

Pyrolysis of *meso* and *rac* I with Their 1,10-Dideuterio Analogs. A sample of the deuterated hydrocarbons, 1.5089 g., was pyrolyzed with 1.4986 g. of *meso* and *rac* I in the manner previously described for the pyrolysis of *meso* and *rac* I. Samples of pyrolyzate fractions III and IV were obtained by preparative v.p.c. on Apiezon column A. The mass spectral cracking patterns (mass spectrometer inlet temperature

170°) of both fractions showed parent molecular ion peaks at  $m/e$  162 (no deuterium), 163 (one deuterium atom/molecule), and 164 (two deuterium atoms/molecule); however, the peak at  $m/e$  163 was the most intense peak of the three in both fractions III and IV.

*Acknowledgment.* We thank the Alfred P. Sloan Foundation and the Robert A. Welch Foundation for financial assistance.

## The Mechanism of the Thermal Decomposition of $\alpha$ -Phenylethylazomethane. A Two-Step Reaction<sup>1</sup>

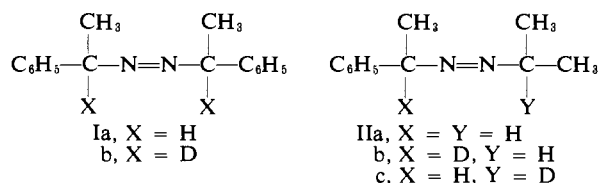
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$\alpha$ -Phenylethylazomethane (IIIa),  $\alpha$ -phenylethyl- $\alpha$ -d-azomethane (IIIb), and  $\alpha$ -phenylethylazomethane- $d_3$  (IIIc) were prepared. The isotope effects in the thermal decomposition,  $k_{IIIa}/k_{IIIb} = 1.13$  and  $k_{IIIa}/k_{IIIc} = 0.97$ , were found. In addition, the  $C^{13}$  effect in the decomposition of  $\alpha$ -phenylethylazomethane- $C^{13}$  is  $k_{12}/k_{13} = 1.0068$ . From these results we conclude that the slow step involves rupture of only the  $\alpha$ -phenylethyl carbon-nitrogen bond; the breaking of the methyl-nitrogen bond in the unstable methylazo radical occurs in a subsequent fast step. An estimate of the lower limit of the rate constant for the second step is obtained from the results. The energy and entropy of activation are discussed.

### Introduction

In previous papers the use of the secondary  $\alpha$ -deuterium isotope effect in determining whether two bonds rupture stepwise or simultaneously was pointed out.<sup>2,3</sup> Azobis- $\alpha$ -phenylethane (Ia) and azobis- $\alpha$ -phenylethane- $\alpha, \alpha'$ - $d_2$  (Ib) were allowed to decompose thermally in ethylbenzene; the observed isotope effect,  $k_{Ia}/k_{Ib} =$



1.27, indicated that both carbon-nitrogen bonds were breaking in a simultaneous process.<sup>2</sup> Decomposition of  $\alpha$ -phenylethylazo-2-propane presented a somewhat different picture. The secondary effects  $k_{IIa}/k_{IIb} = 1.16$  and  $k_{IIa}/k_{IIc} = 1.04$  led to the conclusion that here too both carbon-nitrogen bonds stretch in the same step but to unequal degrees by the time the molecule

reaches the transition state.<sup>3</sup> Since the secondary  $\alpha$ -effect is due, in main part, to the change in H-C-leaving group bending force constant,<sup>4</sup> it was argued that a secondary  $\alpha$ -deuterium isotope effect smaller than the usual effect of about 15% observed in unimolecular decomposition indicates a smaller than usual amount of C-leaving group bond breaking. So in the case of  $\alpha$ -phenylethylazo-2-propane greater stretching of the benzylic-carbon-nitrogen bond than of the 2-propyl-carbon-nitrogen bond has taken place at the transition state. This is consonant with the view that the  $\alpha$ -phenylethyl group is able to delocalize a free electron more efficiently than the 2-propyl group. "Resonance energies" of the  $\alpha$ -phenylethyl and isopropyl radicals differ by more than 15 kcal./mole,<sup>5</sup> and therefore it is not surprising that the decomposition path of lowest energy is that where unstable species are most easily stabilized. Cohen<sup>6b</sup> and Overberger<sup>6c</sup> and their co-workers have suggested previously that differences in rates of decomposition of dialkylazo compounds are probably due to changes in the activation energies brought about by different degrees of resonance stabilization of the particular alkyl radicals produced. The possibility of an unsymmetrical compound decomposing in a symmetrical or an unsymmetrical one-step or two-step mechanism was expressed. However, by studying only the activation energies of decomposition of unsymmetrical dialkylazo compounds, a choice between a symmetrical and an unsymmetrical one-step cleavage is difficult or impossible to make.

A new, more unsymmetrical azo compound,  $\alpha$ -phenylethylazomethane (III), was synthesized. Its rate of decomposition was studied to gain further insight into the factors which determine the relative timing of the rupture of the two carbon-nitrogen bonds in dialkylazo compounds. From the secondary  $\alpha$ -deuterium and  $C^{13}$  isotope effects described in this

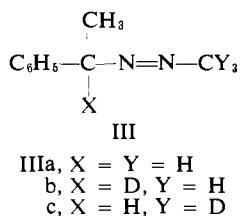
(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission. (b) Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964, p. 4c.

(2) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961).

(3) S. Seltzer, *ibid.*, **85**, 14 (1963).

(4) (a) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, **80**, 2326 (1958); (b) S. Seltzer, *ibid.*, **83**, 1861 (1961); (c) M. Wolfsberg and M. Stern, *J. Pure Appl. Chem.*, **8**, 225 (1964).

(5) (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 50, 51; (b) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **75**, 5504 (1953); (c) see, e.g., C. G. Overberger and A. V. DiGiulio, *ibid.*, **81**, 2154 (1959), and papers cited therein.



paper we conclude that  $\alpha$ -phenylethylazomethane decomposes in two steps. Furthermore, the isotope effects indicate the existence of the  $\text{CH}_3\text{N}_2$  radical, and an approximate rate constant for its decomposition is calculated.

### Experimental

*$\alpha$ -Phenylethylazomethane (IIIa).* A solution containing 58.1 g. of Fisher Scientific acetophenone, 22 g. of methylhydrazine (Metaelectro Corp.), 200 ml. of absolute ethanol, and 2 ml. of glacial acetic acid was refluxed for 24 hr. After removal of ethanol, the hydrazone was distilled at 73.5° (0.25 mm.); yield, 79%,  $n^{23.5\text{D}}$  1.5872; n.m.r. spectra: C-CH<sub>3</sub>,  $\tau$  8.15; N-CH<sub>3</sub>, 7.05; NH, 5.32; aromatic H, 2.30–2.87.

*Anal.* Calcd. for C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>: C, 72.93; H, 8.16. Found: C, 73.10, 72.40; H, 7.87, 7.71.

