ELECTRICAL EFFECTS IN CARBENIC DECOMPOSITION

OF 2,2-DIARYL-1-DIAZOPROPANES

DISSESSATION

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INTRODUCTION

The primary object of this research was to study electronic effects for rearrangement in carbenic (1) decomposition of 2,2-

(1) In this discussion the term "carbene" is used as a general name for divalent carbon intermediates. The simplest such intermediate, :CH₂, is called methylene; other carbenes are named by adding "idene" to the name of the corresponding univalent radical [International Union of Pure and Applied Chemistry Report on Nomenclature, J. Am. Chem. Soc., 82, 5545 (1960)].

diaryl-1-diazopropanes. The purposes were to 1) investigate synthetic pathways to the previously unknown diazo compounds; 2) find optimum conditions for carbenic decomposition of 2,2-diarylpropanal tosylhydrazones; and 3) obtain a quantitative measure of the electrical requirements for rearrangement to the carbenic center by determining migratory aptitudes.

It was also of interest to compare migratory aptitudes for rearrangement in this system with those for 2-diazo-1,1,1-triarylethanones (2). It was hoped that electrical requirements


for rearrangement would be greater for 2,2-diaryl-1-diazopropanes.
than for 2-diazo-1,1,1-triarylethanones since the former system is not as sterically constrained.

For determination of the migratory aptitudes selected 2,2-diaryl-1-diazopropanes were prepared and decomposed in situ (Equations 1, 2, and 3) by base-catalyzed thermal decompositions of their respective p-toluenesulfonylhydrazones in diglyme, a process known to proceed via a carbenic mechanism (3).


\[ \text{Ar}_2C(\text{CH}_3)CH=\text{NNHSO}_2\text{C}_7\text{H}_7 \xrightarrow{\Delta} \text{Ar}_2C(\text{CH}_3)CHN_2^+\text{O}_2\text{SC}_7\text{H}_7+B\text{H} \]  
\[ \text{Ar}_2C(\text{CH}_3)CHN_2 \rightarrow \text{Ar}_2C(\text{CH}_3)CH_2+\text{N}_2 \]  
\[ \text{Ar}_2C(\text{CH}_3)CH_2 \rightarrow \text{ArC(CH}_3)=\text{CHAr} + \text{Ar}_2C(\text{CH}_3) \]  

The products were analyzed by gas chromatography and then oxidized to their respective acetophenones and benzoic acids (Equation 4).

\[ \text{ArC(CH}_3)=\text{CHAr} \xrightarrow{\text{KMnO}_4} \text{ArCOCH}_3 + \text{ArCO}_2\text{H} \]  

The acids were separated and esterified; gas chromatographic analysis provided a quantitative measure of the migratory aptitudes of the substituted phenyl groups.
HISTORICAL

The first attempts (4) to prepare methylene were made before

(4) (a) J. B. Dumas, Ann. chim. phys., [2], 58, 28 (1865).
(b) H. V. Regnault, ibid., [2], 71, 427 (1839). (c) A. Perrot,

the quadravalency of carbon was established. Nef (5) felt that

(5) J. U. Nef, ibid., 298, 202 (1897).

once methylene was prepared it would be stable and readily available.
These early synthetic failures were followed in the first decade of
the twentieth century by postulation of carbenes as intermediates
in many organic reactions. Orlov (6) suggested that methylene was

(1908).

possibly involved in the formation of ethylene from hydrogenation
of carbon monoxide over nickel and palladium; concurrently Curtius
and co-workers (7) proposed methylene as a reaction intermediate in

(7) T. Curtius, A. Darapsky, and E. Muller, Chem. Ber., 41,
3168 (1908).

photolysis of diazomethane.
Staudinger and his colleagues (8) concluded from their work on ketenes and diazo compounds that carbenes are transient diradicals. The observation (9,10) and adequate interpretation (10) of

(9) H. Meerwein, H. Rathjen, and H. Werner, ibid., 75, 1610 (1942).


insertion of methylene and other carbenes into carbon-hydrogen bonds made it clear that carbenes are unique intermediates giving reactions not encountered with radicals. Hine (11) in his studies of

(11) J. Hine, ibid., 72, 2438 (1950), and subsequent papers.

base-catalyzed solvolyses of haloforms and Doering and co-workers (12)


in their work on addition of dihalocarbenes to olefins paved the way for the extensive synthetic and mechanistic research on carbenes that has since appeared in the literature. The preparations and reactions of carbenes have been extensively reviewed (13).
Divalent carbon in a carbene is linked to two groups by covalent bonds and formally possesses two nonbonding electrons which are 1) unpaired and occupy two 2p orbitals resulting in a triplet, or 2) paired in an sp^2 orbital with a 2p orbital vacant resulting in a singlet species.

![Diagram of triplet and singlet carbene structures]

It has been suggested that triplet carbenes should add nonstereospecifically to olefins whereas singlet carbenes should add in a stereospecific manner (14). Methylene produced by photolysis of diazomethane adds stereospecifically to cis- and trans-2-butene (14). On this basis the singlet state was assigned to methylene for this reaction. By similar methods singlet states were assigned
to propylidene (15), cyclopropylidene-(16), dibromomethylene (17), dichloromethylene (18), 2-ketopropylidene (15), and carbethoxy-
methylene (19) as reaction intermediates. Nonstereospecific

(15) P. S. Skell and J. Klebe, ibid., 82, 247 (1960).

addition to olefins was used to assign the triplet state to
propargylidene (15), diphenylmethylene (20), fluorenlylidene (21),
dicyanomethylene (22), and bis(trifluoromethyl)methylene (23).


The use of the stereochemical outcome of additions of carbenes to
olefins as a diagnosis for spin states has been widespread in
spite of warnings that all nonstereospecific additions need not
be due to triplets and that all triplets need not add nonstereo-
specifically (24).

(24) (a) W. B. DeMore and S. W. Benson, Advan. Photochem.,
2, 219 (1964). (b) P. P. Gaspar and G. S. Hammond, "Carbene
1964, p. 235.

Jones (21b) generated triplet fluorenylidene in solution
by collisional deactivation of singlet fluorenylidene with hexa-
fluorobenzene. The triplet apparently adds nonstereospecifically
to olefins, prefers dienes to unconjugated olefins, and reacts
faster with oxygen, while the singlet is stereospecific in its reac-
tion with olefins. In contrast to this work it has recently been
shown (25) that dibenzo[a,d]-cycloheptenylidene (I) and

Soc., 82, 1257 (1967). (b) I. Moritani, S. Murahashi, M. Nishimo,

tribenzo[a,c,e]cycloheptenylidene (II) add to olefins stereospecific-
ally even though formation of hydrogen abstraction products
together with the addition products suggests that considerable amounts of triplet carbene are involved in these reactions.

The existence of triplet ground states has been verified by e.s.r. studies for diphenylmethylen (26), phenylmethylen (27), fluorenylidene (27), cyclopentadienyldiene (28), indenyldene (28), diazomethylen (29), dicyanomethylen (30), cyanomethylen (30), propargyldiene (31), and various para-substituted diphenylmethylenes (32).


(31) R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, ibid., 43, 196 (1965).


Quantum-mechanical calculations for methylen indicate that it has a triplet ground state and a close-lying excited state (33).

Spectroscopic evidence suggests that when diazomethane is photolyzed in an inert gas at high pressure the singlet state is first formed and subsequently decomposes to the more stable triplet (34).


Chemical evidence for this decay is found in that methylene produced in the presence of argon at high pressures adds nonstereo specifically to cis- and trans-2-butenes (35). Photosensitized decomposition of diazomethane in solution thus apparently gives triplet methylene which adds nonstereospecifically to cis- and trans-2-butenes (36). Singlet methylene is initially produced by thermal decomposition of diazomethane.

Carbenes undergo several types of bimolecular reactions. One of the most characteristic reactions of carbenes is insertion into carbon-hydrogen bonds (3,37).


(37) (a) W. v. E. Doering and L. H. Knox, ibid., 78, 4947 (1958). (b) W. v. E. Doering, L. H. Knox, and M. Jones,
Methylene inserts indiscriminantly into the various carbon-hydrogen bonds in n-pentane, 2,3-dimethylbutane, and cyclohexane in the liquid phase (10); however some discrimination occurs in these reactions in the gas phase (38). Insertion of methylene into carbon-hydrogen bonds and addition to double bonds occur at comparable rates. In photolysis of diazomethane in cyclohexene there is no discrimination in insertion into aliphatic and allylic hydrogens; however a slight preference for vinylic hydrogen is indicated (10). For insertion of methylene into secondary carbon-hydrogen bonds of propane in propane-2,2-d₂ there is an isotope effect of \( K_R/K_D = 1.3 \) (39).
insertions between carbon-hydrogen bonds have also been observed.

The ability of carbenes to add to carbon-carbon double bonds is well known and is the basis for many useful syntheses (41).


Although carbon-carbon single bonds are usually inert toward carbenes Yates and Danishefsky (42) have observed a transformation


(Equation 5) which may be viewed as insertion of a carbene across a carbon-carbon single bond. Carbon skeleton rearrangement, which

\[
\text{CH}_3\begin{array}{c}
\text{CH}_3
\end{array} \xrightarrow{\text{Cu, C}_6\text{H}_6} \text{CH}_3\begin{array}{c}
\text{CH}_3
\end{array}
\]

is equivalent to intramolecular insertion across a carbon-carbon single bond, is not a major process in reactions of carbenes of the neopentyl type (3); however such rearrangements are major in thermal decomposition of cyclopropyldiazomethane (37c), diazo-cyclopropane (37d), and diazocyclobutane (37e). Migration of alkyl and aryl groups is the basis of the Wolff rearrangement of \(\alpha\)-diazoketones (43). In thermolysis of 1-diazo-2-methyl-2-phenylpropane (44), phenyl migrates faster than does methyl (10:1).
In rearrangements of 2-phenylpropylidene and 2,2-diphenylethylidene, the order of migration is \( \text{H} > \text{Me} \) (45). Migratory aptitudes for rearrangement in the 2,2,2-triarylethyldiene system are: \( p \)-anisyl, 1.37; \( p \)-tolyl, 1.23; phenyl, 1.00; \( p \)-chlorophenyl, 0.92; \( p \)-nitrophenyl, 0.45 (46). This small range of values is in agreement with the studies of Wilt and co-workers (47) on ring-size effects in neophyl rearrangements; the authors conclude that steric effects play a larger role in determining the migrating ability of a phenyl group than does the electronic nature of the migration terminus.

Rearrangements involving migration of hetero atoms in
carbenic systems have also been reported. Photolysis of 2,2,2-
trifluorodiazoethane produces trifluoroethylene which is derived
from fluorine migration to the carbenic center (Equation 6) (48);

\[
\text{CF}_3\text{CHN}_2 \xrightarrow{h\nu/N_2} \text{CF}_3\text{CH} = \text{CF}_2 = \text{CHF} + \text{CF}_3\text{CH} = \text{CHCF}_3
\]  
(6)

32% 48%

however photolysis of 1-diazo-2,2,3,3,4,4,4-heptafluorobutane gives
rearrangement involving migration of the fluoroalkyl group rather
than migration of fluorine (Equation 7) (48).

\[
\text{C}_2\text{F}_5\text{CF}_2\text{CHN}_2 \xrightarrow{h\nu/N_2} \text{C}_3\text{F}_7\text{CH} = \text{CHC}_3\text{F}_7 + \text{CF}_2 = \text{CH-C}_2\text{F}_5
\]  
(7)

47% 31%

Catalytic decomposition or photolysis of diazoacetaldehyde
diethylacetal leads to products derived from hydrogen and from
alkoxyl migration to the divalent center (Equation 8) (49).

\[
\text{N}_2\text{CHCH(OC}_2\text{H}_5)_2 \xrightarrow{h\nu/N_2} \text{CH}_2 = \text{C(OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_5\text{OCH} = \text{CHOC}_2\text{H}_5
\]  
(8)

Similarly, photolysis of diazoacetaldehyde ethyleneacetal gives
1,4-dioxene via alkoxy migration (Equation 9), and photolysis of 1-diazo-2-methoxy-2-methylpropane yields 1-methoxy-2-methyl-2-propane via a methoxyl shift (Equation 10) (49).

$$\text{N}_2\text{CHCH} \stackrel{h\nu}{\longrightarrow} \text{CH}_2 = \text{C} \bigg\vert \text{O-CH}_2$$

$$\text{CH}_3\text{C}\bigg\vert\text{CH}_2\text{N}_2 \stackrel{h\nu}{\longrightarrow} \text{CH}_3\bigg\vert\text{OCH}_3 + \text{CH}_3\text{C} = \text{C} = \text{C} \bigg\vert\text{OCH}_3$$

Singlet carbenes are electron-deficient species, comparable to carbonium ions; they also possess a nonbonding pair of electrons, analogous to carbanions. Thus the electrophilic or nucleophilic character of singlet carbenes depends strongly on the ability of adjacent groups to withdraw electrons from or supply electrons to the carbene carbon. Although most carbenes exhibit electrophilic character (13) a few nucleophilic carbenes have been reported (50).

(b) U. Schöllkopf and E. Wiskott, ibid., 75, 725 (1963).
DISCUSSION

Much of the research necessary for the solution of this problem involved development of satisfactory synthetic routes to the desired aldehydes. 2,2-Diphenylpropanal has been previously prepared (51) by acid-catalyzed dehydration of the proper diphenylpropylene glycol (Equation 11); however this method was not generally satisfactory for the present research because of difficulties in preparing the pure substituted benzoins required and the possibility of obtaining products other than the desired aldehydes from the dehydrations (2a).

