MECHANISTIC AND SYNTHETIC ASPECTS OF RADICAL CHEMISTRY OF α-AZOCARBINOLS

by

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To my wife, Silvana,

with love

ABSTRACT

α-Phenylazodimethylcarbinol, a new compound in the series of α-azocarbinols prepared in our laboratory, was synthesized by air oxidation of acetone phenylhydrazone to give the hydroperoxide which is subsequently reduced to the α-azocarbinol by the action of triphenylphosphine. The kinetics of thermolysis of this new compound, along with those of α-phenylazodiphenylcarbinol, α-azoethers, and α-azoacetates, were studied under several reaction conditions in an attempt to further elucidate the decomposition mechanism of these new azo compounds.

Radical intermediates are involved in the chemistry of these α-azocarbinols. The evidence presented reinforces the claim that α-azocarbinols decompose by an induced radical chain mechanism. Such a radical chain process permits the application of these α-azocarbinols, which generate a variety of radicals R• (R• is phenyl in this research), to the hydroalkylation (hydrophenylation) of several unsaturated compounds.

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INTRODUCTION

I: Free Radicals[1]

Of all the intermediates in organic chemistry, the free radicals have the longest history. Early in the history of free radical chemistry there were no reliable and generally accepted ways to distinguish between radicals and dimers. Thus, little distinction was made between radicals as functional groups and free radicals as substances.

Early work on free radicals was undertaken in 1900[2] by Gomberg who discovered the first free radical, triphenylmethyl. Since that time more and more work has been done on free radicals. The participation of free radicals as reacting entities in chemical reactions was not generally recognized until after 1937, following the publication of a series of papers by M. S. Kharasch and by P. J. Flory in the United States, and a significant review by D.H. Hey and W.A. Waters in England.

This recognition of free radicals as participants in chemical reactions has had far reaching consequences in organic chemistry. The presently accepted free radical chain mechanism for the addition of hydrogen bromide to alkenes was then proposed by Kharasch[3]. A paper on the kinetics of vinyl polymerization in terms of a free radical chain reaction was published by Flory in 1937[4].

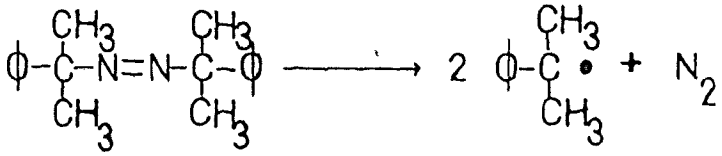
A: Radical Production

In brief, radical reactions can be broken down into three stages: radical production, reactions yielding new radicals, and radical destruction.

The first radical sources to be considered is thermal homolysis. The breaking of chemical bonds at elevated temperatures will form radicals, but below 200°C, the temperature range of ordinary solution chemistry, the bonds that will do so at reasonable rates are limited to a few types, the most common of which are the peroxy bond and the azo linkage. Equations [1] to [3] illustrate a few typical examples.

[1] 

[2] 

[3] 

The complexities of chain induced decompositions can be minimized by choosing an initiator and solvent without easily abstracted hydrogens; under these conditions peroxy and azo compounds decompose unimolecularly at easily measured rates to provide convenient sources of radicals for use in studying other radical processes. The unimolecular decompositions are nevertheless not without their complications.

The fact that stable molecules such as CO_2 and N_2 are produced, in the decomposition of peresters and azo compounds respectively, provides a strong driving force for the dissociation process:

$$RCO\text{-}OCR' \rightarrow CO_2 + R\bullet + R'\bullet$$

$$\text{or} \quad R\text{-}N{=}N\text{-}R' \rightarrow N_2 + R\bullet + R'\bullet$$

The activation energy for the decomposition is decreased as R• increases in stability. Thus, for azo compounds, R-N=N-R, the decomposition is much more facile when R• is resonance stabilized (for example R• = triphenylmethyl) and less favourable when R are primarily alkyl radicals.

Numerous examples of induced decomposition to form free radicals have been reported in the literature. The induced decomposition is a chain reaction caused by the radical products of an initial unimolecular decomposition attacking unreacted initiator molecules to yield new radicals that continue the chain. Benson[5] has reported the induced decomposition of tert-butyl hydroperoxide which he has confirmed by kinetic studies. His results were further confirmed by Hiatt[6] and coworkers who observed the acceleration of the decomposition by the addition of an independent source of radicals.

Potential mechanisms for the induced decomposition of azo compounds are of two types:

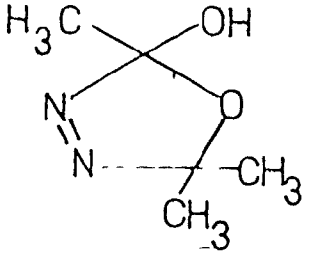
$$[4] \quad R\bullet + X\text{-}N{=}N\text{-}R' \rightarrow RX + N_2 + R'\bullet$$

and

$$[5] \quad R\bullet + X\text{-}Y{-}Z{-}N{=}N{-}R' \rightarrow RX + Y{=}Z + N_2 + R'\bullet$$

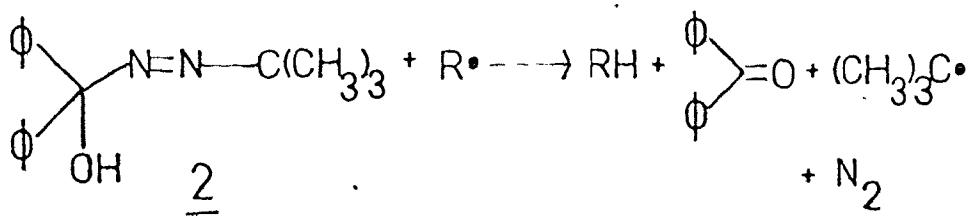
Equation [4] shows radical substitution at an atom situated α to the azo function , whereas equation [5] shows radical substitution at an atom situated γ to the azo function. Azo compounds which are reported to react according to equations [4] and [5] are rare. This rarity is caused, in part, by the absence of a reactive site X (the site susceptible to radical attack) in the above equations.

Reported azo compounds that may decompose according to equation [4] are the following; X=H[7], X= RCO[8], X= RSO_2[9], X= RCO_2[10], and others for which radical substitution was not fully established. For the latter case, equation [5], examples of both cyclic and acyclic azo compounds were provided in this laboratory. Knittel and Warkentin[11] have found that 2-hydroxy-2,5,5-trimethyl-Δ^3-1,3,4-oxadiazoline (1) decomposes via a concerted, radical chain decomposition as depicted in equation [6].

[6]  + R• ⟶ RH + N_2 + $CH_3C(=O)OC(CH_3)_2$•

1

Spin trapping with nitrobenzene, trapping with unsaturated compounds, and several other experiments have confirmed the concerted induced decomposition of the oxadiazoline (1) via attack on the hydroxyl hydrogen. In a similar manner, Yeung and Warkentin[12,13] have shown the induced decomposition of several acyclic azo compounds, of which 2 is the most prominent (Equation [7]).

[7]  + N_2

2

The decomposition of such azo compounds may be either concerted or stepwise. We use the decomposition of azoalkanes as an illustration. In a concerted reaction, the two C-N bonds would break simultaneously (equation [8]), whereas in a stepwise process one radical could be produced first and subsequently the second radical would be produced (equation [9]).

[8] $$R{-}N{=}N{-}R' \longrightarrow R\bullet + N_2 + R'\bullet$$

[9] $$R{-}N{=}N{-}R' \longrightarrow R{-}N{=}N\bullet + R'\bullet$$

$$R{-}N{=}N\bullet \longrightarrow R\bullet + N_2$$

The mechanism of decomposition of azo compounds has been widely investigated. The results support the concerted process (equation [8]) for the symmetrical azo compounds with R• a well stabilized radical such as $(C_6H_5)_2\dot{C}CN$, $(C_6H_5)_2\dot{C}H$, and so forth, but leave open the possibility that in the unsymmetrical cases the mechanism may change to the stepwise one[14].

Crawford and Takagi[15] have examined the gas-phase decompositions of several azo compounds with R=CH_3, tert-butyl, or allyl; they found that most of these compounds, both symmetric and unsymmetric, decompose by the nonconcerted path (equation [9]). Seltzer[16] found, by studying secondary deuterium isotope effects, that in unsymmetrical azo compounds, in which one R group is a much better radical than the other, the bond breaking is stepwise. Other independent evidence[17], favouring the single bond cleavage mechanism for unsymmetric azo compounds, has been found.

Other general methods for the production of radicals, photochemical homolysis, radiolysis, and redox reactions, are beyond the scope of this thesis and will not be discussed.

B: Kinetics of Radical Chain Reactions

The study of kinetics of radical chain reactions is attended by many complications as the rate expressions are generally complex and the reactions are often sensitive to the presence of even traces of catalysts and inhibitors. Nevertheless a number of such studies have successfully been made of gas-phase reactions, among which the classical example of the reaction between hydrogen and bromine vapour, serves as an illustration[18].

$$H_2 + Br_2 \longrightarrow 2\ HBr$$

The actual kinetic measurements are experimentally quite complex and no complete treatment is attempted here. It is important, however, to be aware of the type of information which can be derived from kinetic considerations.

A radical chain reaction consists of chain initiation, chain propagation, and chain termination reactions. An example of this type is given by the halogenation of alkanes (equations [10] to [14], where X_2 is the halogen molecule.

Scheme I

Initiation:

[10] $X_2 \xrightarrow{k_1} 2\,X\bullet$

Propagation:

[11] $X\bullet + RH \xrightarrow{k_2} R\bullet + XH$

[12] $R\bullet + X_2 \xrightarrow{k_3} RX + X\bullet$

Termination:

[13] $2R\bullet \xrightarrow{k_4} R_2$

[14] $R\bullet + X\bullet \xrightarrow{k_5} RX$

non-radical products

In the Scheme I above, $R\bullet$ and $X\bullet$ are called the chain carriers. The kinetic rate laws are usually derived assuming a steady-state approximation. This assumes a) that the concentration of the chain carrier, which is very small, remains essentially constant, and b) the rate of initiation must be equal to the rate of termination. We use Scheme I as an illustration for the derivation of the rate law.

The rate of the overall reaction, obtained from either of the two chain propagation steps (equations [11] and [12]), is given by

$$-\frac{d[RH]}{dt} = \frac{d[XH]}{dt} = k_2[X\bullet][RH]$$

or

$$\frac{-d[X_2]}{dt} = \frac{d[RX]}{dt} = k_3[X_2][R\bullet]$$

Since the rate of initiation must equal the rate of termination, at steady state concentrations,

$$\frac{d[X\bullet]}{dt} = -k_2[X\bullet][RH] + k_3[R\bullet][X_2] = 0 = -\frac{d[R\bullet]}{dt} \qquad \text{(i)}$$

$$2k_1[X_2] = 2\,k_4[R\bullet]^2 + k_5[X\bullet][R\bullet] \qquad \text{(ii)}$$

Solving for [X•] gives

$$[X\bullet] = \frac{k_3\,[X_2]}{k_2\,[RH]}\,[R\bullet] \qquad \text{(iii)}$$

Substituting equation (iii) into equation (ii) gives

$$k_1[X_2] = k_4[R\bullet]^2 + k_5\frac{k_3[X_2]}{k_2[RH]}\,[R\bullet]^2$$

and therefore

$$[R\bullet] = \left(\frac{k_1[X_2]}{k_4 + k_5\dfrac{k_3[X_2]}{k_2[RH]}}\right)^{1/2} \qquad \text{(the positive root)}$$

from which the rate becomes

$$\text{Rate} = \frac{d[RX]}{dt} = k_3[X_2]\left(\frac{k_1[X_2]}{k_4 + k_5\dfrac{k_3[X_2]}{k_2[RH]}}\right)^{1/2}$$

In the derivation of the rate law above, one assumes that the chain length (defined as the number of reaction cycles of the chain carrier before it is destroyed) is long enough, so that the contribution to the overall rate from the initiation reaction is negligible.

The two limiting cases are a) if equation [13] is the only termination reaction, then

$$\text{Rate} = K[X_2]^{3/2} \qquad \text{where } K = \left(\frac{k_3^2\,k_1}{k_4}\right)^{1/2}$$

The rate will be three-halves order in $[X_2]$ and independent of [RH].

(b) If equation [14] is the termination reaction, then

$$\text{Rate} = K'[X_2][RH]^{1/2} \qquad \text{where } K' = \left(\frac{k_1k_3k_2}{k_5}\right)^{1/2}$$

the overall order will be three-halves with first-order dependance on $[X_2]$

and one-half order dependance on [RH].

Essentially all the reactions of α-azocarbinols investigated during this research were of the first order with respect to azocarbinol concentration. For a simple, irreversible, first order process, the rate constant k, is given by a simple integration of the rate equation (Equations [iv] and [v]).

[iv] $$\text{Reactant} \xrightarrow{k} \text{Product(s)}$$

[v] $$\frac{d[\text{Reactant}]}{dt} = -k\,[\text{Reactant}]$$

$$[\text{Reactant}] = [\text{Reactant}]_{\circ}\,\exp(-kt)$$

$$\ln[\text{Reactant}] = \ln[\text{Reactant}]_{\circ} - kt$$

A plot of ln[Reactant] versus time will then give a straight line, if the overall reaction rate is first order. The slope of the line equals -k, where k is the rate constant, usually given in sec^{-1}. A characteristic time is that at which the reactant has decomposed to one-half of its original concentration; this is called the half life ($t_{1/2}$ of the reaction) and is very simply related to k:

from equation [v] $$\frac{[\text{Reactant}]}{[\text{Reactant}]_{\circ}} = 1/2 = \exp(-kt_{1/2})$$

$$\ln 1/2 = -kt_{1/2} \qquad t_{1/2} = \frac{0.6931}{k}$$

Several features highlight the properties of first order reactions. The first is that the concentrations may be replaced by some variable which is proportional to concentration (for example, N.M.R. or I.R. signal intensities). The second feature of first order rate equations is that the validity of the equations is independent of the arbitrary assignment of time zero.

C: Radical Reactions

Bimolecular reactions between radicals and molecules are of several types; substitution, abstraction, and addition. The abstraction of hydrogen atoms from organic compounds is a reaction of frequent occurrence with free radicals, and one characteristic of the species. Addition reactions are the most intensively studied and best understood among radical reactions. They have assumed great practical importance by virtue of their diverse applications in organic synthesis[1]. In this section, only the latter two types of reaction will be discussed.

Abstraction reactions are a special case of substitution reactions. The two most common abstraction reactions of radicals are halogen[19] and hydrogen[20] abstractions, the latter being of interest here. Hydrogen is abstracted from alcohols by several types of radicals, including: alkoxy[21,22], alkyl[23], hydroxyl[24], amino[25,26], and thiyl[27] radicals. The preferable site of attack by free radicals in solution is at the α-CH bond of alcohols and not at the OH bond, tertiary alcohols being the exception[22,28]. Reported cases of hydrogen abstraction from the hydroxyl group have been rare. Diphenylphosphino-radicals have been found[29] to abstract the hydroxylic proton via initial attack on the oxygen atom. Warkentin and coworkers[11,13] have recently found that a variety of radicals abstract hydroxyl hydrogen from several types of α-azocarbinols, 1 and 2.

Many organic radicals will undergo addition reactions with a wide variety of unsaturated compounds such as olefins, aromatic compounds, acetylenes, carbonyl compounds, and azo compounds. The most extensively investigated addition reaction is that with olefins. The following mechanism has become the prototype of a large number of

addition reactions to olefins. In general the reaction may be represented as the addition of XY to the olefin $R'CH=CH_2$ to give $R'CHX-CH_2Y$, depicted as follows (SchemeII):

Scheme II

Initiation:

[16] $\text{Initiator} \longrightarrow R\bullet$

[17] $R\bullet + XY \longrightarrow RX + Y\bullet$

Propagation:

[18] $Y\bullet + R'CH=CH_2 \longrightarrow R'\dot{C}H-CH_2Y$

[19] $R'\dot{C}H-CH_2Y + XY \longrightarrow R'CHX-CH_2Y + Y\bullet$

Termination:

[20] $Y\bullet + Y\bullet \longrightarrow Y-Y$

[21] $2\ R'\dot{C}H-CH_2Y \longrightarrow$ non-radical products

[22] $Y\bullet + R'\dot{C}H-CH_2Y \longrightarrow R'CHY-CH_2Y$

Telomerization:

[23] $R'\dot{C}H-CH_2Y + R'CH=CH_2 \longrightarrow R'\dot{C}HCH_2CHR'CH_2Y$

etc.

The overall reaction rate and the kinetic chain length, which

essentially determine the yield of the 1:1 adduct, thus depend on the processes of initiation, propagation, and termination. Both thermal and photo initiation can be used for studying the chain sequence that leads to 1:1 adducts. The average kinetic chain lengths are usually very large in most radical chain reactions and as result there is little influence by the initial source of radicals on the nature of the addition products.

Chain propagation consists of two steps, one of addition followed by another of chain transfer, to give the 1:1 adduct (equation [19]). Telomerization is often considered as a side reaction, but it would not assume serious proportions if the chain transfer rate constant is much larger than the addition rate constant.

Chain terminations usually occur by radical destroying processes such as dimerization or disproportionation. Termination of radical chains in addition reactions can also be brought about by interaction with metallic halides. Kochi[30] has shown that styrene polymerization is inhibited by cupric or ferric chlorides with the formation of chloro compounds as follows:

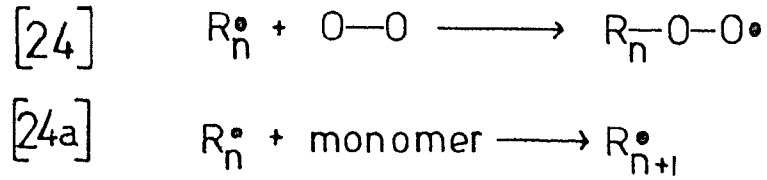
$$R\bullet + \phi\text{—}CH{=}CH_2 \longrightarrow \phi\text{—}\dot{C}H\text{—}CH_2R$$

$$\phi\text{—}\dot{C}H\text{—}CH_2R + FeCl_3 \longrightarrow \phi\text{—}CHCl\text{—}CH_2R + FeCl_2$$

One important feature of these chain processes to be pointed out is that at any time the concentration of the propagating radical species is extremely low. This being so, chain terminating reactions become relatively unimportant and high conversion of the reactants can be realized through the chain propagating steps. On the other hand, small amounts of inhibitors

which can trap or scavenge the propagating radicals are sufficient to slow or inhibit the reaction altogether. Traces of such inhibitors are in fact directly responsible for the induction period in certain reactions.

Inhibitors, in general, are either stable free radicals, (for example: oxygen, nitric oxide, or diphenylpicrylhydrazyl) or substances (eg. 2,4,6-tri-tert-butyl phenol) that can react with radicals to yield stable radicals which do not enter the kinetic chain or initiate a new reaction pathway. Some typical inhibitors are phenols, aromatic amines, quinones, and thiols. Large quantities of oxygen may inhibit a radical reaction; for example the inhibition of radical polymerization by oxygen (equation [24]) competing with equation [24a].Mechanisms of inhibitor



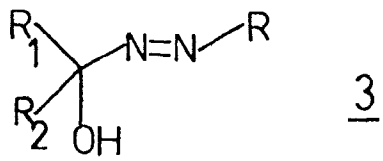
[24] $R_n^{\bullet} + O{-}O \longrightarrow R_n{-}O{-}O^{\bullet}$

[24a] $R_n^{\bullet} + \text{monomer} \longrightarrow R_{n+1}^{\bullet}$

action are complex and not completely understood[1].

II:α-Azocarbinols

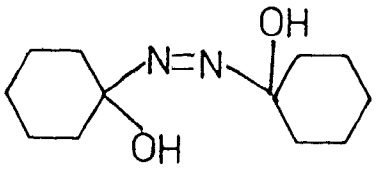
The history of α-hydroxydiazenes (α-azocarbinols) stems back to the early nineteen-sixties. α-Azocarbinol has been the name chosen in our laboratory for a compound of the type 3. Several other names for



3

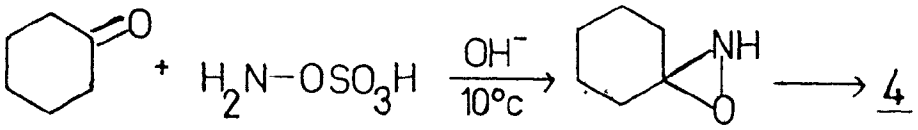
3, such as α-hydroxyazoalkanes, α-hydroxyalkyldiazenes, and semiaminals of diimide, have been used by chemists in the literature.

1,1'- Dihydroxyazocyclohexane (4), which was reported by Schmitz[30,31] in 1963, decomposes readily to give nitrogen, cyclohexanone, hydrazine



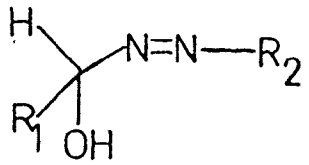
4

and cyclohexanol as major products. Radical chain decomposition may have been the process involved[11]. Compound 4 is a crystalline solid obtained upon treatment of hydroxylamine-O-sulfonic acid with cyclohexanone at 10°C in alkaline solution (equation [25]). An iso-oxime of

[25] 

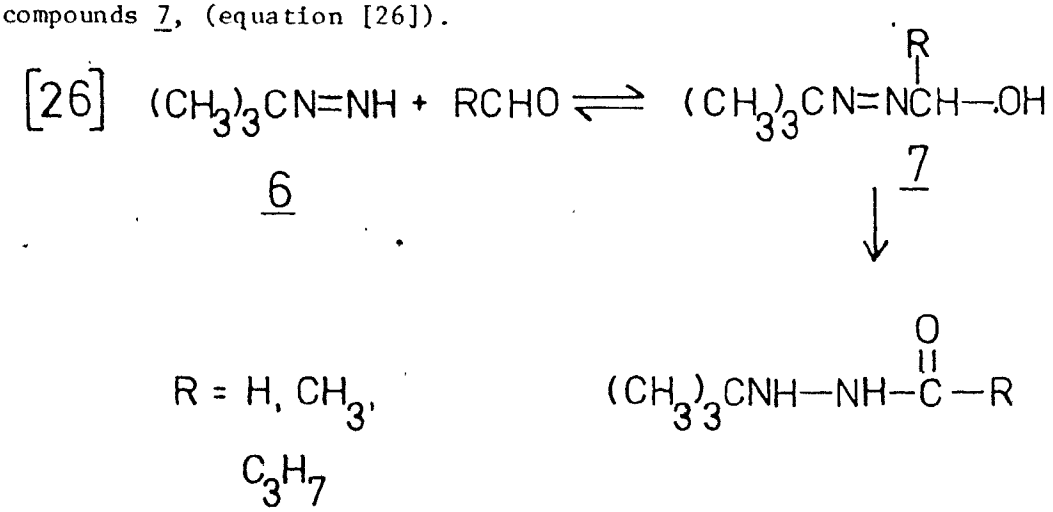
cyclohexanone was suggested as an intermediate in the reaction.

