THE SYNTHESIS AND THERMOLYSIS OF TRIAZOLINES, TRIAZOLINONES AND TRIAZOLINETHIONES

By

ING. LUBOMIRA M. CABELKOVA-TAGUCHI (Hons)

A Thesis

Submitted to the Faculty of Graduate Studies in

Partial Fulfilment of the Requirements for

the Degree

Doctor of Philosophy

McMaster University

June 1977

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DOCTOR OF PHILOSOPHY (1977)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: The Synthesis and Thermolysis of Triazolines, Triazolinones and Triazolinethiones.

AUTHOR: Ing. Lubomira M. Cabelkova-Taguchi (Dipl. ing., SVST, Faculty of Chemistry, Bratislava, CSSR)

SUPERVISOR: Professor J. Warkentin

NUMBER OF PAGES: viii, 159

ABSTRACT

The purpose of this work was to synthesize new triazolines utilizing the lead tetraacetate oxidation method, to establish the mechanism of cyclization and to explore thermal and photochemical decompositions of some triazolines.

The first part of this thesis describes the preparation of two new triazolines (3,3-dimethyl-5-imino-Δ^1-1,2,4-triazoline and 3,3-dimethyl-4-phenyl-5-phenylimino-Δ^1-1,2,4-triazoline) achieved by lead tetraacetate oxidation. The mechanism of LTA cyclization is discussed in the relation to the mechanisms of lead tetraacetate oxidations of semi-carbazones. The second part deals with thermal decomposition studies of 3,3-dimethyl-4-phenyl-5-phenylimino-Δ^1-1,2,4-triazoline, 3,3-dimethyl-4-phenyl-Δ^1-1,2,4-triazoline-5-thione and 3,3-dimethyl-4-phenyl-Δ^1-1,2,4-triazolin-5-one. Possible mechanisms of the decomposition are discussed in the light of a correlation between the rate constants, activation parameters, substituent constants and solvent effects. Exploratory work in the photochemical decomposition of 3,3-dimethyl-4-phenyl-Δ^1-1,2,4-triazolin-5-one is presented in the third part.

ACKNOWLEDGEMENTS

The author would like to express her gratitude to Dr. J. Warkentin for his friendship, knowledgeable guidance and assistance in this work.

To the author's husband, Vince, a special thanks for his drafting of the diagrams and for his patience, encouragement and comfort during these difficult times.

Helpful discussions with the supervisory committee members, Drs. J. J. McCullough and B. L. Hillcoat are also greatly appreciated.

Many thanks for the invaluable help in photochemistry experiments to Dr. J. J. McCullough and his research group, in particular, Rod Miller.

The author is grateful to Dr. N. H. Werstiuk and the Chemistry Department of the University of British Columbia for the experiments in photoelectron spectroscopy.

The technical assistance of Mr. J. I. A. Thompson, Mr. C. Schönfeld, Mrs. B. Spiers and especially Mr. B. G. Sayer is gratefully acknowledged.

Thanks to Mrs. Jan Gallo for her patience, skill, speed and accuracy in typing this thesis.

Financial assistance from the National Research Council of Canada in the form of a scholarship (1972-1975) and from the Chemistry Department of McMaster University in the form of an assistantship is appreciated.

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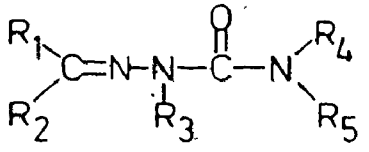
I. OXIDATIVE CYCLIZATION

A. By Lead Tetraacetate

Oxidation of substituted semicarbazones (1) was first reported by Iffland and co-workers.[1] When benzophenone-4,4-diethylsemicarbazone (2) was reacted with lead tetraacetate (LTA), 2-oxo-1,1-diphenylpropyl-

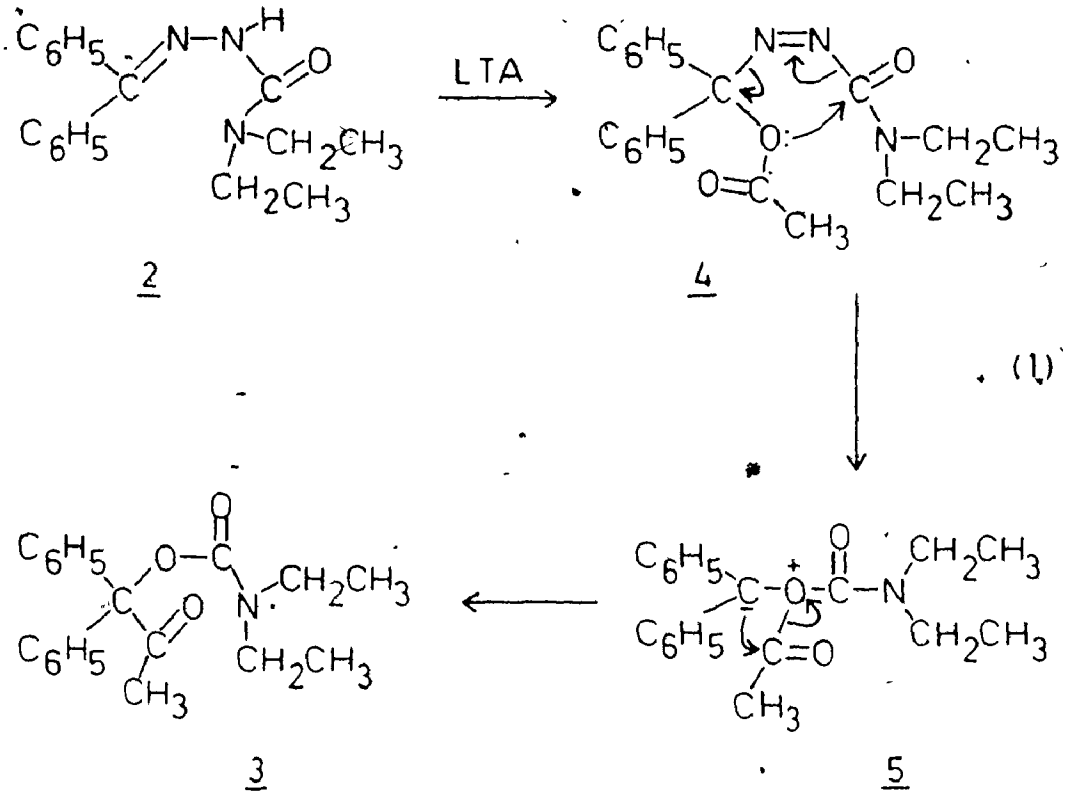


1

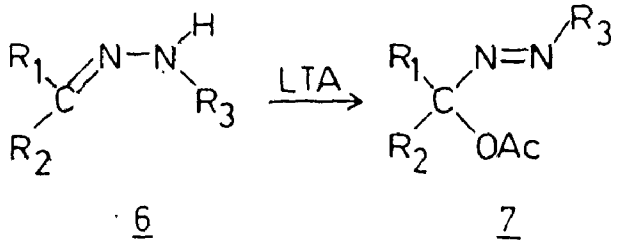
diethylcarbamate (3) was isolated in high yield (eq. (1)). The assumed mechanism involved the azoacetate (4) intermediate and its subsequent rearrangement to 5 by intramolecular nucleophilic displacement at the amide carbonyl and by loss of nitrogen. By a 1,2 shift analogous to the Stevens rearrangement, 5 was converted to the carbamate 3 as indicated in equation (1).

Rabjohn and Chaco[2] explained the LTA oxidation of benzophenone-carbethoxyhydrazones to acetyldiphenylmethylethyl carbonate in a similar fashion. In neither case was the azoacetate isolated or evidence for its existence produced.

These results[1] were different from those obtained with corresponding hydrazones 6 which were converted to azoacetates 7 under the same conditions[3] as shown in eq. (2).

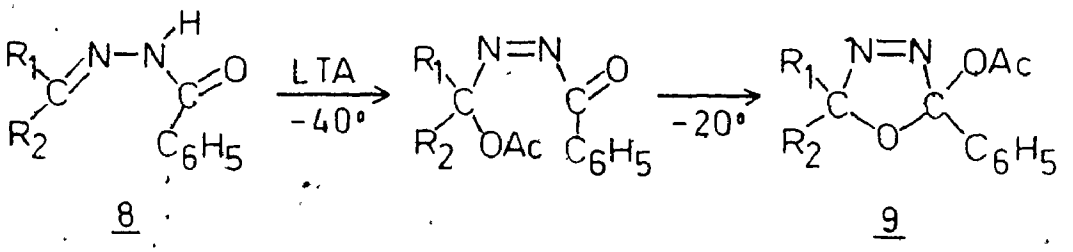


2 4 (1) 5 3



6 7 (2)

The azoacetate intermediate (7, $R_3 = C_6H_5$) was also proposed to exist in the oxidation of some benzoyl hydrazones 8. Hoffmann and Luthardt[4,5] observed that benzoylhydrazones of cyclohexanone, acetophenone and benzophenone undergo cyclization with lead tetraacetate in methylene chloride. At -40°C, a deep red-brown solution, which is the characteristic colour of the benzoylazo chromophor, was observed. Upon warming to -20°C, the colour rapidly faded and the only product isolated was the nearly colourless Δ^3-1,3,4-oxadiazoline (9) (eq. (3)).

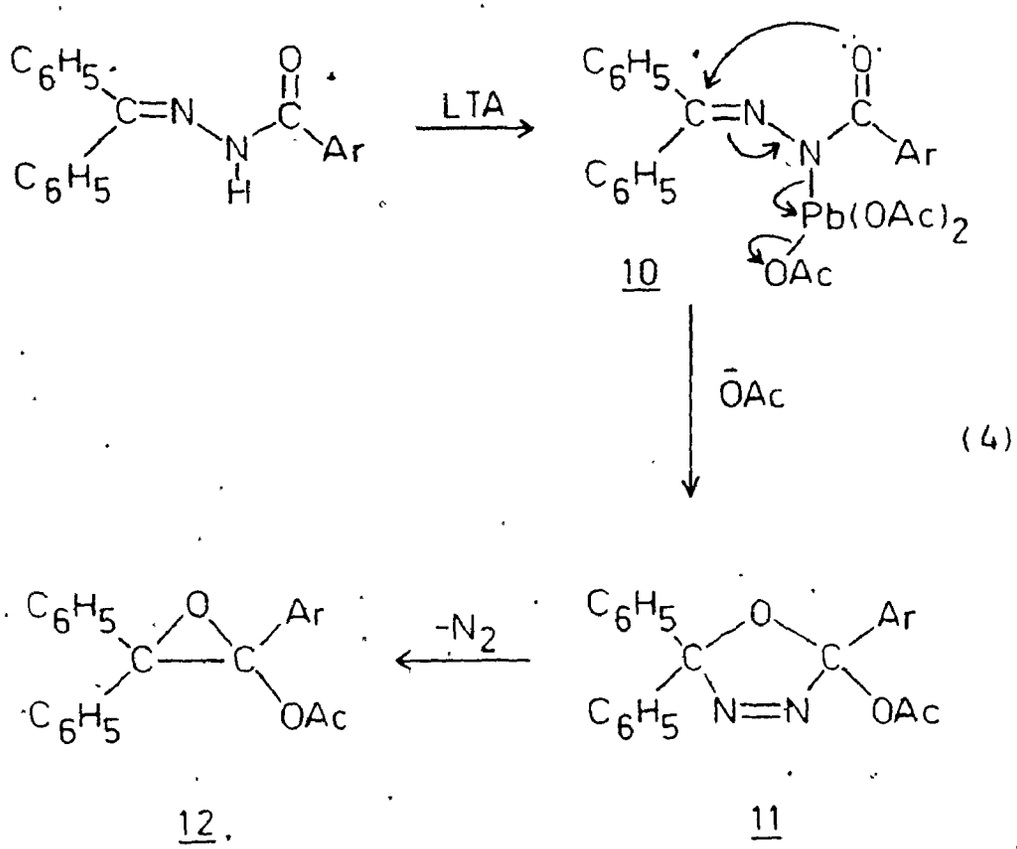


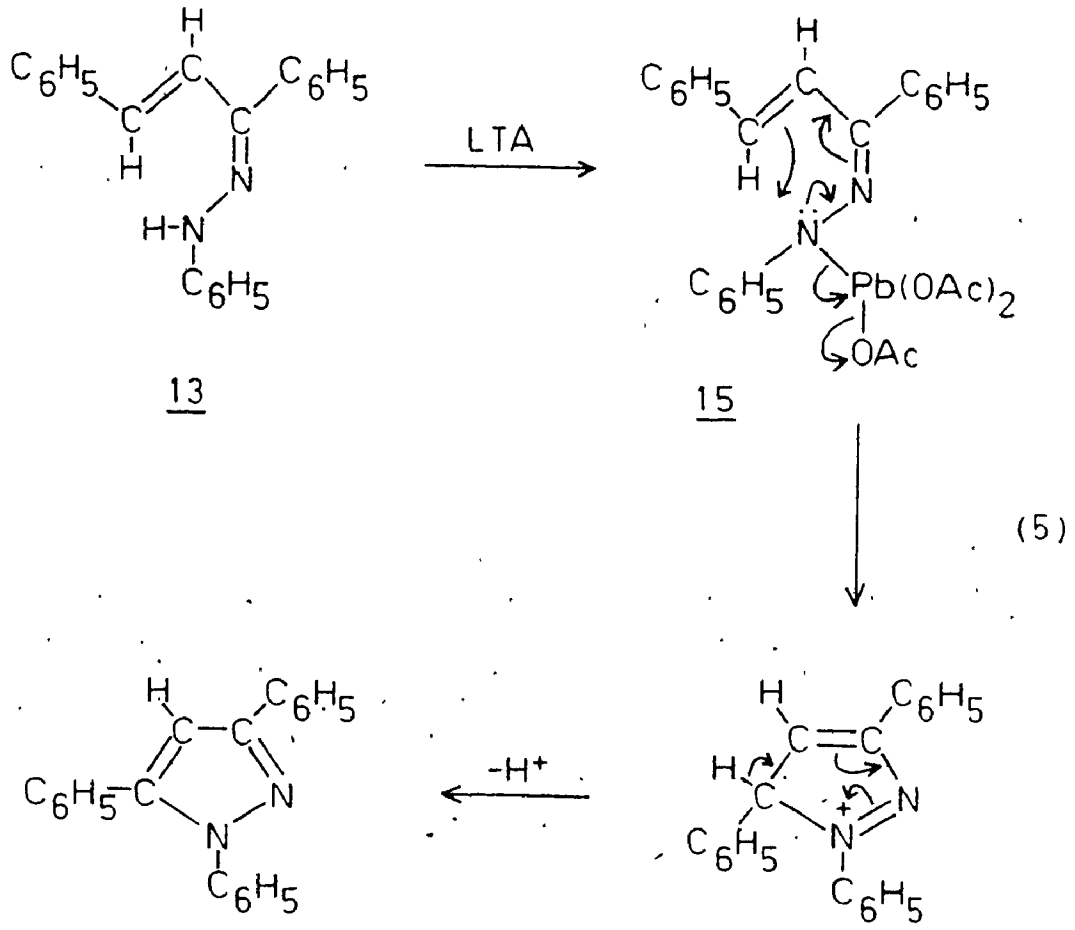
8 9 (3)

Although Hoffmann had suggested an intermediate azoacetate (7) to explain the cyclization of the ketohydrazone, Gladstone and Norman[6] proposed that the reaction actually involved cyclization of an N-Pb complex 10 to an oxadiazoline (11) and subsequent loss of nitrogen to give an epoxide (12) (eq. (4)).

The fact that, when the reaction was carried out in methanol, a methoxyepoxide was obtained, strongly supported this mechanism.

The conversion of chalcone phenylhydrazone (13) to 1,3,5-triphenylpyrazole (14) by lead tetraacetate was observed by Norman[7] as well. Employing a similar mechanism in this case, he envisaged intramolecular nucleophilic attack by the olefinic double bond in an initial intermediate 15 (eq. (5)).

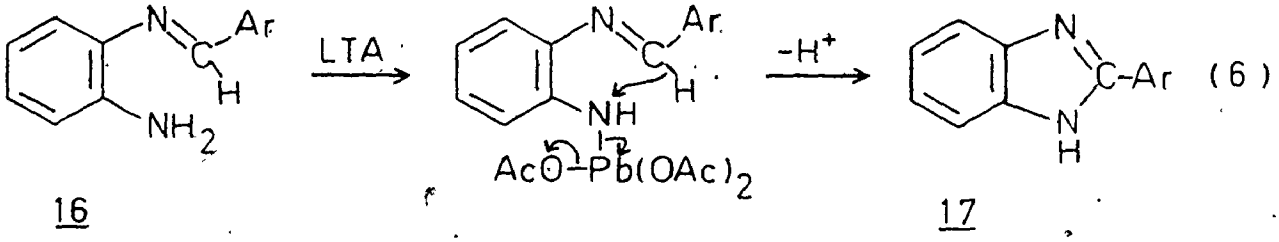

C6H5
C=N
N
H
O
C
Ar
C6H5
LTA
Pb(OAc)2
OAc
10
ŌAc
(4)
C6H5
O
Ar
C
C
C6H5
OAc
-N2
C6H5
O
Ar
C
C
C6H5
N=N
OAc
12
11



13 15 14

(5)

An analogous mechanism was favoured by Norman[7] in the oxidation of the o-phenylenediamine benzaldehyde Schiff bases (16) to benzimidazole (17) (eq. (6)), for which earlier authors[8,18] had suggested free radical alternatives.



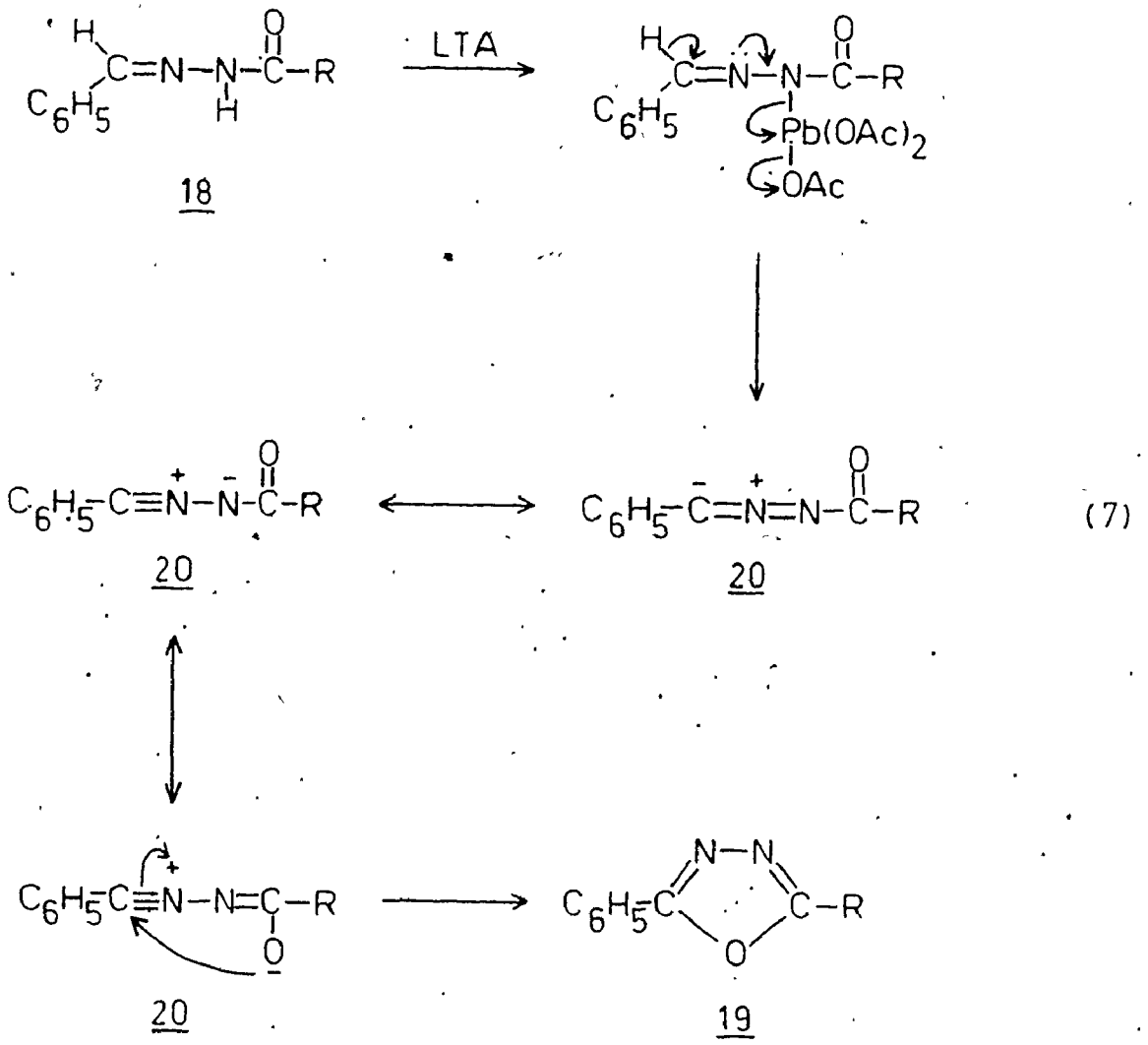
16 17 (6)

Cyclization of aldehyde hydrazones (18) with lead tetraacetate yielded 1,3,4-oxadiazoles (19) and it was proposed[9] that the nitrilimine (20) was formed in the course of reaction (eq. (7)).

Aldehydic semicarbazones (21a, R = aryl) underwent similar cyclization. The authors[10] reported the formation of oxadiazoles (22) in high yield and suggested that the product was formed via an intramolecular 1,5-dipolar cycloaddition of a nitrilimine (23) intermediate (eq. (8)). To support this claim, they cited the fact that, when nitrilimine formation was structurally prevented (21b, R = CH_3) no reaction occurred.

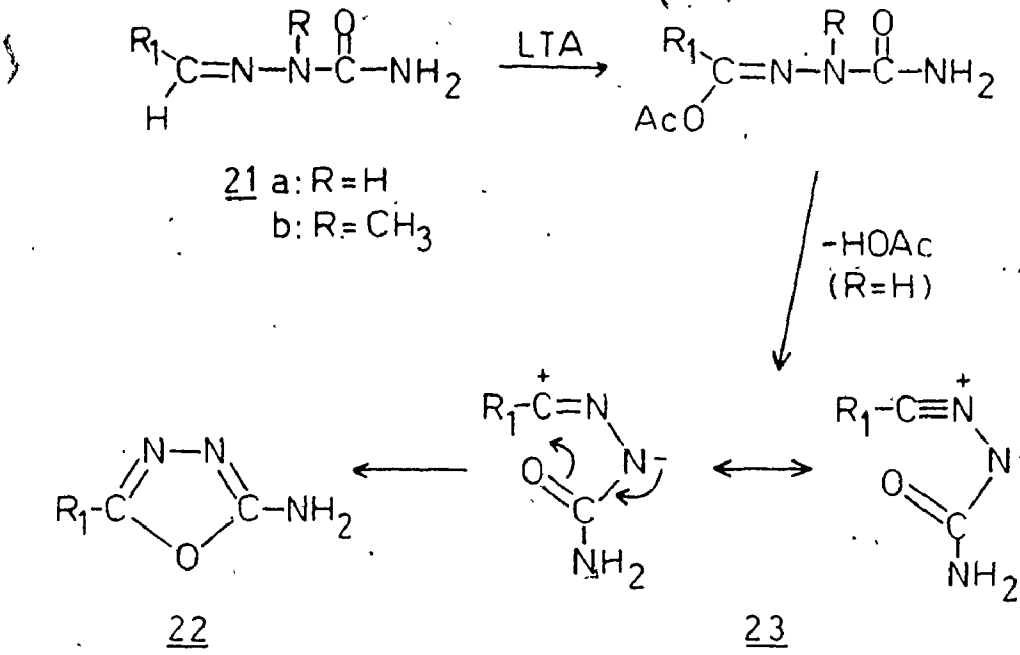
Similarly, preparation of 3-aryl-azo-anthranil-1-oxides (24) was suspected[9] to go through nitrilimines (25) (eq. (9)).

The oxidation of 2-phenylsemicarbazones (26) by LTA, reported by Schildknecht and Hatzman,[11] led to the formation of phenylazomethyl isocyanate (27). According to the authors, the semicarbazone (26) was oxidized to the nitrene (28) which then rearranged via a five-membered ring to the isocyanate (27) as shown in equation (10).



18 20 20 20 19

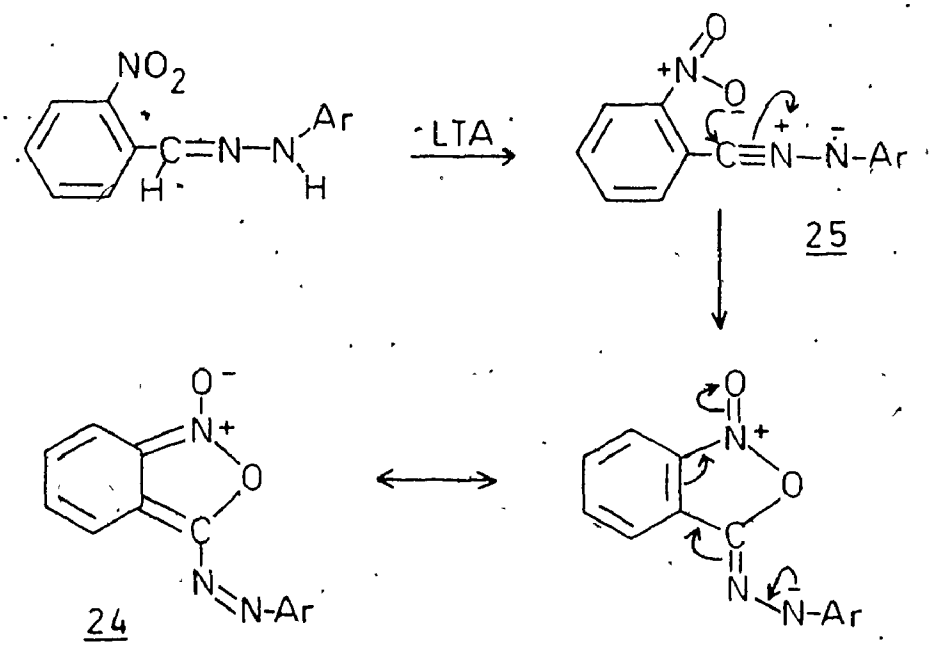
(7)



21 a: R=H
b: R=CH$_3$

(8)

22 23



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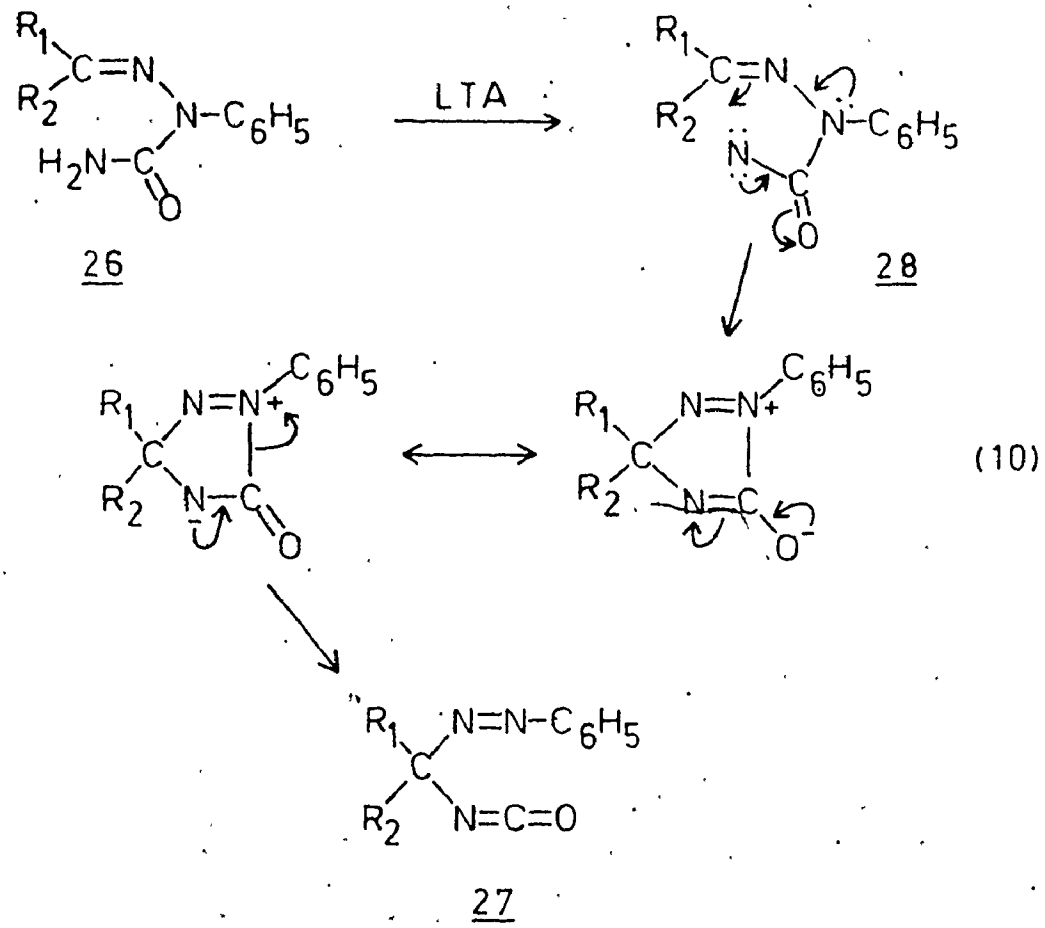
(9)

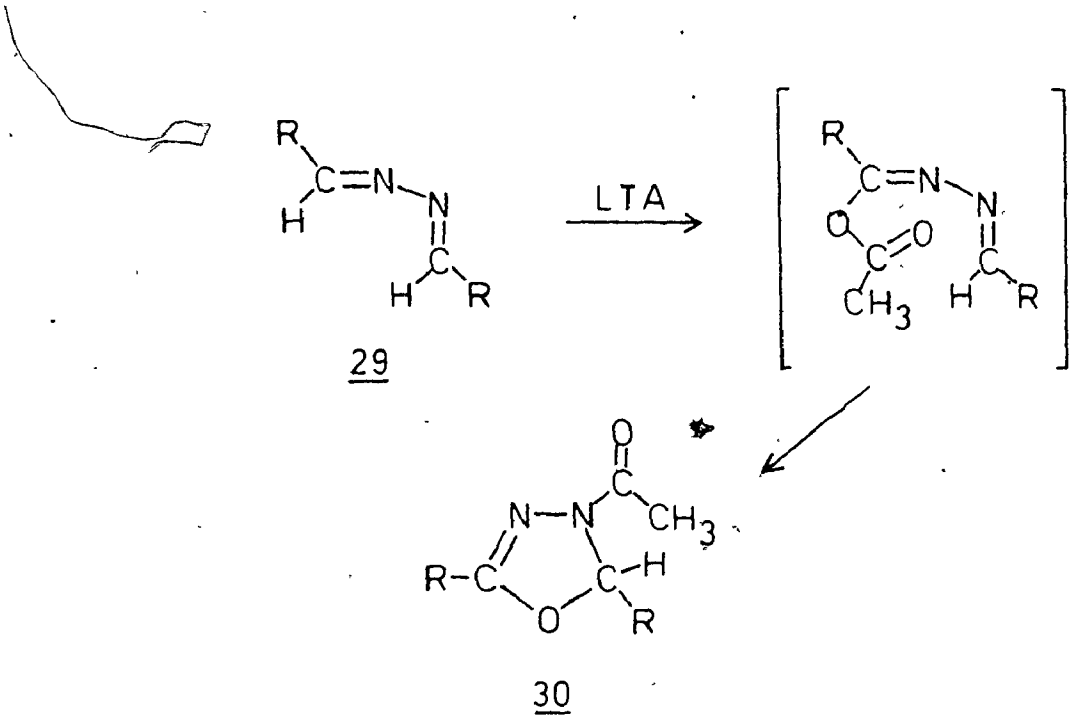
24



26 28 27 (10)

Gillis and La Montagne[12] had studied the LTA cyclization of aldazines and ketazines and found that, while aromatic ketazines did not react with lead tetraacetate, aliphatic ketazines gave α,β-unsaturated "azoacetates". The oxidation of aldazines (29) yielded 1,3,4-oxadiazoles (30) (eq. (11)).

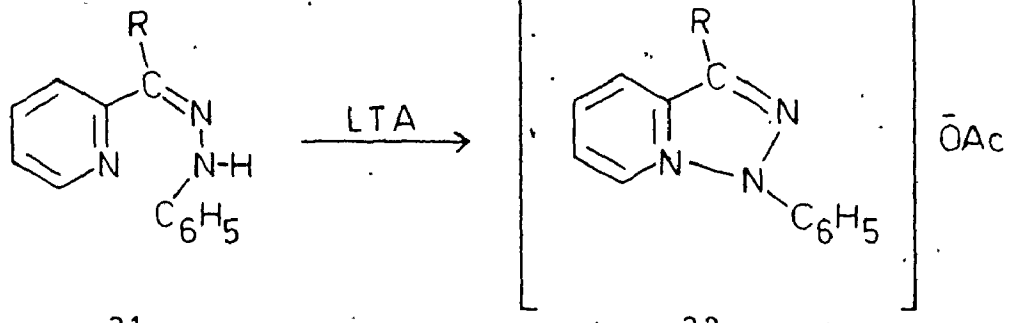
Some fused heterocyclic ring systems were synthesized by lead tetraacetate oxidative cyclization. Kühn[13] employed LTA in glacial acetic acid solution to cyclize 2-acetyl and 2-benzoyl-pyridine phenylhydrazone (31) to the corresponding salts 32 as shown in equation (12):



29

30

(11)



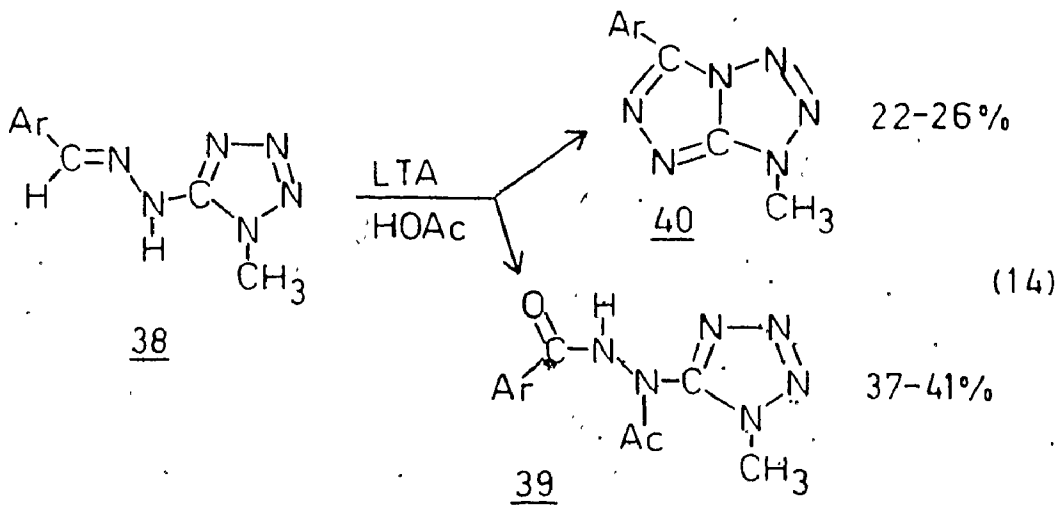
31

32

(12)

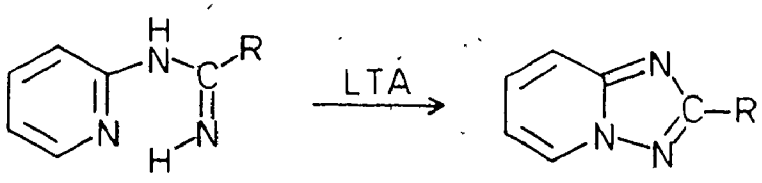
The reaction of lead tetraacetate with 3-phenyl-1,2,4-triazolyl hydrazones (33) was studied by Scott and O'Mahoney.[14] They discovered that under given conditions, besides cyclized products, triazoles (34), an N-acetyl hydrazide (35) was also formed. The reaction was represented as a polar mechanism involving a nitrogen-lead complex (36) and a nitrilimine (37) intermediate (eq. (13)) (see page 12).

Similarly, tetrazolylhydrazones (38) reacted with LTA giving two types of products. Scott[15] discovered that the yield of N-acetylhydrazide derivatives (39) were always higher compared to the cyclized component 40 (eq. (14)).

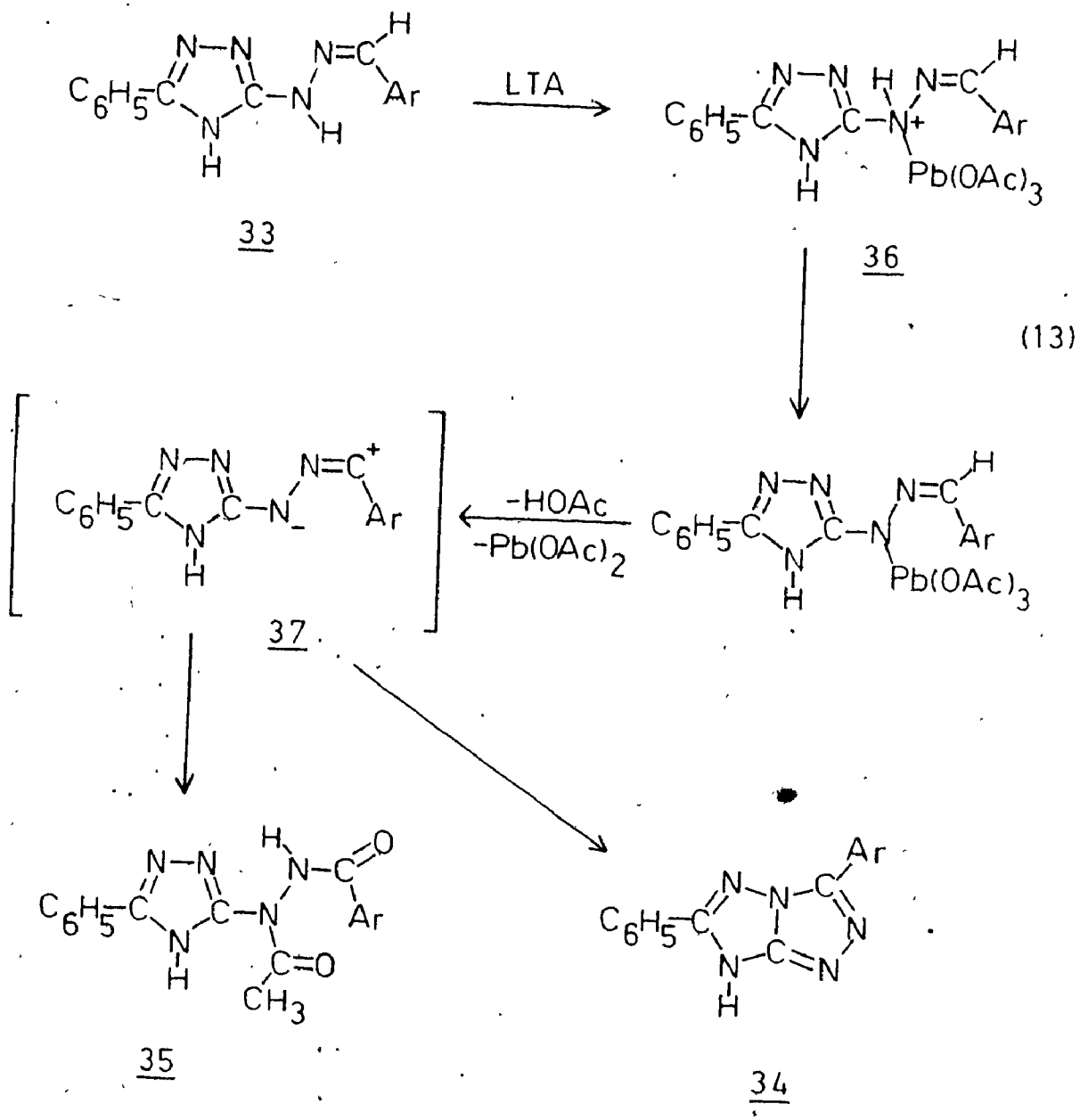


38 40 39 (14)

Lead tetraacetate oxidation of N-(2-pyridyl)amidines (41) yielded[16] the s-triazolo-(1,5-a)-pyridines (42) as equation (15) shows.

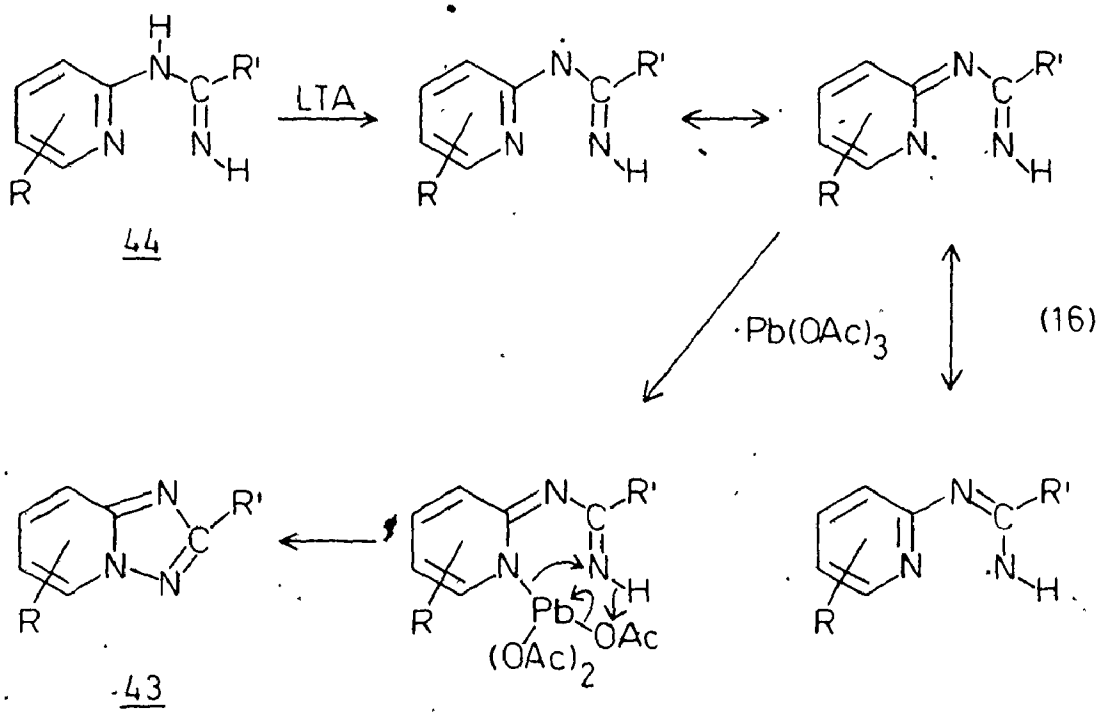


41 42 (15)



(13)

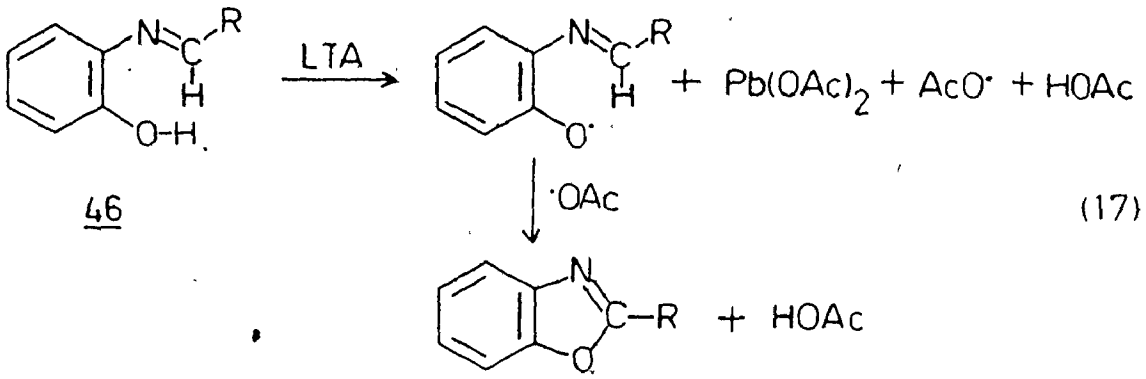
An analogous ring closure was investigated by Potts and co-workers[17] in the preparation of 2-phenyl-s-triazolo-(2,3a)-pyrazines (43) by the cyclization of the corresponding pyridyl amidines (44). The authors suggested a free radical mechanism (eq. (16)).



