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THERMAL DECOMPOSITIONS OF AROMATIC
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AND ARYLDIAZOMETHANES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Gerald Gordon Vander Stouw, B. A.

*****

The Ohio State University
1964

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INTRODUCTION AND HISTORICAL

The chemistry of divalent carbon intermediates (1) has been the

(1) In this discussion the term "carbene" is used as a general
name for divalent carbon intermediates. The simplest such inter­
mediate, \( \cdot \text{CH}_2 \cdot \), is called methylene; other carbenes are named by
adding "-idene" to the name of the corresponding univalent radical.
Thus \( \cdot \text{CH}_3 \cdot \text{CH} \cdot \) is called ethylidene, \( \cdot \text{PhCH} \cdot \) is benzylidene, etc. [Inter­
national Union of Pure and Applied Chemistry Report on Nomenclature,
J. Am. Chem. Soc., 82, 5545 (1960)].

subject of considerable interest during the past several years. Car­
benes have been prepared from a variety of sources and evidence for
their existence has been found in a number of reactions. The prepara­
tions and reactions of carbenes have been extensively reviewed (2).

(2) (a) W. Kirmse, Angew. Chem., 71, 537 (1959). (b) J. Leitich,
Osterr. Chemiker-Ztg., No. 6, 164 (1960). (c) W. Kirmse, Angew. Chem.,
Carbon," The Ronald Press Company, New York, 1964. (g) H. M. Frey,

The addition of carbenes to unsaturated systems is well-known and
provides the basis for many useful syntheses. Many insertions of
carbenes across covalent bonds have also been observed.

In any discussion of carbenes it is necessary to consider the
distribution of the two non-bonded valence electrons in the inter­
mediate. The carbene may be either in the triplet state, with the
two electrons unpaired and each occupying a $2p$ orbital, or in the singlet state, with the two electrons in an $sp^2$ orbital and with a vacant $2p$ orbital.

![Diagram of triplet and singlet states]

Methylene produced by the photolysis of diazomethane adds stereospecifically to cis- and trans-2-butenes (3). On this basis the singlet state was assigned to methylene for this reaction. By similar means the singlet state was assigned to dibromomethylene (4), propylidene (5), carbethoxymethylene (6), and 2-ketopropylidene (5). The occurrence of non-stereospecific addition was used to assign the triplet state to propargylidene (5) and diphenylmethylene (7). The triplet state of diphenylmethylene is confirmed by electron paramagnetic resonance data (8).


(5) P. S. Skell and J. Klebe, ibid., 82, 247 (1960).
Quantum-mechanical calculations for methylene indicate a triplet ground state and a close-lying singlet excited state (9). Spectroscopic evidence suggests that when diazomethane is photolyzed in the presence of a diluent the singlet state is first formed and subsequently decomposes to the more stable triplet (10). Preliminary calculations based on this evidence indicate that the triplet ground state is linear. Chemical evidence for this decay is found in the fact that methylene produced in the presence of argon at high pressures adds non-stereospecifically to cis- and trans-2-butenes (11). The photosensitized decomposition of diazomethane gives triplet methylene which adds non-stereospecifically to cis- and trans-2-butenes (12).


Singlet methylene is produced by the thermal decomposition of diazo-
methane.

It is reasonable to conclude that thermal or direct photolytic
decomposition of diazomethane gives singlet methylene which undergoes
reaction more rapidly than spin inversion to the triplet state. This
should be generally true for carbenes except where certain structural
features facilitate spin inversion or allow direct formation of the
triplet state.

Benzylidene produced by the photolysis of phenyldiazomethane adds
stereospecifically to cis- and trans-2-butenes, indicating the carbene
to be reacting in the singlet state (13). The fact that the addition

(13) C. D. Gutsche, G. L. Bachman, and R. S. Coffey, Tetra-
edron, 18, 617 (1962).

is not completely stereospecific may suggest that the transition to
the triplet state is easier for benzylidene than for methylene.

Thermal and photolytic decompositions of diazo compounds con-
stitute one of the most important sources of carbenes (14). The present

(14) The chemistry of diazo compounds has been reviewed by

review is concerned principally with the preparation and decomposition
of aryldiazoalkanes.

Aryldiazoalkanes are prepared from a variety of sources. The
method first used for the formation of phenyldiazomethane was the
action of concentrated aqueous base on the N-nitroso derivative of
benzylurethan (15). This reaction has also been carried out with the


N-nitroso derivatives of benzylurea (16) and benzylnitroguanidine (17).


A widely used synthesis of aryldiazoalkanes is that of oxidation of the hydrazone of the appropriate aldehyde or ketone with a metallic oxide. Thus mercuric oxide reacts with benzaldehyde hydrazone to give phenyldiazomethane (18) and with benzophenone hydrazone to form diphenyldiazomethane (18,19). A number of ortho-substituted phenyl-

(18) H. Staudinger and A. Gaule, Ber., 49, 1897 (1916).

diazomethanes have been prepared in this way (13,20). Phenyldiazo-


methane prepared by this method is 40% pure (20b). Vacuum distillation increases the purity to 85-90% (20b,21), but the distillation is


reported to be quite hazardous (20b).
Several other procedures for the formation of phenyldiazomethane have been reported. Bamford and Stevens (22) obtained phenyldiazo-

methane by treatment of benzaldehyde tosylhydrazone with sodium ethoxide in ethylene glycol. Phenyldiazomethane is also reported to be formed in 65-70% purity by the reaction of benzaldehyde tosylhydrazone with sodium methoxide in pyridine at 55-65° (23), in 71%

purity by treatment of azibenzi with methanolic sodium hydroxide (24), and in 60% purity by reaction of sodium methoxide with N-nitroso-N-benzyl-p-toluenesulfonamide (25).

Diphenylidiazomethane is prepared by reaction of benzophenone hydrazone with mercuric oxide (18,19) or with iodine in triethylamine (26), or by reaction of oxygen with the adduct of benzophenone imine hydrochloride and ammonia (27). Dimesityldiazomethane is formed by


reduction of N-nitrosodimesitylketimine with lithium aluminum hydride (28).


Treatment of tosylhydrazones with sodium methoxide in aprotic solvents at 100-200° results in products which are believed to be formed from carbenes (29). These reactions apparently proceed through formation of the anion of the tosylhydrazone. The anion loses p-toluenesulfinic acid anion to give the diazo compound, which then loses nitrogen to form the carbene. This procedure has recently been used to generate carbenes from the tosylhydrazones of benzaldehyde, o-tolualdehyde, and mesitaldehyde (30).


The reactivity of benzylidene toward various sites has been studied by Gutsche, Bachman, and Coffey (13). When phenyldiazomethane is photolyzed in a mixture of benzene and cyclohexane, the ratio of phenylcycloheptatriene to benzylcyclohexane in the products indicates that the reactivity of benzylidene toward the aromatic ring is approximately the same as toward aliphatic C-H bonds. A very low reactivity toward the aromatic C-H bond is indicated by the formation of
phenylcycloheptatriene as the only product when the reaction is carried out in pure benzene. This reactivity may be increased by proximity effects; thus, photolysis of 2-(2-deuterophenyl)-phenyldiazomethane gives fluorene in excellent yield (31). In contrast to

\[ \text{(31) D. B. Denney and P. P. Klemchuk, J. Am. Chem. Soc., 80, 3289 (1958).} \]

benzylidene, methylene reacts with benzene to give cycloheptatriene and toluene in the ratio of 3:5 (32). Photolysis of phenyldiazomethane


in pentane results in a ratio of -CH\(_2\)- attack to -CH\(_3\) attack of 6:1 (13). The phenyl group in benzylidene evidently stabilizes the carbene sufficiently to give it a greater discriminatory ability than methylene.

Several examples of intramolecular insertion reactions by substituted benzylidenes have been reported. Gutsche and his coworkers observed 1,5; 1,6; and 1,7 insertions into \(\sigma\)-n-alkyl side chains (13,20). For example, the photolysis of \(\sigma\)-n-butylphenyldiazomethane gives benzosuberan, 2-methyltetralin, and 2-ethylindan in the ratio 1:5:6, along with minor amounts of 1-\(\sigma\)-tolyl-2-butene and 1-\(\sigma\)-tolylbutane (Equation 1). No 1,4 insertion to form 1-\(\sigma\)-propylbenzocyclobutene was observed. The intermediate in this reaction is probably reacting in the singlet state.
Thermal decomposition of dimesityldiazomethane at 140° results in formation of 4,6-dimethyl-1-mesitylbenzocyclobutene in 78% yield (Equation 2)(28).

Decompositions of aryldiazoalkanes have given a variety of products along with those resulting from intramolecular insertions and reactions with solvents. Hantzsch and Lehmann claimed that phenyldiazomethane decomposed to stilbene (15), but this was contradicted by the report of Staudinger and Gaule that benzaldazine was formed in quantitative

Photolysis at 70° of solutions of o-tolualdehyde tosylhydrazone or mesitaldehyde tosylhydrazone and sodium methoxide in cyclohexane is reported not to result in 1,4 insertions to form benzocyclobutenes (30).
yield (16). In the reactions studied by Gutsche and his coworkers, aldehydes, nitriles, azines, and stilbenes were observed. For example, the photolysis of o-n-butylphenyldiazomethane gives o-n-butylbenzaldehyde, o-n-butylbenzonitrile, o,o'-di-n-butylstilbene, and o,o'-di-n-butylbenzaldazine in addition to the hydrocarbons previously listed. The carbenoid decomposition of benzaldehyde tosylhydrazone results in formation of benzaldehyde, benzyl p-tolyl sulfone, stilbene, and benzaldazine (30).

The sulfone in the above case is probably formed by reaction of benzylidene with the p-toluenesulfinate anion (see Results and Discussion). Aldehydes presumably result from reaction of triplet carbenes with atmospheric oxygen. Nitriles are known to be formed from aromatic aldazines both by photolysis (33) and by thermal decomposition in the presence of aryldiazoalkanes (34).


The products of the photolysis of diphenyldiazomethane include 1,1,2,2-tetraphenylethane, benzophenone, and benzophenone azine (35).


The first product probably arises from a free radical process starting with the triplet carbene. A similar mechanism is used to explain the
formation of 2,2′-di(mesitylmethyl)-3,3′,5,5′-tetramethylstilbene as a second product in the thermolysis of dimesityldiazomethane (28).

Benzylidene has been prepared by several routes besides decompositions of phenyldiazomethane. These include the reactions of butyl lithium with benzyl chloride (36), diphenylbenzylsulfonium ion (37), benzal bromide (38), benzyl tosylate (39), and benzyl phenyl ether (40), and the reaction of phenyl lithium with methylene chloride (41). The products reported include those resulting from addition to olefins, those resulting from insertions into solvent C-H bonds (39,41), and also 1,2-diphenylethane (36,39) and stilbene (41).

In the present study phenyldiazomethane and substituted phenyldiazomethanes of high purity have been prepared by vacuum pyrolysis of the sodium salts of the appropriate tosylhydrazones. Benzylidene and substituted benzylidenes have been formed by thermal decomposition of these diazo compounds and by reaction of the tosylhydrazones with sodium methoxide in high-boiling solvents. Monomeric and coupling products have been identified by gas-liquid chromatography and by spectral methods. Particular attention has been focused on monomeric hydrocarbon products.

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(38) G. L. Closs, R. A. Moss, and J. J. Coyle, ibid., 84, 4985 (1962).
SUMMARY

A study has been made of the intramolecular and coupling reactions of substituted phenylmethylenes. Benzylidenes have been generated by the following reactions: thermal decompositions of o-tolualdehyde tosylhydrazone, mesitaldehyde tosylhydrazone, and duraldehyde tosylhydrazone with sodium methoxide in N-methylpyrrolidone or diethyl Carbitol; thermal decompositions of o-tolyldiazomethane in N-methylpyrrolidone and diethyl Carbitol; and thermal decompositions of pure phenyldiazomethane, o-tolyldiazomethane, 2,5-dimethylphenyldiazomethane, and 2,6-dimethylphenyldiazomethane.