A new series of α-azocarbinols of the type 5 was synthesized by Hünig and coworkers[32-35] between 1968 and 1971. These compounds were



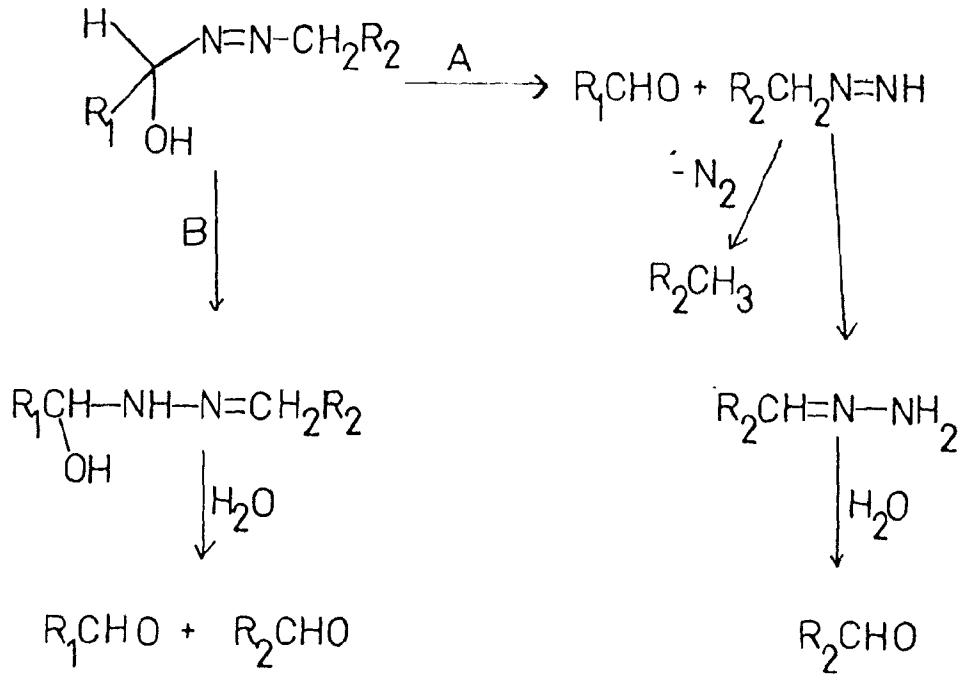
5

prepared by two methods: the action of base on alkoxydiazenium salts, and more generally, the addition of diazenes to carbonyl compounds. For example, addition of tert-butyldiazene 6 to aliphatic aldehydes in aqueous solution reversibly yielded the corresponding α-hydroxyazo compounds 7, (equation [26]).

[26] 

Thermolysis of 5 at room temperature gave a mixture of aldehydes according to the following scheme III. Compounds 5 were shown by U.V. and

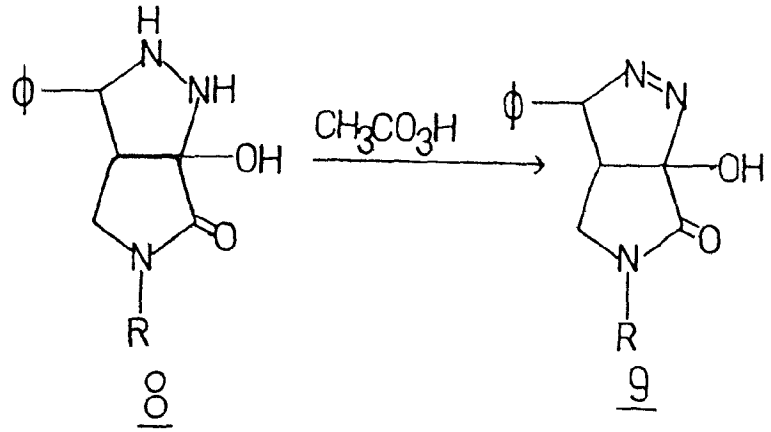
Scheme III



I.R. spectra to possess trans-stereochemistry about the azo double bond with intramolecular hydrogen bonding.[32-35]

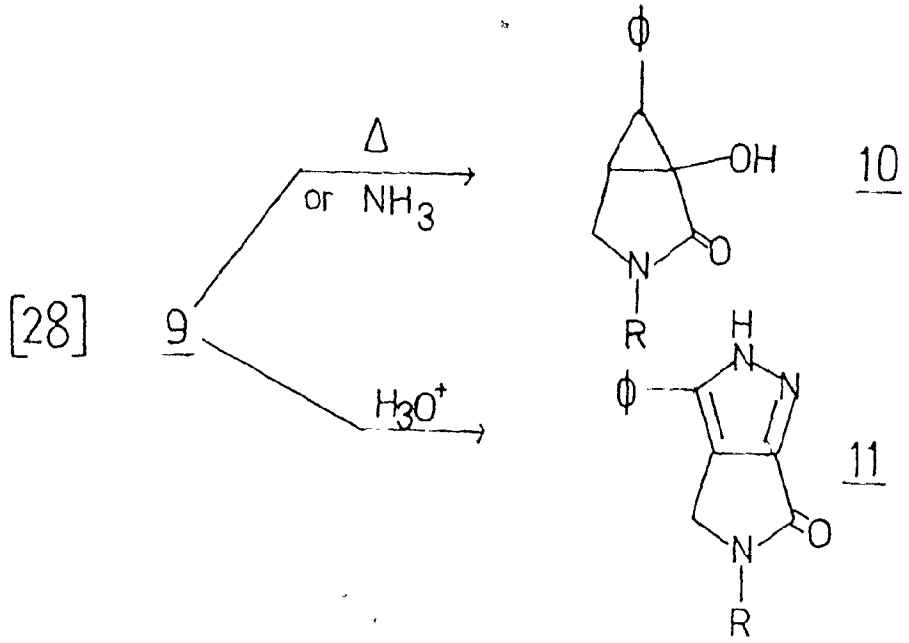
A somewhat more complex example was reported by Southwick and coworkers[36] wherein the oxidation of the ∝-hydroxyhydrazines 8 yielded the azocarbinols 9 (equation [27]). Compound 9 gave typical pyrazoline

[27]

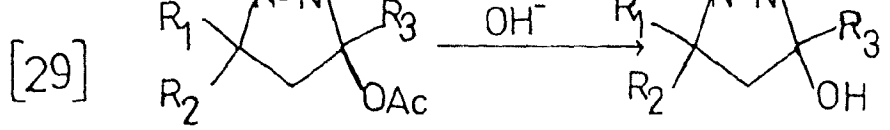


8 9

reactions: thermal decomposition to cyclopropanols 10 and acid-catalyzed dehydration to pyrazoles 11 (equation [28]).

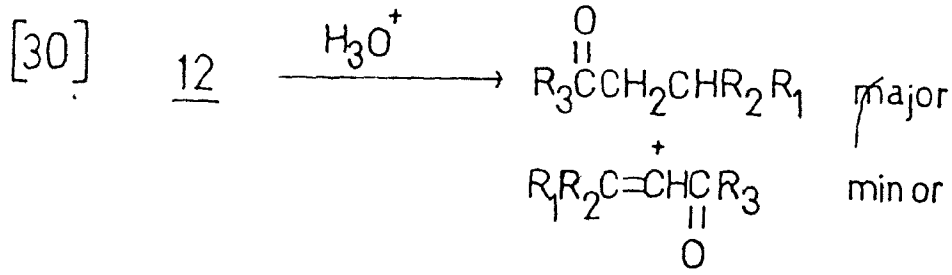


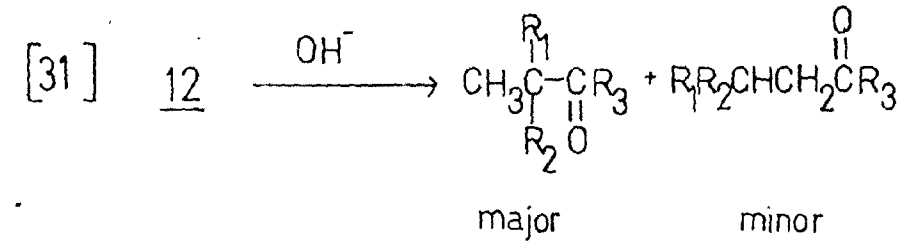
Other cyclic ∝-azocarbinols have also been reported[37,38]. They have been synthesized either by controlled hydrolysis, or by hydrogenolysis with sodium borohydride, of 3-acetoxy- Δ'-pyrazolines, equation [29].



12

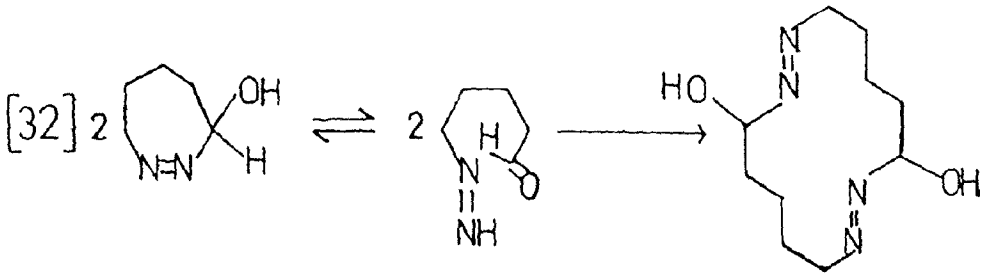
∝-Azocarbinols of the type 12 decompose with acid- and base-catalysis via ring opening to produce both saturated and unsaturated ketones (equations [30] and [31]). Esterification and etherification of the ∝-azocarbinols

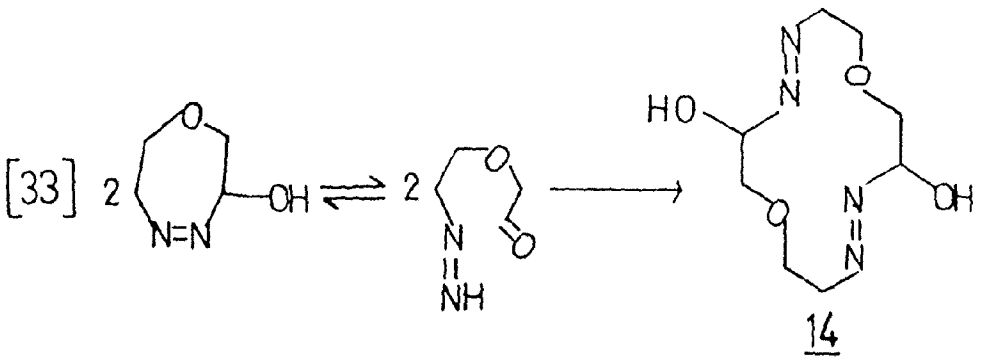




were also reported.

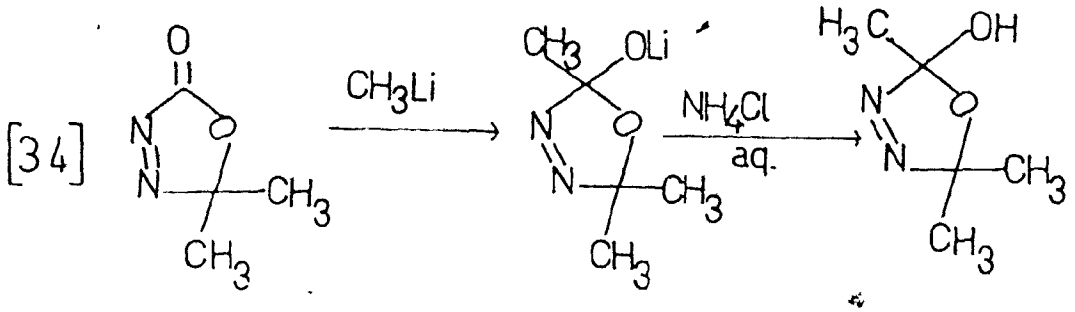
Synthesis of larger rings azocarbinols has also been reported[39,40]. Several 14-membered-ring (13 and 14) azocarbinols have been prepared via dimerization of smaller ring compounds (equations [32] and [33]).





Knittel and Warkentin[11,41] have prepared a new type of α-azocarbinol 1, in this laboratory. Treatment of 5,5-dimethyl-Δ^3-1,3,4-oxadiazolin-2-one (15) with methyllithium in ether at 0°C gave the lithium salt (16). Subsequent hydrolysis of 16 gave 2-hydroxy-2,5,5-

trimethyl-Δ^3-1,3,4-oxadiazoline, 1 (equation [34]). The instability of

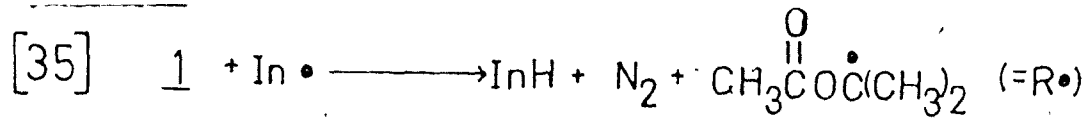
[34] 

15 16 1

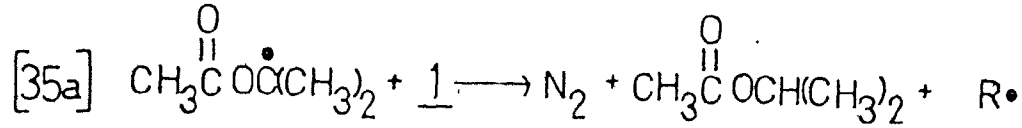
1 made it difficult to isolate but its structure was readily established from its spectra and its decomposition product.

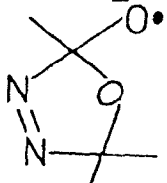
In benzene solutions 1 decomposed at room temperature to produce isopropylacetate in quantitative yield (N.M.R.). It was postulated by the authors that loss of molecular nitrogen must be concerted with hydrogen abstraction to account for the ready decomposition of 1 (equations [35] and [35a]). These findings were supported by several pieces of evidence.

Initiation:

[35] 

Chain Propagation:

[35a] 

One was that addition of a free radical, di-t-butyl nitroxide, greatly enhances the rate of N_2 evolution. This implies that the di-t-butyl nitroxide is capable of H-abstraction from 1 and this can only be believed if it does not lead to  as an intermediate.

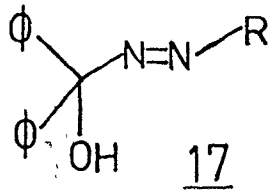
Secondly, addition of phenol, normally an inhibitor of radical chain processes, causes rate enhancement. Thus, in the present case it can be

concluded that phenoxy radicals abstract the hydroxyl hydrogen of 1 in concert with C-N bond cleavage and the partial formation of stable co-products at the transition state lowers the free energy of that state tremendously.

Further evidence to support this radical induced process came from experiments where olefins were converted to adducts of $CH_3CO_2\dot{C}(CH_3)_2$ and H• (equation [36]). The ability of compound 1 to donate an hydrogen atom in a radical chain process has made it a good reagent for radical chain addition in the synthesis of small molecules. The addition of 1 to unsaturated compounds is shown in equation [36]:

[36] 1 + $\overset{}{=}\!\!\!\diagup^{Y}$ ⟶ N_2 + $CH_3C(=O)OC(CH_3)_2CH_2CH_2Y$

More recently Yeung and Warkentin[12,13,42] have synthesized a series of α-azocarbinols of the type 17.

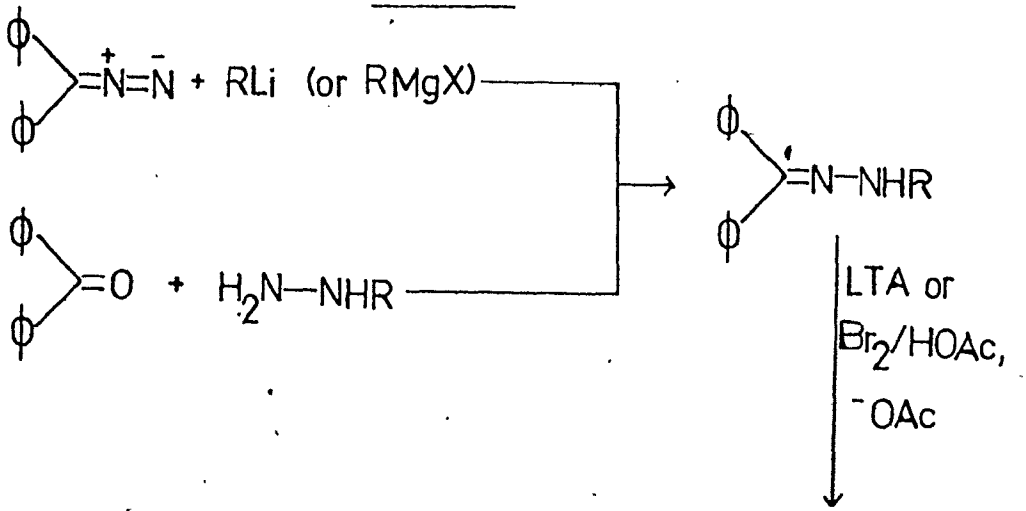


17

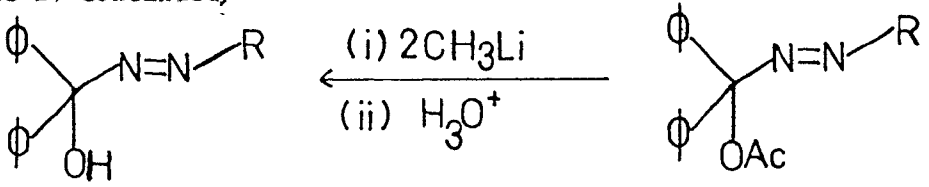
R = Me, Et, i-Pr, t-Bu, Ph, Bz, cyclohexyl, allyl, CH_2CH_2OH

α-Azodiphenylcarbinols were synthesized according to scheme IV[42].

Scheme IV



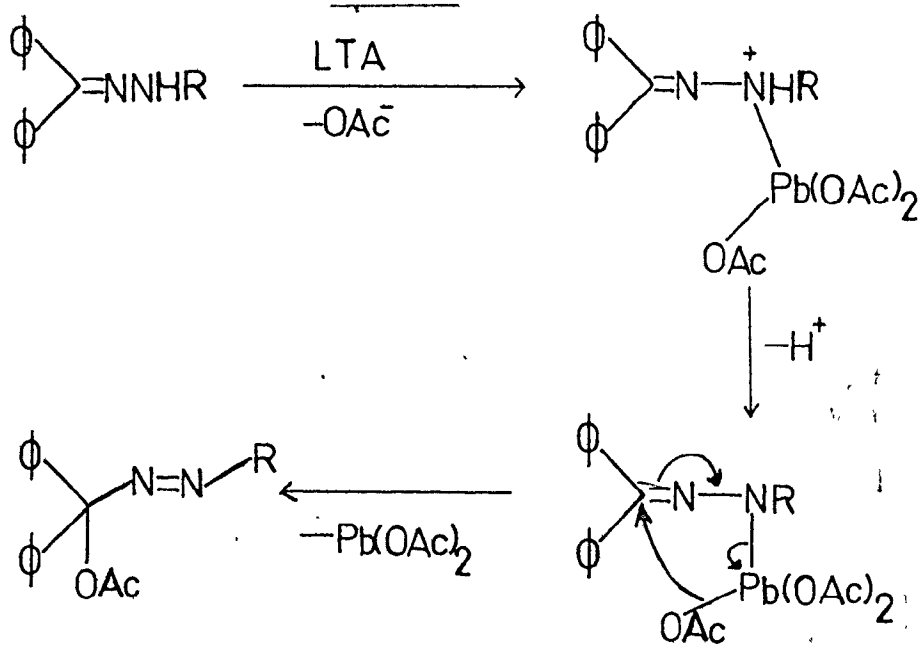
(Scheme IV continued)



17 18

The first step involves the preparation of the benzophenone N-monosubstituted hydrazone, either by direct condensation of benzophenone with the substituted hydrazine or by the reactions of alkyl lithium or Grignard reagents with diphenyldiazomethane. In the second step the hydrazone was converted to the corresponding azoacetate by oxidation with lead tetraacetate (LTA). The following polar mechanism was suggested for the conversion of the hydrazone to the azoacetate (scheme V). The reaction

Scheme V



of bromine with ketohydrazones in acetic acid to yield the azoacetates, was also employed. This method was comparatively less costly and easier to handle than the LTA method, but in general the yields obtained were

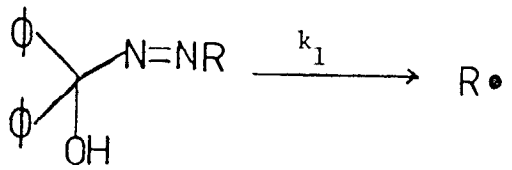
lower. In the final step, the azoacetates (18) were treated with methyllithium in ether at -10°C, followed by acidification with NH_4Cl solution to give the alkylazodiphenylcarbinols (17).