Shortly after the present study was initiated a general method of converting nitriles to aldehydes appeared (52). The

\[
\begin{align*}
\text{O} \quad \text{OH} & \quad \text{CH}_2\text{MgI} & \quad \text{OH} \quad \text{OH} & \quad \varnothing \\
\varnothing \text{-C-CH}-\varnothing & \quad \xrightarrow{\varnothing} \quad \text{CH}_3\text{C-} \quad \text{C-H} & \quad \xrightarrow{\text{H}^+} \quad \text{CH}_3\text{-C} \quad \text{-CHO}
\end{align*}
\]

(11)


method involves reaction of nitriles with lithium triethoxyalumino-hydride. In the present research 2,2-diphenylpropionitrile was
found to react with the reagent under the recommended conditions to give a mixture (approximately 50/50) of 2,2-diphenylpropanal and unreacted nitrile. After considerable experimentation an effective method was developed for preparing the aldehyde.

For generalization of the scheme it was necessary to prepare various new 2,2-diarylpropionitriles. 2-(4-Chlorophenyl)-2-phenylpropionitrile, 2-phenyl-2-(4-tolyl)-propionitrile, and 2-(4-methoxyphenyl)-2-phenylpropionitrile were synthesized by methyllating the corresponding diphenylacetonitrile (Equation 12)

\[
(p)\text{ZCHCN} \xrightarrow{1} \text{NaH} \xrightarrow{2} \text{MeI} \quad \text{CH}_3 - \text{C} - \text{CN} \quad (12)
\]

\(Z=\text{H}, \text{Cl}, \text{Me}, \text{MeO}\)

(53). (p-Chlorophenyl)phenylacetonitrile was obtained from

\[
(p)\text{ZCHCN} \xrightarrow{1} \text{NaH} \xrightarrow{2} \text{MeI} \quad \text{CH}_3 - \text{C} - \text{CN} \quad (12)
\]

(53) The general procedure was that used for preparation of 2,2-diphenylpropionitrile by P. L. Pickard and E. T. Engles, \textit{ibid.}, 73, 864 (1951).

\(\alpha\)-bromo-\(p\)-chlorophenylacetonitrile and benzene (Equation 13) (54);


(p-methoxyphenyl)-phenylacetonitrile and phenyl-p-tolylacetonitrile were prepared in poor yields (55) from \(\alpha\)-cyano benzyl tosylate, the

necessary substituted benzenes, and aluminum chloride (Equation 14); phenyl-p-tolylacetonitrile was also obtained inefficiently (56).

(56) The method used was based on that of D. Shapiro, *ibid.*, 14, 839 (1949).

from α-bromophenylacetonitrile and toluene in the presence of aluminum chloride (Equation 15).

\[
\begin{align*}
(p)\text{ClO}CH_2-CN & \xrightarrow{\text{Br}_2} (p)\text{ClO}CH-CN \xrightarrow{\text{HBr}} (p)\text{ClO}CH-CN \\
& \xrightarrow{\text{AlCl}_3} \phi \\
\phi CH-CN + Z\phi & \xrightarrow{\text{AlCl}_3} \phi CH-CN \\
& \xrightarrow{\text{OSO}_2C_7H_7} \phi Z(p)
\end{align*}
\]

\( Z = \text{Me,MeO} \)

\[ \phi CH_2-CN \xrightarrow{\text{Br}_2} \phi CH-CN \xrightarrow{\text{AlCl}_3} \phi CH-CN \rightarrow \phi CH-CN \]

Extension of the methylation procedure to (p-nitrophenyl)-phenylacetonitrile (57) gave only starting material. Therefore


2-(4-nitrophenyl)-2-phenylpropionitrile was prepared from hydrotroponitrile, p-chloronitrobenzene, and potassium hydroxide (Equation 16) (58).
The general procedure used was that of Davis and Pizzini, Ref. 57.

\[
\begin{align*}
\phi & \quad \overset{\text{KOH, Py}}{\underset{\text{C}_{6}H_{4}NO_{2}(p)}{\text{CH}_{3}-\text{CHCN}}} \quad \phi \\
\phi & \quad \overset{\text{CH}_{3}-\text{C-CN}}{\underset{\phi NO_{2}(p)}{\text{Z=H,Cl,CH}_{3},\text{CH}_{3}O}}
\end{align*}
\]

All of the 2,2-diarylpropionitriles except 2-(4-nitrophenyl)-2-phenylpropionitrile were converted to the corresponding aldehydes by lithium triethoxyaluminohydride (Equation 17) under

\[
\begin{align*}
\phi & \quad \overset{\text{LiAlH(OEt)}_{3}}{\underset{\phi Z(p)}{\text{CH}_{3}-\text{C-CN}}} \quad \phi \\
\phi & \quad \overset{\phi Z(p)}{\underset{\phi Z(p)}{\text{CH}_{3}-\text{C-CHO}}}
\end{align*}
\]

the conditions developed for the parent nitrile. Reactions of 2-(4-nitrophenyl)-2-phenylpropionitrile with the reagent over the temperature range -78 to 25° produced a mixture of products with nitro, nitrogen-hydrogen, and nitrile but no carbonyl absorptions.

Reaction of acid chlorides and lithium tri-\text{t}-butoxyluminohydride is a practical method of preparing aldehydes (59); thus


the reaction sequence in Equation 18 was investigated.
Considerable experimentation was required to convert 2-(4-nitrophenyl)-2-phenylpropionitrile to its carboxylic acid. No reaction occurs with refluxing concentrated hydrochloric acid or with refluxing 10% sulfuric acid; alcoholic potassium hydroxide and hot 70% sulfuric acid give tars. Basic hydrogen peroxide results in a mixture of amide (minor) and nitrile (major). Reaction with refluxing 60% sulfuric acid, however, gave the carboxylic acid in good yield (Equation 19); the acid was converted to its acid chloride by thionyl chloride (Equation 20) and then to the desired aldehyde by lithium tri-t-butoxyaluminohydride (Equation 21).

\[
\begin{align*}
\text{CH}_3\text{-C-CN} & \quad \xrightarrow{60\% \text{ H}_2\text{SO}_4} \quad \text{CH}_3\text{-C-CO}_2\text{H} \\
\text{NO}_2(p) & \quad \text{NO}_2(p)
\end{align*}
\] (19)

\[
\begin{align*}
\text{CH}_3\text{-C-CO}_2\text{H} & \quad \xrightarrow{\text{SOCl}_2} \quad \text{CH}_3\text{-C-COCl} \\
\text{NO}_2(p) & \quad \text{NO}_2(p)
\end{align*}
\] (20)

\[
\begin{align*}
\text{CH}_3\text{-C-COCl} & \quad \xrightarrow{\text{LiAlH(OtBu)}_3} \quad \text{CH}_3\text{-C-CHO} \\
\text{NO}_2(p) & \quad \text{NO}_2(p)
\end{align*}
\] (21)
It was subsequently found that diisobutylaluminum hydride (Dibal-H) converts 2-(4-nitrophenyl)-2-phenylpropionitrile and all the other 2,2-diarylpropionitriles prepared in this study to their aldehydes in good yields in a single operation (Equation 22).

\[
\begin{align*}
\text{CH}_3\text{C}^\text{CN} + \text{AlH}([\text{C}_4\text{H}_9])_2 & \rightarrow \text{CH}_3\text{C}^\text{CHO} \\
\end{align*}
\]

Reduction with Dibal-H provides the most satisfactory method for effecting this transformation.

The synthetic procedures utilized for preparation of 2,2-diarylpropanals in this study are summarized in Charts I-V.

The 2,2-diarylpropanals were converted to the corresponding p-toluenesulfonylhydrazones by reaction with p-toluenesulfonyl hydrazide in refluxing ethanol.

It has been shown that the stoichiometry of the base and the specific base affect the course of decomposition of tosylhydrazones (60). Thus a study was made of stoichiometry of base

---


---

on the decomposition of 2,2-diphenylpropanal tosylhydrazone. The decompositions were effected in diglyme with various amounts of butyllithium, sodium methoxide, or lithium methoxide by slowly
CHART I

\[
\phi\text{CHCN} \xrightarrow{1) \text{NaH}} \phi\text{CH}_2\text{I} \xrightarrow{2) \text{CH}_3\text{I}} \phi\text{CH}_2\text{C-CN} \xrightarrow{\text{LiAlH(OEt)}_3} \phi\text{CH}_2\text{C-CHO}
\]

\[94\% \quad 45\%\]

CHART II

\[(p)\text{Cl}\phi\text{CH}_2\text{CN} \xrightarrow{1) \text{Br}_2} \phi\text{CHCN} \xrightarrow{2) \text{AlCl}_3} \phi\text{Cl(p)} \xrightarrow{1) \text{NaH}} \phi\text{CH}_2\text{I} \xrightarrow{2) \text{CH}_3\text{I}} \phi\text{CH}_2\text{C-CN} \xrightarrow{\text{LiAlH(OEt)}_3 \text{ or AlH(1C}_4\text{H}_9)_2} \phi\text{CH}_2\text{C-CHO} \]

\[73\% \quad 83\% \quad 39\% \quad 64\% \]

CHART III

\[
\phi\text{CHCN} \xrightarrow{\text{AlCl}_3} \phi\text{CH}_3\text{SO}_2\text{C}_7\text{H}_7 \xrightarrow{1) \text{NaH}} \phi\text{CH}_2\text{I} \xrightarrow{2) \text{CH}_3\text{I}} \phi\text{CH}_3\text{C-CN} \xrightarrow{\text{LiAlH(OEt)}_3 \text{ or AlH(1C}_4\text{H}_9)_2} \phi\text{CH}_2\text{C-CHO}
\]

\[34\% \quad 87\% \quad 63\% \quad 51\% \]

\[^a\text{Yield with LiAlH(OEt)}_3, \quad ^b\text{Yield with AlH(1C}_4\text{H}_9)_2.\]
CHART IV

\[ \phi \text{CHCN} \xrightarrow{\text{AlCl}_3} \phi \text{SOCH}_3 \]

\[ \phi \text{CHCN} \xrightarrow{\phi \text{OSO}_2 \text{C}_7 \text{H}_7 \text{H}_3} \phi \text{H}_3 \text{C}-\text{CN} \]

\[ \phi \text{CHCN} \xrightarrow{1) \text{NaH}} \phi \text{C}_3 \text{H}_3 \xrightarrow{2) \text{CH}_3 \text{I}} \phi \text{C}_3 \text{I} \xrightarrow{\text{H}_3 \text{OCH}_3 \text{(p)}} \phi \text{SOCH}_3 \text{(p)} \]

37% 74%

\[ \text{LiAlH(OEt)}_3 \quad \phi \]

56% \footnote{Yield with LiAlH(OEt)_3.}

or \[ \text{AlH(1C}_4\text{H}_9)_2 \quad \phi \text{CH}_3 \text{C}-\text{CHO} \]

\[ \phi \text{SOCH}_3 \text{(p)} \]

59% \footnote{Yield with AlH(1C}_4\text{H}_9)_2.}

CHART V

\[ \phi \text{CH}_2 \text{CN} \xrightarrow{1) \text{NaNH}_2 \text{(NH}_3)_2} \phi \text{CH}_3 - \phi \text{CHCN} \xrightarrow{2) \text{CH}_3 \text{I}} \phi \text{C}_3 \text{H}_3 \xrightarrow{\text{KOH,Py}} \phi \text{C}_3 \text{C}-\text{CN} \]

89% 61%

\[ \phi \text{CH}_2 \text{CN} \xrightarrow{60\% \text{H}_2 \text{SO}_4} \phi \text{CH}_3 - \phi \text{CO}_2 \text{H} \xrightarrow{\text{SOCl}_2} \phi \text{CH}_3 - \phi \text{COC}_1 \xrightarrow{\text{LiAlH(OEt)}_3} \phi \text{H}_3 \text{C}-\text{CN} \]

60% 88%

\[ \phi \text{NO}_2 \text{(p)} \]

CH_3-C-CHO

\[ \phi \text{NO}_2 \text{(p)} \]

-65%

\[ \phi \text{CH}_3 \text{C}-\text{CN} \xrightarrow{\text{AlH(1C}_4\text{H}_9)_2} \phi \text{CH}_3 \text{C}-\text{CHO} \]

\[ \phi \text{NO}_2 \text{(p)} \]

71%

\[ \text{Yield with LiAlH(OEt)}_3. \quad \text{Yield with AlH(1C}_4\text{H}_9)_2. \]
(0.75-1.0 hr.) increasing the temperature to 125° (61). At

(61) Addition of butyllithium to diglyme solutions of the
tosylhydrazone produces a dark red color which disappears with
stirring (unless more than 2.5 equivalents are added); addition
of sodium methoxide or lithium ethoxide produces no color.

approximately 65° with butyllithium or lithium methoxide and ap-
proximately 90° with sodium methoxide the mixtures become cloudy
yellow and nitrogen evolution begins. As the decomposition pro-
cceeds, the amount of precipitated p-toluenesulfinate salt increases,
and the mixtures become more viscous. The product mixtures were
complex and were analyzed by gas chromatography (62). Preparative

gas chromatography (63) was used for separation of the products;

(62) The columns used were 10' x 1/4" FFAP(5%) on Chrom-
sorb G and 15' x 1/4" FFAP(5%) on Chromsorb G.

identification was made by comparison of mass spectra, nuclear
magnetic resonance spectra, and, in most cases, retention times
with authentic samples. The results of the decompositions are
listed in Table 1.