The reactions in N-methylpyrrolidone and diethyl Carbitol result only in minor amounts of monomeric hydrocarbons, along with aldehydes, nitriles, alcohols, and coupling products. Decompositions of pure aryldiazoalkanes give similar products and also the following monomeric hydrocarbons: from o-tolyldiazomethane, benzocyclobutene (4-5%) and styrene (5-9%); from 2,5-dimethylphenyldiazomethane, 4-methylbenzocyclobutene (4%) and p-methylstyrene (7%); from 2,6-dimethylphenyldiazomethane, 3-methylbenzocyclobutene (17%) and m-methylstyrene (3%).

The formation of benzocyclobutenes is believed to result from insertion of carbenes into adjacent methyl groups. The orientation of the methylstyrenes suggests two possible mechanisms for their formation. In one of these a methylbenzylidene undergoes ring
expansion to a cycloheptatrienyldene, which rearranges to a styrene.
The other possible mechanism involves ring closure to a benzobicyclo-
butane, which opens to a styrene.
RESULTS AND DISCUSSION

The present investigation involves study of the intramolecular and coupling reactions of various arylmethylenes. o-Methylbenzylidene, 2,4,6-trimethylbenzylidene, and 2,3,5,6-tetramethylbenzylidene have been generated by reaction of the appropriate tosylhydrazones with sodium methoxide in N-methylpyrrolidone or diethyl Carbitol at 150-200°. Benzylidene, o-methylbenzylidene, 2,5-dimethylbenzylidene, and 2,6-dimethylbenzylidene have also been formed by thermal decomposition of the corresponding aryldiazomethanes. The monomeric and coupling products of these reactions have been identified by isolation, gas-liquid chromatography, and spectral methods. The questions of particular interest were whether a benzylidene will rearrange to a cycloheptatriene carbene (Equation 3) and whether an o-methylbenzylidene will insert into the adjacent methyl group to form a benzo[cyclobutene (Equation 4).

\[
\begin{align*}
\text{CH} & \rightarrow \text{CH} & \rightarrow \text{CH} \\
\text{CH}_2 & \rightarrow \text{CH} & \rightarrow \text{CH}_2
\end{align*}
\]

The occurrence of ring closure to a cyclobutene in the more highly substituted system, dimesitylmethylene, has been observed (28)
Reactions of tosylhydrazones with bases in aprotic solvents at 100–200° constitute an important method of generating carbenes as intermediates (29). These reactions apparently proceed as shown in Equation 5. The anion of the tosylhydrazone loses p-toluenesulfinate anion to form the diazo compound, which then loses nitrogen to give the carbene. A number of insertion reactions of carbenes prepared by this method have been observed (see Introduction and Historical). The possible formation and the subsequent fates of the intermediate benzylidenes as prepared by this method were therefore undertaken.

\[
\begin{align*}
R'-\text{CH}=\text{N}-\text{N-Tos} & \xrightarrow{\text{B}^+} R'-\text{CH}=\text{N}-\text{N-Tos} \xrightarrow{\text{Tos}^\ominus} R'-\text{CH}=\text{N}_2 \xrightarrow{\text{N}_2} R'-\text{CH}
\end{align*}
\]

\hspace{10cm}(5)

\(\alpha\)-Tolualdehyde tosylhydrazone was decomposed by reaction with sodium methoxide in N-methylpyrrolidone (NMP) under nitrogen at 160°. The volatile products were identified by gas-liquid chromatography and their yields were estimated by comparing peak sizes with those from standard samples of \(\alpha\)-xylene. The products identified were \(\alpha\)-xylene (0.3%), \(\alpha\)-tolualdehyde (0.2%), \(\alpha\)-tolunitrile (minor amount), \(\alpha\)-methylbenzyl alcohol (38%), and \(\alpha\)-methylbenzyl p-tolyl sulfone (4%) (Equation 6). The sulfone was isolated from the reaction products and identified by comparison with an authentic sample.
There was a very minor amount of a second C₈ hydrocarbon which had a retention time corresponding to both styrene and benzocyclobutene. Since later experiments showed that thermal decomposition of o-tolyl-diazomethane results in formation of both of these hydrocarbons, definite identification of the product of this experiment cannot be made. There were also two higher-boiling products which could not be identified. These may be compounds resulting from insertion of the carbene into N-methylpyrrolidone.

The source of o-xylene in this system is probably triplet o-methylbenzylidene, which abstracts two H atoms from other species in the system. An example of the same type of reaction is the formation of 1-o-tolylbutane during the photolysis of o-n-butylphenyldiazomethane (13).

The alcohol and the sulfone in this reaction appear to be formed
from an intermediate sulfinate, which undergoes rearrangement to form the sulfone or else is trans-esterified, probably by methanol formed from sodium methoxide, to give the alcohol (Equation 7). The aldehyde may result from splitting of a sulfinate anion (Equation 8) or from reaction of the carbene with oxygen present as an impurity.

\[
\begin{align*}
\text{Ar-CH}_2-\text{O-S-C}_7\text{H}_7 & \xrightarrow{\text{O}} \text{Ar-CH}_2-\text{S-C}_7\text{H}_7 \\
\text{Ar-CH}_2-\text{O-S-C}_7\text{H}_7 & \xrightarrow{\text{O}} \text{Ar-CH}_2-\text{S-C}_7\text{H}_7 \\
\text{Ar-CH}_2-0-\text{S-C}_7\text{H}_7 & \xrightarrow{\text{O}} \text{Ar-CH=0} + \text{C}_7\text{H}_7-\text{S}=\text{O} \\
\text{Ar-CH}_2-\text{N}=\text{H}-\text{SO}_2\text{C}_7\text{H}_7 & \xrightarrow{\text{O}} \text{Ar-CH} = \text{O-S-C}_7\text{H}_7 \\
\text{Ar-CH}_2-0-\text{S-C}_7\text{H}_7 & \xrightarrow{\text{O}} \text{Ar-CH}_2-0-\text{S-C}_7\text{H}_7
\end{align*}
\]

The formation of the sulfinate intermediate from the anion of the tosylhydrazone can be explained in several ways: internal combination of the aryl and sulfinate moieties, with simultaneous expulsion of nitrogen (Equation 9); protonation followed by loss of \text{p-toluene-sulfinate} anion and nitrogen to give a carbonium ion, which then combines with the \text{p-toluene-sulfinate} anion (Equation 10); or formation of the diazo compound, followed by loss of nitrogen, protonation, and combination with the anion in any of several orders (Equation 11). Methanol is probably the proton source in these processes.
The high yield of the alcohol in this reaction is probably related to the ability of N-methylpyrrolidone to function as an ionizing solvent. Other workers in the present laboratory have also obtained poor yields of hydrocarbons from carbenoid decompositions carried out in N-methylpyrrolidone.

The above mechanism may also be used to explain the formation of two alcohols in a total yield of 85% from the reaction of norbornane-1-carboxaldehyde tosylhydrazone with sodium methoxide in N-methylpyrrolidone at 180° (42) (Equation 12). The occurrence of skeletal rearrangement suggests that a carbonium ion process is involved in the

course of this reaction. The above mechanism is further supported by the finding that when the tosylhydrazone contains $^0\text{18}$, there is incorporation of $^0\text{18}$ into the product alcohols.

\[
\begin{align*}
\text{CH=N-N-Tos} & \quad \xrightarrow{\text{NaOCH}_3} \quad \text{OH} + \text{CH}_2\text{OH} \\
\text{NMP} & \quad 180^\circ
\end{align*}
\]

The rearrangement of sulfinate esters to sulfones has been previously observed (43,44). The reaction has been carried out in acid media and in alcohol-water and dioxan-water mixtures. Pure sulfinate esters rearrange thermally in high yield at temperatures above 100°C (43). The reaction in the present study may thus involve thermal rearrangement. The ionic character of the rearrangement (Equation 13) is suggested by substituent effects and by the fact that the reaction is facilitated by ionizing solvents.

\[
\begin{align*}
\text{R-S-OR}^* & \quad \xrightarrow{} \quad \text{R-SO}_2^- + \text{R}^+ \quad \xrightarrow{} \quad \text{R-S-R}^*
\end{align*}
\]

(13)

Mesitaldehyde tosylhydrazone was decomposed by reaction with sodium methoxide in refluxing N-methylpyrrolidone. The only product observed was 2,4,6-trimethylbenzyl $p$-tolyl sulfone (Equation 14), which was isolated in 43% yield and identified by analysis and mixed melting point.
o-Tolualdehyde tosylhydrazone was also decomposed with sodium methoxide in diethyl Carbitol (DEC) under nitrogen at 150°. The volatile products, identified by gas-liquid chromatography, were o-xylene (0.1%), o-tolualdehyde (0.7%), o-tolunitrile (2%), o-methylbenzyl alcohol (8%), cis-o,o'-dimethylstilbene (5%), trans-o,o'-dimethylstilbene (4%), and o-tolualdazine (3%) (Equation 15). There was a second C₈ hydrocarbon (0.2%), which again cannot be definitely identified. There was an additional high-boiling product, intermediate in retention time and peak area between the two stilbenes, which could not be identified but may be a product resulting from insertion of the carbene into diethyl Carbitol.

o-Methylbenzyl alcohol is probably formed by processes similar to those proposed for the reaction in N-methylpyrrolidone. The lower yield of alcohol in diethyl Carbitol may reflect the lesser ability of this solvent to function as an ionizing medium. Similar differences were observed in the reactions studied by Wilt, Schneider, and Parsons (42).
\( \text{CH}_3 \text{CH=N-N=SO}_2\text{C}_7\text{H}_7 \xrightarrow{\text{NaOCH}_3, \text{DEG}, 150^\circ} \text{CH}_3\text{CH} + \text{C}_8\text{H}_6 \)

\( \text{CHO} \xrightarrow{\text{cis} \ 5\%} \text{CH}_3\text{CHO} \)
\( \text{CN} \xrightarrow{\text{trans} \ 4\%} \text{CN} \)
\( \text{CH}_2\text{OH} \xrightarrow{\text{8}\%} \text{CH}_2\text{OH} \)

\text{o-Tolualdazine can arise from reaction of o-methylbenzylidene with o-tolyldiazomethane (Equation 16) or from bimolecular coupling of o-tolyldiazomethane with loss of nitrogen (Equation 17).}

\[
\begin{align*}
\text{Ar-CH+ N=N=CH-Ar} & \xrightarrow{\oplus} \text{Ar-CH=N-N=CH-Ar} \\
\text{Ar-CH=N=N} & \xrightarrow{\ominus \oplus} \text{Ar-CH=N-N=CH-Ar} \\
\text{Ar-CH=N-N=CH-Ar} & \xrightarrow{\ominus \oplus} \text{Ar-CH=N-N=CH-Ar}
\end{align*}
\]
\( \text{o-Tolualdazine is a likely precursor of o-tolunitrile and of the} \)
\( \text{two stilbenes. Benzonitrile is known to be formed by pyrolysis of} \)
\( \text{benzaldazine (45), but the reaction proceeds rapidly only at tempera-} \)
\( \text{tures above 300°. Zimmermann and Somasekhara showed that the pyrolysis} \)
\( \text{occurs at 150° in the presence of a catalytic amount of phenyldiazo-} \)
\( \text{methane (34). These conditions are comparable to those of the present} \)
\( \text{experiment. The mechanism proposed by these authors is shown in} \)
\( \text{Equation 18.} \)
\[
\begin{align*}
\text{Ar-CH=N-N=CH-Ar} + \text{Ar-CH} & \quad \rightarrow \quad \text{Ar-CH=N-N=CH-Ar} \\
& \quad \rightarrow \quad \text{Ar-CH=N-N=CH-Ar} \\
\end{align*}
\]
\( \text{It has also been suggested that the stilbenes in this system} \)
\( \text{result from reaction of benzaldehyde with phenyldiazomethane (Equation} \)
\( 19). \text{Earlier authors had proposed that stilbenes are produced by} \)
\( \text{coupling of phenyldiazomethane (14) (Equation 20).} \)
\[
\begin{align*}
\text{Ar-CH=N-N=CH-Ar} + \text{Ar-CH}=N_2 & \quad \rightarrow \quad \text{Ar-CH=N-N=CH-Ar} \\
& \quad \rightarrow \quad \text{Ar-CH=N-N=CH-Ar} \\
\text{Ar-CH=CH-Ar} + \text{Ar-CH}=N_2 & \quad \rightarrow \quad \text{Ar-CH=N-N=CH-Ar} \\
& \quad \rightarrow \quad \text{Ar-CH=N-N=CH-Ar} \\
\end{align*}
\]
Duraldehyde tosylhydrazone was also decomposed with sodium methoxide in refluxing diethyl Carbitol. It was thought that two o-methyl groups would increase the possibility of intramolecular insertion to form a benzocyclobutene. Preliminary examination of the products by gas-liquid chromatography showed a minor amount of pentamethylbenzene as the only monomeric hydrocarbon present. 2,2', 3,3', 5,5', 6,6'-Octamethylbibenzyl was also formed in minor quantity. This product probably results from coupling of triplet tetramethylbenzyldiene.