The yields of the azoacetates (18) prepared ranged from 20% to 80%. A singlet peak at δ 2.00-2.10 was present in the ^1H N.M.R. spectra of all the azoacetates, corresponding to the protons of the acetate group in the compounds. A strong band near 1760 cm^{-1} was present in the I.R. spectra of all the azoacetates, which was due to the stretching of the C=O bond of the acetate. The presence of the hydroxyl group, in the α-azocarbinols (17) prepared, was confirmed by ^1H N.M.R. spectroscopy which gave a broad singlet near δ 5.80, which disappeared on shaking the sample with D_2O. In the infrared spectrum of compounds 17 a medium intensity band near 3330cm^{-1} was attributed to the OH stretching. The Raman spectrum of tert-butylazodiphenylcarbinol 2 (17, R= tert-butyl), taken in the solid state at room temperature, showed N=N stretching at 1587.0 cm^{-1}.[42]

All the α-azocarbinols (17) prepared decomposed readily at room temperature in carbon tetrachloride giving benzophenone, chloroform, and the corresponding chlorides as major products. The peak at 1650cm^{-1} (C=O of benzophenone) in the I.R. spectra of all the azocarbinols increased in intensity with time as decomposition progressed. For example, 2 decomposes spontaneously at room temperature in carbon tetrachloride to yield benzophenone, tert-butylchloride, and chloroform. Kinetic experiments conducted on 2 in CCl_4 and benzene gave irreproducible apparent first-order rate constants. With undegassed samples (air present) the rate was greatly enhanced. Unimolecular homolysis of 2 was thus excluded and a radical chain mechanism suggested. Scheme VI depicts the proposed radical chain process.[12,13,42]

Scheme VI

Initiation:



17

Propagation:

$$R\bullet + CCl_4 \xrightarrow{k_2} \underline{RCl} + \dot{C}Cl_3$$

$$\dot{C}Cl_3 + \underline{17} \xrightarrow{k_3} \underline{CHCl_3} + \underline{(\phi_2)C{=}O} + N_2 + R\bullet$$

$$R\bullet + \underline{17} \xrightarrow{k_4} RH + (\phi_2)C{=}O + N_2 + R\bullet$$

Termination:

$$2\,R\bullet \xrightarrow{k_5} \text{Combination}$$

$$2\,R\bullet \xrightarrow{k_6} \text{Disproportionation}$$

$$R\bullet + \bullet CCl_3 \xrightarrow{k_7} RCCl_3$$

$$2\,\bullet CCl_3 \xrightarrow{k_8} CCl_3{-}CCl_3$$

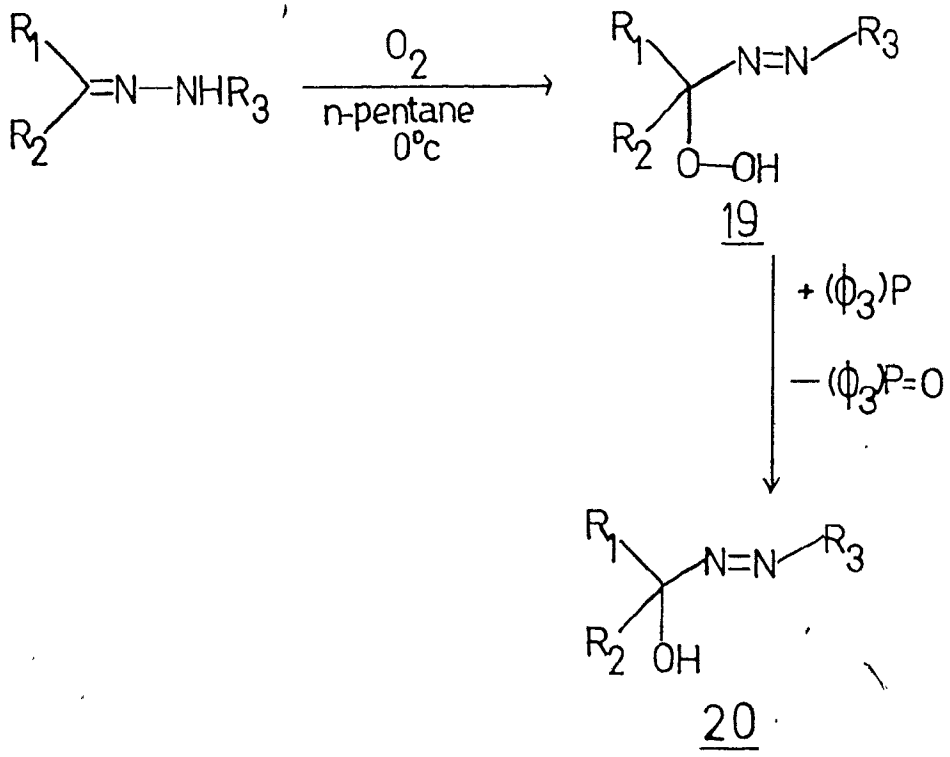
Addition of a small amount of thiophenol to a solution of 2 in carbon tetrachloride gave a very large rate enhancement. Thus thiophenol did not inhibit the radical chain process, as expected, but in fact, thiophenol (0.02M) effectively accelerated the decomposition of 2 in CCl_4. Thus, in the system studied, phenylthiyl radical acts as a chain carrier by abstracting the hydroxyl hydrogen of 2. First-order chain decomposition of 2 in degassed carbon tetrachloride is consistent with chain termination by reaction of trichloromethyl radicals with tert-butyl radicals.

The decomposition of 2 was also well studied in benzene solutions.

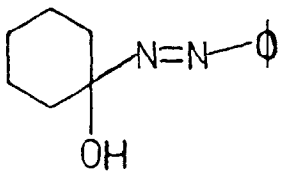
tert-Butylazodiphenylcarbinol (2) decomposed more slowly at room temperature in benzene than in carbon tetrachloride[42]. Solutions of 2 (0.24M) in benzene gave reproducible first-order kinetics if air was excluded[12], suggesting that decomposition of 2 goes by unimolecular, radical bond cleavage under those conditions.

Schulz[43,44] and coworkers have reported the synthesis of trans-α- hydroxydialkyldiazenes (20) from α-alkylazoalkylhydroperoxides (19) according to scheme VII. Compounds 19 formed by autooxidation of alkyl-

Scheme VII



hydrazones are reduced, in high yield, to trans-α-hydroxyalkyldiazenes with triphenylphosphine. The product was isolated by vacuum distillation. According to this synthetic procedure (Scheme VII) the authors[44] prepared 1-phenylazo-1-hydroxycyclohexane (21) (m.p. 31°C, 68% yield) and 1-tert-butylazo-1-hydroxycyclohexane (22). The authors expected compounds 21 and



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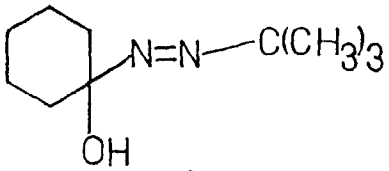
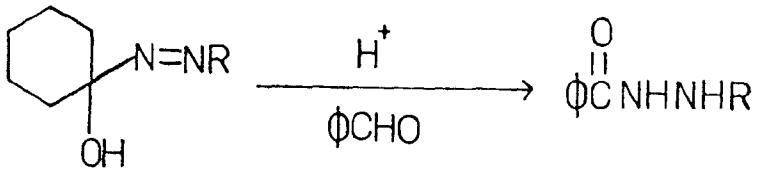


22

22 to fragment to RN=NH and cyclohexanone. Thus, 21 would become a source of $(C_6H_5)N{=}NH$ and 22 a source of $(CH_3)_3CN{=}NH$. The following reaction (equation [37]) supported this hypothesis. Compound 23 also results without acidification on warming

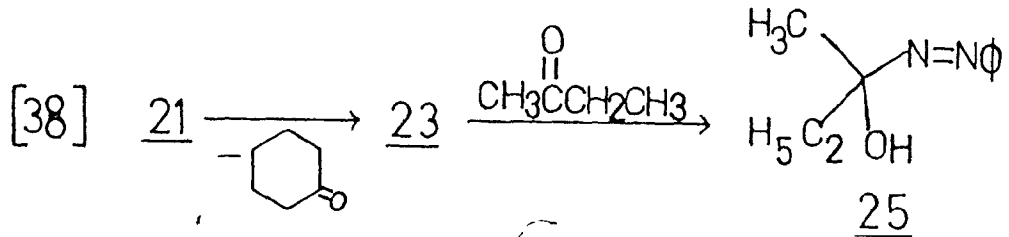
[37] 

21: R=Ph
22: R=t-Bu

23: R=Ph
24: R=t-Bu

21 in the presence of benzaldehyde at 80°C. Yields were: 72% in $HOCH_2CH_2OH$; 61% in EtOH; 48% in $(C_6H_5)Et$.

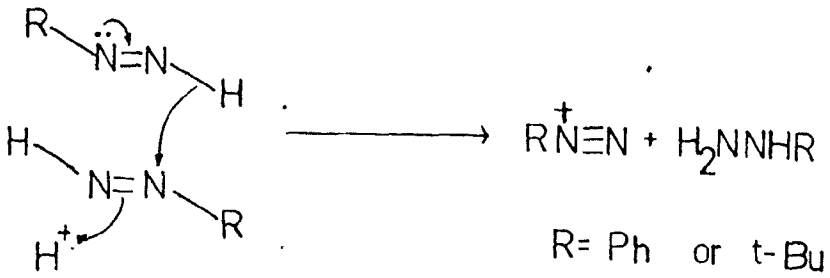
They[44] also observed that the carbonyl component of 21 could be exchanged for $CH_3COCH_2CH_3$ by warming at 80°C for 48 hours. According to them, this observation verified that phenyldiazine adds to ketones. Thus 2-phenylazo-2-hydroxybutane (25) was obtained as a yellow liquid in 82% yield (equation [38]). Reaction of 21 with an ethereal solution of

[38] 

25

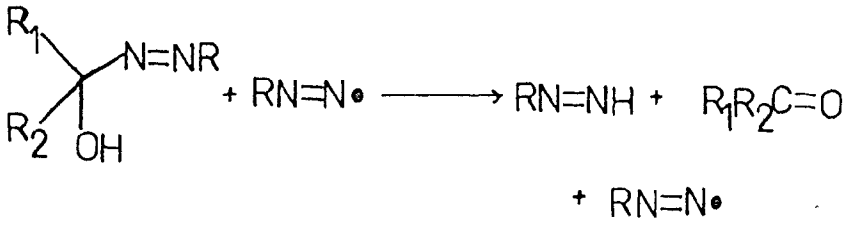
HBF_4 (1:30) gave $(C_6H_5)N_2BF_4$ in 35% yield in addition to $(C_6H_5)NH_2$ (66%),

$(C_6H_5)N_3$ (6%) and $(C_6H_5)N{=}N(C_6H_5)$. These reactions were explained in terms of a bimolecular decomposition of RN=NH (equation [39]). These results

[39] 

indicate an alternative mechanism of azocarbinol decomposition; namely, the alkyldiazene route. Such a mechanism conflicts, at least in the mechanistic detail, with that proposed by Warkentin[11,12,13] and coworkers.

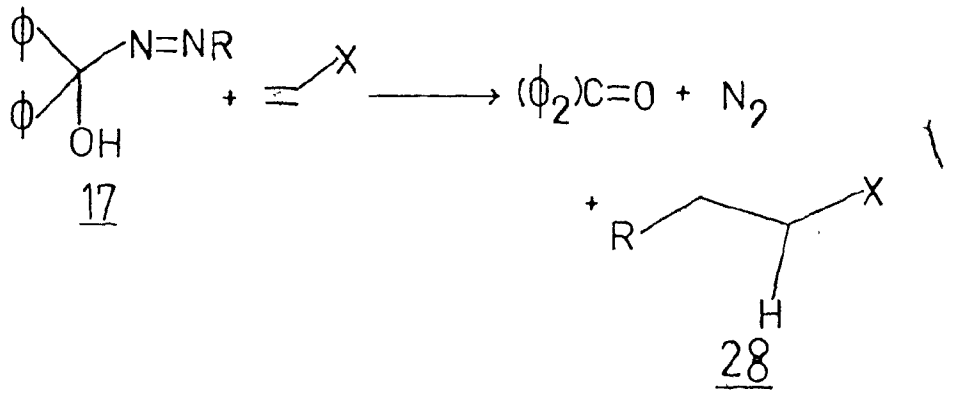
Some of the differences can be smoothed over but others can not. For example, diazene could also come from induced decomposition via a radical chain mechanism (equation [40]). However one can no longer talk

[40] 

about a fully concerted hydrogen abstraction step if Schulz's observations are correct, and if the diazene actually comes from a diazenyl radical. Schulz and coworkers, unfortunately, have no information concerning the mechanism by which RN=NH is formed.

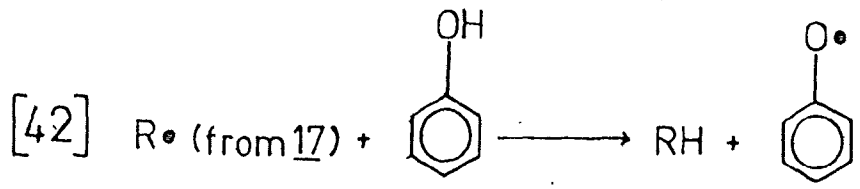
B: Synthetic Utility of α-Azocarbinols

The synthetic utility aspects of α-azocarbinols, for the hydroalkylation of unsaturated compounds, has been a subject of interest in our laboratory[11,13,42]. The apparently excellent chain transfer ability of these α-azocarbinols (17) accounts for their ease of radical chain addition to yield small molecules according to equation [41]. This

[41] 

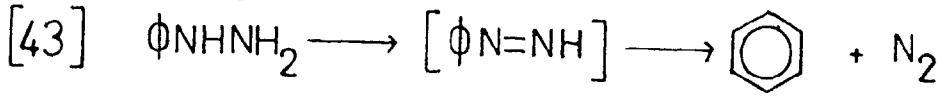
synthetic utility has been demonstrated[42] with a wide variety of olefinic compounds such as acrylonitrile, norbornene, crotonaldehyde, and azobenzene. These unsaturated compounds have been hydro-tert-butylated, hydro-isopropylated, hydro-ethylated, and hydro-methylated, displaying the application of 17 in the synthesis of small molecules.

The radical addition mechanism is a complex sequence of steps, as shown in scheme II (page 11). The addition product (28) (equation [41]) is formed by the chain propagation steps. For good yields the chain length must be as long as possible so that termination products form a small part of the total products. In many cases, phenol was found to increase the yield of the addition product from decomposition of 17 in the presence of an olefin. In other cases, the yields of the addition products were lowered with added phenol because of the competitive reaction (equation [42]) existing for radicals (R•) generated from 17.

[42] 

III: Diazenes

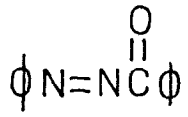
For many years, monosubstituted diazenes were regarded as highly unstable intermediates and were denoted within brackets. The earliest reference to the possibility of an aryldiazene (arylimide[45], ArN-NH) was reported by Widman in 1895[46]. Chattaway explained the formation of benzene and nitrogen from the oxidation of phenylhydrazine[47], (equation [43]), in terms of phenyldiazene as an intermediate. There have



[43]

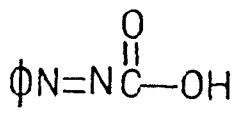
been numerous cases where RN=NH has been cited as an intermediate but no chemist had observed a monosubstituted diazene directly up to 1965[48].

The involvement of monosubstituted diazenes in the deamination by difluoroamine (HNF_2) was first postulated in 1963 by Baumgardner[49]. Several years later Cohen and Nicholson[50] reported that the acid-catalyzed methanolysis of low concentrations of N-phenyl-N'-benzoyl-diazene (29) leads to methyl benzoate, nitrogen and benzene; in the presence of various



29

radical traps, evidence for phenyl radicals was found. The authors postulated that phenyldiazene was formed in the initial step. Simultaneously Kosower and Huang[51] discovered that if phenylazoformic acid (30) is decarboxylated in dilute solution at 25°C, at moderate pH, and



30

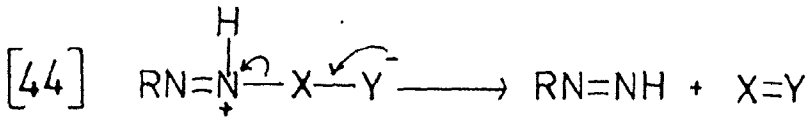
under rigorous exclusion of oxygen, phenyldiazene can be preserved and observed by UV for several hours.

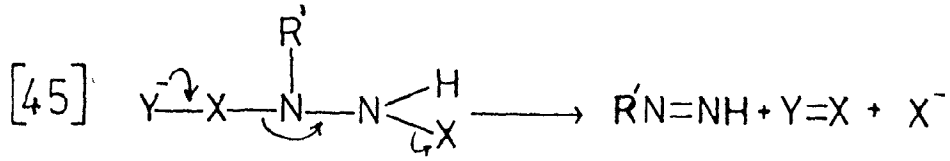
Cram and Bradshaw[52] have provided evidence for the alkyldiazene, 2-phenyl-2-butyldiazene, in the form of similar products produced from alkyldiazene generated in different ways. It has been stated[53] that properties of intermediates should be observed directly rather than being inferred from the nature of the products formed in a reaction. "Intermediates often exhibit surprising behaviour not readily revealed by indirect means". This has been found to be true in the case of phenyldiazene[54].

B: Synthesis of Diazenes

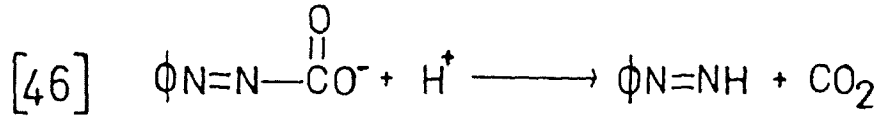
Monosubstituted diazenes can be generated by fragmentation, elimination, and oxidation. The following may serve as examples.

Fragmentation:

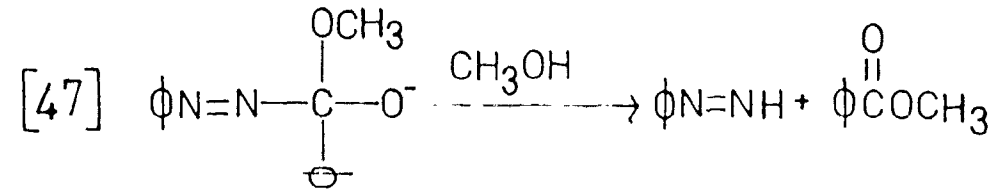
[44] 

[45] 

Decarboxylation:

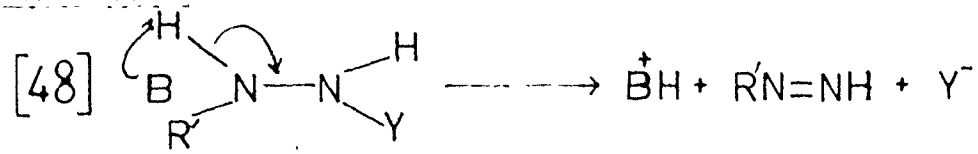
[46] 

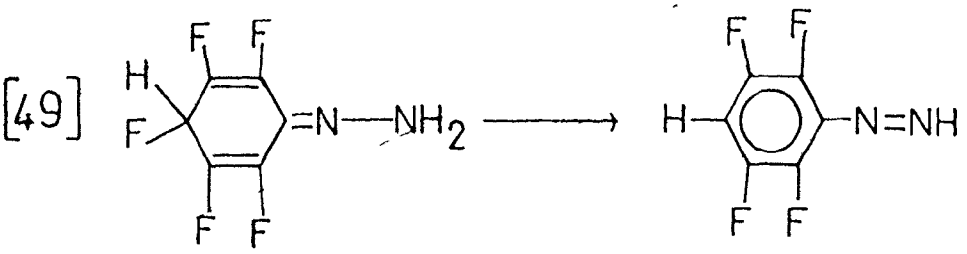
Deesteration:



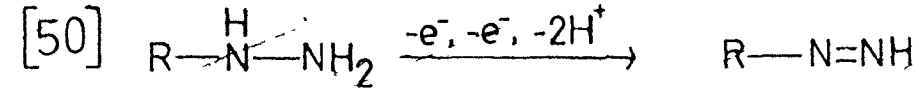
Decarboxylation and deesteration reactions (equations [46] and [47]) are specific examples of the general types of fragmentation reactions [44] and [45]. Equation [49] serves as a specific example of 1,6 elimination[55].

Elimination:





Oxidation:



Complexes with the general constitution $(RN{=}NR)(CuX)_n$, may be formed by the redox reaction between a cupric halide and a suitable hydrazine[56].

Reduction:

[51] $R-\overset{+}{N}\equiv N \xrightarrow[CH_3O^-,\ (n\text{-}C_4H_9)_3SnH]{BH_4^-} R-N=NH$

The two routes, decarboxylation and elimination seem most suitable for the preparation of diazenes.

It is important to note that monosubstituted diazenes are sensitive to oxygen, are subject to bimolecular disappearance, and are reactive toward base. Bimolecular disappearance seems to be the most remarkable reaction of monosubstituted diazenes[54,57]. The products of the reaction are mainly the corresponding hydrocarbon (usually more than 50%) and some other compounds of which the chief one is apparently the hydrazine (equation [52]). However, the mechanism of the reaction is not very clear.