44 43

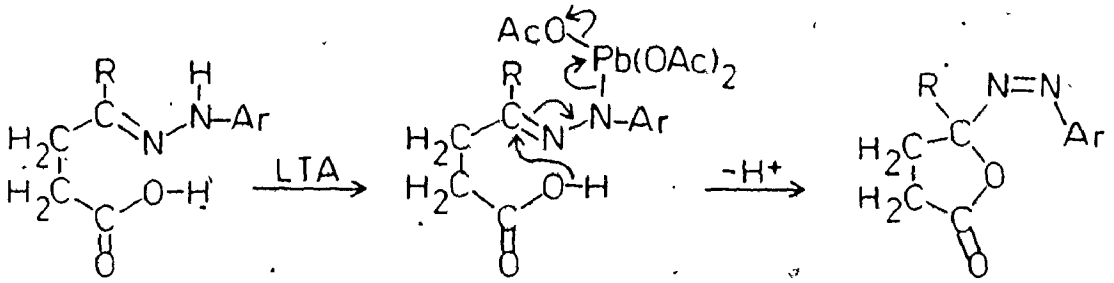
A similar mechanism was proposed by Stephens and Bower[18] for the preparation of some benziminazoles and benzoxazoles 45 from Schiff's bases 46 as shown in equation (17).

Oxidation of ketohydrazones (47) having a suitable cyclization site in the ketone substituents at the fourth or fifth atom from the methine carbon, leads to cyclic products (48); however, azoacetates are formed as by-products as well. The authors[19] proposed a mechanism where

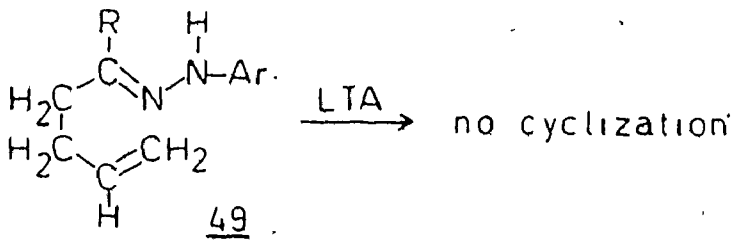


46 (17) 45

nucleophilic attack of the oxygen on the sp^2 carbon is concerted with loss of $Pb(OAc)_2$. Since the cyclization does not occur when the carbonyl group is replaced by a carbon-carbon double bond 49, the possibility of a cationic intermediate, resulting from the loss of $Pb(OAc)_3^-$, on the π-bond, was thought to be unlikely (eq. (18)).

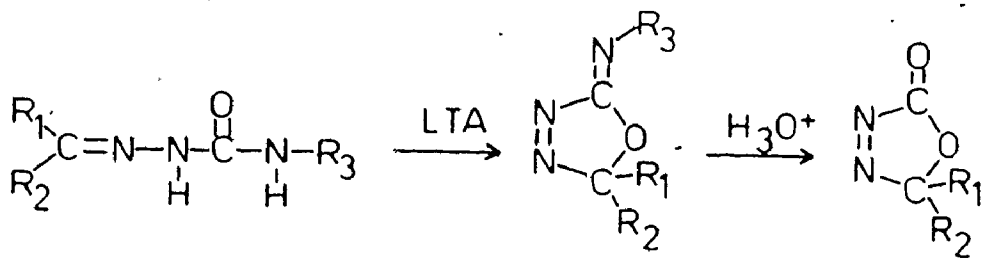


47 48 (18)



49

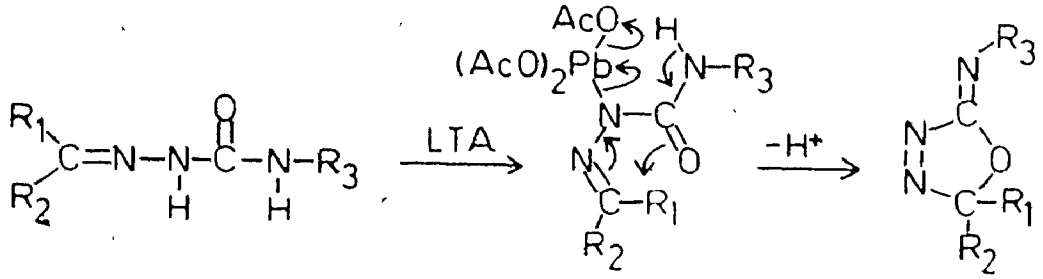
The cyclization of 4-substituted semicarbazones of ketones (50) was examined in considerable detail by earlier workers in this laboratory.[20] By reacting 50 with lead tetraacetate, they prepared a series of oxadiazolines (51, R_3 = Ar), which, in acid media, gives[21] oxadiazolin-2-ones (52) (eq. (19)).



(19)

50 51 52

Cameron and co-workers[22,23] found that the oxidation of 4-substituted semicarbazones with LTA resulted in selective formation of only one of two possible isomers, the Z-isomer (51). The proposed mechanism, similar to Norman's[6,7,9] is shown in equation (20).

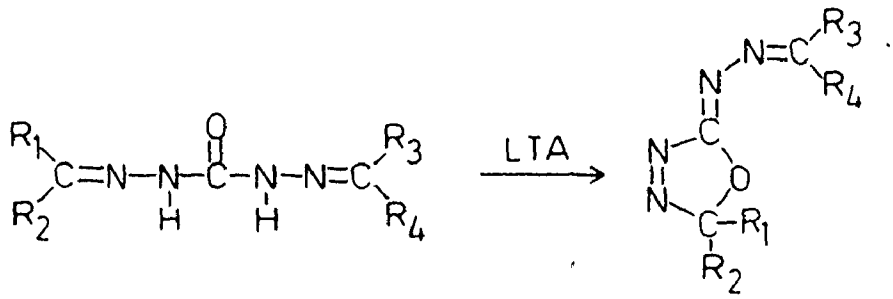


(20)

53 51

The 2-nitrogen-lead complex (53) has steric requirements which force the terminal nitrogen to orient itself in such a way as to minimize steric hindrance. Therefore, closure of the complex 53 results in the Z-isomer exclusively.

When carbohydrazones (54) were oxidized with LTA,[24-26] they generally gave 2-alkylidene-hydrazono-Δ^3-1,3,4-oxadiazolines (55) similar to 51 (eq. (21)).

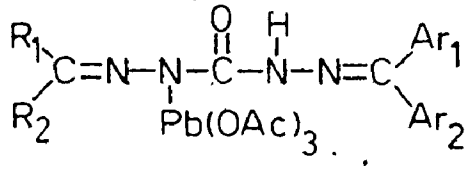


(21)

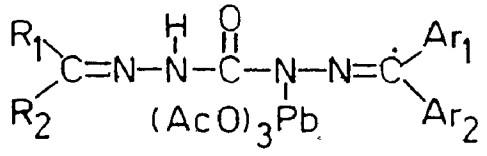
54 55

The cyclization was found to be highly regiospecific. In all the unsymmetrical carbohydrazones studied, with alkyl groups at one end and aryl groups at the other end, cyclization occurred preferentially at the methine carbon bearing the aliphatic substituents. The authors rationale for this fact was the faster formation of the intermediate 56a. The alternative intermediate 56b, according to West and Warkentin, would be disfavoured because of the lower nucleophilicity of the $-NH-N=C-(Ar)_2$

group and because of higher steric hindrance.

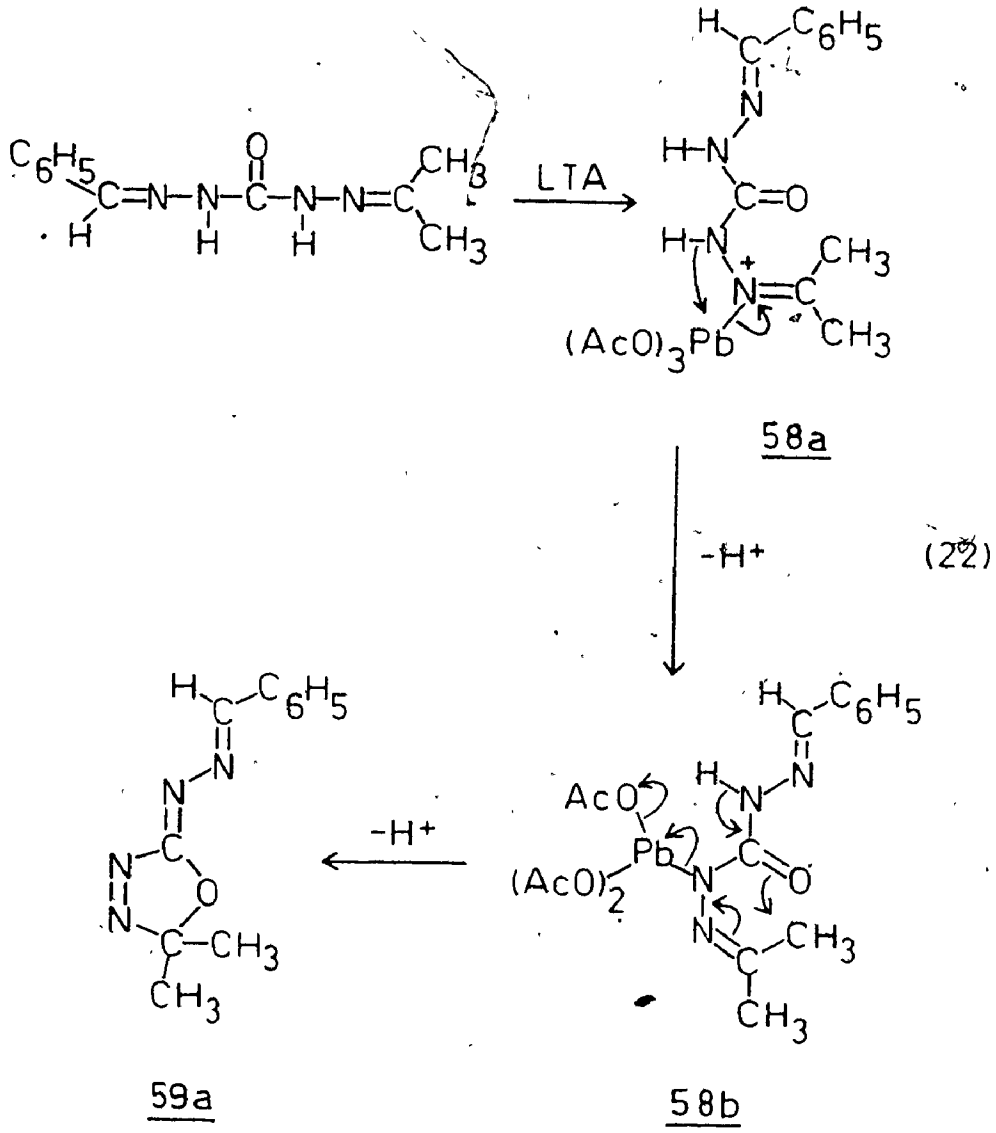


56a

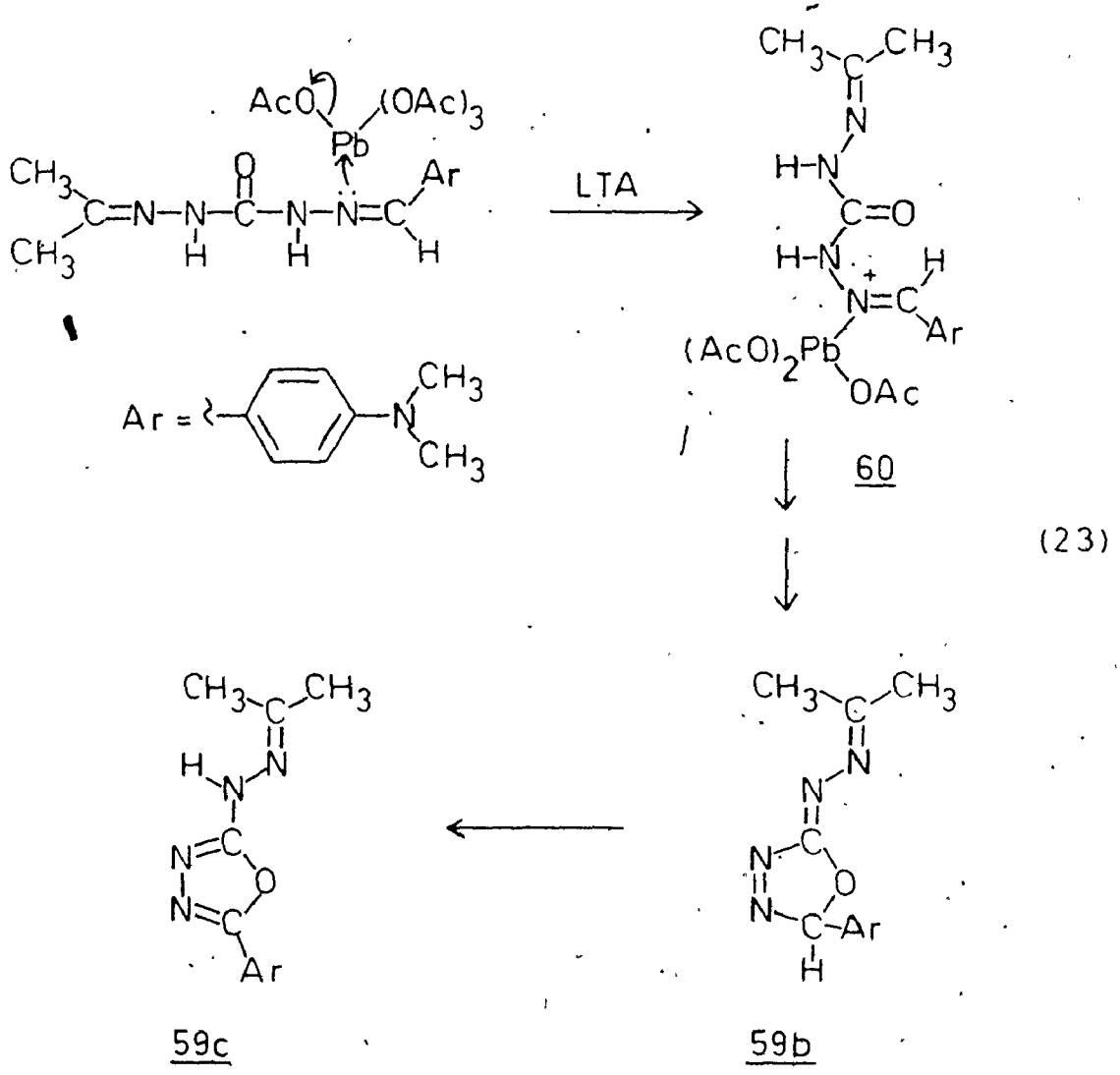


56b

Later, Ramakrishnan[27] investigated this reaction in more detail. Studies of the cyclization of certain carbohydrazones 54 derived from aromatic aldehydes and acetone (54, $R_1 = R_2 = CH_3$, $R_3 = H$, $R_4 = C_6H_5$) provided results which favour an alternative intermediate for this process. When the electron density in the conjugated π system of the starting carbohydrazone (54) was increased by introducing electron donating groups and keeping the steric factors nearly the same, a by-product 57 resulting from the cyclization at the aryl end was formed. It was suggested that in the absence of any electrondonating group, the steric effect is predominant and this effect prevents the lone pair on the imino nitrogen adjacent to the benzene ring from attacking the lead and the product 59a is formed via intermediate 58a (eq. (22)). But, when the benzene ring is substituted with an electrondonating group (e.g., p-dimethylamino), the strong electronic effect offsets the steric effect and the intermediate 60, with lead attached to nitrogen next to aryl group is


LTA
58a
-H+
(22)
-H+
59a
58b

preferred, resulting initially in the product 59b, which tautomerizes to 59c (eq. (23)).

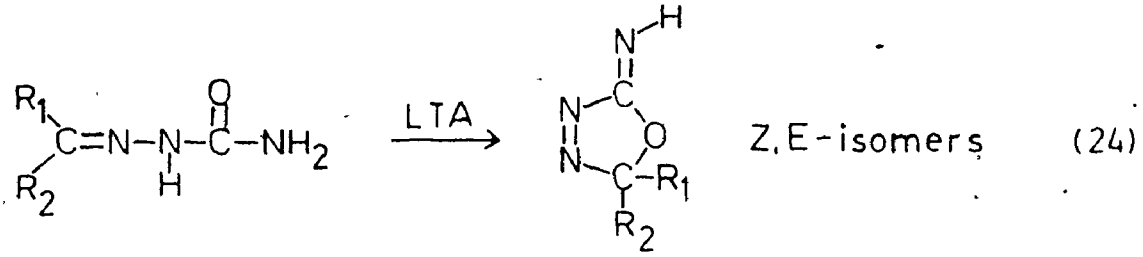


(23)

Ramakrishnan proposed a 1,2-shift of lead, leading to 58b from 58a and thus explained the stereochemistry and regiochemistry of the cyclization. According to him, the bulky $Pb(OAc)_3$ group in 58b forces the side chain

to eclipse the carbonyl oxygen and hence the stereochemistry of the product is determined.

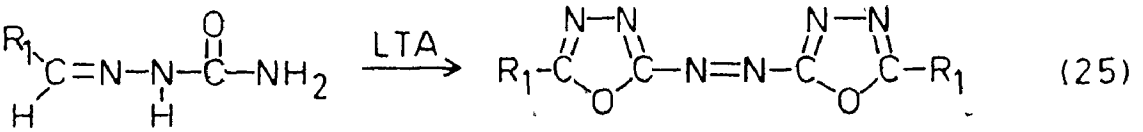
Knittel[28] carried out the LTA oxidation of unsubstituted ketone and aldehyde semicarbazones. Ketone semicarbazones (61) yielded novel, unsubstituted 2-imino-Δ^3-1,3,4-oxadiazolines (62) (eq. (24)).



(24)

61 62

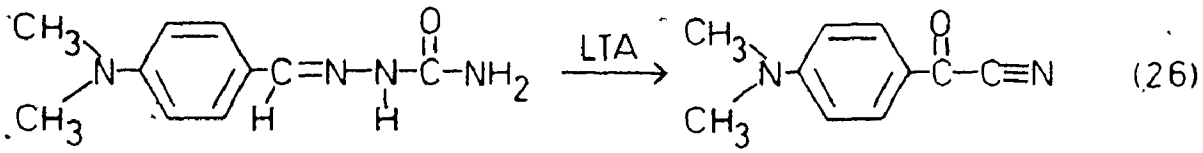
The oxidation of aldehyde semicarbazones (20a) resulted in the formation of 5,5'-disubstituted 2,2'-azobis-1,3,4-oxadiazoles (64) (eq. (25)).



(25)

20a 64

During the course of oxidation, one anomalous result was obtained. Oxidation of p-dimethylaminobenzaldehyde semicarbazone (65) led to a quantitative yield of p-dimethylaminobenzoyl cyanide (66) (eq. (26)).



(26)

65 66

Knittel then suggested a mechanism, closely related to Cameron's, explaining the oxidation of carbonyl derivatives with LTA. The complex, in which lead is attached to the 2-nitrogen is formed and can undergo several reactions, depending on the substituents present. Thus, Iffland's[3] azoacetate product, Hoffman's[4] product, as well as Norman's[6,7] intermediate can be explained by a single mechanism proposed by Knittel (Fig. 1). The anomalous product 66 (eq. (24)) was suggested to result from the unstable iminooxirane (67) formed from oxadiazoline by loss of nitrogen.

B. By Oxidizing Agents Other than Lead Tetraacetate

The ferric chloride oxidative cyclization of aldehyde semicarbazones (20a) was reported as early as 1900 by Young and Whitham.[29] Aryl semicarbazones were heated in alcoholic solution to 130°C with ferric chloride to produce 3-hydroxytriazoles 67 and 68 (eq. (27)).

A similar procedure was used by Young and Oates[30] in synthesis of a series of 1-methyl-5-hydroxytriazoles (69) from 2-methyl semicarbazones (70). Neither work included a mechanistic proposal. However, in 1962, Gibson[31] stated that the mechanism includes a radical intermediate. Later, other workers[32-34] employed the method of Young and Oates to oxidize various 2- and 4-substituted semicarbazones.

FIGURE 1

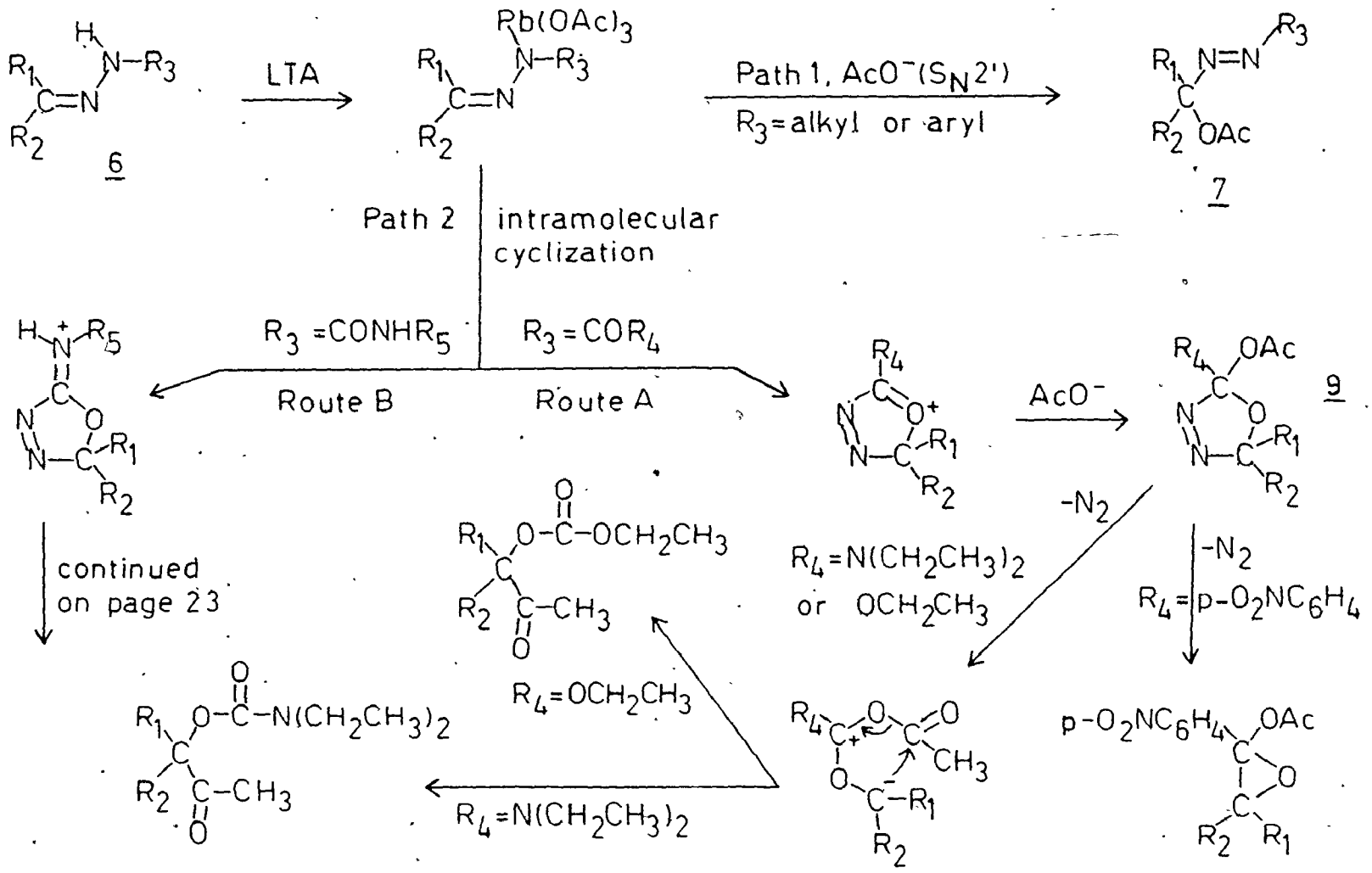
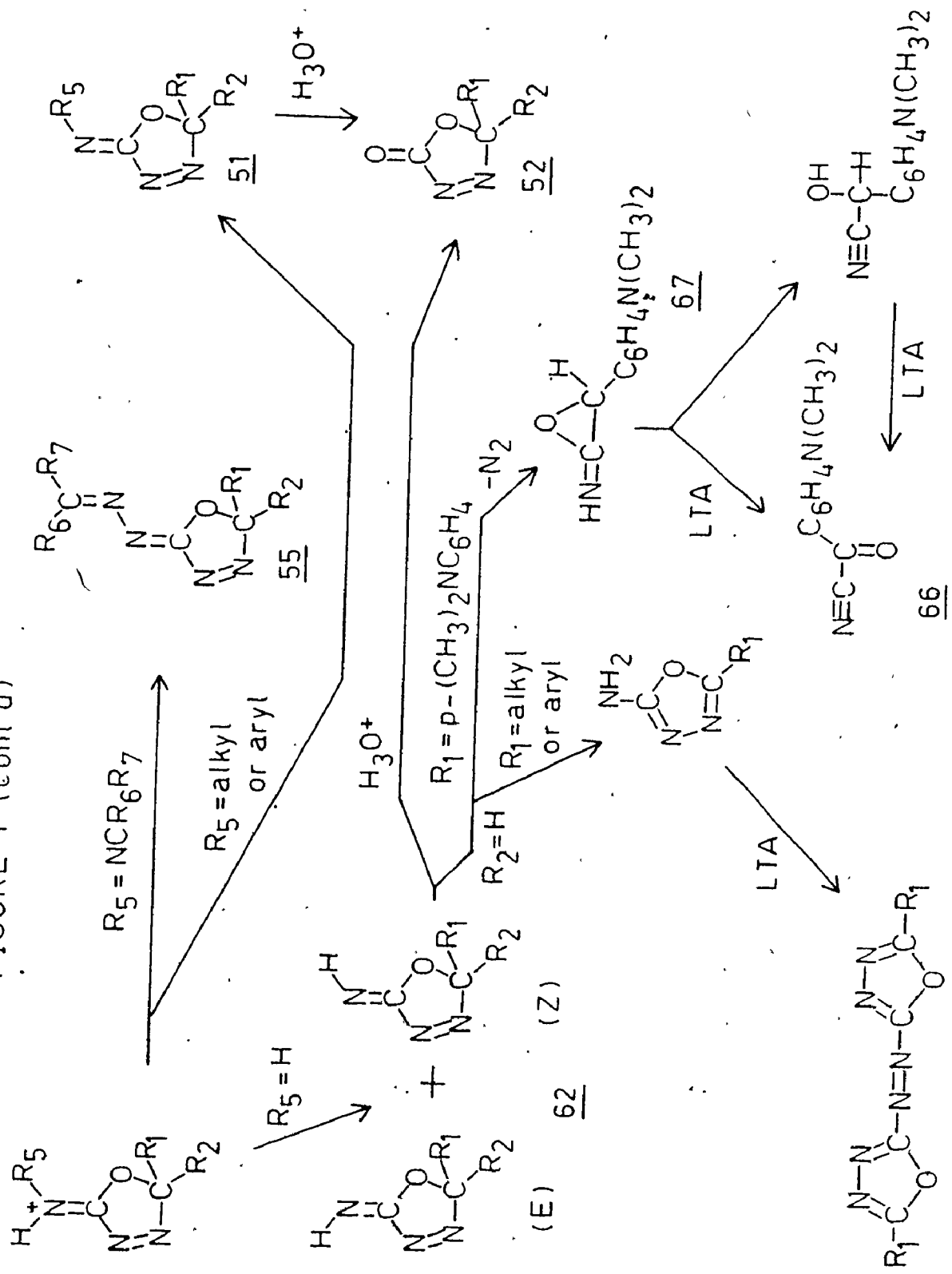
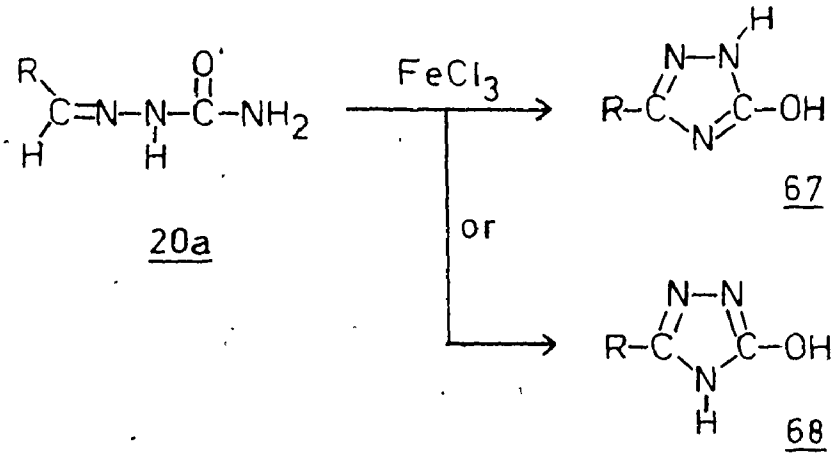
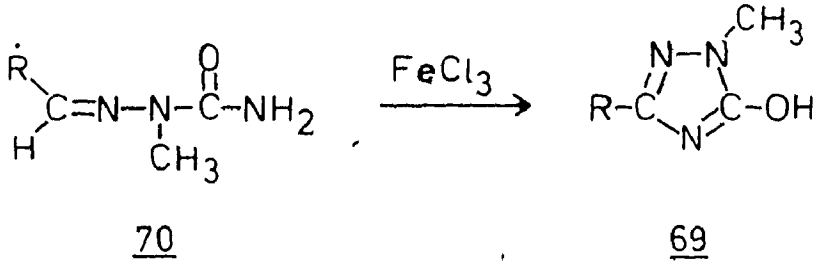

LTA
Pb(OAc)3
Path 1, AcO⁻(SN2')
R3=alkyl or aryl
Path 2
intramolecular cyclization
R3 =CONHR5
R3 =COR4
Route B
Route A
AcO⁻
-N2
-N2
R4=N(CH2CH3)2 or OCH2CH3
R4=p-O2NC6H4
R4=OCH2CH3
R4=N(CH2CH3)2
continued on page 23

FIGURE 1 (cont'd)





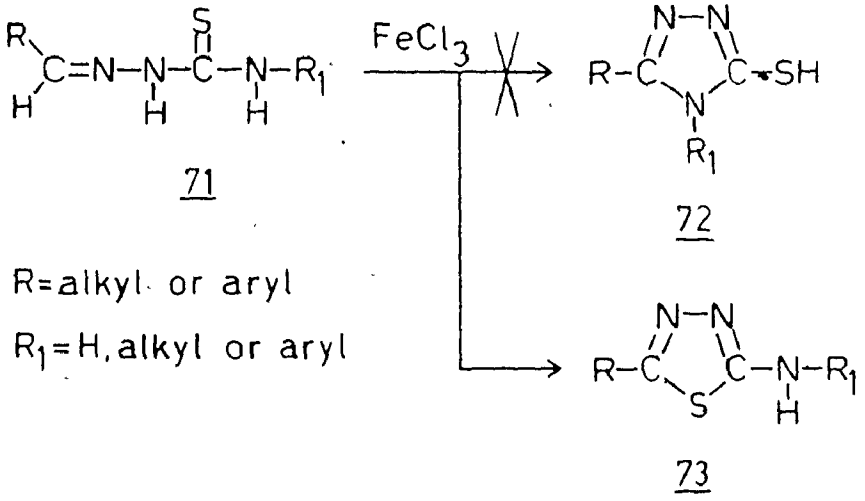
20a 67 68 (27)



70 69 (28)

Oxidation of substituted and unsubstituted aldehydic thiosemicarbazones (71) with ferric chloride was carried out by Young and Eyre.[35] The expected product, mercaptotriazole (72) analogous to hydroxytriazole (68) obtained earlier,[29] was not formed. Instead, 1,3,4-thiadiazole (73) was obtained (eq. (29)).

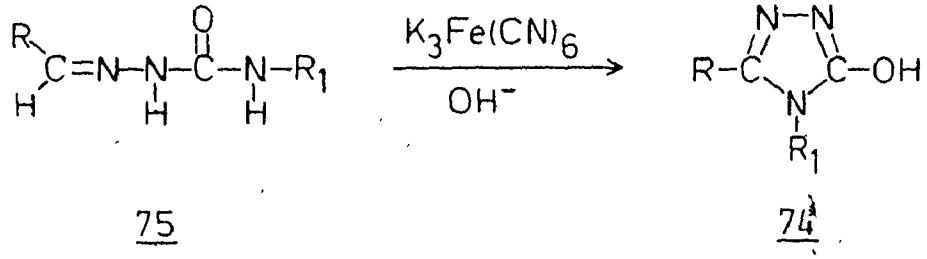
These results were disputed later by Fromm,[36] who claimed that the mercaptotriazole (72) rather than the thiadiazole (73) was present.



(29)

Holmberg[36] in 1955 confirmed the work of Young and Eyre.

A more efficient preparation of hydroxytriazoles (74) from 4-substituted aldehyde semicarbazones (75) was presented by Ramachander and Srinivasan.[38,39] They used alkaline potassium ferricyanide as an oxidizing agent for preparation of 4-aryl-5-hydroxytriazoles (74) (eq. (30)).

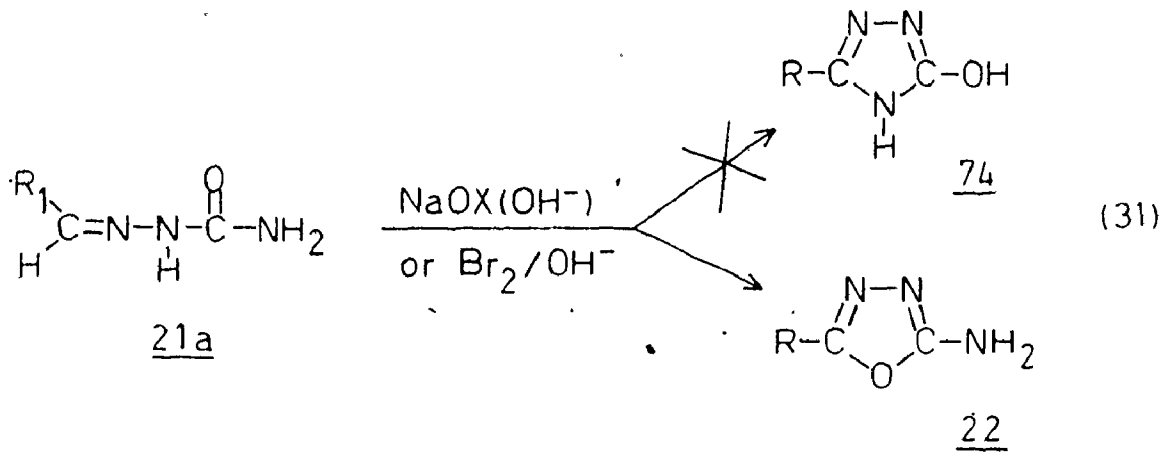


(30)

When 4-arylthiosemicarbazones (71, R_1 = aryl) were oxidized, it was found that 5-hydroxytriazoles were formed instead of the expected thio-compounds. The products 74 apparently resulted from de-

sulfurization of the thiosemicarbazone (71, R_1 = aryl) by the alkaline ferricyanide and subsequent oxidation of the semicarbazone to the hydroxy-triazole.

Different oxidants, namely bromine in alkaline solution and alkaline sodium hypobromite or hypoiodite were used and products other than triazoles (74) were formed.[70,41] Thus, 2-amino-5-phenyl-1,3,4-oxadiazole (22, R = C_6H_5) was prepared from benzaldehyde semicarbazone (21a, R = C_6H_5) using hot alkaline sodium hypobromite or hypoiodite (eq. (31)).

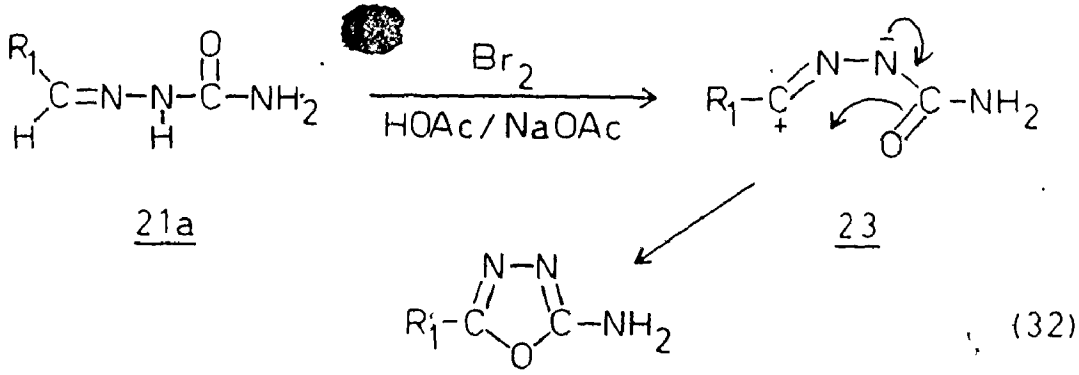


(31)

A number of oxadiazoles were prepared using this route, but no mechanistic proposals were given.

Gehlen and Möckel[42] employed iodine to oxidize some aliphatic and aromatic aldehyde semicarbazones (21a). They, too, discovered that oxadiazoles (22) were formed and, also, that aromatic semicarbazones appeared to have cyclized better (80-90% yield) when compared to aliphatic analogues (10-20% yield).

Gibson[30] in 1962 prepared two oxadiazoles (22) using bromine in acetic acid as the oxidizing agent and suggested a nitrilimine (23) intermediate (eq. (32)). The fact that oxidation under conditions not

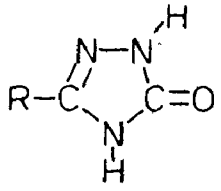


21a 23 (32)

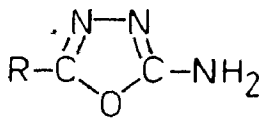
22

leading to nitrilimine formation (e.g., ferric chloride oxidation which Gibson claimed proceeded by a radical mechanism), led to triazoles (74) rather than oxadiazoles, supported his proposal.

Work published by Butler and coworkers[43-46] in the early seventies supported Gibson's[31] theory of the nitrilimine intermediate (23). The authors[43,44] used bromine as the oxidizing agent on arylaldehyde semicarbazones (21a, R = aryl). Using different reaction conditions, they obtained two different products: triazolones (76) and oxadiazoles (22).

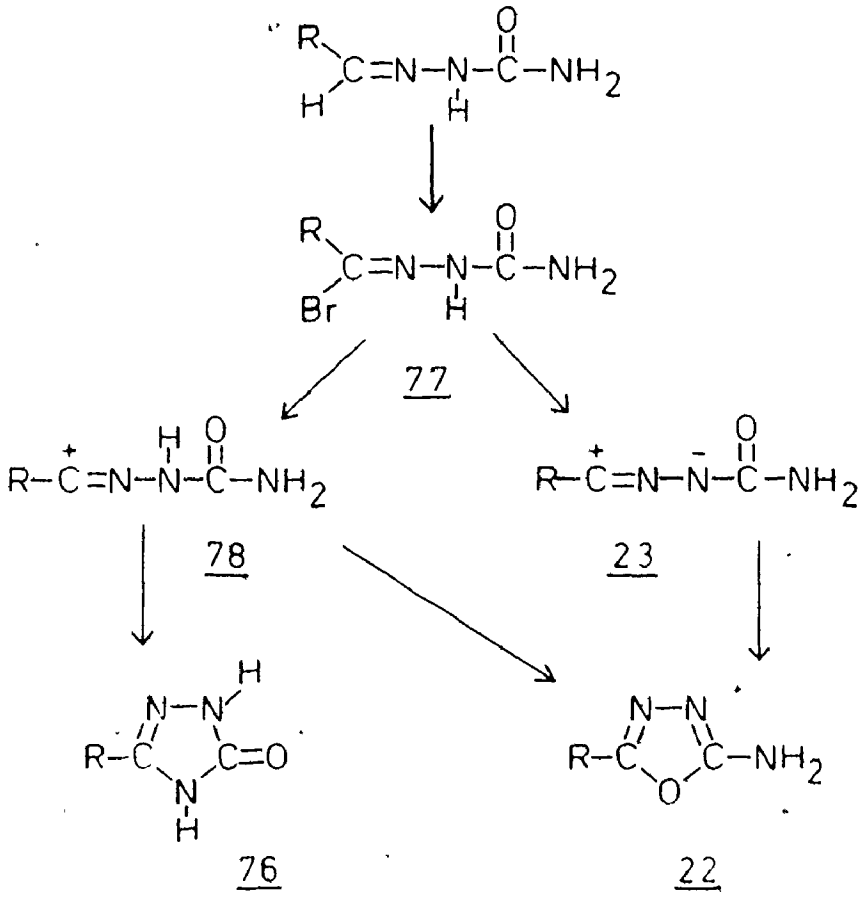


76



22

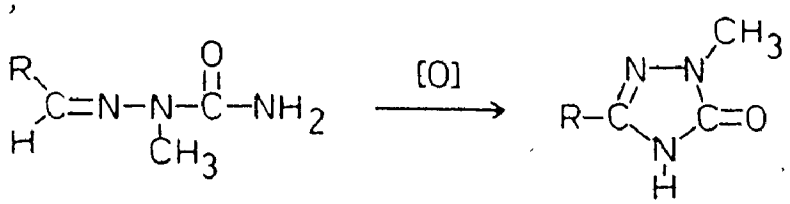
The reaction scheme involves the intermediate 77 which can convert either via the nitrilimine (23) or the carbonium ion (78) to products as shown below (eq. (33)).



(33)

When the nitrilimine formation was structurally prohibited, as in the case of 2-methylsemicarbazone (21b), reaction did not take place under experimental conditions normally leading to oxadiazoles (22). However, when conditions which previously led to triazolones (76) were used, they were formed (79, eq. (34)). These experimental results were

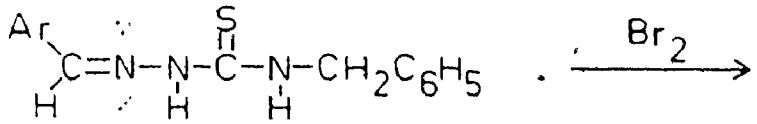
used as further support for the proposed mechanism in equation (31).