During the present study Nozaki, Noyori, and Sisido reported the photolysis of o-tolualdehyde tosylhydrazone and of mesitaldehyde tosylhydrazone in the presence of sodium methoxide in cyclohexane at 70° (30). The products and yields are shown in Equations 21 and 22. Gas-liquid chromatography was not employed by these authors, however.
Since in the present study decompositions of tosylhydrazones resulted in only very minor amounts of intramolecular insertion products, it was decided to isolate and decompose the desired aryldiazoalkanes. Examination of the available methods for preparation of aryldiazoalkanes indicates that the purity of the reported products is less than is desirable. For example, phenyldiazomethane prepared by oxidation of benzaldehyde hydrazone with mercuric oxide is only 40% pure, and purification by distillation is quite hazardous (20b). Other known procedures afford phenyldiazomethane of no better than ca. 70% purity (23-25).

In the present study highly pure aryldiazoalkanes have been prepared by pyrolysis of the sodium salts of the appropriate tosylhydrazones at pressures of 1-2 mm. mercury and bath temperatures of 90-120°. Under these conditions the diazo compounds distill as formed. Thus phenyldiazomethane is formed from the sodium salt of benzaldehyde tosylhydrazone, the sodium salt of o-tolualdehyde tosylhydrazone leads to o-tolyldiazomethane, etc. (Equation 23). 2,5-Dimethyl- and 2,6-dimethylphenyldiazomethanes have also been prepared by this method.
The aryldiazoalkanes are distilled without difficulty; the hazards reported by other workers (20b) may be due to the presence of water or of mercury compounds formed from mercuric oxide.

\[
\text{Ar}-\text{CH}=\text{N} = \text{N} - \text{SO}_2 \text{C}_7\text{H}_7 \xrightarrow{\oplus \text{Na}} \text{Ar}-\text{CH}=\text{N}_2 + \text{NaSO}_2 \text{C}_7\text{H}_7
\]  \hfill (23)

The average yields for these pyrolyses are as follows: phenyldiazomethane, 24%; o-tolyldiazomethane, 25%; 2,5-dimethylphenyldiazomethane, 26%; and 2,6-dimethylphenyldiazomethane, 38%. The low yields appear to be due to decomposition of the diazo compounds to the corresponding azines prior to distillation. The yields could probably be improved by varying the reaction conditions, but no thorough attempt was made to do this, since the primary objective was to obtain products of high purity. Treatment of these aryldiazoalkanes with excess acetic acid in ether at 0-10° results in evolution of 90-110% of the expected nitrogen. Dimethylphenyldiazomethanes appear to be the highest-boiling aryldiazoalkanes that can be obtained by this method; preparation of 2,4,6-trimethylphenyldiazomethane gave material which had undergone considerable decomposition.

o-Tolyldiazomethane was decomposed by addition to both N-methylpyrrolidone and diethyl Carbitol at 160°. The products were identified by gas-liquid chromatography (Equation 24). The reaction in N-methylpyrrolidone gave o-xylene (0.2%), a second C8 hydrocarbon in minor amount, o-tolualdehyde (2%), o-tolunitrile (0.8%), o-methylbenzyl alcohol (4%), \textit{cis}-o,o'-dimethylstilbene (6%), \textit{trans}-o,o'-dimethylstilbene (14%), and o-tolualdazine (6%). In diethyl Carbitol the products
were o-xylene (0.5%), a second C₆ hydrocarbon (minor amount),
o-tolualdehyde (1%), o-tolunitrile (0.7%), o-methylbenzyl alcohol
(0.7%), cis-o,o'-dimethylstilbene (15%), trans-o,o'-dimethylstilbene
(7%), and o-tolualdazine (1%). The reaction in diethyl Carbitol gave
an additional unidentified high-boiling product intermediate in reten-
tion time between the two stilbenes.

\[
\begin{align*}
\text{In NMP} & \quad \text{CH₃} \quad \text{CH=N₂} \quad \text{160°} \quad \text{NMP or DEC} \quad \text{CH₃} + \text{C₆H₆} \\
\text{In DEC} & \quad \text{CH₃} \\
\end{align*}
\]

Because decompositions of o-tolyl diazomethane in high-boiling
solvents did not give substantial yields of C₆H₆ hydrocarbons, it was
decided to decompose pure aryldiazoalkanes. The method primarily used
was that of pyrolytic gas-liquid chromatography. Samples of pure aryldiazoalkanes were injected into a gas chromatograph with the injector heated to sufficiently high temperatures that the diazo compounds decomposed immediately. It is believed that the aryldiazoalkanes decompose in the liquid state upon contact with the hot injector. Products were identified by comparison of their retention times with those of authentic samples. Monomeric hydrocarbon products were collected and studied further by spectral methods. Yields were estimated by comparison of peak sizes with the sizes of peaks from measured samples of aromatic hydrocarbons having the same number of carbon atoms as the aryldiazoalkanes (toluene, o-xylene, mesitylene). Tarry residues were found in the injector after these decompositions, indicating that considerable amounts of the diazo compounds went to form non-volatile and polymeric products. Samples of phenyldiazomethane and o-tolylidiazomethane were also decomposed thermally in reaction flasks under nitrogen and the products were analyzed by gas-liquid chromatography. The products and yields obtained in these experiments were similar to those resulting from pyrolytic gas-liquid chromatography.

Phenyldiazomethane was decomposed both by pyrolytic gas-liquid chromatography and in a reaction flask under nitrogen. Pyrolytic gas-liquid chromatography resulted in formation of benzene (average yield 0.7%), toluene (0.5%), benzaldehyde (0.4%), benzonitrile (2%), benzyl alcohol (1%), cis-stilbene and bibenzyl (2%), trans-stilbene (5%), and benzaldazine (1%). The products of the reaction under nitrogen were benzene (0.1%), toluene (0.1%), benzaldehyde (3%), benzonitrile (3%), benzyl alcohol (0.3%), cis-stilbene and bibenzyl (4%).
trans-stilbene (8%), and o-tolualdazine (3%). The products are shown in Equation 25. cis-Stilbene and bibenzyl cannot be distinguished under the conditions used, so it is not certain whether bibenzyl was formed.

\[
\text{Ph-CH=N}_2 \rightarrow \text{PhH} + \text{PhCH}_3 + \text{PhCHO} + \text{PhCN} + \text{PhCH}_2\text{OH}
\]

(a) Pyrolytic g.l.c. 
(b) Under \( N_2 \)

<table>
<thead>
<tr>
<th></th>
<th>0.7%</th>
<th>0.5%</th>
<th>0.4%</th>
<th>2%</th>
<th>1%</th>
</tr>
</thead>
</table>

+ (Ph-CH=CH-Ph+Ph-CH\(_2\)-CH\(_2\)-Ph) + Ph-CH=CH-Ph

\[
\text{cis} \quad 2\% \quad 5\%
\]

\[
\text{trans} \quad 4\% \quad 8\%
\]

+ Ph-CH=N-N=CH-Ph

(a) 1%
(b) 3%

The formation of benzene probably occurs by thermal fragmentation of some other product or intermediate to give a phenyl radical which then extracts \( \text{H}^+ \). Benzyl alcohol is probably formed by reaction of benzylidene with water present as an impurity.

Decompositions of o-tolylidiazomethane both by pyrolytic gas-liquid chromatography and by pyrolysis under nitrogen gave material corresponding in retention time to both benzocyclobutene and styrene in an average yield of 12%. The spectral data discussed below showed this to be a mixture of the two hydrocarbons. The products from pyrolytic gas-liquid chromatography were thus (Equation 26) toluene (average yield 0.4%), o-xylene (0.2%), benzocyclobutene (4%), styrene (7%), o-tolu-aldehyde (0.5%), o-tolunitrile (2%), cis-o,o'-dimethylstilbene (2%),
29

\[ o,o'\text{-dimethylbibenzyl (5\%), trans-}o,o'\text{-dimethylstilbene (4\%), and} \]
\[ o\text{-tolualaldazine (2\%). The reaction under nitrogen gave toluene (0.3\%),} \]
\[ o\text{-xylene (0.4\%), benzocyclobutene (4\%), styrene (9\%), }o\text{-tolualdehyde} \]
\[ (0.9\%), o\text{-toluntrile (3\%), }o\text{-methylbenzyl alcohol (2\%), cis-}o,o'\text{-} \]
\[ dimethylstilbene (5\%), o,o'\text{-dimethylbibenzyl (11\%), trans-}o,o'\text{-} \]
\[ dimethylstilbene (9\%), and }o\text{-tolualaldazine (2\%).} \]

Samples of the C\textsubscript{8} hydrocarbon product were collected. The infra-
red spectrum of this material (Figure 7) indicated it to be a mixture
of styrene and benzocyclobutene. There was a sharp band of medium
intensity at 10.03\( \mu \) and strong sharp bands at 12.8\( \mu \) and 14.0\( \mu \). The
first of these suggests the presence of a cycloalkyl ring; the latter
two are characteristic of benzocyclobutene (46) (Figure 9). The

(46) M. P. Cava and D. R. Napier, J. Am. Chem. Soc., 80, 2255
(1958).

presence of styrene was confirmed by a maximum at 248 m\( \mu \) in the ultra-
violet spectrum of the collected material (Figure 15). This maximum
is found in the ultraviolet spectrum of an authentic sample of styrene
(Figure 16). Analysis of the collected material by gas-liquid chroma-
tography on a capillary column showed it to be a mixture of 63%
styrene and 37% benzocyclobutene. Decomposition of \( o\text{-tolyldiazo-} \]
methane under nitrogen gave a mixture which was 65% styrene and 35%
benzocyclobutene.

Benzocyclobutene is evidently formed by insertion of the carbene
into the adjacent methyl group (Equation 4). The formation of styrene
is discussed below.
(a) Pyrolytic
(b) Pyrolysis
under N₂
Pure o-tolyldiazomethane was photolyzed for twenty hours at 20° with a 425-watt mercury vapor lamp. The product was a yellow solid which was analyzed by gas-liquid chromatography. The products observed were o-tolualdehyde (minor amount), o-methylbenzyl alcohol (minor amount), cis-o,o'-dimethylstilbene (4%), trans-o,o'-dimethylstilbene (19%), and o-tolualdazine (74%). No insertion products were observed. This is in agreement with the observation of Zimmermann and Paskovich that the photolysis of dimesityldiazomethane does not give insertion to form 4,6-dimethyl-1-mesitylbicyclo[4.3.0]octa-2,5-diene (28).

Decomposition of 2,5-dimethylphenyldiazomethane by pyrolytic gas-liquid chromatography resulted in formation of 4-methylbicyclo[4.3.0]octa-2,5-diene (4%), p-methylstyrene (7%), 2,5-dimethylbenzaldehyde (minor amount), 2,5-dimethylbenzonitrile (3%), 2,5-dimethylbenzyl alcohol (minor amount), 2,2',5,5'-tetramethylstilbenes (63%) and 2,5-dimethylbenzaldazine (6%) (Equation 27).
The two C₉H₁₀ hydrocarbons were collected as a mixture and were identified by spectral data. Other products were identified by their retention times. Yields were estimated by comparing peak sizes with those from standard samples of mesitylene.