[52] $2RN=NH \longrightarrow RH + \overset{H}{\underset{}{RN}}-\overset{H}{\underset{}{NR}}$

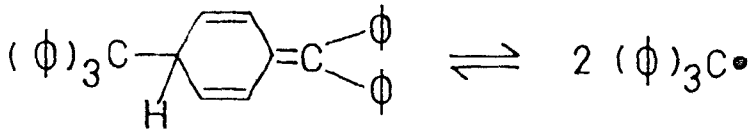
The reaction seems to be very insensitive to solvent. This lack of solvent effect indicates that the rate limiting transition state is not significantly different in charge separation from the initial state[48]. The author[48] further speculates that a steric effect seems to be of some importance in accelerating the reaction. The dissociation of diazenes to a diazenyl radical and a hydrogen atom is ruled out[48] on the basis of the low activation energy, there being little chance that a diazenyl radical (RN=N•) would be so stable.

IV: Stable Free Radicals

One method of testing for induced decomposition of α-azocarbinols (17) is to subject them to radicals under conditions where the azocarbinol alone is stable. In order to do this one must either generate those radicals

in the presence of the azocarbinol (a different route because the latter is thermally and photochemically unstable) or one must introduce preformed or stable radicals.

Triphenylmethyl (trityl), the first known organic free radical[2], was one of the first radicals to be studied by electron spin resonance[58]. Farly measurements showed a serious discrepancy between the observed hyperfine structure and spin densities obtained from the simple molecular orbital theory. Recently it has been shown[59] that the dimer does not have the hexaphenylethane structure originally ascribed to it, but rather 31.



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In 1971 Pryor[60] and coworkers attempted to use trityl radicals to "mop up" secondary radicals and prohibit chain processes, and, in contrast with acetyl radicals, trityl does appear to serve this role. They stated that trityl is a stable radical and a good radical scavenger.

More recently, the transfer of hydrogen atom from thiophenols to trityl radical has been investigated[61]. The hydrogen atom is abstracted from thiophenol or 2,4,6-trimethylbenzenthiol at a rate comparable to that for the establishment of the trityl radical dimerization equilibrium. The results are presented in Tables I and II[61].

Table I: Rate constants for the Reaction of Thiophenol with the Triphenylmethyl Radical in Toluene.

T (°C)	k (exptl.)$M^{-1}s^{-1}$	k (calcd.)*$M^{-1}s^{-1}$
41.1	15.9	16.2
19.2	5.6	5.2
10.9	3.08	3.2

Table II: Rate Constants for the Reaction of 2,4,6-Trimethylbenzenethiol with the Triphenylmethyl Radical in Toluene.

T (°C)	k (exptl.)$M^{-1}s^{-1}$	k (calcd.)**$M^{-1}s^{-1}$
41.89	20.8	20.6
29.87	11.5	11.7
19.6	7.0	7.0
11.0	4.4	4.4

*Calculated from the Arrhenius equation

$$k=6.96X10^{7+/-0.142}\exp(-9540+/-180 cal mol^{-1}/RT)$$

**Calculated from the equation

$$k=3.13X10^{7+/-0.091}\exp(-8910+/-130 cal mol^{-1}/RT)$$

The information from Tables I and II makes it clear that trityl radical can abstract hydrogen from a good hydrogen donor, for example thiophenol. That is, trityl radical is not "stable" under all conditions. Therefore it is a reasonable choice for the experiment in which one wants to observe the induced decomposition of azocarbinol. Tables I and II also indicate that the rate of hydrogen abstraction by trityl radical is temperature dependent; the rate of abstraction increases as the temperature increases.

The difficulty with using trityl is that one can not get the rate constant for its reaction with thiophenol readily; because trityl

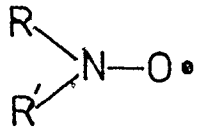
radical is constantly generated from its dimer at a rate that changes with dimer concentration. The authors also used tris-p-tert-butylphenylmethyl radical, which has been shown to be 100% dissociated in solution[62]. This new radical is presumably sterically hindered and tends not to dimerize. Using tris-p-tert-butylphenylmethyl radical, the reaction of the radical with the thiols could be written as follows (Scheme VIII):

Scheme VIII

$$Ar_3C\bullet + Ar'SH \xrightarrow{k_1} Ar_3CH + Ar'S\bullet$$

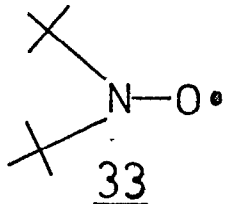
$$Ar_3C\bullet + Ar'S\bullet \xrightarrow{k_2} Ar_3C{-}SAr'$$

The nitroxides (32) are a very stable group of radicals[63], especially if bulky or electronegative groups flank the NO group. These



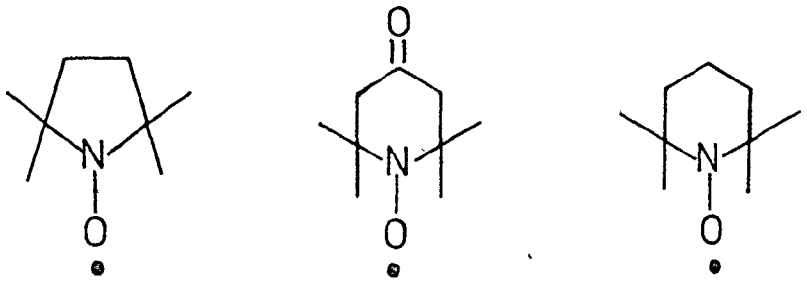
32

radicals do not seem to be able to stabilize themselves by hydrogen abstraction like most carbon radicals; this in spite of the large OH bond energy. This inertness has been used in many ways. For example, the liquid radical di-tert-butylnitroxide (33) can be used as a solvent



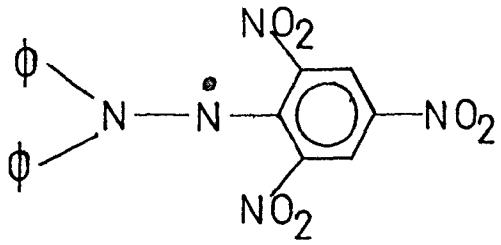
33

for other radicals[64]. Among other stable nitroxides which are most easily obtained are five- and six-membered ring cyclic ditertiary amine-N-oxyls, such as 34, 35, and 36. These are prepared by oxidation of triacetone-



34 35 36

amine with hydrogen peroxide and phosphotungstic acid or other tungsten, molybdenum, or vanadium compounds[65-67]. An interesting analogue of nitroxyl radicals, 2,2-diphenyl-picrylhydrazyl (37) is another type of stable free



37

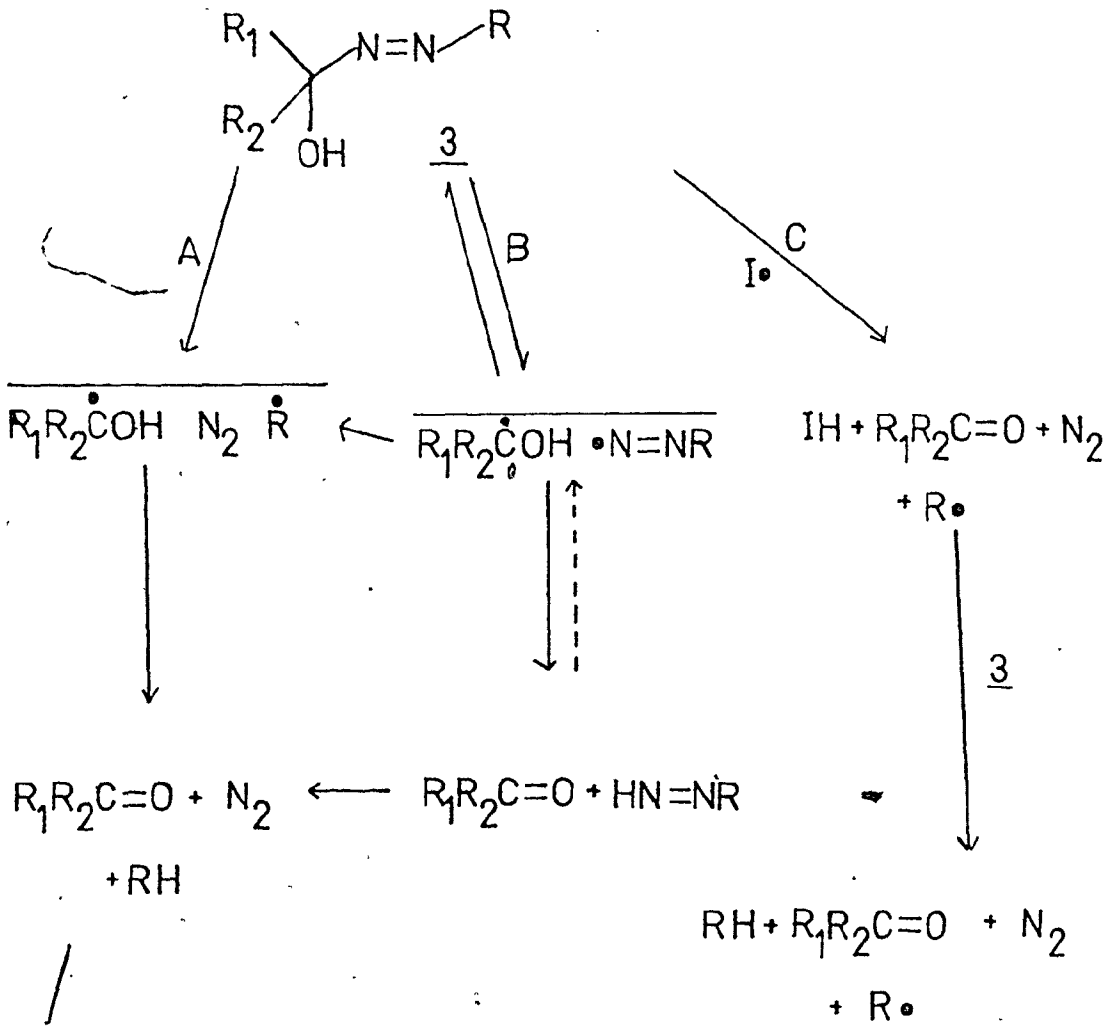
radical[68]. There appears to be no evidence for any dimer in this case.

RESULTS AND DISCUSSION

I: General

The mechanistic possibilities of decomposition of α-azocarbinols (3) may be grouped under three main types of chemistry (Scheme IX):

Scheme IX

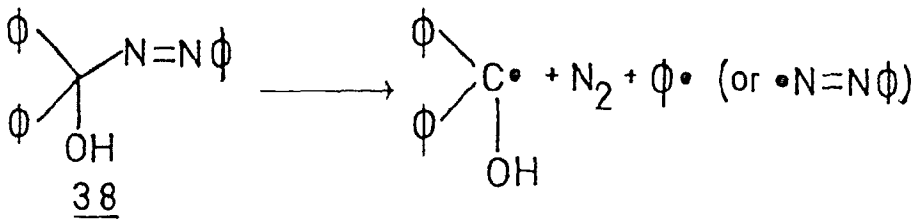


unimolecular fragmentation producing ketyl radicals $R_1R_2\dot{C}OH$ which would most likely disproportionate in the cage (Mechanism A); reversible dissociation to carbonyl compound plus diazene (Mechanism B); and radical chain

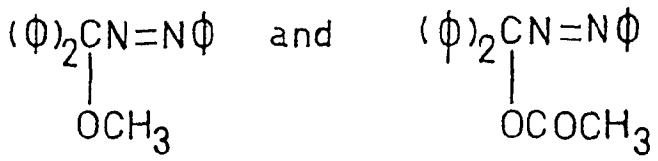
abstraction of hydroxyl hydrogen (Mechanism C). All three modes of decomposition of 3 can lead to the same major products.

Mechanism A was suggested by Southwick[36] and coworkers and by Nagata and Kamata[80] who did product studies for the fragmentation of several α-hydroxydiazenes (for example, pyrazoline 9, equation [28]). Evidence for the operation of mechanism B has been reported by Schulz[44] and Missol and by Hünig's group[32-35]. They have observed the conversion of an added ketone to a new azocarbinol (equation [38]) and have explained this observation in terms of attack of a supposed diazene intermediate on the carbonyl compound; possibly analogous to the reaction shown with the dotted arrow in scheme IX, although the authors did not provide a detailed mechanistic hypothesis. It is also not clear whether or not those workers were sufficiently careful to exclude traces of acid, to avoid an acid catalyzed process. Examination of the decomposition products from 3-hydroxypyrazolines, by Freeman[38] in 1972, has suggested that any of the three mechanisms is possible. The radical chain process involved in mechanism C has been proposed and supported by Warkentin[11,13,12] and co-workers in this laboratory (for more information on this topic the reader is referred to the introduction section).

The initiation step is unlikely to be unimolecular homolysis according to equation [53], because the corresponding methylether (53) and acetate (39) are very stable compared to 38, under similar reaction conditions (Table III). If 38 were decomposing through unimolecular homolysis of the CN bond (mechanism A) then its rate of decomposition would be similar to those of the corresponding azoether 53 and azo-acetate 39, except for small substituent effects. This, however, was

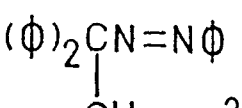
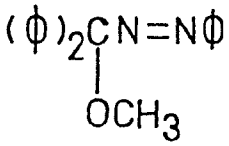
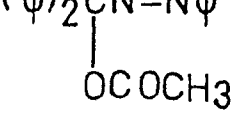
[53] 

38



53 39

Table III:

Compound	Reaction Conditions	k (sec^{-1})	Relative Rate
 38	CCl_4, degassed 80.0+/- 0.1°C	2.47×10^{-4}	211
 53	CCl_4, degassed 80.0+/- 0.1°C	3.64×10^{-6}	3
 39	CCl_4, degassed 80.0+/- 0.1°C	1.17×10^{-6}	1

not found to be the case as the rate of decomposition of 38 was approximately 200 times greater than that of 39 while 53 decomposed at a rate only 3 times faster than that of 39. Thus the order in rate of decompo-

sition is 38 ⟫ 53 ⟩ 39. Hence unimolecular homolysis of 38, via C-N bond cleavage as the rate determining step, could not be the correct interpretation.

Other evidence against mechanism A operating in the decomposition of α-azocarbinols comes from the rate studies of the following compounds (Table IV). Although the decomposition of 41 was done at 35°C and no rela-

Table IV:

Compound	Reaction Conditions	k (sec^{-1})	Relative Rate
$(\phi)_2CN{=}N\phi$ OH 38	CCl_4, degassed 80.0 +/- 0.1°C	2.47×10^{-4}	----
$(CH_3)_2CN{=}N\phi$ OH 41	CCl_4, degassed 35.0 +/- 0.1°C	7.35×10^{-4}	---
Compound	Reaction Conditions	k (sec^{-1})	Relative Rate
$(\phi)_2CN{=}N\phi$ $OCOCH_3$ 39	CCl_4, degassed 80.0 +/- 0.1°C	1.17×10^{-6}	large
$(CH_3)_2CN{=}N\phi$ $OCOCH_3$ 52	CCl_4, degassed 80.0 +/- 0.1°C	Only 12% dissociated after 1,100hrs. (approx.45 days)	1

tive rates were obtainable with comparison to the decomposition of 38, some qualitative information merits mentioning. The results are interesting because if 38 and 41 were decomposing unimolecularly then the rate ratios of 38:41 and 39:52 would be similar in magnitude, however this is not the

case. Also interesting is the fact that 41 decomposes almost instantly at 80°C; ie. 41 decomposes much faster than 38 at 80°C, hence the reason for decomposing 41 at 35°C. Again, this is not reasonable if mechanism A is in operation, since the ketyl radicals generated from the homolysis of 38 and 41, $(C_6H_5)\dot{C}OH$ and $(CH_3)_2\dot{C}OH$ respectively, would have different stabilities; with the former ketyl radical being much more stable due to resonance effects. Hence, if this were the case, 38 should decompose at a rate faster than that of 41.

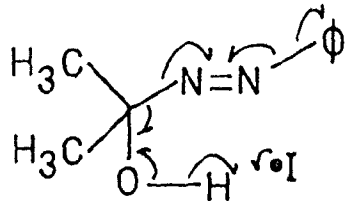
Evidence favouring mechanism B stems from the work of Schulz[44] and coworkers who accounted for these adducts (equations [37] and [38]) by suggesting that the decomposition of azocarbinols occurs via a diazene intermediate. However, kinetics of thermolysis of 41 in different concentrations of benzaldehyde (Section IV: C) showed a first order rate dependance in benzaldehyde. The results do not agree with a mechanism where diazenes are intermediates, but indicate that benzaldehyde reacts directly with undissociated azocarbinol. For more detailed information on this topic the reader is referred to page 57 (Section IV: C). This result is also supported by the owrk of Kosower[54] who states that undissociated phenyldiazene is not a nucleophile toward reactive carbonyl compounds.

Evidence for the decomposition of α-azocarbinols points toward a radical chain mechanism (mechanism C). The fact that 41 decomposes in the presence of trityl radicals (Section IV: E), giving pseudo first order kinetics, with a rate faster than that of the control experiment, is strong evidence for an induced mechanism (equation [69]). The only obscure point here is that one does not know whether phenyldiazenyl radical (51) is generated during the radical chain process of decomposition

of 41 in the presence of trityl radical (equation [69]). However, if generated, 51 cannot live long since it loses[78] molecular nitrogen at a rate of 10^8 sec^{-1}.

There is also the fact that addition of thiophenol to a solution of 41 in carbon tetrachloride causes rate enhancement (equation [67], section IV: D). Thus it is conceivable that thiophenyl radicals act as chain carriers by abstracting the hydroxyl hydrogen of 41.

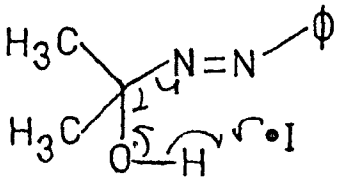
These results and others[11,12,13,42] stemming from this laboratory greatly favour the radical chain mechanism (mechanism C) initiated and propagated by hydroxyl hydrogen abstraction (equation [54]) which

[54] 

$\longrightarrow (CH_3)_2C{=}O + IH + N_2 + \phi\bullet$

41

may be concerted with loss of N_2 or as an alternative produce phenyldiazenyl radical (51) which will rapidly (ie. $k=10^8$ sec^{-1}) lose N_2 to leave behind a phenyl radical (equation [55]).

[55] 

$\longrightarrow (CH_3)_2C{=}O + IH + \bullet N{=}N\phi$ 51

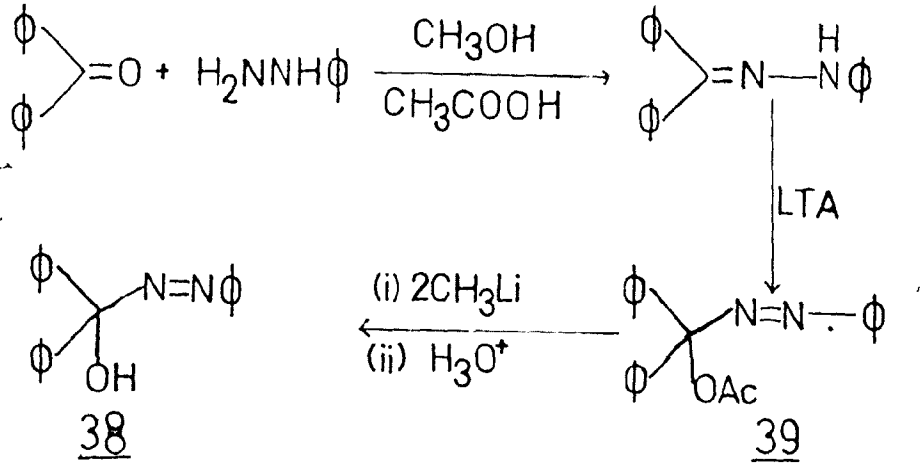
41

51 $\xrightarrow{k=10^8\ sec^{-1}}$ $N_2 + \phi\bullet$

II: Synthesis of α-Azocarbinols

α-Phenylazodiphenylcarbinol, 38, (17, R=Phenyl) was synthesized via the lead tetraacetate (LTA) route, according to scheme X. The first

Scheme X

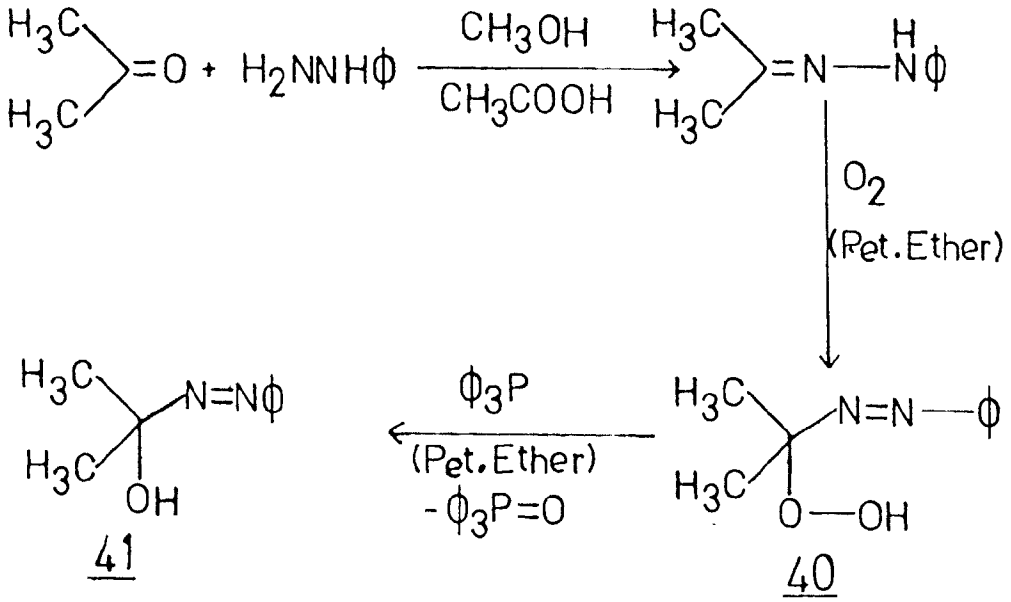


step involves the preparation of benzophenone phenylhydrazone, by direct condensation of benzophenone with phenylhydrazine. In the second step, benzophenone phenylhydrazone is converted to phenylazodiphenylmethylacetate (39) by oxidation with LTA (general mechanism on page 19). In the final step, α-phenylazodiphenylcarbinol (38) was prepared by treatment of the azoacetate (39) with methyllithium in ether at -10°C, followed by acidification with NH_4Cl solution. The yield of 38 was 85%. The resulting azocarbinol, 38, is characterized by a broad singlet peak at δ 5.83 in its ^1H N.M.R. spectrum (this peak disappears on shaking with D_2O), and by a band at 3380 cm^{-1} of medium intensity in the I.R. spectrum; this band is attributed to the O-H stretching frequency.

