

answer to this discrepancy. Assignment of the configurations of cyclohexylamines (and their corresponding alcohols) by analysis of the reactions of the amines with nitrous acid⁹ is unreliable when applied to cases in which the conformations are mobile¹⁰ (e.g., isocarvomethylamine-isocarvomethylol¹¹). Similarly, configurational assignments on the basis of esterification rates of cyclohexanols must be applied with care in mobile systems.¹²

Based on the evidence presented, and the interrelationships of the carvomethylols with the known structures of the carveols,¹³ dihydrocarveols, and sobrerols,¹⁴ the stereochemistry and absolute configurations¹³ of the isomeric carvomethylols may be assigned as follows: D-(−)-carvomethylol (I), D-(+)-neocarvomethylol (II), D-(+)-isocarvomethylol (III), and D-(+)-neoisocarvomethylol (IV).

The reversal of Bose's configurations for iso- and neoisocarvomethylol¹⁵ must of necessity change the configurational assignments which have been based on converting structures of unknown stereochemistry to either of these two carvomethylols.¹⁶ Since completion of the present work, other reports have appeared¹⁷ confirming that isocarvomethylol has configuration III.

Acknowledgment.—J. C. L. expresses appreciation for a National Defense Education Act Fellowship for the years 1960–1963.

(9) J. A. Mills, *J. Chem. Soc.*, 260 (1953); A. K. Bose, *Experientia*, **9**, 256 (1953).

(10) It has been recognized only recently that the isopropyl group is not as bulky as a *t*-butyl group and therefore does not necessarily fix the conformation of a cyclohexane ring as has so often been assumed. For example, A. H. Lewin and S. Winstein, *J. Am. Chem. Soc.*, **84**, 2464 (1962); N. L. Allinger, L. A. Freiberg, and S.-E. Hu, *ibid.*, **84**, 2836 (1962); N. Mori and F. Suda, *Bull. Chem. Soc. Japan*, **36**, 227 (1963).

(11) J. H. Brewster, (a) *J. Am. Chem. Soc.*, **81**, 5483 (1959); (b) *ibid.*, **81**, 5493 (1959).

(12) E. Eliel, *Experientia*, **9**, 91 (1953).

(13) The reversal of the *cis* and *trans* configurations for the carveols (and therefore of all the other related terpenes) as proposed by G. Farges and A. Kergomard [*Bull. soc. chim. France*, 51 (1963)] was rejected on the basis of the above arguments inasmuch as the absolute configurations of the (+)-*cis*- and (+)-*trans*-limonene 1,2-oxides have been established.² This confirmed the absolute configurations of the carveols previously postulated. The direct relationships of (+)-limonene with D-(+)-isopropylsuccinic acid has been shown¹; see also K. Freudenberg and W. Lwowski, *Ann.*, **587**, 213 (1954). The relationships of (+)-limonene → (+)-limonene 1,2-oxides⁴ and of (−)-limonene → (+)-carvone → (+)-*cis*- and (+)-*trans*-carveol have long been known.^{2b} Johnston and Read have previously found that (+)-*cis*-carveol → (+)-carvomethylol and (−)-neoisocarvomethylol and (+)-*trans*-carveol → (−)-neocarvomethylol and (−)-isocarvomethylol.

(14) H. Schmidt, *Ber.*, **83**, 193 (1950); *ibid.*, **88**, 453 (1955); *ibid.*, **88**, 459 (1955); *ibid.*, **86**, 1437 (1953).

(15) Brewster's method for calculating the molecular rotation of saturated cyclic compounds also supports such a reversal of configurational assignments.¹⁰

(16) a) Y. R. Naves and A. V. Grampoloff, *Bull. soc. chim. France*, 37 (1960); (b) Z. Chabudzynski, *Bull. acad. polon. sci., Ser. sci. chim.*, **10**, 157 (1962).

(17) A. Blumann, E. W. Della, C. A. Hendrick, J. Hodgkin, and P. R. Jefferies, *Australian J. Chem.*, **15**, 290 (1962); Z. Chabudzynski, Z. Rykowski, and H. Kuczynski, *Roczniki Chem.*, **37**, 1571 (1963).

(18) Heyden Newport Chemical Corporation, Pensacola Fla.