Both the type of base and the amount of base used have effects
on the course of decomposition; however with slightly greater than
one (1.25) equivalent of sodium methoxide or butyllithium the effect
## TABLE 1

Base-Catalyzed Thermal Decomposition of 2,2-Diphenylpropanal Tosylhydrazone

<table>
<thead>
<tr>
<th>Base</th>
<th>Equiv. C, %</th>
<th>Yield, %</th>
<th>Yl.12</th>
<th>$ \text{C}_6 \text{H}_5 \text{CH} - \text{CH}_2 $</th>
<th>$ \text{CH}_3 $</th>
<th>$ \text{CH}_2 $</th>
<th>$ \text{CH}_2 - \text{CH}_2 \text{CH}_3 $</th>
<th>$ \text{CH}_3 - \text{CH}_2 \text{CO} $</th>
<th>$ \text{CH}_3 - \text{CH}_2 - \text{CN} $</th>
<th>$ \text{CH}_3 - \text{C}_6 \text{H}_5 $</th>
<th>$ \text{CH}_3 - \text{C}_6 \text{H}_5 $</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuLi</td>
<td>0.80</td>
<td>94</td>
<td>2</td>
<td>17</td>
<td>7</td>
<td>-0</td>
<td>38</td>
<td>1</td>
<td>35</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>BuLi</td>
<td>1.00</td>
<td>93</td>
<td>2</td>
<td>22</td>
<td>3</td>
<td>-0</td>
<td>28</td>
<td>1</td>
<td>35</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>BuLi</td>
<td>1.25</td>
<td>89</td>
<td>5</td>
<td>40</td>
<td>trace</td>
<td>16</td>
<td>-0</td>
<td>2</td>
<td>27</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>BuLi</td>
<td>1.50</td>
<td>100</td>
<td>7</td>
<td>42</td>
<td>trace</td>
<td>14</td>
<td>-0</td>
<td>3</td>
<td>26</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>BuLi</td>
<td>2.00</td>
<td>60</td>
<td>30</td>
<td>27</td>
<td>trace</td>
<td>17</td>
<td>-0</td>
<td>5</td>
<td>14</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>BuLi</td>
<td>2.50</td>
<td>50</td>
<td>65</td>
<td>8</td>
<td>trace</td>
<td>-0</td>
<td>0</td>
<td>16</td>
<td>-0</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>BuLi</td>
<td>3.00</td>
<td>22</td>
<td>84</td>
<td>-0</td>
<td>trace</td>
<td>-0</td>
<td>0</td>
<td>16</td>
<td>-0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NaHx</td>
<td>1.25&lt;sup&gt;b&lt;/sup&gt;</td>
<td>95</td>
<td>0</td>
<td>45</td>
<td>trace</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>25</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>LiOHx&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.00&lt;sup&gt;b&lt;/sup&gt;</td>
<td>87</td>
<td>2</td>
<td>48</td>
<td>trace</td>
<td>19</td>
<td>0</td>
<td>0</td>
<td>27</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LiOHx&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.00&lt;sup&gt;d&lt;/sup&gt;</td>
<td>80</td>
<td>0</td>
<td>38</td>
<td>trace</td>
<td>13</td>
<td>17</td>
<td>0</td>
<td>32</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LiOHx&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1.25&lt;sup&gt;d&lt;/sup&gt;</td>
<td>100</td>
<td>0</td>
<td>36</td>
<td>trace</td>
<td>12</td>
<td>19</td>
<td>0</td>
<td>29</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LiOHx&lt;sup&gt;f&lt;/sup&gt;</td>
<td>2.00&lt;sup&gt;d&lt;/sup&gt;</td>
<td>100</td>
<td>0</td>
<td>44</td>
<td>trace</td>
<td>17</td>
<td>5</td>
<td>0</td>
<td>27</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LiOHx&lt;sup&gt;g&lt;/sup&gt;</td>
<td>3.00&lt;sup&gt;d&lt;/sup&gt;</td>
<td>100</td>
<td>0</td>
<td>49</td>
<td>trace</td>
<td>21</td>
<td>0</td>
<td>0</td>
<td>30</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> By nitrogen evolution.  
<sup>b</sup> Corrected for 93% purity of NaHx.  
<sup>c</sup> 4% of an unidentified product was also obtained.  
<sup>d</sup> Corrected for 98.4% purity of LiOHx.  
<sup>e</sup> 7% of an unidentified product was also obtained.
of the base employed is small. The major products result from expected carbenic processes. Phenyl migration to the carbenic center gives cis- and trans-1,2-diphenyl-1-propenes (Equation 23);

\[
\phi \quad \text{CH}_3-\text{C}-\text{CH}=\text{N}-\text{NSO}_2\text{C}_7\text{H}_5 \xrightarrow{-\text{LiSO}_2\text{C}_7\text{H}_7} \phi \quad \text{CH}_3-\text{C}-\text{CH}=\text{N}_2 \xrightarrow{\Delta} \phi \quad \text{CH}_3=\phi \quad \text{CH}_3 \quad \phi
\]

insertion of the carbene across the methyl carbon-hydrogen bond gives 1,1-diphenylcyclopropane (Equation 24).

\[
\phi \quad \text{H}_2\text{C} \quad \text{H} \xrightarrow{\phi \quad \text{C} \quad \text{CH}_2} \quad \text{H} \quad \phi \quad \phi \quad \text{CH}_2 \quad \phi
\]

A small amount of 1,1-diphenyl-1-propene, formally derived by methyl migration to the carbenic center, is also observed (Equation 25).

\[
\phi \quad \text{CH} \xrightarrow{\phi \quad \text{C} \quad \text{CH}} \quad \phi \quad \phi \quad \text{CHCH}_3
\]

2,2-Diphenylpropanal and 2,2-diphenylpropionitrile were present in the decomposition residues. Their formation may result
from pyrolysis of the azine (Equation 26) which is possibly formed

\[
\begin{align*}
\text{CH}_3\text{C}-\text{C}=\text{N} & \rightarrow \text{CH}_3\text{C}-\text{CH}_3 \\
\phi & \begin{array}{c}
\phi \rightarrow \\
\phi \\
\phi
\end{array} \text{CH}_3\text{C}-\text{CH}_3 + \text{H}_2\text{O} \\
\phi & \begin{array}{c}
\phi \\
\phi \\
\phi
\end{array} \phi
\end{align*}
\]

(Equation 26)

by dimerization of the initial diazo compound with loss of nitrogen. 2,2-Diphenylheptane and 1,1-diphenylethane were also obtained. Reaction of the tosylhydrazone salt with butyllithium could possibly give these products (Equations 27 and 28);

\[
\begin{align*}
\text{CH}_3\text{C}-\text{CH}=\text{N}-\text{N}=\text{SO}_2\text{C}_7\text{H}_7 + \text{BuLi} & \rightarrow \text{CH}_3\text{C}-\text{C}=\text{N}-\text{N}=\text{Bu} + \text{Li}^+ \\
\phi & \begin{array}{c}
\phi \\
\phi \\
\phi
\end{array} \phi \\
\phi & \begin{array}{c}
\phi \\
\phi \\
\phi
\end{array} \phi \\
\phi & \begin{array}{c}
\phi \\
\phi \\
\phi
\end{array} \phi
\end{align*}
\]

(Equation 27)

\[
\begin{align*}
\text{CH}_3\text{C}-\text{CH}=\text{N}-\text{N}=\text{SO}_2\text{C}_7\text{H}_7 + \text{BuLi} & \rightarrow \text{CH}_3\text{C}-\text{CH}=\text{N}-\text{N}=\text{Bu} + \text{Li}^+ \\
\phi & \begin{array}{c}
\phi \\
\phi \\
\phi
\end{array} \phi \\
\phi & \begin{array}{c}
\phi \\
\phi \\
\phi
\end{array} \phi \\
\phi & \begin{array}{c}
\phi \\
\phi \\
\phi
\end{array} \phi
\end{align*}
\]

(Equation 28)

however their formation is not well understood and requires further study.
Using less than one equivalent of butyllithium leads to considerable 2,3-diphenyl-1-propene. It is reasonable to conclude that this product is derived from a carbonium ion process which may be concerted (Equations 29 and 30).

\[
\begin{align*}
&\text{CH}_3\text{CCH}_2\text{N}^+\text{N}_2 \rightarrow \text{CH}_3\text{CCH}^+ \rightarrow \text{CH}_3\text{CCH}_2\text{O} \rightarrow \text{CH}_2=\text{CCH}_2\text{O} \quad (29) \\
&\text{CH}_2\text{CCH}_2\text{N}^+\text{N}_2 \rightarrow \text{CH}_2=\text{CCH}_2\text{O} \quad (30)
\end{align*}
\]

Increasing the amount of butyllithium, but not sodium methoxide, significantly changes the product composition. As the amount of butyllithium is increased, the relative amounts of 1,1-diphenylethane and 2,2-diphenylheptane increase at the expense of products derived from carbenic processes, and the amount of nitrogen evolved decreases. Formation of 1,1-diphenylethane and 2,2-diphenylheptane could be explained by Equations 27 and 28; the reason for the decrease in yield of nitrogen is not known.

Use of 1.25 equivalents of lithium methoxide results in formation of 19% of 2,3-diphenyl-1-propene whereas none of this olefin is observed when 1.25 equivalents sodium methoxide are used. A greater excess of lithium methoxide (2-3 equivalents) is required to prevent formation of this olefin which is probably derived from a carbonium ion process (Equations 29 and 30). This difference
in behavior in decomposition of the tosylhydrazone in the presence of lithium and sodium methoxides is probably due to several factors. First, the sodium salt decomposes at a higher temperature than does the lithium salt and thus the diazo compound from the sodium salt has less time than the diazo compound from the lithium salt to react with methanol to form a diazonium ion intermediate before thermolysis occurs. Second, the decomposition temperature of the sodium salt (~90°) is considerably above the boiling point of methanol (65°) whereas that of the lithium salt (~65°) is approximately the same. Thus for a given amount of base the effective concentration of methanol is expected to be relatively greater in decompositions of the lithium salt than of the sodium salt.

When three equivalents of lithium methoxide are used no 2,3-diphenyl-1-propene is observed. Apparently the large excess of lithium methoxide depresses the proton-donor activity of methanol enough to prevent formation of a diazonium ion intermediate.

In order to understand the 2,2-diphenylpropyldene system better, 1-diazo-2,2-diphenylpropane was prepared and decomposed under various conditions. The diazo compound is quite unstable thermally, decomposing fairly rapidly above 0°. Thermolysis of the diazo compound was effected in undried pentane at room temperature for three hours; in a pentane-anhydrous potassium carbonate mixture at 0° for 30 minutes and then at room temperature for 4.75 hours; in a pentane-anhydrous calcium oxide mixture
at $0^\circ$ for 30 minutes and then at room temperature for five hours; in a pentane-sublimed potassium t-butoxide mixture at $0^\circ$ for 35 minutes and then at room temperature for five hours. Photolysis of the diazo compound was effected at $-35^\circ$ (64) in undried pentane using a 100-watt broad spectrum high pressure Hanovia immersion lamp. The products from all the decompositions were analyzed by gas chromatography (62) and identified by comparison of retention times with the previously identified decomposition products of 2,2-diphenylpropanal tosylhydrazone. The results of the decompositions are listed in Table 2.

Except when potassium t-butoxide was added, the compositions of the products from the decompositions are approximately the same; however conversion to 2,3-diphenyl-1-propene is higher in the thermolysis in undried pentane, and the amount of this olefin decreases as the efficiency of the drying agent present increases. This result is in agreement with the results of base-catalyzed decomposition of 2,2-diphenylpropanal tosylhydrazone; both indicate that formation of 2,3-diphenyl-1-propene is enhanced by the proton-donor availability of the environment. The fact that 2,3-diphenyl-1-propene is formed even in the presence of calcium oxide indicates that it may originate in part via intramolecular hydrogen transfer of the carbene (Equation 31).
### TABLE 2

Decomposition of 1-Diazo-2,2-diphenylpropane in Pentane

<table>
<thead>
<tr>
<th>Method</th>
<th>Moles of diazo compd.</th>
<th>Moles of base added</th>
<th>Temp. °C</th>
<th>Yield *</th>
<th>( % )</th>
<th>( \beta \text{CH}_2\text{CH}_3 )</th>
<th>( \beta \text{CH}_3\text{CH}_2)</th>
<th>( \beta \text{CH}_3)</th>
<th>CH2</th>
<th>CH3</th>
<th>CH3-C-CHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>0.00119</td>
<td>none(^b)</td>
<td>25</td>
<td>87</td>
<td>0</td>
<td>22</td>
<td>14</td>
<td>11</td>
<td>20</td>
<td>28</td>
<td>5</td>
</tr>
<tr>
<td>Thermal</td>
<td>0.00087</td>
<td>0.025 ( k_2\text{CO}_3 )</td>
<td>29(^c)</td>
<td>90</td>
<td>0</td>
<td>25</td>
<td>16</td>
<td>9</td>
<td>9</td>
<td>35</td>
<td>6</td>
</tr>
<tr>
<td>Thermal</td>
<td>0.00054</td>
<td>0.11 ( \text{CaO} )</td>
<td>28()</td>
<td>92</td>
<td>0</td>
<td>30</td>
<td>-9</td>
<td>11</td>
<td>5</td>
<td>41</td>
<td>5</td>
</tr>
<tr>
<td>Photo-chem.</td>
<td>0.00119</td>
<td>none(^b)</td>
<td>-35</td>
<td>87</td>
<td>1</td>
<td>27</td>
<td>11</td>
<td>7</td>
<td>7</td>
<td>41</td>
<td>6</td>
</tr>
<tr>
<td>Thermal(^d)</td>
<td>0.00073</td>
<td>0.010 ( \text{KO}_2\text{Bu} )</td>
<td>28()</td>
<td>&gt;90</td>
<td>14</td>
<td>36</td>
<td>trace</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>

* by nitrogen evolution. \(^b\) The pentane was used without drying or distillation. \(^c\) Stirred at 0° for 30 minutes before warming to room temperature. \(^d\) 2,2-Diphenylproponitrile (35%) and an unidentified product (3%) were also obtained.
The formation of a small amount (1%) of 1,1-diphenylethane in the photolysis might result from cleavage of the azine (Equation 32). Production of aldehyde and no nitrile is probably

![Chemical reaction diagram]

the result of reaction of the diazo compound with oxygen.