The infrared spectrum of the hydrocarbon mixture (Figure 10) showed olefinic absorption at 6.16μ and absorption at 10.05μ which is believed to be characteristic of a cycloalkyl ring (46). There was strong absorption at 12.1μ and moderate absorption at 13.7μ. These two absorptions are found in the spectrum of authentic p-methylstyrene.
The absorptions at 12.7 and 14.1 μ which are characteristic of m-methylstyrene (Figure 12) were absent.

The ultraviolet spectrum of the mixture contained a maximum at 254 μ (Figure 17), corresponding to the maximum in the spectrum of authentic p-methylstyrene (Figure 18).

The nuclear magnetic resonance spectrum of the mixture (Figure 21) showed a triplet at 7.72 μ (Ar-CH₃), a singlet at 6.95 μ (cycloalkyl protons in 4-methylbenzocyclobutene), a complex series of absorptions from 4-5.1 μ (olefinic protons), and a multiplet from 2.8-3.2 μ (Ar-H). The cycloalkyl protons in benzocyclobutene absorb at 6.86 μ (47).


The relative areas of the absorptions for the cycloalkyl and olefinic protons indicate that the mixture contains 69% p-methylstyrene and 31% 4-methylbenzocyclobutene. Analysis of the mixture by gas-liquid chromatography at a lower temperature shows that it is 67% p-methylstyrene and 33% 4-methylbenzocyclobutene. The latter figures are believed to be more accurate because of difficulties in correctly integrating the complex olefinic absorptions in the nuclear magnetic resonance spectrum.

Decomposition of 2,6-dimethylphenyldiazomethane by pyrolytic gas-liquid chromatography gave the following monomeric products: 3-methylbenzocyclobutene (17%), m-methylstyrene (3%), 2,6-dimethylbenzonitrile (7%), and 2,6-dimethylbenzyl alcohol (1%) (Equation 28).
The two hydrocarbons were collected as a mixture. The infrared spectrum of this material (Figure 14) showed olefinic absorption at 6.2μ and cycloalkyl absorption at 10.05μ. There were strong bands at 12.7μ and 14.1μ, corresponding to those in the spectrum of authentic m-methylstyrene (Figure 12). The absorptions for o-methylstyrene at 13.0μ and 13.7μ (Figure 11) were absent.

The ultraviolet spectrum of the mixture (Figure 19) exhibited a maximum at 251μ, which is present in the spectrum of authentic m-methylstyrene (Figure 20).

The nuclear magnetic resonance spectrum of the mixture (Figure 22) showed singlets at 7.92τ and 7.77τ (Ar-CH₃), a singlet at 7.01τ (cycloalkyl protons), complex absorptions from 4-5τ (olefinic protons), and a multiplet at 3.2τ (Ar-H).

The relative sizes of the olefinic and cycloalkyl absorptions indicated that the mixture contained 91% 3-methylbenzocyclobutene and
9% \textit{m}-methylstyrene. Analysis by gas-liquid chromatography on a capillary column showed the percentages to be 87% \textit{3}-methylbenzocyclobutene and 13% \textit{m}-methylstyrene.

To determine whether the styrenes found in these decompositions were formed by rearrangement of benzocyclobutenes, it was attempted to rearrange benzocyclobutene by pyrolytic gas-liquid chromatography at 164° and at 237°. In both cases benzocyclobutene was recovered unchanged, indicating that it is probably not an intermediate in the formation of styrene from \textit{o}-tolylidiazomethane.

When benzocyclobutene is synthesized by pyrolysis of 1,3-dihydroisothianaphthene-2,2-dioxide at 770°, the product contains 2% styrene, which is probably formed by thermal rearrangement of benzocyclobutene (48). No styrene is found at lower temperatures, however.

\textit{(48) M. P. Cava and A. A. Deana, J. Am. Chem. Soc., 81, 4266 (1959).}

The five mechanisms given below appear to be plausible routes for the formation of styrenes from \textit{o}-methylbenzylidenedes. Only the last two of these will fit the observations that thermal decomposition of 2,5-dimethylphenyldiazomethane leads to \textit{p}-methylstyrene, while \textit{m}-methylstyrene results from thermolysis of 2,6-dimethylphenyldiazo-

methane.

The first possible mechanism involves proton transfer followed by ring closure to a bicyclic intermediate, which rearranges to a styrene. This process would lead to \textit{m}-methylstyrene from
2,5-dimethylphenyldiazomethane (Equation 29) and to o-methylstyrene from 2,6-dimethylphenyldiazomethane.

A second possible mechanism is that of ring closure and methyl migration to form a 1-methylbenzocyclopropene, followed by opening of the three-membered ring to give a styrene. The preparation of 1,1-dimethyl-3-carbomethoxybenzocyclopropene has recently been reported (49). The products resulting from opening of the three-membered ring have not yet been determined. It seems reasonable to assume that the cyclopropene ring could split in two ways. In the reactions investigated in the present study, this would result in formation of mixtures of methylstyrenes from 2,5-dimethylphenyldiazomethane (Equation 30) and 2,6-dimethylphenyldiazomethane.

Another possible mechanism involves formation of an intermediate benzobicyclobutane. The four-membered ring in this species could open in two ways. One type of ring opening would lead to \( m \)-methylstyrene from 2,5-dimethylphenyldiazomethane (Equation 31) and to \( o \)-methylstyrene from 2,6-dimethylphenyldiazomethane.

Opening of the benzobicyclobutane intermediate in the opposite direction would lead to the methylstyrenes found in the present study: \( p \)-methylstyrene from 2,5-dimethylphenyldiazomethane.
(Equation 32) and \( m \)-methylstyrene from 2,6-dimethylphenyldiazomethane.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{CH} \quad \text{CH} & \quad \text{CH} = \text{CH}_2 \\
\text{CH}_2 & \\
\end{align*}
\]

\((32)\)

Another mechanism which would lead to the methylstyrenes found in the present investigation involves ring expansion to a substituted cycloheptatrienyldiene, which rearranges to a styrene. This pathway also explains the formation of \( p \)-methylstyrene from 2,5-dimethylphenyldiazomethane (Equation 33) and of \( m \)-methylstyrene from 2,6-dimethylphenyldiazomethane.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\text{CH} \quad \text{CH} & \quad \text{CH}_3 \\
\text{CH}_3 & \\
\end{align*}
\]

\[
\begin{align*}
\text{insertion} & \quad \text{H}_3\text{C} \\
\text{CH}_2 & \quad \text{H}_3\text{C} \quad \text{CH} = \text{CH}_2 \\
\end{align*}
\]

\((33)\)

Ring expansions resembling that proposed have been previously observed. For example, cycloheptatriene is a product of the reaction of benzene with methylene (32), and phenylcycloheptatriene is formed by reaction of benzylidene with benzene (13) (Equation 34).

\[
\begin{align*}
& \quad \text{CH} - \text{Ph} \\
& \quad \text{CH} - \text{Ph} \quad \text{CH} - \text{Ph} \\
\end{align*}
\]

\((34)\)
The formation of 2-anilino-7H-azepine from pyrolysis of phenyl azide in the presence of aniline is believed to proceed through intramolecular ring expansion of an aromatic nitrene (50) (Equation 35). This reaction is thus quite similar to that proposed in the present investigation.


There is at present no evidence available which would permit a choice between the two mechanisms which lead to the observed methylstyrenes. The following experiments might be expected to give data on which such a choice could be based.

One approach to the further investigation of the mechanism of styrene formation is that of decomposing appropriate deuterated diazo compounds. For example, thermal decomposition of o-tolyl-α-deutero-diazomethane will result in formation of α-deuterosylene if the reaction proceeds through a benzobicyclobutane intermediate (Equation 36).
If a cycloheptatrienylidene intermediate is involved, the product will be α-deuterostyrene (Equation 37).

The information obtained by use of deuterated materials should be confirmed by decomposition of $^{14}C$-containing aryldiazomethanes. A reaction proceeding through a benzobicyclobutane will give a styrene in which $^{14}C$ is in the α-position of the olefinic group (Equation 38), while the rearrangement of a cycloheptatrienylidene will result in incorporation of $^{14}C$ into the aromatic ring of the product (Equation 39).
Further information about the possibility of a cycloheptatrienylidene intermediate could be gained by generating such carbenes from other sources. Possible approaches to these intermediates would include thermal decompositions of diazocycloheptatrienes, if these compounds can be prepared. The finding of the predicted styrenes in the products of these decompositions would constitute an important indication that cycloheptatrienylidenes are intermediates in the present study.
EXPERIMENTAL

General Information

Melting points.---Melting points were determined on a melting point block manufactured by the Fisher Scientific Company. All melting points are uncorrected.

Elemental analyses.---Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, and by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Infrared spectra.---Infrared spectra were obtained with recording spectrophotometers manufactured by Baird Associates (Model B) and by the Perkin-Elmer Corporation (Infracord Spectrophotometer and No. 137 Sodium Chloride Spectrophotometer). The spectra of solid samples were obtained from potassium bromide wafers, those of liquid samples from liquid films.

Ultraviolet spectra.---Ultraviolet spectra were obtained with a Perkin-Elmer No. 202 recording spectrophotometer.

Nuclear magnetic resonance spectra.---Nuclear magnetic resonance spectra were determined with an A-60 instrument manufactured by Varian Associates.

Gas-liquid chromatography.---Gas-liquid chromatography was carried out on the following instruments: (a) an Aerograph A-90-C gas chromatograph (Wilkens Instrument and Research, Incorporated); (b) an Aerograph A-90-F; (c) a Barber-Colman Series 5000 Selecta-System
(Barber-Colman Company); (d) a Barber-Colman Model 20. Instrument (d) was equipped with a hydrogen flame detector and employed nitrogen as the carrier gas; the others were equipped with thermal conductivity detectors and employed helium as the carrier gas.

The columns used in instruments (a); (b); and (c) were of dimensions 3/8 in. by 5 ft.; 1/4 in. by 5 ft.; and 1/4 in. by 10 ft. Preparative gas-liquid chromatography was done on instrument (b) with 3/8 in. columns; 1/4 in. columns were used for analytical work. The column packings consisted of firebrick coated with ca. 20% adsorbent. The adsorbents used are mentioned with the various experiments. The column used in instrument (d) was a 100 ft. capillary column coated with squalane.

Sample collectors consisted of small test tubes fitted with rubber septa through which were inserted pieces of 3 mm. glass tubing to serve as inlets and outlets. The gas emerging from the chromatograph was passed through a series of two collectors; the first was immersed in ice water and the second in a bath of Dry Ice and acetone or isopropanol.

Peak areas were estimated by multiplying the peak height by the width at the midpoint of the vertical axis. Percentage compositions were estimated by comparing peak areas with the areas of the peaks from measured standard samples. It has been shown that quantitative estimates can be made from peak areas (51). The assumption that

isomers have equal thermal conductivities causes a maximum error of 3.5% (52). Calculations involving components of different molecular


weights were based on the assumption that peak areas are proportional to the weights of the various components (53).


Solvents. — Diethyl Carbitol (diethylene glycol diethyl ether) and N-methylpyrrolidone were purified before use by storage for several days over potassium hydroxide pellets followed by distillation over calcium hydride.

Intermediates

Aromatic aldehydes

α-Tolualdehyde. — α-Bromo-α-xylene (Matheson, Coleman, and Bell Division, Matheson Chemical Corporation) was converted to α-tolu-aldehyde in 77% yield by reaction with the sodium salt of 2-nitro-propane according to the procedure of Hass and Bender (54). Analysis


by gas-liquid chromatography on a Carbowax 20-M column at 140° showed that α-tolualdehyde prepared by this method was not contaminated by isomeric aldehydes or by acetophenone.
2,5-Dimethylbenzaldehyde.—A mixture of 99.9% p-xylene (100 g., 0.94 mole) (Phillips Petroleum Company), glacial acetic acid (290 ml.), concentrated hydrochloric acid (630 ml.), and 37% formaldehyde solution (65 g., 0.77 mole) was stirred vigorously at 50-60° for 24 hours. Additional formaldehyde solution (19 g., 0.23 mole) was added and stirring was continued for 24 hours. The mixture was cooled and extracted three times with benzene (150 ml.). The combined extracts were washed with 10% sodium carbonate solution and water, dried, filtered, and concentrated to give 2,5-dimethylbenzyl chloride (87.7 g., 60%), b.p. 104-106°.