(34)

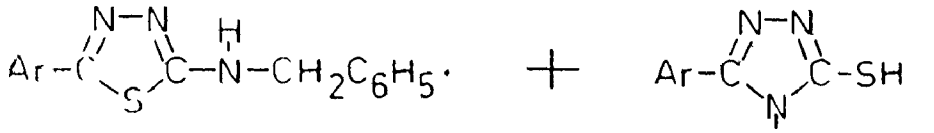
21b 79

Oxidation of the arylaldehyde-4-benzylthiosemicarbazone (80) with bromine also led to two different products, the ratio of which depended on the solvent used for oxidation[47,48] (equation (35)).



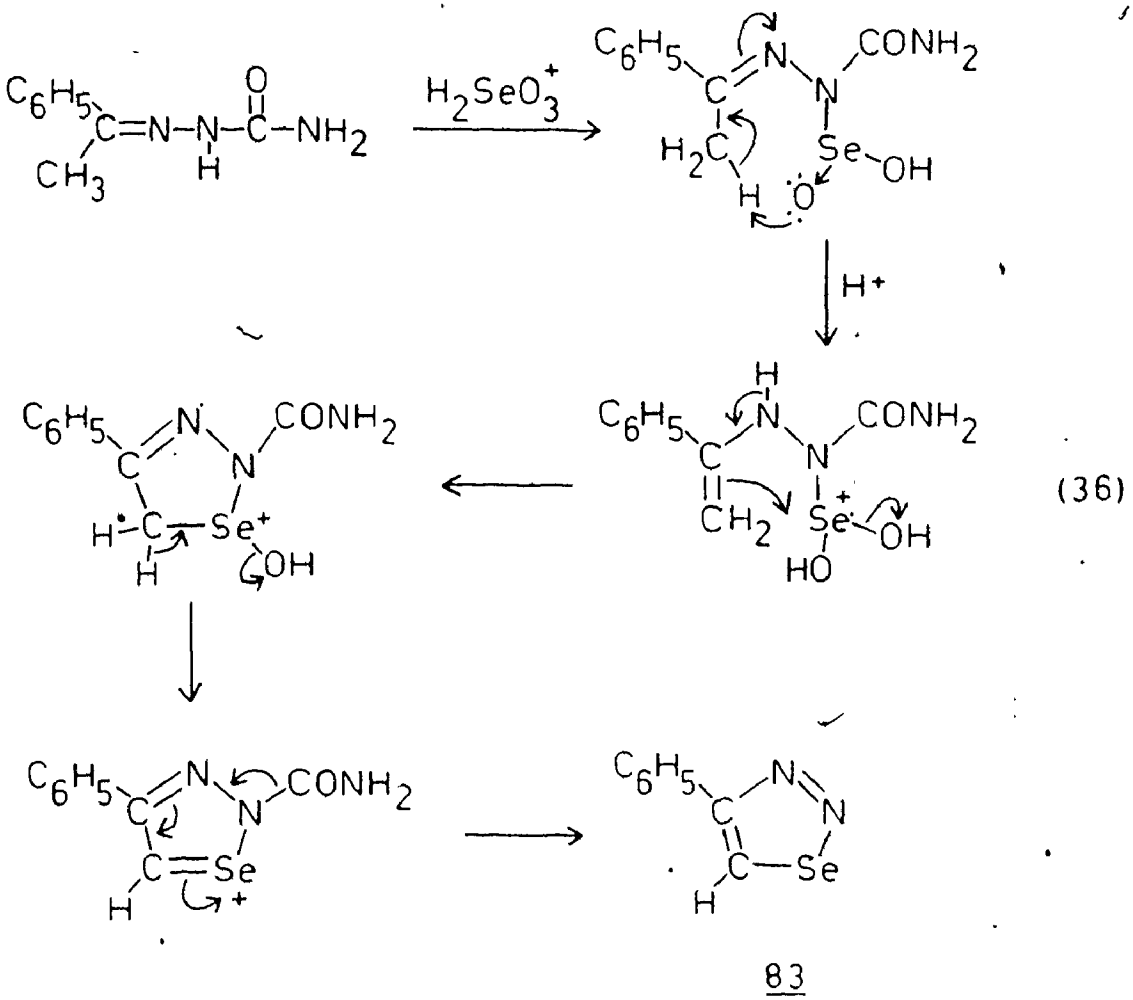
80

(35)



81 82

Recently, selenium dioxide was employed by several authors[49-51] as the oxidizing agent for cyclization of ketosemicarbazones. The five-membered cyclic systems formed have selenium incorporated into rings ... re called 1,2,3-selenadiazoles (83). The mechanism suggested is shown in equation (36).

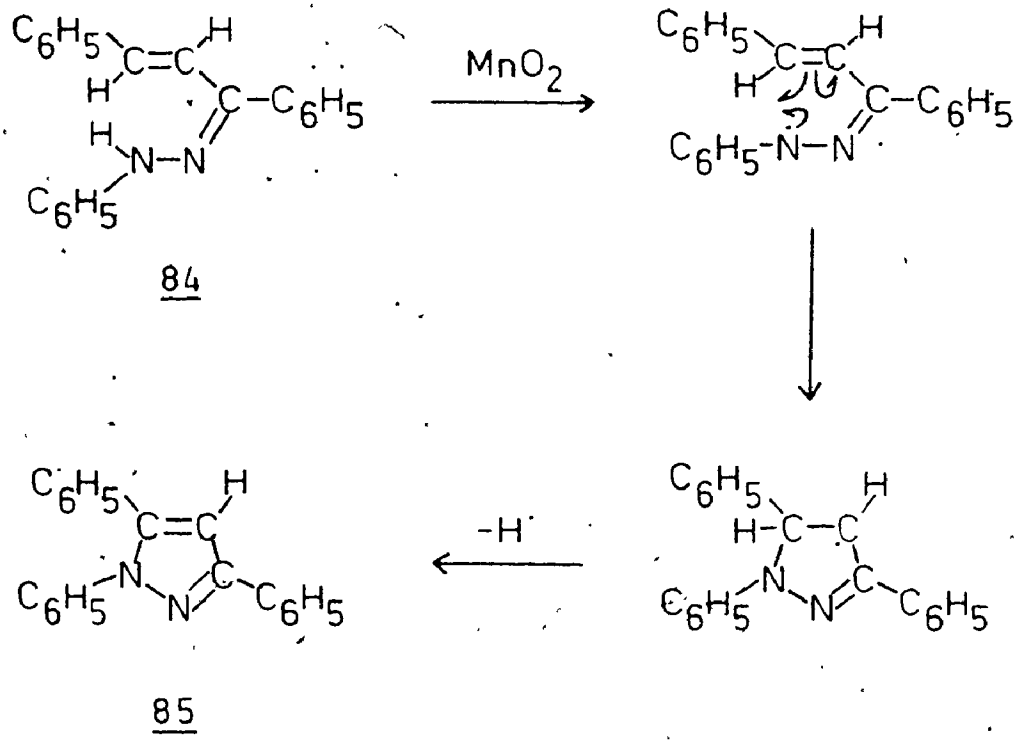


(36)

83

Manganese dioxide was used in the oxidative cyclization of phenyl hydrazones (84) by Bhatnagar and George.[52] They isolated triphenylpyrazole (85) from benzalacetophenone phenylhydrazone (84) and suggested a radical mechanism for the ring closure (eq. (37)).

Other oxidizing agents such as ceric ammonium nitrate,[53] peracetic acid[54] and hydrogen peroxide[55-59] were utilized in cyclization of semicarbazones and thiosemicarbazones, but mechanistic information was not included.



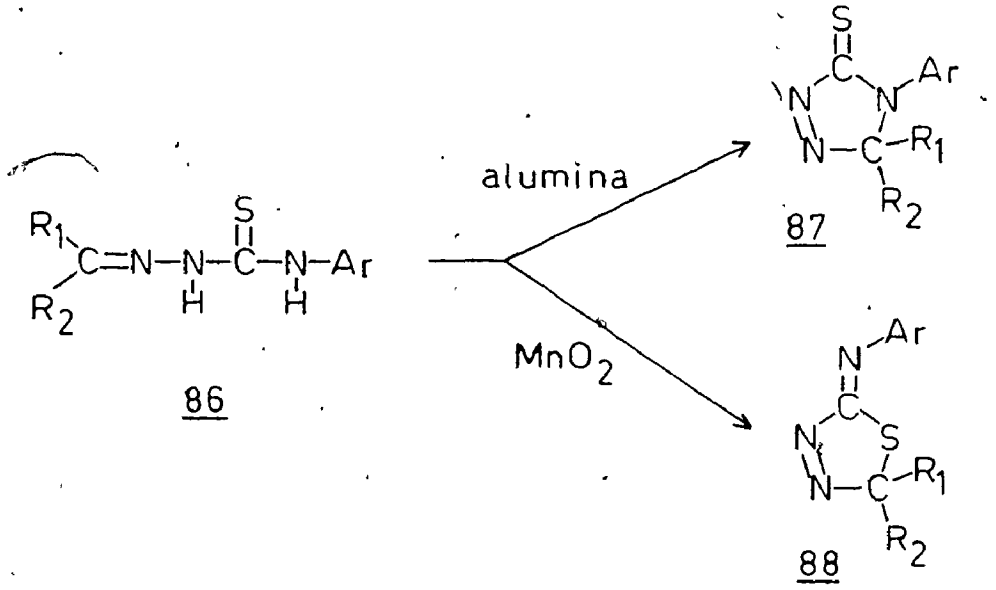
84

85

(37)

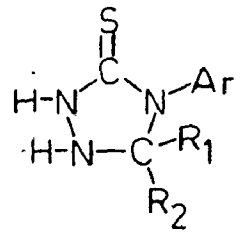
In 1970, Landquist[60] published a report on the oxidation of 4-methyl and 4-aryl ketothiosemicarbazones (86) and 4-aryl ketosemicarbazones. He used chromatographic basic alumina for cyclization and, from 4-substituted thiosemicarbazones (86), he obtained Δ^1-1,2,4-triazolin-5-thiones (87). When manganese dioxide was employed, 5-imino-Δ^3-1,3,4-thiadiazolines (88) were isolated (eq. (38)).

The formation of 87 was explained in terms of the initial formation of triazolidinethiones (89) from addition of the terminal nitrogen

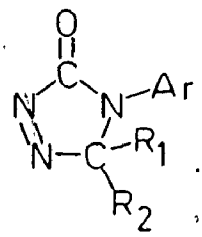


(38)

to the double bond in the thiosemicarbazone. This process was thought to be facilitated by the solid alumina, which held the thiosemicarbazone in a suitable configuration for closure. Then, oxidation by dissolved oxygen led to 87. The mechanism of the manganese dioxide cyclization was not indicated. The triazolinethiones (87) were converted to the triazolinones (90) with mercuric acetate. The latter were prepared independently from 4-substituted semicarbazones via alumina catalyzed oxidation.

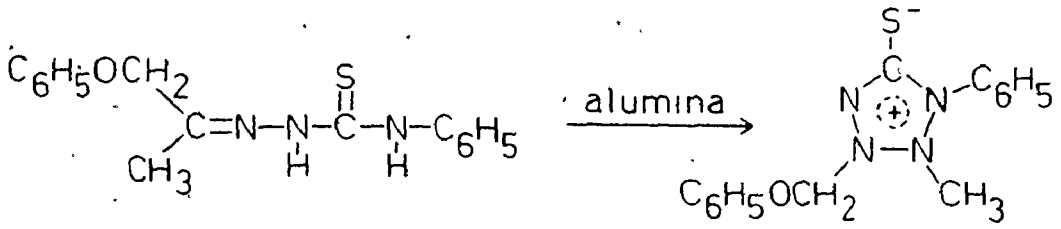


89



90

Landquist also reported[61] the oxidation of phenoxy-acetone-4-phenylthiosemicarbazone (91) on alumina and with manganese dioxide. Along with the expected products such as 87, 88, he isolated inner salt 92, which was proposed to arise from intermediate 89 through a 1,2-shift and oxidation.



(39)

91 92

II. THERMAL DECOMPOSITION OF AZO COMPOUNDS

A. Thermolysis of Azoalkanes and Pyrazolines

Azoalkanes have been used for many years as a convenient source of alkyl radicals, but there remains some doubt as to the nature of the initial mechanistic step involved in their thermolysis. The earliest work dealing directly with this matter was that of Ramsperger,[62] who compared the activation parameters of the unsymmetrical azoalkane R_1-N=N-R_2 (93) to those of the symmetrical azoalkanes, R_1-N=N-R_1 (94) and R_2-N=N-R_2 (95). He predicted that if the thermolysis occurs by simultaneous rupture of both bonds, then the activation energy of R_1-N=N-R_2 (93) should be the average of the activation energies of 94 and 95. That result was observed experimentally. Evidence for the simultaneous cleavage of both carbon-nitrogen bonds, as described by the reaction (40), was found in many other studies.[63-73] It was generally

$$\underset{93}{R_1\text{–}N{=}N\text{–}R_2} \longrightarrow R_1\cdot + N_2 + \cdot R_2 \qquad (40)$$

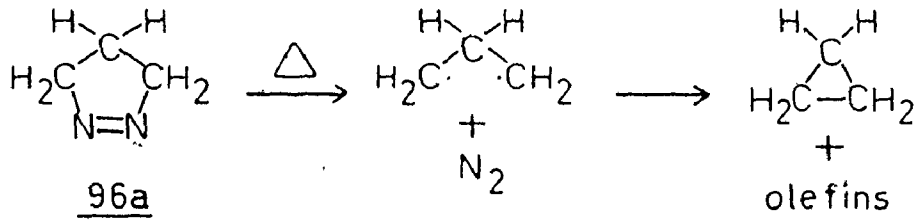
accepted that symmetrical azoalkanes react by the concerted cleavage of both carbon nitrogen bonds. The secondary deuterium kinetic isotope effect studies of Seltzer and coworkers[65,74,75] on the system R_1=R_2=Ph-CH(CH_3)- confirms this. However, studies of unsymmetrical azo-compounds such as R_1=Ph-CH(CH_3)-, R_2=CH_3 and $(CH_3)_2$CH-, revealed definite evidence to support the two-step process as written in equation (41).

$$R_1\text{—}N{=}N\text{—}R_2 \longrightarrow R_1\cdot + \cdot N{=}N\text{—}R_2 \longrightarrow R_1\cdot + N_2 + \cdot R_2 \quad (41)$$

93

Also Rüchardt[76] has published work indicative of symmetrical cleavage (eq. (40)), while Benson and O'Neal[77] have concluded that equation (41) best describes the mechanism for all azoalkanes examined in the gas phase.

Steric factors play an important role in the thermolysis of hindered and cyclic azocompounds.[78-82] Overberger and coworkers,[78-81] using a series of azonitriles, observed that substitution at the α-carbon gave an appreciable change in rate of decomposition. Similarly, Cohen et al.[83] have observed that, in changing the alkyl group in the symmetrical azoalkane $(C_6H_5\text{-}CHR\text{-}N)_2$ from methyl to ethyl to isobutyl, the thermolysis rate changes from 5.45×10^{-5} sec^{-1} to 2.35×10^{-5} sec^{-1} to 7.60×10^{-1} sec^{-1} at 100.4°C. The nature of the steric effects is well demonstrated by the difference in rates observed for diastereomeric azocompounds.[78,84] The thermal decomposition studies of 1-pyrazolines (96a) reported by Overberger and coworkers,[85] indicated that they decomposed much faster than the corresponding open-chain compounds. The enhanced rate is attributed to the weakening of the carbon-nitrogen bonds resulting from the ring constraint (eq. (42)).

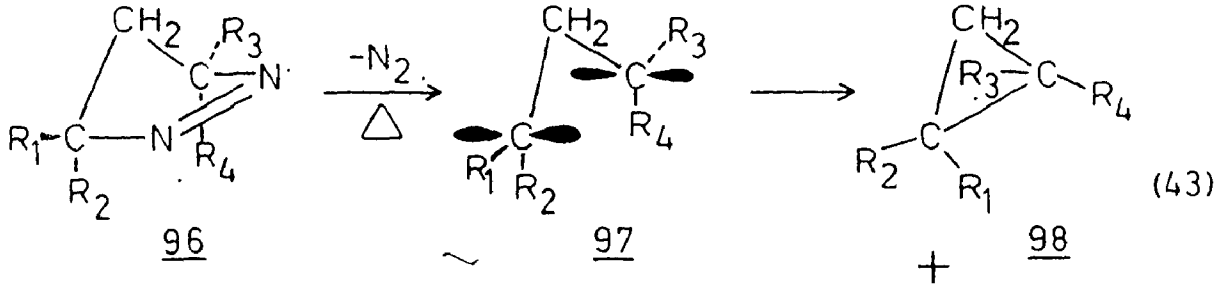


96a (42)

Overberger also found that the cis-3,5-disubstituted compounds decomposed much more rapidly than the corresponding trans-pyrazolines presumably due to the steric interactions in the ground state. The observation that the trans isomer decomposed stereospecifically to the corresponding trans-disubstituted cyclopropanes was rationalized in terms of the fast coupling of the intermediate radicals. The close proximity of the two radical moieties and the greater thermodynamic stability of the resulting cyclopropanes could be the source of the stereospecificity.[85] The observed enhanced rates of thermolysis and high stereospecificity in cyclic azocompounds has been taken as evidence for concertedness of the decomposition.[86-93] However, there is still some doubt about the mechanism involved in the thermolysis of pyrazolines.[94] It has been suggested by several authors[73,95] that that transition state for alkylpyrazolines is best represented as an extension of the normal mode of vibration and that even though kinetic evidence is available to suggest cleavage of the primary carbon-nitrogen bond, quite often a sufficient amount of bonding remains to influence the stereochemical distribution of the products.

Recently Clarke and coworkers[96] disputed the interpretation of work done previously.[63,95,97] They concluded that none of the mechanisms for pyrazoline decomposition considered before,[63,95,97] provides a satisfactory means of accounting for the product distribution. The surprisingly large fraction of optically active product formed from 96b shows that the percentage of product which must have been formed from chiral intermediates (by a pathway which avoids the planar

diradical 97) in 3,5-dialkylpyrazoline decomposition, has been previously underestimated.



(43)

96 ⇌ 97 + 98 + other products

(a) $R_1 = CH_3$, $R_3 = R_2 = H$, $R_4 = CH_2CH_3$

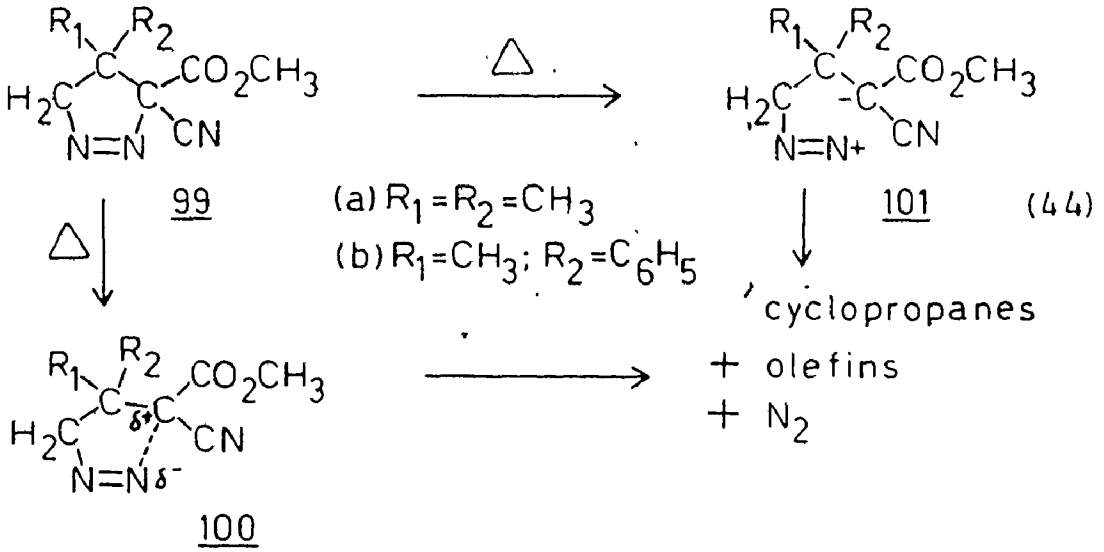
(b) $R_1 = CH_3$, $R_2 = R_4 = H$, $R_3 = CH_2CH_3$

The observation of an isotope effect on the optical purities of chiral product 98a supports this conclusion. It was suggested that competing mechanisms occurred in which diradicals 97 are the source of the achiral part of these product distributions and some other type of pathway accounts for the chiral part. According to Clarke, consideration of Inagaki and Fukui's suggestion[98] that the nitrogen may be eliminated from pyrazolines in a "nonlinear" fashion[99] and Salem and Goddard's prediction that pyramidal (i.e., "canted"[100] or "crabbed"[101]) diradicals can be important intermediates in these reactions, may provide some insight into the data. However, mechanisms generated using these hypotheses must at present be considered speculative. It is also possible (as Freeman and coworkers[102] have suggested) that a true understanding of these reactions will be obtained only after theoretical information on their energy surfaces and reaction dynamics becomes available.

A limited dynamic study of the cyclopropane isomerization has recently been published by Y. Jean and X. Chapuisat.[103] This theory could provide a rationalization for the different product-forming behaviour of "intermediates" generated in pyrazoline and cyclopropane thermolysis.[104,105] It also suggests that mechanistic pathways followed in pyrazoline decomposition will be very sensitive to even rather minor changes in substitution, as is experimentally observed.

The mechanisms discussed above are homolytic in nature and result in the formation of free radicals. However, unlike open-chain azocompounds, cyclic azocompounds sometime exhibit heterolytic bond fission. Thermal decomposition may go through dipolar intermediates depending on the electronegativity of the substituents on the carbons adjacent to the azo functions.[106-117]

McGreer and coworkers[106-112] have studied the thermolysis of a series of pyrazolines containing electron-withdrawing substituents (eq. (44)). It was observed[106] that 99a decomposes faster in polar

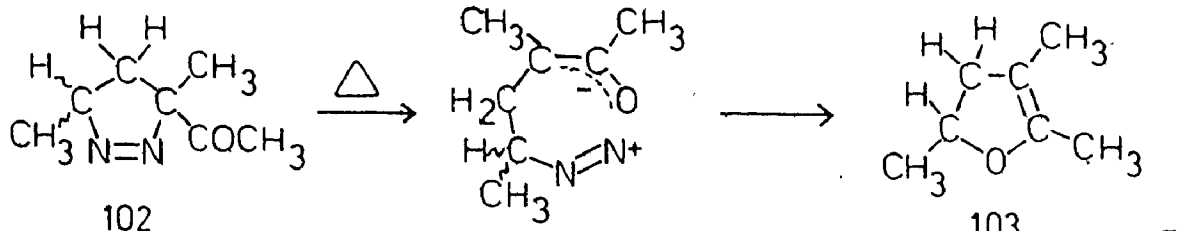


(44)

than in nonpolar solvents. The olefinic products formed must have arisen from the migration of methyl groups from C_4 to C_5 and the stereochemistry of the cyclopropanes formed was different from that in the pyrazolines. This led McGreer to the conclusion that an ionic intermediate 101, with complete ring opening, developed and that the methyl group migrates concurrent with nitrogen loss (eq. (44)). An independent study of Hamelin and Carrie confirmed these results.[113]

Thermolysis studies[110] of 99b showed that the decomposition occurs via a mechanism for which the transition state can be described by 100 in which bond breaking of the C_3 to N bond is well advanced over bond breaking of the N to C_5 bond. This structure has a greater polar character than the starting material, but less than the expected zwitterion 101.

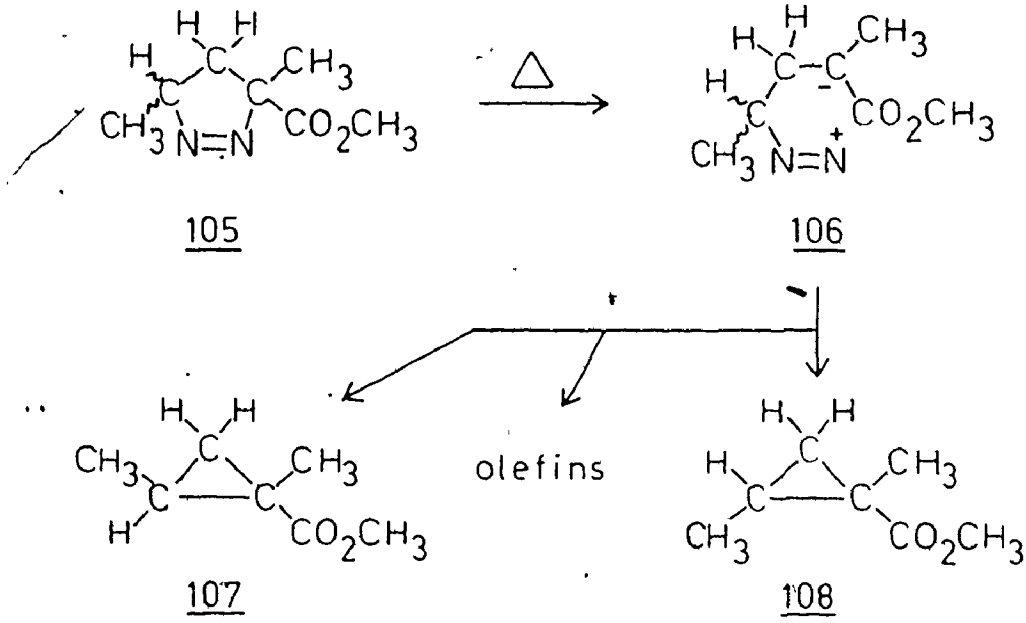
The pyrolysis of cis and trans 3-acetyl-3,5-dimethyl-1-pyrazoline (102) showed that the polarity of the solvent had only a small effect on the rate of decomposition. However, analysis of the products from the isomeric pyrazolines indicated many differences. The cis isomer gave up to 32% of the dihydrofuran (103) (depending on the solvent



102 → 104 → 103 + olefins + cyclopropanes (45)

polarity), formed presumably through the zwitterionic intermediate (104), while the thermolysis of the trans isomer yielded little of 103. The authors[107] suggested a dipolar transition state in which negative charge is delocalized over the carbonyl function and thus oxygen can participate in a ring closure. The intermediate 104 cannot have free rotation around the C_3-C_4 bond and therefore there is some bonding between C_3 and N in the transition state. Ring closure is either concerted with loss of nitrogen or occurs in a subsequent fast step.

A similar study[108] was made of the pyrolysis of cis and trans-3-carbomethoxy-3,5-dimethyl-1-pyrazoline (105) (eq. (46)). The rates of



105 106 107 108 (46)

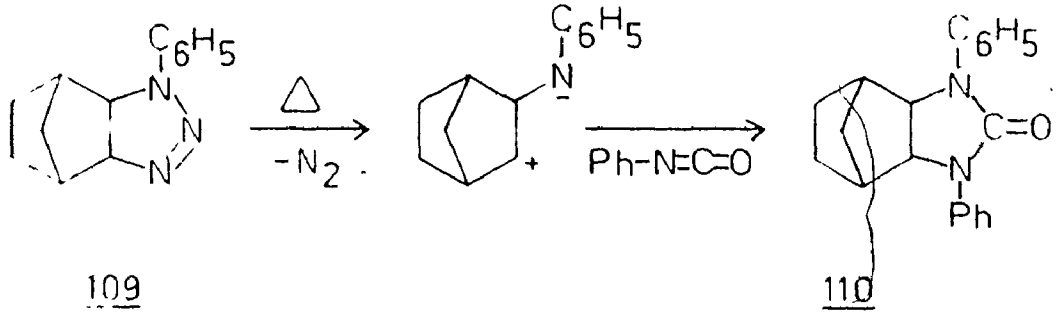
decomposition were not enhanced by polar solvents, nor was methyl methacrylate found in the product mixture. This suggested the absence of any zwitterionic character, such as 106, in the transition state. However, since both cyclopropanes were formed (107 and 108), concerted loss of

nitrogen could not be operative either. McGreer favoured a series of transition states similar to those proposed for open-chain azocompounds. Depending on the ring substituents, the mechanism of thermolysis can range from fully concerted loss of nitrogen to heterolytic bond fission giving a zwitterionic intermediate.[106,109,112] Similar conclusions were reached by Danion-Bougot and Carrie[117] from a study of the pyrolysis of some 1-pyrazolines disubstituted at C_3 with electrophilic groups.

Comprehensive mechanisms including all of the 1-pyrazolines thermolysis studied to-date are not available. The application of mechanistic proposals for new azocompounds must therefore be approached with caution.

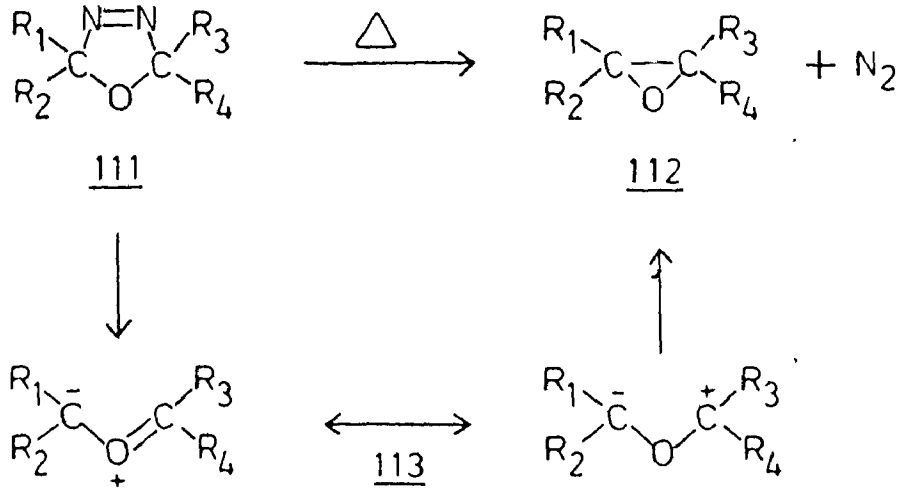
B. Thermal Decomposition of Cyclic Azo Systems Containing Another Heteroatom in the Ring

The pyrolysis of heterocyclic compounds containing the azo function attached to one carbon and to one heteroatom, would be expected to have polar character. Huisgen[118,119] performed a series of experiments on the decomposition of several Δ^2-1,2,3-triazolines in the presence of phenylisocyanate or phenylisothiocyanate. From the products obtained, it was concluded that the decomposition proceeds through a 1,3-dipolar intermediate and is followed by a 1,3-dipolar cycloaddition. For example, the norbornene phenylazide adduct (109) and phenylisocyanate react at 150 °C to give nitrogen and symmetrical urea (110) as given in equation (47).



109 110 (47)

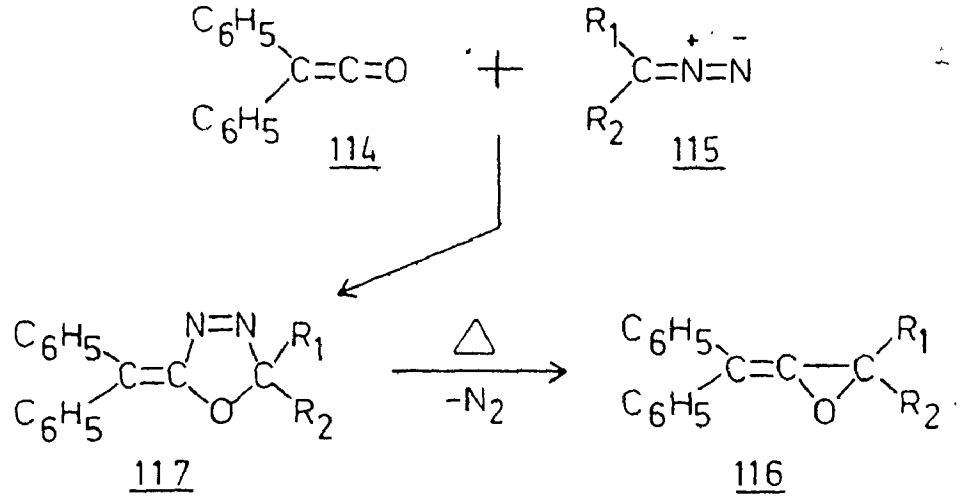
Thermolysis of five-membered heterocyclic rings, where the azo group is not directly attached to the heteroatom (namely oxygen and sulphur) can give products similar to those formed from decomposition of triazolines or more complex mechanisms can be involved. The oxadiazolines, such as 111, were found[6,120,121] to decompose thermally giving epoxides (112) (eq.(48)).



(48)

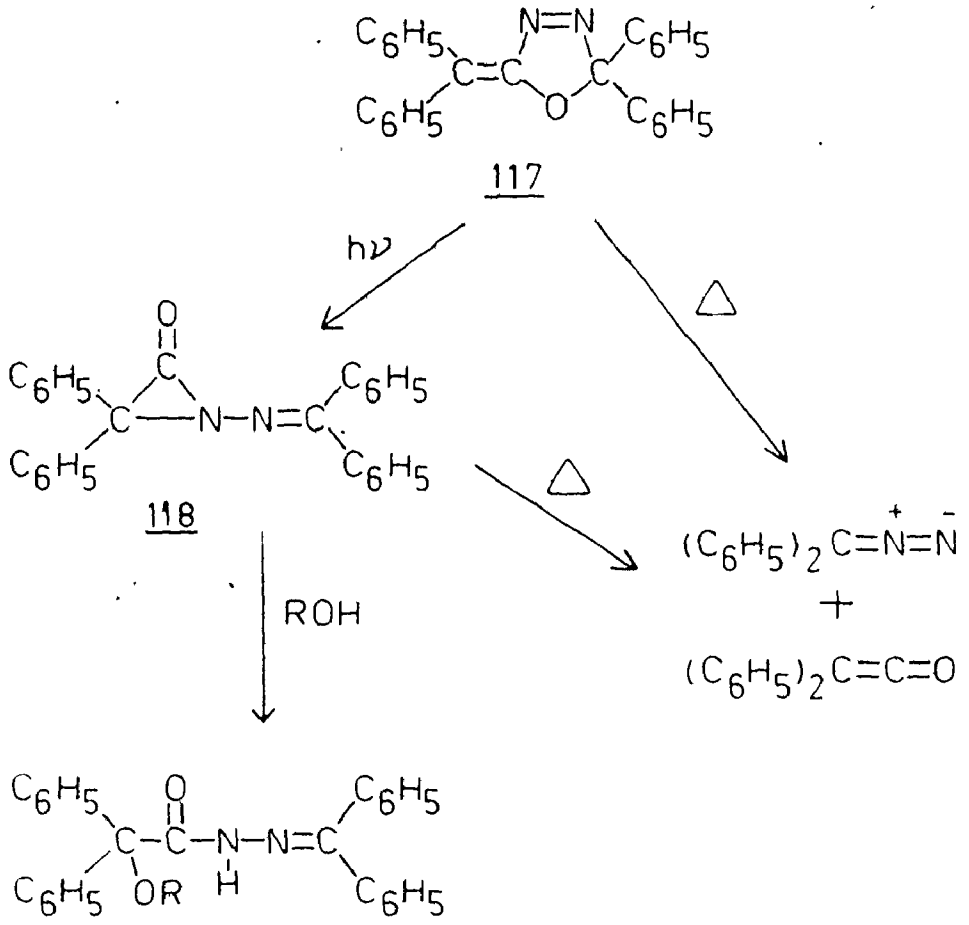
The decomposition of 111 (R_3 = C_6H_5, R_4 = OAc) to 112 was explained[121] by postulating a carbonyl-ylide intermediate 113, formed by loss of nitrogen from 111, which subsequently closed to give 112. The existence of 113 was confirmed by trapping experiments with norbornene and dimethylacetylene dicarboxylate.

In 1921 Staudinger and Reber[122] reacted diphenylketene (114) with several diazomethane derivatives (115). They isolated the epoxides (116) as the major products and suggested that 116 might arise from the intermediate Δ^3-1,3,4-oxadiazoline (117) as shown in equation (49).



(49)

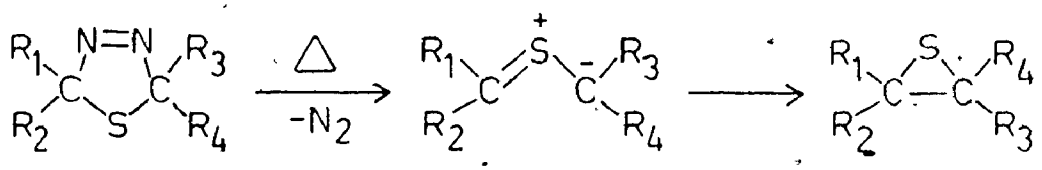
Later, Michejda[123] studied the photolysis and thermolysis of 2,2-diphenylmethylene-Δ^3-1,3,4-oxadiazoline (117, $R_1=R_2=C_6H_5$). According to Michejda, the products, ketene and diazoalkane, were formed from an intermediate α-lactam (118) which was trapped by doing the photolysis in the presence of hydroxylic compounds (eq. (50)).



(50)

Even mild thermolysis of the Δ^3-1,3,4-thiadiazoline ring system (119) releases nitrogen and yields[124-130] thiiranes (120). The proposed

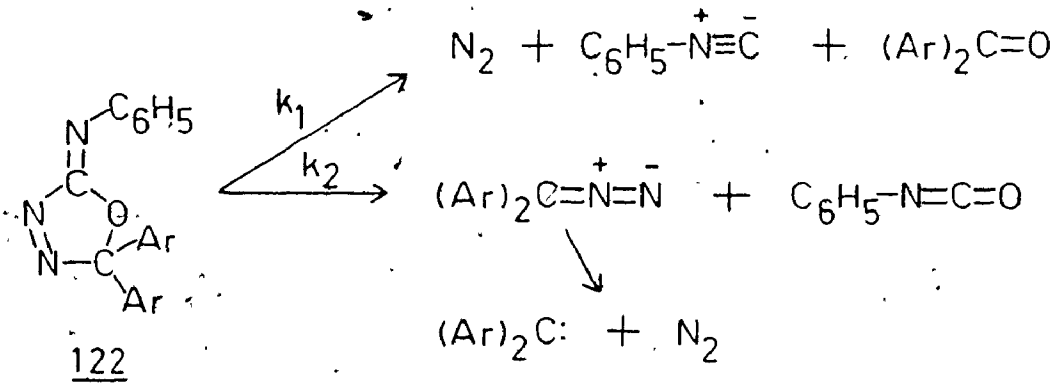
mechanism involves the intermediate thiocarbonyl-ylide (121). Kellogg and coworkers[127-130] found that the reaction obeys the Woodward-Hoffman rules. The predicted conrotatory ring closure occurred with 121 giving thiirane (120) in 100% yield and 100% stereospecificity (eq. (51)). Cycloaddition of 121 occurred with retention of configuration as predicted. The thiocarbonyl ylide 121, generated as a reactive and short-lived intermediate, was trapped by a dialkylazodicarboxylate.



(51)

119 121 120

Warkentin and coworkers[23,26,27,131-134] have investigated the decomposition of a series of Δ^3-1,3,4-oxadiazolines and Δ^3-1,3,4-oxadiazolinones. The thermolysis of 5,5-diaryl-2-(phenylimino)-Δ^3-1,3,4-oxadiazolines (122) followed two parallel first-order processes, as shown below (eq. (52)).

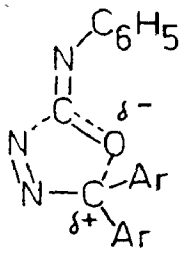


(52)

122

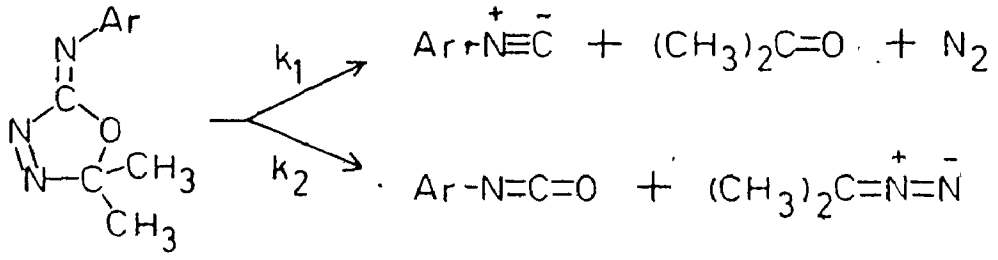
The products other than nitrogen were characterized by their isolation from a partially decomposed sample of oxadiazoline; their melting points and spectra were then compared with those of authentic materials.

Kinetic analysis of this thermolysis required two approaches:
(a) the rate of total nitrogen evolution was determined and
(b) the diazomethane concentration was followed by an infrared technique. Thus the values for both k_1 and k_2 were obtained. West and Warkentin[26] observed that the ratio of the two decomposition pathways was altered when the nature of the aryl group attached to C_5 was changed from electron-donating to electron-withdrawing. A modification of the Hammett equation was used to correlate the rate data. Only three substituted oxadiazolines were available, nevertheless, an approximate value of $\rho = +0.62$ (for pathway with k_1) indicated that electron withdrawing substituents enhanced the rate of decomposition slightly. Because of the limited correlation made, the authors felt that no conclusions, other than the fact that C_5-N bond was breaking in the rate determining step, could be drawn. The magnitude of ρ suggested that there was no full development of charge in the transition state and thus the bond breaking was thought to be a homolytic process. A correlation of structure and rate of decomposition via the retro-1,3-addition reaction (k_2), using the modified Hammett relation of Tsuno and Yukawa[135] gave a ρ value of -1.31. The conclusion drawn in this case was that considerably less positive charge was developed at the decomposition transition state of 51 than in solvolysis of cumyl chlorides. Transition state 123 was suggested, but no conclusion about the extent of C-N bond breaking could be drawn.



123

The pyrolysis of 5,5-dimethyl-2-(arylimino)-Δ^3-1,3,4-oxadiazolines (124) showed[23] that they were thermally more stable than the diaryloxadiazolines (122). Their decomposition in bromobenzene at 150°C led to products similar to those encountered[26] in the decomposition of 5,5-diaryl-2-phenylimino-Δ^3-1,3,4-oxadiazolines (122) (eq. (53)).