Thermolysis of the diazo compound in the presence of potassium t-butoxide results in a considerable change in the composition of products. Relatively large amounts of 1,1-diphenylethane and 2,2-diphenylpropionitrile are observed, and the amount of trans-1,2-diphenyl-1-propene is greatly reduced. Formation of 1,1-diphenylethane and 2,2-diphenylpropionitrile could possibly occur via the sequence in Equation 33; however the effect of potassium t-butoxide on reactions in this system is not well understood.

![Chemical reaction diagram]

Work-up of the thermolysis mixtures produced oily residues which seemed to be oxygen sensitive. On standing, the residues
solidified, and their compositions changed; however the photolysis residue underwent no such transformation. The reason for this difference in behavior is not known.

Base-catalyzed decomposition of 2,2-diphenylpropanal tosylhydrazone (at 65-90°) gives 44% cis- and 27% trans-1,2-diphenyl-1-propene, while decomposition of 1-diazo-2,2-diphenylpropane (at 25°) gives 27% cis- and 39% trans-1,2-diphenyl-1-propene. Thus it is likely that formation of the product of kinetic control (cis-olefin) is favored at higher temperatures whereas the product of thermodynamic control (trans-olefin) is favored at lower temperatures. The other minor differences in the composition of products from the decomposition of diazo compound and tosylhydrazone may well be due to temperature effects.

Several conclusions pertaining to the base-catalyzed decomposition of 2,2-diphenylpropanal tosylhydrazone can be drawn from these experiments: 1) the presence of protons in the environment (use of less than one equivalent of base) results in products derived at least in part from carbonium ion processes; 2) the use of a large excess of a strong base such as potassium t-butoxide or butyllithium leads to products not derived from carbenic processes; 3) thermal decomposition of the tosylhydrazone after treatment with butyllithium, but not with sodium methoxide, yields products which were not obtained from decomposition of the corresponding diazo compound; thus in this system the use of sodium methoxide as base probably results in a more nearly pure carbenic process.

For determination of migratory aptitudes in the
2,2-diarylpropyridene system, the decompositions of selected 2,2-diarylpropanal tosylhydrazones were effected in diglyme containing butyllithium or sodium methoxide. The decompositions were carried out in the same manner as the decomposition of 2,2-diphenylpropanal tosylhydrazone, and similar physical changes were observed (65).

(65) Addition of butyllithium to diglyme solutions of all the tosylhydrazones except 2-(4-nitrophenyl)-2-phenylpropanal tosylhydrazone produces a dark red color which disappears with stirring; addition of butyllithium to the nitro-substituted tosylhydrazone produces a vigorous reaction on the liquid surface to form a yellow solid which "pops" and then dissolves. Addition of sodium methoxide produces neither of these effects.

Some of the decomposition mixtures were analyzed directly by gas chromatography (62); from the results listed in Table 3 it can be seen that the products obtained closely parallel those obtained from decomposition of the unsubstituted tosylhydrazone (Table 1).

Determination of the relative amounts of the two \( \text{cis} \) and \( \text{trans} \) stilbenes (III and IV) produced in the decompositions (Equation 34)

\[
\begin{align*}
\text{CH}_3\text{-C-CHN}_2 & \overset{\text{N}_2}{\longrightarrow} \text{CH}_3\text{-C-CH:} \\
\phi \phi & \rightarrow \text{CH}_3\text{-C}=\text{CH}\phi Z(p) + \text{CH}_3\text{-C}=\text{CH}\phi \\
\phi Z(p) & \quad \phi Z(p) \\
\phi & \quad \phi \\

\text{III} & \quad \text{IV} \\
\text{cis and trans} & \quad \text{cis and trans} \\
\phi Z(p) & \quad \phi Z(p)
\end{align*}
\]

\( Z = \text{MeO,Me,Cl,NO}_2 \)

provides a measure of the migratory aptitude of an aryl group to the carbenic center in this system. With butyllithium the
### TABLE 3

Base-Catalyzed Thermal Decomposition of 2,2-Diarylpropanal Tosylhydrazones

<table>
<thead>
<tr>
<th>$x$</th>
<th>Base</th>
<th>Equiv</th>
<th>Magn ap.</th>
<th>$\delta_{\text{no}}$ (H, L)</th>
<th>$\delta_{\text{H}}$</th>
<th>$\delta_{\text{H}}$</th>
<th>$\delta_{\text{H}}$</th>
<th>$\delta_{\text{H}}$</th>
<th>$\delta_{\text{H}}$</th>
<th>$\delta_{\text{H}}$</th>
<th>$\delta_{\text{H}}$</th>
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<th>$\delta_{\text{H}}$</th>
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<tr>
<td>NaO</td>
<td>BuU</td>
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<td>2.11</td>
<td>2</td>
<td>46</td>
<td>trace</td>
<td>9</td>
<td>0</td>
<td>3</td>
<td>28</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>BuU</td>
<td>1.25</td>
<td>2.38</td>
<td>2</td>
<td>46</td>
<td>trace</td>
<td>12</td>
<td>-0</td>
<td>3</td>
<td>26</td>
<td>5</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>BuU</td>
<td>1.25</td>
<td>0.52</td>
<td>4</td>
<td>42</td>
<td>trace</td>
<td>15</td>
<td>-0</td>
<td>3</td>
<td>24</td>
<td>8</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
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<td>BuU</td>
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<td>0.29</td>
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</tr>
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<td>K</td>
<td>BuU</td>
<td>1.50</td>
<td>1.83</td>
<td>5</td>
<td>43</td>
<td>trace</td>
<td>9</td>
<td>-0</td>
<td>5</td>
<td>28</td>
<td>0</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
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<td>1.43</td>
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<td>8</td>
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<td>11</td>
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<td>BuU</td>
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<td>-0</td>
<td>8</td>
<td>24</td>
<td>0</td>
<td>7</td>
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<td></td>
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<td>BuU</td>
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<td>trace</td>
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<td>27</td>
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<td>trace</td>
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<tr>
<td>$\text{MeO}$</td>
<td>$\text{MeOH}$</td>
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<td>1.92</td>
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<td>trace</td>
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<td>0</td>
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</tr>
<tr>
<td>Cl</td>
<td>$\text{MeOH}$</td>
<td>1.25</td>
<td>0.92</td>
<td>0</td>
<td>52</td>
<td>trace</td>
<td>18</td>
<td>-0</td>
<td>0</td>
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<td>$\text{MeOH}$</td>
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<td>0</td>
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<td>-0</td>
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<td>0</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$\text{MeO}$</td>
<td>$\text{MeOH}$</td>
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<td>0</td>
<td>52</td>
<td>trace</td>
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<td>34</td>
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<td>$\text{Me}$</td>
<td>$\text{MeOH}$</td>
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<td>52</td>
<td>trace</td>
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<td>32</td>
<td>0</td>
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<td>Cl</td>
<td>$\text{MeOH}$</td>
<td>1.50</td>
<td>0.76</td>
<td>3</td>
<td>45</td>
<td>trace</td>
<td>18</td>
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<td>25</td>
<td>9</td>
<td>0</td>
<td></td>
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<td></td>
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<tr>
<td>$\text{NO}_2$</td>
<td>$\text{MeOH}$</td>
<td>1.50</td>
<td>0.26</td>
<td>0</td>
<td>43</td>
<td>0</td>
<td>28</td>
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<td>26</td>
<td>3</td>
<td>0</td>
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</tr>
</tbody>
</table>
α-methylstilbenes comprise an average of 70% of the decomposition products; with sodium methoxide, 80%. Unfortunately it was not possible to establish directly the relative amounts of the two olefins (III and IV) in the decomposition residues because they could not be separated gas chromatographically; two peaks are obtained, but one is for a mixture of cis-III and cis-IV and the other for a mixture of trans-III and trans-IV.

For determination of the relative amounts of III and IV, the decomposition products were oxidized in buffered aqueous acetone with potassium permanganate to a mixture of neutral (containing acetophenone and a substituted acetophenone) and acidic (benzoic acid and a substituted benzoic acid) components (Equation 35). The acids were separated from the neutral components and

\[
\begin{align*}
\text{CH}_3\text{C}=\text{CH}\phi & \quad \phi \text{Z(p)} \\
\phi \text{Z(p)} \quad \text{CH}_3\text{C}=\text{C}0 & \quad \phi \text{Z} \quad \text{KMN}_4 \\
\text{CH}_3\text{C}=\text{CH}\phi & \quad \phi \text{Z(p)} \\
\phi \text{Z(p)} \quad \text{CH}_3\text{C}=\text{C}0 & \quad \phi \text{Z(p)}
\end{align*}
\]

(35)

esterified with diazomethane (Equation 36); the esters were analyzed

\[
\begin{align*}
\phi \text{CO}_2\text{H} \quad (p)\phi \text{CO}_2\text{H} \\
+ \quad \text{CH}_2\text{N}_2 \quad \text{CH}_2\text{N}_2 \\
\text{H}_2\text{N}_2 \quad \text{H}_2\text{N}_2 \\
\phi \text{CO}_2\text{Me} \quad (p)\phi \text{CO}_2\text{Me}
\end{align*}
\]

(36)
by gas chromatography (66). By this procedure analyses of known
mixtures of neutral products from the oxidations were complex and were not quantitatively analyzed; however the presence of the expected acetophenones was verified.

mixtures of $p$-chloro-$\alpha$-methylstilbene (V) and $p'$-chloro-$\alpha$-methylstilbene (VI) deviated less than 4% from the known composition.

\[
\begin{align*}
\text{CH}_3\text{C}=\text{CH}\phi & \quad \text{CH}_3\text{C}=\text{CH}\phi\text{Cl(p)} \\
\phi\text{Cl(p)} & \quad \phi
\end{align*}
\]

V  VI

It was also established that 4-methoxyacetophenone and 4-methylacetophenone are not oxidized by potassium permanganate under the analysis conditions.

The relative amounts of methyl benzoate and substituted methyl benzoate as determined by gas chromatographic peak areas cannot be used as a direct measure of the relative amounts of their olefinic precursors produced in the decompositions because the molecular weights of the olefins are identical but those of the esters are different. Rather, it is necessary to multiply the observed ratio of the peak areas of substituted methyl benzoate to methyl benzoate by the ratio of the molecular weights of methyl benzoate to substituted methyl benzoate in order to determine the true relative amounts of the olefins present.