α-Phenylazodimethylcarbinol, 41, a new compound in the series of α-azocarbinols prepared in our laboratory, was synthesized according

to Scheme XI . This route involves the air oxidation of the hydrazone

Scheme XI



to give the hydroperoxide which is then reduced to the ∝-azocarbinol by the action of triphenylphosphine.The hydrazone is converted to the hydroperoxide (40) via oxidation with oxygen at room temperature in petroleum ether. The reaction was judged to be complete when no more oxygen was taken up. The fact that the reaction was complete was also checked by ^{1}H N.M.R. In the final step, the hydroperoxide (40) (in petroleum ether) was reduced, in 75% yield, by the action of triphenylphosphine, to phenylazodimethylcarbinol (41), with triphenylphosphine oxide as the biproduct of the reaction.

The O-H stretching frequency of 41 occurs at 3425 cm^{-1} in the I.R. spectrum. A pure sample of 41 shows singlets in the ^{1}H N.M.R. spectrum at δ 4.57 and at δ 1.43 corresponding to the O-H proton and the gem-dimethyl protons, respectively. The new ∝-azocarbinol (41) has also been characterized by its ^{13}C N.M.R. spectrum. The spectroscopic data for all of the compounds prepared appear on pages 43 and 44 (Table V).

Table V: Spectral Data of Compounds Prepared

Compound	Yield (%)	M.P.(°C)	^{1}H N.M.R. (δ, ppm)	I.R. (cm^{-1})
$(\phi)_2C{=}N\underset{H}{N}\phi$	95	137-138	3.38 (s,1), 6.72 - 7.62 (m, 15)	3345, 3090, 3060, 3030, 1960, 1880, 1820, 1770, 1600, 1500, 1450, 1340, 1315, 1300, 1250, 1190, 1175, 1125, 1105, 1070, 1030, 965, 920, 885, 690, 660
$(\phi)_2C(OCOCH_3)N{=}N\phi$	80	100-102	2.18 (s,3), 7.20 - 7.83 (m, 15)	3650, 1950, 1850, 1750, 1480, 1440, 1360, 1220, 1195, 1175, 1145, 1080, 1035, 1020, 955, 910, 695, 685
$(\phi)_2C(OH)N{=}N\phi$	70	75-76 (decomposes)	5.83 (s, 1) 7.10 - 7.80 (m, 15)	3380, 3050, 1950, 1870 1800, 1650, 1600, 1480 1450, 1380, 1310, 1210 1185, 1160, 1100, 1070 1030, 940, 900, 700
$\phi(Br_2)C{-}CH{<}^{Br_2}$	1.5	oil	7.43 (s, 1) 7.33 (s, 5)	Mass Spectometry (MS) 426, 424, 422, 420, 418 ratios 1:4:6:4:1

Table V: Spectral Data of Compunds Prepared

Compound	Yield (%)	M.P.(°C)	^{1}H N.M.R. (δ, ppm)	I.R. (cm^{-1})
$(CH_3)_2C{=}NN(H)\phi$	90	B.P. 140-143	1.73 (s, 3) 1.97 (s, 3) 6.57 - 7.30 (m, 6)	3350, 3058, 2995, 2909, 1597, 1500, 1422, 1367, 1318, 1271, 1248, 1177, 1129, 1041, 890, 760, 705
$(CH_3)_2C(OCOCH_3)N{=}N\phi$	75	----	1.60 (s, 6) 2.07 (s, 3) 7.33 - 7.73 (m, 5)	3065, 2998, 2943, 2888, 1750, 1481, 1455, 1435, 1370, 1310, 1243, 1195, 1169, 1140, 1070, 1018, 935
$H_3C(H_3C)C(OH)N{=}N\phi$	82	----	^{1}H N.M.R. 1.43 (s, 6) 4.57 (s, 1) 6.87-7.57 (m, 5) ^{13}C N.M.R. 27.04 ($2C_1$) 122.8 (C_2) 128.3, 128.8, 129.2, 131.1, 131.9, 132.4 — Phenyl Carbons	3425, 3072, 2993, 2961, 2939, 2878, 1482, 1456, 1439, 1381, 1362, 1311, 1220, 1200, 1121, 1072, 1023, 979, 929

The reduction of hydroperoxides to alcohols by phosphines has been studied extensively by Hiatt[70-72] and coworkers. Earlier stereochemical studies[73] had shown that the phosphine abstracts the hydroxyl oxygen (equation [56]); the speeding of the reduction and the absence of inhi-

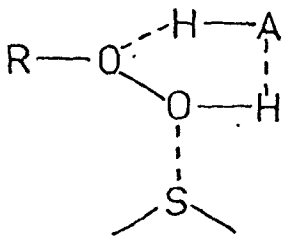
$$[56] \quad RO_2H + R'_3P \longrightarrow ROH + R'_3PO$$

bition by trinitrobenzene[74] had suggested a polar rather than a radical mechanism[73,74]. However, there was evidence that the reduction could be inhibited, or at least retarded, by impurities[70], and misgivings about its cleanness when applied to non-tertiary hydroperoxides had been expressed[75]. Such findings suggested a free radical chain mechanism[70] propagated by reactions [57] and [58] as follows:

$$[57] \quad RO_2\bullet + R'_3P \longrightarrow RO\bullet + R'_3PO$$

$$[58] \quad RO\bullet + RO_2H \longrightarrow ROH + RO_2\bullet$$

It was then shown[70] that the reduction of hydroperoxides by triphenylphosphine did not involve a free radical chain, but had similar characteristics to reductions by organic sulfides. The sulfide reduction appears to require a greater degree of assistance in transferring the proton from one oxygen to the other, 42, whereas the lower sensitivity of the



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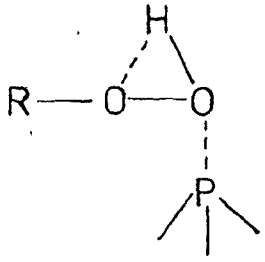


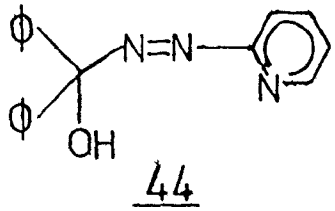
43

RO_2H-$(C_6H_5)_3P$ reaction need not to be interpreted as a concerted proton shift, as in 43; more likely it reflects a transition state where there is little weakening of the O-H bond. This conclusion was supported by the low activation energy and the insensitivity to solvent polarity.

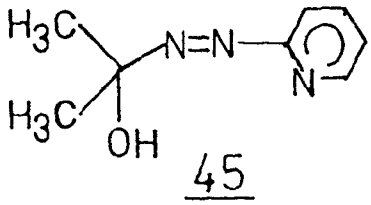
The present results support a non-radical mechanism for the reaction of hydroperoxides with $(C_6H_5)_3P$. A radical process would require that the radical $(CH_3)_2\overset{O\bullet}{C}N=N-\phi$ lives long enough to attack hydroperoxide at low concentrations of the latter. This is most unlikely, in view of the excellent leaving group properties of $\bullet N=NR$, coupled in this case with the driving force for formation of a carbonyl group.

Attempts to air oxidize other hydrazones, such as benzophenone phenylhydrazone and acetophenone phenylhydrazone, were not successful as air oxidation was very slow for these compounds.

Attempts to synthesize α-azocarbinols 44 and 45 were not successful by either scheme X or XI.



44

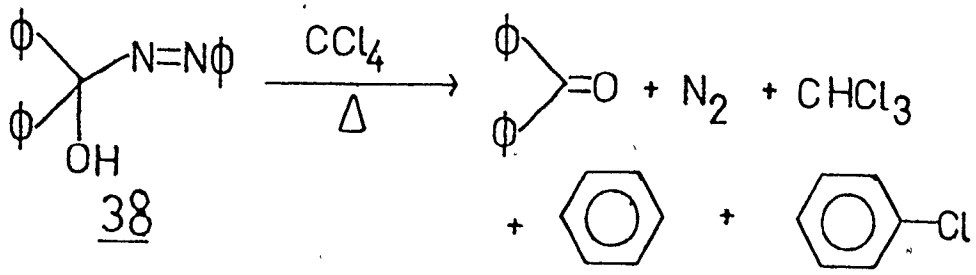


45

III: Chemistry of Phenylazodiphenylcarbinol

A: Thermal Decomposition in Carbon Tetrachloride

α-Phenylazodiphenylcarbinol (38), in refluxing carbon tetrachloride, decomposes to give benzophenone, chloroform, benzene and chlorobenzene as major products (equation [59]). Nitrogen evolution was al

[59] 

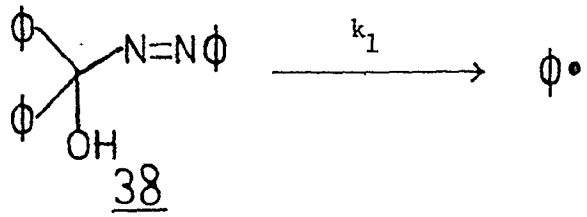
38

observed during decomposition of 38. Vacuum distillation of the reaction mixture afforded a clear distillate which, when subjected to gas chromatography analysis using several glpc columns and authentic samples permitted identification of benzene, chlorobenzene, and chloroform. These findings are in accordance with previous results[42] on the decompositon of 38 in carbon tetrachloride at room temperature, the only exception being that benzene was not detected in the latter case.

The kinetics of decomposition of 38 in carbon tetrachloride are gathered in Table VI, page 49. As proposed[13,42] a few years ago these results indicate that the decomposition of 38 is a radical chain process. Particularly relevant is the fact that 38 decomposes much more rapidly than either the corresponding methyl ether or the corresponding acetate. Moreover, it decomposes more slowly than 41, which is explicable in terms of a chain process but not in terms of unimolecular homolysis. The specific proposed mechanism of decomposition of 38 in carbon tetrachloride involves phenyl radicals as shown in scheme XII, page 48.

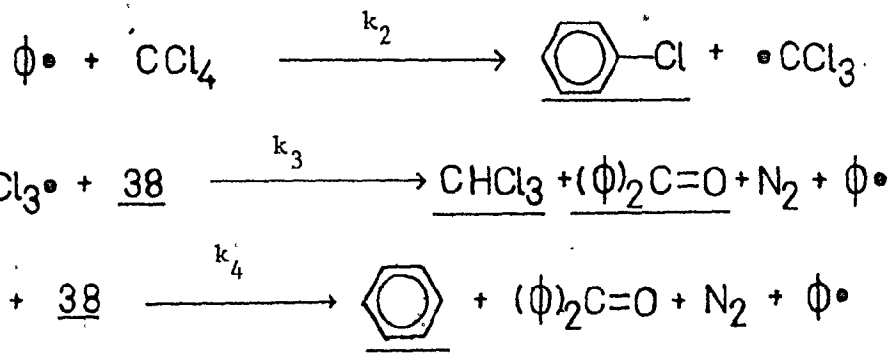
Scheme XII

Initiation:

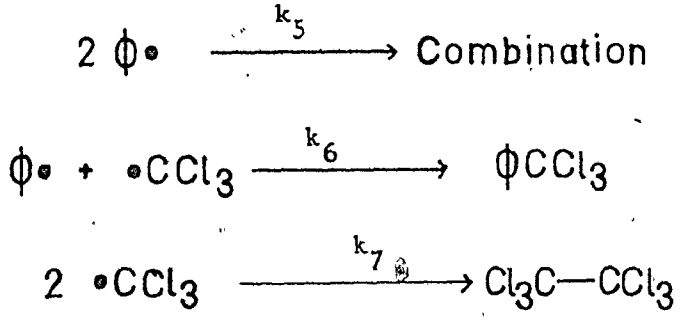


38

Propagation:



Termination:



(Compounds underlined indicate that they were detected).

Table VI: Rate Constants for Compounds Studied

Expt. No.	Compound	Reaction Conditions	Rate Constant (sec^{-1}) (least squares)	Correl Coeff.
1	$(C_6H_5)\underset{\underset{OH}{|}}{C}N=N(C_6H_5)$	CCl_4, degassed 80.0 +/- 0.1°c	2.47×10^{-4}	0.9950
2	$(C_6H_5)\underset{\underset{OCH_3}{|}}{C}N=N(C_6H_5)$	CCl_4, degassed 80.0 +/- 0.1°C	3.64×10^{-6}	0.9707
3	$(C_6H_5)\underset{\underset{OCOCH_3}{|}}{C}N=N(C_6H_5)$	CCl_4, degassed 80.0 +/- 0.1°C	1.17×10^{-6}	0.9987
4	$(CH_3)_2\underset{\underset{OH}{|}}{C}N=N(C_6H_5)$	CCl_4, degassed 35.0 +/- 0.1°C	7.76×10^{-4} 6.95×10^{-4}	0.9932 0.9879
5	$(CH_3)_2\underset{\underset{OCOCH_3}{|}}{C}N=N(C_6H_5)$	CCl_4, degassed 80.0 +/- 0.1°C	ca 3×10^{-8} *	-----

*1. Experiment No. 5: Only 12% decomposed after a period of 1,100 hours (approximately 45 days).

Table VI: continued

Expt. No.	Compund	Reaction Conditions	Rate Constant (s^{-1}) (least squares)	Correl Coeff.
6	$(CH_3)_2\underset{\underset{OH}{|}}{C}N=N(C_6H_5)$	neat Benzaldehyde (10M) degassed 35.0 +/- 0.1°C	k_{obs}= 2.74 X 10^{-4} ($k=2.74X10^{-5}M^{-1}s^{-1}$)	0.9830
7	$(CH_3)_2\underset{\underset{OH}{|}}{C}N=N(C_6H_5)$	Benzaldehyde (5M)/Benzene degassed 35.0 +/- 0.1°C	k_{obs}= 1.64 X 10^{-4} ($k=3.28X10^{-5}M^{-1}s^{-1}$)	0.9893
8	$(CH_3)_2\underset{\underset{OH}{|}}{C}N=N(C_6H_5)$	Benzaldehyde (2M)/Benzene degassed 35.0 +/- 0.1°C	k_{obs}= 6.00 X 10^{-5} ($k=3.00X10^{-5}M^{-1}s^{-1}$)	0.9860
9	$(CH_3)_2\underset{\underset{OH}{|}}{C}N=N(C_6H_5)$	$(C_6H_5)SH$ ($1.0X10^{-3}$M)/CCl_4 degassed 35.0 +/- 0.1°C	k_{obs}= 3.21 X 10^{-3} ($k=3.21\ M^{-1}s^{-1}$)	0.9972
10	$(CH_3)_2\underset{\underset{OH}{|}}{C}N=N(C_6H_5)$	$(C_6H_5)SH$ ($5.0X10^{-4}$M)/CCl_4 degassed 35.0 +/- 0.1°C	k_{obs}= 1.64 X 10^{-3} ($k = 3.28\ M^{-1}s^{-1}$)	0.9891

2. Experiments 6, 7, and 8: Molar Ratios 20:1 = $(C_6H_5)CHO$:Azocarbinol.

Table VI: continued

Expt. No.	Compound	Reaction Conditions	Rate Constant (s^{-1}) (least squares)	Correl Coeff.
11	$(CH_3)_2\underset{\underset{OH}{|}}{C}N{=}N(C_6H_5)$	$(C_6H_5)_3C^{\bullet}$ (1.55×10^{-2}M)/Benzene** degassed, 35.0+/-0.1°C (1:3 = Radical:Azo)	$k_{obs} = 3.66 \times 10^{-5}$ ($k=4.41\times10^{-3}M^{-1}s^{-1}$)	0.9912
12	$(CH_3)_2\underset{\underset{OH}{|}}{C}N{=}N(C_6H_5)$	Benzene, control experiment	3.80×10^{-6}	0.9810
		degassed, 35.0+/-0.1°C	4.12×10^{-6}	0.9935
13	$(CH_3)_2\underset{\underset{OH}{|}}{C}N{=}N(C_6H_5)$	2,2,6,6-tetramethylpiperidine (36) (0.12M)/Benzene degassed, 35.0+/-0.1°C (10:1 = Radical :Azo)	$k_{obs} = 1.01 \times 10^{-6}$ $k_{obs} = 9.31 \times 10^{-7}$ ($k_{ave}=8.1\times10^{-6}M^{-1}s^{-1}$)	0.9897 0.9913
14	$(CH_3)_2\underset{\underset{OH}{|}}{C}N{=}N(C_6H_5)$	2,2-diphenyl-1-picryl-hydrazyl (37) (0.15M)/Benzene degassed, 35.0+/-0.1°C (10:1 = Radical:Azo)	$k_{obs} = 8.08 \times 10^{-6}$ $k_{obs} = 8.71 \times 10^{-6}$ ($k_{ave}=5.6\times10^{-5}M^{-1}s^{-1}$)	0.9952 0.9792

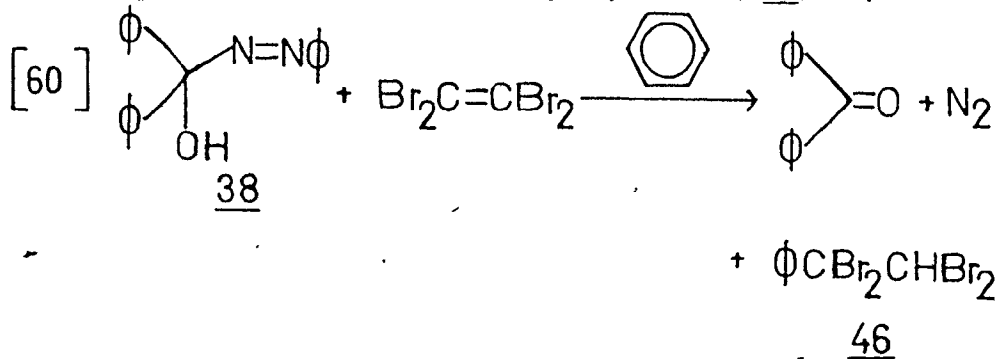
3. ** Expt. No. 11: The concentration of trityl radical was kept essentially constant by having present a large excess of the dimer, with which it is in equilibrium (see experimental).

B: Product Composition from the Thermolysis of 38 in Carbon Tetrachloride

Product composition from the thermolysis of 38 in carbon tetrachloride was studied as a function of initial concentration of the α-azocarbinol (38). For each initial concentration of 38 a product analysis was done using gas chromatography techniques. Of interest were the relative yields of benzene, chloroform, and chlorobenzene produced (equation [59]). The results (Table VII, page 53) are as follows. First, the chlorobenzene to chloroform ratio is close to unity as expected. This is a result of phenyl radicals (produced from 38) abstracting chlorine atoms from carbon tetrachloride with the resulting trichloromethyl radical, a good chain transfer agent, attacking the hydroxyl hydrogen of 38 to give chloroform (scheme XII). Secondly, the amount of chlorobenzene, relative to that of benzene, increases as the concentration of 38 decreases. These results are in agreement with the radical chain mechanism depicted in scheme XII (page 48).

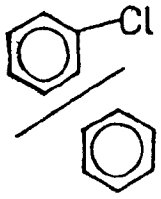
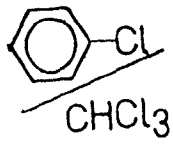
C: Trapping with Tetrabromoethylene

Decomposition of phenylazodiphenylcarbinol, 38, in a solution of tetrabromoethylene in benzene gave, besides benzophenone and nitrogen, the addition product 1,1,2,2-tetrabromophenylethane, 46, (equation [60]).



Benzophenone was identified as a reaction product (^{1}H N.M.R., I.R., m.p., and M.S.: m/e = 182). The addition product, 46, was obtained in low yield

Table VII: Composition of the Products from the Thermolysis of 38 in Carbon Tetrachloride

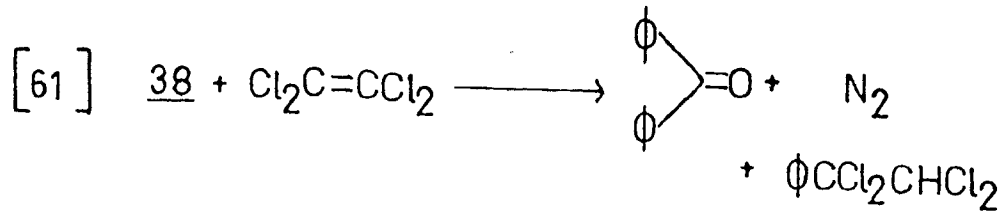
I_o (M)	 *	 *
0.6	1.39	0.96
0.35	2.9	0.98
0.26	3.8	1.1
0.17	5.7	0.7
0.09	11	1.5
0.04	24	0.5
0.01	large**	0.8

* These ratios have been corrected for the gas chromatograph response. The most reliable ones are those in which the absolute amounts were highest, ie. the ones for large I_o values.