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RECEIVED MARCH 6, 1964

The Reaction of Methyl Radicals with Dimethylmercury Sir:

In a recent publication¹ from this laboratory, acetone-*d*₆ was photolyzed in the presence of dimethyl-

(1) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **85**, 3086 (1963).

mercury in the gas phase. The following reaction was postulated



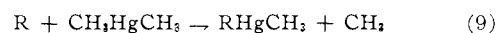
Evidence for the occurrence of this reaction in the gas phase was based mainly on the appearance of CH₃ as an important radical specie. In order to verify this interpretation, further experiments have been carried out with mixtures in which the deuteration has been reversed, as CH₃COCH₃-CD₃HgCD₃. In this way the rate of formation of CD₃, which may tentatively be ascribed to the reaction



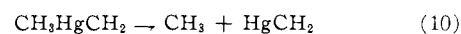
was studied and compared to the rate of formation of CH₃ which was ascribed to reaction 1 in the previous paper. The values obtained for $k_1'/k_8^{1/2}$ were found to be a factor of three lower than those ascribed previously to $k_1'/k_8^{1/2}$. k_8 and k_8' are the rate constants for the combination reactions



Because this is an unusually large deuterium isotope effect for this type of process, serious doubts arose as to the correctness of the original interpretation. For this reason attempts were made to determine the actual rate of formation of CH₃HgCD₃ produced in these systems. In order to obtain reliable yields of this product, conversions had to be increased from 0.5% in the original work to about 5.0%. Blank runs carried out for long periods of time indicated that in the absence of light, the formation of CD₃HgCH₃ in CD₃COCD₃-CH₃HgCH₃ mixtures at 453°K. was negligible. However, CD₃HgCH₃ is a product when CD₃COCD₃ is photolyzed in the presence of CH₃HgCH₃. On the basis of the yield of this product as determined by mass spectrometry a value of $6.0 \times 10^{-3} \text{ l.}^{1/2} \text{ mole}^{-1/2} \text{ sec.}^{1/2}$ was calculated for the rate constant ratio $k_1'/k_8^{1/2}$. Although the determination of this product does provide a more unambiguous proof for the occurrence of process 1, it should be noted that the rate constant ratio is considerably lower than the value of $30.0 \times 10^{-3} \text{ l.}^{1/2} \text{ mole}^{-1/2} \text{ sec.}^{-1/2}$ reported in the previous study. It is clear, therefore, that in the CD₃COCD₃-CH₃HgCH₃ system, CH₃ radicals are also produced by processes other than 1, such as



and/or



This is also substantiated in the earlier work in which the ratio (ethane + 1/2 methane)/CO is greater than unity at the highest temperature. Reaction 10 was not considered originally as a likely process because the quantum yield of the decomposition of dimethylmercury was reported to be independent of temperature from 26 to 198°.² Likewise, it was excluded on the basis of the pyrolytic studies of Gowenlock, *et al.*,³ which were carried out in a flow system. However, as pointed out by Srinivasan,⁴ the possibility exists that in a static system

(2) R. E. Rebbert and E. W. R. Steacie, *Can. J. Chem.*, **31**, 631 (1953).

(3) B. G. Gowenlock, J. C. Polanyi, and E. Warhurst, *Proc. Roy. Soc. (London)*, **A218**, 269 (1953).

(4) R. Srinivasan, *J. Chem. Phys.*, **28**, 895 (1958).

the CH_3HgCH_2 radical may decompose on the wall of the reaction vessel.

Finally it should be mentioned that a mixture of CH_3HgCH_3 and CD_3HgCD_3 does exchange to form CH_3HgCD_3 when left standing in a Pyrex vessel at room temperature in the dark. However, contrary to a recent suggestion,⁵ there is no exchange within the mass spectrometer itself. Mass spectrometric analysis, carried out on a Consolidated Model 21-103, of an equimolar mixture of CH_3HgCH_3 and CD_3HgCD_3 which was analyzed on the mass spectrometer immediately after mixing gave less than 0.7% CH_3HgCD_3 . It must thus be concluded that the buildup of CH_3HgCD_3 reported for this compound in the liquid phase experiments occurred mainly during the manipulations of the sample. This, however, does not affect any of the conclusions reached concerning the lack of a hot-radical effect in the liquid nor the cage recombination of the methyl radicals. This latter conclusion was based on the small amount of CH_3CD_3 formed from a freshly prepared mixture of CH_3HgCH_3 - CD_3HgCD_3 -2,3-dimethylbutane. Likewise it does not affect the conclusion that reaction 1 occurs in the liquid phase since this was based mainly on the azomethane experiments.

Acknowledgment.—We wish to thank Drs. Ralph E. Weston, Jr., and Stanley Seltzer for their communications with us and for bringing to our attention the possible occurrence of reaction 10 in our system.

(5) R. E. Weston, Jr., and S. Seltzer, *J. Phys. Chem.*, **66**, 2192 (1962).

