ether were obtained from Foote Mineral Co.; concentration was determined by proton nmr. Other materials were all reagent grade. Diethyl ether, cyclohexane, benzene, and Skelly B, used as solvents, were purified by lengthy reflux over LiAlH$_4$. Toluene was purified by refluxing over sodium. All were distilled immediately prior to use.

The bis(organosilyl)hydrazines and bis(organosilyl)methylhydrazines were prepared as described in earlier papers.[5,6,8] Tris(trimethylsilyl)hydrazine[10] and 1-trimethylsilyl-1,2-dimethylhydrazine[32] were made according to published procedure. Properties of these compounds agreed with those reported in the literature.

The various silylhydrazines were purified by preparative gas–liquid chromatography on an Aerograph Model A700 gas chromatograph equipped with a thermal conductivity detector. Isomers were separated using a $^3/_8$ in. × 15 ft aluminum column packed with 20% SE-30 on 40–60 mesh Chromosorb W, and a helium flow rate of 200 cc/min.

Formation of Anions. Gas chromatograph collection tubes and Varian nmr sample tubes were carefully cleaned with various solvents and dried in a 160° oven for at least 1 hr. They were then flushed with dry nitrogen and capped with a rubber septum. Samples were prepared immediately after collection from the gas chromatograph. Care must be taken to prevent traces of oxygen or water from entering the system.

In a typical preparation 50 μl (0.240 mmol) of 1,2-bis(trimethylsilyl)methylhydrazine was syringed into a capped nmr tube containing 0.3 ml of diethyl ether. The solution was cooled to $-78°$ and 0.143 ml (0.240 mmol) of 1.68 *M* methyllithium in ether was slowly added. The solution was carefully mixed while warming to room temperature. Methane is allowed to escape through a hypodermic needle connected to the dry nitrogen system. Best results were obtained with fresh methyllithium solution and when the hydrazide anion solution remained colorless or very slightly yellow. Concentrations of the anions were usually 10–15% (v/v) since too large a concentration causes lithium hydrazide salt precipitation. The nmr tubes, if carefully sealed, gave reproducible nmr spectra for several weeks.

The silylhydrazine anions can also be prepared on a larger scale using standard glassware and nitrogen atmosphere before transferring the solution by syringe to the capped nmr tube.

Proton Nmr Spectra. The proton nmr spectra were obtained with a Varian A60-A spectrometer using cyclohexane (τ 8.56) as internal standard. The appropriate regions for each sample were scanned at 50 or 100 cycle sweep width. The sweep time was 250 sec in all cases. Variable-temperature spectra were obtained with a Varian V-6040 variable-temperature controller and probe. Temperatures were checked before and after each spectrum was taken by measuring the chemical shift difference in the absorption peaks of methanol at low temperature and ethylene glycol at high temperature. Temperatures are estimated to be accurate to $\pm 1°$. Temperature-dependent spectra are reproducibly reversible in all cases.

The peak areas were measured by planimeter or the method of triangulation. The measurement precision is estimated as $\pm 2\%$.

Rearrangement and Insertion Reactions of 2-Methylbenzylidenes

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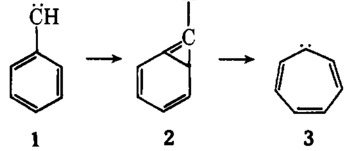
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received February 13, 1971*

Abstract: (2-Methylphenyl)diazomethane (**4**), generated by thermolysis of the sodium salt of 2-methylbenzaldehyde tosylhydrazone, decomposes at 150° to styrene (**6**), benzocyclobutene (**7**), and *o*-xylene along with *cis*- and *trans*-2,2′-dimethylstilbenes, 2,2′-dimethylbibenzyl, 2,2′-dimethylbenzaldazine, 2-methylbenzonitrile, and 2-methylbenzaldehyde. At higher temperatures conversion of **4** to **6** and **7** is increased; **6** is not formed, however, by isomerization of **7**. Pyrolysis of (2,5-dimethylphenyl)diazomethane (**8**) and (2,6-dimethylphenyl)diazomethane (**13**) was investigated to determine which methylstyrenes are produced. At 179–181° **8** decomposes to 4-methylstyrene (**10**), *cis*- and *trans*-2,2′,5,5′-tetramethylstilbenes, 2,2′,5,5′-tetramethylbenzaldazine, and 2,5-dimethylbenzonitrile; 3-methylstyrene is not formed. Neat **13** thermolyzes (176–194°) to 3-methylstyrene (**12**), 3-methylbenzocyclobutene (**15**), 2,6-dimethylbenzonitrile, and bimolecular products; 2-methylstyrene is not obtained. Conversion of α-deuterio(2-methylphenyl)diazomethane (**33**) at 350° to 2-deuteriostyrene (**35**) and 1-deuteriobenzocyclobutene (**36**) provides additional mechanistic information concerning isomerization of 2-methylbenzylidenes. In conversion of **4**, **8**, **13**, and **33** to **6**, **10**, **12**, and **35**, respectively, the intermediate 2-methylbenzylidenes (**17**) may isomerize to fused cyclopropenes **25** and their corresponding 2-methylcycloheptatrienylidenes (**26**) which (1) undergo carbon–hydrogen insertion to yield fused alkylidenecyclopropanes (**27**) and then styrenes and/or (2) rearrange to fused cyclopropenes **29** which isomerize to 1-phenyl-1-ethylidenes and their subsequent styrenes. An alternate possibility involves direct conversion of cyclopropenes **25** to cyclopropenes **29** and then to styrenes. The consequences of other possible isomerization processes in these systems are discussed.

Recently benzylidene (**1**) and 4-methylbenzylidene, as generated by pyrolysis (250°) of the sodium salts of the tosylhydrazones of benzaldehyde and 4-methylbenzaldehyde, respectively, were found to give heptafulvalene and dimethylheptafulvalene, apparently by dimerization of cycloheptatrienylidene (**3**) and methylcycloheptatrienylidene derived by isomerization (eq 1) of their parent carbenes.[1] Shortly thereafter, it was communicated that 4-, 3-, and 2-methylbenzylidenes, upon generation from the corresponding diazo compounds at 450°, each yield styrene (**6**) and benzocyclobutene (**7**) by multiple processes possibly involving intraconversion of the carbenes *via* intermediate cycloheptatrienylidenes.[2] We should like to report in detail



1 **2** **3** (1)

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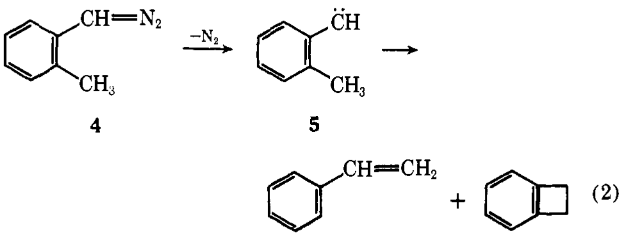
[1] (a) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969); (b) P. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *ibid.*, **92**, 2147 (1970); (c) C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, **53**, 1459 (1970).