(53)

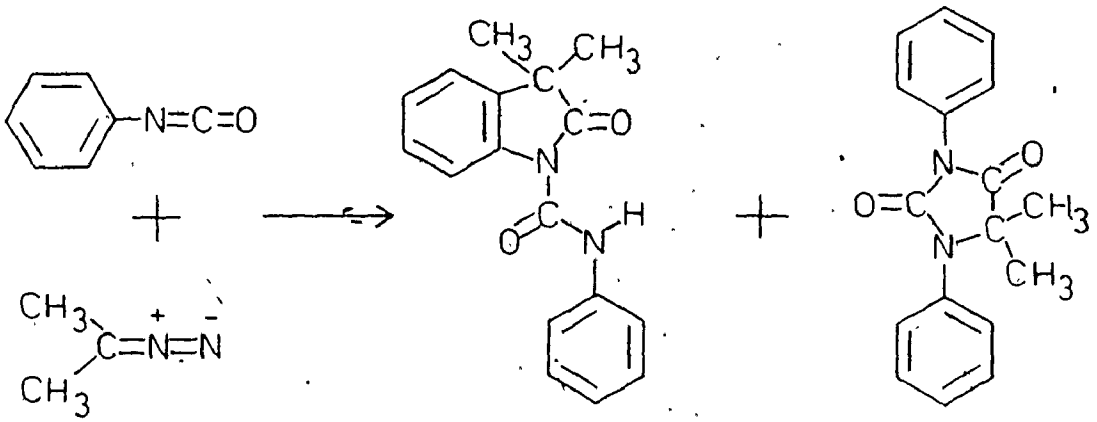
124

However, only acetone and arylisocyanate were positively identified in the infrared spectra. The diazomethane as well as arylisocyanide

could not be detected using the infrared technique, although the characteristic odour of isocyanide was detectable, indicating a low concentration to be present. Kinetic measurements of pyrolysis gave a value for $(k_1 + k_2)$ of 7.63×10^{-4} sec^{-1} at 150°C, using a gas evolution method. The formation of phenylisocyanate, followed by the intensity of the isocyanate absorption at 2256 cm^{-1} in the infrared region, was surprisingly not first order. It was observed that the isocyanate concentration rose to 23% of the theoretical maximum, then decreased.

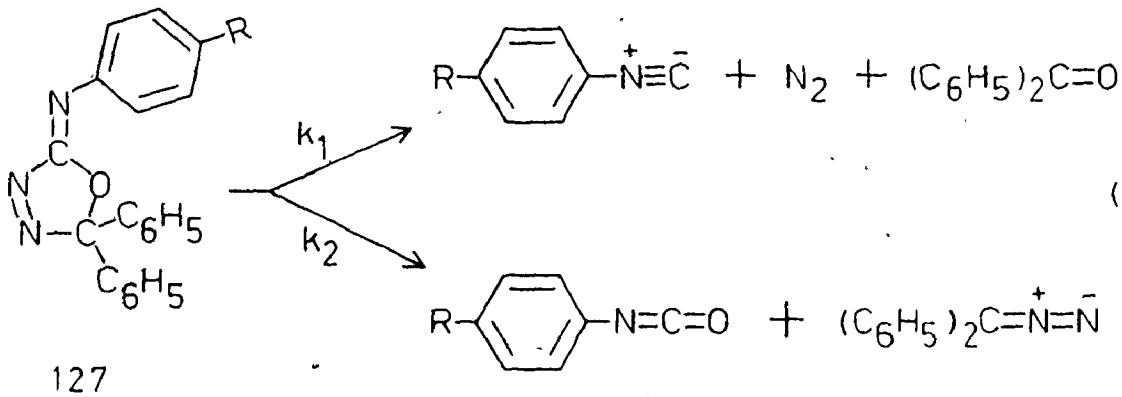
Later studies[134] of the thermolysis of 124 in the presence of an excess of phenylisocyanate indicated that other products (e.g., 125 and 126) were formed from the subsequent reaction of phenylisocyanate and diazomethane (eq. (54)).

(54)



125 126

Cameron[23] also investigated the effect of changing the substituents of the exocyclic aryl group on the rates and products of the thermolysis of 127. The two modes of decomposition are given below (eq. (55)).

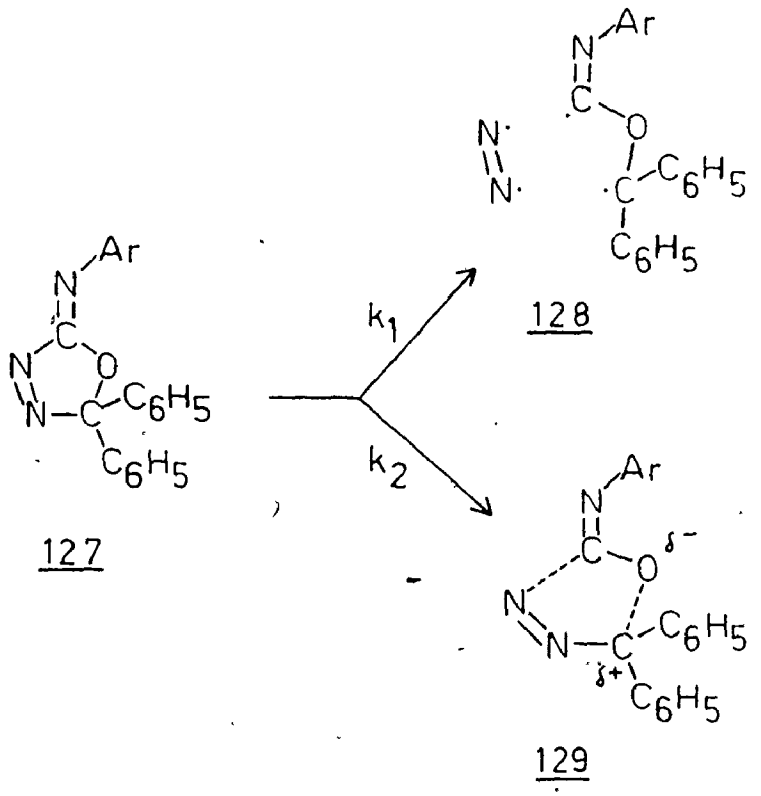


(55)

127

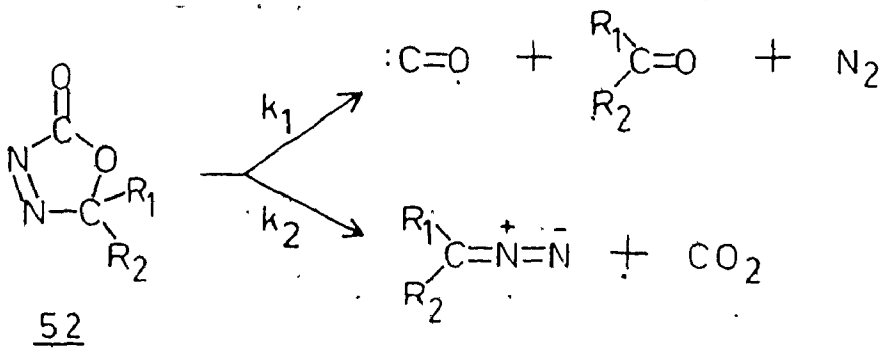
Both pathways were kinetically first order and the rates of the reaction were correlated with σ by the Hammett relation. The ρ value for the formation of benzophenone was +1.0 and for the formation of isocyanate was +1.1. These results, together with the solvent effect experiments, led to the conclusion that a homolytic process (transition state 128) is likely in the decomposition pathway with k_1 as shown in equation (56). The transition state for the retro-1,3-dipolar addition (k_2) appeared to be more ionic than the starting material. This confirmed the previously suggested transition state by West,[26] where the extent of C-N bond cleavage is most likely smaller than that of C-O bond cleavage.

Similarly,[133] two parallel first order processes occur in the thermal decomposition of 5,5-dialkyl-Δ^3-1,3,4-oxadiazolin-2-ones (52) obtained from corresponding 2-imino-Δ^3-1,3,4-oxadiazolines by acid catalyzed



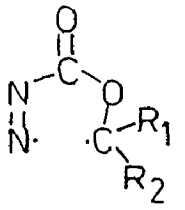
(56)

hydrolysis.[21,136,137] One of the processes results in the formation of a ketone, nitrogen and carbon monoxide while the other leads to the appropriate diazoalkane and carbon dioxide (eq. (57)).

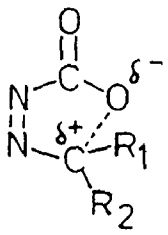


(57)

The production of a ketone (k_1) was thought to involve a diradical-like 130, rather than a dipolar transition state, since changing the solvent from carbon tetrachloride to methanol had little effect on the magnitude of k_1. However, a concerted process involving two or three bonds could



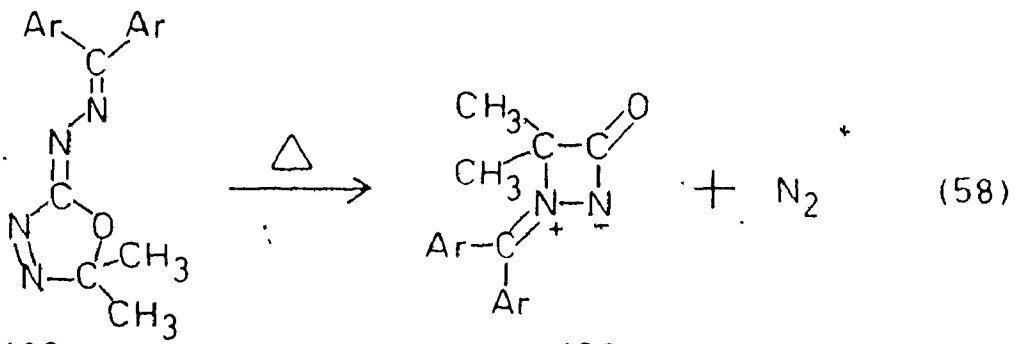
130



131

not be ruled out on the basis of the available evidence. In contrast, changing the polarity of solvent caused a large increase in k_2 and therefore the production of carbon dioxide and diazoalkane was judged to involve a more polar transition state 131. Again, a concerted process for the decomposition could not be ruled out.

Work[131,138] on the pyrolysis of 5,5-dimethyl-2-(hydrazono)-Δ^3-1,3,4-oxadiazolines (132) led to the four-membered azomethine imine ylids (133) in about 40% yield (eq. (58)).

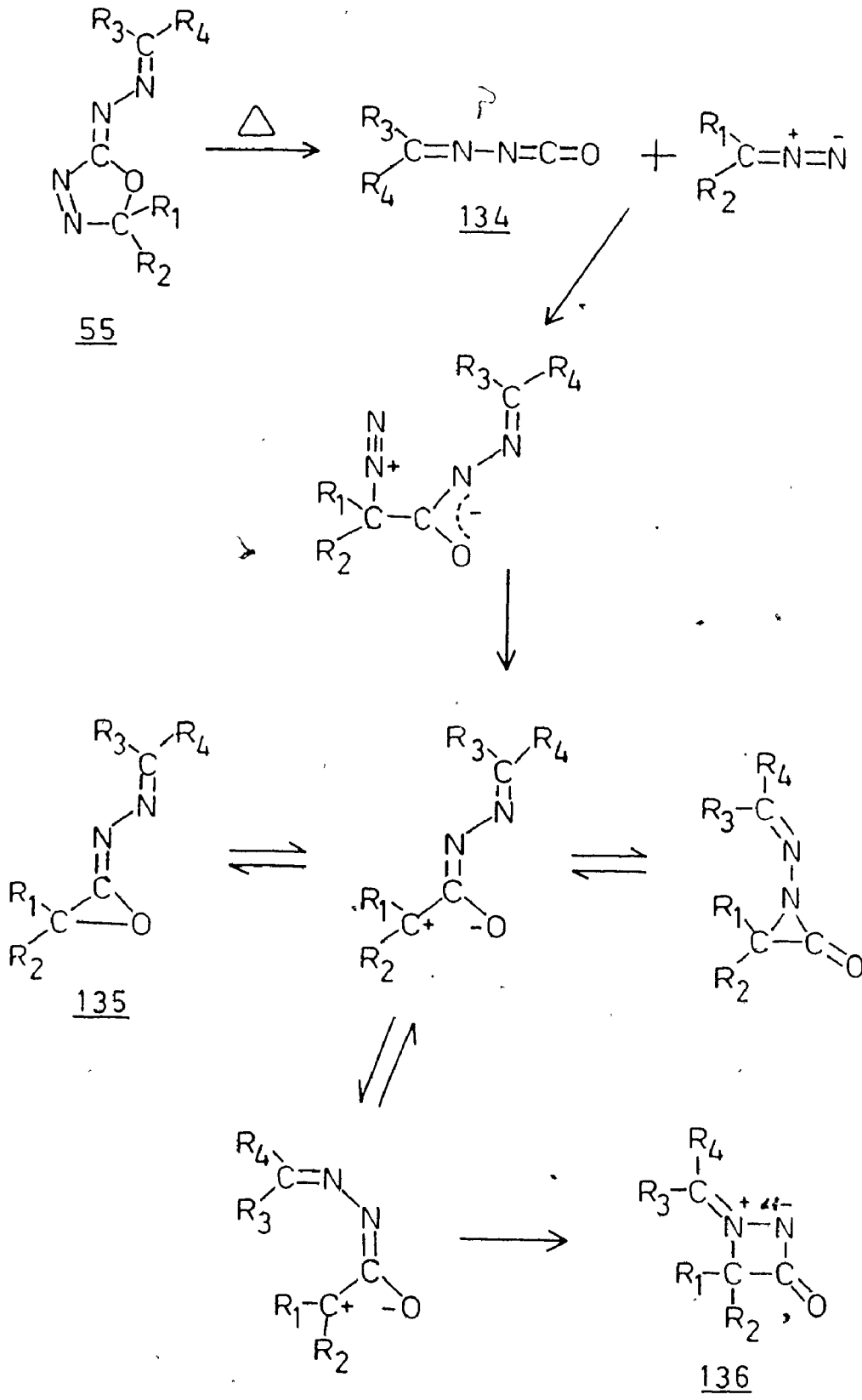


132 133 (58)

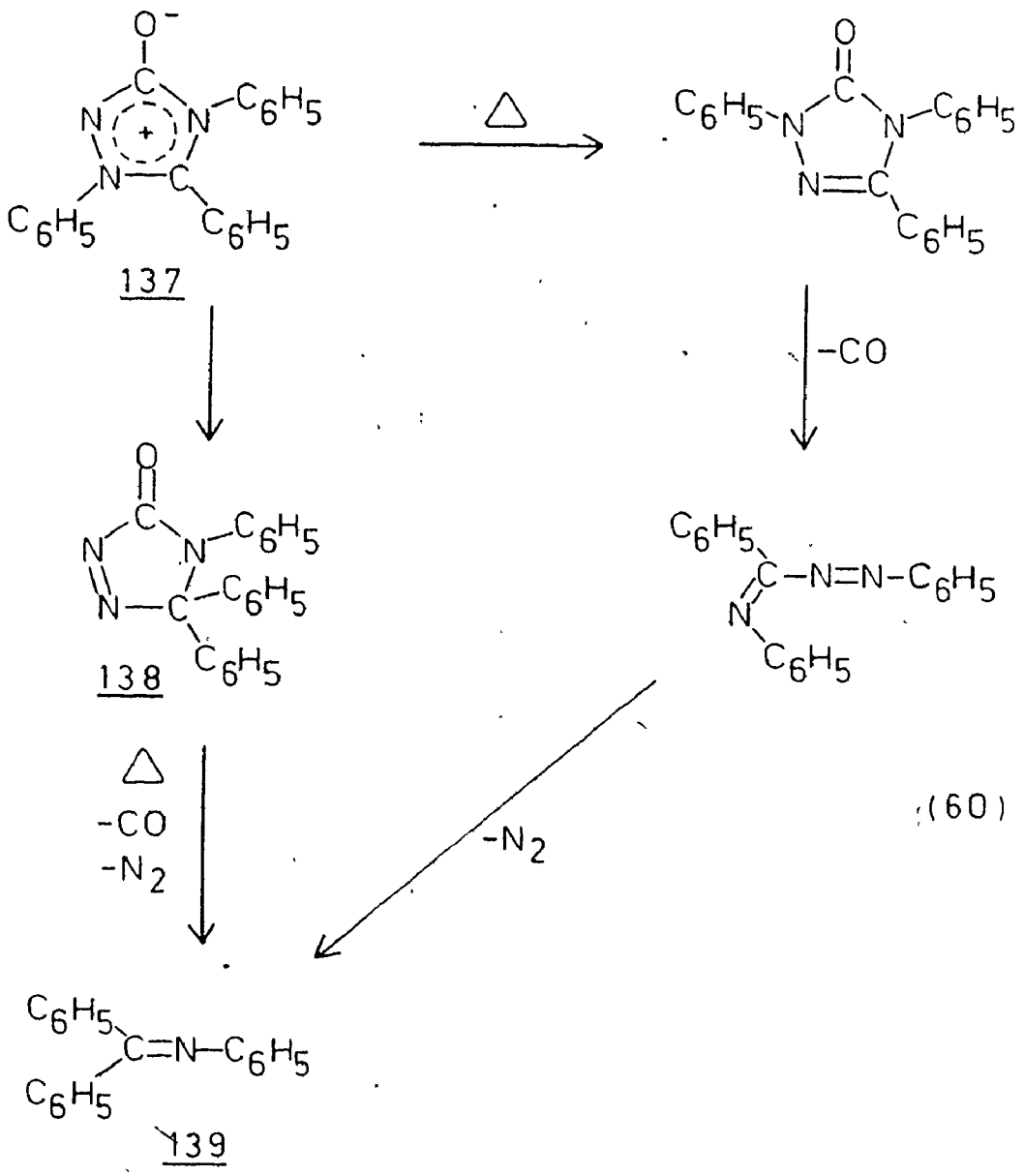
The proposed[138] mechanism involved the formation of N-isocyanatoimine (134) and, perhaps, iminooxirane (135) by analogy to the known thermal decomposition of 1-pyrazolines to cyclopropanes[106-108] as shown in equation (59).

As it was not possible to isolate and characterize the intermediates involved in this process, experiments were carried out to trap them chemically. Trapping experiments with phenylisocyanate and phenylisothiocyanate established the presence of an N-isocyanatoimine intermediate (134) during the pyrolysis.

Pyrolysis of azo compounds, with heteroatom (nitrogen) not directly attached to the azo group has not been studied in great detail. Recent work of Kato and coworkers[139] deals also with the thermolysis of the triphenyltriazolone (137) at 350°C and the proposed mechanism which accounts for the products included intermediate triazolinone (138) as described in equation (60). The g.l.c. analysis showed the presence of N-(diphenylmethylen)-aniline (139), but in no case was fragmentation into phenylisocyanate detected.



(59)



(60)

EXPERIMENTAL

The experimental section has been divided into three parts. The first part deals with the synthesis of several new triazolines. The second part describes the kinetic procedures used in the study of the thermal decomposition of 3,3-dimethyl-4-phenyl-5-phenylimino-Δ^1-1,2,4-triazoline (140a), 3,3-dimethyl-4-phenyl-Δ^1-1,2,4-triazolin-5-ones (141a,b,c,d,e) and 3,3-dimethyl-4-phenyl-Δ^1-1,2,4-triazoline-5-thione (142). The third section describes photochemical studies of 141a.

GENERAL

The proton magnetic resonance spectra were recorded on Varian Associates Models HA-100, T-60, or EM-390 spectrometers, using deuteriochloroform as the solvent (unless otherwise indicated) and the resonances are reported in parts per million (δ) from tetramethylsilane (TMS), the internal standard for both ^1H and ^{13}C spectra. Spectra are reported in the format: chemical shift, multiplicity (s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet), and relative integral. The ^{13}C magnetic resonance spectra were recorded on a Brüker WH-90 instrument.

The infrared spectra were recorded on Perkin-Elmer Models 521, 337, or 283 and Beckman IR-5 spectrophotometers. The spectra were run in carbon tetrachloride solutions in 0.1 mm sodium chloride or potassium bromide cells, and the data are presented in reciprocal centimeters referred to polystyrene bands at 1601 and 1984.5 cm^{-1}.

Ultraviolet spectra were obtained on a Cary Model 14 spectrophotometer using quartz cells with 95% ethanol (spectroscopic grade) as the solvent and the data are given in nanometers, followed by a bracketed number describing log ε.

Gas chromatographic analyses were done on a Varian Aerograph A90-P3 instrument using a 5' x 1/4", 15% SE 30 on 60-80 mesh chromosorb P column at 65°C and flow rate 50-60 ml/min of the carrier gas, helium.

The high resolution mass spectra were obtained on a Consolidated Electrodynamics Inc. Model 21-110b instrument. Gas samples were analysed on the Hitachi-Perkin Elmer Model RMV-6A mass spectrometer.

Melting points were determined on a Thomas-Hoover Unimelt Capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

SOLVENTS

Benzene and toluene (Mallinckrodt Anal. Reagent) were heated with concentrated sulfuric acid, washed several times with water, and dried with calcium chloride. Decanted liquids were then refluxed for 2 hrs. with sodium wire present and redistilled. Fractions of 80-81°C (for benzene) and 110-111°C (for toluene), respectively, were collected. Purified solvents were kept in dark bottles over Molecular sieves (BDH Chemicals).

Chlorobenzene (Fisher Certified Reagent) was shaken repeatedly with portions of sulfuric acid until the acid was no longer coloured. It was washed with water and with 0.1 N potassium bicarbonate solution, dried with calcium chloride and fractionally distilled. The fraction

boiling at 130-131°C was redried over phosphorus pentoxide and again distilled.

Chloroform (Mallinckrodt, Anal. Reagent) was washed with H_2SO_4, dilute sodium carbonate solution (0.1 N) and water. It was dried, first with calcium chloride and then over P_2O_5, and distilled twice. It was kept in a dark bottle over $CaCl_2$.

Methylene chloride (J. T. Baker Anal. Reagent) was washed with water and sodium carbonate solution, refluxed overnight over calcium chloride and distilled at 40°C.

Nitrobenzene (BDH Chemicals, Anal. Reagent) was dried with phosphorus pentoxide and distilled under reduced pressure. It was kept in a dark bottle over molecular sieves.

Light petroleum ether (Mallinckrodt Anal. Reagent, boiling range 30-60°C) was distilled and the fraction boiling between 30-40°C was used for column chromatography.

A. SYNTHESES

Lead tetraacetate

The method of Fieser[140] was employed here. A solution of 600 ml of glacial acetic acid (CIL, C. P. reagent) and 400 ml of acetic anhydride (BDH analytical reagent) was transferred to a three-necked, three-liter, round bottom flask and placed in an oil bath which was maintained at 55-80°C. The mixture was continuously stirred with a mechanical stirrer, as red lead oxide (lead tetraoxide, 700 g, 1.03 mol) was added in approximately 20 g lots. A new addition was made only after the orange colour from the previous addition had disappeared. After the addition of lead tetraoxide was completed (~ 10 hrs), the brownish reaction mixture was cooled to room temperature and the crude product was filtered, washed with cold acetic acid and recrystallized from hot acetic acid. The product obtained in 78% yield was kept in a dark bottle in the refrigerator.

3,3-Dimethyl-5-imino-Δ^1-1,2,4-triazoline (143)

The synthesis consists of two steps. Firstly, acetone guanylhydrazone acetate (144) was prepared by a slightly modified version of the method of Baiocchi et al.[141] To a solution of 30 g (0.33 mol) of aminoguanidine bicarbonate (Eastman) in 75 ml of water was added slowly 30 ml of acetic acid (25 g, 0.44 mol) until the pH of the solution was less than 7. The solution was filtered to remove trace amounts of insoluble solids. The acidic filtrate was heated to ca. 60°C, acetone (13 g, 0.22 mol) was slowly added and solution was left stirring at room temperature for about 16 hrs. The crude product was filtered off and recrystallized from 95% ethanol yielding 30 g (78%) of 144 as white

crystals, m.p. 221-222°C (lit[141] m.p. 222°C).

Acetone guanylhydrazone acetate (1.7 g, 0.01 mol) in 75 ml of methylene chloride was cooled to 0°C in an ice bath. Anhydrous sodium carbonate (2.1 g, 0.025 mol) was added to the solution and the mixture was left stirring in the ice bath under dry nitrogen for about 3 hr. Lead tetraacetate was washed with petroleum ether (Mallinckrodt Anal. Reagent, 30-60°C) and added (2.2 g, 5 mmol) to the reaction mixture, which turned yellow. The slurry was stirred for about 10 minutes and then a cold solution of $NaHCO_3$ (Fisher Certified Reagent) in water (5.0 g in 20 ml of water) was quickly poured into the reaction mixture. A dark brown slush was formed, which was stirred for an additional 15 minutes and then filtered through Celite (Johns-Manville, 535). The organic layer was separated, washed three times with ice water, and dried over magnesium sulfate. The evaporation of methylene chloride at ~ 10°C using a rotary evaporator gave a white solid as the crude product. Sublimation of the crude material at room temperature and 10^{-2} Torr yielded 0.25 g (28%) of crystalline 143, m.p. 70°C (d).
I.r.: ν_{NH} 3550, 3490 and $\nu_{C=N}$ 1680 cm^{-1} (s), pmr δ 1.5 (s), uv λ_{max} 285 (2.375). Anal. calcd. for $C_4H_8N_4$: C 42.86, H 7.16, N 50.00. Found: C 42.80, H 7.09, N 50.11.

Oxidation of 144 with Br_2 instead of LTA gave 143 in lower yield. Acetone guanylhydrazone acetate (1.7 g, 0.01 mol) in 50 ml of methanol was stirred in an ice bath with anhydrous sodium carbonate (2.1 g, 0.025 mol) for about 1 hr. Bromine (0.6 g, 7.5 mmol) was then added dropwise to the reaction mixture, which turned yellow. After 15 minutes of stirring, excess of sodium carbonate was filtered off, filtrate was evaporated to

dryness and to the residue, 25 ml of ether and 25 ml of water were added. The mixture was shaken several times, the ether layer was separated, washed with water and dried over anhydrous calcium chloride. The excess of ether was evaporated and the residue was sublimed at room temperature and 10^{-2} Torr, giving 0.15 g (17%) of white 143, m.p. 70°C (d). I.r.: ν_{NH} 3550, 3490 and $\nu_{C=N}$ 1680 cm^{-1} (s), pmr δ 1.5 (s), uv λ_{max} 285 (2.374).

3-Amino-5-methyl-1-phenyl-1,2,4-triazole (145)

Acetophenone guanylhydrazone acetate (146) was prepared by modified procedure of Baiocchi.[141] Acetic acid (30 ml, 0.44 mol) was slowly added to a solution of aminoguanidine bicarbonate (30 g, 0.22 mol in 75 ml of water) and then the solution was filtered to remove impurities. The filtrate was warmed up to ca. 60°C and after addition of acetophenone (26.4 g, 0.22 mol), it was left stirring at room temperature for 24 hrs. The crude product was filtered off and recrystallized from 95% ethanol giving 36 g (69%) of 146 as white needles, m.p. 208-209°C (lit[141] 207-209°C).

The solution of 146 (2.4 g, 0.01 mol) in 75 ml of methylene chloride was cooled to 0°C in an ice bath. After addition of anhydrous sodium carbonate (2.1 g, 0.025 mol), the mixture was left stirring under dry nitrogen for about 3 hrs. Lead tetraacetate (2.2 g, 5 mmol), washed with petroleum ether prior to use, was added and the reaction mixture was stirred for 15 minutes. A cold solution of $NaHCO_3$ (5 g in 20 ml of water) was poured into the vessel; the brown slurry was stirred for an additional 15 minutes and then filtered through Celite. The organic layer was separated, washed three times with ice water, and dried over

magnesium sulfate. The methylene chloride was removed with a rotary evaporator and crude material was purified by column chromatography using silica gel (J.T. Baker, 80-200 mesh) and a solution of petroleum ether (30-60°) in ether (1:1). Recrystallization from methanol yielded 0.5 g (36%) of 145, m.p. 185-186° (lit[142,143] 186°C).

I.r.: ν_{NH} 3500 and 3400 (m), 1650 and 1598 (s) cm^{-1} (lit[142] 3320, 3185, 1650, 1598 cm^{-1}). Pmr: δ 2.4 (s,3H), 7.2-7.45 (m) and 7.7-7.9 (m) (together 5H), 4.3 (s,broad,1H); ^{13}Cmr: δ 160.6, 150.1, 141.8, 128.7, 128.2, 126.5, 13.6; uv: λ_{max} 315 (3.51), 265 (3.63), 235 (4.11); m/e (mol ion) 174. Anal. calcd. for $C_9H_{10}N_4$: C 62.07, H 5.75, N 32.18. Found: C 61.83, H 6.29, N 31.99. (Two ν_{max} reported in literature[142] were not observed in the ir spectrum of 145 and it was assumed that they are due to impurities.)

Third fraction from the column contained 0.4 g (29%) of acetophenone azine, yellow crystals melting at 119-120°C (lit[157] 121°C, lit[158] 122-124°C).

Ir: ν_{max} 1620 and 1580 cm^{-1}, pmr: δ 2.25 (s,3H), 7.3-7.9 (m,5H) (lit[158] δ 2.30 (s,3H, 7.25-7.55, 7.89 (m,5H)). ^{13}Cmr: δ 157.8, 138.6, 129.7, 128.4, 126.7, 15.02. Anal. calcd. for $C_{16}H_{16}N_2$: C 81.36, H 6.78, N 11.86. Found: C 82.05, H 7.01, N 11.25. The lack of correlation between the C, H, N analyses or melting point with the structure may be attributed to impurities in the sample. Mixture m.p. with authentic sample (120-121°) was 119-121°C.

3,3-Dimethyl-4-phenyl-5-phenylimino-Δ^1-1,2,4-triazolines (140a,b)

(i) The acetone-4-phenyl-thiosemicarbazone (147) required in the

synthesis was prepared according to the method of Wilson and Burns[144] by heating under reflux 30 g of 4-phenyl-thiosemicarbazide (Eastman) with 175 ml of 95% ethanol and 70 ml of acetone until solution was effected. On cooling, the thiosemicarbazone (147) separated in a pure state, melting at 178-179°C (lit.[144,145] 179°C). The yield was 78%.

(ii) Methylation of 147 was achieved by a modified version of Kirsten and Smith's[146] method of methylation of thioureas. The solution of 147 (21 g, 0.1 mol) in 200 ml of absolute ethanol was cooled to 0°C in an ice bath and then methyl iodide (15 g, 0.1 mol) was added quickly. The flask was stoppered tightly and left stirring in an ice bath for 3 hrs. After this period of time, the mixture in the tightly-sealed flask was left stirring for an additional 12 hrs at room temperature. During this period, the white suspension turned into a clear yellow solution. The bulk of the ethanol was evaporated on a rotary evaporator and the resulting viscous yellow oil was purified by column chromatography, using silica gel (J.T. Baker, 80-200 mesh). The second fraction (1:1 petroleum ether/CCl_4) contained purified S-methyl-4-phenyl-acetone thiosemicarbazone iodide (148), which, after recrystallization gave 16.5 g (79%) of white crystals melting at 43-44°C. Pmr: δ 2.05 (s,3H), 2.10 (s,3H), 2.4 (s,3H), 7.25 (s,broad, 5H), 8.20 (s,broad,1H).

(iii) Again, the procedure of Kirsten and Smith[146] was modified to prepare 1,3-diphenyl-2-(isopropylideneamino)-guanidinium iodide (149). The product (148), prepared in the previous step, was dissolved (18 g, 0.05 mol) in 50 ml of dry benzene and redistilled aniline (BDH Reagent,

4.65 g, 0.05 mol) was added. The mixture was placed on a steam bath under an air condenser for approximately 24 hr, or until the smell of methanethiol ceased. The excess of benzene was removed with a rotary evaporator and the crude syrupy material was used directly in the next step (yield 87%).

(iv) About 4.0 g (0.01 mol) of 149 was dissolved in 75 ml of methylene chloride and cooled to 0°C in an ice bath. While stirring under a stream of nitrogen, 1.0 g (0.012 mol) of anhydrous Na_2CO_3 (Fisher Certified Reagent) was added and left stirring for 2 hr. Lead tetraacetate (3.3 g, 7.5 mmol) was washed with light petroleum ether (Mallinckrodt, 30-60°C) and then added rapidly to the reaction vessel. The yellow solution turned to a light brown slurry and this was stirred for an additional 10 minutes. A cold solution of $NaHCO_3$ (5.0 g of $NaHCO_3$ in 20 ml of water) was poured quickly into the reaction mixture. A dark brown slush formed, which was stirred for 15 minutes and then filtered through Celite (Johns-Manville, 535). The organic layer was separated, washed once with 300 ml of a saturated solution of sodium bicarbonate, three times with 300 ml of ice water and dried over anhydrous magnesium sulfate. Evaporation of methylene chloride at ~ 10°C using a rotary evaporator gave a dark brown oil. A solution of petroleum ether (30-60°C) in ether (50 ml, 1:1) was added to the flask with the residue and left stirring for 12 hr. The colourless solution above the residue turned to a dark orange colour and was decanted. The extraction procedure was repeated twice and the combined solutions were evaporated using a rotary evaporator. The brown orange crude material was further purified by column chromatography using silica gel

(J.T. Baker, 80-200 mesh) and a solution of petroleum ether (30-60°C) in ether (4:1). Recrystallization from hexane/ether (1:1) yielded 1.2 g (40%) of orange crystals of 140a melting at 89.5-90°C (d). R_f = 0.50. Pmr: δ 1.66 (s,6H), 7.16 (s,broad,5H), 7.3 (s,broad,5H); ^{13}Cmr: δ 156.11, 147.53, 135.79, 129.55, 128.44, 127.40, 126.78, 123.73, 123.37, 102.60, 24.06. Ir: $\nu_{C=N}$ 1680 (s) and $\nu_{N=N}$ 1590 cm^{-1} (m); uv: λ_{max} 410 (3.38), 345 (3.67), 235 (4.11); m/e (mol. ion) 264. Anal. calcd. for $C_{16}H_{16}N_4$: C 72.73, N 6.10, N 21.19. Found: C 72.97, H 6.45, N 20.97.

Also isolated from the column was 0.03 g (1%) of an isomer of 140a, yellow crystals 140b, m.p. 93-94°C, ir, pmr and ^{13}Cmr data as above, R_f = 0.67, uv: λ_{max} 395 (3.88), 338 (3.93), 230 (4.69); m/e (mol. ion) 261. Anal. calcd. for $C_{16}H_{16}N_4$: C 72.73, H 6.10, N 21.19. Found: C 72.75, H 6.38, N 20.86. Mixture melting point (140a and 140b): 85-87°C.

Isomerization of 140b to 140a

In freshly distilled aniline (10 ml) was dissolved 0.08 g of 140b isomer and 3 drops of concentrated HCl was added. The solution was heated to about 45°C for 4 hrs and, after cooling, the uv spectrum was taken. The spectrum showed a new absorption at 410 nm which was not present in the spectrum of a control sample of aniline and HCl (3 drops) which was also heated at 45°C for 4 hrs. The solution with 140a,b was freed from aniline under vacuum and the residue was chromatographed on silica gel (ligroine in ether 1:1). The uv spectrum and the R_f value of the second fraction were identical to that of 140a. Isolated 0.041 g (0%) of 140a (m.p. 89-90°C).

3,3-Dimethyl-4-phenyl-Δ^1-1,2,4-triazoline-5-thione (142)

The procedure followed was essentially that of Landquist.[60] Acetone-4-phenylthiosemicarbazone (147) (5 g, 0.024 mol), prepared as described on page 61, was dissolved in dry chloroform (100 ml) and stirred with fresh basic alumina (Fisher Certified Reagent, Brockmann Activity I, 80-200 mesh) in an Erlenmeyer flask, with drying tube attached, at room temperature, for 5 days. Alumina was filtered off, washed with chloroform, and the orange coloured filtrate was concentrated. The resulting crude material was purified by column chromatography on silica gel (methylene chloride) and recrystallized from 95% ethanol yielding 3.5 g (67%) of red crystals melting at 174°C (lit[160] 172-174°C). Pmr: δ 1.60 (s,6H), 7.15-7.75 (m,broad,5H); ir: $\nu_{C=S}$ 1300 cm^{-1} (lit[60] 1300 cm^{-1}).

3,3-Dimethyl-4-aryl-Δ^1-1,2,4-triazolin-5-ones (141a-e)

(i) Acetone semicarbazone was prepared by the usual method from acetone and semicarbazide hydrochloride (Fisher Certified Reagent) to give a white powder, m.p. 187-188°C (lit[147] 187-188°C). Following the method of Borsche,[148] 58 g (0.5 mole) of acetone semicarbazone was reacted in 200 ml of bis(2-methoxyethyl)ether (J.T. Baker) under reflux, with aniline (95 g, 1.0 mole) (Fisher Certified Reagent, redistilled) or para substituted aniline, respectively (Eastman), at 145-160°C to yield 25-35% of crude acetone-4-aryl semicarbazones (150a-e). The physical properties and spectroscopic data are given below.

Acetone-4-aryl-semicarbazones (150a-e):

150a (Ar=C_6H_5) m.p. 154-155°C (lit[147] 155-156°C)

p.m.r.: δ 1.97 (s,3H), 2.05 (s,3H), 7.3-7.6 (m,broad,5H)

i.r.: ν_{max} 1690 cm^{-1}

150b (Ar=p-C_6H_4-Cl) m.p. 170°C (lit[23] 169-170°C)

p.m.r.: δ 1.95 (s,3H), 2.05 (s,3H), 7.2-7.6 (m,broad,4H), 8.45 (s,broad,1H); 9.2 (s,broad,1H)

i.r.: ν_{max} 1690 cm^{-1}

150c (Ar=p-C_6H_4-Br) m.p. 172-173°C (lit[149] 174°C)

p.m.r.: δ 1.95 (s,3H), 2.05 (s,3H), 7.4-7.8 (m,broad,4H), 8.5 (s,broad,1H), 9.25 (s,broad,1H)

i.r.: ν_{max} 1690 cm^{-1}

150d (Ar=p-C_6H_4-CH_3) m.p. 173-174°C (lit[150] 174-175°C)

p.m.r.: δ 1.95 (s,3H), 2.00 (s,3H), 2.25 (s,3H), 6.95-7.4 (m,4H), 8.1 (s,broad,1H), 8.3 (s,broad,1H).

i.r.: ν_{max} 1690 cm^{-1}

150e (Ar=p-C_6H_4-OCH_3) m.p. 169-170°C (lit[23] 167-169°C)

p.m.r.: δ 1.90 (s,3H), 2.00 (s,3H), 3.65 (s,3H), 6.8-7.4 (m,broad,4H)

i.r.: ν_{max} 1680 cm^{-1}

(ii) Substituted semicarbazone (150a-e) (~ 2 g), fresh basic alumina (Fisher Certified Reagent, Brockmann Activity I, mesh 80-200) (~ 50 g) and dry chloroform (100 ml) were stirred at room temperature for 7 days. The solvent was evaporated from the filtered solution and the crude product was recrystallized from 95% ethanol, yielding 35-80% of cyclized compound (141a-e). The triazolinones (141a-e) which were prepared are listed below, together with melting points, i.r., u.v., p.m.r. spectral data, as well as analyses:

3,3-dimethyl-4-aryl-Δ^1-1,2,4-triazolin-5-ones (141a-e):

141a (Ar=C_6H_5) m.p. 142-143°C (lit[60] 143-144°C)
p.m.r.: δ 1.58 (s,6H), 7.0-7.6 (m,5H)
u.v.: λ_{max} 275 (3.35), 375 (2.63)
i.r.: $\nu_{C=O}$ 1750 cm^{-1} (s)

141b (Ar=p-C_6H_4-Cl) m.p. 107°C
p.m.r.: δ 1.6 (s,6H), 7.0-8.15 (m,4H)
u.v.: λ_{max} 281 (3.47), 378 (2.64), m/e (mol. ion): 223
i.r.: $\nu_{C=O}$ 1750 cm^{-1} (s)
Anal. calcd. for $C_{10}H_{10}N_3Cl_0$: C 53.69, H 4.47, N 18.79; Cl 15.92. Found: C 53.82, H 4.50, N 18.88, Cl 16.05.

141c (Ar=p-C_6H_4-Br) m.p. 126-127°C
p.m.r.: δ 1.58 (s,6H), 7.0-8.2 (m,4H)
u.v.: λ_{max} 282 (3.67), 378 (3.02), m/e (mol. ion): 268
i.r.: $\nu_{C=O}$ 1750 cm^{-1} (s)

Anal. calcd for $C_{10}H_{10}N_3BrO$: C 44.77, H 3.73, N 15.67, Br 29.85. Found: C 44.88, H 3.96, N 15.55, Br 29.68

141d (Ar=p-C_6H_4-Cl_3) m.p. 109-110°C

p.m.r.: δ 1.60 (s,6H), 2.40 (s,3H), 7.0-7.6 (m,4H)

u.v.: λ_{max} 280 (3.45), 385 (2.69), m/e (mol. ion): 203

i.r.: $\nu_{C=O}$ 1750 cm^{-1} (s)

Anal. calcd. for $C_{11}H_{13}N_3O$: C 65.02, H 6.40, N 20.69. Found: C 64.72, H 6.34, N 20.73

141e (Ar=p-C_6H_4-OCl_3) m.p. 230°C

p.m.r.: δ 1.55 (s,6H), 3.70 (s,3H), 6.7-7.6 (m,4H)

u.v.: λ_{max} 285 (3.41), 390 (2.87)

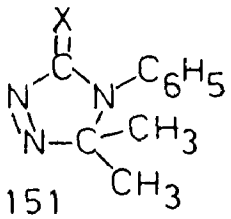
i.r.: $\nu_{C=O}$ 1755 cm^{-1}

Anal. calcd. for $C_{11}H_{13}N_3O_2$: C 60.27, H 5.94, N 19.18. Found: C 60.31, H 6.09, N 19.03.

B. THERMAL DECOMPOSITION STUDIES

GENERAL

Thermal decomposition of the following series of compound 151 and 141a-e in solution was studied.

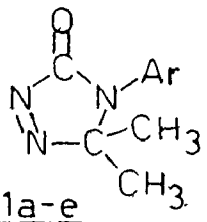


151

where X = N-C_6H_5 (140)

X = O (141a)

X = S (142)



141a-e

where Ar = C_6H_6 (141a)

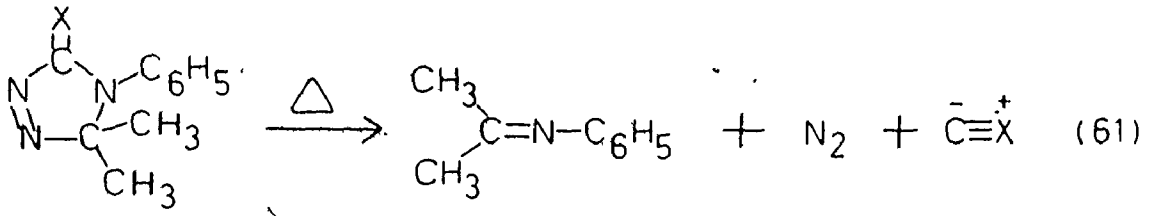
Ar = p-C_6H_4-Cl (141b)

Ar = p-C_6H_4-Br (141c)

Ar = p-C_6H_4-CH_3 (141d)

Ar = p-C_6H_4-OCH_3 (141e)

In view of the chemical and physical properties of the starting material and the formed products (eq. (61)), pmr was chosen as the method for following the rate of disappearance of starting materials (151). The peak heights of 151 at any time were compared to the peak height of an added known amount of internal standard toluene (J.T. Baker). The average



151 152 (61)

of five or more peak heights was used and these were converted into

molarities using a calibration chart. The resulting data were fed into the computer, which computed the first order rate constants and the activation parameters using a standard linear least square method. The error was calculated from estimates of standard deviation.