The results of base-catalyzed decomposition of 2,2-diarylpropanal tosylhydrazones are listed in Table 4. The migratory aptitudes appear to be independent of the specific base and the amount of base employed. Slow increase of the temperature of the
TABLE 4

Decomposition of 2,2-Diarylpropanal Tosylhydrazones

<table>
<thead>
<tr>
<th>Substituents</th>
<th>Base</th>
<th>Equivalents base</th>
<th>Grams tosylhydrazone</th>
<th>Migratory aptitude</th>
</tr>
</thead>
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<tr>
<td>H, MeO</td>
<td>BuLi</td>
<td>1.10</td>
<td>2.00</td>
<td>1.65</td>
</tr>
<tr>
<td>H, MeO</td>
<td>BuLi</td>
<td>1.00</td>
<td>2.00</td>
<td>1.83</td>
</tr>
<tr>
<td>H, MeO</td>
<td>BuLi</td>
<td>1.01</td>
<td>2.00</td>
<td>1.96</td>
</tr>
<tr>
<td>H, MeO</td>
<td>BuLi</td>
<td>1.25</td>
<td>0.500</td>
<td>2.11</td>
</tr>
<tr>
<td>H, MeO</td>
<td>NaOMe</td>
<td>1.50</td>
<td>0.500</td>
<td>1.56</td>
</tr>
<tr>
<td>H, MeO</td>
<td>BuLi</td>
<td>1.50</td>
<td>0.500</td>
<td>1.83</td>
</tr>
<tr>
<td>H, MeO</td>
<td>NaOMe</td>
<td>1.25</td>
<td>0.500</td>
<td>1.92</td>
</tr>
<tr>
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<td>BuLi</td>
<td>1.01</td>
<td>2.00</td>
<td>1.59</td>
</tr>
<tr>
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<td>BuLi</td>
<td>1.00</td>
<td>2.00</td>
<td>1.53</td>
</tr>
<tr>
<td>H, Me</td>
<td>BuLi</td>
<td>1.00</td>
<td>2.00</td>
<td>1.22</td>
</tr>
<tr>
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<td>2.00</td>
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<tr>
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<td>BuLi</td>
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<td>0.500</td>
<td>1.38</td>
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<tr>
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<td>0.500</td>
<td>1.32</td>
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<tr>
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<td>BuLi</td>
<td>1.50</td>
<td>0.500</td>
<td>1.43</td>
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<tr>
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<td>0.500</td>
<td>1.47</td>
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<tr>
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<td>BuLi</td>
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<tr>
<td>H, Cl</td>
<td>BuLi</td>
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</tr>
<tr>
<td>H, Cl</td>
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<td>0.500</td>
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<td>H, Cl</td>
<td>NaOMe</td>
<td>1.25</td>
<td>0.500</td>
<td>0.92</td>
</tr>
<tr>
<td>H, NO₂</td>
<td>BuLi</td>
<td>1.25</td>
<td>0.500</td>
<td>0.29</td>
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<tr>
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</tr>
<tr>
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<td>0.500</td>
<td>0.23</td>
</tr>
<tr>
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<td>BuLi</td>
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<td>0.500</td>
<td>0.18</td>
</tr>
<tr>
<td>H, NO₂</td>
<td>BuLi</td>
<td>1.25</td>
<td>0.500</td>
<td>0.19</td>
</tr>
</tbody>
</table>
reaction mixtures should have allowed decomposition and rearrangement at relatively low temperatures and presumably with selectivity. Nevertheless, the effect of substituents on the migratory aptitude of a phenyl group in this system is quite small. The migratory aptitude of p-anisyl is 1.83; p-tolyl, 1.41; phenyl, 1.00; p-chlorophenyl, 0.90; and p-nitrophenyl, 0.23.

In a related carbonium ion process, acid-catalyzed rearrangement of symmetrical aromatic pinacols to their pinacolones, the migratory aptitudes are: p-anisyl, 500; p-tolyl, 15.7; phenyl, 1.0; and p-chlorophenyl, 0.66 (67). In carbenic rearrangement of


2-methyl-2-phenylpropylidene the phenyl:methyl migration ratio is 10:1 (44), and in thermal rearrangement of triarylmethyl azides, (68) a process postulated to proceed via the nitrogen analog of

(68) W. H. Saunders, Jr. and J. C. Ware, ibid., 80, 3328 (1958).

a carbene, the migratory aptitudes are: p-anisyl, 2.5; p-tolyl, 1.8; phenyl, 1.0; p-chlorophenyl, 0.39; p-nitrophenyl, 0.20.

The small substituent effect on rearrangement to the carbenic center indicates that the activation energy for decomposition must be fairly small and the overall process somewhat indiscriminate. If a carbene is indeed formed via thermolysis, it is of great
reactivity. It is also of interest that a greater substituent effect on rearrangement is observed in the present system than in the more sterically crowded triphenylethylidene system where the migratory aptitudes are: p-anisyl, 1.37; p-tolyl, 1.23; phenyl, 1.00; p-chlorophenyl, 0.92; and p-nitrophenyl, 0.45. (2,69). The replacement of a phenyl by a methyl group appears to allow more selectivity in rearrangements in the less crowded 2,2-diphenylpropylidene system.

The relative rates of migration observed are in the order expected for rearrangement to an electron deficient center. Thus VII is a reasonable representation of the transition state for rearrangement. The results are also consistent with the supposition that the carbenic center in this system is of singlet character (14a); if a triplet were involved it might be expected to have radical-like
properties (14a), and thus all the para-substituted groups would have migratory aptitudes greater than phenyl (70).


The relationship of the observed migratory aptitudes to the Hammett equation (71) was determined. A linear free energy relationship exists between the migratory aptitudes and the \( \sigma_p \) substituent constants of the rearranging aryl groups (Figure 1). The correlation coefficient is 0.98 and \( \rho \) is -0.824. Thus there is resonance and inductive interaction between the p-substituent of the migrating group and positive charge developed in the electron-deficient transition state; furthermore the sensitivity of the rearrangement to electrical effects of substituents is small.

The corrected migratory aptitudes found for the triphenyl-ethylidene system (2,69) are also correlated by \( \sigma_p \) substituent constants (Figure 2); the correlation coefficient is 0.99 and \( \rho \) is -0.499 indicating that this system is even less sensitive to electrical effects of substituents than the 2,2-diphenylpropylidene system.
Figure 1. Hammett correlation of migratory aptitudes for 2,2-diaryl-1-diazo propanes with $\sigma_p$ substituent constants.
Figure 2. Hammett correlation of migratory aptitudes for 2-diazo-1,1,1-triarylethanes with $\sigma_p$ substituent constants.
The conclusions concerning rearrangement of 2,2-diaryl-1-diazopropanes drawn from this study are as follows:

1. The most desirable conditions for carbenic decomposition of 2,2-diarylpropanal tosylhydrazones involve use of excess sodium methoxide in aprotic solvents. Large excesses of very strong bases such as butyllithium and potassium t-butoxide or the presence of protons in the environment lead to products derived from non-carbenic processes.

2. In carbenic decomposition of 2,2-diarylpropanal tosylhydrazones the effects of substituents on the migratory aptitude of an aryl group and on the overall composition of products is small. These results indicate that the free energy difference between the competitive rearrangement processes is small and imply that the carbenic intermediate is highly indiscriminate.

3. The linear free energy relationship between the migratory aptitudes and $\Phi_p$ substituent constants with a negative $\rho$ correlation indicates that the rearrangement proceeds through an electron deficient transition state which is stabilized by resonance and inductive contribution of electron-donating substituents on the migrating group. The results also indicate that the carbenic processes in this system are electrophilic.

4. The effect of substituents on migratory aptitudes in the 2,2-diaryl-1-diazopropanes is larger than in the more sterically crowded 2-diazo-1,1,1-triarylethane system. Thus relief of steric compression at the migration origin has a smaller effect on rearrangement in the less crowded system.
To gain further insight into the rearrangement of diazo compounds, the decompositions of triphenylacetaldehyde tosylhydrazone and 2-diazo-1,1,1-triphenylethane were effected in a deuterium-donor solvent. Decomposition of triphenylacetaldehyde tosylhydrazone in ethylene glycol-d$_2$ (72) with less than one equivalent of butyllithium by quickly (ca. 3 min.) warming the mixture to 150° yields only triphenylethylene, 85% of which contains deuterium in the 2 position (Equation 37) (73) (Table 5).

(72) The glycol contained 1% ethylene glycol.

(0.80-0.87) equivalent of butyllithium by quickly (ca. 3 min.) warming the mixture to 150° yields only triphenylethylene, 85% of which contains deuterium in the 2 position (Equation 37) (73) (Table 5).

(73) The position and the amount of deuterium in the triphenylethylene were determined by NMR and mass spectra at low voltage.

\[ \phi_3^C=NC=H\text{SO}_2\text{C}_7\text{H}_7 \xrightarrow{\text{BuLi} \Delta \text{to} 150°} \phi_2^C=\text{CH}\phi + \phi_2^C=\text{CD}\phi \]  
\[ 15\% \quad 85\% \]  

When 2-diazo-1,1,1-triphenylethane was dropped into hot (140°) ethylene glycol-d$_2$ (72) the only product isolated was triphenylethylene; however in this case only 2% of the product contains deuterium at the 2 position (Equation 38) (73) (Table 6).

\[ \phi_3^C=CN_2 \xrightarrow{\text{DOCH}_2\text{CH}_2\text{OD} \ 140°} \phi_2^C=\text{CH}\phi + \phi_2^C=\text{CD}\phi \]  
\[ 98\% \quad 2\% \]
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*A Scale divisions.  *  
*B Triphenylethylene.
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<th>Deuterated triphenylethylene intensity$^{a}$</th>
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$^{a}$ Scale divisions.  
$^{b}$ Triphenylethylene.
The presence and the extent of incorporation of the deuterium in the triphenylethylene is probably largely the result of an isotope effect in decomposition of the diazonium compound formed by deuteration of the diazo compound on carbon (Equation 39);

\[
\begin{align*}
\text{C}_3\text{CCH}_2 & \overset{\text{ROD}}{\rightleftharpoons} \text{C}_3\text{CCHD}_2^+ \overset{-\text{N}_2}{\rightarrow} \text{C}_3\text{CCHD}^+ \rightarrow \text{C}_2\text{CCHD}^0 \\
\text{C}_3\text{CCH}_2 & \overset{-\text{H}^+}{\rightarrow} \text{C}_2\text{CCH}_2 \overset{-\text{D}^+}{\rightarrow} \text{C}_2\text{CCHD}_2^+ = \text{CD}^0
\end{align*}
\] (39)

however, a large isotope effect \((K_H/K_D=5.7)\) is required to explain the results obtained. Thus it is likely that part of the deuterium incorporation is due to deuterium exchange between the salt of the tosylhydrazone and solvent (Equation 40) and diazo compound and solvent (Equation 41).

\[
\begin{align*}
\text{C}_3\text{CCH} = \text{N} - \text{NSO}_2\text{C}_7\text{H}_7 & \rightleftharpoons \text{C}_3\text{CCHD} = \text{N} - \text{NSO}_2\text{C}_7\text{H}_7 \overset{\text{ROD}}{=} \text{C}_3\text{CCHD} = \text{N} - \text{NSO}_2\text{C}_7\text{H}_7 \\
\text{C}_3\text{CCH} = \text{N} - \text{NSO}_2\text{C}_7\text{H}_7 & \overset{\text{RO}^-}{\rightarrow} \text{C}_3\text{CCH} = \text{N} - \text{NSO}_2\text{C}_7\text{H}_7 \overset{\text{RO}^-}{\rightarrow} \text{C}_3\text{CCH} = \text{N} - \text{NSO}_2\text{C}_7\text{H}_7
\end{align*}
\] (40)

\[
\text{C}_3\text{CCH}_2 + \text{ROD} \rightarrow \text{C}_3\text{CCD}_2 + \text{ROH}
\] (41)

The great difference in the amount of deuterium incorporated in the two experiments is probably due to solubility factors and the different methods of decomposition employed. First, the tosylhydrazone salt is much more soluble in ethylene glycol-d_2.
than is the diazo compound and thus has greater opportunity to undergo deuterium exchange with the solvent. Second, the salt was warmed quickly in the solvent from room temperature to 150° whereas the diazo compound was dropped into the solvent heated to a temperature above that for decomposition of the diazo compound. Thus in decomposition of the tosylhydrazone there is greater contact with solvent before decomposition occurs and a correspondingly greater opportunity for deuterium exchange and for formation of the diazonium ion intermediate. It is quite likely that much of the decomposition of the tosylhydrazone proceeds through the intermediate diazonium ion whereas the diazo compound decomposes primarily by a thermal carbenic process.
EXPERIMENTAL

General

Melting points. Melting points were determined on a modified Hershberg melting point apparatus using uncalibrated Anschutz thermometers unless otherwise noted.

Boiling points. Boiling points were obtained as the compounds distilled. Thermometer corrections were not made.

Infrared spectra. The infrared spectra of compounds prepared in this research were obtained with a Perkin-Elmer Infracord Spectrophotometer. Spectra of solid samples were obtained from potassium bromide wafers and those of liquid samples from liquid films.

Nuclear magnetic resonance spectra. Nuclear magnetic resonance spectra were determined in carbon tetrachloride with a Varian Associates A-60 instrument using tetramethylsilane as internal standard.

Mass spectra. Mass spectra were obtained on an Associated Electrical Industries MS-9 high resolution mass spectrometer.

Elemental analyses. Elemental analyses were performed by Microanalysis, Inc., Wilmington, Delaware

Solvents. Ether was purified by distillation from lithium aluminum hydride. Diglyme [bis(2-methoxyethyl)ether] was predried
by storage over calcium hydride and distilled under reduced pressure from lithium aluminum hydride. Reagent grade benzene and toluene were dried by distillation of 25% of the material. Reagent grade pentane was distilled and used without further purification.

**Intermediates**

2,2-Diphenylpropionitrile. Diphenylacetonitrile (262 g., 1.35 moles) in benzene (375 ml.) and ether (100 ml.) was added in 90 minutes to a stirred slurry of sodium hydride (53.4% mineral oil dispersion, 60.7 g., 1.35 moles) in ether (175 ml.). The mixture was refluxed and stirred for 30 hours. Addition of methyl iodide (192 g., 1.35 moles) in benzene (100 ml.) to the cooled reaction mixture over a 4.5 hour period produced continuously a precipitate of sodium iodide (74). The mixture was

(74) The procedure used was essentially that of P. L. Pickard and E. L. Engles, Ref. 53.

stirred for an hour after addition was complete, cooled in an ice bath, and washed with cold 10% acetic acid (200 ml.) to destroy unreacted sodium hydride. The layers were separated; the aqueous layer was extracted with ether (2 x 100 ml.); the combined organic portions were dried over calcium chloride, filtered, and concentrated under reduced pressure. Distillation yielded 2,2-diphenylpropionitrile [263 g., 1.27 moles, 94% yield, b.p. 144-147°/1.8 mm., lit. (53) b.p. 135°/1 mm.].
2,2-Diphenylpropanal. Ethyl acetate (13.22 g., 0.150 mole) was added in 45 minutes to a cold (0°) stirred slurry of lithium aluminum hydride (3.80 g., 0.100 mole) in ether (100 ml.). The mixture was stirred for 30 minutes at 0°, and then 2,2-diphenylpropionitrile (20.73 g., 0.100 mole) was added in three minutes (75). After stirring 30 minutes at room temperature the mixture was cooled to 0° and hydrolyzed with 5 N sulfuric acid (100 ml.). The layers were separated; the aqueous layer was extracted with ether (2 x 50 ml.); the combined ether solutions were washed with saturated sodium bicarbonate (50 ml.) and then with cold water (6 x 25 ml.) to remove ethyl alcohol, dried over sodium sulfate, filtered, and concentrated at reduced pressure to give an oil (19.6 g.). The infrared spectrum of the product showed carbonyl and aldehyde C-H absorptions and was identical to the infrared spectrum of 2,2-diphenylpropanal prepared by the method of Greene (51). Distillation gave 2,2-diphenylpropanal [9.41 g., 0.0448 mole, 45% yield, b.p. 117-119°/1.5 mm., lit. (51) b.p. 111-113°/1 mm.]. The semicarbazone derivative [m.p. 191.5-192.5°, lit. (76) m.p. 192°] was prepared.