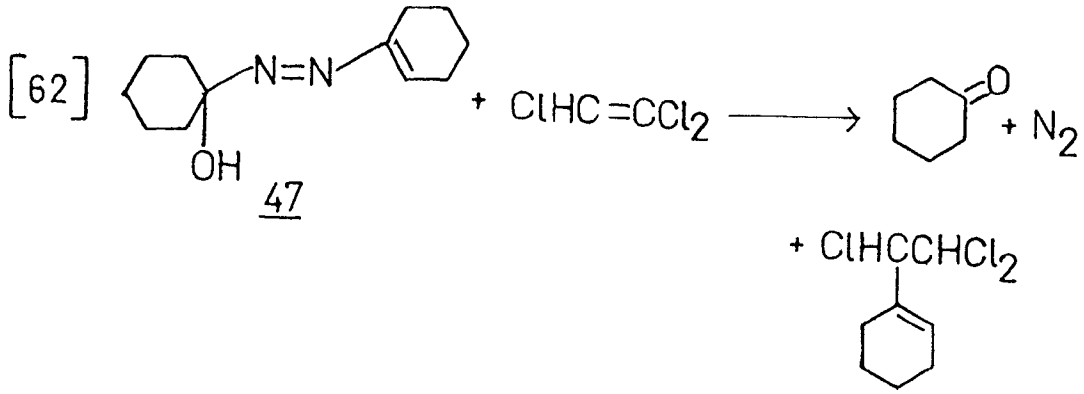
** Benzene not detected.

(1.5%). Compound 46, however, has been prepared in high yield by bromination of phenylacetylene[76].

Equation [60] further illustrates the use of azocarbinols for radical chain hydrophenylation of olefinic substrates, although the yield is only 1.5%. Other examples of this have been reported in our laboratory[77]. Equation [61] serves as an example. Hydro-1-alkenylation of olefinic sub-

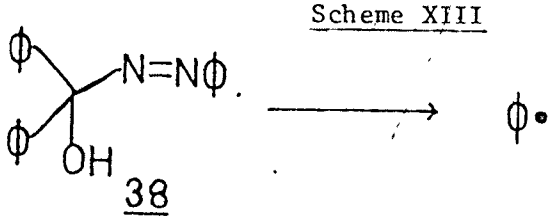
[61] 

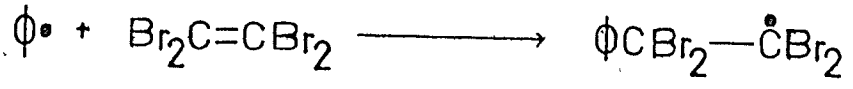
strates was also reported in the same study (equation [62]). The radical

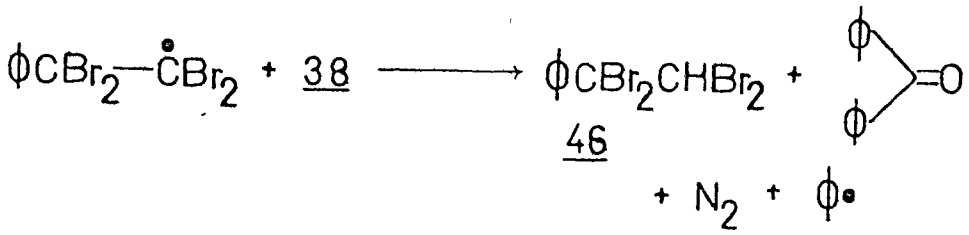
[62] 

chain hydrophenylation mechanism involving the chain transfer ability of 38 is depicted in scheme XIII. The low yield is probably the result of

Scheme XIII







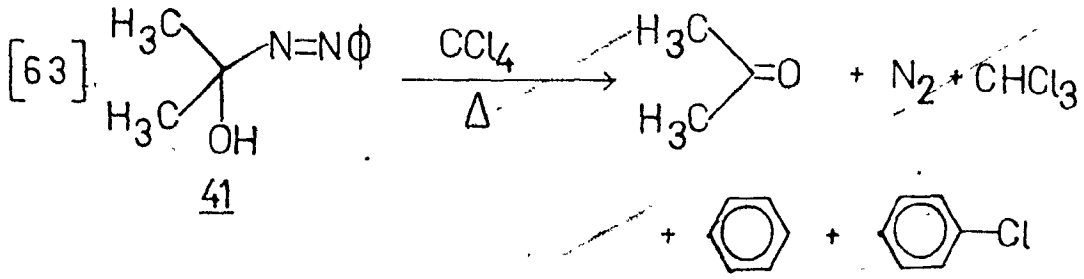
bromine atom loss from the first-formed adduct, to form $\phi C(Br)=CBr_2$. The hydro-1-alkenylation mechanism using 41 as the azocarbinol is analogous.

These additions (equations [61] and [62]) and others reported from our laboratory[13,42] demonstrate the utility of these azocarbinol compounds. Since simple alcohols are poor donors of hydroxyl hydrogen to radicals, it is probable that alkoxy radical intermediates are avoided in the reaction mechanism of azocarbinols. In such a mechanism hydrogen abstraction is concerted with C-N bond scission.

IV: Chemistry of Phenylazodimethylcarbinol

A: Thermal Decomposition in Carbon Tetrachloride

α-Phenylazodimethylcarbinol, 41, decomposes in the presence of carbon tetrachloride (35.0+/-0.1°C) giving acetone, benzene, chloroform, and chlorobenzene as reaction products. The thermolysis of 41 (equation [63]) is similar to that of 38; the difference being the carbonyl



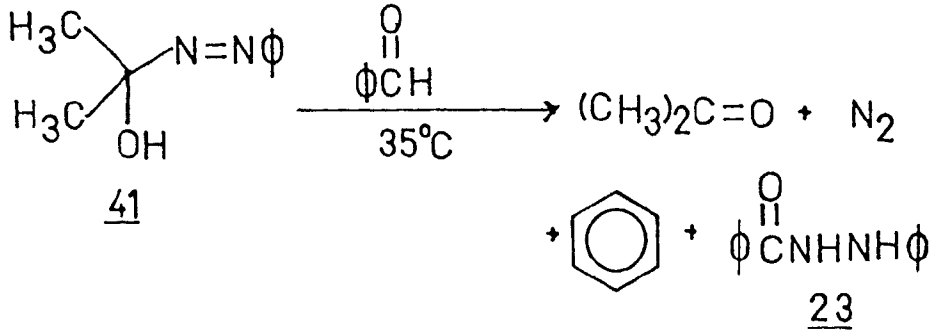
41

compound produced.

The molecular formula of 41 affords a convenient way of following the kinetics of its decomposition. The disappearance of the gem-dimethyl peak (δ 1.43 ppm) and the appearance of the acetone peak, (δ 2.1 ppm) can be easily normalized against an internal standard (usually dimethyl carbonate; (δ 3.73 ppm) during a kinetic run. The decomposition of 41 in carbon tetrachloride (35.0+/-0.1°C) obeys first order kinetics, $k=7.36 \times 10^{-4}$ sec^{-1} (mean of two runs).

B: Thermal Decomposition in Benzaldehyde

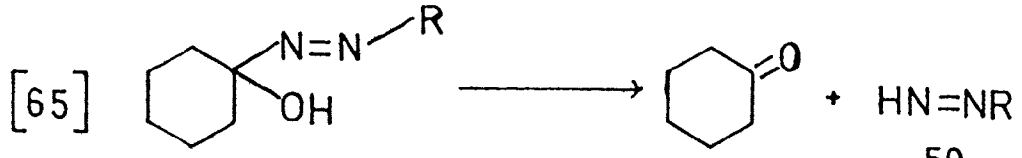
In the presence of benzaldehyde (degassed conditions) 41 decomposes at 35.0+/-0.1°C according to equation [64]. The reaction

[64] 

41

mixture contained a solid which was characterized as benzoic acid-2-phenylhydrazide (23) (M.P. 165-166°C, M.S.: m/e=212). Acetone and benzene were characterized as the other two products by comparing their retention times with those of authentic samples by the use of a gas chromatograph and several glpc columns.

The products of this experiment agree with the results found by Schulz[44] and coworkers. They did similar experiments (equation [37]) (see introduction, pages 23-25) with other azocarbinols (21 and 22) that led them to the conclusion that diazenes (50) were intermediates in the decomposition of 21 and 22 (equation [65]). In light that 50

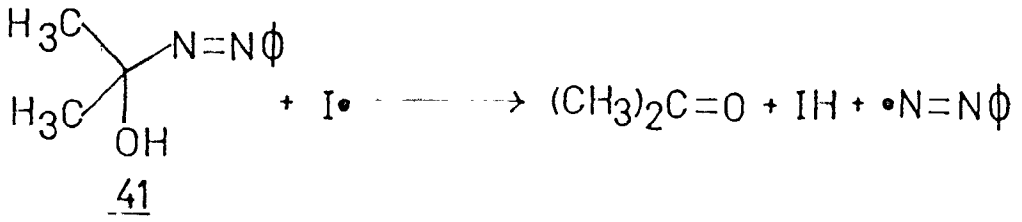
[65] 

21: R = Phenyl

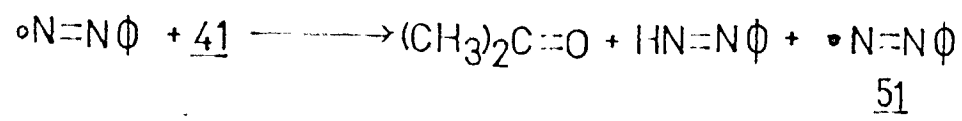
22: R = tert-Butyl

could be intermediates in the decomposition of α-azocarbinols one has to envisage a new radical chain mechanism (Scheme XIV) yielding phenyl

Scheme XIV

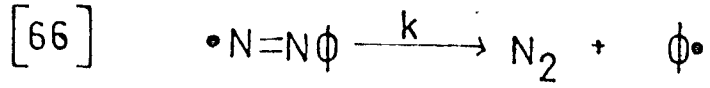


41



51

diazenyl radicals (51) which propagate the chain. Moreover, 51 could give phenyl radicals (equation [66]) which are required to account for the benzene produced.



Scheme XIV, however, is not a reasonable scheme, given that $k=10^8$ sec^{-1} for equation [66][78]. To compete with this reaction, the reaction of $\bullet N{=}N(C_6H_5)$ with 41 (second step of scheme XIV) would have to be very fast indeed.

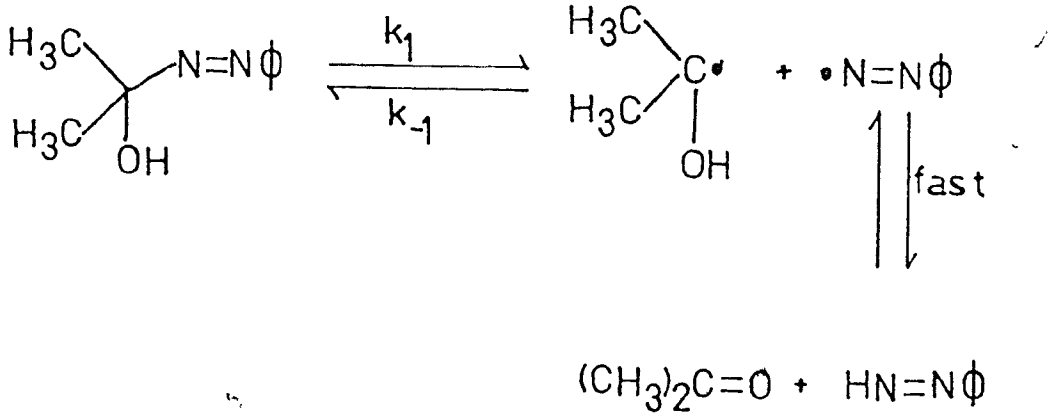
C: Kinetics of Decomposition of 41 in Benzaldehyde

Kinetic studies of 41 in benzaldehyde ([ϕCHO]=10M or neat, 5M, and 2M) were done in order to establish the rate dependance on [ϕCHO]. Results appear on Table VI (page 50). It was found that as the concentration of benzaldehyde (in benzene) doubles, the rate of decomposition also doubles, hence the rate dependance is first order in benzaldehyde. From this result one could exclude the possibility that benzal-

dehyde reacts with phenyldiazene generated from the decomposition of 41 (Scheme XIV, page 57).

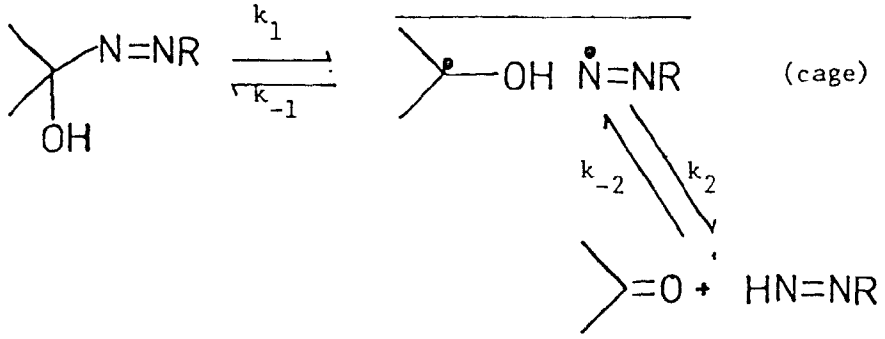
Most important is the fact that the rate of decomposition of 41 in the presence of benzaldehyde does not show a levelling effect; ie. in neat benzaldehyde (10M) the rate is still changing. This implies that phenyldiazene does not add reversibly to acetone, if phenyldiazene is at all formed (Scheme XV). The present results indicate that Scheme

Scheme XV



XV is not very likely and that benzaldehyde reacts directly with undissociated azocarbinol (41). Furthermore, $(C_6H_5)N{=}N\bullet$ decomposes to phenyl radicals[78] and molecular nitrogen (equation [66]) with a rate constant of the order of $10^8 sec^{-1}$. With such a large rate constant $(C_6H_5)N{=}N\bullet$ would probably not survive long enough to find azocarbinol (41) in scheme XIV. This is further supported by the fact that the yield of $(C_6H_5)CONHNH(C_6H_5)$ (23) from the decomposition of 41 in benzaldehyde (equation [64]), was 77% indicating relatively little loss of N_2.

Mechanism B (page 35) could be further subdivided into categories in which the N=N-R bond is retained.

1. 

$$HN{=}NR + \phi CHO \xrightarrow{k_3} \text{Product}$$

$$\frac{-d}{dt}[Azo] = k_1[Azo] - k_{-1}[cage] \qquad (i)$$

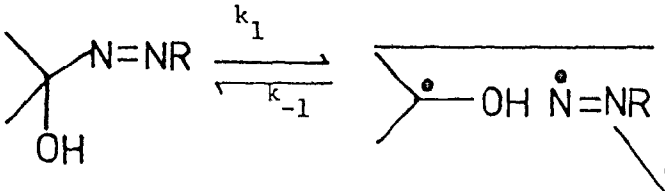
Since [cage] is a radical pair, which must be short-lived because radical reactions are fast, one can use the steady-state approximation. Also $k_{-2} \cong 0$[51]. Therefore

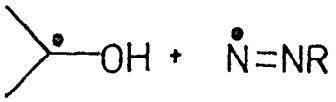
$$\frac{d}{dt}[cage] = 0 = k_1[Azo] - k_{-1}[cage] - k_{-2}[cage]$$

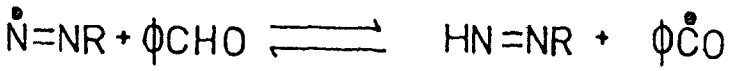
therefore $[cage] = k_1[Azo]/k_{-1} + k_2$ which when substituted into (i) gives;

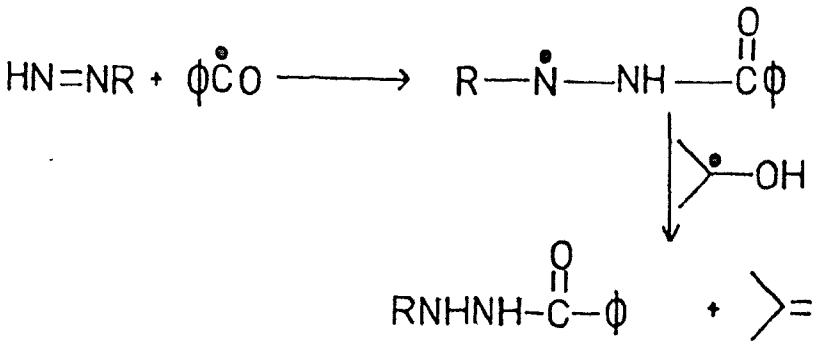
$$\frac{-d}{dt}[Azo] = k_1[azo] - k_{-1}\left(\frac{k_1[Azo]}{k_{-1}+k_2}\right) = k_1[Azo]\left(1 - \frac{k_{-1}}{k_{-1} + k_2}\right)$$

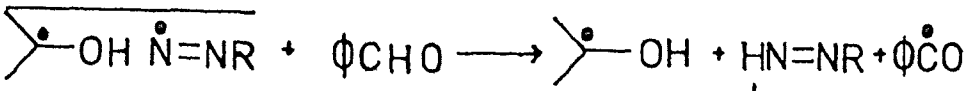
This is clearly not first order in benzaldehyde.

2. 
N=NR
k1
k-1
OH
OH N=NR
diffusion


OH + N=NR

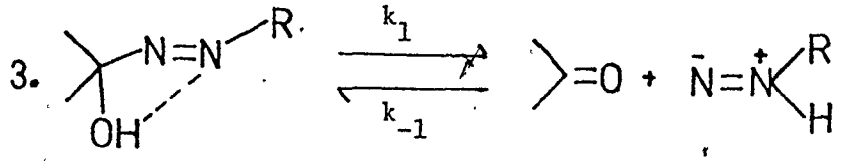

N=NR + ϕCHO
HN=NR + ϕCO

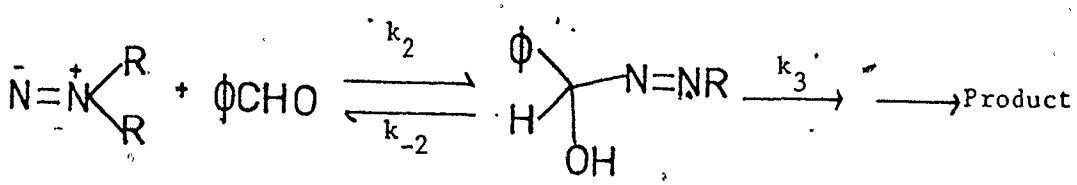

HN=NR + ϕCO
R—N—NH—Cϕ
O
OH
RNHNH–C–ϕ
O
=O

and 
OH N=NR + ϕCHO
OH + HN=NR + ϕCO
as above


=O + RNHNHCOϕ

If this were the mechanism, then benzaldehyde would have to be scavenging from the cage to get first order dependance on benzaldehyde. That is simply unreasonable, for the reaction would have to compete with diffusion and with cage disproportionation, both of which must be very fast.





$$\frac{-d}{dt}[Azo] = k_1[azo] - k_{-1}[\rangle=O][\bar{N}=\overset{+}{N}-HR] \qquad (ii)$$

$$\frac{d}{dt}[\bar{N}=\overset{+}{N}-HR] = 0 = k_1[Azo] - k_{-1}[\rangle=O][\bar{N}=\overset{+}{N}-HR] - k_2[\phi CHO][\bar{N}=\overset{+}{N}-HR] + k_{-2}[Azo']$$

$$[\bar{N}=\overset{+}{N}-HR] = \frac{k_1[Azo] + k_{-2}[Azo']}{k_{-1}[\rangle=O] + k_2[\phi CHO]}$$

which when substituted into (ii) gives;

$$\frac{-d}{dt}[Azo] = k_1[Azo] - k_{-1}[\rangle=O]\ \frac{k_1[Azo] - k_{-2}[Azo']}{k_{-1}[\rangle=O] + k_2[\phi CHO]}$$

If $k_{-2}[Azo']$ is zero or small

$$\frac{-d}{dt}[Azo] \cong k_1[Azo]\left(1 - \frac{k_{-1}[\rangle=O]}{k_{-1}[\rangle=O] + k_2[\phi CHO]}\right)$$

$$\cong k_1[Azo]\left(\frac{k_2[\phi CHO]}{k_{-1}[\rangle=O] + k_2[\phi CHO]}\right)$$

This mechanism could fit, for this reduces to

$$\frac{-d}{dt}[Azo] = k_1[Azo]\left(\frac{k_2[\phi CHO]}{k_{-1}[\rangle C{=}O]}\right) \qquad \text{if } k_{-1}[\rangle C{=}O] \gg k_2[\phi CHO]$$

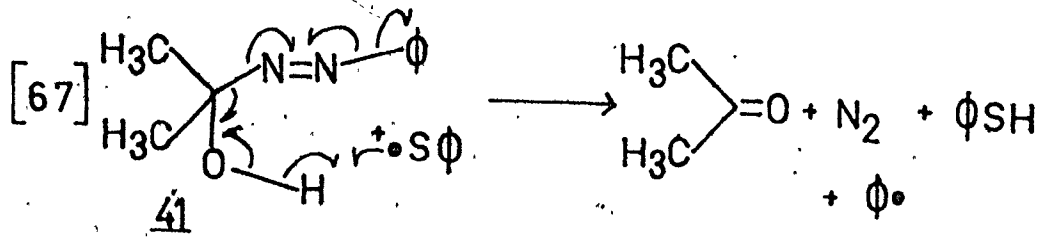
However, the requirement that $k_{-1}[\rangle C{=}O] \gg k_2[\phi CHO]$ can not be met at high [ϕCHO], since k_2 is probably greater than k_{-1} (aldehydes more reactive than ketones). Thus, the first order dependance might be expected only at low [ϕCHO] but not in neat [ϕCHO].

In view of the results that the decomposition of 41 is first order in benzaldehyde concentration, we would have to speculate that a different mechanism is involved in the formation of 23; a mechanism different than that involving phenyldiazene as an intermediate,

D:Kinetics of Thermolysis of 41 in Carbon Tetrachloride in the Presence of Thiophenol

Azocarbinol 41 decomposes in carbon tetrachloride with a 4-fold rate enhancement when thiophenol (1.0×10^{-3}M) was present as opposed to the case when 41 decomposes in carbon tetrachloride alone. This rate enhancement was also observed by Yeung[42], (although more pronounced) when he attempted to inhibit chain reactions of azocarbinol 2 in carbon tetrachloride by adding phenol. In fact, phenol (0.02M) was found to be an effective accelerator of decomposition of 2 in carbon tetrachloride.