[2] W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *J. Amer. Chem. Soc.*, **92**, 4739 (1970).[3]

our studies of multiple rearrangement of 2-methylbenzylidene (**5**), 2,5-dimethylbenzylidene (**9**), and 2,6-dimethylbenzylidene (**14**). These results and their possible interpretation involving isomerization of benzylidenes to cycloheptatrienylidenes and subsequent reorganization have been summarized previously;[4,5] however, present investigators have not been aware of these early studies. We should also like to describe our investigation of the intramolecular chemistry of α-deuterio-2-methylbenzylidene (**34**), a study proposed in our initial work[1a] and initiated shortly thereafter.[6]

Results and Discussion

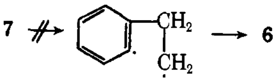
Pure (2-methylphenyl)diazomethane (**4**), prepared by vacuum thermolysis of the sodium salt of 2-methylbenzaldehyde tosylhydrazone at 90–120°, was first pyrolyzed under nitrogen in Pyrex at 150°. The diazo compound decomposed violently and gave along with intractables the volatile products: styrene (**6**, eq 2, 9%), benzocyclobutene (**7**, 4%), *o*-xylene (0.4%), *cis*-2,2′-dimethylstilbene (5%), *trans*-2,2′-dimethylstilbene (9%), 2,2′-dimethylbibenzyl (11%), 2,2′-dimethylbenzaldazine (∼2%), 2-methylbenzonitrile (3%), and 2-methylbenzaldehyde (∼1%). Similar results were obtained upon injection of **4** into a heated glass liner (157–168°) of a gas–liquid chromatograph. Conversion of **5** to **6** (11%), **7** (16%), and *o*-xylene (2%) was improved upon decomposing **4** at 250°. At 350°, *o*-xylene was not formed and the yields of **6** and **7** were 11 and 25%, respectively. The thermal and photolytic behaviors of **4** are decidedly different;[7] irradiation of neat **4** at 20° with a 425-W mercury lamp yielded 2,2′-dimethylbenzaldazine (74%), *cis*-2,2′-dimethylstilbene (4%), *trans*-2,2′-dimethylstilbene (19%), and neither **6** nor **7**.[8]



6 **7** (2)

Intramolecular carbenic conversion of **5** at 150–350° to **7** is formally analogous to decomposition of dimesityldiazomethane at 140° to 4,6-dimethyl-1-mesitylbenzocyclobutene.[9] Conversion of **5** to 2,2′-dimethylbibenzyl, particularly at lower pyrolytic temperatures in Pyrex, presumably arises from environmental hydrogen transfer to triplet 2-methylbenzylidene and dimerization of 2-methylbenzyl radicals. *o*-Xylene apparently results from intermolecular hydrogen transfer to the 2-methylbenzyl radicals. Conversions of **4** to 2,2′-dimethylbenzaldazine, *cis*- and *trans*-2,2-dimethylstilbenes, and 2-methylbenzonitrile have ample precedent.[10,11]

The observation of principal interest in the present study is thermal conversion of **4** to **6**, a process which must involve at least double rearrangement of **5** and cannot involve isomerization of **7** (eq 3). It has been previously reported that **7** containing only 2% **6** is produced by pyrolysis of 1,3-dihydroisothianaphthene 2,2-dioxide at 770°;[12] **6** is not formed at lower temperatures.[12] In the present investigation, **7** has been found not to convert to **6** using pyrolytic gas–liquid chromatographic methods under conditions (150–350°) at which **6** is formed from **4**.[13]



(3)

As a first step in studying the mechanisms of formation of styrenes, thermal decompositions of (dimethylphenyl)diazomethanes were examined. The principal objective of these experiments was to determine whether mixtures or single methylstyrenes were formed from each diazo compound, and which of the possible isomeric methylstyrenes was obtained if there were only one such product from each diazo compound.

Decomposition of (2,5-dimethylphenyl)diazomethane (**8**) at 179–181° yielded 4-methylstyrene (**10**, 7%) and 4-methylbenzocyclobutene (**11**, 4%) as intramolecular products of **9** (eq 4); 3-methylstyrene (**12**) could not be detected. Additional products from **8** were *cis*- and *trans*-2,2′,5,5′-tetramethylstilbenes (63%), 2,2′,5,5′-tetramethylbenzaldazine (6%), and 2,5-dimethylbenzonitrile (3%).

The study of intramolecular reactions of 2-methylbenzylidenes was then extended to 2,6-dimethylbenzylidene (**14**). Thermolysis of pure (2,6-dimethylphenyl)-

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(3) In an accompanying communication, J. A. Myers, R. C. Joines, and W. M. Jones, *J. Amer. Chem. Soc.*, **92**, 4740 (1970)) report that diarylmethylidenes pyrolyze to arylcycloheptatrienylidenes and that arylcycloheptatrienylidenes ring contract to biphenylmethylidenes; see also ref 1c.

(4) (a) G. G. Vander Stouw, *Diss. Abstr.*, **25** (12), 6974 (1965), in summary of a Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1964; University Microfilms (Ann Arbor, Mich.), 65-5684; (b) G. G. Vander Stouw, *Chem. Abstr.*, **63**, 13126b (1965); (c) the results of these investigations have been presented at the Carbene Symposium, Lockport, Ill., April 3, 1965, and at the Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 10, 1968.

(5) The sponsorship of this research by the National Science Foundation (G 15559 and GP 22545) and the National Institutes of Health (CA 11185-03) is gratefully acknowledged.

(6) We should like to acknowledge the contributions of R. L. Larrabee, Jr., 1967, in this effort.

(7) (a) Reaction of 2-methylbenzaldehyde tosylhydrazone with sodium methoxide (1.25 equiv) in *N*-methylpyrrolidone at 160° did not give **6** or **7**; the principal products are 2-methylbenzyl alcohol (38%) and 2-methylphenyl 4-methylphenyl sulfone (4%) along with *o*-xylene and 2-methylbenzonitrile. Extensive formation of 2-methylbenzyl alcohol in this solvent system apparently results from methanolysis of 2-methylbenzyl 4-methylbenzenesulfinate; isomerization of the sulfinate may give its sulfone. (b) Similar complications in base-catalyzed decomposition of sulfonylhydrazones have been reported by J. W. Wilt and C. A. Schneider, *Chem. Ind. (London)*, 865 (1963).

(8) H. Nozaki, R. Noyori, and K. Sisido (*Tetrahedron*, **20**, 1125 (1964)) report that photolysis of the sodium salt of 2-methylbenzaldehyde tosylhydrazone in cyclohexane at 70° results in 2-methylbenzaldehyde (8%), *trans*-2,2′-dimethylstilbene (41%), 2,2′-dimethylbenzaldazine (15%), and 2-methylbenzaldehyde *N*-(2-methylbenzyl)tosylhydrazone. Similar results were obtained from 2,4,6-trimethylbenzaldehyde tosylhydrazone. Benzocyclobutenes and styrenes were not observed in these experiments.