(75) The general procedure was that of H. C. Brown and C. P. Garg, Ref. 52.

2,2-Diphenylpropanal tosylhydrazone. 2,2-Diphenylpropanal (24.90 g., 0.119 mole) and p-toluenesulfonyl hydrazide (tosyl hydrazide, 22.08 g., 0.119 mole) were dissolved in absolute ethanol (500 ml.) and concentrated hydrochloric acid (2 ml.). The solution was refluxed for two hours, and part of the ethanol (425 ml.) was removed by distillation. After filtering and cooling the solution, crystals were collected; recrystallization from ethanol gave 2,2-diphenylpropanal tosylhydrazone (30.74 g., 0.0813 mole, 69% yield, m.p. 156.5-157.5°).

Anal. Calcd. for \(C_{22}H_{22}N_2O_2S\): C, 69.81; H, 5.86; N, 7.40

Found: C, 69.80; H, 5.65; N, 7.69.

2,2-Diphenylpropylamine. (a) 2,2-Diphenylpropionitrile (5.00 g., 0.0241 mole) in ether (20 ml.) was added slowly to a stirred slurry of lithium aluminum hydride (1.14 g., 0.0301 mole) in refluxing ether (40 ml.). The mixture was refluxed and stirred for 12 hours. It was then cooled to 0° and hydrolyzed by adding successively water (1.2 ml.), 20% sodium hydroxide (0.90 ml.), and water (4.2 ml.) (77).


The granular inorganic solid was filtered and washed with ether. The combined ether portions were washed with water (15 ml.), dried over potassium carbonate, filtered, and concentrated under reduced pressure. The infrared spectrum of the oily residue
(5.27 g.) showed N-H absorption and no C=NN absorption. Distillation gave 2,2-diphenylpropylamine [4.36 g., 0.026 mole, 86% yield, b.p. 117-120°/0.1 mm., lit. (78) b.p. 156-157°/4 mm.].


(b) Diisobutylaluminum hydride (25% solution in hexane, 14.22 g., 0.100 mole) was added with stirring to 2,2-diphenylpropionitrile (20.73 g., 0.100 mole) at such a rate that the temperature did not exceed 40°. After addition was complete the mixture was stirred for one hour at room temperature. The addition product was then decomposed by heating for three hours at 180-195° (79).


Gas evolution began at about 180°. The residue solidified on cooling and was dissolved in ether (100 ml.). The product was hydrolyzed with 20% sodium hydroxide (90 ml.); the layers were separated; the aqueous layer was extracted with ether (3 x 50 ml.); the combined ether solutions were washed with water (2 x 100 ml.), dried over potassium carbonate, filtered, and concentrated under reduced pressure to give an oil (24.0 g.). Distillation gave 2,2-diphenylpropylamine (9.52 g., 0.045 mole, 45% yield, b.p. 123-125°/0.2 mm.). Its infrared spectrum was identical to that of the amine prepared above.
Ethyl N-2,2-diphenylpropyl carbamate (2,2-diphenylpropylurethane). Sodium carbonate (11.47 g., 0.108 mole) and ethyl chloroformate (9.13 g., 0.0915 mole) were added to a stirred aqueous suspension (50 ml.) of 2,2-diphenylpropylamine (17.57 g., 0.0832 mole). The solid which formed was thoroughly trituated. After excess sodium carbonate was added, the mixture was filtered and washed with water. Recrystallization from petroleum ether (65-110°) gave 2,2-diphenylpropylurethane [20.17 g., 0.0712 mole, 86% yield, m.p. 114.2-115.2°, lit. (80) m.p. 114-115°].

(80) G. Berti, Gazz. chim. ital., 90, 559 (1960).

1-Diazo-2,2-diphenylpropane. Anhydrous sodium acetate 17.50 g., 0.213 mole) was added to a cold (0°) solution of dinitrogen tetroxide [9.92 g., 0.107 mole (dinitrogen trioxide was removed by passing an oxygen stream through the liquid for 15 minutes)] in carbon tetrachloride. Ethyl N-2,2-diphenylpropyl carbamate (20.17 g., 0.0712 mole) was added with stirring to the mixture. After 20 minutes the mixture was poured into ice (75 g.)-water (75 ml.) (81). The layers were separated, the aqueous layer

(81) The general procedure used was that of E. H. White, J. Am. Chem. Soc., 77, 6008 (1955).

was extracted with ether (50 ml.); the combined organic portions were washed successively with water (100 ml.), 5% sodium carbonate (75 ml.), and water (100 ml.), dried over sodium sulfate, filtered,
and concentrated under reduced pressure to give a yellow viscous liquid (22.55 g.) which resisted attempts at crystallization. Its infrared spectrum showed N-NO absorption and no N-H absorption. Because of its instability N-carbethoxy-N-nitroso-2,2-diphenylpropylamine was reacted further without distillation.

Sodium methoxide (0.135 g., 0.00250 mole) in methanol (7 ml.) was added to N-carbethoxy-N-nitroso-2,2-diphenylpropylamine (3.12 g., 0.0100 mole) in ether (60 ml.) and maintained at -20° for 1.5 hours. Cold water (25 ml.) was added, and the layers were separated; the aqueous layer was extracted with ether (2 x 25 ml.); the combined ether portions were washed with cold water (25 ml.) and cold saturated sodium chloride solution (25 ml.); the solution was filtered and concentrated at -20° in a stream of dry nitrogen and finally under reduced pressure. 1-Diazo-2,2-diphenylpropane (2.22 g., 0.010 mole, 100% yield, m.p. ~ -5°) is an orange crystalline solid with strong infrared absorption at 2080 cm.-1. Purity as determined by nitrogen evolution from the acetic acid-catalyzed decomposition of a weighed sample was 100%. The diazo compound decomposed fairly rapidly above 0°.

(p-Chlorophenyl)-phenylacetonitrile. Bromine (176.0 g., 1.10 moles) was added slowly (1.5 hours) to hot (105-110°) stirred p-chlorophenylacetonitrile (151.6 g., 1.00 mole). Heating was continued for 15 minutes after addition was complete. Hydrogen bromide was removed by passing nitrogen over the surface of the liquid for 30 minutes. The reaction mixture was then transferred to an addition funnel, mixed with benzene (100 g., 1.30
moles), and added slowly (2 hours) to aluminum chloride (133.4 g., 1.00 mole) in refluxing benzene (368 g., 4.70 moles) (54). The mixture was refluxed for an hour after addition was complete and then cooled and hydrolyzed by pouring into a mixture of ice (1 kg.) and concentrated hydrochloric acid (100 ml.). The layers were separated; the aqueous layer was extracted with ether (2 x 250 ml.); the combined organic portions were washed successively with water (500 ml.), saturated sodium bicarbonate (250 ml.), and water (500 ml.). The organic solution was dried over sodium sulfate, filtered, and concentrated under reduced pressure to give a brown solid (220 g.). The residue was transferred to a Claisen flask and distilled under reduced pressure (b.p. 150-178°/3 mm.) to yield a yellow solid (196.0 g.) which after recrystallization from isopropanol gave (p-chlorophenyl)-phenylacetonitrile [165.5 g., 0.727 mole, 73% yield, m.p. 75.0-76.0°, lit. (55) m.p. 75-76°].

2-(4-Chlorophenyl)-2-phenylproponitrile. (p-Chlorophenyl)-phenylacetonitrile (159.4 g., 0.700 mole) in benzene (190 ml.) and ether (50 ml.) was reacted with a stirred slurry of sodium hydride (53.4% mineral oil dispersion, 31.5 g., 0.700 mole) in ether (90 ml.) and then with methyl iodide (99.4 g., 0.700 mole) in benzene (50 ml.) as was diphenylacetonitrile. There was obtained after distillation under reduced pressure, treatment of the distillate with neutral alumina (49.7 g.) in ether (311 ml.) to remove the red color, and a final distillation under reduced pressure 2-(4-chlorophenyl)-2-phenylpropionitrile (140.9 g., 0.619 mole, 83% yield, b.p. 138-140°/0.5 mm.).
Anal. Calcd. for $C_{15}H_{12}ClN$: C, 74.53; H, 5.01; Cl, 14.67; N, 5.80

Found: C, 74.32; H, 5.12; Cl, 14.61; N, 5.87.

2-(4-Chlorophenyl)-2-phenylpropanal. (a) 2-(4-Chlorophenyl)-2-phenylpropionitrile (12.09 g, 0.0500 mole) was reduced with lithium triethoxyaluminumhydride [0.0500 mole, prepared by adding ethyl acetate (6.61 g, 0.0750 mole) to lithium aluminum hydride (1.90 g, 0.0500 mole) in ether (50 ml.) at 0°] for 30 minutes in the same manner as 2,2-diphenylpropionitrile to give, after distillation under reduced pressure, 2-(4-chlorophenyl)-2-phenylpropanal (4.72 g, 0.0195 mole, 39% yield, b.p. 125-134°/0.5 mm.) (82).

(b) Diisobutylaluminum hydride (25% solution in hexane, 6.48 g., 0.0455 mole) was added in 25 minutes to cold (0-5°) stirred 2-(4-chlorophenyl)-2-phenylpropionitrile (10.00 g., 0.414 mole) in toluene (75 ml.). A nitrogen atmosphere was maintained during the reduction. After addition of all the hydride, the mixture was stirred for 30 minutes at room temperature. The clear solution
Figure 3.

Figure 4.
was then poured into a stirred mixture of ice (100 g.) and 10% sulfuric acid (50 ml.). Almost no reaction occurred until the mixture was warmed to 30° whereupon considerable gas was evolved. After standing 30 minutes at 30° the layers of the mixture were separated; the aqueous layer was extracted with benzene (2 x 25 ml.); the combined organic solutions were washed with saturated sodium bicarbonate (25 ml.) and water (30 ml.), dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation gave 2-(4-chlorophenyl)-2-phenylpropanal (6.75 g., 0.0263 mole, 64% yield, b.p. 121-124°/0.1 mm.).

2-(4-Chlorophenyl)-2-phenylpropanal tosylhydrazone. 2-(4-Chlorophenyl)-2-phenylpropanal (10.00 g., 0.0408 mole) and p-toluenesulfonyl hydrazide (7.63 g., 0.0410 mole) were dissolved in absolute ethanol (400 ml.) and concentrated hydrochloric acid (1 ml.). The solution was refluxed for 1.5 hours and part of the ethanol (350 ml.) was distilled. After filtering and cooling the solution, the crystals were collected. Recrystallization from ethanol gave 2-(4-chlorophenyl)-2-phenylpropanal tosylhydrazone (10.50 g., 0.0255 mole, 62% yield, m.p. 130.0-131.5°).

*Anal.* Calcd. for C₂₂H₂₁ClN₂O₃S:  C, 63.99; H, 5.13;
Cl, 8.59; N, 6.79

Found: C, 64.30; H, 5.29;
Cl, 8.18; N, 6.79.
α-Cyanobenzyl p-toluenesulfonate. α-Cyanobenzyl p-toluenesulfonate (m.p. 58-59°) was prepared from benzaldehyde, p-toluenesulfonyl chloride, and potassium cyanide by the method of Sisido et al (55) in 65% yield.

Phenyl-α-p-tolylacetonitrile. (a) α-Cyanobenzyl p-toluenesulfonate (200 g., 0.695 mole) in toluene (217 g., 2.36 moles) was added slowly (2 hours) to a stirred slurry of aluminum chloride (92.7 g., 0.695 mole) in refluxing toluene (167 g., 1.81 moles). The mixture was refluxed for two hours after addition was complete, cooled, and poured into a mixture of ice (800 g.) and concentrated hydrochloric acid (80 ml.) (55). The layers were separated; the aqueous layer was extracted with ether (3 x 100 ml.); the combined organic portions were washed successively with water (3 x 75 ml.), saturated sodium bicarbonate (3 x 50 ml.), and water (3 x 75 ml.). The organic solution was dried over sodium sulfate, filtered, concentrated under reduced pressure, and distilled (b.p. 100-123°/0.1 mm.) to give a viscous slightly yellow oil (137.9 g.) which crystallized on seeding. Three recrystallizations from ethanol gave phenyl-α-p-tolylacetonitrile [49.6 g., 0.239 mole, 34% yield, m.p. 61.0-62.0°, lit. (83) m.p. 62°].