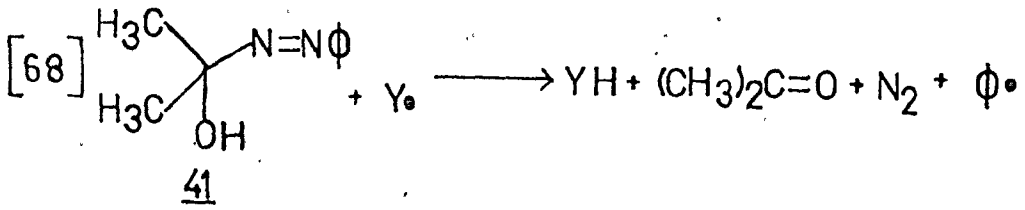
These findings support a mechanism in which thiophenyl radicals directly attack the azocarbinol 41 possibly by a fully concerted mechanism as in equation [67] with a partly concerted mechanism (through



$(C_6H_5)N{=}N\bullet$) as an alternative. Thus in this case thiophenyl radical acts as a chain carrier by abstracting the hydroxyl hydrogen of 41. Phenyl radical then abstracts hydrogen from thiophenol regenerating the chain carrying radical. There was no chloroform and no chlorobenzene detected from decomposition runs of 41 with thiophenol present, indicating that essentially all phenyl radicals were trapped by thiophenol rather than by carbon tetrachloride.

E: Decomposition in the Presence of Triphenylmethyl Radical

The decomposition of 41 was studied in the presence of a stable free radical; triphenylmethyl. The aim of this study was to set up a model for the chain-carrying hydrogen abstraction step in the decomposition of α-azocarbinols as depicted in equation [68]. If Y•, a stable



41

free radical, causes decomposition of the azocarbinol at a temperature where the azocarbinol is relatively stable, then one can surely conclude that decomposition is induced by other radicals also.

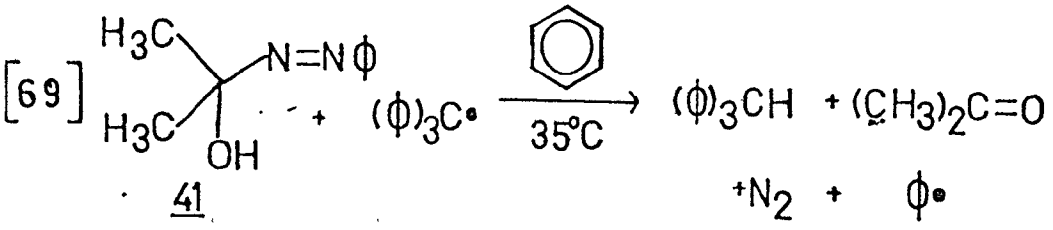
In this study trityl radical (dimer included) was in excess of 41 by approximately fourteen fold, making the trityl radical concentration effectively constant throughout the reaction (ie. bimolecular between 41 and trityl radical). The $K_{eq}^{35°}$ for dimer $\rightleftharpoons$ 2trityl was estimated from Lewis[89] to be $7.5X10^{-4}$ mole/L. The trityl radical concentration was therefore about $1.55X10^{-2}M$ which, in turn, is used to calculate the second order rate constant, $2.6X10^{-3}$ $M^{-1}s^{-1}$, for the attack on 41 by trityl radical.

The rate of decomposition of 41 (0.05M, initial) in benzene at

35.0°C was found to be more than eight times greater in the presence of trityl radical (8.3×10^{-3}M) than in its absence. In both cases decomposition of 41 was first order in 41 to about 90% completion. The observed eight fold increase is a large factor and surely indicates that trityl radical induces the decomposition of the azocarbinol 41 in degassed benzene solution.

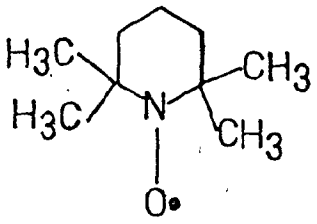
Identification of the products from decomposition of 41 in the presence of trityl radical indicated acetone and triphenylmethane as major products. Two other minor products were not identified.

These results are important because they mean that the mechanism proposed by Schulz is not general, if it applies at all. From the present study we can conclude that trityl radical abstracts the hydroxyl hydrogen of 41, at a temperature where the azocarbinol alone is relatively stable. The decomposition of 41 in the presence of trityl radical obeys pseudo-first-order kinetics with trityl in large excess and produces acetone and triphenylmethane as major products (equation [69]).

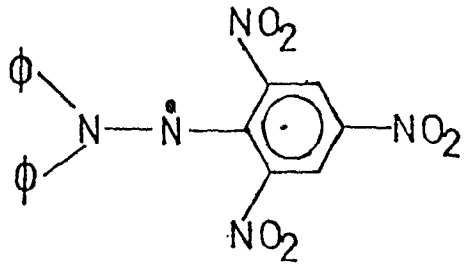


F: Decomposition in the Presence of Other Stable Free Radicals

Other stable free radicals were used in an attempt to show the induced decomposition of 41. These are, 2,2,6,6-tetramethylpiperidinoxy (36) and 2,2-diphenyl-1-picrylhydrazyl (37) (see introduction pages 33-34).



36



37

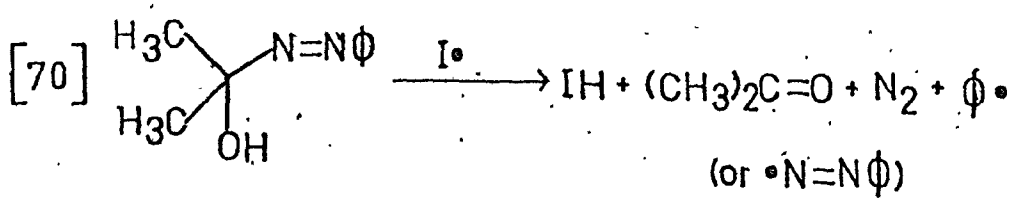
The results are of interest because 36 is actually rate retarding whereas 37 enhances the rate of decomposition by twofold (see Table VIII).

Table VIII

Compound	Reaction Conditions	k (sec^{-1})	Relative Rate
$(CH_3)_2CN{=}N\phi$ OH 41	Control experiment Benzene, degassed 35.0 +/- 0.1°C	3.96×10^{-6}*	1
41	36 (0.12M)/ Benzene degassed 35.0 +/- 0.1°C	$k_{obs.}$ = 9.71×10^{-7}*	0.24
41	37 (0.15M)/ Benzene degassed 35.0 +/- 0.1°C	$k_{obs.}$ = 8.40×10^{-6}*	2.04

(* These numbers are averages of the duplicate kinetic runs which appear on Table VI, page 51)

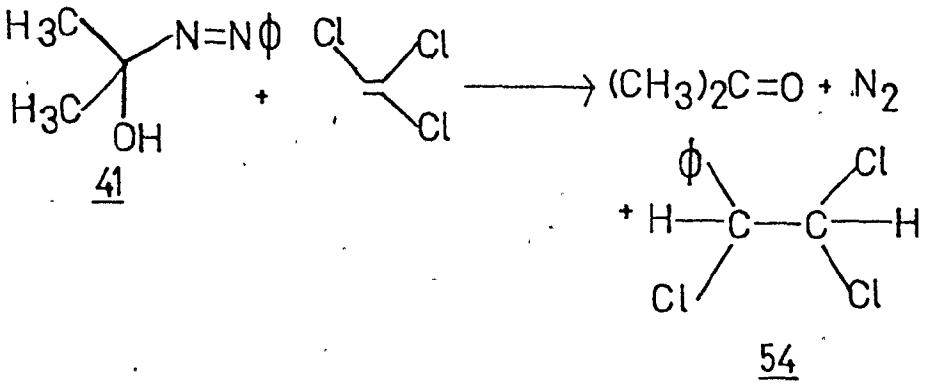
The key step in the mechanism of α-azocarbinols decomposition is radical abstraction of hydroxyl hydrogen from the hydroxydiazene in concert with C-N bond cleavage[88]. This avoids formation of an alkoxy radical intermediate (equation [70]) and provides enough lowering of the free energy



from coproducts of [70] to allow even stabilized radicals to act as chain carriers. This has been found to be true in the case where the free radicals (I•) were phenoxy, thiophenoxy, trityl, and 2,2-diphenyl-1-picrylhydrazyl (37). Such an explanation, however, does not hold true for 2,2,6,6-tetramethylpiperidinoxy (36), which is in effect rate retarding. The free radical 36 could be "mopping up" the phenyl radicals produced from decomposition of 41 rather than it (36) directly attacking 41 by hydroxyl hydrogen abstraction, thus slowing down the rate of decomposition.

G: Trapping with Trichloroethylene

The decomposition of 41, in benzene or in carbon tetrachloride solutions is induced by radicals through abstraction of hydroxyl hydrogen in concert with scission of at least one C-N bond (for example equation [69]). This mode of decomposition is analogous to that of azocarbinol 38 investigated in this research, and to others (1 and 17) reported from this laboratory by Warkentin[11,12,13] and coworkers. Thus, 41 decomposes in the presence of trichloroethylene (equation [71]) to give acetone and

[71] 

41 54

the addition product (54), 1,1,2-trichloro-2-phenylethane. The known[79] compound 54 was characterized in the crude state by ^{1}H N.M.R. spectroscopy; comparing the chemical shifts to those of the same compound prepared in this laboratory[77] by hydrophenylation of trichloroethylene with the α-azo-

carbinol 38. Acetone was characterized by adding a minute amount of an authentic sample to the nmr tube containing the reaction mixture and observing increase of the suspected acetone peak at δ 2.12. The yield of the addition product (54) was estimated to be of the order of 40%.

V: Conclusion

α-Phenylazodiphenylcarbinol (38) was synthesized by mild deacetylation (with methyllithium) of the corresponding azoacetate (39). The thermal decomposition of 38 in carbon tetrachloride was studied with a detailed analysis of the product composition and kinetic measurements. A new acyclic azocarbinol, α-phenylazodimethylcarbinol (41), was synthesized via air oxidation of acetone phenylhydrazone to the hydroperoxide (40) which is itself reduced to 41 by the action of triphenylphosphine.

Evidence from this research points toward a radical chain, induced decomposition by attack at the hydroxyl hydrogen of 41, in a process where phenyl radicals or phenyldiazenyl radicals are generated. This evidence was provided from kinetic measurements of the thermal decomposition of 41 and of several azoacetates and azoethers, as well as from decomposition of 41 in the presence of several substrates (benzaldehyde and thiophenol) and of stable free radicals. Some of the latter have been shown to induce decomposition of 41 at a temperature where the azocarbinol is relatively stable. Evidence disfavouring other possible competing mechanisms was also found.

The synthetic utility of 38 and 41 was also investigated briefly. This potential synthetic utility of these azocarbinols was illustrated through their hydrophenylation of several olefinic compound.

EXPERIMENTAL

I: General

Proton magnetic resonance spectra were obtained with Varian T-60 or Varian EM-390 instruments using carbon tetrachloride as the solvent and tetramethyl silane (TMS) as internal reference (unless otherwise indicated). The resonances are reported in δ values (P.P.M), followed in brackets by the multiplicity symbol (s=singlet, d=doublet, t=triplet, q=quartet, and m=multiplet) and the relative number of protons. ^{13}C nmr (or ^{13}C N.M.R.) spectra were taken on a Bruker WH-90 or a Bruker WP-80 instrument using $CDCl_3$ as the solvent and TMS as internal reference.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. The spectra were taken in CCl_4 solutions (unless otherwise indicated) in 0.5mm KBr cells. The data are presented in reciprocal centimeters.

Mass spectral molecular weights were obtained from a high resolution Consolidated Electrodynamics Corporation (C.E.C.) 21-110 instrument.

Gas chromatography analysis were done on a Varian Aerograph A90-P3 or on a Varian Model 3700 Gas Chromatograph.

Electron spin resonance spectra were obtained using a JES-3BS-X esr instrument, using Mn^{++} as marker.

Melting points were determined on a Thomas Hoover Capillary Melting Point apparatus.

Starting materials were commercially available, and were used without purification unless otherwise specified.

The spectral properties of the compounds prepared are assembled in Table V (pages 43 and 44) . The rate constants of the compounds studied appear in Table VI (pages 49-51). The kinetic rates were calculated using peak heights or integral areas obtained from ^{1}H N.M.R. spectra (unless otherwise indicated) of the reaction mixture under investigation. Appendix I contains the structural formulae with their assigned numbers and may be used as a quick reference.

II: A: Preparation of Lead Tetraacetate (LTA)

The method used was similar to that of Fieser[81]. A mixture of acetic acid (1200 ml) and acetic anhydride (800 ml), in a three litre, three necked, round-bottomed flask, was heated to 55°C and stirred vigorously with a mechanical stirrer. Lead tetraoxide (red lead oxide) (1400g) was added in portions of 15-20g over a period of five hours. A fresh addition was made only after the colour due to the preceding portion had largely disappeared. The temperature was kept between 55°C and 60°C at all times. The thick slurry precipitate was collected by filtration, washed with cold acetic acid, and recrystallized from hot acetic acid to give white crystals (700g, 80% yield). These were kept in a closed container in a dry box.

B: Preparation of Benzophenone Phenylhydrazone

Benzophenone, 54.6g (0.30 mole) was dissolved in methanol (100 ml), to which solution 30 ml of glacial acetic acid was added. To the resulting solution was added phenylhydrazine (29.4 ml, 0.30 mole). The mixture was refluxed under nitrogen for several hours. Colourless crystals, which appeared on cooling to ice temperature, were collected by suction filtration and recrystallized from hot methanol; m.p. 137-138°C (literature[82] 137-139°C). The yield was 67.8g (83%).

III: A: Preparation of Phenylazodiphenylmethylacetate (39)

The procedure was similar to that of Iffland[73]. A solution of benzophenone phenylhydrazone (27.2g, 0.10 mole), dissolved in methylene chloride (100 ml), was added, in the course of fifteen minutes, to a stirred solution, at 0°C to -10°C (dry-ice-acetone bath) under nitrogen, of lead tetraacetate (44.3g, 0.1 mole) dissolved in methylene chloride (200 ml). The resulting solution was warmed up to room temperature and stirred for twenty more minutes. To the stirring solution was added cold water (200 ml) and the brown sludge formed was removed by filtering the entire mixture through a bed of Celite. The methylene chloride layer was separated and washed successively with water and with dilute sodium bicarbonate solution (5%) until free of acetic acid. After drying over anhydrous Na_2SO_4, the solvent was removed under vacuum with a rotary evaporator. The pale yellow solid which remained was recrystallized from methanol to give 26g (80%) of pure product.

B: Kinetics of Decomposition of 39 in Carbon Tetrachloride

A solution of phenylazodiphenylmethylacetate (39) (0.2M) in carbon tetrachloride, with dimethyl carbonate as the internal standard, was prepared and kept at ice temperature. An aliquot of this solution was placed in an nmr tube connected to a ground-glass joint, which was put through 3 or 4 freeze-pump-thaw cycles (vacuum line pressure: $5X10^{-3}$ mm Hg) before sealing. The tube was heated in a constant temperature oil bath (80.0+/-0.1°C). N.M.R. spectra were recorded at selected time intervals throughout the course of the reaction, starting with time zero. The reaction was stopped by cooling the tube quickly in liquid nitrogen and the time outside the bath was not counted. Peak heights of N.M.R. signals (methyl acetate peak of 39 at δ 2.18 ppm) were normalized with reference to that

of the internal standard. Standard first order treatment of the data gave straight, least-squares fits to the equation $\ln \frac{a}{a-x} = kt + c$.

IV: Chemistry of Phenylazodiphenylcarbinol (38)

A: Preparation[12]

Phenylazodiphenylmethylacetate (39) (3. , 0.01 mole) was dissolved in dry ether (25 ml) and the solution was cooled to -10°C in a dry-ice-acetone bath. Methyllithium (5 ml, 2M reagent in ether) was added, under nitrogen, dropwise from a syringe within 10 minutes. The solution was stirred for fifteen minutes more and ice-cold, saturated NH_4Cl solution (20 ml) was added slowly. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined ethereal solution was dried over Na_2SO_4 and concentrated (no heating) under reduced pressure with a rotary evaporator. The pale yellow residue which remained was recrystallized from n-pentane. The yield was of the order of 70%.

B: Thermolysis in Carbon Tetrachloride

Phenylazodiphenylcarbinol (38) (576mg, 0.002 mole) was dissolved in carbon tetrachloride (5 ml) and the solution was refluxed for The major products from the decomposition were benzophenone, chloroform, benzene, and chlorobenzene. Vacuum distillation (aspirator pressure, 70°C) gave a clear distillate which afforded the identification of the last three products mentioned above by comparing their retention times on several glpc columns with those of authentic samples. The residue has been previously derivatized[43] to give a 2,4-di-nitro-phenylhydrazone, m.p. 238°C (literature[83] m.p. 238°C), thus confirming the presence of benzophenone.

C: Kinetics of Decomposition in Carbon Tetrachloride

The reaction was followed by monitoring the growth of the carbonyl

stretch of benzophenone in the infrared spectrum (1665 cm^{-1}) at selected time intervals. A calibration curve was worked out for the carbonyl stretching band as a function of concentration of benzophenone in carbon tetrachloride.

A solution of 38 (0.002M) in CCl_4 was prepared and kept cold. Four samples of this solution were placed in different tubes equipped with joints to attach to the vacuum line. Each tube was sealed and then heated at 80.0 +/- 0.1°C for a prescribed period of time. When taken out of the bath each sample was quickly cooled in liquid nitrogen. The tube was then broken and the I.R. spectrum of the mixture was recorded. Standard first-order treatment of the data gave good fits to the first order rate equation with least squares correlation coefficients better than 0.990.

D: Composition of the Products from Thermolysis of 38 in Carbon Tetrachloride

Solutions of 38 in CCl_4 (0.6M, 0.35M, 0.26M, 0.17M, 0.09M, 0.04M, and 0.01M) were placed in small tubes, each of which was degassed, at the vacuum pump, and sealed. The tubes were placed in a constant temperature oil bath (80.0+/-0.1°C) and heated for several hours. Each mixture was then analyzed for product composition using a 10 foot FFAP (10%) column, on a Varian Model 3700 Gas Chromatograph. The data from each individual injection were obtained from a Varian CDS111 recorder (connected to the Gas Chromatograph) which gives the peak time, area, and per-cent area. Each sample was injected approximately six or seven times to minimize statistical errors and an average of the results was taken. The product composition in CCl_4 was studied as a function of initial concentration of 38 (I_o). The results (Table VII, page 53) have been corrected for the G.C. response to known concentrations of products (benzene, chloroform, and

chlorobenzene).

E: Trapping with Tetrabromoethylene

Tetrabromoethylene (5g, 0.015 mole) was added to a solution of 38 (576mg, 0.002 mole) in benzene (4.0 ml). The mixture was stirred (or shaken) until it became homogeneous after which it was heated at 100°C for one hour. Vigorous gas evolution was observed. The reaction mixture was chromatographed on silica gel (60-120 mesh) using petroleum ether as the eluant. The excess tetrabromoethylene was identified as the first eluant (m.p. 55-56°C, literature 56.4°C; M.S. was identical to that of an authentic sample). Benzophenone was also identified as a reaction product (N.M.R., I.R., M.S. m/e=182). The addition product, 1,1,2,2-tetrabromophenylethane, was obtained as a colourless oil (12.8mg, 1.5% yield). The yield was calculated by N.M.R. using cyclohexanone as the internal standard. The same addition product can be obtained in high yield by bromination of phenylacetylene[80].

V: A: Preparation of Acetone Phenylhydrazone

Acetone (22.0ml, 0.3 mole), methanol (100ml), glacial acetic acid (5.0ml), and phenylhydrazine (29.4ml, 0.3 mole) were placed in a round-bottomed flask and the solution was refluxed overnight (approximately 12 hours). The excess solvent was removed under vacuum with a rotary evaporator. The resulting solution was washed with dilute bicarbonate solution (5%) until free of acetic acid. The solution was then dried over Na_2SO_4. The product, described[84] as a straw coloured oil had a b.p. of 140-143°C (literature[84]; b.p.=140-145°C) and was obtained in 85% yield. The compound was characterized in the N.M.R. spectrum, by two singlets at δ 1.73 ppm and δ 1.97 ppm corresponding to the two methyl groups of the hydrazone. Other properties may be found on Table V (page 44).

B: Preparation of Phenylazodimethylmethylacetate (52)

A solution of acetone phenylhydrazone (1.5g, 0.01 mole) in methylene chloride (50 ml) was added in the course of fifteen minutes to a stirred solution, at 0°C to -10°C, under nitrogen, of lead tetraacetate (4.6g, 0.01 mole) in methylene chloride (75 ml). The resulting solution was stirred for twenty minutes more after which cold water (100 ml) was added. The mixture was then filtered and the methylene chloride layer was separated and washed with a sodium bicarbonate solution (5%). After drying the solution over anhydrous Na_2SO_4, the solvent was removed under vacuum with a rotary evaporator. The yellow oil left behind was triturated with hot petroleum ether to deposit insoluble impurities. The solvent was again removed to leave behind a yellow oil (1.70g, 83% yield).

A strong band near 1750 cm^{-1} is present in the I.R. spectrum of 52 (Table V, page 44), which is due to the stretching of the C=O bond of the acetate. Singlet peaks at δ 1.60 ppm (s,6) and δ 2.07 ppm (s,3) in the ^1H N.M.R. spectrum of 52 are due to the protons of the gem-dimethyl groups and the protons in the acetate group, respectively. The aromatic protons of the phenyl group appear at δ 7.33-7.73 ppm (m,5).