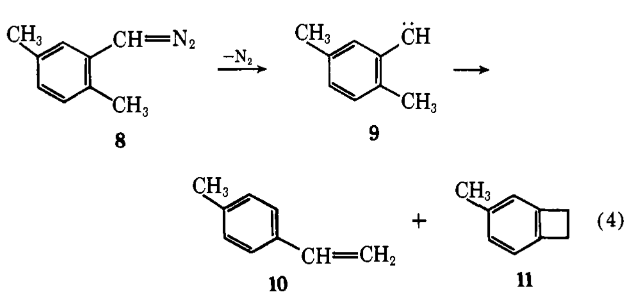
(9) H. E. Zimmerman and D. H. Paskovich, *J. Amer. Chem. Soc.*, **86**, 2149 (1964).

(10) Examples and references of thermal and photochemical conversions of phenyldiazomethanes to azines are contained in (a) H. Staudinger and A. Gaule, *Ber.*, **49**, 1897 (1916); (b) C. D. Gutsche, E. F. Jason, R. S. Coffey, and H. E. Johnson, *J. Amer. Chem. Soc.*, **80**, 5756 (1958); (c) W. Kirmse, L. Horner, and H. Hoffman, *Justus Liebigs Ann. Chem.*, **614**, 19 (1958); and (d) V. Franzen and H. I. Joschek, *ibid.*, **633**, 7 (1960).

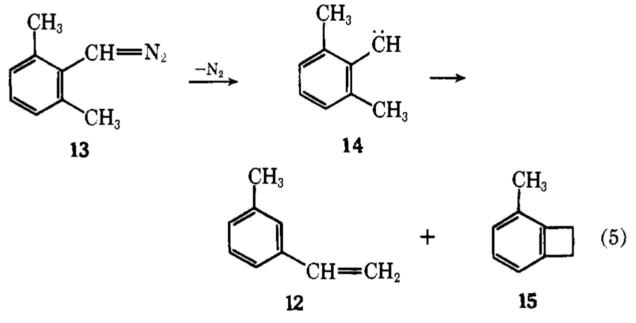
(11) Thermal decomposition of benzaldazines with loss of nitrogen to give stilbenes and nitriles by chain reactions involving catalysis by aryldiazomethanes has been studied by H. E. Zimmerman and S. Somasekhara, *J. Amer. Chem. Soc.*, **82**, 5865 (1960), and references therein.

(12) M. P. Cava and A. A. Deana, *ibid.*, **81**, 4266 (1959).

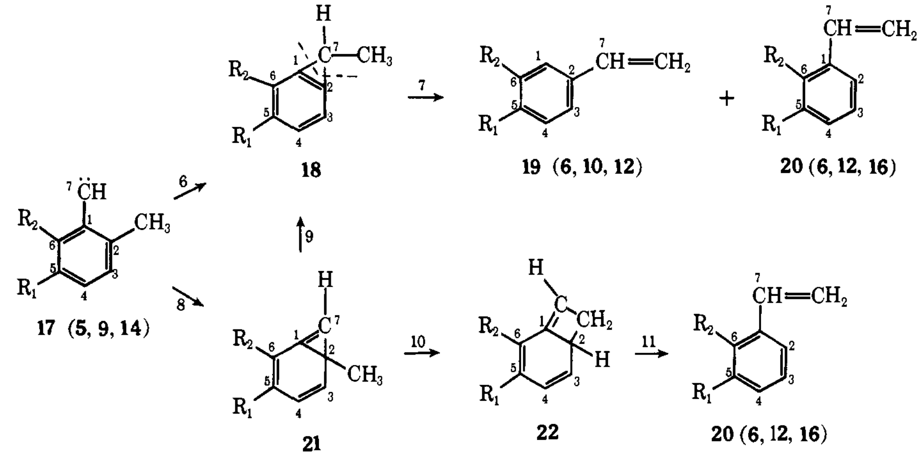
(13) Rupture of the 1,2 rather than the 2,3 carbon–carbon bonds of the cyclobutene ring in 4,6-dimethyl-1-mesitylbenzocyclobutene occurs at 215° to give eventually 2,2′-di(mesitylmethyl)-3,3′,5,5′-tetramethylstilbene; dimethylstyrenes were not obtained.[9]



diazomethane (13) at 176–194° gave (eq 5), along with bimolecular products, 3-methylstyrene (12, 3%), 3-methylbenzocyclobutene (15, 17%), and 2,6-dimethyl-



benzonitrile (7%); 2-methylstyrene (16) was not found. The conversion of 14 to benzocyclobutene 15 relative to styrene 12 is considerably greater than that for analogous processes for 5 and for 9.



Conversions of 9 to 10 and 14 to 12 indicate that the mechanisms of conversion of the 2-methylbenzylidenes (17) to their styrenes do not involve benzocyclopropenes (18), formed either by carbon–carbon insertion (eq 6) or by structural reorganization to the fused cyclopropenes 21 (eq 8) and then methyl migration to 18 (eq 9).[14a–d] Such processes are expected to result in mixtures of styrenes (19 and 20, eq 7).[14c] Isomerization of 21 (or 17) with hydrogen rearrangement and ring expansion to cyclobutenes 22 (eq 10) are also not involved. Such processes would result in single styrenes (20, eq 11) isomeric with those found.[14e]

One mechanism which would account for the conversion of 17 (5, 9, and 14) to their respective styrenes is that fused cyclopropenes 21 (eq 12 and 13) isomerize with 1,3-hydrogen rearrangement to C-1 with formation of fused bicyclobutanes 24 (eq 13) and then their styrenes 19 (6, 10, and 12, eq 14). Much more likely processes for conversion of the (2-methylphenyl)diazomethanes 4, 8, and 13 to their respective styrenes 28 (6, 10, and 12) involve intramolecular attack (eq 15) at C-6[15] of the 2-methylbenzylidenes 17 (5, 9, and 14) and valence isomerization of the resulting fused cyclopropenes 25 to their corresponding 2-methylcycloheptatrienylidenes (26)[16] (eq 16). The cycloheptatrienylidenes (26) may undergo either (1) carbon–hydrogen insertion (eq 17) into their 2-methyl groups to give fused, conjugated alkylidenecyclopropanes (27) which reorganize (eq 18) possibly *via* bicyclobutanoid processes to their respective styrenes 28 (6, 10, and 12) and/or (2) bicyclization[17] (eq 19) at their C-3 positions and isomerization (eq 21) of the resulting fused cyclopropenes 29 to 1-phenyl-1-ethylidenes[18] (30) and their subsequent styrenes 28 (eq 22; 6, 10, and 12). An alternate possibility is direct valence isomerization[2,3] of fused cyclopropenes 25 to fused cyclopropenes 29 and their conversion to styrenes 28 (eq 20 and 21).