About 15 g. of the above hydrazone was dissolved in 150 ml. of ethyl acetate and 4 g. of 5% palladium on charcoal (Baker Co.) was added. The hydrazone was catalytically reduced with a starting pressure of hydrogen of 28 p.s.i. Reduction was complete in 1.3 hr. The n.m.r. spectrum of the residue, obtained after filtration and evaporation of solvent, indicated that the material was pure enough to be used in the next step without further distillation; n.m.r. spectra: N-CH<sub>3</sub>,  $\tau$  7.60; C-CH<sub>3</sub>, 8.77; N-H, 6.80; tertiary H, 6.09; aromatic H, 2.80.

The N- $\alpha$ -phenylethyl-N'-methylhydrazine obtained from reduction was dissolved in 70 ml. of benzene and treated with 30 g. of yellow mercuric oxide. After stirring for 2 hr., the mixture was filtered and the solvent was evaporated. The azo compound was distilled at 33.5–35.5° (0.1 mm.);  $n^{25\text{D}}$  1.5088; ultraviolet  $\epsilon_{331\text{m}\mu}$  34.6; n.m.r.: C-CH<sub>3</sub>,  $\tau$  8.52; N-CH<sub>3</sub>, 6.37; tertiary H, 5.42; aromatic H, 2.67.

*Anal.* Calcd. for C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>: C, 72.93; H, 8.16. Found: C, 73.53, 71.66; H, 7.64, 8.20.

*$\alpha$ -Phenylethyl- $\alpha$ -d-azomethane (IIIb).* One gram of 5% palladium on charcoal suspended in 20 ml. of D<sub>2</sub>O–50 ml. of dioxane was equilibrated with deuterium gas. Then 8.0 g. of the acetophenone methylhydrazine was added and reduced at atmospheric pressure. The requisite amount of D<sub>2</sub> was taken up in 2.25 hr. The catalyst was removed by filtration and the solution was stirred with 25 g. of fresh yellow mercuric oxide. After filtering and evaporation of solvent, the azo compound was distilled, b.p. 32° (0.2 mm.); yield, 3.0 g.,  $n^{25\text{D}}$  1.5070. The n.m.r. spectrum was the same as that for IIIa except that the tertiary H quartet at  $\tau$  5.42 had practically vanished. The C-CH<sub>3</sub> doublet at  $\tau$  8.52 in IIIa collapsed to a singlet in IIIb.

*$\alpha$ -Phenylethylazomethane-d<sub>3</sub> (IIIc).* Carboethoxyhydrazine was prepared by the method of Diels,<sup>6</sup> b.p. 106° (20 mm.), yield, 70%. A solution of 124 g. of carboethoxyhydrazine, 200 ml. of absolute ethanol, 2

ml. of glacial acetic acid, and 145 g. of acetophenone was refluxed for about 20 hr. The product, acetophenone carboethoxyhydrazone, crystallized as white needles as the solution cooled. Recrystallization from absolute ethanol gave 203 g., m.p. 118.8–119.6°; reported m.p. 119–120°.<sup>7</sup> Acetophenone carboethoxyhydrazone (20 g.) was dissolved in 200 ml. of ethyl acetate. The hydrazone was reduced on a Parr shaker after the addition of 1 g. of 5% palladium on charcoal catalyst. After 48 hr., shaking was discontinued and white crystals were obtained after filtration and evaporation of the solvent. Recrystallization from ligroin (b.p. 110–115°) yielded 17.7 g. of solid, m.p. 55.5–57.2°; after two more recrystallizations, m.p. 57.2–58.2°; n.m.r. spectrum: ethylic methyl,  $\tau$  8.83; benzylic methyl, 8.77; methylene, 5.97; tertiary proton, 5.85; benzylic NH, 5.85; NH neighboring to carbonyl group, 3.07; aromatic protons, 2.77.

*Anal.* Calcd. for C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 63.44; H, 7.74. Found: C, 63.11, 63.23; H, 7.87, 7.38.

The N-carboethoxy-N'- $\alpha$ -phenylethylhydrazine (15 g.), in previously dried and distilled Fisher tetrahydrofuran, was added dropwise to a slurry of 5.0 g. of LiAlD<sub>4</sub> (Metal Hydrides, Inc.) in 250 ml. of the same tetrahydrofuran. The mixture was stirred and refluxed for 70 hr.<sup>8</sup> At first there developed a brown-orange color which changed to light green. A small amount of saturated sodium potassium tartrate solution was added to decompose the excess LiAlD<sub>4</sub>. Then ether followed by more saturated tartrate solution was added until two liquid layers formed. The ether layer, which was separated from solid material and the aqueous layer, was washed twice with water. The solution was mixed with about an equal amount of benzene to make one phase. Yellow mercuric oxide (25 g.) was stirred with the mixture overnight and then filtered. The filtrate was dried and the solution was distilled; b.p. 34° (0.2 mm.);  $n^{25\text{D}}$  1.5060; yield, 1.10 g.; n.m.r.: benzylic methyl,  $\tau$  8.52; benzylic proton, 5.47; aromatic proton, 2.73.

*Free radicals* were shown to be involved by three methods: (a) A sample of the neat azo compound IIIa was heated to 165° while its e.p.r. spectrum was observed.<sup>9</sup> Although the spectrum appeared too complicated for rapid assignment it did, however, indicate a high concentration of radical species. (b) Styrene, containing 4-*t*-butylpyrocatechol, was mixed with a small amount of the azo compound to give about a 1% solution. The temperature of the solution was maintained at 160° in an atmosphere of N<sub>2</sub> for 13 min. After this period of time the flask was removed and inverted; the contents did not flow. Treatment of styrene containing 4-*t*-butylpyrocatechol in the same manner produced a liquid more viscous than the original material but yet quite fluid. (c) A dilute solution of diphenylpicrylhydrazyl in diphenyl ether changed its color from violet to brown-orange in 2 min. when heated at 160° with azo compound in an atmosphere of N<sub>2</sub>, while the same solution remained violet for 10 min.

*Kinetics.* The rate of evolution of N<sub>2</sub> from the decomposition of azo compounds in diphenyl ether—

(7) W. Borche, *ibid.*, 38, 831 (1905).

(8) R. L. Hinman, *J. Am. Chem. Soc.*, 78, 1645 (1956).

(9) We thank Dr. B. Bielski for the e.p.r. measurements.

(6) O. Diels, *Ber.*, 47, 2183 (1914).

benzoquinone solution at 161° was measured as previously described.<sup>3</sup> Approximately 65 points were taken during each run and these were processed by an IBM 7094 computer to obtain the nonlinear least-squares solution of the first-order rate constant.

In addition, the rate of decomposition of natural  $\alpha$ -phenylethylazomethane (IIIa) was measured in *n*-hexadecane (Distillation Products, Inc.,  $n^{25}_D$  1.4328, reported<sup>10</sup>  $n^{25}_D$  1.4325) at the same temperature using the same technique.