(83) J. Hoch, Compt. rend., 197, 770 (1933).

(b) Phenylacetonitrile (117.1 g., 1.00 mole) and bromine (176.0 g., 1.10 moles) were reacted in the same manner as p-chlorophenylacetonitrile. To the crude stirred α-bromophenylacetonitrile in
toluene (461 g., 5.00 moles) maintained at 45-50° was added alumi-
num chloride (133.4 g., 1.00 mole) during 45 minutes. The
reaction mixture was heated for one hour at 60-65° and then
hydrolyzed by ice (1 kg.)-concentrated hydrochloric acid (100 ml.)
(56). The layers were separated; the aqueous layer was extracted
with ether (2 x 250 ml.); the combined organic portions were
washed successively with water (500 ml.), saturated sodium
bicarbonate (250 ml.), and water (500 ml.). The organic solu-
tion was dried over sodium sulfate, filtered, concentrated under
reduced pressure, and distilled (b.p. 143-147°/1 mm.) to give an
oil (122.4 g.) which crystallized on seeding. Three recrystal-
lizations from ethanol gave phenyl-p-tolylacetonitrile [64.5 g.,
0.315 mole, 31% yield, m.p. 61.0-62.0°, lit. (83) m.p. 62°].

2-Phenyl-2-(4-tolyl)-propionitrile. Phenyl-p-tolylacetono-
itride (114.5 g., 0.552 mole) in benzene (150 ml.) and ether
(40 ml.) was reacted with a stirred slurry of sodium hydride
(53.4% mineral oil dispersion, 24.8 g., 0.552 mole) in ether
(100 ml.) and then with methyl iodide (78.4 g., 0.552 mole) in
benzene (40 ml.) as was diphenylacetonitrile. There was obtained
after distillation under reduced pressure, treatment of the
distillate with neutral alumina (33 g.) in ether (100 ml.), and
final distillation under reduced pressure 2-phenyl-2-(4-tolyl)-
propionitrile (106.3 g., 0.480 mole, 87% yield, b.p. 129-132°/0.5 mm.).

Anal. Calcd. for C₁₆H₁₅N: C, 86.84; H, 6.83; N, 6.33
Found: C, 86.39; H, 7.02; N, 6.16.
2-Phenyl-2-(4-tolyl)-propanal. (a) 2-Phenyl-2-(4-tolyl)-
propionitrile (22.13 g., 0.100 mole) was reacted with lithium
triethoxyaluminohydride [0.100 mole, prepared by adding ethyl
acetate (13.22 g., 0.150 mole) to lithium aluminum hydride
(3.80 g., 0.100 mole) in ether (100 ml.) at 0°] for 15 minutes
in the same manner as 2,2-diphenylpropionitrile. Distillation
under reduced pressure gave a mixture (80-20) of 2-phenyl-2-
(4-tolyl)-propanal [14.24 g. (80% of 17.80 g.), 0.625 mole,
63% yield, b.p. (mixture) 118-124°/0.5 mm.] and an unidentified
higher boiling product.

(b) 2-Phenyl-2-(4-tolyl)-propionitrile (10.00 g., 0.432 mole)
in toluene (70 ml.) was reacted with diisobutylaluminum hydride
(25% solution in hexane, 7.07 g., 0.0497 mole) in the same
manner as 2-(4-chlorophenyl)-2-phenylpropionitrile to give after
distillation under reduced pressure 2-phenyl-2-(4-tolyl)-propanal
(5.20 g., 0.0232 mole, 51% yield, b.p. 130-133°/1.5 mm.).

Anal. Calcd. for C_{16}H_{16}O: C, 85.67; H, 7.19
Found: C, 85.75; H, 7.35.

2-Phenyl-2-(4-tolyl)-propanal tosylhydrazone. 2-Phenyl-2-
(4-tolyl)-propanal (2.24 g., 0.0100 mole) and p-toluenesulfonyl
hydrazide (1.88 g., 0.0101 mole) were dissolved in absolute
ethanol (125 ml.) and concentrated hydrochloric acid (1 ml.).
After refluxing the solution for four hours, part of the ethanol
(100 ml.) was distilled. The solution was filtered and cooled
and the crystals collected. Recrystallization from ethanol
gave 2-phenyl-2-(4-tolyl)-propanal tosylhydrazone (2.53 g., 0.00644 mole, 64% yield, m.p. 144.5-146.5°).

Anal. Calcd. for C_{23}H_{23}N_{2}O_{2}: C, 70.38; H, 6.16; N, 7.13
Found: C, 70.50; H, 6.17; N, 7.38.

(p-Methoxyphenyl)-phenylacetonitrile. Aluminum chloride (108.5 g., 0.890 mole) was added with stirring in small portions during one hour to a-cyanobenzyl p-toluenesulfonate (213.0 g., 0.740 mole) in anisole (392.0 g., 3.63 moles) maintaining the temperature at 5-10°. The mixture was then heated at 93-95° for seven hours, cooled, and poured into a mixture of ice (740 g.) and concentrated hydrochloric acid (74 ml.) (55). The layers were separated; the aqueous layer was extracted with benzene (2 x 100 ml.); the combined organic portions were washed successively with water (2 x 100 ml.), saturated sodium bicarbonate (2 x 100 ml.), and water (2 x 100 ml.) and steam distilled to remove the anisole. The residue was extracted with benzene (2 x 100 ml.); the benzene solution was dried over sodium sulfate, filtered, and concentrated at reduced pressure to yield a yellow solid (166.0 g.) which after recrystallization from ethanol gave (p-methoxyphenyl)-phenylacetonitrile [60.5 g., 0.271 mole, 37% yield, m.p. 129.5-130.0°, lit. (83) m.p. 130-131°].

2-(4-Methoxyphenyl)-2-phenylproponitrile. (p-Methoxyphenyl)-phenylacetonitrile (60.5 g., 0.271 mole) in benzene (300 ml.) and ether (70 ml.) was reacted with a stirred slurry of sodium hydride (53.4% mineral oil dispersion, 12.2 g., 0.271 mole) in ether (50 ml.) and then with methyl iodide (38.5 g., 0.271 mole)
in benzene (20 ml.) in the same manner as diphenylacetonitrile.
There was obtained after distillation under reduced pressure
(b.p. 142-164°/0.5 mm.) and treatment of the distillate with
neutral alumina (20 g.) in ether (125 ml.) a mixture of white
crystals and a cloudy colorless liquid. The crystals (starting
material, 6.0 g., 0.027 mole) were removed by filtration. A
second distillation under reduced pressure (b.p. 141-150°/0.5 mm.)
of the liquid (53.8 g.) gave a cloudy distillate which separated
into two layers after centrifugation. The layers were separated;
the upper layer (mineral oil) was discarded and the lower layer
distilled under reduced pressure to give 2-(4-methoxyphenyl)-2-
phenylpropionitrile [42.76 g., 0.180 mole, 74% yield (correcting
for 6.0 g., 0.027 mole of recovered starting material) b.p.
148-150°/0.5 mm.].

**Anal.** Calcd. for C_{16}H_{15}NO: C, 80.98; H, 6.37; N, 5.90
Found: C, 81.10; H, 6.50; N, 6.10.

2-(4-Methoxyphenyl)-2-phenylpropanal. (a) 2-(4-Methoxy-
phenyl)-2-phenylpropionitrile (20.00 g., 0.0843 mole) was reacted
with lithium triethoxyaluminohydride [0.0843 mole, prepared by
adding ethyl acetate (11.13 g., 0.126 mole) to lithium aluminum
hydride (3.20 g., 0.0843 mole) in ether (100 ml.) at 0°] for
30 minutes in the same manner as 2,2-diphenylpropionitrile.
Distillation under reduced pressure gave 2-(4-methoxyphenyl)-2-
phenylpropanal (11.28 g., 0.0470 mole, 56% yield, b.p. 154-
155/1.0 mm.).
Anal. Calcd. for C\textsubscript{16}H\textsubscript{16}O\textsubscript{2}: C, 79.97; H, 6.71

Found: C, 80.11; H, 6.71.

(b) 2-(4-Methoxyphenyl)-2-phenylpropionitrile (18.22 g., 0.0768 mole) in toluene (75 ml.) was reacted with diisobutylaluminum hydride (25\% solution in hexane, 12.00 g., 0.0845 mole) in the same manner as 2-(4-chlorophenyl)-2-phenylpropionitrile to give after distillation under reduced pressure 2-(4-methoxyphenyl)-2-phenylpropanal (10.85 g., 0.0452 mole, 59\% yield, b.p. 145-148°/0.5 mm.).

2-(4-Methoxyphenyl)-2-phenylpropanal tosylhydrazone.

2-(4-Methoxyphenyl)-2-phenylpropanal (5.00 g., 0.00208 mole) and \textit{p}-toluenesulfonyl hydrazide (3.87 g., 0.00208 mole) were dissolved in absolute ethanol (200 ml.) and concentrated hydrochloric acid (1 drop). The solution was refluxed for five hours, and part of the ethanol (160 ml.) was removed by distillation. After filtering and cooling the solution the crystals were collected; recrystallization from ethanol gave 2-(4-methoxyphenyl)-2-phenylpropanal tosylhydrazone (6.09 g., 0.00149 mole, 72\% yield, m.p. 120.5-122.0°).

Anal. Calcd. for C\textsubscript{23}H\textsubscript{23}N\textsubscript{2}O\textsubscript{3}: C, 67.62; H, 5.92; N, 6.86

Found: C, 67.78; H, 6.07; N, 6.93.

2-(4-Methoxyphenyl)-2-phenylpropylamine. 2-(4-Methoxyphenyl)-2-phenylpropionitrile (5.00 g., 0.0211 mole) and lithium aluminum hydride (1.00 g., 0.0263 mole) were reacted in refluxing ether (45 ml.) for 30 hours in the same manner as 2,2-diphenylpropionitrile to give, after distillation under reduced pressure,
2-(4-methoxyphenyl)-2-phenylpropylamine (4.36 g., 0.0181 mole, 86% yield, b.p. 147-150°/0.1 mm.).

**Anal.** Calcd. for C₁₆H₁₉NO: C, 79.65; H, 7.94; N, 5.81

Found: C, 79.25; H, 8.17; N, 5.76.

2-Phenylpropionitrile (hydratroponitrile). Phenylacetonitrile in liquid ammonia was treated with sodium amide and then methyl iodide by the procedure of Hauser to give 2-phenylpropionitrile (b.p. 91.0-91.5°/4 mm.) in 89% yield (84).


2-(4-Nitrophenyl)-2-phenylpropionitrile. 2-Phenylpropionitrile (hydratroponitrile, 33.1 g., 0.252 mole) was added to a cold (0°) stirred mixture of p-chloronitrobenzene (39.8 g., 0.252 mole) and powdered potassium hydroxide (84.9 g., 1.51 moles) in pyridine (399 g., 5.05 moles) (58). The dark blue mixture was stirred at 0° for 10 hours and then filtered to remove the potassium bromide-potassium hydroxide mixture. The pyridine solution was concentrated under reduced pressure and the liquid residue distilled to give, besides unreacted p-chloronitrobenzene (2.0 g., 0.05 mole) and an undetermined amount of hydratroponitrile, 2-(4-nitrophenyl)-2-phenylpropionitrile [39.0 g., 0.155 mole, 61% yield, b.p. 188-192°/0.5 mm., m.p. (from ethanol) 75.8-76.8°].

**Anal.** Calcd. for C₁₅H₁₂N₂O₂: C, 71.41; H, 4.80; N, 11.11

Found: C, 71.60; H, 4.73; N, 10.90.
2-(4-Nitrophenyl)-2-phenylpropanal. 2-(4-Nitrophenyl)-2-phenylpropionitrile (5.00 g., 0.0198 mole) in toluene (50 ml.) was reacted with diisobutylaluminum hydride (25% solution in hexane, 3.10 g., 0.0216 mole) in the same manner as 2-(4-chlorophenyl)-2-phenylpropionitrile to give, after distillation under reduced pressure, 2-(4-nitrophenyl)-2-phenylpropanal (3.59 g., 0.0141 mole, 71% yield, b.p. 187-189°C/0.5 mm.).

Anal. Calcd. for C_{15}H_{13}NO: C, 70.58; H, 5.13; N, 5.49

Found: C, 70.53; H, 5.21; N, 5.79.

2-(4-Nitrophenyl)-2-phenylpropanal tosylhydrazone. 2-(4-Nitrophenyl)-2-phenylpropanal (8.97 g., 0.0351 mole) and p-toluene-sulfonyl hydrazide (6.56 g., 0.0352 mole) were dissolved in absolute ethanol (360 ml.) and concentrated hydrochloric acid (1 ml.). The solution was refluxed for two hours, and part of the ethanol (300 ml.) was removed by distillation. After filtering and cooling the solution the crystals were collected. Recrystallization from ethanol gave 2-(4-nitrophenyl)-2-phenylpropanal tosylhydrazone (9.54 g., 0.0373 mole, 64% yield, m.p. 146.4-147.4°C).