The mechanisms of conversion of 2-methylbenzylidenes (17) to styrenes 19 *via* 21, 23, and 24 predict that the parent carbenes (17) labeled at C-7 with deuterium will give styrenes 19 having the isotope in the α positions of the vinyl groups. On the other hand, rearrangement of C_7-D benzylidenes 17 to 25 and thence *via* 26 and 27 or 29 and 30 will yield styrenes 28 having deuterium at the 2 positions of the benzene rings. To obtain information concerning the mechanisms of conversion of 17 to styrenes, a study has been made of the intramolecular products of decomposition of the so-

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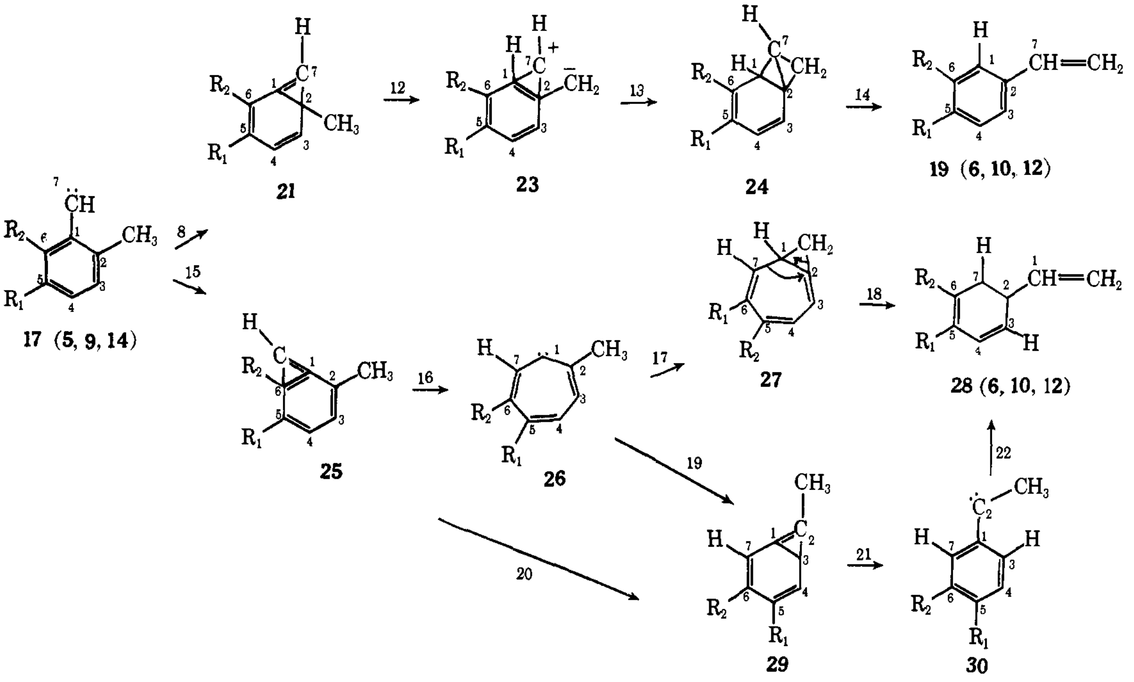
(14) (a) These processes have previous analogy in that (1) aromatic substitution involving carbenic insertion may occur by singlet or triplet processes,[14b] (2) 3-methyl-3*H*-indazoles, presumably *via* their isomeric diazo compounds, lose nitrogen and reorganize carbenically to 1-methylbenzocyclopropenes which convert thermally to styrenes,[14c] (3) phenylnitrene and 2-pyridylmethylidene apparently intraconvert *via* processes having the structural character of nitrogen-containing valence tautomers of 21 and of azacycloheptatrienylidene,[14d] and (4) cyclobutenes isomerize to 1,3-butadienes.[14e] (b) M. J. S. Dewar and K. Narayanaswami, *J. Amer. Chem. Soc.*, 86, 2422 (1964), and G. Baum, R. Bernard, and H. Shechter, *ibid.*, 89, 5307 (1967). (c) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *ibid.*, 89, 3376 (1967) and R. Anet and F. A. L. Anet, *ibid.*, 86, 525 (1964). (d) M. Appl and R. Huisgen, *Chem. Ber.*, 92, 2961 (1959), and W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 6149 (1968). (e) H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Amer. Chem. Soc.*, 87, 3019 (1965), and references therein.

(15) In 14, C-2 and C-6 are identical.

(16) The previous basis for processes of this type is indicated in ref 3c–d, 4, 1, 2, and 3.

(17) This mechanistic route has been suggested in ref 2.

(18) Thermolysis of 1-phenyl-1-diazoethane yields styrene.



dium salt **32** of α-deuterio-2-methylbenzaldehyde tosylhydrazone (**31**). Salt **32** was prepared upon exchange of 2-(2-methylphenyl)-1,3-dithiane with *n*-butyllithium, quenching with deuterium oxide and hydrolysis to α-deuterio-2-methylbenzaldehyde,[19] synthesis of **31**, and reaction with sodium hydride.

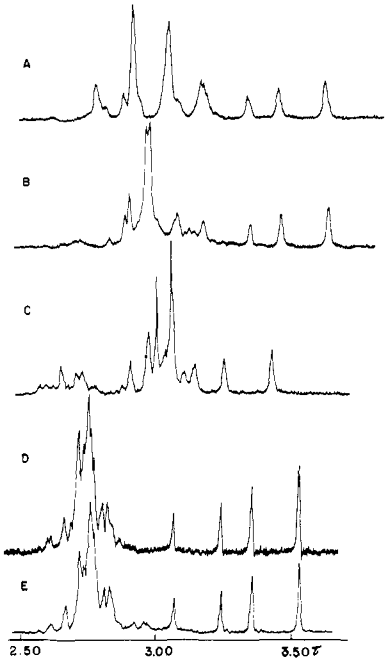
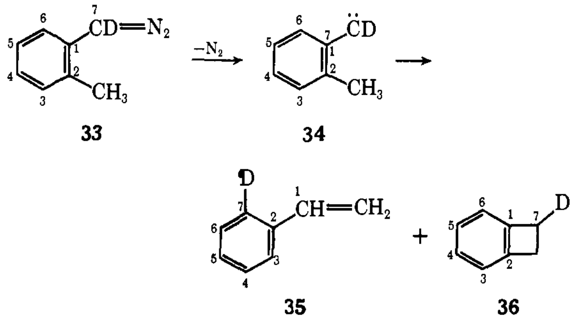


Figure 1. Nmr spectra (60 MHz; TMS as internal standard) measured in CCl_4 for (A) 4-methylstyrene, (B) 3-methylstyrene, (C) 2-methylstyrene, (D) 2-deuteriostyrene (authentic sample), (E) 2-deuteriostyrene produced *via* 2-methylbenzylidene.