A well-insulated (5" thick asbestos and glass wool insulation) bath of Silicone Oil (Dow-Corning Silicone Ltd., 550 Fluid) was stirred rapidly using a mechanical stirrer (Gerald K. Heller Co.). The temperature of the oil was controlled by means of a thermoregulator (Magna-Set T 260) and a Fisher Transistor relay. The temperature of the bath did not vary from day-to-day at a given regulator setting within the limits (± 0.1°C) of the thermometer used. An Anschuts thermometer that had been calibrated by the Physical Chemistry Laboratory of the National Research Council of Canada was employed to measure the exact temperature of the bath. An electric timer (Precision Scientific Co.) was employed to measure time.

The technique involved sealing 0.3 ml aliquots of stock solution of the prepared compounds in different solvents. Each sample was degassed at least three times by freeze-pump-thaw cycles and then sealed under vacuum. At specific intervals, sealed tubes of samples were removed from the oil bath and quickly fully-immersed in liquid nitrogen. At the completion of the experiment, each tube was opened, the sample transferred into an nmr tube and scanned through the 1.3-3.0 δ region on the Varian HA-100 instrument. The peak heights of the internal standard toluene (at approximately δ 2.3,s), starting material (at approximately δ 1.6,s), and acetone anil (152) (at approximately δ 2.1 and 1.7,s) were recorded.

The solvents used for thermolysis were benzene (J.T. Baker Anal.

Reagent), chlorobenzene (Fisher Certified Reagent), nitrobenzene (Fisher Certified Reagent), and also carbon tetrachloride (J.T. Baker analytical reagent) when the thermolysis of 140 was studied. The solvents used in the thermolysis were distilled and thoroughly dried prior to use as described earlier in General Experimental Section (pg. 56).

Thermolysis of 3,3-dimethyl-4-phenyl-5-phenylimino-Δ^1-1,2,4-triazoline (140a)

(i) Product Studies

A solution of 140a (50 mg) in 3 ml of carbon tetrachloride was degassed using a freeze-pump-thaw cycle and then sealed under vacuum in the glass tube. The compound was thermolysed at about 100°C until the reaction was completed. The tube was opened and the dark brown solution was divided into several portions. The composition of the products was obtained by spectroscopic and by gas-liquid chromatographic techniques. Qualitative analyses of the pmr spectra of the products showed the presence of acetone anil (152) (δ 2.05,s,3H; 1.70,s,3H; 7.0-7.4,m; lit[151,152] 2.08, s,3H; 1.68,s,3H), phenylisocyanide (153) (δ 7.6,s) and traces of acetone (2.05,s) and aniline (6.5-7.2,m). There was no evidence indicating the presence of other products such as diazopropane.

The products, tentatively assigned in this way, were further identified as follows:

Acetone anil (152): A sample of 152 was prepared independently by the method of Kuhn and Jochims.[153] α-Anilinoisobutyronitrile was mixed with 1,6-hexanediol (Eastman) and slowly distilled at 16 Torr. The crude liquid anil was redistilled twice and the fraction between 80-81° was collected.

α-Phenylamino-isobutyronitrile was synthesized from acetone and aniline in the presence of glacial acetic acid (lit.[154]). To the solution was added aqueous KCN and the mixture was kept in an ice bath for about one hour. After this period of time, the solution was filtered and the α-phenylamino-isobutyronitrile salt was recrystallized from an ethanol-water mixture. The product was dried under vacuum pump and used immediately for the preparation of 152 as described above.

The pmr spectrum (δ 2.08,s,3H; 1.68,s,3H; 7.0-7.4,broad,5H) of the synthesized acetone anil was identical to that of the anil obtained in the thermolysis. Similarly, the ir spectrum showed in both cases, a strong band at 1660 cm^{-1}, in agreement with the ir data given in the literature.[155]

The prepared sample of 152 was also used for the identification of acetone anil in the thermolysis mixture using the gas-liquid chromatographic technique. Upon addition of the prepared sample of 152 to the mixture, the area of the peak assigned to acetone anil, increased. When a drop of water was added, (or if the sample was left open in the air) both samples of 152 (synthesized and from thermolysis) decomposed rapidly giving acetone and aniline.

Quantitative studies using a pmr calibration plot of signals at δ 2.1 and 1.6 (methyl group singlets) indicated that the yield of 152 formed under strictly dry conditions was 90%. This plot had been prepared by recording the pmr peak heights of standard solutions of acetone anil and toluene (internal standard).

Phenylisocyanide (153): A sample of 153, prepared in another laboratory

was redistilled and its spectral data used for identification of its presence in the mixture of products obtained by the thermolysis of 140. The ir spectrum of the sample had an intense single peak at the same frequency (2125 cm^{-1}) as the absorption observed in the thermolysis mixture. The pmr spectra were also consistent in displaying a sharp singlet in the aromatic region, at δ 7.58. Additional evidence for the assignment was the same penetrating malodorous odour of the decomposition residue and the synthetic sample.

Acetone and Aniline: Traces of these two compounds were present only if the solvent was not extremely dry. Any small amount of moisture from the air absorbed by the solvent, caused hydrolysis of acetone anil (152) and the formation of acetone and aniline. Since both compounds are well-known and readily available, their identification through pmr, ir and glc was a simple matter.

(ii) Kinetic Studies of 140a

The technique used was the same as that described in the General Kinetic Studies Section. The thermolyses were studied at different temperatures (79.0, 90.6, 97.4, 100.8, 103.7, 106.1, 111.6, 119.2, 133.6) in several different solvents (chloroform, carbontetrachloride, benzene, chlorobenzene, nitrobenzene). All data tabulated in Tables (1-3) and graphs (Figs. 2-6) are discussed in the Results Section.

Thermolysis of 3,3-dimethyl-4-phenyl-Δ^1-1,2,4-triazolin-5-ones (141a-e)

(i) Product Studies

A procedure similar to the one performed in product studies of

140a was applied here.

A solution of 141a (75 mg) in 3 ml of benzene was degassed, sealed under vacuum and thermolysed at about 175°C for 5 hr. The composition of the products (after the complete reaction) was obtained from pmr spectra and by glc. Quantitative analysis of the pmr spectra using a peak-height calibration chart showed the presence of 52 mg (98%) of acetone anil (152). The gaseous products were not examined. Only four peaks were observed on the chromatogram when the thermolysis mixture was subjected to glc analysis. The peaks were positively assigned to the solvent (benzene) and the products: acetone anil (152), acetone, and aniline. The ir spectrum of the thermolysis mixture displayed a strong band at 1660 cm^{-1} (152) and no absorption at 2270 cm^{-1} (phenyl-isocyanate) was observed.

(ii) Kinetic Studies

Thermolysis of 141a (benzene, chlorobenzene, nitrobenzene) and of 141b-e (nitrobenzene) by the procedure already described on pg. 69 gave the data in Tables 4-7 and Figures 7-11 of the Results Section.

Thermolysis of 3,3-dimethyl-4-phenyl-Δ^1-1,2,4-triazoline-5-thione (142)

(i) Product Studies

Similarly, as described in the Product Studies of 140a and 141a, a solution of 142 (100 mg) in 5 ml of dry nitrobenzene was degassed, sealed under vacuum in the glass tube and thermolyzed at 175°C for 3 hrs. At the end of the 3 hr period, qualitative analysis of the dark brown solution using pmr and ir techniques indicated that, as in previous cases,

acetone anil and traces of acetone and aniline were present. Again, there was no evidence for the presence of the other possible products, such as diazopropane, acetone azine, or phenylisothiocyanate. More detailed qualitative studies of other products were carried out.

Acetone Anil (152): The presence of 152 was established by ir, pmr and glc techniques as described in detail previously (pg. 71). Quantitative analysis, using pmr calibration chart indicated that 84% of 152 was formed.

Nitrogen: The formation of nitrogen in the thermolysis of 142 was qualitatively demonstrated by using mass spectrometry. About 0.5 g of the sample of 142, dissolved in 20 ml of chlorobenzene, was placed in the assembly sketched below (Figure 16).

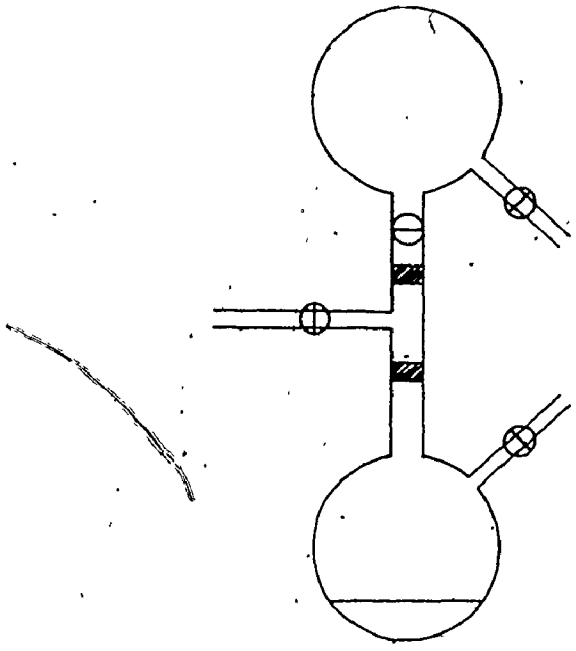


FIGURE 16

The whole system was thoroughly degassed several times and argon was purged through the solution, until the gas sample taken from the system did not show any peaks in the mass spectrum indicating the presence of air. After 4 hrs at about 150°C, the lower flask was inserted into a dry ice-acetone bath, left there for 20 minutes and then the upper flask, with collected gas sample, was detached. The mass spectrum of the gas sample showed a large parent peak at m/e = 28 (nitrogen), m/e = 40 (argon) and a weak peak at m/e = 32 (oxygen). The small amount of oxygen is believed to be present due to the partial diffusion of air into the gas sample in the process of handling and heating rather than to its formation in the reaction.

Carbon Monosulfide (155): The presence of 155 was at first established in its polymeric form C_xS_y in the pyrolysis residue. A solution of 142 (0.3 g) in dry chlorobenzene (20 ml) was sealed in a thick glass tube under vacuum and inserted into an oil bath at ~ 175°C for 3 hrs. After this period of time, the tube was cooled, opened and the solvent was distilled off under vacuum. The residue was fractioned by column chromatography (silica gel) and fractions were analyzed by nmr. The pmr spectra showed no peaks (i.e., no ^1H's present) in most fractions and the results of an elemental analysis indicated that the 56% polymers contained mainly carbon and sulphur (C 67.8, S 30.5 and C 53.4, S 44.7, and C 48.9, S 47.6). Traces of N and H were found in two (23%) of the analyzed samples (C 51.03, S 37.21, N 7.52, H 3.45 and C 64.47, S 23.43, H 6.74, N 4.68).

Attempts were made to trap 155 with different organic compounds, such as cyclohexene, anthracene, phenylisocyanate, phenylisothiocyanate,

chlorobenzene, nitrobenzene, benzil, fumaronitrile, triphenylphosphine, 4,4-bis-(dimethylamino)-benzophenone (Michler's ketone), and $Rh((C_6H_5)_3P)_3Cl$. The trapping experiments were carried in the same manner as described above. Approximately 0.2 g of 142 was dissolved in 25 ml of dry chlorobenzene and about 10 fold excess of trap was added. The mixture was sealed into a thick glass tube under vacuum, thermolysed at ~ 170°C for 3 hrs and after removal of solvent, the residue was analyzed by pmr and chromatography techniques. With liquid traps, decomposition was carried in neat trap, without solvent present. The pmr spectra of chromatographic fractions either had no peaks present or, in two cases, had a broad bump in the hydrocarbon region. The elemental analysis of some fractions revealed that mainly C_xS_y polymer was formed in the process (C 52.34, S 43.71 and C 47.12, S 50.91 and C 73.41, S 33.78).

In two cases, the products of trapping experiments were positively identified by mass spectrometry as those formed from the reaction of 155 and the traps (cyclohexanone and sulphur):

About 0.2 g of 142 was dissolved in cyclohexanone (30 ml) and the solution was purged with argon. To the round bottom flask was attached a short (10 cm) distillation column and to the top a round bottom flask for catching gas sample (top part of diagram, pg. 75). The system was evacuated, purged with argon for 20 minutes and sealed off from the atmosphere. The solution was slowly refluxed for 6 hrs, cooled with dry ice-acetone and the gas sample from the top round bottom flask was analyzed by mass spectrometry. There were peaks at m/e = 60 (COS), m/e = 40 (argon) and m/e = 28 (nitrogen). A gas sample of simultaneously decomposed 142 in chlorobenzene in the presence of oxygen was analyzed and this did not

have mass peaks corresponding to COS and argon. In a similar manner, decomposition of 142 was carried out using sulphur as a trap. The thermolysis was carried out in chlorobenzene (35 ml) with sulphur present in large excess (1.5 g of S_8 and 0.2 g of 142) in the same experimental set up as described above. The gas sample analyzed by mass spectrometry showed a peak at m/e = 76, which was assigned to CS_2. Again, a blank solution run simultaneously but without sulphur present did not have a mass peak corresponding to CS_2 in the mass spectra of the gas sample. The residue from the decomposition of 142 in the presence of sulphur was chromatographed and two fractions which were sent for elemental analysis had large amounts of sulphur incorporated into the polymer (C 21.78, S 78.21 and C 13.21, S 81.33).

(ii) Kinetic Studies of 142

The studies were carried out in the same manner as described in the General Kinetic Studies Section. Rate constants and activation parameters are given in the Results Section (Tables 8-10, Figures 12-15).

C. PHOTOCHEMICAL DECOMPOSITION

GENERAL

The photochemical reaction of 141a was done in a Srinivasan-Griffin Photochemical Reactor (Rayonet), manufactured by the Southern New England Ultraviolet Company, using 12 lamps (2537 Å). Aliquots were analyzed by proton magnetic resonance spectrometry and/or by gas-liquid chromatography. All pmr spectra were run on a Varian EM-390 or HA-100 spectrometer and all spectra were taken in deuteriochloroform solution. Where pmr was used to determine the abundance of one or more materials, peak heights were measured. The average of a minimum of five peak heights was used.

Gas chromatographic analyses were done on a Varian Aerograph Model A90-P3 using a 5' x 1/4", 15% SE 30 on 60/80 mesh chromosorb P column, at 65°C and helium flow rate of 50-60 ml/min.

Quantum yield experiments were performed on a small optical bench using a Bausch and Lomb Model 33-86-01 high intensity monochromator, fitted with an achromatic condenser lens and coupled to an Osram HBO 200W super pressure mercury lamp.

The total amount of the starting material disappearing in quantum yield was followed by pmr by comparing the peak heights of the starting material 141a with the peak height of an added known amount of internal standard, 1,3,5-trimethoxybenzene (Aldrich Chemical Co. Inc.). The ratio of the peak heights of the two peaks was then juxtaposed to a calibration graph, a plot prepared by pmr studies of known mixtures of both the internal standard and the starting material, where the exact weight of 141a at different times was determined (methyl singlets at δ 1.64 and

3.75 were observed).

Absorbances (O.D.) of ferrioxalate actinometry solutions were recorded on a Bausch and Lomb Precision Spectrophotometer, Model 33-26-50, at 510 nm. The instrument was calibrated prior to use according to the procedure of Hatchard and Parker.[156]

1. Irradiation of 141a. Product Studies

A solution of 0.15 g (0.02 mol) of 140a in 50 ml of methanol (spectroscopic grade) was irradiated through quartz with 12 lamps (2537 Å) in the Rayonet Photochemical reactor. Prior to and during the irradiation, a stream of argon was passed through the solution. The reaction was stopped at 1 hr intervals, to withdraw 1 ml aliquots which were analyzed by pmr. To each aliquot was added one ml of a stock solution of 1,3,5-trimethoxybenzene in methanol, the solvent was evaporated off using a rotary evaporator and the methyl singlet at δ 1.64 was observed. After 5 hrs of irradiation, when no starting material was observed in the pmr spectrum of the withdrawn aliquot, the photolysis was stopped. The solution was divided into two parts. One part was analyzed by glc, where acetone and aniline were demonstrated to be present. The second part had the solvent and volatile products removed under vacuum using a rotary evaporator. The oily residue, analyzed by pmr, ir and uv, showed that only aniline was present.

2. Quantum Yield Measurements

(i) Direct Irradiation of 141a

Irradiations were performed using a Bausch and Lomb Model 33-86-01 High Intensity Monochromator, fitted with an achromatic condenser lens.

A mercury high pressure arc lamp (Osram HBO 200W) was used as a source of light and the uv-vis grating had entrance and exit slit widths set to give a band pass of 15 nm at 313 nm. The parallel beam from the monochromator was split by a quartz plate, 2 x 2 x 1/8 in, fixed at an angle of 45° to the beam. About 7% of the beam was reflected into cell A which always contained actinometer, a 0.006 M potassium ferrioxalate solution. The transmitted beam was incident on cell B, which contained 39 mg (2.065×10^{-4} mole) of 141a in 13 ml of methanol in run 2 and actinometer in runs 1 and 3. In run 2, cell C was placed behind cell B, to measure light transmitted by the triazolinone solution. Cells A and C in run 2 and cell B in runs 1 and 3 were 5.0 cm long by 2.5 cm in diameter and contained 26 ml of actinometer. Cell B in run 2 and cell A in runs 1 and 3 were 2.5 cm in length, 2.5 cm in diameter and had a volume of 13 ml. The cells were of Suprasil quartz, made by the Hallma Co., Gmbh, Germany. All solutions were purged with argon for a period of 20 min prior to irradiation and throughout the irradiation period. Light intensities were measured by ferrioxalate actinometry, according to the procedure of Hatchard and Parker.[156] The splitting ratio of reflected to transmitted beam intensities was determined in runs 1 and 3 and this was used in calculation of light incident on the triazolinone 141a solution during run 2. Thus, irradiation for 10 hrs at 313 nm led to the absorption of 7.29×10^{-4} Einsteins of light by the solution of 141a. Analysis by pmr, using 1,3,5-trimethoxybenzene as an internal standard showed the disappearance of 9 mg (4.762×10^{-5} mol) of starting material, giving a value of 0.065 for the quantum

yield of product formation. A duplicate run gave a value of 0.064. Table 11 of the Results Section gives the pertinent data for the quantum yields.

(ii) Sensitized Irradiation of 141a

The benzophenone sensitized photolysis was performed in an analogous manner as described in previous pages. The solution cell contained 39 mg (2.065×10^{-4} mol) of 141a and 234 mg (1.286×10^{-3} mole) of benzophenone (BDH Chemicals, Anal. Reagent) in a solution made from 13 ml of methanol. The quantum efficiency of conversion of ferrioxalate was taken as 1.23. Duplicate quantum yields were measured by the pmr method (using 1,3,5-trimethoxybenzene as the internal standard) and the data obtained are listed in Table 12 in the following section (pg.135). Thus, irradiation for 10 hrs at 313 nm led to the absorption of 2.56×10^{-4} Einsteins of light by benzophenone, giving a value of 0.20 for the quantum yield of the sensitized decomposition of 141a. A duplicate run gave a value of 0.22.

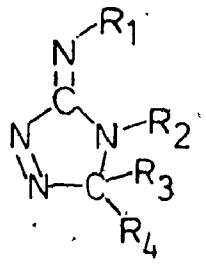
(iii) Irradiation of 141a with a Quencher Present

The photolysis was performed in an analogous manner as described on pg. 80. The solution cell contained 39 mg (2.065×10^{-4} mol) of 141a and 84 mg (0.01 mol) of freshly distilled 1,3-cyclohexadiene in 13 ml of methanol. Again, the disappearance of starting material was followed by pmr using 1,3,5-trimethoxybenzene as the internal standard. After 10 hrs of irradiation, the amount of the starting material present in the irradiated solution was unchanged from the original value.

RESULTS AND DISCUSSION

A. SYNTHESES OF TRIAZOLINES AND MECHANISM OF LTA OXIDATION OF GUANYL HYDRAZONES

Despite the fact that triazolines were known as far back as 1900, none of the published work deals with preparation of triazolines of the type 156:



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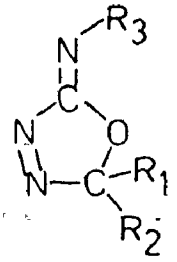


157

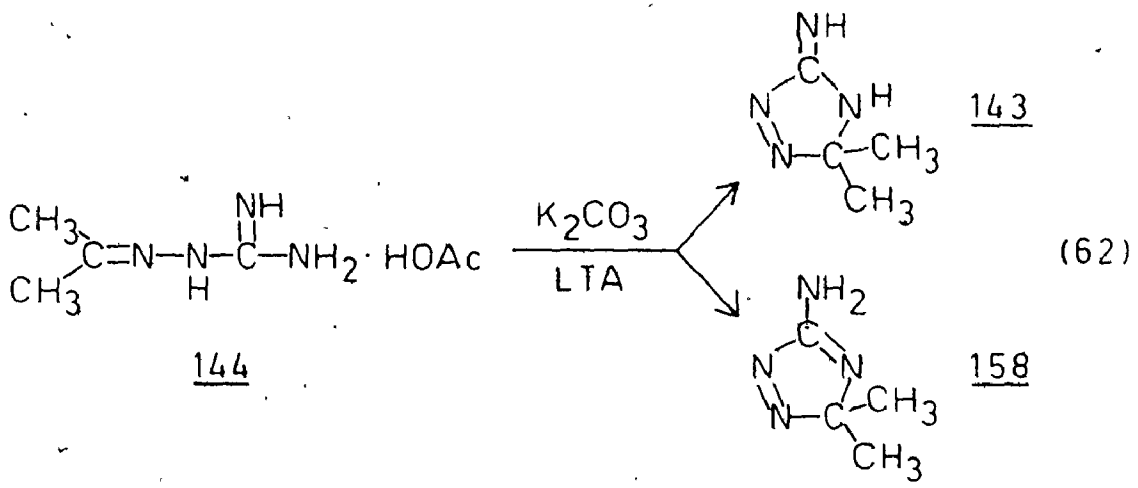
where $R_1 = R_2$ = H, alkyl or aryl $R_1 = R_2 = R_3$ = alkyl or aryl

$R_3 = R_4$ = alkyl or aryl

One of the aims of this work was to prepare compounds 156, using the general approach developed by Warkentin and coworkers[23-26] for the oxygen analogues 157. The latter are readily obtained by oxidative cyclization of semicarbazones with lead tetraacetate and it seemed likely that 156 might be obtained similarly, by oxidative cyclization of guanylhydrazones.

We carried out the LTA oxidation of two unsubstituted ketone guanylhydrazone acetates (144 and 146). Cyclization of acetoneguanyl-

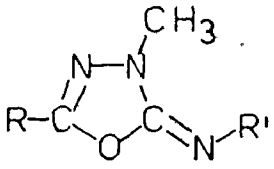
hydrazone acetate (144), the nitrogen analogue of acetone semicarbazone, in methylene chloride containing anhydrous potassium carbonate to remove acetic acid, led to a new product. An examination of spectroscopic (pmr) and analytical evidence, led to the conclusion that the product differed in molecular formula from the substrate by only two hydrogens. The pmr spectrum of the product showed one methyl singlet absorption at δ 1.50, indicating that the two methyl groups from 144 had become equivalent. On the basis of this evidence and the semicarbazone-to-oxadiazoline analogy,[22-26] a cyclic structure was tentatively assigned. However, there are two possible tautomeric forms of a heterocyclic compound that would fit the elemental analysis and pmr results, 143 and 158 (eq. 62).



(62)

The pmr spectra of the two methyl groups in both cases would give just one singlet and NH group absorption (broad line), which was not observed in some pmr spectra, is a weak structural criterion. We believe, mainly on the basis of infrared data, that 143 and 158 can be distinguished, since it is well known that the exocyclic C=N group

gives a very strong absorption as compared to an endocyclic C=N group. Najer and coworkers[159-162] studied the ir spectra of oxadiazolines (159). N-Alkylimino groups in such compounds strongly absorb at 1700-1710 cm^{-1},[159,162] and N-arylimino groups at lower frequency (1600-1680 cm^{-1}).[160,161] Other



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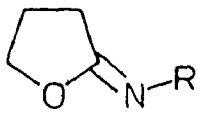

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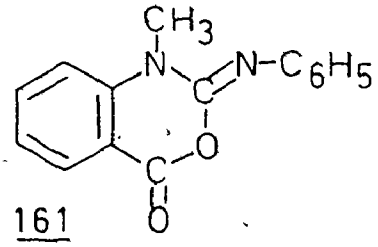


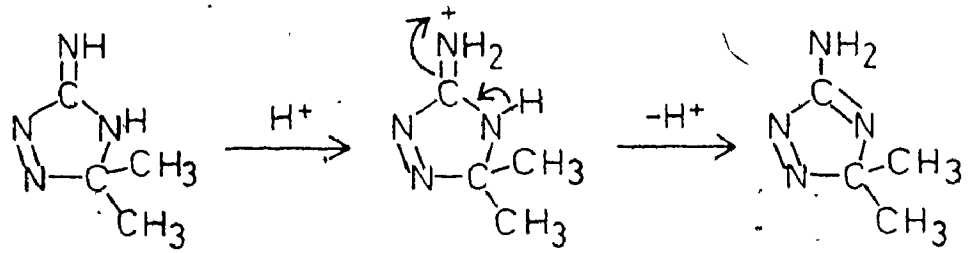
161

workers[163,164] have reported exocyclic C=N absorption of lactone imines (160) in the same region. Kurihara and Yoda[165] found that the imino stretching frequency becomes more intense relative to carbonyl when made exocyclic in the benzoxazine (161). West[26] and Cameron[23] also observed that oxadiazolines 157 exhibit strong absorption at about 1700 cm^{-1} frequency and thus assigned it to the exocyclic C=N group.

Indeed, a strong peak at 1630 cm^{-1} was observed in the ir spectrum of the product of cyclization of 144 and therefore the structure 143, rather than 158 was assigned to it. Also, two separate broad peaks were seen in some of the pmr spectra and these could be assigned to two different NH groups in 143, but could not readily be explained by structure 158.

It was expected that 143 would isomerize giving 158 and experiments were done to isolate a possible tautomer 158 (eq. 63). The triazoline (143) was dissolved in chloroform, 1 ml of dilute acid was added and the

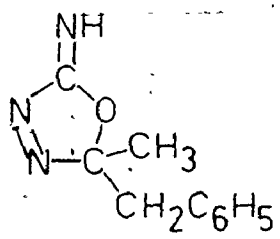
mixture was stirred virogously for 1 hr. The expected product 158 was



143 158 (6.3)

not detectable, but instead, acetone was found to be formed (pmr, ir). The acetone was isolated by glc and its identity confirmed by comparison with an authentic sample. Attempts to isomerize 143 in an anhydrous acid system (glacial acetic acid and acetic anhydride) were not successful either. The pmr spectrum of 143 dissolved in $CDCl_3$, in a sealed tube, showed after a few minutes, besides the singlet representing 143, a peak at δ 2.1 (acetone), which gradually increased with time until a constant value of the ratio of the two peaks was attained. It is believed that hydrolysis occurred and that when all moisture from the solvent was used up, the reaction stopped. The formation of acetone supports this claim. However, because of insufficient evidence, the mechanism cannot be determined.

A compound similar to 143, oxadiazoline 162 was synthesized from methylbenzylketone semicarbazone by Knittel.[28] He observed two imino signals (broad lines) in the pmr spectrum of 162 and suggested that those two signals come from the E and Z isomers of the imine. Knittel could not separate the isomers, nor could he reproduce the spectrum. On the



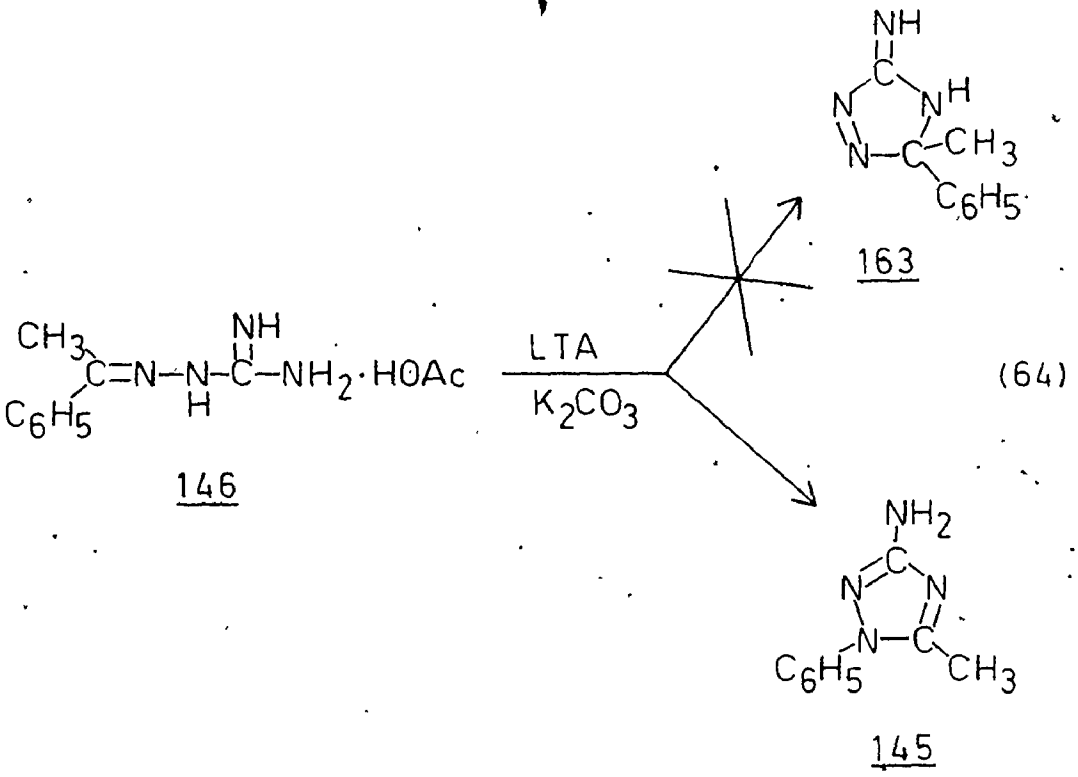
162

basis of our pmr evidence, it cannot be established whether 143 existed as a mixture of E,Z isomers, or whether just one isomer was present, or whether rapid interconversion of the two was occurring. However, since our system is very similar to Knittel's, in the sense that the pmr spectra are sample-dependent, it is tempting to postulate that there is indeed rapid averaging in some environments.

Since the yield of 143 was low (10-30%), attempts were made to use other oxidizing agents instead of lead tetraacetate. Bromine was employed in some experiments, however, yields of 143 were even lower than when LTA was used. Cameron[23] also investigated the possibility of using other oxidizing agents for preparation of oxadiazolines and she concluded that LTA was the most satisfactory reagent for the cyclization of semicarbazones.

Acetophenoneguanylhydrazone acetate (146) was oxidized by LTA under the same condition as 144, however, the expected product 163 was

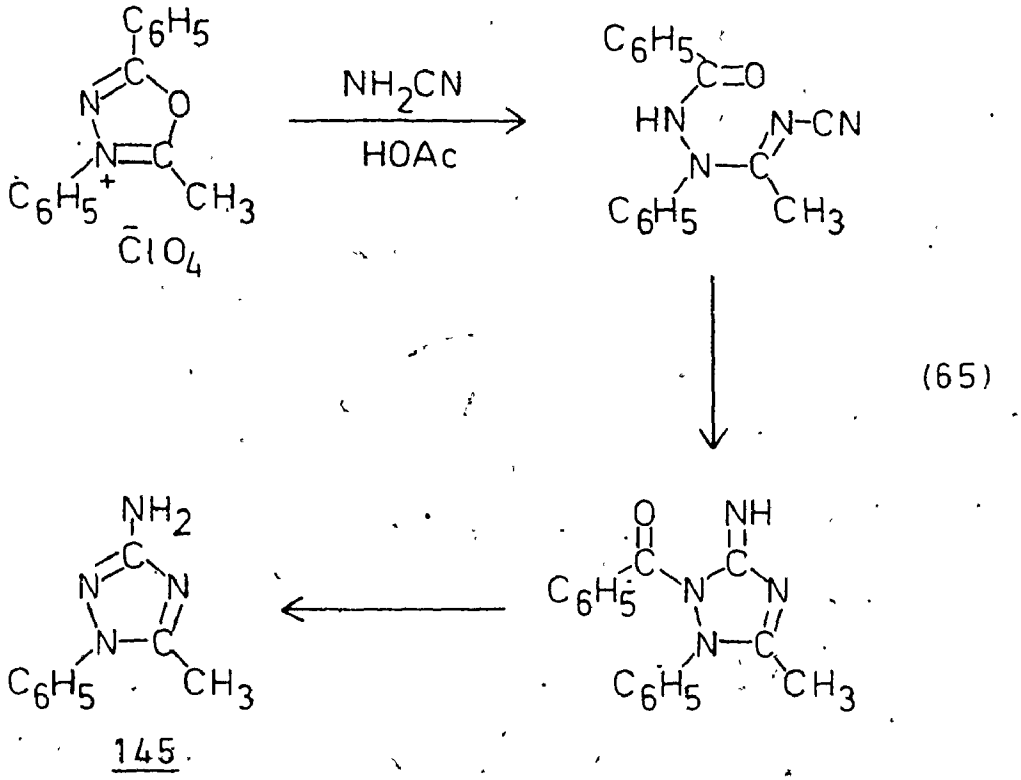
not isolated. Instead, 3-amino-5-methyl-1-phenyl-1,2,4-triazole (145) was obtained in 36% yield (eq. 64). The melting point and spectroscopic data of 145 are in agreement with those given in the literature.[142,143]



(64)

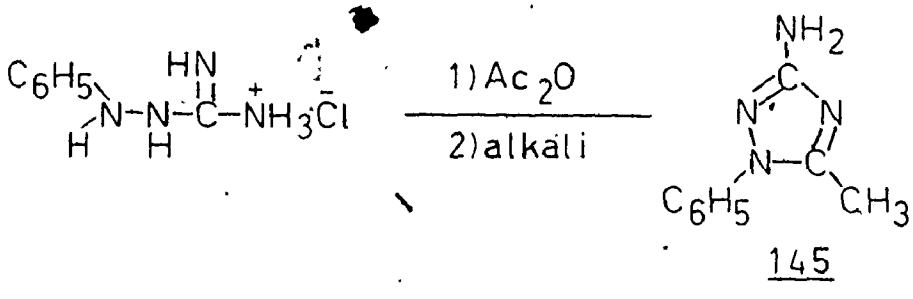
Boyd and Dando[142] prepared 145 from the corresponding oxadiazolium salt, by heating it with cyanamide in acetic acid medium (eq. 65) (page 89).

Cuneo's[143] method of preparation involves acylation of aminoguanidines (eq. 66). Thus, although the product 145 is not new, the LTA oxidation of 146 is a new synthetic route to 145 and potentially to some other members of that family.



(65)

145

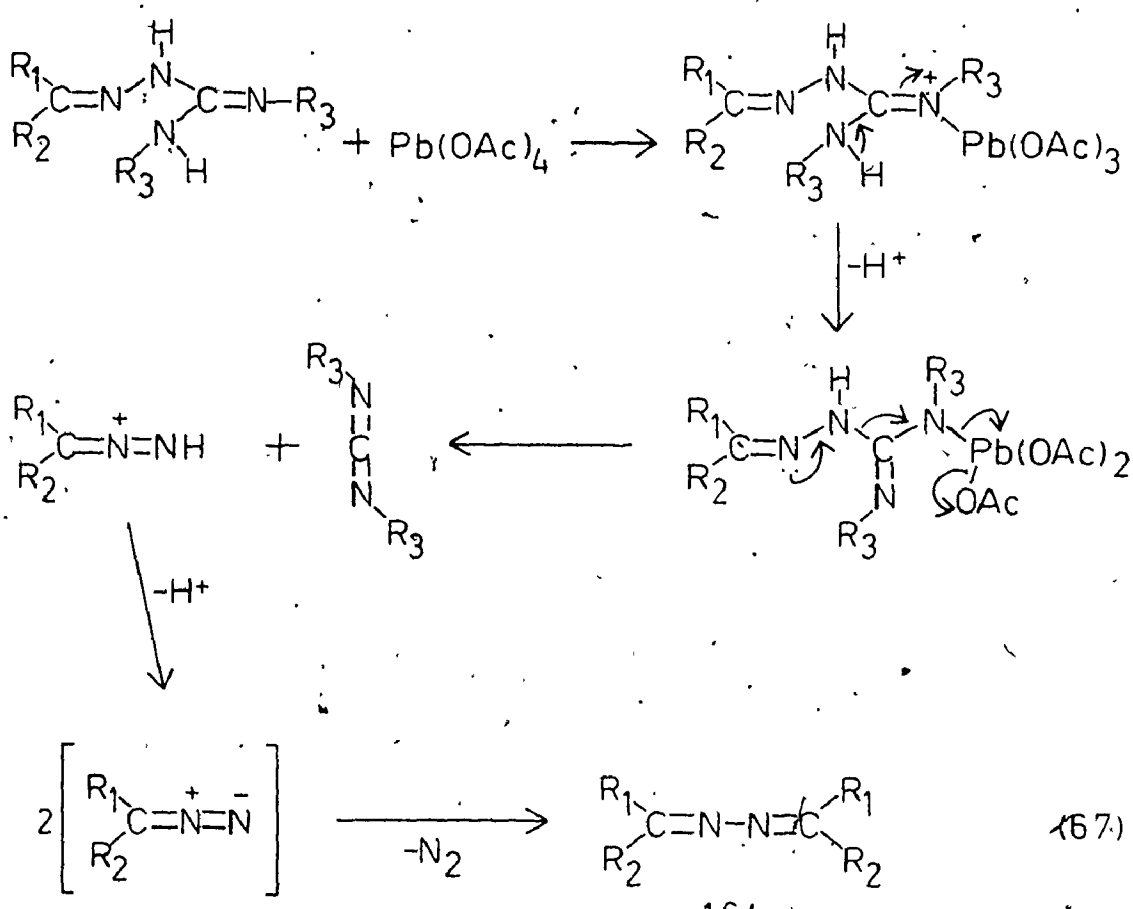


(66)

145

Besides 145, acetophenoneazine was also isolated (29%) from the reaction mixture. The byproduct was not isolated in the pure state, however, its identity was firmly established by comparison of its ir, pmr, and ^{13}Cmr spectra with those of an authentic sample.

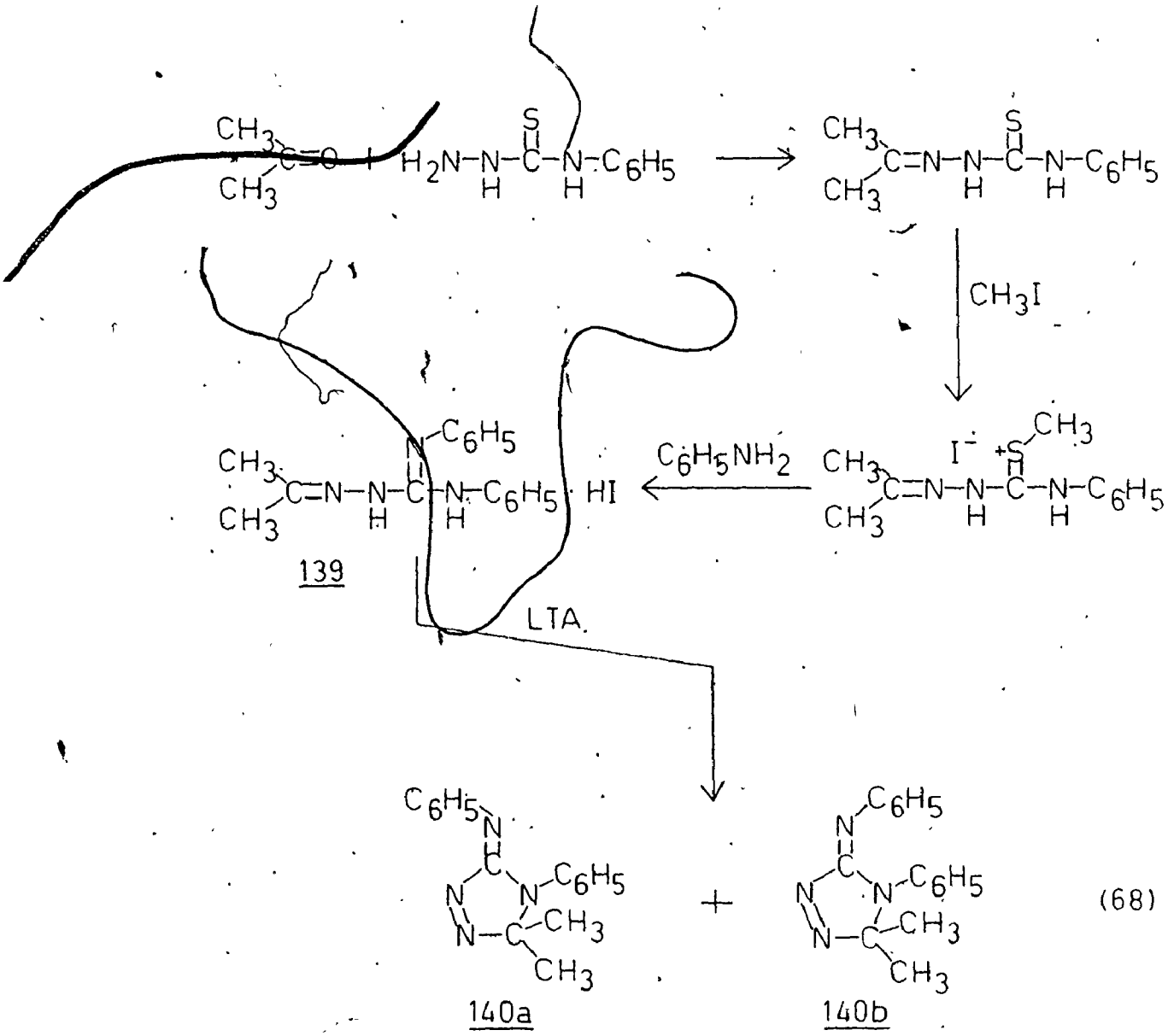
The formation of azine (164) in the LTA oxidation of guanyl hydrazones can be readily explained by a reaction mechanism involving oxidation of the guanyl hydrazone with LTA to the diazocompound, which is known[166] to decompose to the corresponding azine (eq. 67).



(67)

164

One N,N'-disubstituted acetoneguanylhydrazone acetate (139) was cyclised by LTA. The preparation of 139 was achieved via several steps (eq. 68). Oxidation with LTA produced two isomers 140a and 140b in the ratio 40:1, respectively.



(68)

These isomers, which were separated by column chromatography differed mainly in colour (140a orange, 140b yellow), R_f value (silica gel, petroleum ether, ether 1:1) (140a: R_f = 0.50, 140b: R_f = 0.67), melting point (140a m.p. 89-90°C, 140b m.p. 93-94°C), and uv spectra (140a: λ_{max} 410(3.38), 345 (3.67), 235 (4.11); 140b: λ_{max} 395(3.88), 388(3.93), 230(4.69)). Results of elemental analysis, pmr, and ^{13}Cmr were identical. The mixture melting point of the two products exhibited depression by 2-3°C below the lower melting point of the two. Thus, on the basis of data presented above, it was concluded that the compounds are two different stereoisomers, 140a and 140b. The basis for assigning the Z configuration (140a) to the major isomer is discussed below.