**$C^{13}$ -Isotope Effects.** Methane was collected together with nitrogen when the natural azo compound (IIIa) was allowed to decompose in *n*-hexadecane. In the decompositions carried to completion, the gases nitrogen and methane were allowed to expand into evacuated bulbs until the pressure of the gas remaining in the apparatus for decomposition was insignificant compared to the quantity of gas removed. The gas was then passed through a radiator trap<sup>11</sup> immersed in a Dry Ice-acetone mixture and adsorbed on charcoal at liquid  $N_2$  temperature. In the runs where only a fraction of the sample was allowed to decompose thermally, the flask containing the solvent was not connected to the manometer but just placed in the bath, flushed with  $N_2$ , and partially evacuated in the usual way. The azo compound in 3 ml. of hexadecane was admitted followed by 2 ml. of hexadecane. At prescribed times the flask was removed from the bath and cooled. The fraction of reaction,  $f$ , was determined by comparison with the kinetics determined on complete decomposition. The flask and contents were connected through a radiator trap to a charcoal trap on a high vacuum line. The flask and radiator trap were cooled to Dry Ice temperature while the charcoal trap, cooled with liquid  $N_2$ , adsorbed the methane and  $N_2$ . The contents of the flask was warmed to room temperature a few times in standard degassing technique to remove completely all volatile materials. Almost complete separation between nitrogen and methane was obtained by warming the charcoal trap, cooled to liquid  $N_2$  temperature, to  $-123^\circ$  (*n*-butyl chloride) and simultaneous pumping to about  $15 \mu$  in a high vacuum system. In this way no methane was lost and the sample was enriched by a factor of 15:1 in methane, as shown by control experiments and vapor phase chromatography. The methane sample containing a small amount of nitrogen was combusted over copper oxide to  $CO_2$  as described previously.<sup>12</sup> The 45/44 ratio, obtained on a Consolidated-Nier Model 21-201 mass spectrometer, was corrected for collector resolution error ( $\rho = 0.00010$ ) and  $O^{17}$  abundance (0.00083) to get true  $C^{13}O_2/C^{12}O_2$  ratios.<sup>12</sup>

A portion of the same methylhydrazine that was used in the synthesis of the natural compound was added dropwise to a sulfuric acid-methanol solution. The final solution was strongly acidic. Precipitated  $CH_3NHNH_2 \cdot H_2SO_4$  was recrystallized three times from methanol, m.p. 142.4–143.2°; reported m.p. 142°.<sup>13</sup>

(10) F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Carnegie Press, Carnegie Institute of Technology, Pittsburgh, Pa., 1953, p. 34.

(11) D. R. Christman, *et al.*, *Anal. Chem.*, **27**, 1345 (1955); **28**, 1345 (1956).

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

(13) J. Thiele, *Ber.*, **42**, 2575 (1909).

**Anal.** Calcd. for  $CH_8N_2O_4S$ : C, 8.33; H, 5.59. Found: C, 8.26; H, 5.15.

The salt was burned over active CuO and the product  $CO_2$  purified by v.p.c. on a silicone oil column at room temperature. In one instance (last entry of Table III) the salt was burned in an analytical combustion line and the  $CO_2$  chromatographed. The  $C^{13}/C^{12}$  ratios were determined as described above.

**Product Analysis.** Approximately 1 g. of the natural azo compound IIIa was allowed to decompose thermally in 75 ml. of 0.13 *M* benzoquinone in diphenyl ether at 160° in an atmosphere of nitrogen. At the top of the flask where the neck protruded from the bath white needles were deposited. The white solid, m.p. 172–173°, was identified as hydroquinone by its ultraviolet and n.m.r. spectra being identical with that from authentic hydroquinone.

The remaining brown solution was steam distilled and the distillate was extracted with ether. The ether layer was washed with KOH solution to remove any hydroquinones and then washed with saturated sodium bicarbonate and water. The ether layer was dried and the solvent was evaporated, leaving a small amount of an impure brown semisolid. Its n.m.r. spectrum in  $CCl_4$  indicated a doublet at  $\tau$  8.44 and a probable quartet at 4.90. The aromatic region was obscure because of diphenyl ether contamination.

The solutions from partial and total decomposition of the natural azo compound IIIa in hexadecane were combined and heated at 160° to ensure complete decomposition of undecomposed azo compound. The temperature of the pot was raised until a small amount of the lowest boiling material was distilled. An n.m.r. spectrum of the distillate in  $CCl_4$  indicated, in addition to hexadecane, the presence of cumene. The observed peaks were: doublet,  $\tau$  8.77 ( $CH_3$ ); complex, 7.30; singlet, 2.79 (aromatic proton). Authentic cumene in  $CCl_4$  has the following peaks: doublet,  $\tau$  8.76 ( $CH_3$ ); septet, 7.13 (benzylic proton); singlet, 2.79 (aromatic proton).

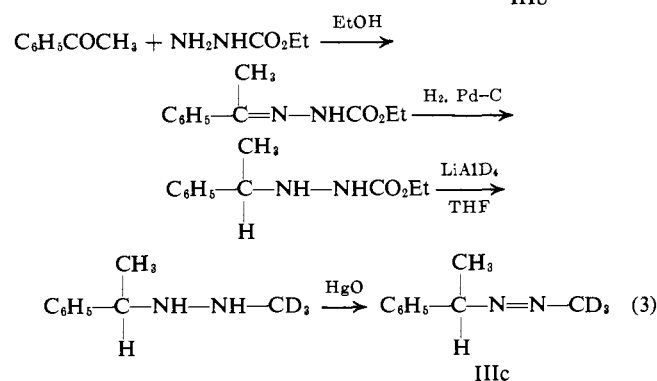
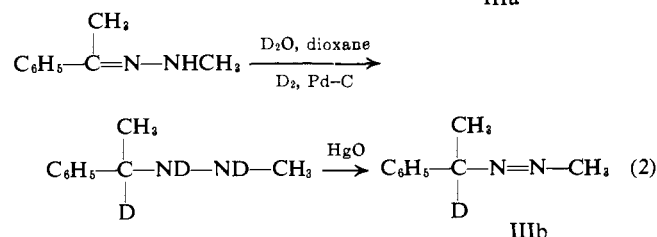
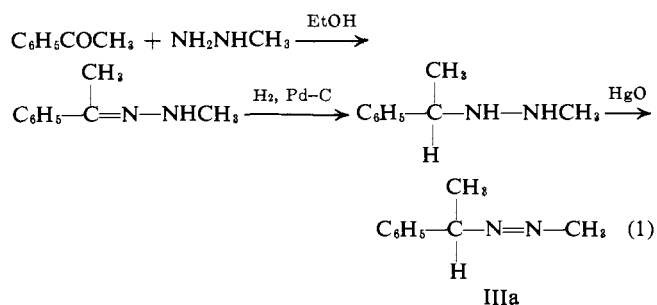
In one experiment,  $\alpha$ -phenylethyl- $\alpha$ -*d*-azomethane (0.4328 g.) was mixed with 25.0 ml. of hexadecane and placed in a thick-walled glass tube. The solution was degassed on a high vacuum line using standard techniques and then sealed. The tube was then submerged in a thermostated bath at 171° for 11.2 hr. The cooled tube was opened and the contents was removed. Predistilled cumene (0.9691 g.) was added and reisolated from the solution by distillation. The recovered cumene amounted to 0.591 g. and shown to be relatively pure by vapor phase chromatography and comparison with an authentic sample. Deuterium analysis of the recovered cumene indicated that it contained 0.69 atom % D, equivalent to a  $26 \pm 2\%$  yield of cumene from the initial azo compound.