Thermolysis of **33** as generated from **32** at 350° resulted in 2-deuteriostyrene (**35**) and 1-deuteriobenzocyclobutene[20] (**36**, eq 23) in a 1.0:3.0 ratio. The nmr



(23)

of **35** reveals the location of its deuterium in that (1) the resonance of its vinyl protons is identical, but that of its phenyl protons is different from that of undeuterated styrene,[21] (2) its vinyl and phenyl hydrogens integrate in a ratio of 3.0:4.0, (3) the splitting of its phenyl protons is distinctly different from that of 3- and 4-methylstyrenes[22] (Figure 1), and (4) its phenyl protons at sweep

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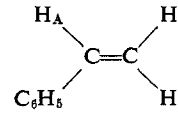
[19] An adaption of the method of D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, **31**, 4303 (1966).

[20] In naming benzocyclobutene derivatives, the methylene carbon atoms are numbered 1 and 2.

[21] Styrene

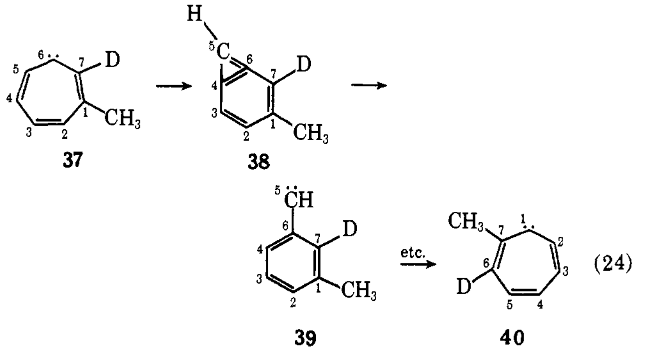


and **35** (Figure 1) have the following vinyl proton nmr: H_A, τ 3.30 (quartet); H_B, 4.33 (d of doublets); H_C, 4.81 (d of doublets); $J_{AB} = 17.6$ Hz; J_{AC} 10.8 Hz; and $J_{BC} = -1.4$ Hz. For analysis of the nmr spectra of styrene and α-deuteriostyrene, see E. I. Snyder, *J. Phys. Chem.*, **67**, 2873 (1963).

[22] (a) The coupling constants for phenyl protons are $J_{\text{ortho}} = 6.0$–9.4 Hz, $J_{\text{meta}} = 1.2$–3.1 Hz, and $J_{\text{para}} = 0.2$–1.5 Hz. Since a coupling constant with deuterium is smaller ($J_{H,H} = J_{H,D} \times 6.514$) and often lessened by broadening due to the quadrupole moment of deuterium,[22b] in deuterated phenyl groups $J_{\text{ortho}}{}^{H,D}$ will be $\sim$1 or less and $J_{\text{meta}}{}^{H,D}$ and $J_{\text{para}}{}^{H,D}$ will be negligible. Thus, deuterium in a phenyl group has little effect on the splitting of the ring protons. Since the effect of a methyl group on the splitting of phenyl hydrogen approximates that of deuterium,[22c] the nmr (Figure 1) of the aromatic regions of 2-, 3-, and 4-methylstyrenes, respectively, was compared with that of the styrene from **34** in order to assign the position of its isotopic label. From the spectra of 3- and 4-methylstyrenes it can be concluded that the rearrangement product of **34** is neither 3-deuterio- nor 4-deuteriostyrene. However, it could not be conclusively decided from the spectra of 2-methylstyrene, probably because of steric interaction of the methyl and vinyl groups, that the styrene from **34** has *all* of its deuterium in the 2 position. Therefore, 2-deuteriostyrene was synthesized and its spectra compared with that of **35**. (b) L. M. Jackman and S. Stern-

widths of 50 and 100 Hz show the same shape and splitting as does authentic (>95%) **35** (Figure 1). The position of deuterium in **36** is located by nmr at τ 6.92 (singlet) and 3.02 (multiplet) in a ratio of 3.0:4.0.

Isomerization of **34** thus does not involve C_7–D bicyclobutane **24** (eq 13 and 14) upon conversion to **35**. Choice cannot be made presently as to whether isomerization of **34** *via* **35**-C_7–D to **35** involves eq 16, 17, and 18, eq 16, 19, 21, and 22, and/or eq 20–22.[23,23a] Ring contractions of 4-methyl- and 3-methylcycloheptatrienylidenes appear to be involved in the conversion of 4-methyl- and 3-methylbenzylidenes to 2-methylbenzylidenes (processes analogous to eq 19 and 21) and intermediates such as **27** might be expected to isomerize possibly in part to methylenecycloheptatrienes. Conversion of **34** to **36** apparently occurs by a direct carbenic process which is favored relative to isomerization to **35** as the reaction temperature is increased. On the basis of essentially 100% location of deuterium as indicated in **36**, redistributive isomerization of **34** to 3-deuterio-2-methylbenzylidene, and then insertion to give 3-deuteriobenzocyclobutene, is an unimportant process. Isomerization of **34** to **21**-C_7–D (eq 8) and then to 2-deuterio-3-methylcycloheptatrienylidene (**37**) may be occurring;[24] however, **37** must reverse to **25**-C_7–D *via* **34** or else isomerize by a lengthy series of ring contractions and expansions (eq 24) to 3-deuterio-2-methylcycloheptatrienylidene (**40** = **26**-C_3–D) before yielding **35**.[24]



37 **38** **39** **40** (24)

Experimental Section

2-Methylbenzaldehyde. α-Bromo-*o*-xylene (Matheson Coleman and Bell Division, Matheson Chemical Corporation) was converted by the sodium salt of 2-nitropropane to pure 2-methylbenzaldehyde[25] (77%).

2,5-Dimethylbenzaldehyde. A mixture of 99.9% *p*-xylene (100 g, 0.94 mol), glacial acetic acid (290 ml), 12 *N* hydrochloric acid (630 ml), and 37% formaldehyde solution (65 g, 0.77 mol) was stirred at 50–60° for 24 hr. Additional formaldehyde solution (19 g, 0.23 mol) was added, and after 24 hr, the mixture was cooled and extracted with benzene. The combined extracts were washed with 10% sodium carbonate solution and water, dried, and concentrated to 2,5-dimethylbenzyl chloride (87.7 g, 60%), bp 104–106° (2 mm).

Sodium (13.1 g, 0.57 mol) was dissolved in absolute ethanol (500 ml) and 2-nitropropane (50.7 g, 0.57 mol) and then 2,5-dimethylbenzyl chloride (87.7 g, 0.57 mol) was added. The stirred solution was filtered after 4 hr, concentrated, and then diluted with ether and water. The ether layer was washed with 10% sodium hydroxide solution and water, dried, and distilled to yield 2,5-dimethylbenzaldehyde (57.8 g, 76%), bp 66° (3 mm).

2,6-Dimethylbenzaldehyde. A solution of thionyl chloride (29.3 g, 0.25 mol) in benzene (75 ml) was added in 30 min to stirred 2,6-dimethylbenzyl alcohol[26] (30.5 g, 0.23 mol) in benzene (200 ml) and pyridine (19.5 g). After the mixture had been refluxed for 2 hr, water was added and the benzene layer was separated, washed with water, dried, and distilled to yield 2,6-dimethylbenzyl chloride (20.6 g, 59%), bp 101–102° (10 mm).