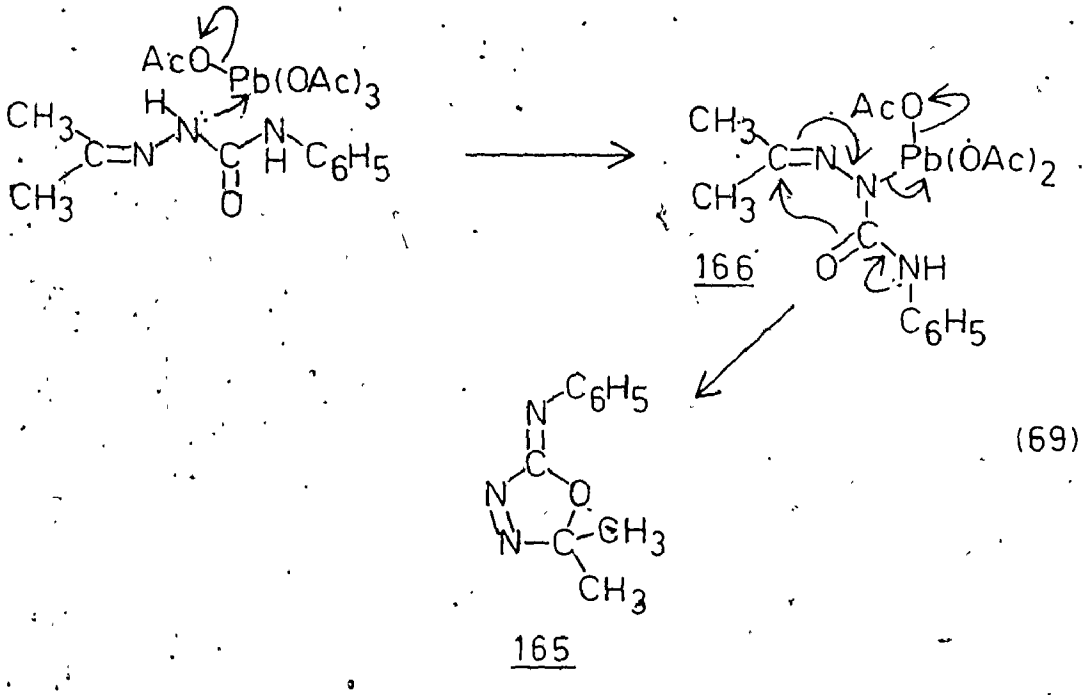
Molecular models of the isomers indicate that the phenyl rings can be more nearly coplanar with the triazoline ring and with each other in the Z-isomer, 140a. In the E-isomer, the phenyl groups interfere with each other unless one or both are turned out of the plane of the five-membered ring. Two predictable consequences of these structural features are that the Z-isomer should show longer wavelength absorptions in the uv and visible spectra and that it should be the more stable, thermodynamically, of the two. On the basis of the electronic spectra, the Z-configuration was assigned to the major, orange-coloured isomer and the E-configuration to the minor, yellow isomer.

An attempt to equilibrate the isomers provided support for the above assignment. In a buffer solution of anilinium ion in aniline, the minor isomer was isomerized in about 50% yield (isolated) to the major isomer. An equilibrium constant could not be measured and other,

unidentified products attributed to decomposition reactions were observed. Nevertheless, the spectroscopic data and the isomerization experiment, taken together, leave no doubt that the major and minor isomers are 140a and 140b, respectively.

Products formed in LTA cyclization of substituted and unsubstituted guanylhydrazones, as presented on previous pages, suggest that the mechanism of cyclization involves a nitrogen-lead intermediate, similar to that proposed by other authors.[23-28]

Cameron's[23] investigation of the oxidation of acetone-4-arylsemicarbazones, revealed that only one oxadiazoline, the Z-isomer (165). was formed (eq. 69).

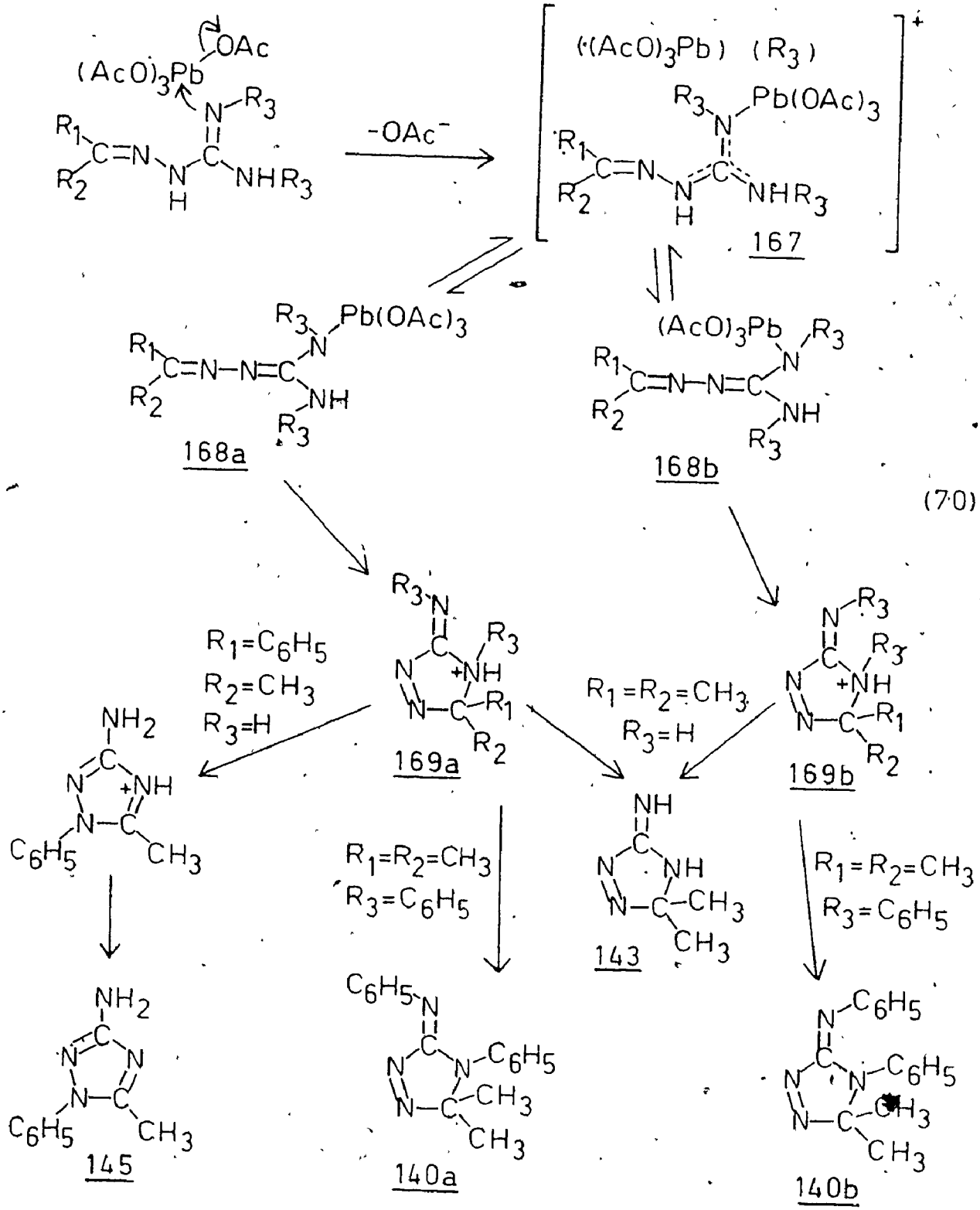


(69)

An X-ray crystal structure of 2-[(p-bromophenyl)-imino]-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline[22] firmly established the Z-stereochemistry at the imine function. The stereospecificity of the oxidative cyclization of 4-substituted semicarbazones was used as a clue to the mechanism of the reaction. Rotation in a lead-nitrogen species 166 was expected to involve large steric requirements. Such a steric requirement would force the large phenyl group to a position as distant as possible from the Pb-N bond, which would result in the production of the isomer in which the phenyl group is syn to the ring oxygen system.

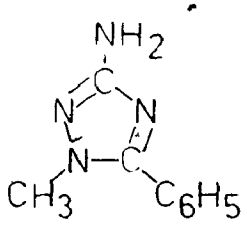
Steric crowding of the bulkier N-C_6H_5 group in triazolines 140a and 140b, as compared to oxygen in oxadiazolines, has to be considered when proposing the mechanism of LTA oxidation. Moreover, the basicity of a guanylhydrazone is greater than that of a semicarbazone and therefore it is very likely that the nucleophilic attack on lead will be by the most basic nitrogen, i.e., the imino nitrogen (intermediate 167) and not by N-2 (or N-1) as has been suggested for semicarbazones (intermediate 166, eq. 69). A general mechanism of LTA cyclization of guanylhydrazones, based on observed results, is given (eq. 70).

In the case of unsubstituted guanylhydrazones, (R_3 = H) the imino-nitrogen site of the molecule is sterically unhindered and therefore even more likely to be the favoured site of attack. When R_3 = H, the two conformations of the proposed lead derivative (168a and 168b) give rise to distinguishable isomers, 140a and 140b, respectively. One way of accounting for the fact that the major isomer is 140a, is to postulate that 168a is the preferred conformation of the proposed lead derivative.



(70)

As mentioned previously, when acetophenone guanylhydrazone (R_3 = H, R_1 = C_6H_5, R_2 = CH_3) was oxidized with LTA, product 145 was obtained. Its formation can be accounted for in terms of a 1,2 shift of the phenyl group from 169a,b. The migratory aptitudes of phenyl, hydrogen and methyl were compared by several authors.[167-170] The multiplicity of factors affecting the migratory aptitudes of groups makes it difficult to establish orders of intrinsic migratory aptitudes. In general, it appears that aryl groups are most mobile, followed by hydrogen and alkyl groups. This is consistent with the requirement that, in the transition state of the 1,2 shift, the migrating group should be able to accommodate a substantial proportion of the positive charge of the carbonium ion, and some MO calculations support the sequence.[171] Bachmann and Fergusson[172] studied the migratory aptitudes of substituted phenyl groups in pinacol rearrangement of symmetrical glycols and they found a 500-fold preference for p-methoxyphenyl migration versus phenyl migration. Applying these facts to our system and taking into account mechanism suggested above, it can be explained why 170 was not formed. The poorer migratory aptitude of the methyl group is the most likely reason for the isolation of product 143 from acetoneguanylhydrazone acetate rather than 171.



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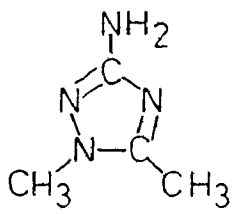
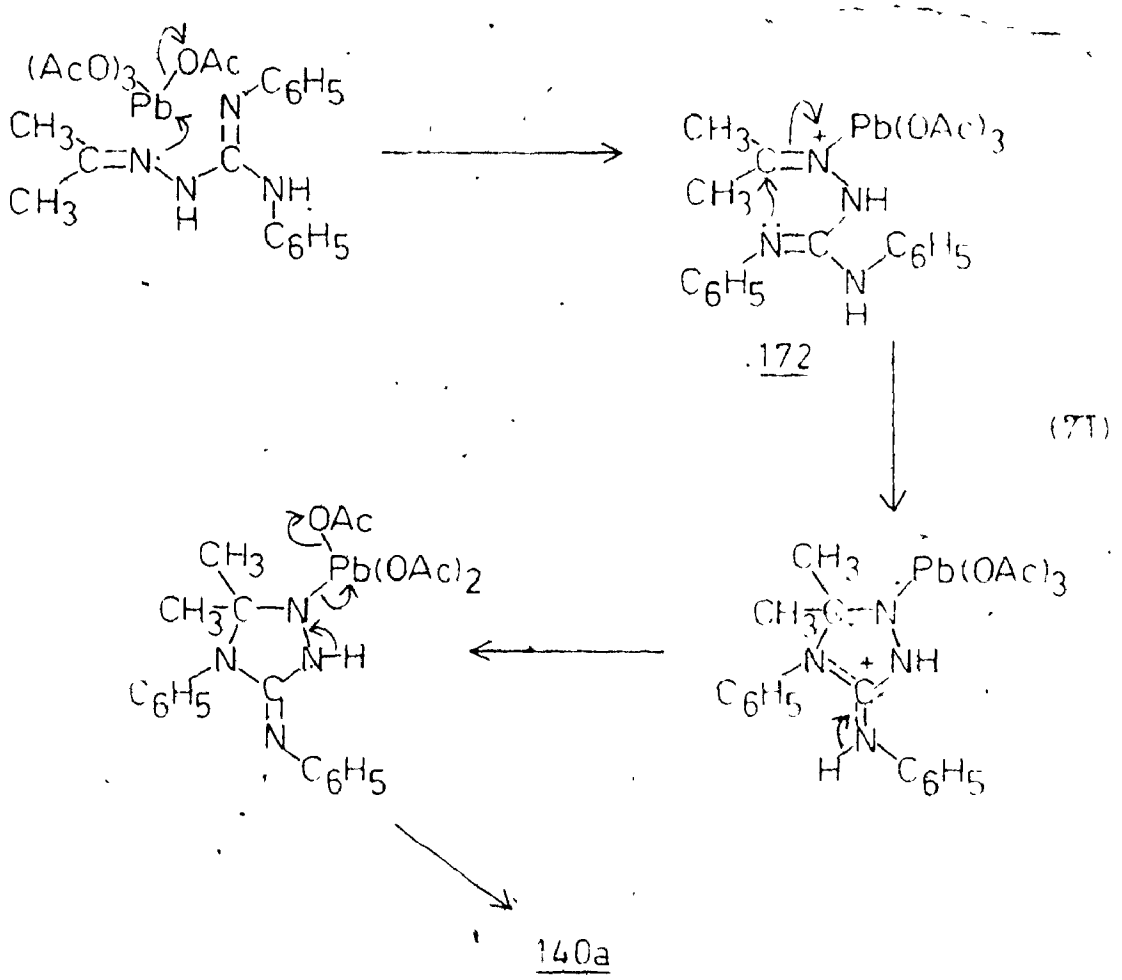


171

Phenylsubstituted guanylhydrazones ($R_1R_2C{=}NNHC(NPh)NHPh$) differ from unsubstituted guanylhydrazones in two important aspects. First, they are less basic and second they are more hindered to attack by bulky electrophiles at the guanidine nitrogens. Hence, another mechanism has to be considered for their oxidative cyclization by LTA. The initial nucleophilic attack could involve the other imino nitrogen which is comparably hindered, leading to intermediate 172 (eq. 71).

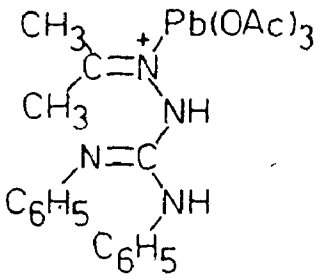


(71)

172

140a

The intermediate 172 accounts also for the stereochemistry of the major product 140a. The other possible intermediate 173, which would lead eventually to 140b is not favoured since two phenyl groups are eclipsed and more congested.



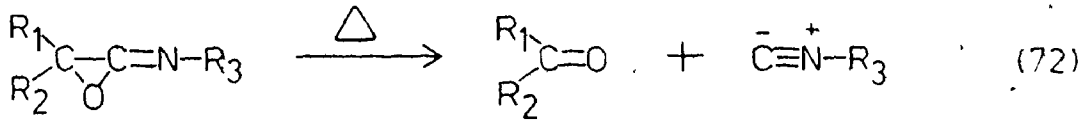
173

An analogous nucleophilic attack on lead by imino nitrogen of a carbohydrazone was proposed by Ramakrishnan[27] in order to explain the stereochemistry of his products.

B. THERMAL DECOMPOSITION OF 140a, 141a, 142

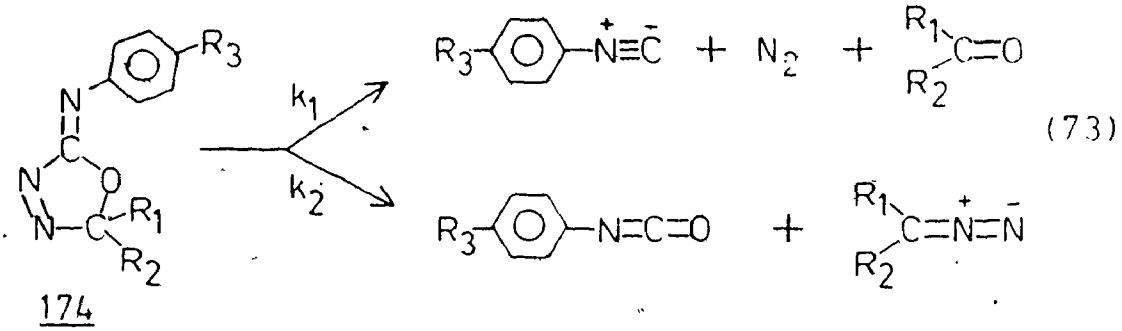
1. PRODUCT STUDIES

Thermolysis of 1-pyrazolines almost invariably leads to cyclopropanes, via different mechanisms.[75-103,106-112] The oxadiazoline ring system has one of the carbon atoms of the 1-pyrazolines replaced by an oxygen. Therefore, the analogous product of thermolysis would be a three membered ring system such as an oxirane or iminooxirane. Staudinger[122] isolated an epoxide (eq. 49, pg. 43) believed to be formed by the thermolysis of Δ^3-1,3,4-oxadiazoline (117) (pg. 43 in Introduction). Thiadiazolines decompose readily[124-130] upon heating giving thiiranes (eq. 51, page 45). Oxadiazolines, containing the exocyclic iminogroup (157) were expected to decompose via iminooxiranes. It is known that iminooxiranes are extremely reactive. They are known to decompose to isonitrile and carbonyl compound as shown below[173] (eq. 72).



(72)

As described in the Introduction (pg. 49), thermolysis of 174 was found[23] to proceed by two different pathways (eq. 73).



174

(73)

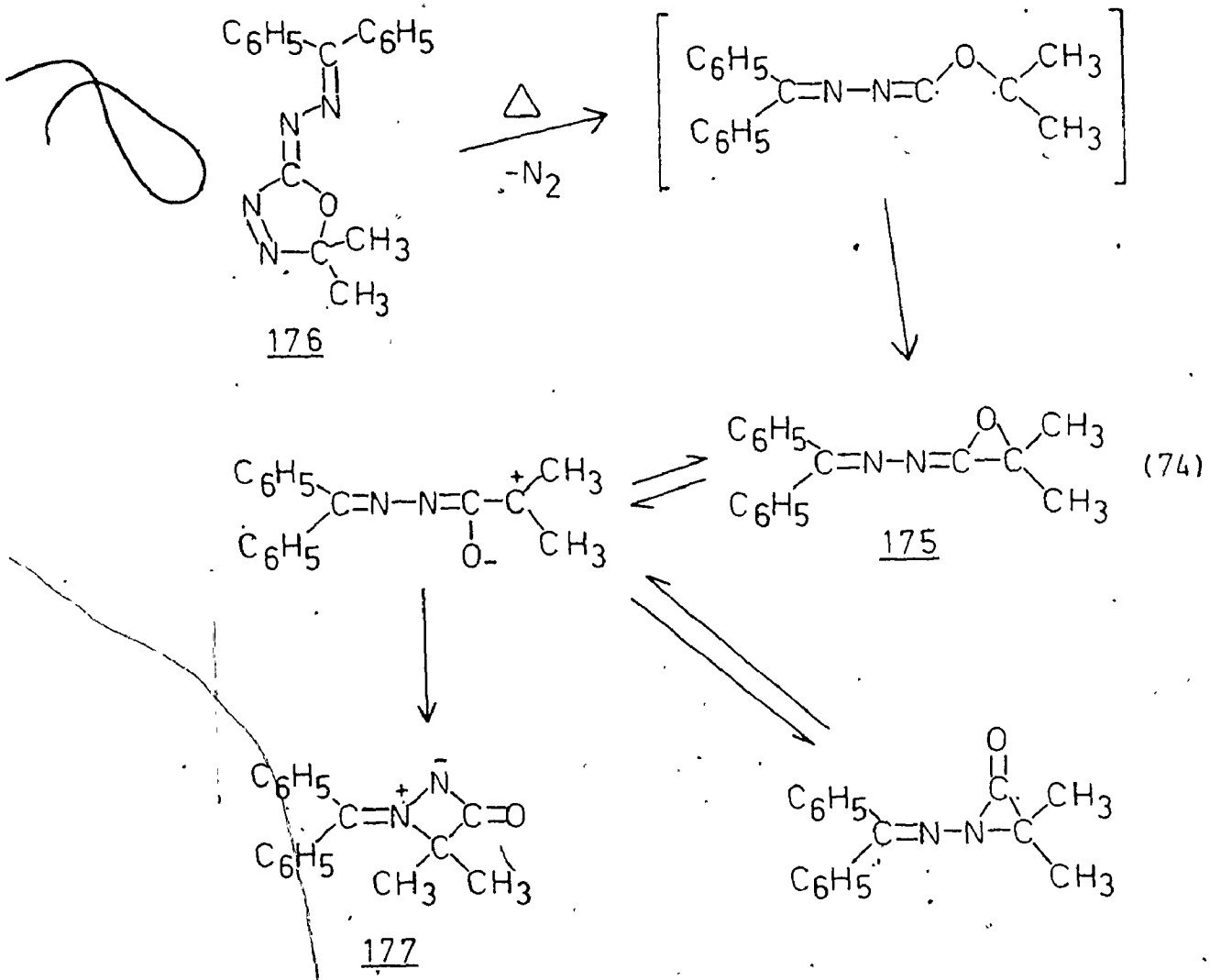
Cameron did not suggest an iminooxirane intermediate, however, the possibility that the thermal decomposition is "normal" through the three-membered intermediate should be considered. The products of the pyrolysis via pathway k_1 could be formed from iminooxirane as well as from direct three-bond cleavage of 174.

When another nitrogen was introduced into the side chain, the products of thermolysis were found to be different. Ip[131] proposed that the process is homolytic in nature, with the initial formation of the iminooxirane (175). For example, 2-diphenylmethylenehydrazono-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (176) decomposed thermally giving 1-diphenylmethyl-3-oxo-1,2-diazetidinium hydroxide, inner salt (177), a mesoionic compound (eq. 74) (pg. 101). Ip was not able to isolate or even detect the iminooxirane intermediate. Similarly, Knittel[28] had suggested the intermediate iminooxirane to explain the formation of benzoyl cyanide in LTA oxidation of p-dimethylaminobenzaldehyde semicarbazone (see pages 20-21).

Unpredictable results obtained from thermolysis of oxadiazolines (174 and 176) prompted us to investigate the analogous triazolines; compounds similar to oxadiazolines, where oxygen is replaced by the N-C_6H_5 group. The aim of the work was to establish the products of thermolysis and possible mechanism by which decomposition takes place.

The qualitative and quantitative product analysis established that, contrary to oxadiazolines, all three compounds studied (140a, 141a, 142) decompose exclusively by one pathway (eq. 75) (pg. 102).

Since, as mentioned previously, oxadiazolines 174 undergo two



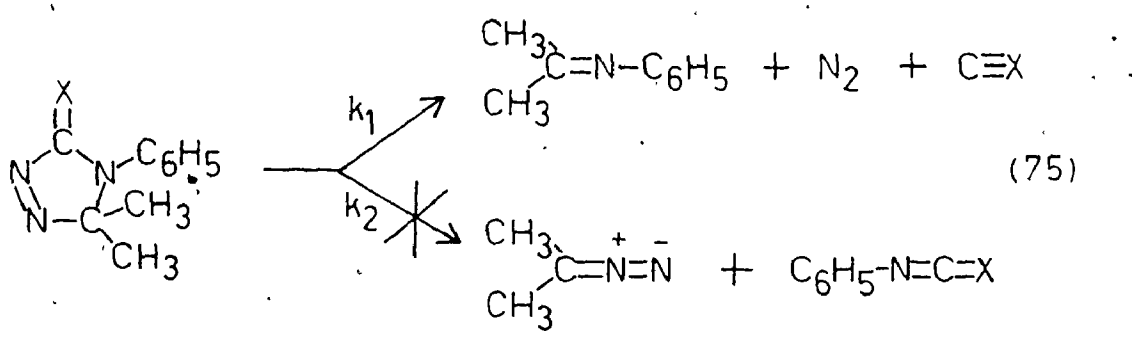
176

175

177

(74)

modes of decomposition, special attention was given to the detection of the other possible products of thermolysis (eq. 75). For example, if 141a had thermolysed via pathway k_2, diazopropane and phenylisocyanate or products from their reaction with each other would have to be present. Such products include oxindoles and hydantoins, which have been prepared independently in this laboratory from phenylisocyanate and diazo alkanes.[174] They would have been detected and identified readily had they



(75)

140a : X = N-C_6H_5 141a : X = O 142 : X = S

been formed from 141a. As mentioned above, none of the other possible products were observed.

Besides acetone anil (152), phenylisocyanide (153) was formed in the process of thermolysis of 140a. It was identified by comparison of ir and pmr spectra with those of an independently prepared sample (Experimental, page 72). Carbon monooxide and nitrogen were shown to be present in the gas sample from thermolysed 141a, by mass spectrometry.

The formation of carbon monosulfide (155) from 142 was, at first, deduced from the confirmed presence of acetone anil and nitrogen rather than from direct observation or from detection of products of its further reactions. A literature search showed that CS has been prepared previously by several different methods.[175-180] However, as many authors reported,[181-185] carbonmonosulfide is very unstable and even at very low temperature (-178°C) readily polymerizes forming the polymer C_xS_y. The ratio of x and y is not known and it appears that it varies considerably from $x >> y$, to $y >> x$. The polymer itself oxidizes at higher

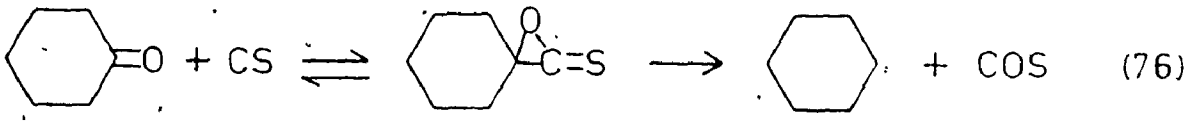
temperatures (~ 200°C). When 142 was thermolysed in solution, the solution turned dark quickly and the residue after evaporation of solvent had polymeric consistency. Column chromatography of the residue gave fractions which had no pmr absorption and elemental analysis indicated that mainly carbon and sulphur were present (Experimental, page 76). Traces of N and H were found in two of the samples analysed. These could have been incorporated into the polymer from the attack of CS on either the product 152 or on the starting material 142. Since kinetic results showed that the decomposition is of first order, attack on the product is suspected.

The formation of CS in the process of thermolysis of 142 was further confirmed by UPS and by trapping experiments.

The ultraviolet photoelectron spectroscopy (UPS) was carried out on the products of vacuum thermolysis of 142. The spectrum showed that CS_2 (I.P., 10.17, 12.80, 14.47, 16.16 eV) and N_2 (I.P., 15.57, 16.6-17.8 envelope, 18.73 eV) were the major volatile products. A small quantity of CS was indicated by the band at 11.28 $\pm$ 0.05 eV. That the CS_2 was the product of the gas phase thermolysis of 142 can be explained by the presence of intermediate CS. Richardson and coworkers[186] also observed that CS is converted to CS_2 at room temperature via a heterogeneous wall reaction.

Trapping experiments with cyclohexanone and with sulphur gave further indication that CS is an intermediate in the thermolysis of 142. A sample of the gas swept out of a flask containing 142 in hot cyclohexanone (Experimental, page 77) contained COS (m/e = 60). Similarly, CS_2 (m/e = 76) was obtained from the decomposition of 142 in chlorobenzene containing S_8. It is difficult to rationalize the formation of COS and CS_2 without involving the intermediacy of CS which is expected to have

carbene-like properties and might attack cyclohexanone as shown in the following equation (eq. 76).



(76)

In both cases, control experiments were carried out, where the traps were absent and the products, CS_2 and COS, respectively, were not observed. Thus, it can be concluded that these were formed only from the reaction of carbonmonosulfide with the corresponding trap.

The carbene-like reactivity of carbonmonosulfide was also observed by Steudel.[187,188] He reported that CS, prepared in a high frequency discharge tube, undergoes heterogeneous reactions to form CSSe and CSTe if the walls of the discharge tube are covered with Se and Te, respectively (eq. 77).

$$CS + Se \rightarrow S = C = Se$$
$$CS + Te \rightarrow S = C = Te \qquad (77)$$

Similarly, halogens (Cl_2, Br_2 and I_2) reacted, forming thiocarbonyl halides (eq. 78).

$$CS + Cl_2(Br_2, I_2) \rightarrow S = CCl_2(Br_2, I_2) \qquad (78)$$

The products were identified by ir at -190°C in CS_2 matrix or by mass spectrometry. The reaction was done on a small scale and yields were low due to polymerization of CS. Recent work by Klabunde and coworkers[189]

deals with several gram quantities of carbonmonosulfide. They condensed CS with excess of a halogen or a mixed halogen, to prepare compounds of general formula CSX_4 (eq. 79).

$$CS + 2Cl_2(Br_2) \rightarrow CSCl_4(Br_4)$$

$$3CS + 7BrCl \rightarrow CSCl_4 + CSBr_4 + Cl_2BrCSCl + Br_2 \qquad (79)$$

From the equation above, it can be seen that two molecules of halogen added to one molecule of carbonmonosulfide (155). However, when hydrogen halide was reacted with CS, only 1:1 addition occurred and the thioformyl halide (HC(X) = S) were generated. These compounds were previously unknown.

The reactions mentioned above are the only ones reported so far in the literature. Therefore, we decided to investigate the possibility of trapping CS to functionalize organic molecules; that is, to utilize it in organic synthesis.

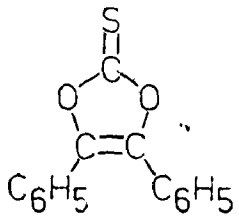
The organic traps that were investigated can be divided into two groups:

a) traps which might react by utilizing the carbene-like character of 155 to trap it through addition to C=C or C=O bonds,

b) an organometallic species known to coordinate CO and CS.

Potential traps for group (a) were selected by considering that CS might have either electrophilic or nucleophilic properties. Cyclohexene, anthracene, phenylisocyanate, phenylisothiocyanate, fumaronitrile, 4,4'-bis(dimethylamino)-benzophenone (Michler's ketone) and benzil were chosen. Chlorobenzene and nitrobenzene, which were used as solvents for

some of the trapping attempts, could potentially act as traps themselves. It was by no means clear what ultimate products should be expected, for some initially-formed adducts might not survive the temperature (175°C) required to generate CS. Hence, the workup consisted of a general search for tractable products such as 178 from benzil or 179 from Michler's ketone.



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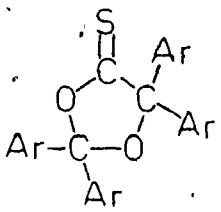
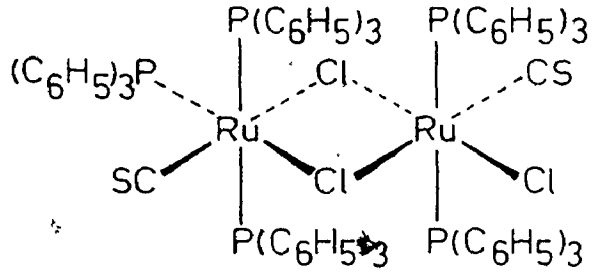


179

None of the attempts to capture CS with group (a) traps showed any promise of synthetic utility. In fact, the products were found to be mainly of C_xS_y polymeric nature.

For category (b), the organometallic substance $Rh((C_6H_5)_3P)_3Cl$ was used, since the existence of organometallic compounds, containing the CS moiety in the structure, has been known for several years.[190,191] They are complexes of the transition metals Ru and Rh in which one of the ligands is CS (180, 181, 182). However, none of these complexes (180, 181, 182) were prepared directly by the reaction of CS and organometallic compound, but through carbon disulfide. The mechanism of the rearrangement is not really known, but on the basis of spectroscopic evidence, the intermediate 183 has been suggested[191] as shown in eq. 80.



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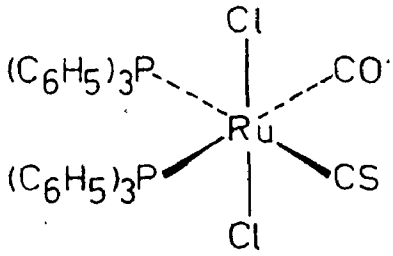

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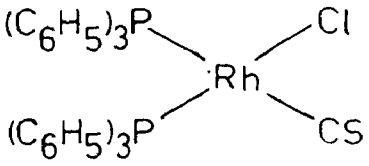

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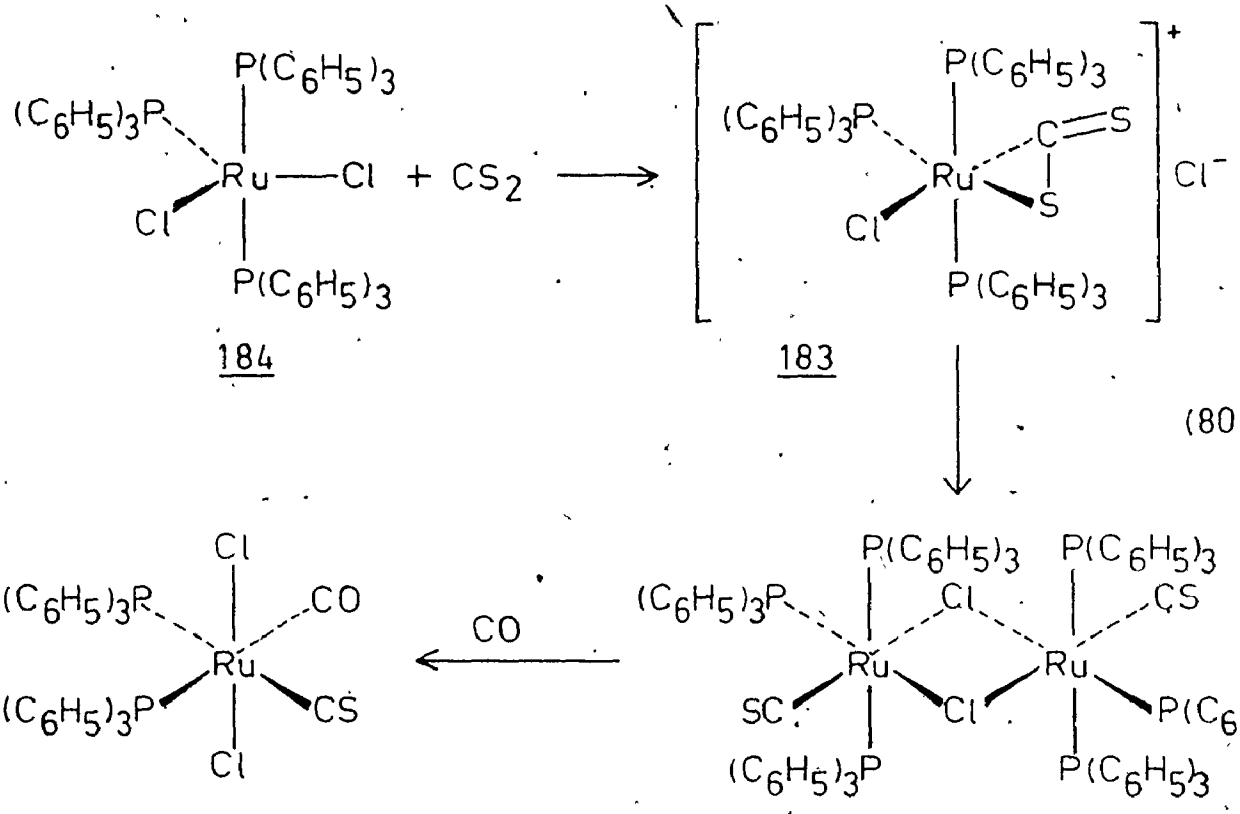


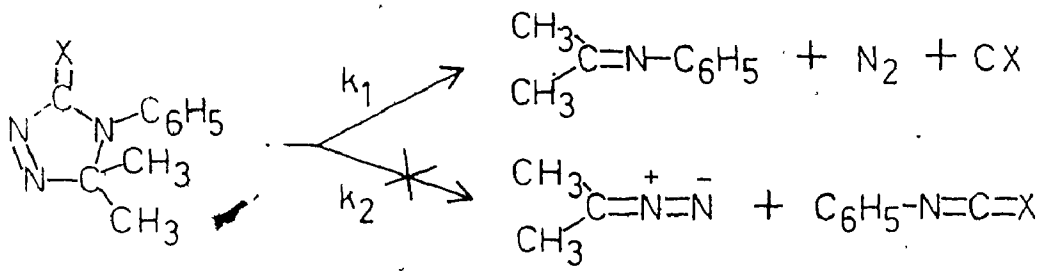
184 183

(80)

It was hoped that the apparent stability of the compounds of the type 180, 181 and 182 would be a driving force for the reaction of CS with the corresponding organometallic starting material, e.g., 184. However, the organometallic substance $Rh((C_6H_5)\ P)\ Cl$ was not successful either in trapping carbonmonosulfide and thus it appears that under our experimental conditions (relatively high temperature), CS is not useful synthetically.

(2) KINETIC STUDIES

Analysis of the products from pyrolysis of 140a, 141a and 142, revealed that only acetone anil, nitrogen and phenylisocyanide (or carbon monooxide and carbonmonosulfide, respectively) were formed in the process. Thus, it could be concluded that one mode of decomposition took place exclusively (eq. 80).



(80)

140a: X = N-C6H5 141a: X = O 142: X = S

In order to determine possible mechanisms and to seek information about the transition states involved in thermolyses, kinetic studies were carried out. Mechanistic probes included:

(i) kinetic order

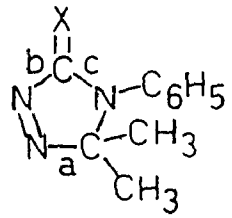
(ii) solvent polarity dependence of k.

(iii) substituent effects on k

(iv) activation parameters.

The investigation of concentration dependence of the rate constants confirmed first-order kinetics for all three compounds studied (Tables 2, 5, 9). As can be observed from Tables 1-10, all compounds (140a, 141a, 142) gave similar results and therefore all three of them are considered together in the discussion of the mechanism of decomposition.

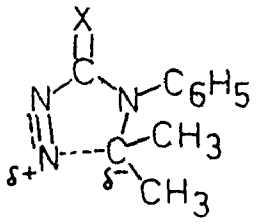
According to the results of product analysis, it can be concluded that three bonds were broken overall in the thermolysis. Let's call them a, b, c as in 185 below, for simplicity.



185

The cleavage of the bonds in 185 can occur via many possible ways:

(i) One bond broken at a time. This can proceed through three different transition states for each bond considered; two of them polar but with opposite polarities and one nonpolar. For example, for bond a, they are: 186, 187, 188. Analogous transition states can be drawn for the cleavage of bonds b and c, thus giving nine overall for this case.



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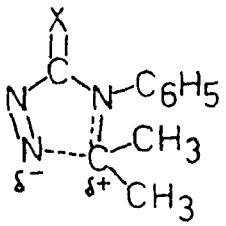

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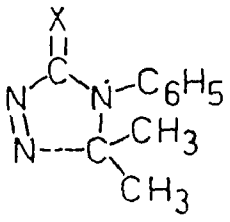
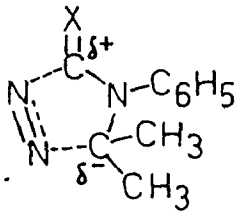


188

(ii) Simultaneous two bond scission. There are, again, nine possibilities, three for each pair of bonds. Thus, for example, when bonds a and b are being cleaved at a time, possible transition states can be represented by 189, 190, 191.



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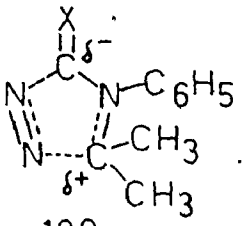

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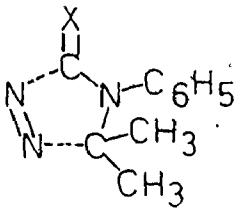
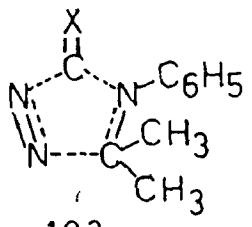


191

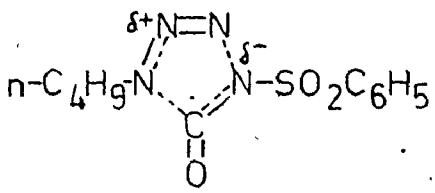
Similarly, for pairs b and c, and a and c, analogous representatives of transition states can be considered.

(iii) When three bonds cleave simultaneously, the number of possibilities for transition states increases dramatically, since there are five atoms in the ring, on each of which a partial charge can be written as δ^+ or δ^-. For δ^+ on a given atom, there are four choices for δ^-. Therefore, the number of polar transition states becomes twenty. One other possibility has to be considered, when the simultaneous bond cleavage if without a charge separation, i.e., the fully concerted non-polar process represented by 192.



192

From this large number of possibilities (39 overall), solvent effect studies eliminate heterolytic bond cleavage for all three compounds (140a, 141a, 142). The investigation showed that increasing polarity of the solvent (E_T value of solvents ranged from 32.5-42.5) did not increase the rate of thermolysis (Tables 1, 4, 8). Polar transition states such as 186, 187, 189, 190, would be better stabilized by more polar solvents and thus the rate of thermolysis would have increased with solvent polarity, which was not observed. For example, Cameron's[23] studies showed that, for thermolysis of 5,5-diphenyl-2-(p-tolylimino)-Δ^3-1,3,4-oxadiazoline (157, $R_1=R_2=C_6H_5$, $R_3=C_6H_4-CH_3$), $k_{(C_6H_5NO_2)} = 2k_{(C_6H_5Cl)}$ at 85°. Cameron concluded that the transition state was more polar than the starting material. Also, L'Abbé[192] and coworkers, when studying cycloreversions of 1,3-dipole adducts, discovered that the decomposition rate constants for 1-n-butyl-4-sulfonyl-Δ^2-tetrazolin-5-one at 125°C in chlorobenzene and nitrobenzene were 26.4×10^{-4} and 70×10^{-4} min^{-1}, respectively. On the basis of all their results they suggested a transition state involving charge development as shown in 193. McGreer and coworkers[109-112]



193

observed a similar effect on the thermolysis rates of some substituted pyrazolines and proposed polar transition states.

The substituent effect studies, carried out with 141a-e, also point to a non-polar transition state (Table 7). The small ρ value (-0.17) obtained (Fig. 11) indicates that there is very little stabilization or destabilization of the transition state by substituents. Larger ρ values could be expected if the transition state had polar character. For example, when West[26] and later Cameron[23] studied the decomposition of oxadiazolines, they observed a strong influence of substituents on the rate constants of retro-1,3-dipolar cycloaddition. Their ρ values were -1.31 and +1.0, respectively, and they concluded that the transition state of a retro-1,3-dipolar cycloaddition possessed partial ionic character.

In view of the negligible effects of solvent polarity and substituents on the rates of thermolysis of 140a, 141a and 142, all transition states more polar than the corresponding starting material are unlikely and only seven of the overall thirty-nine possibilities remain.