In duplicate experiments, approximately 0.02 *M* natural  $\alpha$ -phenylethylazomethane in hexadecane was placed in a glass tube with a break-seal and the solution was thoroughly degassed before sealing. After heating the contents at 160° for more than 48 hr. the solution was cooled and the tube was opened under high vacuum conditions. The gases were removed by standard degassing techniques and Toeppler-pumped into sample bulbs to be analyzed by mass spectrometry and vapor phase chromatography (silica gel column). The ratio

of the partial pressures of methane to nitrogen in the product gases was observed to be  $0.65 \pm 0.03$  by both methods.

## Results

$\alpha$ -Phenylethylazomethane (IIIa) and its deuterated isomers, IIIb and IIIc, were prepared according to the reactions given in eq. 1–3. It should be pointed out



that in the reduction of acetophenone methylhydrazone with deuterium to prepare the desired N-methyl-N'- $\alpha$ -phenylethyl- $\alpha$ -d-hydrazine, it is necessary to perform this in a deuterioxylic solvent in order to exchange the N-H proton of the precursor hydrazone. Catalytic reduction of this hydrazone with deuterium in the absence of  $\text{D}_2\text{O}$ , e.g., in ethyl acetate, leads to a hydrazine product with only 0.35 atom of deuterium in the  $\alpha$ -position.

N.m.r. indicated that the benzylic hydrogen position contained 0.95 atom of D while less than 0.1 atom of D was found in the methyl group. Similar reductions have shown only trace incorporation of deuterium into the aromatic ring.<sup>2</sup> The trideuteriomethyl isomer IIIc contained 2.89 atoms of deuterium as determined from its n.m.r. spectrum. The kinetics of nitrogen evolution were determined separately for each compound in a staggered order to minimize any possible trends in the bath temperature over long periods of time. The nonlinear least-squares solution of the first-order rate law for each run is given in Table I. Correction of  $k_{\text{IIIa}}/k_{\text{IIIb}}$  and  $k_{\text{IIIa}}/k_{\text{IIIc}}$  to 1.00 and 3.00 atoms of deuterium in the  $\alpha$ - and  $\alpha'$ -positions yields 1.13 and 0.97, respectively.<sup>14</sup>

(14) R. R. Johnson and E. S. Lewis, *Proc. Chem. Soc.*, 52 (1958).

**Table I.** First-Order Rate Constants of Decomposition of  $\alpha$ -Phenylethylazomethane<sup>a</sup>

$k_{\text{IIIa}}$ $\times 10^4$ , sec. <sup>-1</sup>	$k_{\text{IIIb}}$ $\times 10^4$ , sec. <sup>-1</sup>	$k_{\text{IIIc}}$ $\times 10^4$ , sec. <sup>-1</sup>
1.156	1.068	1.183
1.169	1.041	1.192
1.163	1.032	1.182
1.158	1.034	1.195
1.157	1.048	1.215
Av. $1.161 \pm 0.004$	$1.04 \pm 0.01$	$1.19 \pm 0.01$
$k_{\text{IIIa}}/k_{\text{IIIb}} = 1.12 \pm 0.01$	$k_{\text{IIIa}}/k_{\text{IIIc}} = 0.97 \pm 0.01$	

<sup>a</sup> In diphenyl ether-benzoquinone solution,  $t = 161.00 \pm 0.05^\circ$

As a check on the small, actually slightly inverse, secondary  $\alpha$ -deuterium isotope effect in the decomposition of the methyl- $d_3$  compound, the  $\text{C}^{13}$ -isotope effect in the methyl group was determined on natural abundance (1%  $\text{C}^{13}$ ) material. When  $\alpha$ -phenylethylazomethane (IIIa) decomposes in *n*-hexadecane, methane is produced from hydrogen atom abstraction by free methyl radicals and the first-order rate constant is the same, within experimental error, as when the reaction is carried out in benzoquinone-diphenyl ether solution. No detectable amount of ethane was observed in the methane-nitrogen product gas mixture as shown by vapor phase chromatography. The methane, at partial and essentially total decomposition, was collected and burned to  $\text{CO}_2$ . Analysis of the  $\text{CO}_2$  on a Consolidated-Nier Model 21-201 isotope ratio mass spectrometer indicated a very small  $\text{C}^{13}$ -isotope effect; the data are given in Table II.

**Table II.**  $\text{C}^{13}$ -Isotope Effect in the Decomposition of  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)-\text{N}=\text{N}-\text{C}^{13}\text{H}_3$ <sup>a</sup>

45/44	$f^b$	Cor. ratio <sup>c</sup>	$k_{12}/k_{13}$
0.011622	1.00	0.010692	
0.011554	0.19	0.010624	1.0065
0.011547	0.15	0.010617	1.0071
0.011611	1.00	0.010681	
Av.			$1.0068 \pm 0.0006$

<sup>a</sup> In hexadecane at  $161.0^\circ$ . <sup>b</sup> Corrected for  $\text{O}^{17}$  abundance and collector resolution. <sup>c</sup> Fraction of reaction.

The  $\text{C}^{13}$  abundance in the starting material, methylhydrazine, was also determined. Methylhydrazine was converted to its acid sulfate salt in order to decompose any carbonate salt formed from atmospheric carbon dioxide. The sulfate was burned to  $\text{CO}_2$  and the  $\text{CO}_2$  was analyzed for carbon-13 as described above. The results are shown in Table III.

**Table III.**  $\text{C}^{13}$ - $\text{C}^{12}$  Ratio in Methylhydrazine

45/44 <sup>a</sup>	Cor. ratio <sup>b</sup>
0.011612	0.010682
0.011611	0.010681
0.011596	0.010666
0.011587	0.010657
Av. $0.010672 \pm 0.000010^c$	

<sup>a</sup> Corrected to the same common 45/44 ratio for the same standard  $\text{CO}_2$  sample as in Table II. <sup>b</sup> Corrected for  $\text{O}^{17}$  abundance and collector resolution. <sup>c</sup> Average deviation.