Sodium (13.1 g., 0.57 mole) was dissolved in absolute ethanol (500 ml.). 2-Nitropropane (50.7 g., 0.57 mole) and 2,5-dimethylbenzyl chloride (87.7 g., 0.57 mole) were added and the solution was stirred for four hours. The solution was filtered and concentrated and the residue was diluted with ether (100 ml.) and water (150 ml.). The ether layer was washed twice with 10% sodium hydroxide solution (50 ml.) and with water (50 ml.), dried, and concentrated. Distillation of the residue gave 2,5-dimethylbenzaldehyde (57.8 g., 76%), b.p. 63-69°.

2,6-Dimethylbenzaldehyde.—2,6-Dimethylaniline (100 g., 0.83 mole) (Aldrich Chemical Company, Incorporated) was added to 48% hydrogen bromide solution (250 ml.) at 0°. The resulting suspension was stirred at 0-5° and a solution of sodium nitrite (58 g., 0.84 mole) in water (100 ml.) was added slowly. The resulting solution was added in thirty minutes to a boiling solution of cuprous bromide (66 g.) and 48% hydrogen bromide solution (67 ml.). The product was steam-distilled and the distillate was extracted with ether. The
ether solution was washed with 5% sodium hydroxide solution and water, dried, and concentrated. Distillation of the residue gave 2,6-dimethylbromobenzene (51.7 g., 34%), b.p. 65-67°C.

A solution of 2,6-dimethylbromobenzene (51.7 g., 0.28 mole) and bromoethane (61 g.) in anhydrous ether (280 ml.) was added in ninety minutes to magnesium turnings (24 g.) and anhydrous ether (42 ml.) under nitrogen. The resulting solution of 2,6-dimethylphenylmagnesium bromide was poured onto stirred Dry Ice (168 g.). A hard dark solid was formed and was treated with 20% hydrochloric acid (225 ml.). The solid went into solution and ether and water layers separated. The ether layer was washed with water and extracted with 10% sodium hydroxide solution (250 ml.). The extract was acidified with 20% hydrochloric acid (70 ml.). The resulting precipitate was filtered, washed with water, and dried to give 2,6-dimethylbenzoic acid (32 g., 76%), m.p. 120-121°C, lit. m.p. 116°C (55).


2,6-Dimethylbenzoic acid (42.5 g., 0.28 mole) and thionyl chloride (52.2 g., 0.44 mole) were refluxed for two hours. Distillation of the product gave 2,6-dimethylbenzoyl chloride (43.4 g., 91%), b.p. 79-80°C. A solution of the chloride in anhydrous ether (115 ml.) was added slowly to a solution of lithium aluminum hydride (9.25 g., 0.24 mole) in anhydrous ether (1 l.). The resulting solution was stirred for twenty hours. Water was added cautiously to destroy excess lithium aluminum hydride and the solution was poured onto ice and 10%
hydrochloric acid (600 ml.). The ether layer was washed with 10% sodium bicarbonate solution, dried, and concentrated to give 2,6-dimethylbenzyl alcohol (30.5 g., 87%), m.p. 85-86°, lit. m.p. 91-92° (55). Analysis by gas-liquid chromatography on a Carbowax 20-M column at 160° showed that the alcohol was not contaminated with 2,5-dimethylbenzyl alcohol.

A solution of thionyl chloride (29.3 g., 0.25 mole) in benzene (75 ml.) was added in thirty minutes to a stirred solution of 2,6-dimethylbenzyl alcohol (30.5 g., 0.23 mole), benzene (200 ml.) and pyridine (19.5 g.). An exothermic reaction began and refluxing was continued for two hours. Water (150 ml.) was added and the benzene layer was separated, washed with water, dried, and concentrated. Distillation gave 2,6-dimethylbenzyl chloride (20.6 g., 59%), b.p. 101-102°.

A solution of 2,6-dimethylbenzyl chloride (20.6 g., 0.13 mole) in absolute ethanol (50 ml.) was added slowly to a stirred solution of sodium (3.1 g., 0.13 mole) and 2-nitropropane (11.6 g., 0.13 mole) in absolute ethanol (130 ml.). Stirring was continued for three hours. The solution was concentrated and the residue was diluted with ether and water. The ether layer was washed with 10% sodium hydroxide solution and water, dried, and concentrated. The residue was distilled to give 2,6-dimethylbenzaldehyde (11.4 g., 63%), b.p. 76-82°.

Mesitaldehyde (2,4,6-trimethylbenzaldehyde)—Mesitaldehyde was purchased from the Aldrich Chemical Company, Incorporated.
Duraldehyde (2,3,5,6-tetramethylbenzaldehyde).—Chloromethyldurene was prepared by chloromethylation of durene according to the procedure of Aitken, Badger, and Cook (56).


Chloromethyldurene (20 g., 0.11 mole) was added in small portions to a stirred solution of commercial sodium methoxide (6.5 g., 0.12 mole) and 2-nitropropane (10.8 ml.) in anhydrous methanol (1 l.). The stirred solution was refluxed for ten hours. The solution was concentrated and the residue was diluted with ether (20 ml.) and water (30 ml.). The ether layer was washed with 10% sodium hydroxide solution (20 ml.) and water (20 ml.), dried, and concentrated. The crude duraldehyde was used without further purification.

Tosylhydrazones

Tosylhydrazide.—Tosylhydrazide was prepared from p-toluenesulfonyl chloride and hydrazine by the procedure of Friedman, Litle, and Reichle (57).


General procedure for tosylhydrazones.—The aromatic aldehyde was dissolved in sufficient anhydrous methanol to make a 20-30% solution. An equivalent amount of tosylhydrazide and a few drops of dilute hydrochloric acid or sulfuric acid were added and the solution was
stirred overnight. The crystalline material which appeared was filtered, washed with anhydrous ether at -20°, and dried under vacuum.

The tosylhydrazones were stable indefinitely at room temperature.

Benzaldehyde tosylhydrazone.—m.p. 127-129°, lit. m.p. 128° (22).

Anal. Calcd. for C_{14}H_{14}N_{2}O_{2}S: C, 61.29; H, 5.14.
Found: C, 60.66; H, 4.84.

o-Tolualdehyde tosylhydrazone.—m.p. 136-138°, lit. m.p. 143-144° (30).

Anal. Calcd. for C_{15}H_{16}N_{2}O_{2}S: C, 62.48; H, 5.60.
Found: C, 61.85; H, 5.59.

2,5-Dimethylbenzaldehyde tosylhydrazone.—m.p. 145-146°.

Anal. Calcd. for C_{16}H_{18}N_{2}O_{2}S: C, 63.55; H, 6.00; N, 9.26.
Found: C, 62.75; H, 6.04; N, 9.20.

2,6-Dimethylbenzaldehyde tosylhydrazone.—m.p. 155-158°.

Anal. Calcd. for C_{16}H_{18}N_{2}O_{2}S: C, 63.55; H, 6.00; N, 9.26.
Found: C, 63.32; H, 5.98; N, 9.12.

Mesitaldehyde tosylhydrazone.—m.p. 159-161°, lit. m.p. 158-160° (30).

Anal. Calcd. for C_{17}H_{20}N_{2}O_{2}S: C, 64.53; H, 6.37.
Found: C, 65.55; H, 6.50.

Duraldehyde tosylhydrazone.—m.p. 172-174°.

Anal. Calcd. for C_{18}H_{22}N_{2}O_{2}S: C, 65.43; H, 6.71.
Found: C, 64.99; H, 7.11.

Sodium salts of tosylhydrazones

General procedure.—The tosylhydrazone (5-20 g.) was dissolved in anhydrous ether (ca. 150 ml.) and an equivalent amount of a 53.4%
suspension of sodium hydride in mineral oil (Metal Hydrides, Incorporated) was added. The mixture was stirred overnight at room temperature. The resulting white or light pink solid was filtered, washed with anhydrous ether, and dried under vacuum.

The salts were hygroscopic and were kept under vacuum until used. Ordinarily the salts were used within two or three days.

**Aryldiazooalkanes**

**General procedure.**—The sodium salt of the appropriate tosylhydrazone (5-20 g.) was placed in a round-bottomed flask fitted with a distillation head which was attached to a receiver immersed in ice water. The system was evacuated to 1-2 mm. Hg and the salt was slowly heated with an oil bath. Decomposition occurred at bath temperatures of 90-110° and the diazo compound distilled as a red oil. The oil was diluted with pentane and the solution was filtered and then concentrated under dry nitrogen. Yields ranged from 15-45%. It appeared that the yields are lowered by decomposition of the diazo compounds to the corresponding azines prior to distillation.

**Phenyldiazomethane.**—Pyrolysis of benzaldehyde tosylhydrazone sodium salt gave phenyldiazomethane as a dark red oil with characteristic infrared absorption at 4.91μ (58) (Figure 1). The average yield for several preparations was 24%.

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Phenyldiazomethane (1.65 g.) was dissolved in anhydrous ether
(200 ml.) and the solution was cooled to 0°. A solution of acetic acid (4 g.) in anhydrous ether (25 ml.) was added dropwise to the stirred solution. There was evolution of 346 ml. (110%) of nitrogen, corrected to STP and corrected for the vapor pressure of water.

**o-Tolyldiazomethane.**—Decomposition of o-tolualdehyde tosylhydrazone sodium salt gave o-tolyldiazomethane as a dark red oil with strong infrared absorption at 4.86μ (Figure 2). The average yield for several preparations was 25%.

**o-Tolyldiazomethane (1.40 g.)** was dissolved in anhydrous ether (100 ml.) and the solution was cooled to 5°. A solution of acetic acid (4 g.) in anhydrous ether (30 ml.) was added dropwise to the stirred solution. There was evolution of 257 ml. (108%) of nitrogen, corrected to STP and corrected for the vapor pressure of water.

**2,5-Dimethylphenyldiazomethane.**—Pyrolysis of 2,5-dimethylbenzaldehyde tosylhydrazone sodium salt resulted in formation of 2,5-dimethylphenyldiazomethane as a dark red oil with strong infrared absorption at 4.88μ (Figure 3). The average yield for four preparations was 26%.

A solution of 2,5-dimethylphenyldiazomethane (1.42 g.) in anhydrous ether (250 ml.) was cooled to 5° and a solution of acetic acid (4 g.) in anhydrous ether (30 ml.) was added dropwise to the stirred solution. There was evolution of 199 ml. (91%) of nitrogen, corrected to STP and corrected for the vapor pressure of water.

**2,6-Dimethylphenyldiazomethane.**—2,6-Dimethylbenzaldehyde tosylhydrazone sodium salt was pyrolyzed to give 2,6-dimethylphenyldiazomethane as a yellowish-red oil with strong infrared absorption at
A solution of 2,6-dimethylphenyldiazomethane (0.66 g.) in anhydrous ether (250 ml.) was cooled to 5° and a solution of acetic acid (4 g.) in anhydrous ether (30 ml.) was added dropwise to the stirred solution. There was evolution of 115 ml. (110%) of nitrogen, corrected to STP and corrected for the vapor pressure of water.

**Attempted preparation of 2,4,6-trimethylphenyldiazomethane.**—Mesit-aldehyde tosylhydrazone sodium salt (16 g.) was heated slowly at 1-2 mm. Hg as described in the general procedure. Decomposition occurred suddenly at a bath temperature of 115°. The distillate was dissolved in pentane, filtered, and concentrated. The resulting reddish-yellow oil showed strong infrared absorption at 4.91 μ (2,4,6-trimethylphenyldiazomethane), 4.55 μ (2,4,6-trimethylbenzonitrile), and 5.94 μ (2,4,6-trimethylbenzaldehyde) (Figure 5). The diazo compound is evidently sufficiently high-boiling to undergo extensive decomposition prior to distillation.