The possibility of a fully-concerted process (192) can be considered. The Woodward-Hoffmann orbital symmetry correlations are used to predict the stereochemical course of a pericyclic reaction.[193] By these rules, a concerted process is allowed thermally for completely suprafacial reactions, when $m + n + p = 4q + 2$ (where m, n, etc. are numbers of π electrons in the open-chain reactants and q is an integer,

e.g., 0, 1, 2, 3,...). In our case, the reaction fulfills the criterion ($m + n + p = 6$) and therefore the concerted cycloreversion reaction is thermally allowed. The thermolysis of 185 in concerted fashion can be classified as a cheletropic process, in which two σ bonds broken terminate at a single atom. That is, all three bonds in 185 may be partially broken at the transition state. It must be borne in mind that although the reaction is symmetry-allowed according to the Woodward-Hoffmann rules, it does not necessarily mean that a concerted process takes place. Rules do not give any guidance as to the degree of synchroneity of concerted processes.

A fully concerted process is generally characterized by high changes in activation entropies $\Delta S^{\ddagger}$ accompanied by a relatively small enthalpy of activation $\Delta H^{\ddagger}$ ($\Delta H^{\ddagger} < 25$ kcal/mole).[194] In practically every case of Diels-Alder reactions examined, it was found that the strongly negative entropies of activation, $\Delta S^{\ddagger}$, are remarkably constant. An average value of about -35 e.u. points to a highly ordered rate-determining transition state.[195-199] According to Sauer,[194] the strongly negative values of $\Delta S^{\ddagger}$ must be regarded as important evidence of synchronous bond formation.

However, it is not true that dissociative concerted reactions show large positive values of $\Delta S^{\ddagger}$. In a concerted retro cycloaddition, for example, the atoms are restricted similarly in both reactant and transition state. In the latter, the σ bonds which break are slightly "engthened," compared to those in the reactant, but the remaining bonding

is strengthened and new rigidity is coming in with the onset of π-bonding in the developing fragments. Such a process might therefore be expected to have a $\Delta S^{\ddagger}$ value near zero. In a stepwise, non-polar, retro cycloaddition where only one bond breaks to give an open-chain intermediate, the ordering of the system is relaxed on going to the transition state which leads to the intermediate, so that a positive entropy of activation is expected.

Results obtained from the investigation of thermolysis of trans-3,5-diphenyl-1-pyrazoline and trans-3,5-bis(-p-methoxyphenyl)-1-pyrazoline led Timberlake and Bandlish[90] to conclude that the thermal mode of decomposition of those compounds was a concerted, two-bond cleavage. Energies of activation were 27.5 and 26.1 kcal $mole^{-1}$, respectively.

Schneider and Ströhacker[73] argued that the stereochemistry of products (cis-cyclopropane mainly was formed) of thermolysis of cis-3,5-diphenyl-1-pyrazoline and the activation parameters ($\Delta H^{\ddagger} \simeq 25$ kcal $mole^{-1}$, $\Delta S^{\ddagger} \simeq 0 \pm 3$ cal.K^{-1}.$mole^{-1}$) provide a strong point in favour of a concerted process.

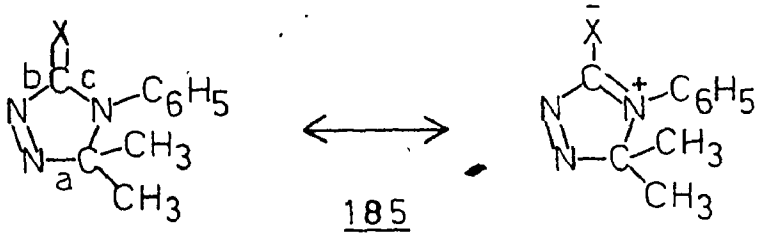
Crawford and Ohno's studies[69] on thermolysis of some pyrazolines indicated a stepwise process ($\Delta H^{\ddagger} \simeq 40$ kcal $mole^{-1}$, $\Delta S^{\ddagger} \simeq 11$ cal.K^{-1}.$mole^{-1}$).

As many authors[96] have pointed out, the interpretation of activation parameters data and other kinetic evidence has to be done with caution. The total evidence has to be considered in choosing a probable reaction mechanism from among the ones that are possible.

Our kinetic experimental results (Tables 1-10) suggest that the thermal decomposition of triazolinone 141a ($\Delta H^{\ddagger} \simeq 35$ kcal $mole^{-1}$, $\Delta S^{\ddagger} \simeq 6$-8 cal.$K^{-1}$.$mole^{-1}$) is a stepwise process involving homolytic

cleavage of bonds, while 140a ($\Delta H^{\ddagger} \approx 28$ kcal mole^{-1}, $\Delta S^{\ddagger} \approx 0$-2 cal.K^{-1}.mole^{-1}). and 142 ($\Delta H^{\ddagger} \approx 33$ kcal mole^{-1}, $\Delta S^{\ddagger} \approx 0$ cal.K^{-1}.mole^{-1}) may decompose via a concerted reaction.

If thermolysis of 141a is assumed to be stepwise, there is still the question as to which bond might break first. There is precedent for stepwise decomposition of unsymmetrical azo compounds. From the secondary deuterium kinetic isotope effect studies of unsymmetrical azo compounds, Seltzer and coworkers[65,74,75] concluded that the first step of the thermal decomposition is the formation of a short-lived diazenyl radical (eq. 41, page 35). Since the substances studied here (185) are highly unsymmetrical azo compounds, it is reasonable to suggest stepwise, one-bond cleavage characteristic of such compounds. Thus, three possible fissions can occur (bonds a, b, c). Rupture of bond c, as a first step of thermolysis, seems very unlikely, since that bond has a bond order greater than unity, as shown with the accompanying resonance structures.



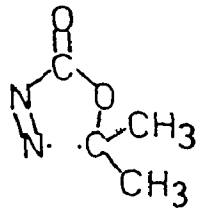
185

It is known that amides do not readily cleave at the N-CO bond in thermal processes. Moreover, Cameron[22] found from X-ray studies that the bond between the oxygen and the sp^2 carbon in oxadiazoline 174 (R_1=R_2=CH_3, R_3=Ar), has considerable double bond character. Thus, breaking of bond c in the rate-determining step need not be considered seriously.

The possibility of cleavage of bond b in the first step cannot be dismissed as easily, although it is also more than a single bond, because of hydrazyl resonance in the diazenyl radical. It was attempted to use mass spectrometry for clarification of the decomposition mechanism, for there are often similarities between thermal and mass spectrometric fragmentations. The high resolution mass spectrum of 141a revealed the presence of the N_2CO fragment (calculated mass 56.0056, observed mass 56.0077, error +0.00213). When sample 142 was subjected to the same high resolution mass spectrum-computer analysis the N_2CS fragment was not observed. The observation of a mass peak corresponding to the N_2CO species indicates that bond b probably is not broken in the first step of the thermolysis of 141a. The rise of thermal decomposition studies to confirm mass spectral assignments has interested several authors.[200-202] The decomposition of pyrazine-2,3-dicarboxylic anhydride,[200] phthalic anhydride[201] and 2,5-diphenyl-1,3,4-oxadiazole[202] have been studied in this regard. Also, West[26] analyzed mass spectra of several of the oxadiazolines in terms of two modes of decomposition and found quite good correlation of electron-impact induced reaction and thermal decomposition.

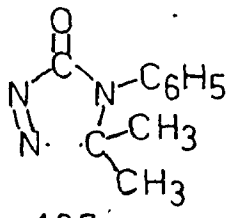
By eliminating primary cleavage of bond b and c, it seems very likely that bond a is first broken in the process of thermolysis. Cameron's[22] X-ray structure of oxadiazoline 174 ($R_1=R_2=CH_3$, $R_3=Br$) revealed that corresponding bond a is the longest bond in the ring system. The analogous structural feature can be expected in triazoline system 185. Studies of β-deuterium kinetic isotope effects on the rate of decomposition of oxadiazolinones carried out in our laboratory[203] also imply the rupture of

the corresponding bond a in the rate determining step and intermediate 186 was suggested.



186

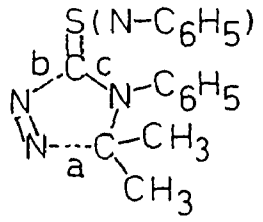
On the basis of all available evidence including the above-mentioned analogies to the related oxadiazolines and oxadiazolinones, the most likely mechanism for thermolysis of the triazolinone involves the diradical intermediate 187.



187

As mentioned previously, the kinetic data (entropies) obtained from thermolysis of 140a and 142 suggest concerted rather than stepwise bond cleavages. Detailed mass spectrometry-computer analysis of 142 failed to reveal the fragment N_2CS, thus suggesting that bond b is broken in the initial electron-impact-induced fragmentation step. As mentioned before, analogy can be drawn between mass spectrometric and thermolytic mechanisms and, therefore, the absence of N_2CS supports our suggestion that a concerted process is most likely in the decomposition of 142 and 140a. It is very difficult to draw any conclusion, on the basis of available evidence, as to whether the process is fully con-

certed (i.e., all three bonds are broken at once) or whether just elimination of nitrogen is concerted. However, since it is expected that bond c is the shortest and strongest bond, it seems quite likely that its cleavage is not part of the rate determining step. Thus, transition state 188 seems to be the most probable, where bonds a and b are broken simultaneously, but a fully concerted process cannot be excluded.

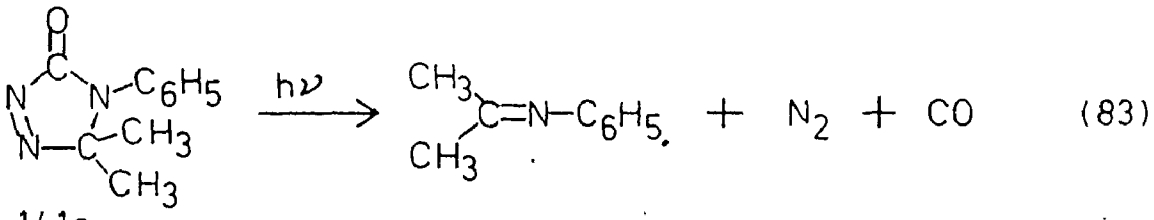


188

C. PHOTOCHEMICAL DECOMPOSITION OF 3,3-DIMETHYL-4-PHENYL-Δ^1-1,2,4-TRIAZOLIN-5-ONE (141a)

The aim of this part of the work was to compare the products of thermal and photolytic decomposition of 141a and to establish the multiplicity of the excited state from which the photodecomposition takes place.

As mentioned in the Experimental Section (page 80), 141a upon irradiation decomposes giving acetone anil; the same product as that of thermolysis (page 83).



141a

In order to identify the excited state involved in photolysis of 141a, a quantitative study, utilizing quantum yield techniques, was made of the direct and sensitized photolysis of 141a, as well as of direct photolysis with a quencher present. The experiments revealed that the quantum yield of direct photolysis was 0.065 (Table 11). Upon addition of sensitizer (benzophenone, E_T = 69 kcal mole^{-1}), the quantum yield of the photolytic process increased to 0.22 (Table 12). When a large excess of quencher (1,3-cyclohexadiene) was added to the solution, no decomposition of 141a was observed after 10 hrs. of irradiation. Since 1,3 dienes are known to quench triplet states,[204] it can be concluded that the reaction in direct photolysis must certainly involve the triplet state (T_1) of starting material. The low quantum yields (0.065) observed can be explained in terms of inefficient intersystem crossing (ISC) (eq. 84).

$$\underline{141a} \xrightarrow{h\nu} (\underline{141a})^*_{S_1}$$

$$(\underline{141a})^*_{S_1} \rightarrow (\underline{141a})^*_{T_1} \qquad \text{(ISC)} \qquad (84)$$

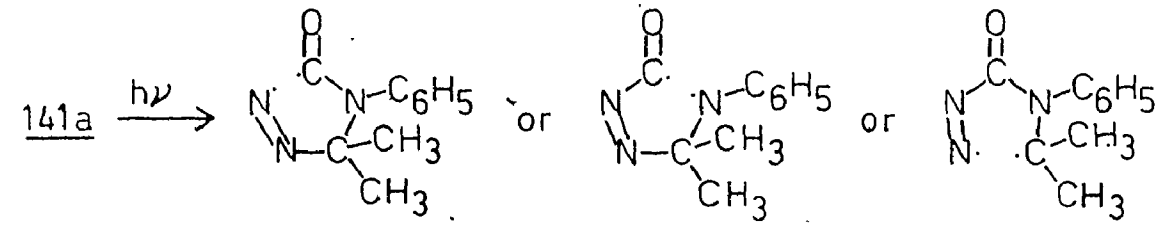
$$(\underline{141a})^*_{T_1} \rightarrow \text{products}$$

Several mechanisms can be proposed for photolytic dissociation of triazolinone (141a).

(i) A fully-concerted process, involving simultaneous cleavage of three bonds can be ruled out, since according to the Woodward-Hoffman rules, this process is not photochemically allowed, since m + n + p = 6 (see page 112).

(ii) A stepwise process could involve one or two bonds being broken at the same time and there are several possibilities.

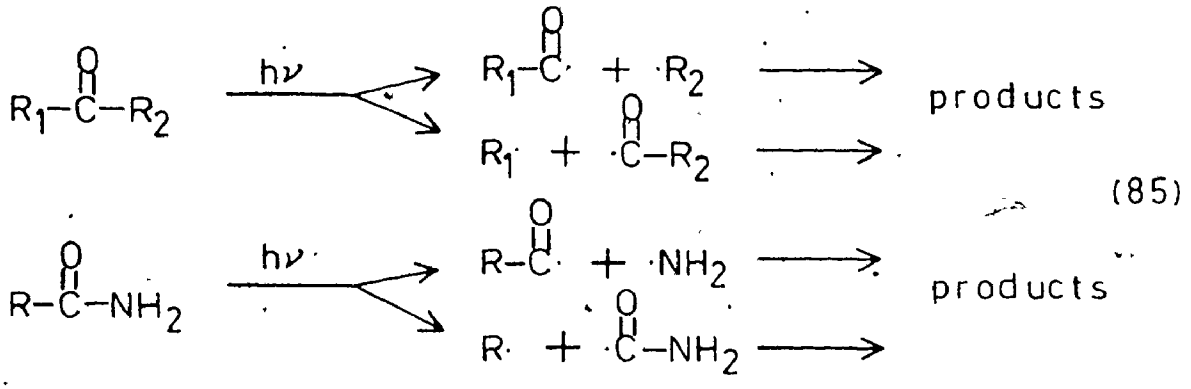
(a) Cleavage of one bond could lead to any one of the three intermediates shown below:



189 190 191

Processes involving intermediates 189 and 190 can be viewed as Norrish type I reactions. Most aldehydes and ketones,[205] as well as amides[205] in inert solvents undergo this type of reaction (eq. 85).

Which one of the two R-CO bonds of an unsymmetrical ketone cleaves, depends on the relative stabilities of the two possible R·



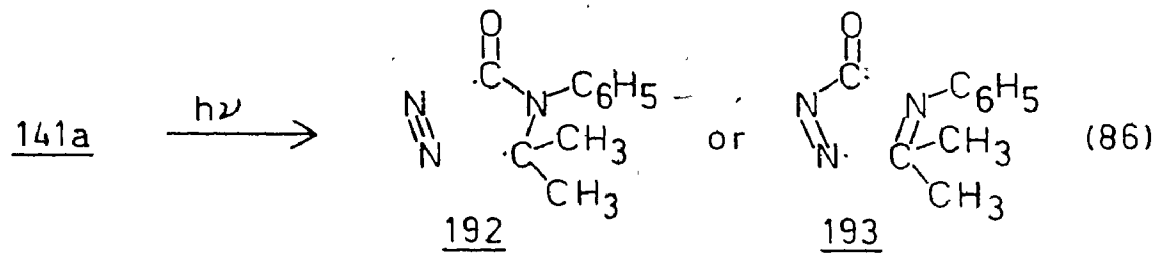
(85)

radicals. The initial cleavage is reversible and thus quantum yields of this reaction never approach one, even for very reactive ketones.[204]

From the point of view of radical stability, the process involving 190 appears to be more likely than that involving 189, since benzylic conjugation should provide better stabilization than hydrazyl type resonance ($R\text{-}\ddot{N}\text{=}\ddot{N}\cdot \leftrightarrow R\text{-}\dot{N}^{+}\text{=}\ddot{N}:^{-}$) in the diazenyl radical.

The other possible pathway of photolysis, with intermediate 191 cannot be excluded either.

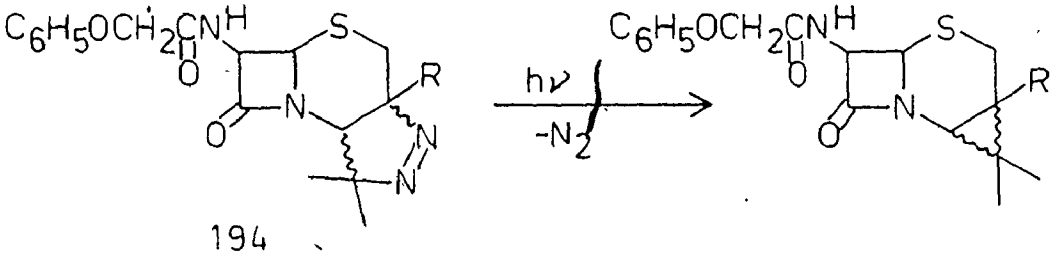
(b) Cleavage of two bonds (eq. 86).



192 193 (86)

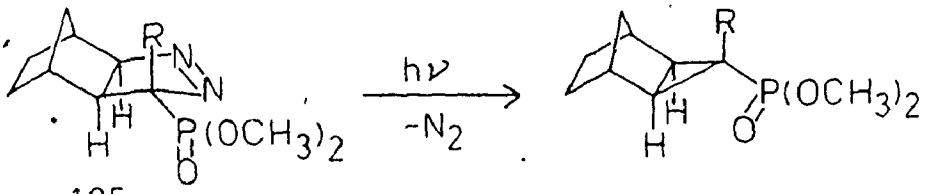
The intermediate 192 is similar to that in the photochemical decomposition of 1-pyrazolines. Photoreactions of this type provide a useful synthetic route to cyclopropane derivatives. Irradiation of several steroidal 4'-β,5-dihydro-[17α,1b-c]pyrazoles leads exclusively by elimination of nitrogen to cyclopropa[16α,17α] compounds.[206] The

cephalosporin derivatives (194) are similarly converted into the cyclopropanes[207] (eq. 87).



194 (87)

Complete retention of configuration is observed in the direct photolysis of 1-pyrazolines (195), whereas in the corresponding benzophenone-sensitized irradiation, mixture of isomers are obtained.[208]



195

Singlet and triplet excited states, respectively, are believed to be implicated. Quantum yields for the elimination of nitrogen from a series of substituted 1-pyrazolines have been determined and range from 0.12-0.88.[209] It is believed that cyclic azo compounds decompose predominantly via the singlet state in the absence of sensitizer.[210] Since it has been demonstrated that 141a decomposes via the triplet state, intermediate 192 seems unlikely, but it cannot be ruled out. Neither can a mechanism involving 193 be excluded.

SUMMARY

The oxidative cyclization of substituted and unsubstituted guanylhydrazones have been investigated. This led to the new compounds, Δ^1-1,2,4-triazolines and to a postulate for the mechanism of their formation.

Studies of the thermal decomposition of several triazolines revealed that only one pathway is followed. The thermolytic process was investigated kinetically and it is suggested that a stepwise process, involving homolytic cleavage of one bond, is involved in the case of 3,3-dimethyl-4-phenyl-Δ^1-1,2,4-triazolin-5-one. Concerted elimination of nitrogen is proposed as a possible mechanism for the thermolysis of 3,3-dimethyl-4-phenyl-5-phenylimino-Δ^1-1,2,4-triazoline and 3,3-dimethyl-4-phenyl-Δ^1-1,2,4-triazoline-5-thione.

In the process of thermolysis of 3,3-dimethyl-4-phenyl-Δ^1-1,2,4-triazoline-5-thione, the formation of carbon monosulfide was established. The intermediacy of the CS species was confirmed by some trapping experiments and by photoelectron spectroscopy. Attempts to utilize the high reactivity of carbon monosulfide in synthesis were not successful.

Exploratory work on photochemical decomposition of 3,3-dimethyl-4-phenyl-Δ^1-1,2,4-triazolin-5-one was carried out. It was established that the process of photochemical decomposition leads to the same products as the thermolytic process. Quantum yield experiments revealed that the photolysis involves the triplet state of the starting material. The most likely process of photodecomposition is thought to be Norrish type I, involving the cleavage of the N_4-C_5 bond.

Table 1. Rate of Thermal Decomposition of 140a

Temp. [°C]	CCl_4 k x 10^4 (sec^{-1})	C_6H_6 k x 10^4 (sec^{-1})	C_6H_5-Cl k x 10^4 (sec^{-1})	C_6H_5-NO_2 k x 10^4 (sec^{-1})
79.0	0.361 ± 0.007	0.290 ± 0.003	0.212 ± 0.004	0.124 ± 0.002
90.6	1.74	1.56	1.17	0.745
97.4	3.08	2.52	1.59	1.133
100.8	3.58 ± 0.02	3.43 ± 0.04	2.62 ± 0.02	1.35 ± 0.01
103.7	5.21 ± 0.04	4.27 ± 0.03	3.41 ± 0.03	2.03 ± 0.02
106.1	6.80 ± 0.07	5.20 ± 0.06	3.97 ± 0.04	2.50 ± 0.02
111.6	12.09 ± 0.09	10.94 ± 0.08	7.87 ± 0.08	4.45 ± 0.04
119.2	26.63 ± 0.13	20.33 ± 0.15	17.15 ± 0.13	10.40 ± 0.13
133.6	98.65 ± 0.81	85.71 ± 0.73	63.04 ± 0.52	38.16 ± 0.37

Note: deviations quoted are standard deviations, for average values of several runs. Where no deviation is given, a single determination was made.

Table 2. Concentration Dependence Studies of 140a

(t = 100.8°C)

Solvent	Initial conc. (mol l^{-1})	k x 10^4 * [sec^{-1}]
CCl_4	0.0137	3.58
	0.0275	3.52
	0.0580	3.60
	0.1116	3.57
C_6H_5-NO_2	0.010	1.33
	0.020	1.37
	0.080	1.38
	0.160	1.32
$CHCl_3$	0.0124	2.72
	0.0248	2.78
	0.0496	2.75
	0.0992	2.73

* single determination was made.

Table 3. Activation Parameters for Thermal Decomposition of 140a

Solvent	$\Delta H^{\ddagger}$ (kcal.mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	$\Delta F^{\ddagger}$ (kcal.mol^{-1})	Ea (kcal.mol^{-1})
CCl_4	28.5 ± 0.4	1.6 ± 1.2	27.9 ± 0.9	29.3 ± 0.4
C_6H_6	28.8 ± 0.6	2.3 ± 1.5	28.0 ± 0.2	29.6 ± 0.6
C_6H_5Cl	28.8 ± 0.1	1.8 ± 0.2	28.2 ± 0.5	29.7 ± 0.2
$C_6H_5NO_2$	28.6 ± 0.3	0.2 ± 0.7	28.5 ± 0.4	29.4 ± 0.3

Table 4. Rates of Thermal Decomposition of 141a

Temp. [°C]	C_6H_6 $k \times 10^4$ (sec^{-1})	C_6H_5Cl $k \times 10^4$ (sec^{-1})	$C_6H_5NO_2$ $k \times 10^4$ (sec^{-1})
148.0	2.550 ± 0.009	1.916 ± 0.010	1.116 ± 0.010
152.5	4.54 ± 0.02	3.54 ± 0.014	2.787 ± 0.009
157.1	7.57 ± 0.03	5.20 ± 0.02	4.64 ± 0.04
161.8	9.82 ± 0.05	7.65 ± 0.03	5.99 ± 0.05
166.6	16.38 ± 0.07	12.76 ± 0.07	7.74 ± 0.07
172.5	31.10 ± 0.21	21.20 ± 0.13	12.16 ± 0.11
200.6	300.6 ± 2.8	222.1 ± 1.9	130.1 ± 1.5

Note: deviations quoted are standard deviations for average values of several runs.

Table 5. Concentration Dependence Studies of 141a

(t = 152.5°C)

Solvent	Initial conc. (mol l^{-1})	$k \times 10^4$* [sec^{-1}]
C_6H_6	0.0142	4.56
	0.0284	4.58
	0.0568	4.57
	0.1136	4.52
$C_6H_5NO_2$	0.0113	2.81
	0.0226	2.77
	0.0452	2.79
	0.0904	2.77

* single determination was made

Table 6. Activation Parameters for 141a

Solvent	$\Delta H^{\ddagger}$ (kcal.mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)	$\Delta F^{\ddagger}$ (kcal.mole^{-1})	Ea (kcal.mole^{-1})
C_6H_6	35.1 ± 1.2	7.8 ± 2.6	31.8 ± 2.2	36.0 ± 0.9
C_6H_5Cl	34.9 ± 0.5	6.8 ± 1.1	32.1 ± 0.9	35.8 ± 0.4
$C_6H_5NO_2$	35.0 ± 0.2	5.8 ± 0.5	32.5 ± 0.3	35.9 ± 0.3

Table 7. Correlation of Rates of Decomposition of 141a by Hammett Equation

solvent: nitrobenzene

temperature: 172.5 ± 0.1°C

Substituent	σ	k x 10^3 (s^{-1}) (a)	log $\frac{k_i}{k_o}$ (b)
p-OCH_3	-0.268 ± 0.02	1.343 ± 0.007	0.0431 ± 0.004
p-CH_3	-0.170 ± 0.02	1.301 ± 0.012	0.0293 ± 0.006
p-H	-0.00	1.216 ± 0.011	0.0000 ± 0.006
p-Cl	0.227 ± 0.02	1.110 ± 0.009	-0.0390 ± 0.04
p-Br	0.227 ± 0.02	1.113 ± 0.008	-0.0384 ± 0.04

(a) The precision of the kinetic results is expressed as standard deviation.

(b) The deviation quoted is obtained from the limiting values of the expressed fraction.

Table 8. Rates of Decomposition of 142

Temp. [°C]	C_6H_6 $k \times 10^4$ (sec^{-1})	C_6H_5Cl $k \times 10^4$ (sec^{-1})	$C_6H_5NO_2$ $k \times 10^4$ (sec^{-1})
148.0	0.855 ± 0.018	0.642 ± 0.011	0.455 ± 0.009
152.5	1.59 ± 0.04	1.30 ± 0.017	0.697 ± 0.015
154.8			0.876 ± 0.017
157.1	2.46 ± 0.03		1.32 ± 0.023
161.8	2.82 ± 0.07	2.19 ± 0.05	1.71 ± 0.04
172.5	8.13 ± 0.20	6.68 ± 0.12	4.64 ± 0.09
178.5	13.77 ± 0.11	10.20 ± 0.13	
181.5	18.72 ± 0.32	13.19 ± 0.21	
200.6	76.66 ± 1.33	56.83 ± 1.18	41.05 ± 0.83

Note: deviations quoted are standard deviations, for average values of several runs.

Table 9. Concentration Dependence Studies of 142

(t = 152.5°C)

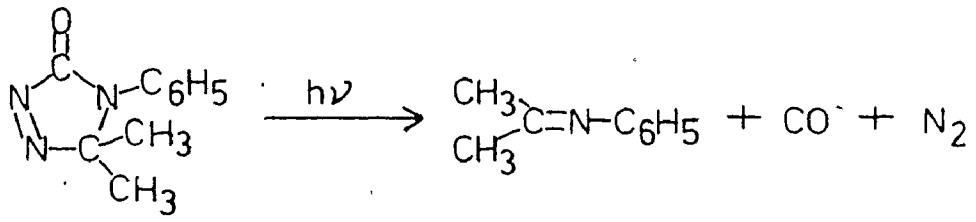
Solvent	Initial conc. (mol l^{-1})	k x 10^4 * [sec^{-1}]
C_6H_6	0.0121	1.63
	0.0242	1.58
	0.0482	1.61
	0.0964	1.55
$C_6H_5NO_2$	0.0129	0.698
	0.0258	0.710
	0.0516	0.713
	0.1022	0.689

* Single determination was made.

Table 10. Activation Parameters for 142

Solvent	$\Delta H^{\ddagger}$ (kcal.mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)	$\Delta F^{\ddagger}$ (kcal.mole^{-1})	Ea (kcal.mole^{-1})
C_6H_6	32.9 ± 0.3	0.5 ± 0.7	32.7 ± 0.5	33.9 ± 0.3
C_6H_5Cl	32.9 ± 1.0	-0.15 ± 0.4	32.8 ± 1.2	33.8 ± 1.1
$C_6H_5NO_2$	33.0 ± 0.8	-0.6 ± 1.8	33.3 ± 1.6	33.9 ± 0.7

Table 11. Quantum Yield of Direct Decomposition of 141a



141a

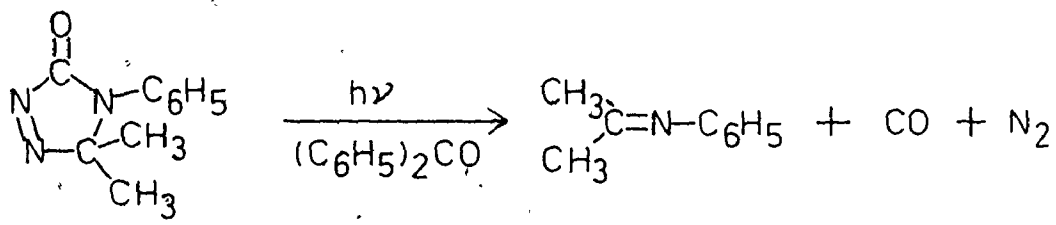
Light absorbed by Starting material (Einsteins x 10^4)	Amount of Starting material disappeared (moles x 10^5)	Quantum Yield
7.29	4.76	0.065
6.61	4.23	0.064

Solvent: methanol

Concentration of 141a: 8.466×10^{-5} M

Temperature: $9 \pm 1°C$

Table 12. Quantum Yield of Sensitized Decomposition of 141a



141a

Light absorbed by benzophenone (Einsteins x 10^4)	Amount of Decomposition Starting material (moles x 10^4)	Quantum Yield
2.56	0.51	0.20
2.97	0.65	0.22

Solvent: methanol

Concentration of 141a: 8.466×10^{-5} M

Concentration of benzophenone: 9.892×10^{-2} M

Temperature: 9 ± 1°C

FIGURE 2

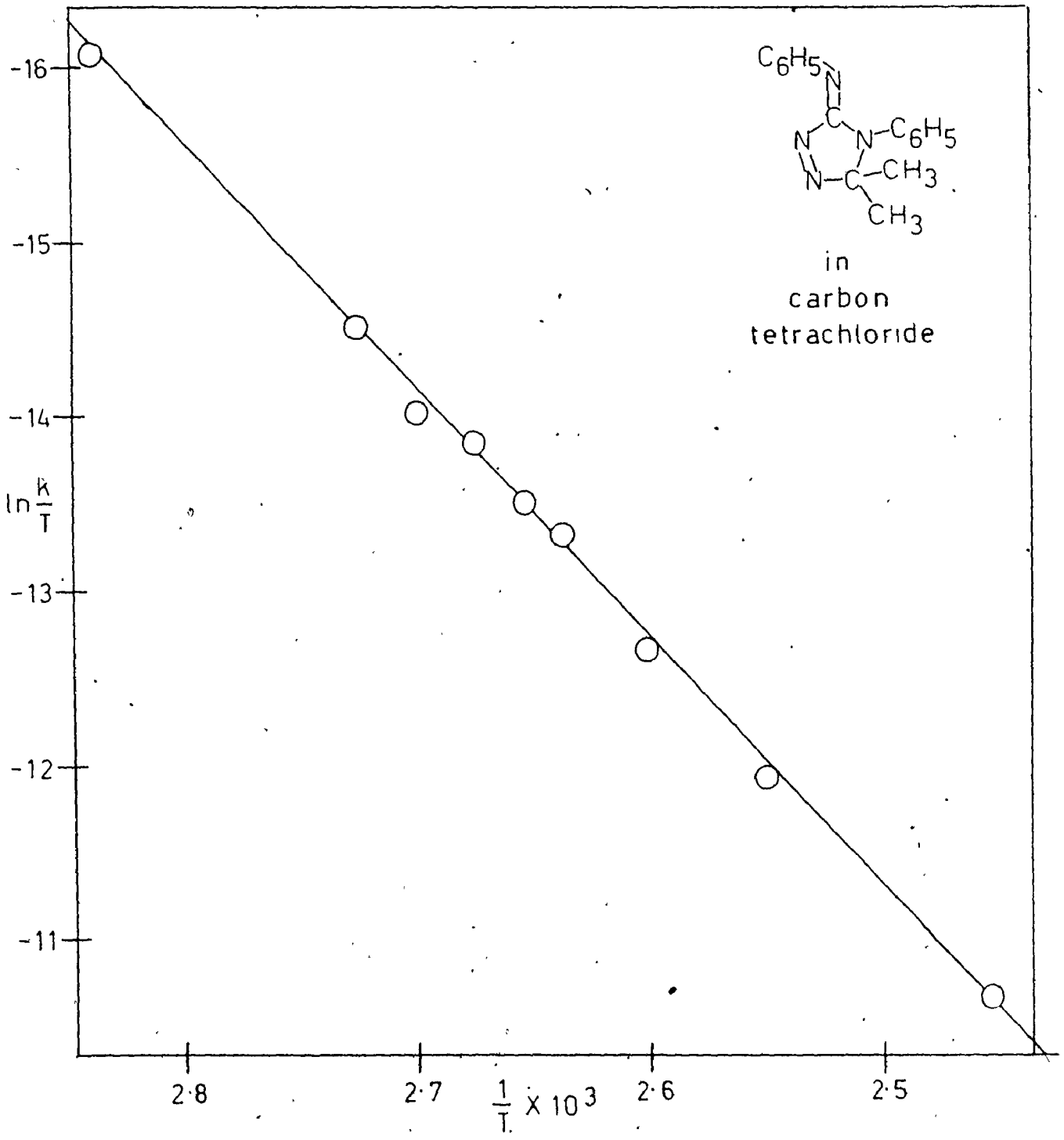

-16
-15
-14
-13
-12
-11
ln k/T
2·8
2·7
1/T X 10³
2·6
2·5
C6H5
N
C
N-C6H5
N
N-C-CH3
CH3
in
carbon
tetrachloride

FIGURE 3

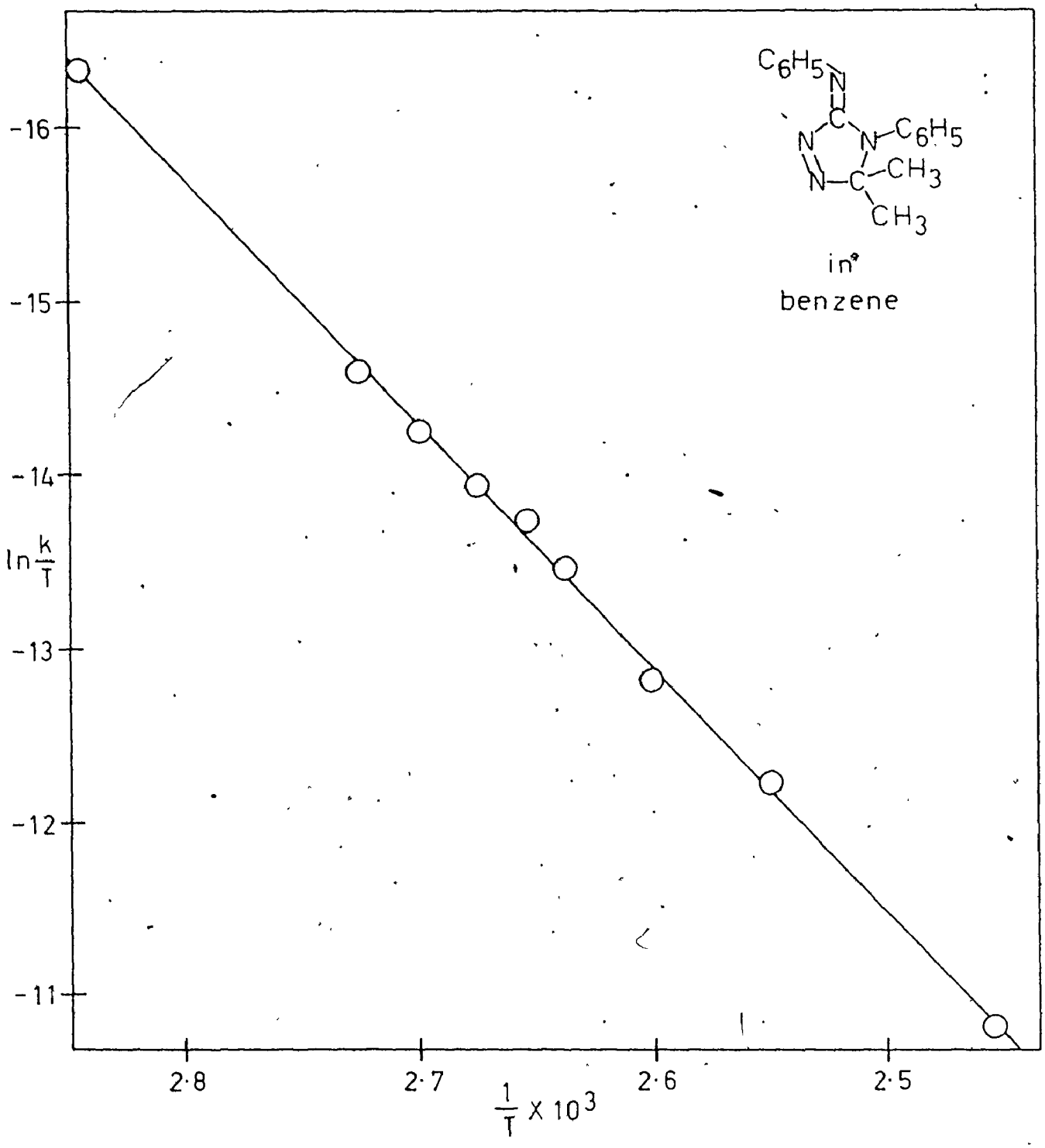

-16
-15
-14
-13
-12
-11
ln k/T
2·8
2·7
2·6
2·5
1/T X 10^3
C6H5
N
H
C
N
C6H5
N
N
C
CH3
CH3
in
benzene

FIGURE 4 -

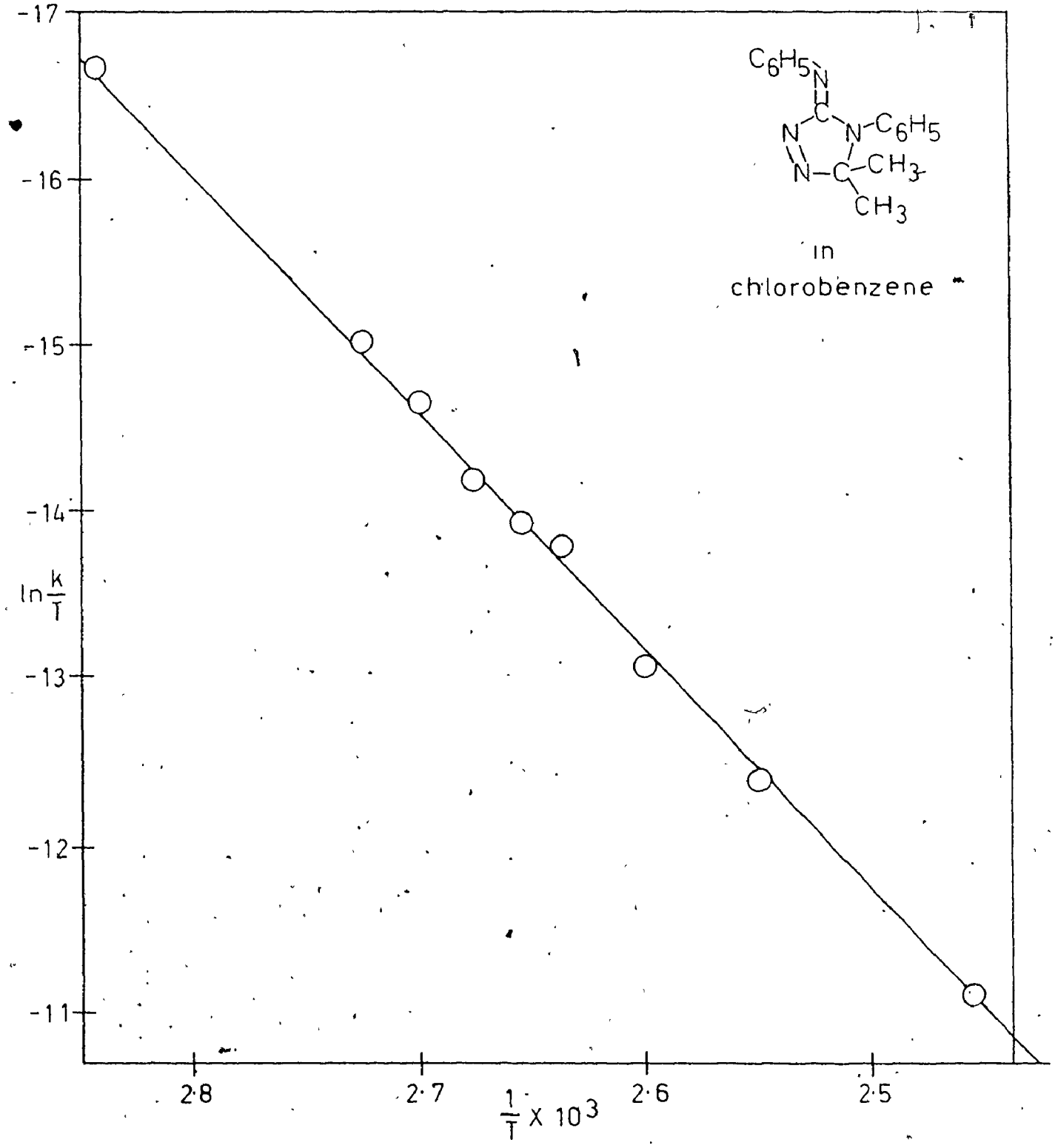

-17
-16
-15
-14
-13
-12
-11
ln k/T
2·8
2·7
2·6
2·5
1/T X 10³
C6H5
N
H
C
N
N
C6H5
N
C
CH3
CH3
in
chlorobenzene