2,6-Dimethylbenzyl chloride (20.6 g, 0.13 mol) in absolute ethanol (50 ml) was added to a stirred solution of sodium (3.1 g, 0.13 mol) and 2-nitropropane (11.6 g, 0.13 mol) in absolute ethanol (130 ml). After 3 hr, the mixture was concentrated and then diluted with ether and water. The ether layer was washed with 10% sodium hydroxide solution and water, dried, and upon distillation gave 2,6-dimethylbenzaldehyde (11.4 g, 63%), bp 79° (3 mm).

Preparation of Tosylhydrazones. The benzaldehyde was dissolved in sufficient anhydrous methanol to make a 20–30% solution. An equivalent 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 vacuum-dried. The tosylhydrazones were stable indefinitely at room temperature.

The properties of the tosylhydrazones prepared are: 2-methylbenzaldehyde tosylhydrazone, mp 136–138° (lit.[8] mp 143–144°); 2,5-dimethylbenzaldehyde tosylhydrazone, mp 145–146° (*Anal.* Calcd for $C_{16}H_{18}N_2O_2S$: N, 9.26. Found: N, 9.20); and 2,6-dimethylbenzaldehyde tosylhydrazone, mp 155–158° (*Anal.* Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.55; H, 6.00; N, 9.26. Found: C, 63.32; H, 5.98; N, 9.12).

Sodium Salts of Tosylhydrazones. 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, Inc.) was added. The mixture was stirred overnight at room temperature. The resulting white or light pink solid was filtered, washed with anhydrous diethyl ether, and dried under vacuum. The salts were hygroscopic and were kept under vacuum until used. Ordinarily the salts were used within 3 days.

Phenyldiazomethanes (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 cooled to 0°. The system was evacuated to 1–2 mm and the salt was slowly heated. 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 nitrogen. The yields of pure phenyldiazomethanes by this procedure range from 15 to 45%. Purity was emphasized in these preparations and thus the salts of the tosylhydrazones were decomposed slowly and at relatively low temperatures; under these conditions there is extensive conversion of the diazo compounds to azines in the distillation flask. Rapid decomposition of the tosylhydrazone salts gives the phenyldiazomethanes in excellent yields; however, the products are contaminated by volatile products of decomposition of the azines formed. The phenyldiazomethanes gave strong infrared absorptions ($C{=}N_2$) at 4.86–4.88 μ and their purity was established (~100%) gasometrically from the nitrogen evolved from an aliquot in anhydrous ether upon addition of acetic acid. The phenyldiazomethanes can be stored in a freezer for a few days without much change; after 2 weeks or longer, there is extensive conversion of the diazo compounds to azines.

2,2′-Dimethylbenzaldazine. (2-Methylphenyl)diazomethane (**4**) on storage for several weeks decomposed to a yellow solid which on crystallization from methanol gave 2,2′-dimethylbenzaldazine, mp 96–97° (lit.[27] mp 100°).

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hell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 142. (c) The phenyl group will not be sufficiently perturbed to affect the splitting of the ring protons and possible long-range coupling to the methyl protons would only broaden the peaks.

(23) 2-Methylcycloheptatrienylidene has been reported to isomerize to styrene.[3]

(23a) Note Added in Proof. After the present manuscript had been submitted (Feb 13, 1971) for publication, E. Hedaya and M. E. Kent, *J. Amer. Chem. Soc.*, **93**, 3283 (1971), submitted (March 15, 1971) a Communication to the Editor reporting that *p*-[^{13}C]tolyldiazomethane is converted at 700° to [4-^{13}C]benzocyclobutene and [4-^{13}C]styrene. The apparent mechanisms for isomerization of *p*-[^{13}C]tolylmethylidene thus are consistent with that proposed for α-deuteriobenzylidene in the present manuscript.

(24) Similarly, **17** (**9**, **14**) might convert to **21** before isomerizing to **10** and **12**.

(25) H. B. Hass and M. L. Bender, *Org. Syn.*, **30**, 99 (1950).

(26) (a) Prepared by reduction of 2,6-dimethylbenzoic acid, mp 120–121° (lit.[26b] mp 116°) with lithium aluminum hydride; (b) B. van Zanten and W. Th. Nauta, *Recl. Trav. Chim. Pays-Bas*, **79**, 1211 (1960).

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.

2,2′,5,5′-Tetramethylbenzaldazine. (2,5-Dimethylphenyl)diazomethane (**8**), after 10 days at 20–25°, gave a yellow solid which was recrystallized from methanol to yield 2,2′,5,5′-tetramethylbenzaldazine, mp 129–130°.

Anal. Calcd for $C_{18}H_{20}N_2$: N, 10.60. Found: N, 10.59.

Gas–Liquid Chromatographic Standards. Authentic 4-, 3-, and 2-methylstyrenes (**10**, **12**, and **16**) were purchased from the Columbia Organic Chemicals Co., Inc. Dr. M. P. Cava, then of the Department of Chemistry, The Ohio State University, Columbus, Ohio, provided benzocyclobutene (**7**). 2,2′-Dimethylbibenzyl was prepared by vibrationally stirring a mixture of sodium and α-bromo-*o*-xylene in hexadecane under nitrogen at 160° for 1 hr. *o*-Xylene, 2,5-dimethylbenzonitrile, 2,5-dimethylbenzyl alcohol, and 2,6-dimethylbenzonitrile were available or prepared by traditional procedures. *cis*- and *trans*-2,2′-dimethylstilbenes and *cis*- and *trans*-2,2′,5,5′-tetramethylstilbenes were prepared *via* phosphoranylic methods as described.

2,2′-Dimethylstilbenes and 2,2′,5,5′-Tetramethylstilbenes. A solution of α-bromo-*o*-xylene (10 g, 0.054 mol) and triphenylphosphine (14.2 g, 0.054 mol) in benzene (50 ml) was stirred for 10 hr. The (2-methylbenzyl)triphenylphosphonium bromide formed was washed with benzene and dried; white crystals, mp 270–271°.

Sodium hydride (1.22 g of a 53.4% suspension in mineral oil, 0.027 mol) was washed with pentane and then dissolved in dimethyl sulfoxide (50 ml). The yellow solution was stirred under nitrogen at 65° until hydrogen ceased evolving and was then cooled to 25°. A slurry of (2-methylbenzyl)triphenylphosphonium bromide (12 g, 0.027 mol) in dimethyl sulfoxide (30 ml) was then added.