**Stability of aryldiazoalkanes.**—The aryldiazoalkanes described above could be stored in a freezer for a few days. After two weeks or longer, decomposition to the corresponding azines had occurred to a considerable extent. The aryldiazoalkanes could be kept for only a few hours at room temperature without decomposition.

**Standards**

**Benzyl p-tolyl sulfones**

**General procedure.**—The benzyl halide (1 g.) and an equivalent amount of p-toluenesulfonic acid sodium salt were dissolved in
anhydrous methanol (10 ml.) and the solution was refluxed overnight. The solution was concentrated and the residue was diluted with ether and water. The ether layer was washed with water, dried, and concentrated. The residue was recrystallized from methanol.

**o-Methylbenzyl p-tolyl sulfone**. — m.p. 115-116°.

Anal. Calcd. for C_{15}H_{16}O_2: C, 69.00; H, 6.15.

  Found: C, 69.54; H, 6.52.

**p-Methylbenzyl p-tolyl sulfone**. — m.p. 151-152°, lit. m.p. 156-157° (59).


**2,4,6-Trimethylbenzyl p-tolyl sulfone**. — m.p. 135-136°.

**2,3,5,6-Tetramethylbenzyl p-tolyl sulfone**. — m.p. 188-189°.

**Standards for gas-liquid chromatography**

The compounds used as standards for gas-liquid chromatography were, unless listed below, prepared as intermediates in the syntheses of aromatic aldehydes, or were provided by members of the Department of Chemistry, The Ohio State University.

**Benzocyclobutene**. — Benzocyclobutene was provided by Dr. M. P. Cava, Department of Chemistry, The Ohio State University.

**Benzaldehyde**. — Phenyldiazomethane (0.8 g.) was added dropwise to an evacuated distillation flask set in an oil bath at 160°. Most of the phenyldiazomethane was distilled. The residue was recrystallized from methanol to give benzaldehyde as a yellow solid, m.p. 87-92°, lit. m.p. 93° (60), λ_{max}^{EtOH} 304 μm, lit. λ_{max} 304 μm (61).

o-Tolualdazine.—A sample of o-tolyldiazomethane which had been stored for several weeks was found to have decomposed to a yellow solid. Recrystallization from methanol gave o-tolualdazine, m.p. 96-97°, lit. m.p. 100° (62).


Anal. Calcd. for C_{16}H_{16}N_2: C, 81.32; H, 6.83; N, 11.85. 
Found: C, 81.37; H, 7.17; N, 11.49.

2,5-Dimethylbenzaldazine.—A sample of 2,5-dimethylphenyldiazo-
methane was kept for ten days at room temperature. The resulting yellow solid was recrystallized from methanol to give 2,5-dimethylphenyldiazomethane, m.p. 129-130°.

Anal. Calcd. for C_{18}H_{20}N_2: C, 81.77; H, 7.63; N, 10.60
Found: C, 80.89; H, 7.70; N, 10.59.

o,o'-Dimethylstilbene.—α-Bromo-o-xylene (10 g., 0.054 mole) and triphenylphosphine (14.2 g., 0.054 mole) were dissolved in benzene (50 ml.) and the solution was stirred for ten hours. The resulting white solid was filtered, washed with benzene, and dried to give o-tolyltriphenylphosphonium bromide, m.p. 270-271°.

Sodium hydride (1.22 g. of a 53.4% suspension in mineral oil, 0.027 mole) was washed with pentane and then dissolved in dimethyl
sulfoxide (50 ml.). The yellow solution was stirred under nitrogen at 65-68° until evolution of hydrogen ceased and was then cooled to room temperature. A slurry of o-tolyltriphenylphosphonium bromide (12 g., 0.027 mole) in dimethyl sulfoxide (30 ml.) was added. The occurrence of an intense brownish-red color indicated the formation of the expected phosphorane.

A solution of o-tolualdehyde (3.24 g., 0.027 mole) in dimethyl sulfoxide (20 ml.) was added slowly to the phosphorane solution. The solution was stirred for four hours, during which time the brownish-red color disappeared. The solution was then poured onto ice. The resulting mixture was extracted with methylene chloride. The extract was concentrated and the residue was diluted with petroleum ether. The solution was filtered to remove triphenylphosphine oxide, dried, and concentrated.

The product was a yellow oil. Analysis of this material by gas-liquid chromatography on an SE-30 column indicated the presence of two main components in approximately equal concentration. During two days most of the material of higher retention time crystallized. Both this material and the remaining oil showed strong infrared absorption at 10.4μ (Figure 6), which is characteristic of stilbenes (63).


Recrystallization of the solid material from 95% ethanol gave trans-o,o'-dimethylstilbene, m.p. 82-83°, lit. m.p. 82.5-83° (64).

The other main component was concluded to be \textit{cis-o,o'-dimethylstilbene}.

\textit{2,2',5,5'-Tetramethylstilbene.--}2,5-Dimethylbenzyl chloride (10 g., 0.065 mole) and triphenylphosphine (17 g., 0.065 mole) were dissolved in benzene (50 ml.). The stirred solution was refluxed overnight. The solid which appeared was filtered, washed with benzene, and dried to give 2,5-dimethylbenzyltriphenylphosphonium chloride, m.p. \( >300^\circ \) (17.2 g., 64%).

Sodium hydride (1.22 g. of a 53.4\% suspension in mineral oil, 0.027 mole) was washed with pentane and then dissolved in dimethyl sulfoxide (50 ml.) under nitrogen. The solution was stirred for two hours at 65\(^\circ\) and then cooled. A slurry of 2,5-dimethylbenzyltriphenylphosphonium chloride (11.2 g., 0.027 mole) in dimethyl sulfoxide (30 ml.) was added slowly to give a bright orange solution. A solution of 2,5-dimethylbenzaldehyde (3.56 g., 0.027 mole) in dimethyl sulfoxide (20 ml.) was added slowly. The resulting solution was stirred for four hours, during which time the bright orange color disappeared.

The solution was poured onto ice and the resulting mixture was extracted twice with methylene chloride (100 ml.). The combined extracts were washed three times with water (100 ml.). The solution was concentrated and then diluted with petroleum ether. The solution was filtered to remove triphenylphosphine oxide, dried, and concentrated to give a light yellow solid with strong infrared absorption at 10.4\mu. Analysis of this solid by gas-liquid chromatography on an SE-30 column at 269\(^\circ\) indicated that the solid was a mixture of the stilbenes. This material was used without further purification.
**o,o'-Dimethylbibenzyl.**—A mixture of sodium (2.99 g., 0.08 mole) and hexadecane (200 ml.) was heated to 170° under nitrogen while being agitated with a vibrating stirrer (A. G. fur Chemie-Apparatebau) and was then cooled without stirring. The sodium settled out as a sand. The agitated mixture was heated to 160° and a solution of α-bromo-α-xylene (20 g., 0.08 mole) in hexadecane was added in one hour. Agitation was stopped and the solution was cooled and analyzed by gas-liquid chromatography on an SE-30 column at 252°. Only one peak corresponding to a coupling product was observed. This component was intermediate in retention time between cis- and trans-o,o'-dimethyl-stilbenes and was concluded to be o,o'-dimethylbibenzyl. This hydrocarbon is also formed by the reaction of α-chloro-α-xylene with magnesium (65).


**Methylstyrenes.**—Samples of o-, m-, and p-methylstyrenes were obtained from the Columbia Organic Chemicals Company, Incorporated.

**2,5-Dimethylbenzonitrile.**—2,5-Dimethylaniline (20 g., 0.17 mole) was added to a stirred mixture of 36% hydrochloric acid (32 ml.) and crushed ice (160 g.). A solution of sodium nitrite (11.6 g., 0.17 mole) in water (33 ml.) was added in thirty minutes to the stirred suspension at 0-5°. Anhydrous sodium carbonate (9 g.) was added to neutralize the solution.

Cuprous cyanide (18.6 g., 0.21 mole) and potassium cyanide (22.4 g., 0.36 mole) were dissolved in water (120 ml.) at 60°.
The solution was cooled to 0° and toluene (50 ml.) was added. The mixture was stirred vigorously and the diazonium solution was added in thirty minutes. Stirring was continued while the mixture was warmed to room temperature. The toluene layer was separated and washed twice with 2N potassium hydroxide solution (16 ml.) and water and then steam-distilled. The toluene layer in the distillate was separated, dried, and concentrated. The crude liquid 2,5-dimethylbenzonitrile was used without further purification.

2,5-Dimethylbenzyl alcohol.—2,5-Dimethylbenzoic acid (2 g., 0.013 mole) and thionyl chloride (2.43 g., 0.02 mole) were refluxed for two hours. The crude 2,5-dimethylbenzyl chloride was dissolved in anhydrous ether (5 ml.). The solution was added dropwise to a stirred solution of lithium aluminum hydride (0.4 g., 0.01 mole) in anhydrous ether (50 ml.). Stirring was continued for twenty hours. Water was added in small portions to destroy excess lithium aluminum hydride. The mixture was poured onto ice and 10% hydrochloric acid (30 ml.). The ether layer was washed with 10% sodium bicarbonate solution and water, dried, and concentrated. The crude liquid 2,5-dimethylbenzyl alcohol was used without further purification.

2,6-Dimethylbenzonitrile.—2,6-Dimethylaniline (100 g., 0.83 mole) was added to 36% hydrochloric acid (160 ml.) and crushed ice (800 g.). The resulting suspension was stirred at 0-5° and a solution of sodium nitrite (58 g., 0.84 mole) in water (165 ml.) was added in thirty minutes. Anhydrous sodium carbonate (45 g.) was added to neutralize the solution.

Cuprous cyanide (93 g., 1.04 moles) and potassium cyanide (112 g.,
1.72 moles) were dissolved in water (600 ml.) at 60°. The solution was cooled to 0° and toluene (245 ml.) was added. The mixture was stirred vigorously at 0-5° and the diazonium solution was added slowly. Stirring was continued while the solution was slowly warmed to room temperature.

The toluene layer was separated and steam-distilled. The distillate was concentrated and the residue was dissolved in ether (200 ml.). This solution was washed twice with 2N potassium hydroxide solution (85 ml.) and with water, and concentrated. The residue was recrystallized from benzene and from petroleum ether to give 2,6-dimethylbenzonitrile (16 g., 15%), m.p. 90-92°, lit. m.p. 89-91° (66).


Thermal Decompositions of Tosylhydrazones

Decomposition of o-tolualdehyde tosylhydrazone in N-methylpyrrolidone. Experiment I.—o-Tolualdehyde tosylhydrazone (10 g., 0.035 mole) was added to N-methylpyrrolidone (50 ml.) at 160° under nitrogen. Commercial sodium methoxide (2.4 g., 0.044 mole) was added in small portions to the stirred solution. There was evolution of 623 ml. (80%) of nitrogen, corrected to STP.

The solution was diluted with ether (100 ml.) and water (100 ml.). The ether layer was washed five times with water (100 ml.), dried, filtered, and concentrated. The residue was a dark brown oil. After
one day solid material appeared. This was filtered and was recrystal-
lized from 95% ethanol to give o-methylbenzyl p-tolyl sulfone, m.p.
115-116°, which did not depress the melting point of an authentic
sample.

The remaining oil (2.6 g.) was analyzed by gas-liquid chromatog-
raphy on a Carbowax 20-M column at 153° and on an SE-30 silicone column
at 261°. The volatile products are shown in Table 1.

TABLE 1.—Volatile products from the reaction of o-tolualdehyde tosyl-
hydrazone with sodium methoxide in N-methylpyrrolidone at 160°

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative peak area</th>
<th>Estimated percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Xylene</td>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td>C₈H₈ a</td>
<td>trace</td>
<td>--</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>0.7</td>
<td>--</td>
</tr>
<tr>
<td>o-Tolualdehyde</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>o-Tolunitrile</td>
<td>trace</td>
<td>--</td>
</tr>
<tr>
<td>o-Methylbenzyl alcohol</td>
<td>165</td>
<td>38</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>27</td>
<td>--</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>32</td>
<td>--</td>
</tr>
</tbody>
</table>

a The C₈H₈ hydrocarbon was present in too small concentration to
permit distinguishing between styrene and benzocyclobutene. These
two compounds have identical retention times under the conditions
employed.