FIGURE 5

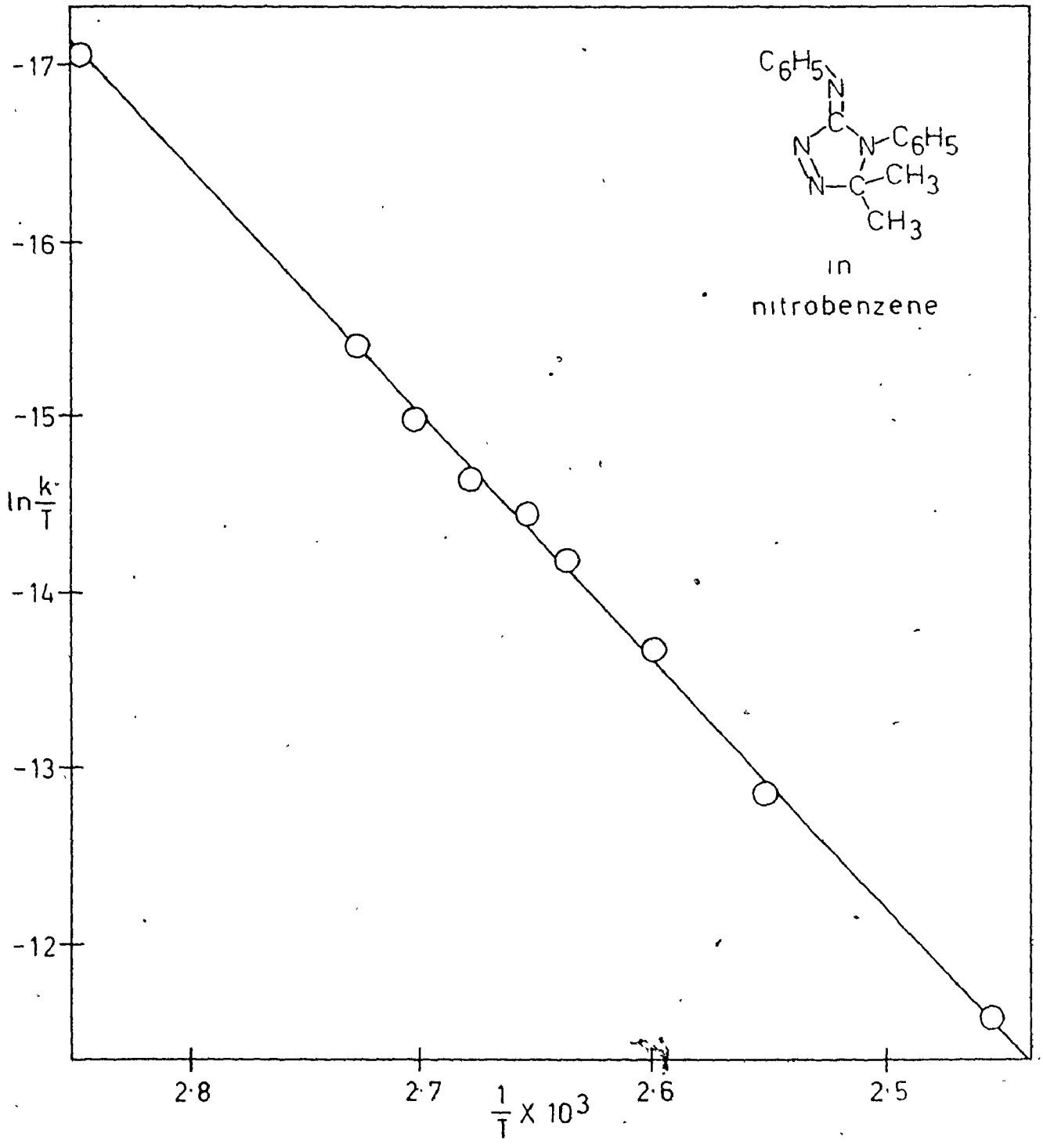
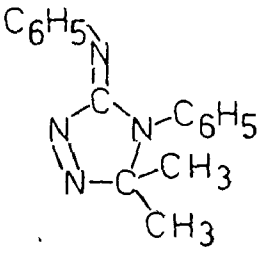

-17
-16
-15
-14
-13
-12
$\ln \frac{k}{T}$
2·8
2·7
2·6
2·5
$\frac{1}{T} \times 10^3$
C_6H_5
N
C
N
C_6H_5
N
C
CH_3
CH_3
in
nitrobenzene

FIGURE 6


C6H5
N
C
N
C6H5
N
C
CH3
N
C
CH3

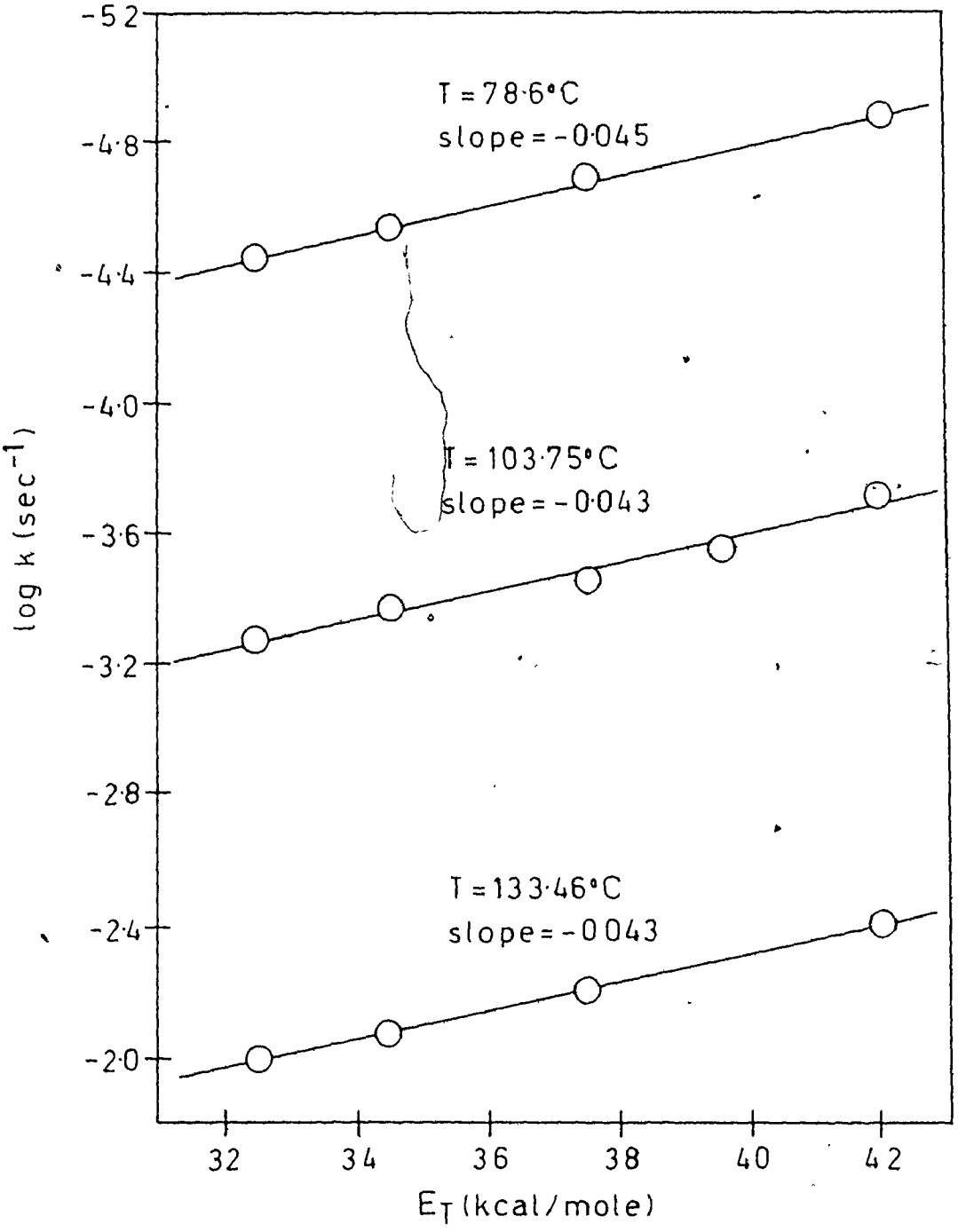

-5·2
-4·8
-4·4
-4·0
-3·6
-3·2
-2·8
-2·4
-2·0
log k (sec⁻¹)
T = 78·6°C
slope = -0·045
T = 103·75°C
slope = -0·043
T = 133·46°C
slope = -0·043
32
34
36
38
40
42
E_T (kcal/mole)

FIGURE 7

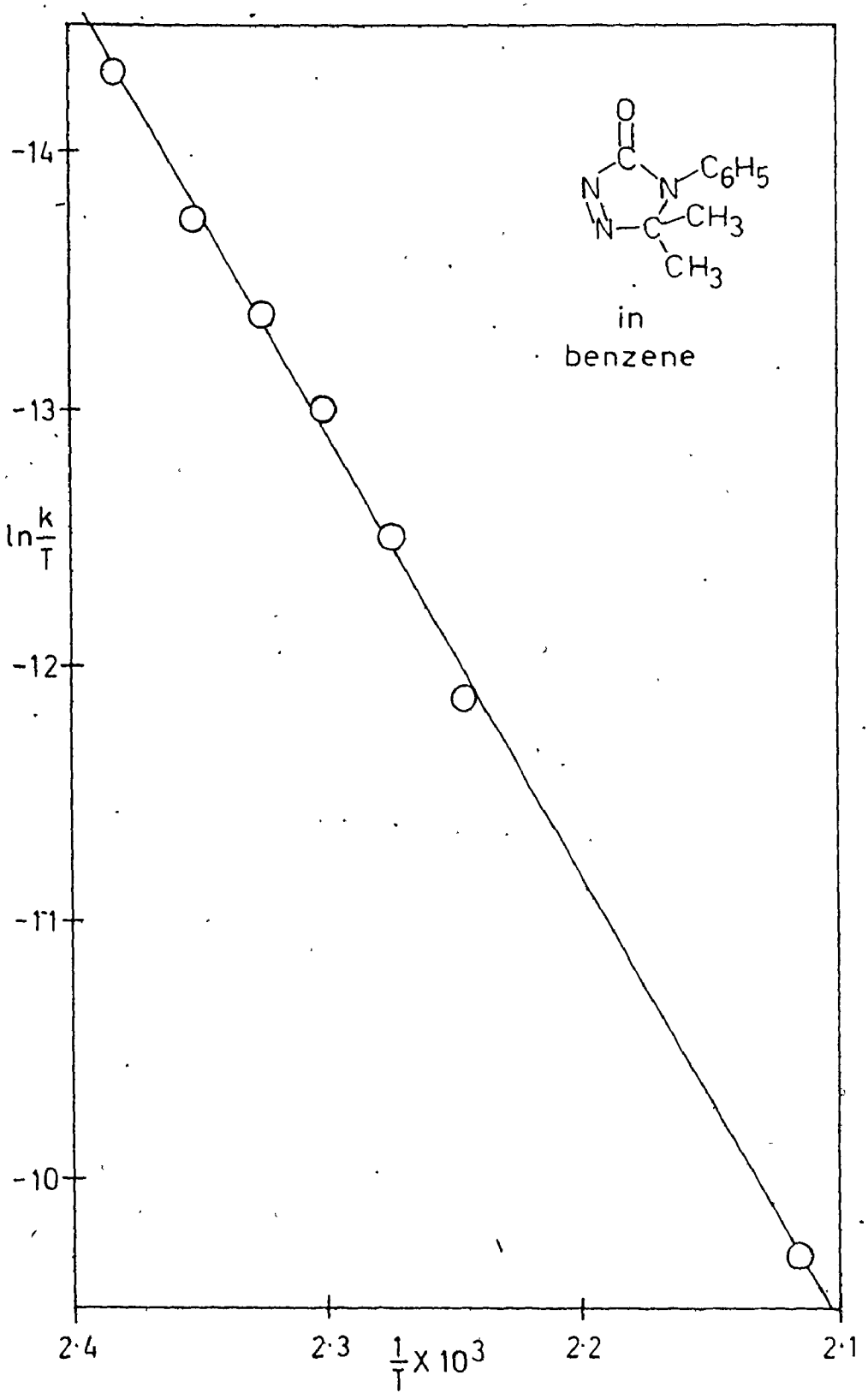


FIGURE 8

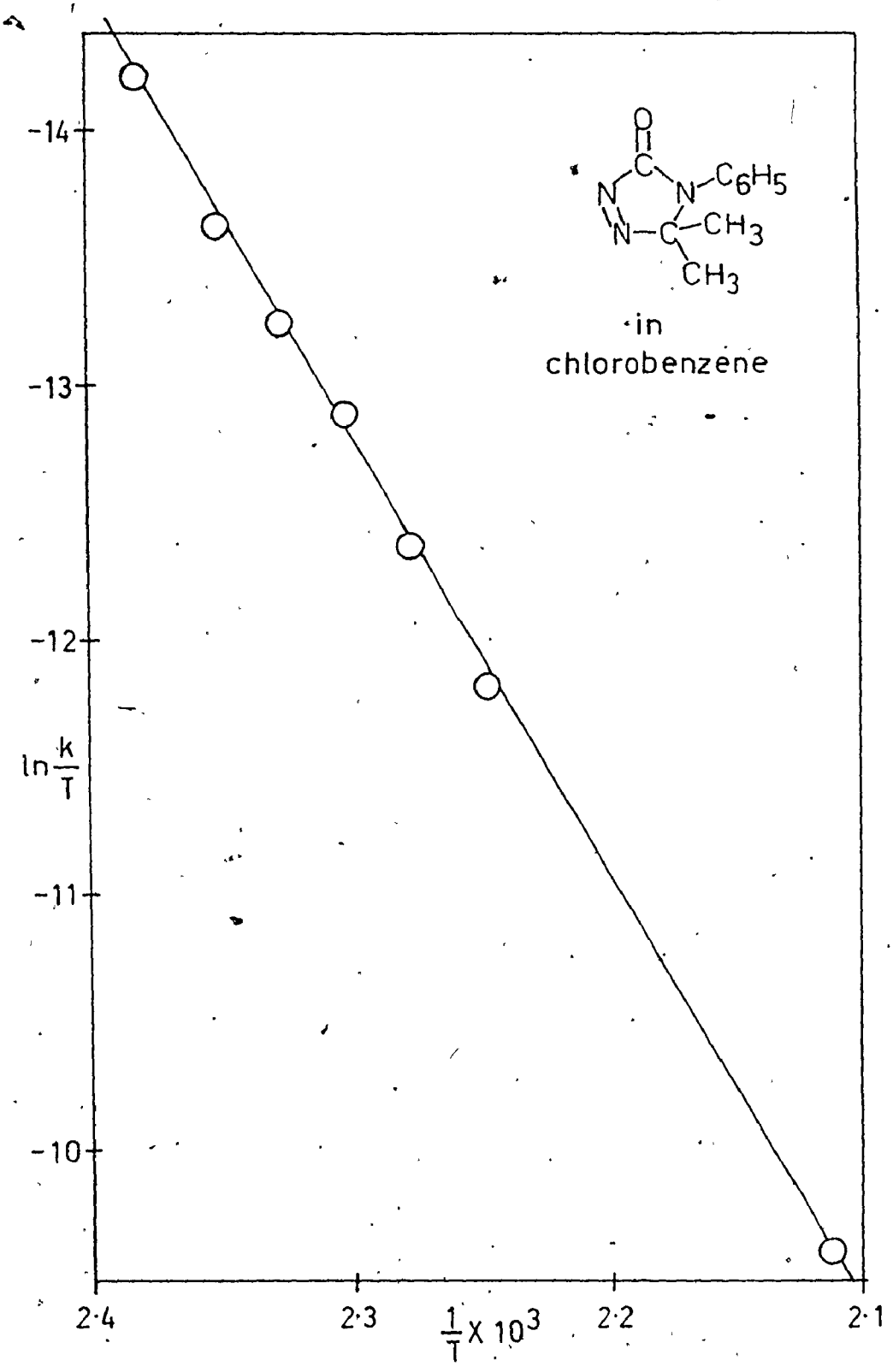

-14
-13
-12
-11
-10
ln k/T
2·4
2·3
2·2
2·1
1/T X 10³
C6H5
CH3
CH3
in
chlorobenzene

FIGURE 9

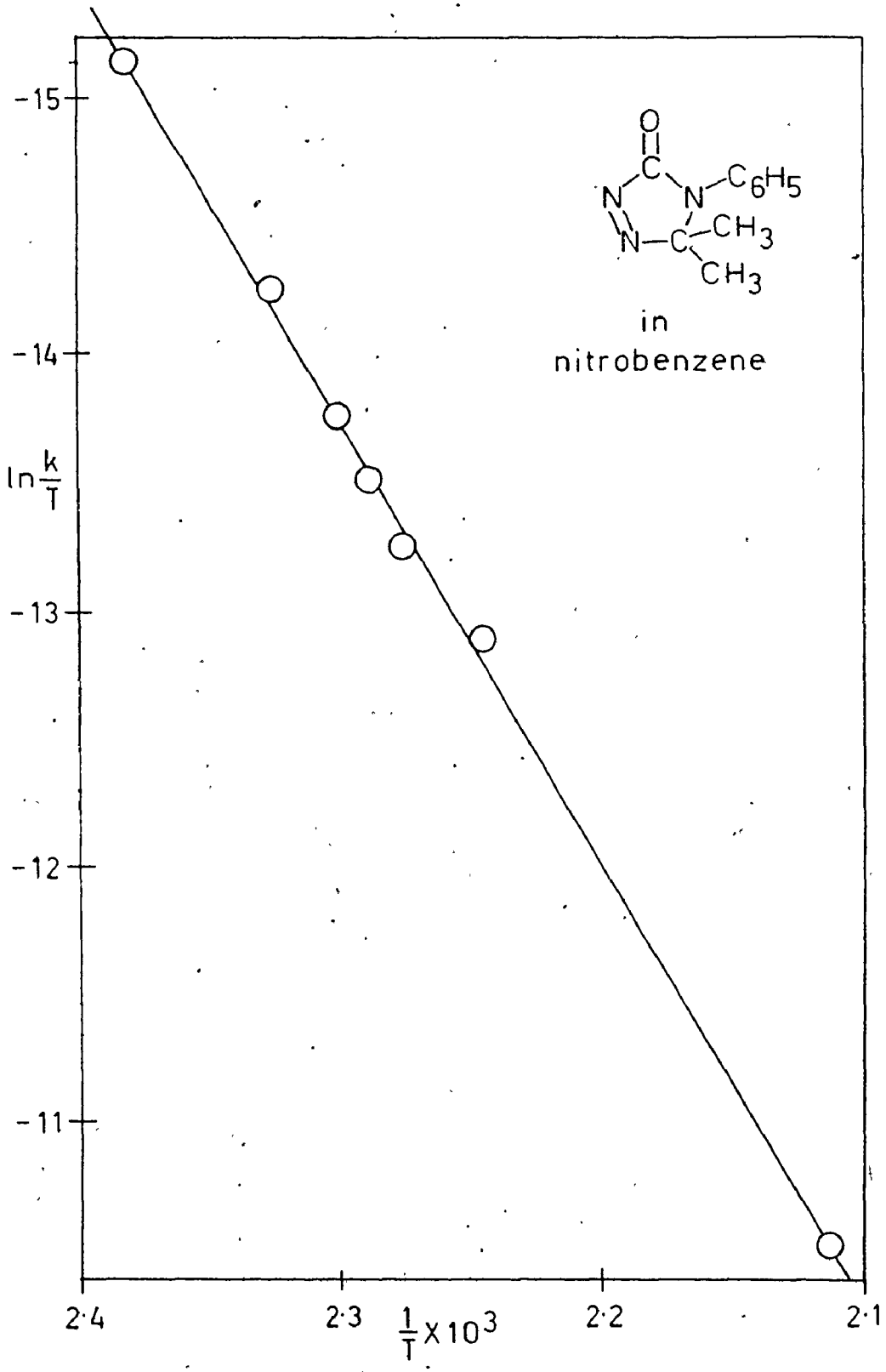
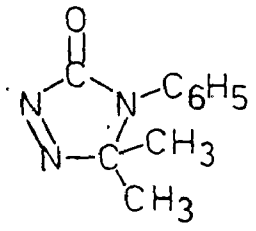


FIGURE 10


O
C
N
N
C6H5
N
C
CH3
CH3

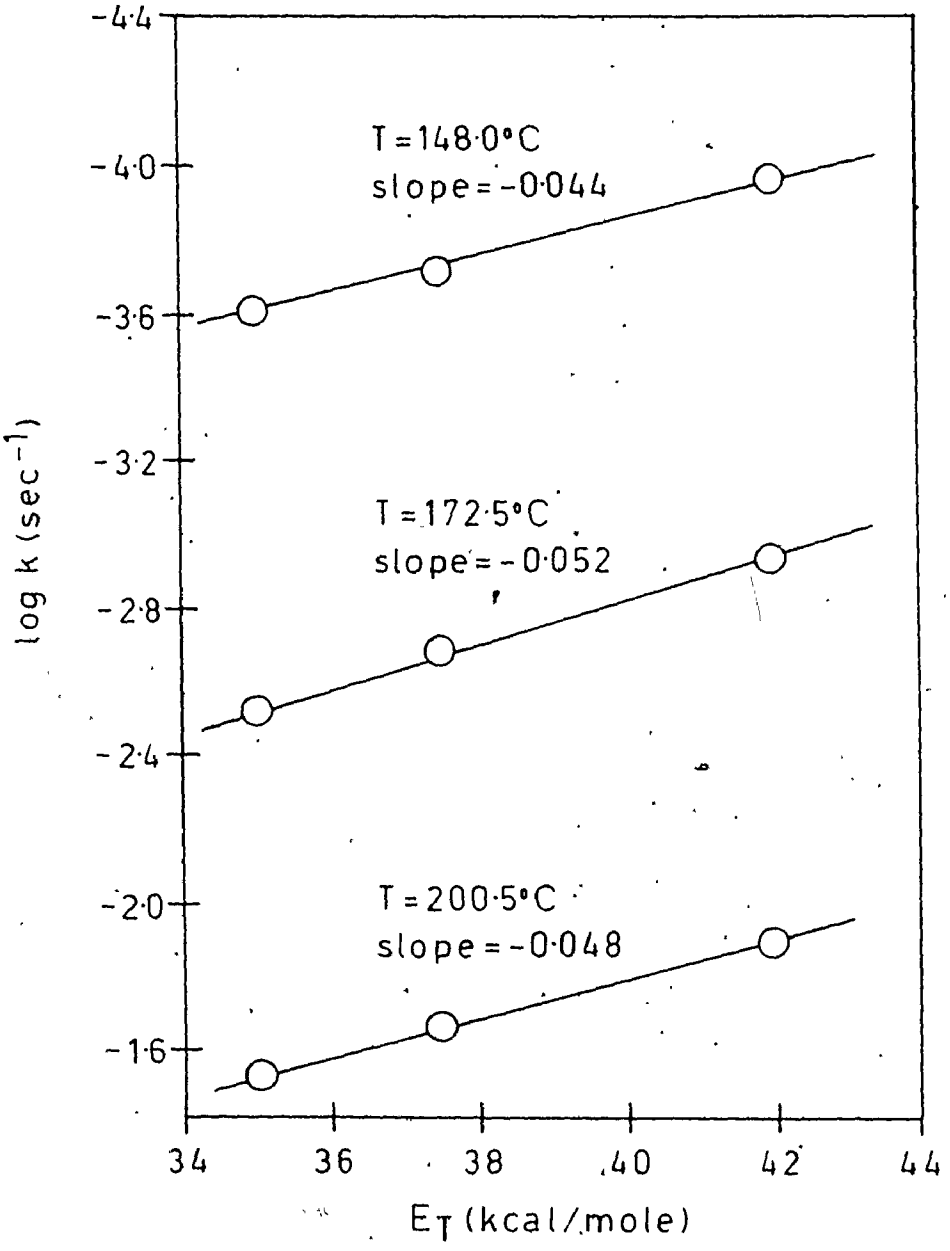
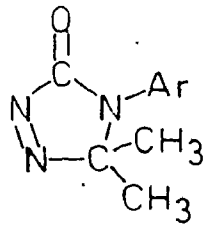

-4·4
-4·0
-3·6
-3·2
-2·8
-2·4
-2·0
-1·6
log k (sec⁻¹)
T = 148·0°C
slope = -0·044
T = 172·5°C
slope = -0·052
T = 200·5°C
slope = -0·048
34
36
38
40
42
44
ET (kcal/mole)

FIGURE 11

CORRELATION OF RATES OF THERMOLYSIS OF 141a-e



141a-e

BY THE HAMMETT EQUATION

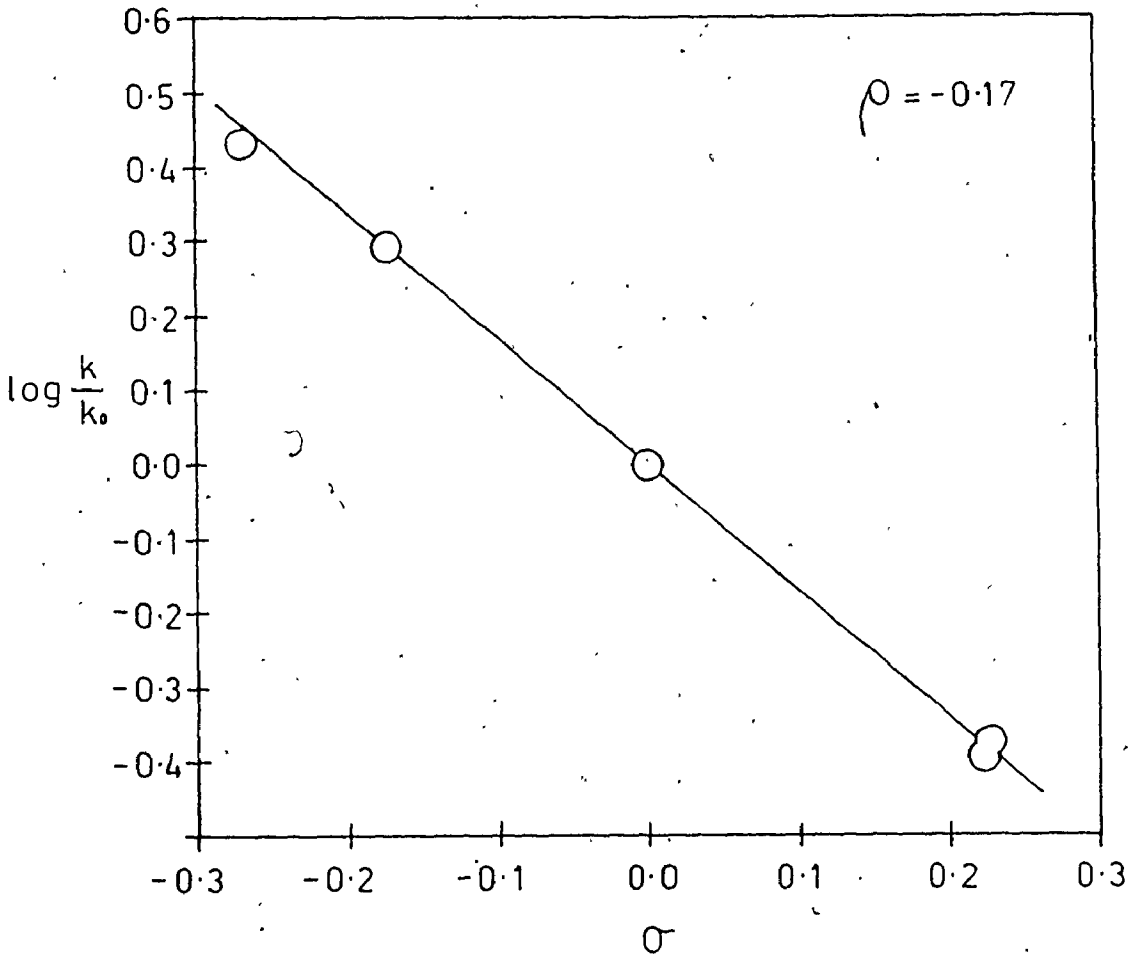


FIGURE 12

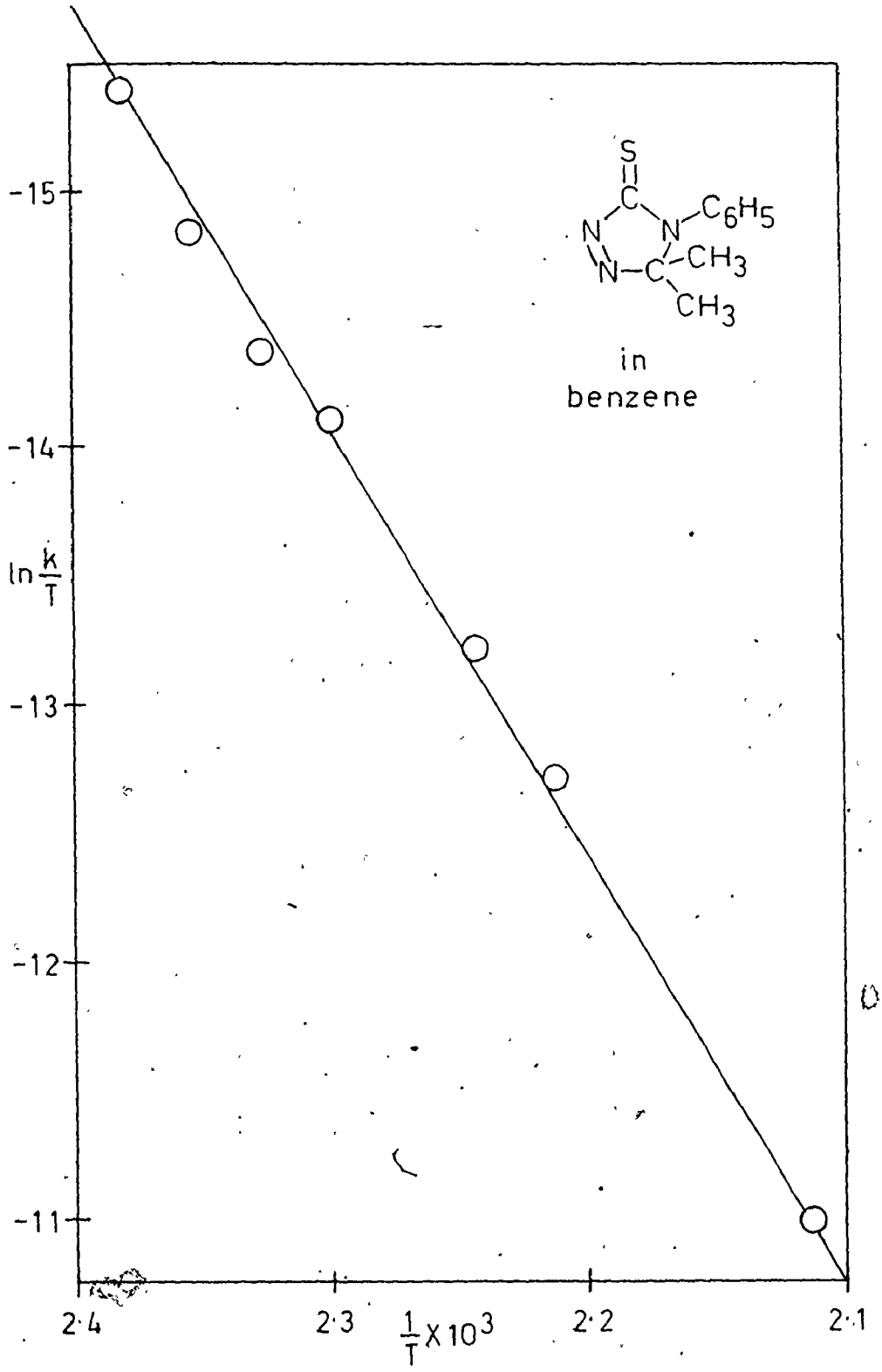


FIGURE 13

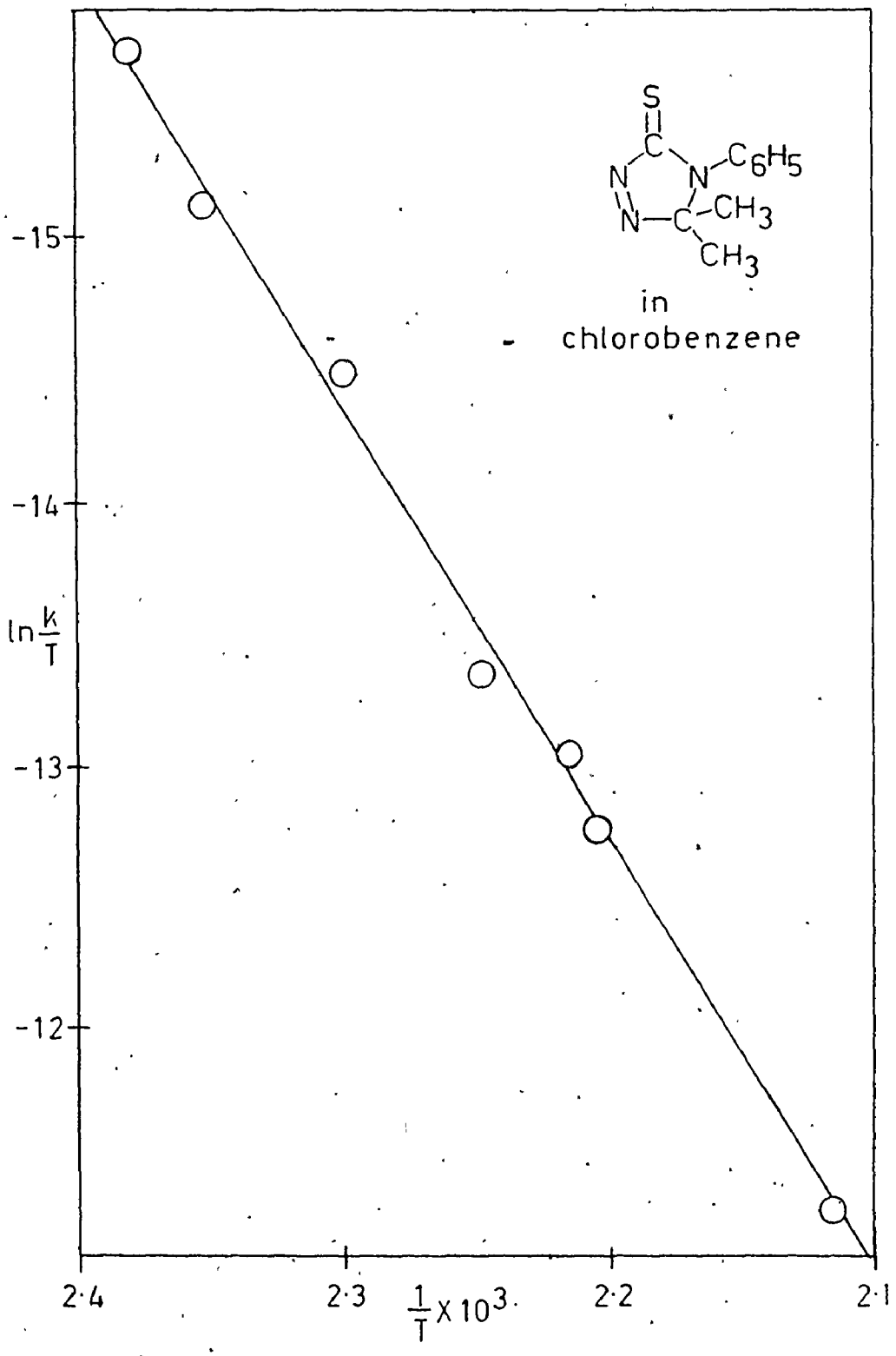

S
C
N
N
N
C
C6H5
CH3
CH3
in
chlorobenzene
-15
-14
-13
-12
ln k/T
2·4
2·3
1/T X 10³
2·2
2·1

FIGURE 14

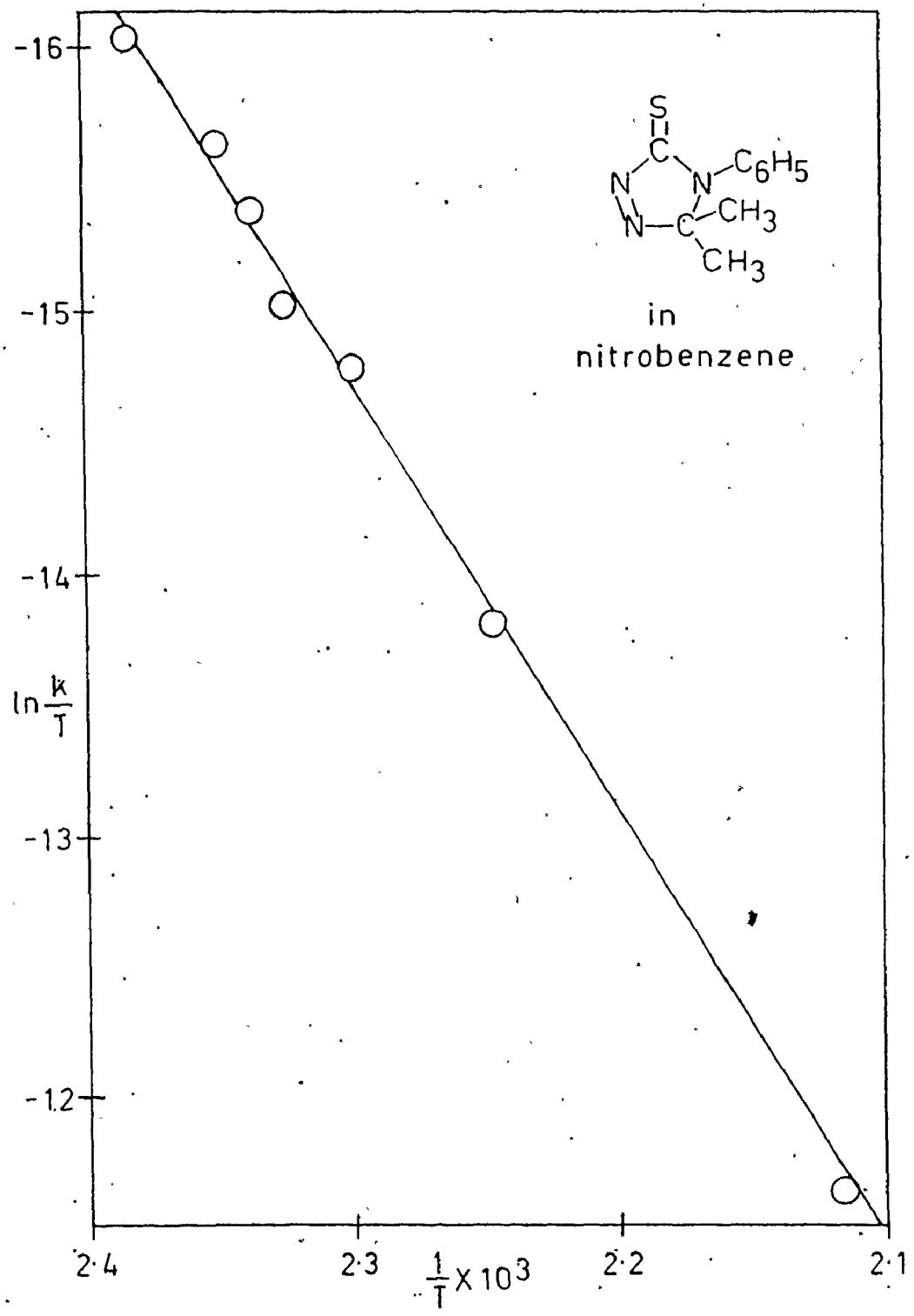
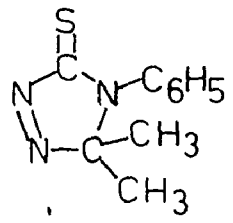
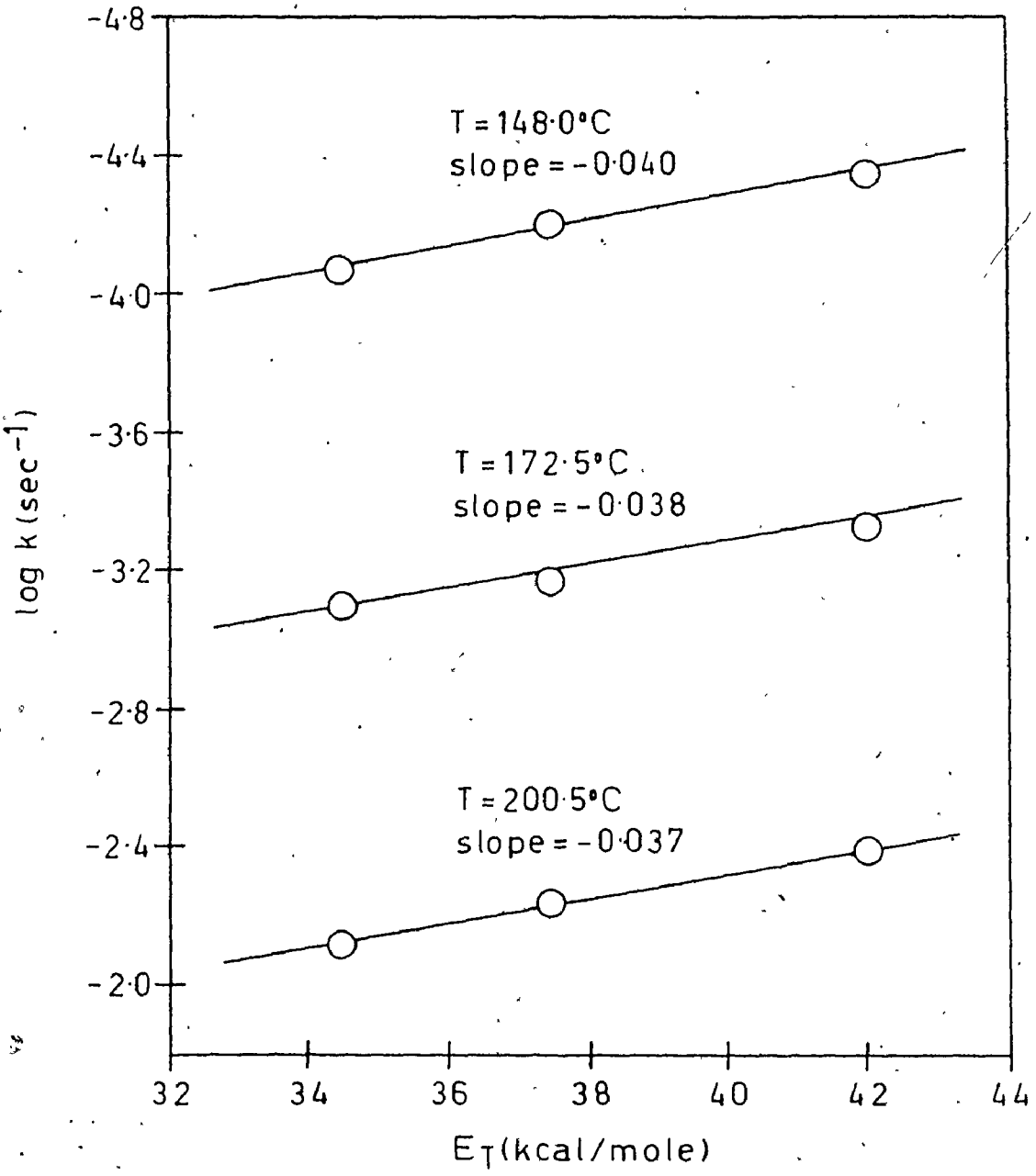

-16
-15
-14
-13
-1.2
ln k/T
2·4
2·3
1/T X 10³
2·2
2·1
S
C
N
N
C6H5
CH3
CH3
in
nitrobenzene

FIGURE 15


S
C
N
N
C6H5
N
C
CH3
CH3


T = 148·0°C
slope = -0·040
T = 172·5°C
slope = -0·038
T = 200·5°C
slope = -0·037
log k (sec⁻¹)
-4·8
-4·4
-4·0
-3·6
-3·2
-2·8
-2·4
-2·0
32
34
36
38
40
42
44
ET (kcal/mole)

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