2-Methylbenzaldehyde (3.24 g, 0.027 mol) in dimethyl sulfoxide (20 ml) was dropped slowly into the phosphorane solution. After 4 hr the mixture was poured onto ice and extracted with methylene chloride. The extract was evaporated, diluted with petroleum ether, filtered to remove triphenylphosphine oxide, and concentrated. The yellow product on analysis by gas–liquid chromatography on an SE-30 column indicated the presence of two main components in approximately equal concentrations. In 2 days most of the material of higher retention time crystallized. Both this product and the remaining oil showed strong infrared absorption of 10.4 μ characteristic of stilbenes.[28] Recrystallization of the solid material from 95% ethanol gave *trans*-2,2′-dimethylstilbene, mp 82–83° (lit.[29] mp 82.5–83°); the remaining product was *cis*-2,2′-dimethylstilbene.

cis- and *trans*-2,2′,5,5′-tetramethylstilbenes were prepared from (2,5-dimethylbenzyl)triphenylphosphonium chloride by reaction with sodium methylsulfinylmethide and then 2,5-dimethylbenzaldehyde by procedures identical with that used for synthesis of 2,2′-dimethylstilbenes. The isomeric tetramethylstilbenes were separated by gas–liquid chromatography on an SE-30 column at 269°.

Thermal Decomposition of (2-Methylphenyl)diazomethane (4). **(a) Static Pyrolysis.** Neat **4** (2.1 g) was added slowly to a Pyrex flask flushed with dry nitrogen and heated at 150°. The diazo compound decomposed violently on contact with the heated flask to give a dark brown material which on gas–liquid chromatography with a Carbowax 20-M column at 152° and with an SE-30 column at 280° contained the following volatile products in the indicated per cent yields: toluene (0.3%), *o*-xylene (0.4%), benzocyclobutene (**7**, 4%), styrene (**6**, 9%), 2-methylbenzaldehyde (0.9%), 2-methylbenzonitrile (3%), 2-methylbenzyl alcohol (2%), *cis*-2,2′-dimethylstilbene (5%), 2,2′-dimethylbibenzyl (11%), *trans*-2,2′-dimethylstilbene (9%), and 2,2′-dimethylbenzaldazine (≫2%). The yields were estimated by comparison of gas–liquid chromatographic peak areas with those from measured samples of authentic standards. The C_8H_8 hydrocarbon mixture was analyzed at 100° with an SE-30 column.

(b) Pyrolytic Gas–Liquid Chromatography. Samples of **4** were syringed into a heated glass-lined injector of an Aerograph A-90-P chromatograph. For production and analysis of the relatively low boiling products in various experiments the injector ranged from 162 to 200° and a Carbowax 20-M column was used at 138–162°. For generation of the higher boiling volatile products, the injector was heated from 268 to 277° and analyses were effected on an SE-30 column at 239–256°. A large nitrogen peak appeared within a few seconds after each injection, indicating that decomposition had occurred immediately. Peaks appeared corresponding to the various products, each of which was identified, and their yields were determined by comparison of their retention times and peak areas with those of authentic standards. The presence or absence of clean or dirty glass inserts did not affect the nature of the products of decomposition of **4**. For preparative purposes the C_8 hydrocarbons were collected as a mixture, characterized by their infrared and ultraviolet spectra, and then analyzed on a squalane column (100 ft) at 92°.

A typical experiment in which an aliquot of **4** was syringed into the injector heated to 168° and a second aliquot was added later to the injector at 239° resulted in identification of **6** (7%), **7** (4%), *o*-xylene (0.1%), 2-methylbenzonitrile (3%), *cis*-2,2′-dimethylstilbene (1%), *trans*-2,2′-dimethylstilbene (3%), 2,2′-dimethylbibenzyl (5%), and 2,2′-dimethylbenzaldazine (1%).

(c) Flash Pyrolysis of Sodium 2-Methylbenzaldehyde Tosylhydrazone. 2-Methylbenzaldehyde tosylhydrazone (1 equiv) was converted to its sodium salt by reaction with sodium hydride (1.1 equiv) in either anhydrous diethyl ether or methylene chloride. The salt was filtered, dried *in vacuo*, and dropped into a Pyrex flask heated to 250° (1 mm). Decomposition was instantaneous and the volatile product was condensed in a liquid nitrogen trap. The condensate was analyzed by nmr methods and then by gas–liquid chromatography on a 1,2,3-tris(β-cyanoethoxy)propane (20%)–Chromosorb P (80%) column at 75°. Comparison with authentic samples showed that the C_7–C_8 hydrocarbon products were toluene (5.6%), *o*-xylene (2.0%), **6** (10.6%), and **7** (15.5%).

(d) Hot Tube Techniques. The sodium salt of 2-methylbenzaldehyde tosylhydrazone, prepared as described previously, was placed in a Pyrex flask and the pressure was reduced to 1 mm. Generation of **4** was achieved by heating the salt slowly from 100 to 180°. Decomposition of **4** was effected at 350° in a tube packed with glass beads. The volatile product was collected in a liquid nitrogen trap; **6** (11% yield) and **7** (25% yield) were then analyzed, preparatively chromatographed, and characterized further by their ir and nmr spectra. Nmr of **7** occurred at τ 2.97 (m, Ar-*H*) and at 6.90 (s, C*H*$_2$).

(e) Photolysis. Stirred **4** (1.3 g) was irradiated for 20 hr at 20° with a 425-W mercury vapor lamp (Hanovia Lamp Division, Engelhard Hanovia, Inc.). The product, a yellow solid, was analyzed by gas–liquid chromatography on Carbowax 20-M (184°) and SE-30 (238°) columns. The components observed were 2-methylbenzaldehyde (minor amount), 2-methylbenzyl alcohol (minor amount), *cis*-2,2′-dimethylstilbene (4%), *trans*-2,2′-dimethylstilbene (19%), and 2,2′-dimethylbenzaldazine (74%).

Attempted Decomposition of Benzocyclobutene (7). Samples of **7** were syringed into an Aerograph-A-90-P chromatograph in which the temperature of the injector ranged from 164 to 350°. The gas chromatographic and spectral properties of the exit product were identical with that of initial **7**.

Thermal Decomposition of 1-Diazo-1-phenylethane. The lithium salt of acetophenone tosylhydrazone was pyrolyzed at 0.08–0.5 mm at 105–135° to give 1-diazo-1-phenylethane as a purple-colored liquid which was collected at −20° and showed strong infrared absorption for a diazo group at 4.90 μ. The yield of the diazo compound was approximately 65%.

Decomposition of the 1-diazo-1-phenylethane was effected upon injection of neat samples into a heated injector of a gas–liquid chromatograph. Analysis on a 3% SF-96 column showed styrene and nitrogen to be the only products of thermolysis.

Thermal Decomposition of (2,5-Dimethylphenyl)diazomethane (8). Pure **8** was decomposed by pyrolytic gas–liquid chromatography at an injector temperature of 179° and a Carbowax 20-M column at 170°. Higher boiling materials were determined from the injector heated to 296° and an SE-30 column at 269°. The products obtained were 4-methylstyrene (**10**, 7%), 4-methylbenzocyclobutene (**11**, 4%), 2,5-dimethylbenzonitrile (3%), *cis*- and *trans*-2,2′,5,5′-tetramethylstilbenes (63%), and 2,2′,5,5′-tetramethylbenzaldazine (6%).

