

TABLE VI

MASS SPECTROGRAPHIC DETERMINATION OF CARBON MONOXIDE AND CARBON DIOXIDE FOR THE CHROMIC ACID OXIDATION OF TRIPHENYLACETALDEHYDE

Sample <sup>a</sup>	28	Peak 32	44
Air	1527	166	4.5
Reaction product	2562	8.4	584
Reaction product (cor. for air present)	2485	0	584
CO	3010	...	....
CO <sub>2</sub>	..	...	3440

<sup>a</sup> All corrected to pressure = 35.1  $\mu$ ; background subtracted from all samples.

The arms of the reactions cell were placed in a Dry Ice-acetone-bath and the system was evacuated by a mercury diffusion pump. The cell was allowed to warm to room temperature, the contents were again frozen, and the cell was re-evacuated. The solutions were mixed by inverting the reaction cell after warming to room temperature. After allowing the reaction to proceed for 17 hr., the reaction mixture was frozen in a Dry Ice-acetone-bath and the gas above the reaction mixture was analyzed mass spectrometrically. One solution contained 4.00 ml. of 0.0940  $M$  (in Cr<sup>6</sup>) of sodium dichromate plus 2.00 ml. of 0.900  $M$  perchloric acid both in 91% acetic acid. The other solution contained 0.1535 g. (0.564 mmole) of triphenylacetaldehyde in 10.0 ml. of 91% acetic acid solution. The final concentrations were: ((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CCHO) = 0.0353  $M$ , (Cr<sup>6</sup>) = 0.0235  $M$  and (HClO<sub>4</sub>) = 0.113  $M$ . The mass spectral data are given in Table VI. The mole percentages of

carbon monoxide (82%) and carbon dioxide (17%) were calculated from these data.

**Triphenylacetic Acid in Chromic Acid.**—A mixture of 0.100 g. (0.348 mmole) of triphenylacetic acid, 6.00 ml. of 0.0940  $M$  (in Cr<sup>6</sup>) of sodium dichromate and 3.00 ml. of 0.900  $M$  perchloric acid in a total of 20.0 ml. of 91% acetic acid was prepared. The mixture was poured into 30 ml. of 0.2  $M$  sodium arsenite solution in 2  $M$  hydrochloric acid after 48 hr. at 30°.

The mixture was filtered and 0.04 g. of triphenylacetic acid, m.p. 258–260° dec. (uncor.) (lit.<sup>26</sup> m.p. 264–265°) was collected. The filtrate was extracted with three 50-ml. portions of methylene chloride and the combined methylene chloride extracts were washed with two 10-ml. portions of water. Concentration of the methylene chloride extract, after drying over magnesium sulfate, gave 0.05 g. of triphenylacetic acid, m.p. 258–260° dec. (uncor.). The total amount of recovered triphenylacetic acid was 0.09 g. (90% recovery).

**Carbon Monoxide in Chromic Acid.**—Carbon monoxide (Matheson C.P.) was bubbled through 50.0 ml. of 91% acetic acid solution which was 0.0302  $M$  in chromium(VI) and 0.126  $M$  in perchloric acid. Aliquots (2.00 ml.) were analyzed titrimetrically by a method previously used by Wiberg and Mill.<sup>8</sup> No change in titer was noted over a 100-hour period.

**Calculation of Concentrations by Numerical Integration.**—The concentrations were determined from the differential equations appropriate to the system and the rate constants given in the results section using fourth order Runge-Kutta numerical integration.<sup>27</sup> An IBM-709 computer was used in performing the numerical calculations. Independent checks of this method indicate that the results will be in error by less than 0.1%.

(27) W. E. Milne, "Numerical Calculus," Princeton University Press, Princeton, N. J., 1949.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

## Homologation of the Triphenylmethyl Cation

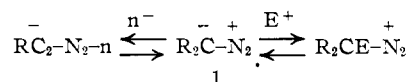
By H. W. WHITLOCK, JR.

RECEIVED JANUARY 19, 1962

Homologation of the triphenylmethyl cation by diazomethane affords, as end products, triphenylethylene and 1,2,3-triphenylpropene. Homologation by phenyldiazomethane affords stilbene and tetraphenylethylene. Homologation by diphenyldiazomethane affords tetraphenylethylene, the triphenylmethyl cation serving as a catalyst. The results are interpreted in terms of simple carbonium ion behavior.

### Introduction

Reactions of diazo compounds may be best interpreted in light of resonance structure 1.