Experiment II.—o-Tolualdehyde tosylhydrazone (3 g., 0.01 mole)
was decomposed as described for Experiment I. There was evolution of
200 ml. (77%) of nitrogen, corrected to STP. The resulting oil gave
on standing crystalline material which was recrystallized from methanol
to give o-methylbenzyl p-tolyl sulfone, m.p. 112-114°, which did not
depress the melting point of an authentic sample.

Decomposition of mesitaldehyde tosylhydrazone in N-methylpyrrol-
idone. — Commercial sodium methoxide (7.55 g., 0.14 mole) was added in
small portions to a stirred refluxing solution of mesitaldehyde tosyl-
hydrazone (44 g., 0.14 mole) in N-methylpyrrolidone (700 ml.). The
total evolution of nitrogen, corrected to STP, was 2740 ml. (88%).

The solution was diluted with ether, washed three times with
water, dried, and concentrated. The resulting solid was recrystal-
lized from methanol to give 2,4,6-trimethylbenzyl p-tolyl sulfone
(17.6 g., 43%), m.p. 136-137°, which did not depress the melting point
of an authentic sample.

Decomposition of o-tolualdehyde tosylhydrazone in diethyl Carbitol.--
o-Tolualdehyde tosylhydrazone (5 g., 0.017 mole) was dissolved in
diethyl Carbitol (50 ml.) at 150°. Commercial sodium methoxide (1.03 g.,
0.019 mole) was added in small portions to the stirred solution.
There was evolution of 392 ml. (100%) of nitrogen, corrected to STP.

The solution was cooled and diluted with water (300 ml.). This
mixture was extracted three times with ether (100 ml.). The combined
ether extracts were washed six times with water (100 ml.), dried, and
concentrated to give a dark brown oil (1.2 g.). The oil was analyzed
by gas-liquid chromatography on a Carbowax 20-M column at 164° and on
an SE-30 column at 242°. The volatile products are shown in Table 2.
TABLE 2.—Volatile products from the reaction of o-tolualdehyde tosylhydrazone with sodium methoxide in diethyl Carbitol at 150

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative peak area</th>
<th>Estimated percent yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Xylene</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>C_8H_8</td>
<td>1.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>6.3</td>
<td>--</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>2.6</td>
<td>--</td>
</tr>
<tr>
<td>o-Tolualdehyde</td>
<td>6.4</td>
<td>0.7</td>
</tr>
<tr>
<td>o-Tolunitrile</td>
<td>17.4</td>
<td>2</td>
</tr>
<tr>
<td>o-Methylbenzyl alcohol</td>
<td>72.5</td>
<td>8</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>6.8</td>
<td>--</td>
</tr>
<tr>
<td>cis-o,o'-Dimethylstilbene</td>
<td>35.6</td>
<td>5</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>33.7</td>
<td>--</td>
</tr>
<tr>
<td>trans-o,o'-Dimethylstilbene</td>
<td>28.2</td>
<td>4</td>
</tr>
<tr>
<td>o-Tolualdazine</td>
<td>20</td>
<td>2</td>
</tr>
</tbody>
</table>

Decomposition of duraldehyde tosylhydrazone in diethyl Carbitol—

Duraldehyde tosylhydrazone (10 g., 0.03 mole) was added in small portions to a stirred refluxing solution of commercial sodium methoxide (1.70 g., 0.03 mole) in diethyl Carbitol (100 ml.). The total nitrogen evolution, corrected to STP, was 635 ml. (94%). The mixture was cooled and was diluted with water (600 ml.). The oil which separated was dissolved in ether and the resulting solution was washed several times with water.

A small amount of solid material separated from the solution.
This was filtered and was recrystallized from methanol to give 2,2'-3,3',5,5',6,6'-octamethylbibenzyl, m.p. 239-241°, lit. m.p. 235-236° (67). The infrared spectrum of this compound was identical to that of an authentic sample.


The ether solution was concentrated to a yellow oil, which was analyzed by gas-liquid chromatography on a Dow-Corning 550 silicone oil column at 165°. The only product which was identified was pentamethylbenzene, which was present in very small concentration. No other C₁₁ hydrocarbons appeared to be present.

Thermal Decompositions of Aryldiazoalkanes

Decomposition of o-tolyldiazoethane in N-methylpyrrolidone.---A solution of o-tolyldiazoethane (1.80 g., 0.014 mole) in N-methylpyrrolidone (5 ml.) was added dropwise to stirred N-methylpyrrolidone (25 ml.) under nitrogen at 160°. The nitrogen evolution, corrected to STP, was 203 ml. (66%). The solution was cooled, diluted with ether (50 ml.), washed five times with water (100 ml.), dried, and concentrated to a yellow oil (1.1 g.). The oil was analyzed by gas-liquid chromatography on a Carbowax 20-M column at 153° and on an SE-30 column at 285°. The volatile products are shown in Table 3.
TABLE 3.—Volatile products from thermal decomposition of o-tolyl-
diazomethane in N-methylpyrrolidone at 160°

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative peak area</th>
<th>Estimated percent yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Xylene</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>C₆H₈</td>
<td>trace</td>
<td>--</td>
</tr>
<tr>
<td>o-Tolualdehyde</td>
<td>10.8</td>
<td>2</td>
</tr>
<tr>
<td>o-Tolunitrile</td>
<td>3.3</td>
<td>1</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>11.8</td>
<td>--</td>
</tr>
<tr>
<td>o-Methylbenzyl alcohol</td>
<td>15.8</td>
<td>4</td>
</tr>
<tr>
<td>cis-o,o'-Dimethylstilbene</td>
<td>24.6</td>
<td>6</td>
</tr>
<tr>
<td>trans-o,o'-Dimethylstilbene</td>
<td>56.2</td>
<td>14</td>
</tr>
<tr>
<td>o-Tolualdazine</td>
<td>27.2</td>
<td>6</td>
</tr>
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</table>

Decomposition of o-tolyl diazomethane in diethyl Carbitol.—A solution of o-tolyl diazomethane (1.75 g., 0.013 mole) in diethyl Carbitol (5 ml.) was added dropwise to stirred diethyl Carbitol (20 ml.) under nitrogen at 160°, with evolution of 237 ml. (80%) of nitrogen, corrected to STP. The mixture was worked up as described for the preceding experiment to give a yellow oil (1.6 g.). This was analyzed by gas-liquid chromatography on a Carbowax 20-M column at 153° and on an SE-30 column at 285°. The volatile products are shown in Table 4.
TABLE 4.—Volatile products from thermal decomposition of o-tolyldiazomethane in diethyl Carbitol at 160°

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative peak area</th>
<th>Estimated percent yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Xylene</td>
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<tr>
<td>C₈H₈</td>
<td>trace</td>
<td>--</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>0.6</td>
<td>--</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>1.1</td>
<td>--</td>
</tr>
<tr>
<td>o-Tolualdehyde</td>
<td>2.8</td>
<td>1.2</td>
</tr>
<tr>
<td>o-Tolunitrile</td>
<td>1.5</td>
<td>0.7</td>
</tr>
<tr>
<td>o-Methylbenzyl alcohol</td>
<td>1.7</td>
<td>0.7</td>
</tr>
<tr>
<td>cis-ortho Dimethylstilbene</td>
<td>27.8</td>
<td>15</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>11.6</td>
<td>--</td>
</tr>
<tr>
<td>trans-ortho Dimethylstilbene</td>
<td>13.4</td>
<td>7</td>
</tr>
<tr>
<td>o-Tolualdazine</td>
<td>2.2</td>
<td>1</td>
</tr>
</tbody>
</table>

Thermal decomposition of aryl diazoalkanes by pyrolytic gas-liquid chromatography. General procedure.—Pyrolytic gas-liquid chromatography was carried out on instrument b, the Aerograph A-90-P. The temperatures of the injector, column, and detector of this instrument are set separately. The injector was always heated to at least 150°, so that it would be sufficiently hot that the aryl diazoalkanes would decompose instantly upon injection. It is probable that the diazo compounds decomposed in the liquid state upon contact with the walls of the injector. The exact temperatures and columns used for the decompositions are given with the individual experiments.
Decompositions were carried out by injecting samples of the aryl-diazoalkanes directly into the heated injector. The samples used were generally 1-10 micro-liters. Samples of 0.1-0.5 ml. were used when products were to be collected. In every case a large nitrogen peak appeared within a few seconds after injection, indicating that the decomposition occurred immediately. This peak was then followed by peaks corresponding to the various products. The retention times of the product peaks were compared to those of authentic samples.

In some cases the injector was lined with a clean glass insert. It was found that the presence or absence of the insert did not affect the nature and yields of the products from the decomposition of a particular sample of phenyldiazomethane.

Yields of volatile products were estimated by comparison of the peak areas with those from measured samples of standard hydrocarbons. Whenever the glass insert was examined after a decomposition a considerable amount of tarry residue was found. This indicated that much of the diazo compound went to form non-volatile or polymeric products.

**Thermal decomposition of pure phenyldiazomethane. Experiment I.**

Phenyldiazomethane was decomposed by pyrolytic gas chromatography according to the general procedure. A Carbowax 20-M column was used. The injector was at 180° and the column at 148° for the determination of lower-boiling products. Higher-boiling components were studied with the column at 225°. The products and amounts are shown in Table 5.
Experiment II.—Phenyldiazomethane was decomposed according to the general procedure. A Carbowax 20-M column was used. The injector was at 254° and the column at 206°. The volatile products and quantities are shown in Table 5.

Experiment III.—The general procedure was followed. Lower-boiling products were determined using a Carbowax 20-M column, with the injector at 160° and the column at 142°. For higher-boiling compounds an SE-30 column was used. The injector was at 282° and the column at 233°. Products and amounts are shown in Table 5.

Experiment IV.—Phenyldiazomethane was decomposed according to the general procedure, using a Carbowax 20-M column. The temperature of the injector was 170°; the column was at 98°. The only peak which appeared at this temperature was identical in retention time to benzene.

Experiment V.—A round-bottomed flask was filled with dry nitrogen and placed in an oil bath at 160°. Phenyldiazomethane (1.5 g.) was added dropwise. The product was a dark brown oil. This material was analyzed by gas-liquid chromatography on a Carbowax 20-M column at 150° and on an SE-30 column at 251°. The products and yields are shown in Table 5.

Thermal decomposition of pure o-tolyldiazomethane. Experiment I.—o-Tolyldiazomethane was decomposed by pyrolytic gas-liquid chromatography according to the procedure given. A Carbowax 20-M column was used at 162°, with the injector at 168°, for determination of the lower-boiling products. Higher-boiling components were studied with
<table>
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<tr>
<td></td>
<td>Rel. peak area</td>
<td>Est. yield</td>
<td>Rel. peak area</td>
<td>Est. yield</td>
<td>Rel. peak area</td>
<td>Est. yield</td>
<td>Rel. peak area</td>
<td>Est. yield</td>
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<tr>
<td>Benzene</td>
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<td>52</td>
<td>2</td>
<td>4</td>
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<tr>
<td>Toluene</td>
<td>21</td>
<td>0.3</td>
<td>25</td>
<td>0.5</td>
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<td>0.7</td>
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<td>--</td>
<td>42</td>
<td>--</td>
<td>11</td>
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</tr>
<tr>
<td>Benzenaldehyde</td>
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<td>Benzonitrile</td>
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<td>100</td>
<td>2</td>
<td>100</td>
<td>2</td>
<td>100</td>
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<td>Benzyl alcohol</td>
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<td>0.5</td>
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<td>2</td>
<td>96</td>
<td>2</td>
<td>13</td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>33</td>
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<tr>
<td>cis-Stilbene or bibenzyl a</td>
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<td>3</td>
<td>81</td>
<td>2</td>
<td>64</td>
<td>1</td>
<td>117</td>
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<td>--</td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>30</td>
<td>--</td>
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<tr>
<td>trans-Stilbene</td>
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<td>8</td>
<td>240</td>
<td>5</td>
<td>96</td>
<td>2</td>
<td>299</td>
<td>8</td>
</tr>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>98</td>
<td>--</td>
</tr>
<tr>
<td>Benzaldazine</td>
<td>-- b</td>
<td>-- b</td>
<td>-- b</td>
<td>-- b</td>
<td>46</td>
<td>1</td>
<td>131</td>
<td>3</td>
</tr>
<tr>
<td>Unidentified compound</td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>40</td>
<td>--</td>
</tr>
</tbody>
</table>

*a cis-Stilbene and bibenzyl could not be distinguished under the conditions employed.*

*Not volatile at the temperatures employed.*
an SE-30 column at 239°, with the injector at 277°. The volatile products and the yields are given in Table 6.