A sample of **8** was decomposed with the injector at 181° and an SE-30 column at 121°. The C_9 hydrocarbons were collected as a mixture and characterized as follows. The ir spectrum of the mixture exhibited olefinic absorption at 6.16 μ and cycloalkane absorption at 10.05 μ. There was strong absorption at 12.1 μ and weak absorption at 13.7 μ which correspond to peaks in the spectrum of authentic **10**. Absorptions shown by authentic 3-methylstyrene (**12**) at 12.7 and 14.1 μ were absent. The uv spectrum of the hydrocarbon mixture had a maximum at 254 mμ which corresponds to that of **10**.

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(27) S. Pietra and C. Trinchera, *Gazz. Chim. Ital.*, **85**, 1705 (1955).

(28) S. F. D. Orr, *Spectrochim. Acta*, **8**, 218 (1956).

(29) R. M. Beale and E. M. F. Roe, *J. Amer. Chem. Soc.*, 74, 2302 (1952).

The nmr spectrum of the hydrocarbon mixture exhibited a triplet at τ 7.72 (ArCH_3), a singlet at 6.95 (CH_2 protons in **11**), complex absorptions from 4.0 to 5.1 (olefinic H in **10**), and a multiplet from 2.8 to 3.2 (Ar-H). Analysis by nmr methods revealed the mixture to be 69% **10** and 31% **11**. By gas-liquid chromatography the mixture was found to be 67% **10** and 33% **11**.

Thermal Decomposition of (2,6-Dimethylphenyl)diazomethane (13). Decomposition of **13** was effected gas-liquid chromatographically in an injector at 194° and on a Carbowax 20-M column at 178°. The low boiling products were 3-methylstyrene (**12**, 3%), 3-methylbenzocyclobutene (**15**, 17%), 2,6-dimethylbenzonitrile (7%), and 2,6-dimethylbenzyl alcohol (1%).

The hydrocarbon product was preparatively collected as a mixture and revealed an ultraviolet absorption maximum at 251 mμ which corresponded to that of authentic **12**. The mixture displayed olefinic absorption at 6.2 μ and cycloalkane absorption at 10.05 μ. Strong absorptions were obtained at 12.7 and 14.1 μ corresponding to those in the spectrum of authentic **12**; absorptions characteristic of 2-methylstyrene (**16**) at 13.0 and 13.7 μ were absent.

The nmr spectrum of the mixture showed singlets at τ 7.92 and 7.77 (ArCH_3), a singlet at 7.01 (CH_2 protons in **15**), complex absorptions from 4.0 to 5.0 (olefinic protons in **12**), and a multiplet at 3.2 (ArH). Integration of the olefinic and the methylene hydrogen resonances indicated that the product was 7% **12** and 93% **15**. Analysis of the mixture chromatographically on a 100-ft squalane column at 58° indicated that 13% **12** and 87% **15** were present; there was no evidence for formation of **16** in these experiments.

Thermal Decomposition of the Sodium Salt 32 of α-Deuterio-2-methylbenzaldehyde Tosylhydrazone (31). α-Deuterio-2-methylbenzaldehyde was converted to **31** by tosylhydrazide in tetrahydrofuran and then to **32** by sodium hydride in anhydrous diethyl ether. Decomposition of dry **32** was effected at 350° using the hot tube techniques previously described. The volatile product was shown to be **6** and **7** in a 1:3 ratio by analytical gas-liquid chromatography. The hydrocarbons were separated and collected using a gas-liquid chromatographic column of tetracyanoethylated pentaerythritol (20%) on Chromosorb P (80%) at 80°. The location of deuterium in **35** and **36** was revealed by their nmr spectra (see Figure 1 and previous discussion).

Authentic 2-Deuteriostyrene (35). The reaction of pure 2-bromotoluene with magnesium in anhydrous diethyl ether and decomposition of the resulting Grignard reagent with 99.5% deuterium oxide yielded 2-deuteriotoluene. Oxidation of the 2-deuteriotoluene with chromyl chloride[30] and hydrolysis of the subsequent adduct gave 2-deuteriobenzaldehyde (50%) which was converted to 1-(2-deuteriophenyl)-1-ethanol by reaction with methylmagnesium bromide in diethyl ether and hydrolysis. Dehydration of the deuterated alcohol to **35** was accomplished by adding a drop of sulfuric acid, heating the mixture, and distilling away the volatile product.

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[30] H. Law and E. Perkin, *J. Chem. Soc.*, **91**, 258 (1907).

Bond-Stretch Isomerism and Polytopal Rearrangements in $(CH)_5^+$, $(CH)_5^-$, and $(CH)_4CO$

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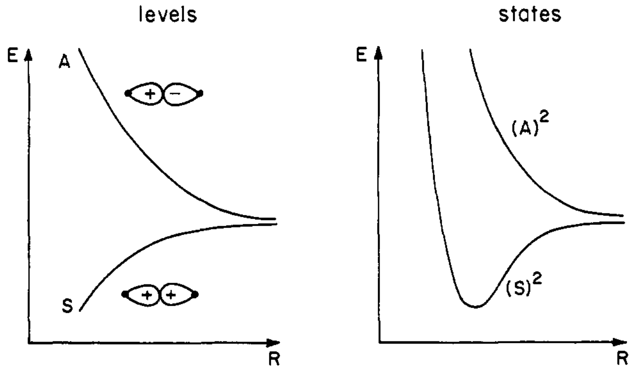
Abstract: Following a general outline of the theoretical prerequisites for creating a double energy minimum upon simple stretching of a single bond we present an analysis of one such case, the tricyclo[2.1.0.0^{2,5}]pentane system. The 3-carbonium ion of this molecule exhibits a clear double minimum upon stretching the central bicyclobutane bond, created by interaction of the carbonium ion p orbital with a σ^* level. The resulting $(CH)_5^+$ potential surface shows typical Jahn–Teller behavior—open and closed C_{2v} minima circumventing a D_{3h} structure. The C_{2v} structures, as well as other $(CH)_5^+$ isomers, appear to be unstable with respect to a square pyramidal C_{4v} cation. The quantum mechanical calculations allow a qualitative evaluation of the energy barriers to various polytopal rearrangements of this species, as well as of $(CH)_5^-$. A similar case of bond-stretch isomerism is predicted for $(CH)_4CO$, whose rearrangements are more inhibited than those of $(CH)_5^+$.

Awareness of orbital symmetry constraints on chemical reactions permits one to make a qualitative judgment as to the relative stabilities of molecules with respect to the reactive channels open to them. Highly strained molecules, such as Dewar benzene or bicyclo[2.1.0]pentene, owe their relative stability to the fact that a forbidden reaction, a change in predominant electronic configuration, separates them from their geometrically close and thermodynamically much more stable isomers.[1] In further development of these ideas, we have been exploring a novel type of isomerism in which two or more stable conformations of a molecule related to each other by a simple bond stretching differ in their electronic configurations.

Consider the consequences of stretching a normal single bond, described by a symmetric (S) σ level and an antisymmetric (A) σ^* level. As the interatomic separation increases from the equilibrium value, the S and A levels approach each other. The ground state of the system is adequately described by the configura-



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