Rates of thermolysis of the azo compound in the same diphenyl ether-benzoquinone solution were determined over a 20° range and their first-order rate constants are listed in Table IV together with those observed in *n*-hexadecane at 161°.

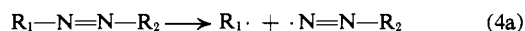
**Table IV.** First-Order Rate Constants for Thermal Decomposition of  $\alpha$ -Phenylethylazomethane (IIIa) vs. Temperature

	$k \times 10^4, \text{sec.}^{-1}$	$E_a,$ kcal./mole	$\Delta S^*,$ e.u.
151.00	$0.435 \pm 0.002 (3)^a$		
161.00	$1.16 \pm 0.00 (5)^a$		
171.10	$3.48 \pm 0.02 (2)^a$	38.6	14.0
161.0	$1.20 \pm 0.04 (2)^b$		

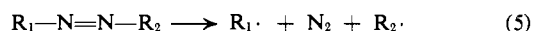
<sup>a</sup> In diphenyl ether-benzoquinone solution. <sup>b</sup> In *n*-hexadecane.

## Discussion

Our present knowledge concerning the mode of decomposition of dialkylazo compounds is mainly due to Overberger<sup>5c</sup> and Cohen<sup>15</sup> and their co-workers. These compounds thermally decompose to yield N<sub>2</sub> and alkyl radicals by a one- or two-step process. That radicals are produced in the thermolysis of  $\alpha$ -



or



phenylethylazomethane (III) is shown by its: (a) rapid discoloration of diphenylpicrylhydrazyl solution, (b) polymerization of styrene, and (c) complex e.p.r. spectrum.

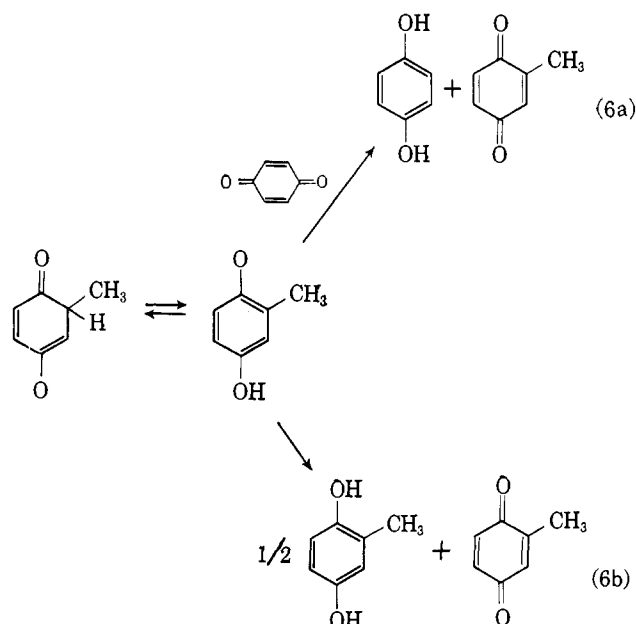
In benzoquinone-diphenyl ether solution the only gas that is produced is nitrogen; free methyl radicals must therefore add to the aromatic solvent or benzoquinone. The low concentration of  $\alpha$ -phenylethylazomethane ( $\sim 0.03 M$ ) precludes attack by methyl radicals.  $\alpha$ -Phenylethyl radical prefers to dimerize<sup>2</sup> or to add to diphenyl or benzoquinone rather than to abstract hydrogen. Further confirmation of this was seen in the good first-order kinetic plots.<sup>16</sup> When the reaction is carried out in benzoquinone-diphenyl ether solution, the only easily identifiable product was found to be hydroquinone. Methyl radical prefers to add to benzoquinone rather than to diphenyl ether by a factor of about 125 under the conditions of the present study.<sup>17</sup> Addition is probably to carbon<sup>17b</sup> to produce the semiquinone which eventually can lose or gain a hydrogen atom to give toluoquinone or toluohydroquinone, respectively. In the presence of benzoquinone, it can be calculated from oxidation-reduction potentials of quinones<sup>18</sup> that more than 99.9% of the semitoloquinone will proceed to stable products by path 6a rather than by 6b. Our expectation of hydroquinone

(15) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 3628 (1955), and papers cited therein.

(16) Early runs, not included here, did show some curvature in their first order plots. This was remedied by more careful purification of the substrate.

(17) (a) M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **77**, 1949 (1955); (b) A. Rembaum and M. Szwarc, *ibid.*, **77**, 4468 (1955).

(18) (a) A. G. Stromberg and L. M. Reinus, *J. Gen. Chem. USSR*, **16**, 1431 (1946); *Chem. Abstr.*, **41**, 5479 (1947); (b) M. I. Bobrova, *Zh. Fiz. Khim.*, **26**, 822 (1952); *Chem. Abstr.*, **46**, 10961 (1952).



and no toluohydroquinone is confirmed by experiment. However, we were not able to isolate any toluoquinone or a compound having the  $\alpha$ -phenylethyl group when the reaction was carried out in diphenyl ether-benzoquinone.

Decomposition of the azo compound in *n*-hexadecane yields approximately 0.65 equiv. of methane by hydrogen abstraction from the solvent. Isotopic dilution studies (see Experimental) indicate that for every mole of  $\alpha$ -phenylethylazomethane decomposed under these conditions 0.26 mole of cumene forms (arising most probably from cage recombination of  $\alpha$ -phenylethyl and methyl radicals).<sup>19</sup> At least 91% of the nitrogen-bonded methyl groups have been accounted for while only 26% of the  $\alpha$ -phenylethyl have been definitely found. The remaining 74% would be expected to dimerize<sup>2</sup> or to couple with the hexadecyl radical formed in close proximity to it.

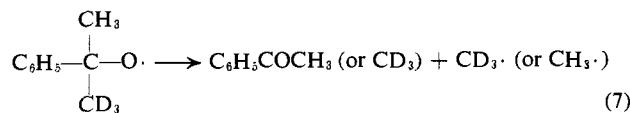
As noted in the Introduction, the symmetrical azo-bis- $\alpha$ -phenylethane decomposes in an apparently symmetrical simultaneous rupture of both carbon-nitrogen bonds while the corresponding reaction with  $\alpha$ -phenylethylazo-2-propane proceeds by an unsymmetrical simultaneous breaking of its two carbon-nitrogen bonds. The rationalization given for this observation was the difference in the "resonance energies" of the  $\alpha$ -phenylethyl vs. the 2-propyl radicals. If this is true, one might observe a more unsymmetrical mode of decomposition if the groups bonded to either side of the  $-N=N-$  linkage were to differ by more than the 15 kcal./mole in resonance energy quoted above. In compound III, the two groups,  $\alpha$ -phenylethyl and methyl, differ by about 25 kcal./mole in "resonance energy."<sup>5a</sup>