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RECEIVED MARCH 31, 1964

Free-Radical Addition to Azobenzene in Cumene Solution. Electron Paramagnetic Resonance Spectra of Some Long-Lived Radical Intermediates

Sir:

One aspect of the photochemistry of aromatic azo compounds, the *cis-trans* isomerization, has been the subject of many investigations. However, relatively little attention has been given to the possibility of free-radical attack at the azo bridge.¹ Free-radical addition to the azo bridge has been suggested by Kharasch, *et al.*,² and Blaisdell³ has demonstrated the ability of the azo bridge to abstract hydrogen atoms in the photoreduction of azobenzene in isopropyl alcohol solution.

We wish to report the results of a preliminary investigation in which we have obtained evidence for free-radical attack at the azo site. A stable free radical was photochemically produced and observed spectroscopically by irradiation of an azobenzene-cumene solution in an e.p.r. cavity. Product analysis coupled with a theoretical calculation to aid in interpretation of the e.p.r. spectrum served to identify the long-lived radical intermediate.

A degassed solution of azobenzene in cumene was irradiated at room temperature in the microwave cavity of a Varian V4500 e.p.r. spectrometer with 100-kc. field modulation. The light source was a PEK

(1) For a detailed review, see H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

(2) M. S. Kharasch, M. Zimmermann, W. Zimmt, and W. Nudenberg, *J. Org. Chem.*, **18**, 1045 (1953).

(3) B. E. Blaisdell, *J. Soc. Dyers Colourists*, **65**, 618 (1949).

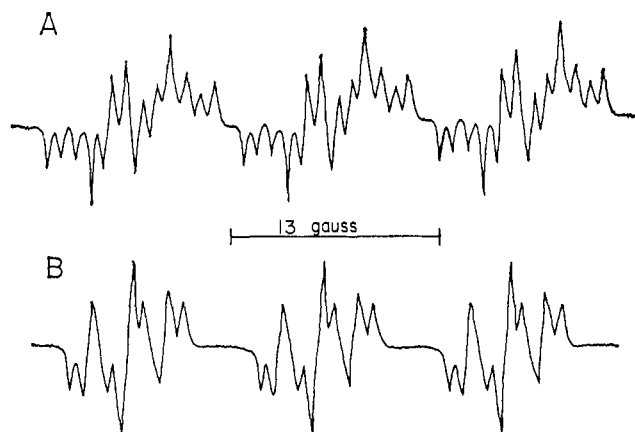
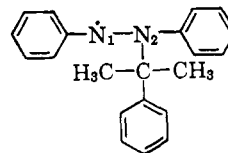


Fig. 1.—First derivative of e.p.r. absorption spectra of irradiated azobenzene-cumene solution (A), and irradiated 4,4'-dimethoxyazobenzene-cumene solution (B).

mercury high pressure lamp equipped with filters which absorbed wave lengths shorter than 4000 Å.

During irradiation at room temperature an e.p.r. spectrum was readily observed with an intensity dependent upon the initial concentration of azobenzene. The spectrum exhibited 36 lines (Fig. 1A) and persisted for several hours after irradiation was terminated. The spectrum is a triplet, each component of which contains four groups of lines of which the intensities follow a 1:3:3:1 binominal distribution. Each of these groups is further split into three lines of approximately equal intensity.

The radical structure consistent with the observed spectrum is



The primary triplet of the spectrum is ascribed to the strong interaction of nitrogen atom N_1 with the unpaired electron. The four groups of lines within the triplet are ascribed to isotropic hyperfine interactions of the three equivalent *ortho* and *para* protons of the phenyl group attached to N_1 . The three lines within each group may be due to weak interaction with the second nitrogen atom.

With this assignment, and use of the McConnell⁴ relation, $A_H = -22.5\rho_C$, and the equation⁵ $A_N = Q_N\rho_N - \sum Q_i\rho_i$ where $Q_N = 24$ and $Q_i = 49$, the experimental coupling constants and spin densities shown in Table I were obtained. The theoretical spin densities given in Table I were calculated on the monophenylaminy fragment of the radical using the Hückel method.⁶ These values serve to substantiate the above interpretation of the observed e.p.r. spectrum.

Separate experiments were carried out on a larger scale in which the reaction mixture was subjected to liquid chromatography techniques after irradiation. $\text{N,N}'$ -Diphenyl- N -(1-methyl-1-phenylethyl)hydrazine was eluted from a 3-ft. column which was packed

(4) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956); H. M. McConnell and D. B. Chestnut, *ibid.*, **28**, 107 (1958).

(5) H. Veda, Z. Kuri, and S. Shida, *ibid.*, **36**, 1676 (1962).

(6) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.