**Experiment II.** -- o-Tolyldiazomethane was decomposed as described in the preceding experiment. Lower-boiling products were studied with a Carbowax 20-M column at 138° and the injector at 200°; higher-boiling compounds were determined with the injector at 269° and an SE-30 column at 256°. The products and quantities are shown in Table 6.

**Experiment III.** -- o-Tolyldiazomethane was decomposed by pyrolytic gas-liquid chromatography with the injector at 163° and a 3/8-in. Carbowax 20-M column at 107°. A sample of the C8 hydrocarbon product, which corresponded in retention time to both benzocyclobutene and styrene, was collected. Comparison of the infrared spectrum of this sample (Figure 7) with the spectra of authentic samples of styrene and benzocyclobutene (Figures 8 and 9) indicated that the collected material was a mixture of the two hydrocarbons. The ultraviolet spectrum of the collected material (Figure 15) exhibited a maximum at 248 μμ, which is found in the ultraviolet spectrum of an authentic sample of styrene (Figure 16).

**Experiment IV.** -- o-Tolyldiazomethane was decomposed as described for Experiments I and II. For the determination of lower-boiling products, the injector was at 170° and a Carbowax 20-M column was at 150°; higher-boiling compounds were studied with the injector at 268° and an SE-30 column at 248°. The products are shown in Table 6.

Two portions of this sample of o-tolyldiazomethane were decomposed with the injector at 157° and a 3/8-in. Carbowax 20-M column
at 104° and the C₈ hydrocarbon product was collected. A total of 0.148 g. (11.5%) of hydrocarbon was obtained from 1.63 g. of o-tolyl-diazomethane. The collected material had an infrared spectrum identical to that of the material collected in Experiment III. The collected product was analyzed by gas-liquid chromatography on a 100-ft. squalane capillary column at 92°. Comparison of retention times with those of authentic samples showed the collected material to be a mixture of styrene (63%) and benzocyclobutene (37%).

**Experiment V.**—A round-bottomed flask was flushed with dry nitrogen and set in an oil bath at 150°. o-Tolyldiazomethane (2.1 g.) was added slowly. The diazo compound decomposed violently on contact with the flask. The product was a dark brown oil. This material was analyzed by gas-liquid chromatography with a Carbowax 20-M column at 152° and with an SE-30 column at 280°. The volatile products and quantities are shown in Table 6. Analysis with an SE-30 column at 100° showed that the C₈ hydrocarbon product in this reaction was a mixture of styrene (65%) and benzocyclobutene (35%).

**Photolysis of o-tolyldiazomethane.**—Stirred o-tolyldiazomethane (1.3 g.) was irradiated for 20 hours at 20° with a 425-watt mercury vapor lamp (Hanovia Lamp Division, Engelhard Hanovia, Incorporated). The product was a yellow solid. This material was analyzed by gas-liquid chromatography on a Carbowax 20-M column at 184° and on an SE-30 column at 238°. The components observed were o-tolualdehyde (minor amount), o-methylbenzyl alcohol (minor amount), cis-o,o'-dimethylstilbene (4%), trans-o,o'-dimethylstilbene (19%), and o-tolu-aldazine (74%).
TABLE 6.—Products from thermal decomposition of pure o-tolyldiazomethane

<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Rel. peak area</td>
<td>Est. yield</td>
<td>Rel. peak area</td>
<td>Est. yield</td>
</tr>
<tr>
<td>Toluene</td>
<td>13</td>
<td>0.2</td>
<td>19</td>
<td>0.6</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>3</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>9</td>
<td>0.1</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>Benzocyclobutene</td>
<td>680</td>
<td>4</td>
<td>490</td>
<td>4</td>
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<tr>
<td>Styrene</td>
<td>7</td>
<td>7</td>
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<td>7</td>
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<tr>
<td>o-Tolualdehyde</td>
<td>33</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
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<tr>
<td>o-Tolunitrile</td>
<td>100</td>
<td>1</td>
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<td>3</td>
</tr>
<tr>
<td>o-Methylbenzyl alcohol</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>cis-2,2'-Dimethylstilbene</td>
<td>195</td>
<td>3</td>
<td>43</td>
<td>1</td>
</tr>
<tr>
<td>o,2'-Dimethylbibenzyl</td>
<td>316</td>
<td>5</td>
<td>187</td>
<td>5</td>
</tr>
<tr>
<td>trans-2,2'-Dimethylstilbene</td>
<td>343</td>
<td>6</td>
<td>191</td>
<td>3</td>
</tr>
<tr>
<td>o-Tolualdazine</td>
<td>126</td>
<td>2</td>
<td>39</td>
<td>1</td>
</tr>
</tbody>
</table>
Recrystallization from methanol gave o-tolualdazine, m.p. 99-100°, lit. m.p. 100° (62).

Attempted decomposition of benzocyclobutene by pyrolytic gas-liquid chromatography. **Experiment I.** A sample of benzocyclobutene was injected into the Aerograph A-90-P with the injector at 164° and a 3/8-in. Carbowax 20-M column at 104°. The infrared spectrum of the material which was collected was identical to that of unreacted benzocyclobutene.

**Experiment II.** The above experiment was repeated with the injector at 238° and an SE-30 column at 104°. The collected material again had an infrared spectrum identical to that of an authentic sample of benzocyclobutene.

**Thermal decomposition of 2,5-dimethylphenyldiazomethane.**—2,5-Dimethylphenyldiazomethane was decomposed by pyrolytic gas-liquid chromatography using a Carbowax 20-M column with the injector at 179° and the column at 170°. Higher-boiling products were determined with an SE-30 column at 269° with the injector at 296°. The products are shown in Table 7.

A sample of 2,5-dimethylphenyldiazomethane was decomposed with the injector at 181° and a 3/8-in. SE-30 column at 121°. The two C9 hydrocarbons were collected as a mixture and were identified by the following data.
TABLE 7.—Products from thermal decomposition of pure 2,5-dimethylphenyldiazomethane

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative peak area</th>
<th>Estimated percent yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unidentified compound</td>
<td>5</td>
<td>--</td>
</tr>
<tr>
<td>4-Methylbenzocyclobutene</td>
<td>268</td>
<td>4</td>
</tr>
<tr>
<td>p-Methylstyrene</td>
<td>trace</td>
<td>--</td>
</tr>
<tr>
<td>2,5-Dimethylbenzaldehyde</td>
<td>trace</td>
<td>--</td>
</tr>
<tr>
<td>2,5-Dimethylbenzonitrile</td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>2,5-Dimethylbenzyl alcohol</td>
<td>trace</td>
<td>--</td>
</tr>
<tr>
<td>2,2',5,5'-Tetramethylstilbenes</td>
<td>1560</td>
<td>63</td>
</tr>
<tr>
<td>2,5-Dimethylbenzaldazine</td>
<td>151</td>
<td>6</td>
</tr>
</tbody>
</table>

The ultraviolet spectrum of the hydrocarbon mixture (Figure 17) had a maximum at 254 m✉, corresponding to the maximum in the spectrum of authentic p-methylstyrene (Figure 18).

The infrared spectrum of the mixture (Figure 10) showed characteristic olefinic absorption at 6.16μ and cycloalkane absorption at 10.05μ. There was strong absorption at 12.1μ and weak absorption at 13.7μ, corresponding to the peaks in the spectrum of authentic p-methylstyrene (Figure 13). The absorptions shown by m-methylstyrene at 12.7μ and 14.1μ (Figure 12) were absent.

The nuclear magnetic resonance spectrum of the mixture (Figure 21) exhibited a triplet at 7.72τ (ArCH3), a singlet at 6.95τ (cycloalkyl protons in 4-methylbenzocyclobutene), complex absorptions from 4-5.1τ (olefinic protons), and a multiplet from 2.8-3.2τ (Ar-H). Comparison
of the sizes of the absorptions for the olefinic protons with that for the cycloalkyl protons suggests the mixture to be 69% \( p \)-methylstyrene and 31% 4-methylbenzocyclobutene. Analysis of the mixture by gas-liquid chromatography on an SE-30 column at 134° indicated that the mixture contained 67% \( p \)-methylstyrene and 33% 4-methylbenzocyclobutene.

**Thermal decomposition of 2,6-dimethylphenyldiazomethane.**

2,6-Dimethylphenyldiazomethane was decomposed by pyrolytic gas-liquid chromatography with a Carbowax 20-M column at 178° and the injector at 194°. The monomeric products and the quantities are shown in Table 8.

A mixture of the two hydrocarbons was collected when 2,6-dimethylphenyldiazomethane was decomposed with the injector at 176° and a 3/8-in. SE-30 column at 124°. The structures are based on the following data.

**TABLE 8.** Products from thermal decomposition of pure 2,6-dimethylphenyldiazomethane

<table>
<thead>
<tr>
<th>Product</th>
<th>Relative peak area</th>
<th>Estimated percent yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unidentified compound</td>
<td>7</td>
<td>--</td>
</tr>
<tr>
<td>3-Methylbenzocyclobutene</td>
<td>270</td>
<td>17</td>
</tr>
<tr>
<td>( m )-Methylstyrene</td>
<td>270</td>
<td>3</td>
</tr>
<tr>
<td>2,6-Dimethylbenzonitrile</td>
<td>100</td>
<td>7</td>
</tr>
<tr>
<td>Unidentified compound</td>
<td>25</td>
<td>--</td>
</tr>
<tr>
<td>2,6-Dimethylbenzyl alcohol</td>
<td>19</td>
<td>1</td>
</tr>
</tbody>
</table>
The ultraviolet spectrum of the collected material (Figure 19) exhibited a maximum at 251 m\(\mu\), corresponding to the maximum in the spectrum of authentic \(m\)-methylstyrene (Figure 20).

The infrared spectrum of the mixture (Figure 14) showed olefinic absorption at 6.2\(\mu\) and cycloalkane absorption at 10.05\(\mu\). There were strong absorptions at 12.7\(\mu\) and 14.1\(\mu\) corresponding to those in the spectrum of authentic \(m\)-methylstyrene (Figure 12); the absorptions shown by \(o\)-methylstyrene at 13.0\(\mu\) and 13.7\(\mu\) (Figure 11) were absent.

The nuclear magnetic resonance spectrum of the mixture (Figure 22) showed singlets at 7.92\(\tau\) and 7.77\(\tau\) (Ar-CH\(_3\)), a singlet at 7.01\(\tau\) (cycloalkyl protons in 3-methylbenzocyclobutene), complex absorptions from 4-5\(\tau\) (olefinic protons), and a multiplet at 3.2\(\tau\) (Ar-H).

Comparison of the relative sizes of the olefinic and cycloalkyl absorptions suggested that the mixture contained 93\% 3-methylbenzocyclobutene and 7\% \(m\)-methylstyrene. However, the gas-liquid chromatographic data given below probably provide a more reliable estimate.

The mixture was analyzed by gas-liquid chromatography on a 100-ft. squalane capillary column at 92\(^\circ\) and at 58\(^\circ\). At the lower temperature \(o\)- and \(m\)-methylstyrenes could be distinguished. The styrene product was found to correspond in retention time to \(m\)-methylstyrene. The peak areas indicated that the mixture contained 87\% 3-methylbenzocyclobutene and 13\% \(m\)-methylstyrene.
APPENDIX I

INFRARED SPECTRA
FIGURE 10

FIGURE 11

FIGURE 12
APPENDIX II

ULTRAVIOLET SPECTRA
APPENDIX III

NUCLEAR MAGNETIC RESONANCE SPECTRA