Decomposition of III was studied in the same solvent as the previous compound (II) and the secondary  $\alpha$ -deuterium effect, corrected for 1.00 atom of D in the benzylic  $\alpha$ -position, is  $k_{IIIa}/k_{IIIb} = 1.13$ . This is

(19) That this is a true cage reaction is further supported by the fact that when a mixture of azomethane and azomethane-*d*<sub>6</sub> are photolyzed in isooctane solution less than 0.3% of mixed ethanes are produced (R. K. Lyon and D. H. Levy, *J. Am. Chem. Soc.*, **83**, 4290 (1961)). If it is difficult for methyl radical to escape from its neighbor under these conditions, it would be expected that the  $\alpha$ -phenylethyl radical, because of its greater mass, could not escape easily from methyl.

indeed the expected value for such an effect when that carbon-nitrogen bond is stretched substantially at the transition state.<sup>2</sup> It compares favorably with 1.13 per D atom and 1.15 per D atom in the decompositions of azobis- $\alpha$ -phenylethane and  $\alpha$ -phenylethylazo-2-propane, respectively, when in each molecule deuterium is located at the benzylic  $\alpha$ -position.<sup>20</sup> The secondary effect when the methyl group is fully deuterated is  $k_{\text{IIIa}}/k_{\text{IIIc}} = 0.97$  and requires further discussion.

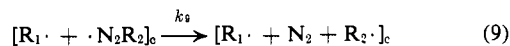
*A priori* the secondary  $\alpha$ -effect per D atom generated by the change in H-C-leaving group bending force constant in breaking a CH<sub>3</sub>-X bond should not be significantly different from that when the  $\alpha$ -D atom is part of a group more complex than methyl. However, some early work, the gas phase thermolysis of dimethyl-*d*<sub>6</sub>-mercury, indicated the secondary  $\alpha$ -effect to be abnormally low.<sup>12</sup> The source of the discrepancy is unknown but perhaps it may be due to nonthermal equilibrium effects.<sup>21</sup> Because of this anomaly, the secondary  $\alpha$ -effect in the breaking of a methyl-X bond was studied in another system where nonthermal equilibrium effects are absent, *viz.*, the decomposition of cumyloxy radical. The isotope effect here,  $k_{\text{H}}/k_{\text{D}} = 1.12$  per D atom at 75° (1.11 at 105°, extrapolated),<sup>22</sup> falls closely in line with those observed for "unimolec-



ular" reactions in more branched systems.<sup>2</sup>

With these results in mind, we infer that the secondary effect,  $k_{\text{H}}/k_{\text{D}} = 0.97$  (3 D atoms) when IIIc decomposes, indicates that the CH<sub>3</sub>-N bond is not stretching in the slow step; the reaction coordinate of the rate-controlling step is concerned with the two fragments,  $\alpha$ -phenylethyl and azomethyl radicals moving apart. In the absence of other force constant changes, there should be a mass effect in the ratio of imaginary frequencies,  $k_{\text{H}}/k_{\text{D}} \approx 1.025$  (3 D atoms), if one makes the simplifying assumption that the movement of these two fragments away from each other is along the direction of the bond between the nitrogen and benzylic-carbon atoms.<sup>23</sup> The fact that there is a slight inverse effect as compared to 1.025 might indicate that as the methylazo radical moves away the CH<sub>3</sub>-N bond tightens slightly, thereby increasing the H-C-N bending force constant.

To test the interpretation derived from the secondary  $\alpha$ -deuterium effect we determined the C<sup>13</sup> effect in the decomposition of C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)N=NC<sup>13</sup>H<sub>3</sub>. In hexadecane as solvent, approximately a 65% yield of methane is produced; the following sequence of reactions can be written

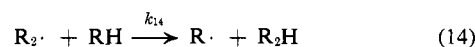
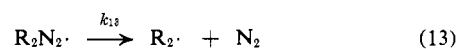
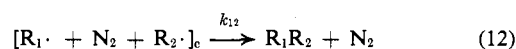
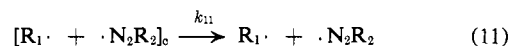
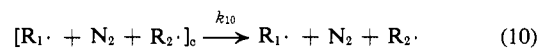


(20) Of course to compare these more precisely correction to the same temperatures should be made; see ref. 4b.

(21) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **85**, 2365 (1963).

(22) A. A. Zavitsas and S. Seltzer, *ibid.*, **86**, 1265 (1964); **87**, 1534 (1965).

(23) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 30 (1950).



where A = azo compound, R<sub>1</sub>· = C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)·, R<sub>2</sub>· = CH<sub>3</sub>·, RH = hexadecane and c = cage. Starting with eq. 8 and integrating consecutively, an equation (not given here because of space limitations) can be derived which expresses the yield of CH<sub>4</sub> as a function of A<sub>0</sub>, t, and all the rate constants; a similar expression is derived for C<sup>13</sup>H<sub>4</sub> as a function of A<sub>0</sub>' t, and (k'), where the primes refer to the C<sup>13</sup> molecules. Simplification of these equations is obtained by realizing that k<sub>8</sub> is much smaller than all the other rate constants given in the scheme above and leads to eq. 15. The assumption, that the rate constant for the back reaction of eq. 8 (*i.e.*, k<sub>-8</sub>) is much smaller than k<sub>9</sub>, is made.

$$\frac{[\text{C}^{13}\text{H}_4]}{[\text{C}^{12}\text{H}_4]} = \frac{\frac{1}{k_9' + k_{11}'} \left[ k_{11}' + \frac{k_9' k_{10}'}{k_{11}' + k_{12}'} \right] A_0' (1 - e^{-k_8 t'})}{\frac{1}{k_9 + k_{11}} \left[ k_{11} + \frac{k_9 k_{10}}{k_{11} + k_{12}} \right] A_0 (1 - e^{-k_8 t})} \quad (15)$$

At  $t = \infty$ , the equation reduces to

$$\frac{[\text{C}^{13}\text{H}_4]}{[\text{C}^{12}\text{H}_4]} = \frac{\alpha'}{\alpha} = \frac{\frac{1}{k_9' + k_{11}'} \left[ k_{11}' + \frac{k_9' k_{10}'}{k_{11}' + k_{12}'} \right] A_0'}{\frac{1}{k_9 + k_{11}} \left[ k_{11} + \frac{k_9 k_{10}}{k_{11} + k_{12}} \right] A_0} \quad (16)$$

and  $\alpha'/\alpha$  is determined. At partial reaction, eq. 15 can be rewritten as

$$\frac{[\text{C}^{13}\text{H}_4]}{[\text{C}^{12}\text{H}_4]} = \frac{\alpha' (1 - e^{-k_8 t'})}{\alpha (1 - e^{-k_8 t})} \quad (17)$$

By setting  $[\text{C}^{13}\text{H}_4]/[\text{C}^{12}\text{H}_4] = N_x$ ,  $\alpha'/\alpha = N_{x_0}$ , and  $f$ , the fraction of decomposition that A undergoes, =  $(1 - e^{-k_8 t})$ , one obtains the familiar equation derived by Bigeleisen<sup>24</sup>; the low yield of methane does

$$\frac{N_{x_0}}{N_x} = \frac{1 - (1 - f)^{k_8'/k_8}}{f} \quad (18)$$

not offer any difficulty because all isotope effects concerned in the partitioning of methyl and azomethyl radicals cancel when comparing the C<sup>13</sup>/C<sup>12</sup> ratio at partial and complete decomposition. The C<sup>13</sup>-kinetic isotope effect refers to the fractionation in the slow step whatever it is. The very small C<sup>13</sup> effect forces one to conclude that the C<sup>13</sup>-N bond is not breaking in the slow step.