Anal. Calcd. for C_{22}H_{21}N_3O_8: C, 62.39; H, 5.00; N, 9.92


2-(4-Nitrophenyl)-2-phenylpropanoic acid. 2-(4-Nitrophenyl)-2-phenylpropionitrile (2.00 g., 0.00793 mole) and 60% sulfuric acid (7 ml.) were heated for 10 hours at 155-160°C. The resultant dark mixture was cooled to room temperature and diluted with water (10 ml.); the crystals were collected and washed with cold water.
After two recrystallizations from ethanol (with charcoal treatment) there was obtained 2-(4-nitrophenyl)-2-phenylpropanoic acid (1.28 g., 0.000472 mole, 60% yield, m.p. 187-188.5°).

Anal. Calcd. for C_{15}H_{13}NO_{4}: C, 66.41; H, 4.83; N, 5.16

Found: C, 65.97; H, 4.71; N, 5.42.

2-(4-Nitrophenyl)-2-phenylpropanoyl chloride. Thionyl chloride (30.85 g., 0.259 mole) and 2-(4-nitrophenyl)-2-phenylpropanoic acid (7.83 g., 0.0288 mole) were reacted at 90° for three hours. Benzene (25 ml.) was added and the solution concentrated under reduced pressure to remove thionyl chloride; this process was repeated three times. Recrystallization from petroleum ether (65-110°) gave 2-(4-nitrophenyl)-2-phenylpropanoyl chloride (7.32 g., 0.0253 mole, 88% yield, m.p. 98.3-99.3°). Identification of the product is based on the infrared spectrum which showed 0 C-Cl and no OH absorption (Figure 4, p. 58).

2-(4-Nitrophenyl)-2-phenylpropanal tosylhydrazone. t-Butyl alcohol (2.47 g., 0.0334 mole) (85) was added in 40 minutes to a stirred slurry of lithium aluminum hydride (0.422 g., 0.111 mole) in diglyme (10 ml.). The resultant diglyme solution of lithium tri-t-butoxyaluminoxydride was transferred to an addition funnel and added in 50 minutes to a solution of 2-(4-nitrophenyl)-2-phenylpropanoyl chloride (3.22 g., 0.0111 mole) in cold (-78°) diglyme (15 ml.). The mixture was warmed to room temperature,
stirred for 55 minutes, and poured onto ice (50 g.). Benzene (50 ml.) was added, and the mixture was filtered; the layers were separated, and the aqueous layer was extracted with benzene (25 ml.). The combined organic portions were washed with water (5 x 15 ml.), dried over magnesium sulfate, filtered, and concentrated at reduced pressure. The infrared spectrum of the resulting oil (2.054 g.) showed C=O and C-H absorption. The product was dissolved in absolute ethanol (85 ml.) and concentrated hydrochloric acid (2 drops); p-toluenesulfonyl hydrazide (1.50 g., 0.0080 mole) was added, and the solution was refluxed for five hours; part of the ethanol (55 ml.) was removed by distillation during the last two hours. Further concentration and cooling produced no crystals; thus the product was chromatographed over silica acid (40% Celite). Concentration of the eluant gave 2-(4-nitrophenyl)-2-phenylpropanal tosylhydrazone [1.51 g., 0.0036 mole, 32% yield (from acid chloride), m.p. 148.4-150.0°]. Mixed melting point with 2-(4-nitrophenyl)-2-phenylpropanal tosylhydrazone prepared above was 143-146°.

Triphenylacetaldehyde tosylhydrazone. Triphenylacetaldehyde tosylhydrazone, m.p. 214.5-215.5° (86), was prepared as previously described (2a).

(86) The melting point was determined on a Fisher melting point block using an uncalibrated thermometer.
2-Diazo-1,1,1-triphenylethane. 2-Diazo-1,1,1-triphenylethane, decomposition point 81.0-83.0°C, was prepared as described previously (2a).

**Thermal decomposition and rearrangement of tosylhydrazones**

**General techniques**

The same general procedure was used for the decomposition of all the tosylhydrazones. Base (sodium methoxide, lithium methoxide, or butyllithium), tosylhydrazone, and solvent (diglyme) were mixed at room temperature. Sodium methoxide (87) and lithium methoxide (88) were weighed into dried tared containers in an environment of low relative humidity (~20%) and added to the solution quickly all at once; butyllithium (89) was added slowly by syringe. The mixture was then slowly (0.75-1.0 hr.) heated

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(87) Sodium methoxide (Matheson, Coleman, and Bell) was standardized by titration with standard hydrochloric acid using phenolphthalein indicator and found to be 93% pure. It was stored under nitrogen and sealed with paraffin wax.

(88) Lithium methoxide (Alfa Inorganics) having a titrated purity of 98.4% was kindly furnished by Mr. Gary Kauffman.

(89) Butyllithium (Foote Mineral Co., 15% solution in hexane) was standardized by titration with standard hydrochloric acid using phenolphthalein indicator.
to 125°. The volume of nitrogen evolved was measured using a gas buret previously described (90). The measuring apparatus con-

sisted of a reaction flask (50 ml.), condenser, gas buret, and manometer with a leveling bulb to adjust the mercury level in the manometer and buret. The measured volume was corrected to STP.

**Analysis of rearrangement products**

The decomposition products of all the tosylhydrazones were analyzed by the same procedure. The diglyme solution of the decomposed tosylhydrazone was diluted with water (15 ml.), and ether (15 ml.) was added; the layers were separated and the aqueous portion extracted with ether (2 x 10 ml.); the combined ether solutions were washed with water (5 x 10 ml.) to remove the diglymes, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residual oil was analyzed by gas chromatography. The chromatographic column employed for all except the decomposition products of the nitro-substituted tosylhydrazone was 10' x 1/4" FFAP (5%) on Chromsorb G; for the nitro-substituted tosylhydrazone the column was 5' x 1/8" FFAP (5%) on Chromsorb W (91). Representative analyses are shown in

(91) The instrument used in this case was a model 600D Aerograph.

Figures 5-7.
1. $\Phi_2CHCH_3$
2. $\Phi C(CH_3) = CH\Phi$(cis)
3. $\Phi_2C = CHCH_3$
4. $\Phi$
5. $\Phi CCH_2\Phi$
6. $\Phi C(CH_3)CH_2Bu$
7. $\Phi C(CH_3) = CH\Phi$(trans)
8. $\Phi_2C(CH_3)CHO$
9. $\Phi_2C(CH_3)CN$

Figure 5.

Figure 6.

Figure 7.
The remaining residue was dissolved in a mixture of acetone (15 ml.), water (5 ml.), and acetic acid (0.5 ml.) and oxidized with potassium permanganate (4:1 molar ratio) at room temperature for one hour (92). The excess permanganate was destroyed with sodium bisulfite, and the mixture was filtered; the precipitate was washed with acetone and hot water. The acetone was removed in an air stream on a steam bath, and the residue was extracted with ether (3 x 15 ml.). The ether was washed with saturated sodium bicarbonate solution (3 x 10 ml.) to remove the acidic components. The bicarbonate solution was acidified with hydrochloric acid and extracted with ether. The ether solution of aromatic acids was concentrated, and an ethereal solution of diazomethane (prepared from N-nitroso-N-methylurea) was added until the yellow diazomethane color did not fade. The ether solution was dried over magnesium sulfate and concentrated; the aromatic esters were analyzed by gas chromatography. The chromatographic column employed was 15 ft x 1/4" Dow Corning silicon oil #550 (5%) on Fluoropack.

Gas chromatography

A model A-90-C Aerograph gas chromatograph equipped with thermal conductivity cell detectors (helium carrier gas) and connected to a 2.5 millivolt full scale deflection Brown recorder.
was used for the analyses unless otherwise noted. All stationary phases and solid supports used in this research were purchased from Varian Aerograph, Walnut Creek, California.

Peak areas, calculated by multiplying the peak height by the peak width at half-height, were used to determine product composition. Quantitative measurements of the compositions of many mixtures of organic compounds can be made by using the peak areas resulting from gas chromatographic analyses (93). No


corrections were made for differences in thermal conductivities of the compounds involved (94).

(94) Studies of a representative mixture containing aromatic, cyclic, and aliphatic hydrocarbons, acetone, acetaldehyde, and methyl and ethyl alcohols indicate that the maximum error resulting from the assumption that all the compounds possess the same thermal conductivity is 3.5%. [K. Dimbat, P. E. Porter, and F. H. Stross, ibid., 28, 290 (1956)]. In the present study analyses made of known mixtures of methyl benzoate and methyl-\(\text{p}\)-chlorobenzoate, methyl benzoate and methyl-\(\text{p}\)-methoxybenzoate, and methylbenzoate and methyl-\(\text{p}\)-toluate deviated less than 2% from the known composition.

Decomposition of 2,2-diphenylpropanal tosylhydrazone.

2,2-Diphenylpropanal tosylhydrazone (0.500 g., 0.00132 mole) was dissolved in diglyme (8 ml.). Butyllithium (1.665 N in hexane, 0.99 ml., 0.00165 mole) was syringed in, and the stirred mixture was heated slowly to 126°. The mixture turned yellow, and nitrogen evolution began at approximately 65°. The entire heating process
required 0.75 hr., and the nitrogen (27.0 ml., 91% yield) was collected. The diglyme solution was diluted with water (15 ml.), and ether (15 ml.) was added; the layers were separated; the aqueous layer was extracted with ether (2 x 10 ml.); the combined ether portions were washed with water (5 x 10 ml.), dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give a red oil (0.4073 g.) (95). After analysis by gas chromatography, the remaining residue was oxidized with potassium permanganate as previously described to give benzoic acid in 49% yield.

(95) Diglyme could not be completely removed, and thus the amount of residue obtained is greater than the theoretical value.

gas chromatography, the remaining residue was oxidized with potassium permanganate as previously described to give benzoic acid in 49% yield.

Thermolysis of 1-diazo-2,2-diphenylpropane. 1-Diazo-2,2-diphenylpropane (0.120 g., 0.00054 mole) was dissolved in a cold (0°) mixture of pentane (50 ml.) and anhydrous calcium oxide (0.614 g., 0.0109 mole). The mixture was stirred for 30 minutes at 0° to remove any water present and then warmed to room temperature (~25°) and stirred for five hours to effect the decomposition. Nitrogen (18.6 ml., 92% yield) was collected. After removing the inorganic solids by filtration the solution was concentrated under reduced pressure to give an oil (0.159 g.) which was analyzed by gas chromatography (62).

Photolysis of 1-diazo-2,2-diphenylpropane. Attempts to photolyze 1-diazo-2,2-diphenylpropane (0.243 g., 0.00109 mole) in pentane (250 ml.) at -78° in a Pyrex vessel using first a
Westinghouse 125-watt sunlamp for 40 minutes and then a 450-watt broad spectrum high pressure Hanovia external lamp for two hours were unsuccessful. The solution was transferred to a quartz vessel; attempted photolyses at -78° using the 125-watt sunlamp for one hour and then a 100-watt broad spectrum high pressure Hanovia immersion lamp for 1.25 hours failed. Photolysis was effected by warming the solution to -35° and using the 100-watt Hanovia lamp for 1.25 hours. Nitrogen (22.2 ml., 87% yield) was collected. Concentration of the solution at reduced pressure gave an oil which was analyzed by gas chromatography (62).

Decomposition of triphenylacetalddehyde tosylhydrazone. Butyl-lithium (2.23 ml., 1.627 N in hexane, 0.00363 mole) was added with stirring to ethylene glycol-d$_2$ (7 ml.) (96). After the mixture had cooled to room temperature, triphenylacetalddehyde tosylhydrazone (1.84 g., 0.00418 mole) was added through Gooch tubing without exposure to the atmosphere. The stirred mixture was then plunged into a hot (150°) oil bath to effect the decomposition. Within two minutes the orange diazo compound began to form and decompose. After eleven minutes the mixture was cooled to room temperature, diluted with water, and made basic with sodium hydroxide solution. The layers were separated; the aqueous portion was extracted with petroleum ether (b.p. 30-60°, 2 x 20 ml.); the combined organic portions were washed with water (8 x 15 ml.), dried over magnesium sulfate, filtered, and concentrated under reduced pressure to

(96) The ethylene glycol-d$_2$ was shown by nuclear magnetic resonance to contain 1% protioethylene glycol.
give an oil (0.988 g.). The oil was chromatographed over silicic acid (15% Celite) to give, after crystallization from ethanol, triphenylethylene [0.3814 g., 0.00149 mole, 37% yield, m.p. 65.5-67.2°, lit. (97)m.p. 65.0-67.5°]. The nuclear magnetic resonance spectrum showed very little 1-hydrogen in the product; mass spectral analysis indicated that the product contained 85% 1-deuterio-1,2,2-triphenylethylene (Table 5).

**Decomposition of 2-diazol,1,1,1-triphenylethane.** 2-Diazo-1,1,1-triphenylethane (0.509 g., 0.00198 mole) was added in three minutes to hot (140°) stirred ethylene glycol-d₂ (6 ml.). Instant decomposition with nitrogen evolution occurred on the liquid surface to give a red oil. Water (25 ml.) and petroleum ether (b.p. 30-60°, 50 ml.) were added, and the layers were separated; the petroleum ether portion was washed with water (5 x 15 ml.), dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give an oil (0.867 g.). After crystallization from ethanol there was obtained triphenylethylene (0.223 g., 0.000871 mole, 44% yield, m.p. 66.0-68.0°). The nuclear magnetic resonance spectrum showed approximately as much 1-hydrogen as did the spectrum of an authentic sample of triphenylethylene. Mass spectral analysis indicated that the product contained 2% 1-deuterio-1,2,2-triphenylethylene (Table 6).