C: Kinetics of Decomposition of 52 in Carbon Tetrachloride

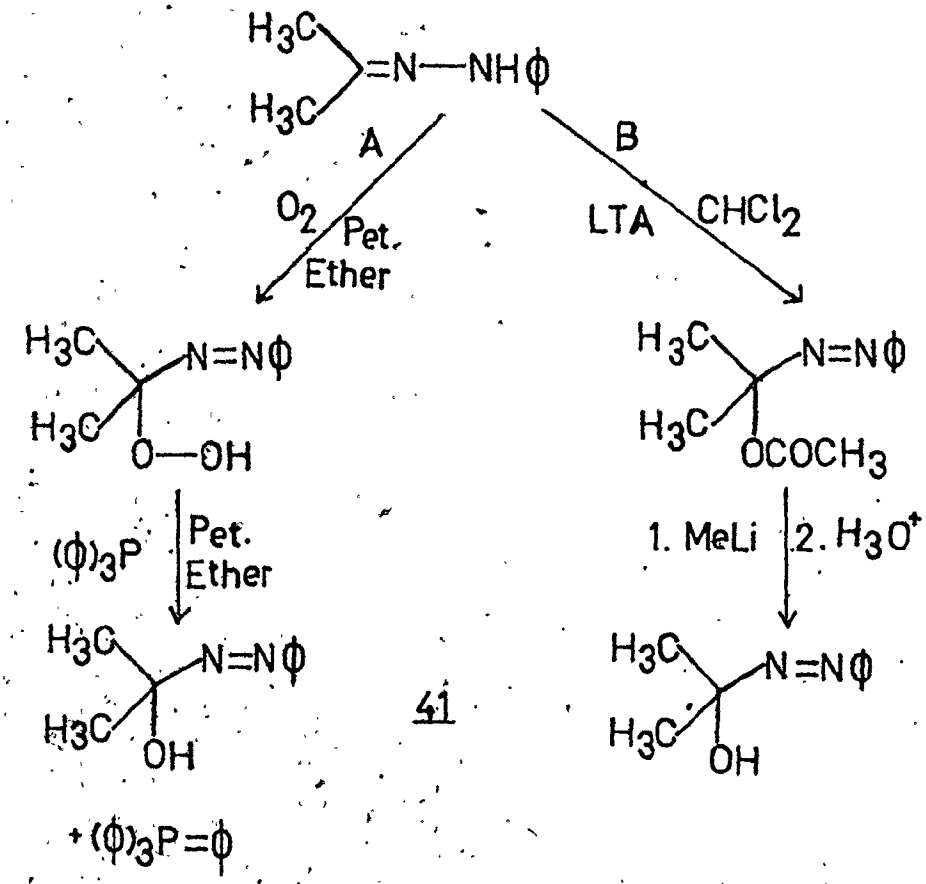
To a solution of 52 (0.2M) in carbon tetrachloride (5.0 ml) was added dimethyl carbonate (0.1 ml) as the internal standard. An aliquot of this solution was transferred into an nmr tube which was degassed and sealed (vacuum line pressure=5.0×10^{-3} mm Hg). The rate of decomposition at 80.0+/-0.1°C was followed by N.M.R. by monitoring the decay of the methyl acetate peak normalized to that of the internal standard. The reaction was followed for a period of 1,100 hours (approximately 45 days) after which time only 12% of 52 had decomposed.

VI: Chemistry of Phenylazodimethylcarbinol (41)

A: General

Phenylazodimethylcarbinol may be synthesized via several routes starting from the acetone phenylhydrazone (Scheme XVI). Thus far, in our

Scheme XVI



laboratory, several ∝-azocarbinols have been synthesized via route (B)[43]. In the course of the present study, the ∝-azocarbinol (41) was synthesized via the oxidation route (A). This route is simpler, more efficient, and less costly.

B: Preparation of 41 by the Oxidation Route

Acetone phenylhydrazone (7.4g, 0.05 mole) was dissolved in petroleum ether (200 ml) and the solution was allowed to take up oxygen. The amount of oxygen consumption was monitored. The reaction was stopped

when no more oxygen was taken up. Reaction progress was also checked by recording the ^1H N.M.R. spectrum of the reaction mixture which shows the disappearance of the two methyl singlets of acetone phenylhydrazone (δ 1.73 ppm and δ 1.97 ppm) and the appearance of the gem-dimethyl singlet of the hydroperoxide (40) at approximately δ 1.45 ppm. The hydroperoxide solution was then added to a solution of triphenylphosphine (13g, 0.05 mole) in petroleum ether (400 ml). A precipitate quickly formed which, when collected and dried, melted at 150-153°C, and after several recrystallizations from chloroform-petroleum ether , had a m.p. of 153-154°C (literature[70,73], m.p. = 153.5°C). The precipitate was triphenylphosphine oxide. The solution was left overnight to deposit more triphenylphosphine oxide before the filtrate was collected and concentrated. The filtrate was then distilled bulb-to-bulb (vacuum line pressure: 5.0×10^{-3} mm Hg) for a period of approximately five hours to give phenylazodimethylcarbinol as a yellow oil, in 82% yield.

C: Kinetics of Decomposition in Carbon Tetrachloride

Thermolysis of 41 in carbon tetrachloride (0.25 ml, 0.0015 mole, per 1.0 ml) containing dimethyl carbonate (0.15 ml, 0.0015 mole) as internal standard was done in a sealed tube at 35 +/- 0.1°C. The kinetics were followed by monitoring the decay of the gem-dimethyl signal (δ 1.43 ppm) in the ^1H N.M.R. spectra recorded at selected time intervals. This signal and the reference signal were integrated at least three times. Standard first order treatment of the data gave good fits to the first order rate equation and the rate constant was evaluated from a least-squares treatment. The major products of the reaction were acetone, (new peak at δ 2.10 ppm) benzene, chloroform, and chlorobenzene (new peak near δ 7.20 to 7.30 ppm). The presence of these products was confirmed by comparing their

retention times, on several glpc columns (Gas Chromatography), against those of authentic samples.

D: Thermal Decomposition in Benzaldehyde

A solution of 41 in benzaldehyde (0.6M) was placed in a thick-walled tube, degassed and sealed. The tube was heated at 35°C for a period of 48 hours, after which time a solid appeared in the tube. Gas chromatography analysis of the filtrate showed the presence of acetone and benzene as the other reaction products. The solid, from the reaction, was identified as benzoic acid-2-phenylhydrazide (24a); m.p. 165-167°C (literature m.p.=168°C), M.S. m/e=212, (77.2% yield).

E: Kinetics of Decomposition in Benzaldehyde

Three solutions of benzaldehyde (10M or neat, 5M, and 2M) in benzene were prepared. To each solution 41 was added (C_6H_5CHO=0.01M, 41= $5.0X10^{-4}$M) along with an equivalent molar amount (to that of 41) of dimethyl carbonate as the internal standard. Aliquots of this solution were transferred into nmr tubes which were degassed and sealed. The tubes were heated in a constant temperature water bath (35.0+/-0.1°C). The kinetics of each run were followed by normalizing the decaying gem-dimethyl signal of 41 against that of the internal standard. The rate constants were then calculated from the data obtained with good fits to the first order rate equation (pseudo first order conditions).

F: Kinetics of Decomposition of 41 in CCl_4 in the Presence of Thiophenol

Two solutions of thiophenol (0.001M and 0.0005M) in CCl_4 were prepared. To these solutions (5.0 ml each) 41 was added (100 µl, $6.0X10^{-4}$ mole) along with dimethyl carbonate (internal standard). An aliquot of each solution was placed in an nmr tube which was degassed and sealed. The tubes were heated at 35°C and the reaction was followed by recording

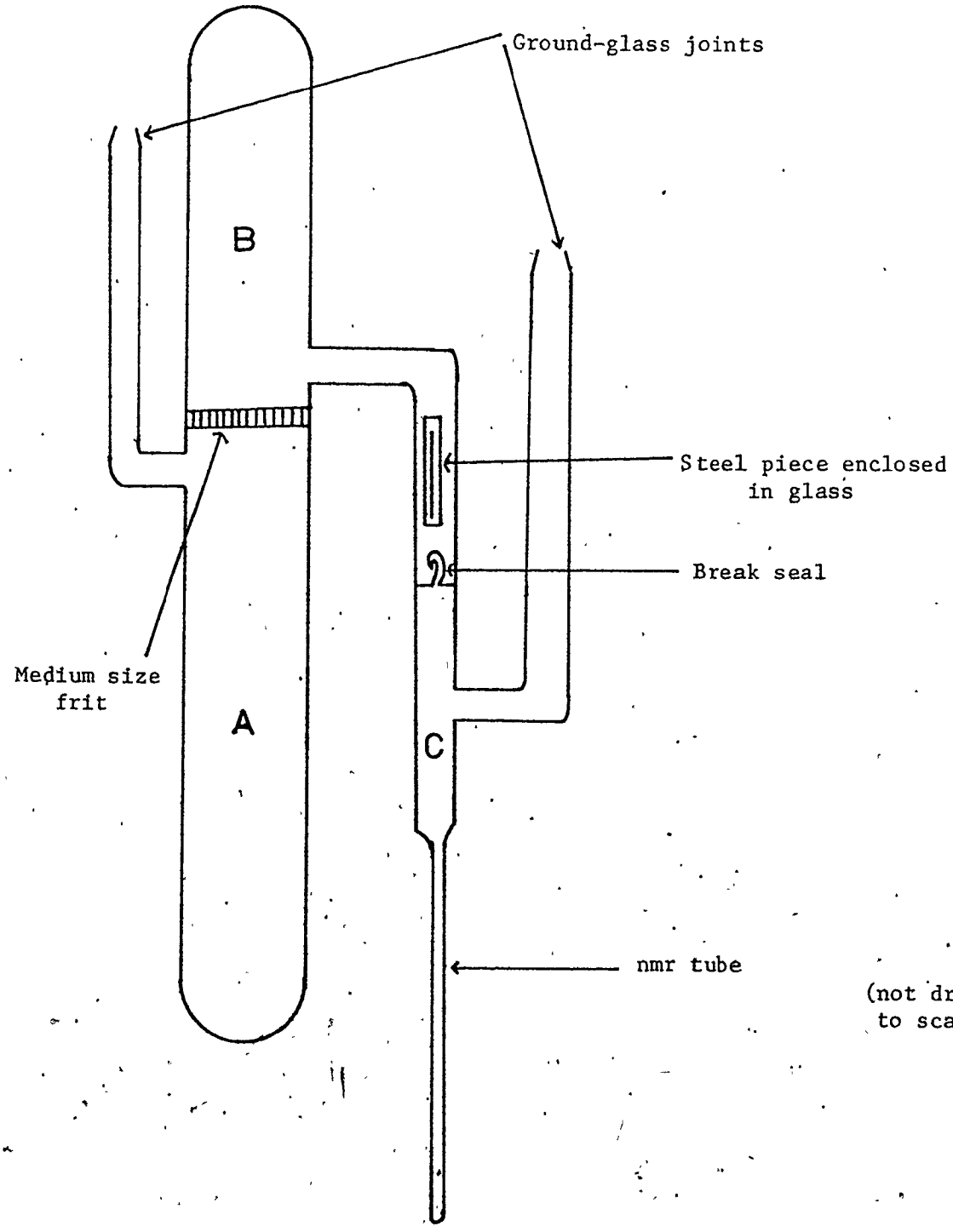
N.M.R. spectra at selected time intervals to at least three half lives. The first order rate constants were then calculated as described in section VI C.

G: Kinetics of Decomposition of 41 in the Presence of Triphenylmethyl Radicals

A solution of triphenylmethyl radicals in benzene was prepared by a procedure modelled after that of Hammond, Ravve, and Modic[85]. The apparatus (Figure I, page 79) was completely modified from that used by the authors, in order to assure proper sealing against oxygen which would react rapidly with the radicals being formed. In a typical preparation, triphenylmethyl chloride (2.4g, $8.6X10^{-3}$ mole) in benzene (10 ml) was placed in compartment A of figure I. To this solution, mercury (5.0g) was added along with Na_2CO_3(1.0g) (to eliminate traces of acid). This solution was degassed at the vacuum pump ($5.0X10^{-3}$mm Hg pressure) and the pumping arm was sealed. The apparatus was then shaken on a mechanical shaker for a period of approximately 48 hours. The colour change, from dark orange to yellow, in the course of the reaction gave an indication of when the reaction was complete.

Azocarbinol 41 (0.1 ml, 0.6 mmole), benzene (3.0 ml), and dimethyl carbonate (0.6 mmole) were then placed in compartment C of figure I. Compartment C was then degassed and sealed and the whole apparatus was inverted so that the trityl radical solution filtered through the frit into compartment B, with the inorganic salts of mercury left behind. The break seal was then broken by using the weight of the glass enclosed steel piece. The two solutions were thus mixed in compartment B, after which an aliquot was run into the nmr tube which was quickly sealed. This nmr tube was kept frozen, in liquid nitrogen, until an E.S.R. spectrum

Figure I: Apparatus for Generation of Triphenylmethyl Radicals and Reaction with 41 Under Sealed Conditions



was taken to confirm the presence of trityl radicals.

The sealed nmr tube was then heated at 35°C in a constant temperature water bath. N.M.R. spectra were taken periodically, to monitor the integral of the gem-dimethyl peak of 41 against that of the internal standard. The fit to first order kinetics was excellent (see Table VI, page 51).

H: Product Identification from Decomposition of 41 in the Presence of Trityl Radicals

The solution of trityl radicals in benzene containing 41 (left behind in compartment B of figure I from section VI G) was allowed to react (at 35.0+/-0.1°C) for a period of several weeks. One millilitre of this solution was distilled and the clear distillate collected was subjected to Gas Chromatography using several glpc columns. Acetone was identified as a reaction product by comparing its retention time to that of an authentic sample.

The fraction left behind in the distillation eventually crystallized and when subjected to thin layer chromatography showed three spots, indicating the presence of at least three products. This fraction was sublimed under vacuum ($5.0X10^{-3}$ mm Hg) to give a fine white powder. The same fraction showed three peaks when subjected to Gas Chromatography analysis, one of which was attributed to triphenyl methane by comparing the retention time to that of an authentic sample using three chromatographic columns (5% OV-17, 5%OV-101, and 5% SE-30). Injections of the sublimate (in ether) into the Gas Chromatograph (Varian Aerograph A90-P3) afforded the collection of minute quantities of the reaction product. This material had a melting point of 92-95°C (literature value for $(C_6H_5)_3CH$ is 94°C) and signals in the ^1H N.M.R. spectrum (δ 5.47 (s,broad), δ 6.97 to 7.27 (m)) corresponding

to those found in the literature[86] (δ 5.50 and δ ca 7.15).

I: Kinetics of Decomposition of 41 in Benzene as a Control Experiment

A solution of 41 (0.05 ml), dimethyl carbonate (0.03 ml), and benzene (3.0 ml) was prepared and kept cold. An aliquot of this was transferred to an nmr tube which was degassed and sealed. The reaction was run simultaneously, and in the same constant temperature water bath (35.0+/-0.1°C) as that of the trityl radical experiment (section VI G).

J: Kinetics of Decomposition in the Presence of Other Stable Free Radicals

The kinetics of decomposition of 41 were done, in separate experiments, in the presence of 2,2,6,6-tetramethylpiperidinoxy (36) (0.12M; 10:1 = Radical:Azocarbinol) and of 2,2-diphenyl-1-picrylhydrazyl (37) (0.15M; 10:1 = Radical:Azocarbinol) under sealed conditions. Benzene was used as the solvent and dimethyl carbonate as the internal standard. Both reactions were done at 35°C and followed by N.M.R. spectroscopy to at least three half lives, using integral areas and integrating the signals at least three times. Both experiments were done in duplicate and their respective rate constants were evaluated from a least squares treatment. The results are gathered in Table VI, page 51.

K: Trapping with Trichloroethylene

Azocarbinol 41 (328 mg, 2.0 mmole) was added to trichloroethylene (5.0 ml) and the solution was stirred for one hour at room temperature. The flask was vented with a syringe needle throughout the course of the reaction. Upon completion the excess trichloroethylene was removed by distillation at atmospheric pressure. The N.M.R. spectrum of the crude reaction showed authentic[77] peaks of the addition product, $\phi CH(Cl)CHCl_2$; N.M.R.: δ 7.50 (m,5); δ 6.02 (1H, J=5.9Hz); δ 5.21 (1H, d, J=5.9Hz). Acetone was also identified as a reaction product (^{1}H N.M.R. δ 2.12) from

a sample of the reaction mixture before distillation. No attempt was made to purify the addition product.

VII: Kinetics of Decomposition of Methoxydiphenylphenylazomethane[87] (53)

Thermolysis of 53 in carbon tetrachloride (300 mg, 0.001 mole, per 4.5 ml) containing dimethyl carbonate as internal standard was done in a sealed tube at 80.0+/-0.1°C. The decomposition was followed by ^{1}H N.M.R. spectroscopy; by monitoring the decay of the methoxy peak at δ 3.27. The results, when fitted to the first order rate equation, gave $k^{80°C}$(53) = 3.64 X10^{-6} sec^{-1}(c.c.=0.9707), (Table VI, page 49).

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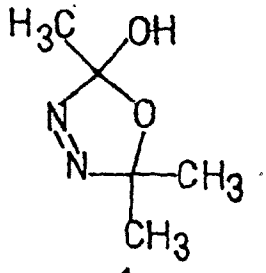
APPENDIX I

Structural Formulae of Compounds



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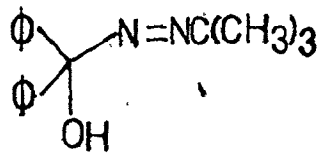

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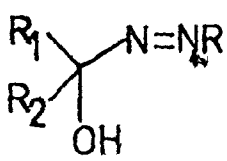

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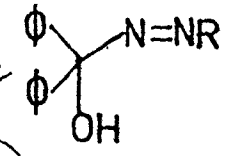

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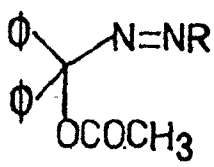

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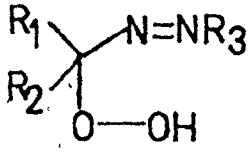

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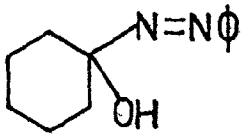

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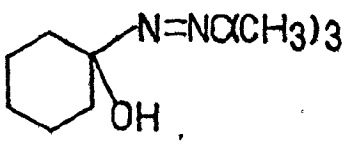

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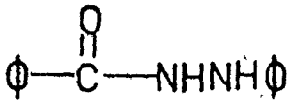

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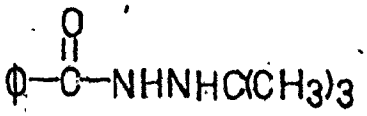

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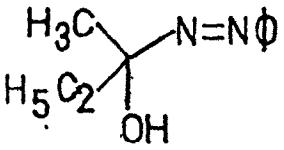

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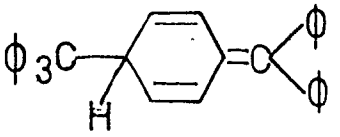

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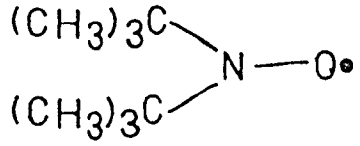

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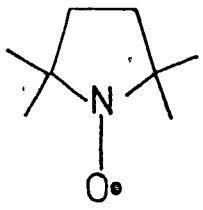

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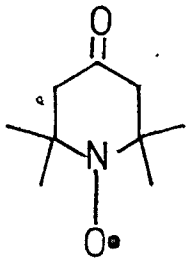

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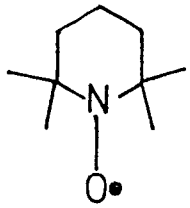

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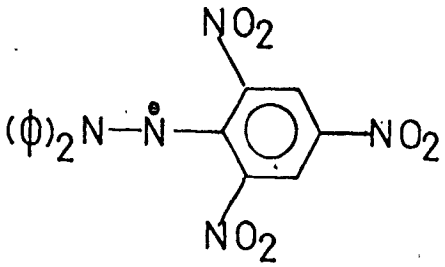

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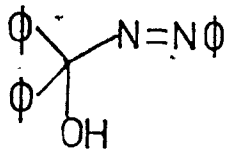

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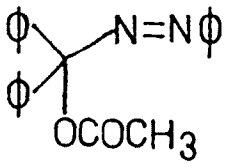

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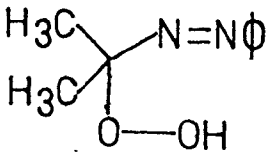

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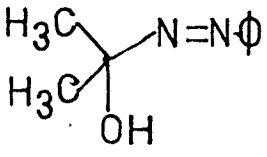

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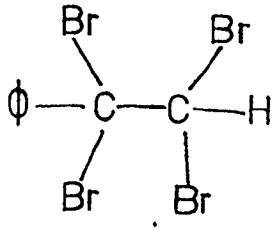

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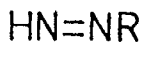

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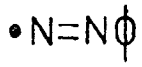

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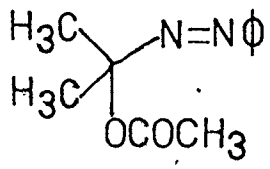

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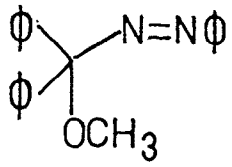

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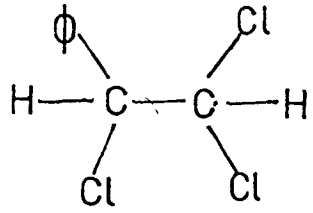

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