As shown in Table II, the C<sup>13</sup>-isotope effect, in the decomposition of C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)N=NC<sup>13</sup>H<sub>3</sub>, is  $k_{12}/k_{13} = 1.0068 \pm 0.0006$ . This is to be contrasted with

(24) J. Bigeleisen, *Science*, **110**, 14 (1949).

effects of 1.02–1.04 when a C<sup>13</sup>–X bond is breaking in the rate-controlling step.<sup>25</sup> Furthermore, the C<sup>13</sup> effect can be classified as a secondary mass effect. Again, if the fragments azomethyl and  $\alpha$ -phenylethyl are moving apart, the expected effect on the ratio of imaginary frequencies is 1.0082. That the calculated effect is larger than the observed isotope effect may be another hint that the carbon–nitrogen bond in the incipient methylazo group is tightening in going from reactant to the transition state in the slow step of the reaction. In summary, both effects indicate that with compound III the mechanism has changed to a two-step reaction which is probably caused by the greater difference in resonance energy stabilization between the two groups R<sub>1</sub> and R<sub>2</sub> in III than in I or II.

In addition to the indication of a change of mechanism, the isotope effects establish the transitory existence of the CH<sub>3</sub>N<sub>2</sub> radical. Ramsperger<sup>26</sup> concluded, from examination of the activation energies for thermal decomposition of azomethane, methylazo-2-propane, and azo-2-propane, that the unsymmetrical methylazo-2-propane decomposed by simultaneous rupture of its two carbon–nitrogen bonds. Trotman-Dickenson<sup>27</sup> and Gowenlock<sup>28</sup> and their co-workers, on the other hand, felt that the current thermochemical evidence was not compelling enough to make a choice between simultaneous two-bond rupture or consecutive two-step decomposition of azomethane. The latter two groups, however, did agree that the methylazo radical, if it existed, could possibly be stabilized by a three-electron bond (actually five electrons) between nitrogen atoms. Although a three-electron bond is more favored between identical atoms than between neighboring elements of the periodic chart,<sup>29</sup> nevertheless one might expect a small degree of free electron density between carbon and its neighboring nitrogen atom. This stabilization would imply that there would be a tightening of the nitrogen–nitrogen bond and to a lesser degree a tightening of the carbon–nitrogen bond. As noted above, the isotope effects provide weak evidence to support this hypothesis.

As shown in Table III, the C<sup>13</sup> abundance in the methylhydrazine used to synthesize  $\alpha$ -phenylethylazomethane is, within experimental error, identical with that observed in the methane obtained from complete decomposition of the azo compound in hexadecane. If the plausible assumption that no C<sup>13</sup>-isotope effect operates in the synthesis (see eq. 1) is made, then eq. 19 follows from eq. 16.

$$\frac{\alpha'/\alpha}{A_0'/A_0} = 1.001 \pm 0.001 =$$

$$\frac{\frac{1}{k_9' + k_{11}'} \left[ k_{11}' + \frac{k_9' k_{10}'}{k_{11}' + k_{12}'} \right]}{\frac{1}{k_9 + k_{11}} \left[ k_{11} + \frac{k_9 k_{10}}{k_{11} + k_{12}} \right]} \quad (19)$$

(25) Reference 23, pp. 68, 72, 73.

(26) H. C. Ramsperger, *J. Am. Chem. Soc.*, **51**, 2134 (1929).

(27) M. Page, H. O. Pritchard, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3878 (1953).

(28) B. G. Gowenlock, J. R. Majer, and D. R. Snelling, *Trans. Faraday Soc.*, **57**, 670 (1961).

(29) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 341–343.

Furthermore, at  $t = \infty$ ,

$$[\text{CH}_4]/A_0 \cong 0.65 \cong \frac{1}{k_9 + k_{11}} \left[ k_{11} + \frac{k_9 k_{10}}{k_{11} + k_{12}} \right] \quad (20)$$

The rate constant  $k_9$ , for rupture of the methyl–nitrogen bond in the solvent cage, would be expected to be  $\sim 2\text{--}4\%$  greater than the corresponding rate constant,  $k_9'$ , for cleavage of the methyl–C<sup>13</sup>–nitrogen bond. With this in mind, the two ways for the quotient of rate constants in eq. 19 to equal unity are for  $k_9 \gg k_{11}$  or  $k_{11} \gg k_9$ ; the latter condition, however, does not satisfy eq. 20 readily. In fact it is necessary that  $k_9 \gg k_{11}$ . Equation 19 reduces to

$$1.001 \cong \frac{k_{10}'(k_{11}' + k_{12}')}{k_{10}/(k_{11} + k_{12})} \quad (21)$$

if  $k_9 \gg k_8$ ; eq. 20 simplifies to eq. 22.

$$0.65 \cong \frac{k_{10}}{(k_{11} + k_{12})} \cong \frac{k_{10}}{k_{12}} \left( 1 + \frac{k_{11}}{k_{12}} \right) \quad (22)$$

Since  $k_{10} < (k_{11} + k_{12})$  and  $k_{10} > k_{11}$ ,  $k_{12}$  must be greater than  $k_{11}$ ; the equality

$$1.001 \cong \left[ \frac{k_{10}'/k_{12}'}{k_{10}/k_{12}} \right] \left[ \frac{1 + k_{11}/k_{12}}{1 + k_{11}'/k_{12}'} \right] \quad (23)$$

is obtained where the second term in the brackets is probably very close to unity since  $k_{12} > k_{11}$ . The transition state for radical coupling would be expected to look very much like reactants<sup>30</sup> and therefore the ratio  $k_{12}'/k_{12}$  is determined almost entirely by the ratio of imaginary frequencies.<sup>23</sup> The ratio  $k_{10}'/k_{10}$ , since it describes movement of the same two radicals R<sub>1</sub> and R<sub>2</sub> away from each other, would be expected to be controlled by the same function that determines  $k_{12}'/k_{12}$ ,<sup>31</sup> and hence these two ratios can be anticipated to be equal.

This treatment reveals that the rate constant for rupture of the methyl–nitrogen bond is larger than the rate constant for diffusion of the methylazo radical from the solvent cage. The lifetime of cages has been estimated to be of the order of  $3 \times 10^{-11}$  sec. for the diffusion of iodine atoms in a hexane cage.<sup>32</sup> Simple calculations<sup>33</sup> of the diffusion constant from the estimated viscosity of hexadecane at 160°<sup>34</sup> and use of this to calculate<sup>32,35</sup> the lifetime of the cage restricting the methylazo and  $\alpha$ -phenylethyl radicals also yield about  $4 \times 10^{-11}$  sec. Therefore the rate constant for escape of these two partners from the cage is about  $2.5 \times 10^{10}$  sec.<sup>-1</sup>, which in turn is the lower limit of the rate constant for decomposition of the methyl–nitrogen bond.<sup>36</sup> Because of the approximations involved, the limit may

(30) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(31) (a) J. H. Arnold, *ibid.*, **52**, 3937 (1930); (b) G. Ertl and H. Gerscher, *Z. Elektrochem.*, **66**, 560 (1962); (c) W. P. A. Haas, G. Seidel, and N. J. Poullis, *Physica*, **26**, 834 (1960); (d) R. K. Lyon, *J. Am. Chem. Soc.*, **86**, 1907 (1964).

(32) S. Benson, "The Foundation of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 495, 496.

(33) R. H. Stokes, P. J. Dunlop, and J. R. Hall, *Trans. Faraday Soc.*, **49**, 886 (1953).

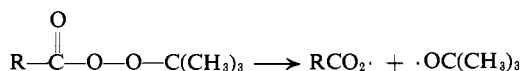
(34) "Handbook of Chemistry and Physics," 44th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1962–1963, p. 2261, lists the viscosity of hexadecane at 20° as 3.34 cp. We estimate that  $\eta_{160^\circ} = 1$  cp.

(35) F. W. Lampe and R. M. Noyes, *J. Am. Chem. Soc.*, **76**, 2140 (1954).

(36) Previous workers, e.g., Lampe and Noyes, ref. 35, have utilized the cage effect to help determine relative rate constants.

be off by as much as a factor of three or four. Furthermore, the possibility of backside attack of the methylazo radical by the  $\alpha$ -phenylethyl radical to give  $N_2$  and cumene while in the cage was neglected because of the lack of knowledge of this type of reaction. Inclusion of such a displacement in the scheme as an important reaction lowers the limit for  $k_9$ .

**Activation Parameters.** The entropy of activation and the Arrhenius energy of activation for III were measured and are shown together with those for I and II in Table V. In reactions involving similar compounds capable of giving two or three fragments it might be expected that the entropy of activation would be greater when three particles are being produced than when two particles are being formed, due to the increase in rotational freedom. This is not the case. The general order is similar to that observed for the decomposition of peresters by Bartlett and co-workers.<sup>37</sup> In a series of compounds, they noted a decrease of energy of activa-



tion with concurrent decrease of entropy of activation as R varied. When R is phenyl, the incipient carboxy radical could be stabilized in the transition state by delocalization of the free electron on the ring. This can be seen as a lowering of the activation energy in the rupture of the oxygen-oxygen bond when compared to the parent molecule, *t*-butyl peracetate. Such stabilization, however, generally creates steric restrictions in the transition state in that the phenyl group is not free to rotate; it was suggested that this is the cause for the simultaneous decrease in  $\Delta S^*$ .<sup>37</sup> Similar arguments can

(37) P. D. Bartlett, *Experientia Suppl.*, 7, 275 (1957). The authors thank Dr. Leon Gortler for citing this paper.

be made to explain the trends in entropy and energy of activation for the decomposition of I, II, and III. In I, both phenyl groups help to delocalize the free electrons on the benzylic carbons. Therefore rotation of both rings is restricted in order that its  $\pi$ -orbitals overlap with the half-filled p-orbital being formed at the benzylic carbon. The isotope effects in the decomposition of II were interpreted as showing little progress in the rupture of the nitrogen-2-propyl-carbon bond. This would mean little requirement for stabilization of the hardly formed 2-propyl radical and in turn little restriction on the geometry of the isopropyl group; the energy and entropy of activation increase in going from I to II. Finally in the decomposition of III we have shown that only the benzylic carbon-nitrogen bond ruptures in the slow step. The methyl group contributes little stabilization and therefore is free to rotate, as seen by the increase in energy and entropy of activation.

**Table V.** Activation Parameters in the Thermal Decomposition of Azo Compounds

	$E_a$ , kcal./ mole	$\Delta S^*$ , e.u.	Ref.
$C_6H_5CH(CH_3)N=N(CH_3)CHC_6H_5$ (I)	32.6	7.0	15
$C_6H_5CH(CH_3)N=NCH(CH_3)_2$ (II)	36.5	9.3	5c
$C_6H_5CH(CH_3)N=NCH_3$ (III)	38.6	14.0	This work

**Acknowledgment.** The authors are indebted to Mr. Theodore Middleton for mass spectrometric determinations and to Dr. D. R. Christman and Mrs. C. Paul for v.p.c. analyses.

## The Optical Activity of Butylethylhexylpropylmethane<sup>1</sup>

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*Contribution from the Department of Organic Chemistry of The University, Bloemsingel 10, Groningen, The Netherlands. Received March 8, 1965*

*A synthetic route to an asymmetric hydrocarbon, butylethylhexylpropylmethane, is described. Within the limits of experimental error it is established that both enantiomers exhibit no rotation of plane-polarized light between 280 and 580  $m\mu$ . This finding is in accord with predictions based on empirical calculations.*

Most textbooks introduce the subject of stereoisomerism by stating that an asymmetric carbon atom in a molecule gives rise to rotation of the plane of polarized light. The two enantiomers differ from one another by the fact that their rotation is opposite in direction.

However, van't Hoff<sup>3</sup> in his first publications nearly a century ago already recognized that the degree of

difference between the four substituents at the asymmetric center might determine whether optical activity would be observed or not.

A particularly instructive test case appeared to be a tetraalkyl methane of type A. The question we wished to answer was "Is the difference in the length of the four alkyl groups a sufficient condition for optical activity to be observed with present day instruments?" It has been predicted<sup>4</sup> that a paraffin with three or four flexible chains at the asymmetric center should be almost completely optically inactive.

An asymmetric hydrocarbon of a somewhat dif-

(3) J. H. van't Hoff, "Voorstel tot uitbreiding der tegenwoordig in de scheikunde gebruikte structuurformules in de ruimte," Utrecht, 1874; "La chimie dans l'espace," Rotterdam, 1875; *Bull. soc. chim. France*, 23, 295 (1875).

(4) (a) J. H. Brewster, *J. Am. Chem. Soc.*, 81, 5475, 5483, 5493 (1959); *Tetrahedron*, 13, 106 (1961); (b) D. H. Whiffen, *Chem. Ind.* (London), 964 (1956).

(1) Part of this work was presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 31-Sept. 4, 1964.

(2) To whom inquiries should be sent.