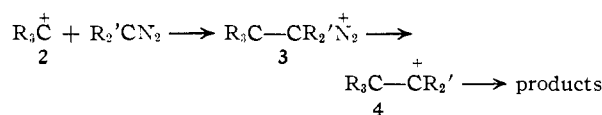
In accordance with this structure, reactions of diazo compounds with electrophiles (E<sup>+</sup>) proceed *via* electrophile-carbon bond formation. Similarly, reactions with nucleophiles (n<sup>-</sup>) proceed *via* nucleophile-nitrogen bond formation. Many examples of this ambivalent character of diazo compounds are found in the literature—reactions with metal salts, acid chlorides,  $\alpha,\beta$ -unsaturated carbonyl and nitro compounds, carboxylic and non-carboxylic acids, simple carbonyl groups, Grignard reagents, diazonium salts and even other diazo compounds<sup>1</sup> being known.

As set forth in a previous communication,<sup>2</sup> we have now extended this list by proposing the re-

(1) R. Huisgen and R. Fleischmann, *Ann.*, **623**, 47 (1959).

(2) H. W. Whitlock, Jr., *Tetrahedron Letters*, 593 (1961).

action between diazo compounds and carbonium ions. The proposed reaction involves formation of a primary adduct 3 followed by rapid loss of nitrogen to afford a new carbonium ion 4. The subse-



quent pathways of reaction which are open to 4 then will be determined by the nature of R and R', Wagner-Meerwein rearrangements followed by either proton loss or reaction with a nucleophile being most likely.<sup>3</sup> That the reaction as formulated is feasible has been already demonstrated by the one-step preparation of dibenz[b,f]oxepin, dibenzo[b,f]thiopin and N-methyldibenz[b,f]azepin from the heterocyclic xanthylium, thiaxanthylium and N-methylacridinium cations, respectively.<sup>2</sup> Another example of the generality of this reaction is

(3) (a) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); (b) B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *J. Am. Chem. Soc.*, **83**, 3654 (1961).

the formation of pentaphenylcyclopentadiene from the reaction between triphenylcyclopropenium fluoroborate and phenyldiazomethane.<sup>4</sup>

Before proceeding to more complex examples of this reaction, it was desired to investigate briefly the type of diazo compounds which might be used and the possibility of variable stoichiometry (e.g., 1:2 cation-diazo compound adducts), employing a relatively simple cation whose behavior toward diazo compounds could be readily interpreted. The trityl (triphenylmethyl) cation was chosen for this purpose, its perchlorate salt being employed in order to eliminate the possibility of nucleophilic capture of any intermediate cations. As will be seen, reactions of the trityl cation with diazo compounds can be interpreted best in terms of simple carbonium ion behavior.

### Results and Discussion

The dropwise addition of an ethereal solution of diazomethane to an equivalent of trityl perchlorate in ether at 0° led to a 62% yield of triphenylethylene. However, when trityl perchlorate was added to an excess of ethereal diazomethane, there was isolated in addition to a 34% yield of triphenylethylene a 27% yield of 1,2,3-triphenylpropene as a polymorphic modification, m.p. 53°. Its identity was established by direct comparison with an authentic sample of 1,2,3-triphenylpropene, m.p. 63°, prepared by dehydration of dibenzylphenylcarbinol. No other homogeneous material could be isolated from this reaction. In no instance was there found any evidence for formation of polymethylene. The proposed mechanism is presented<sup>5</sup> in Fig. 1.

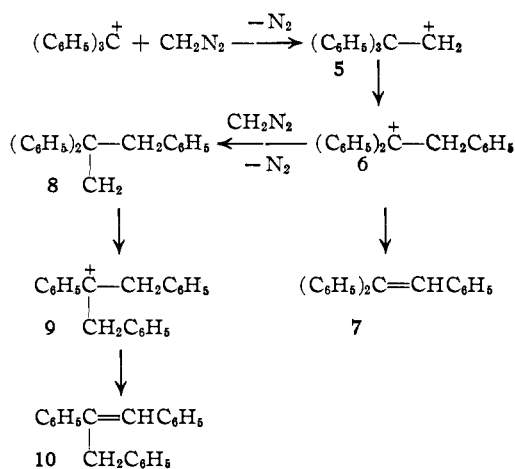


Fig. 1.

It is difficult to rationalize the observed products except on the basis of a carbonium ion mechanism.<sup>6</sup> Formation of both triphenylethylene (7) and 1,2,3-triphenylpropene (10) can best be interpreted by

(4) R. Breslow, reported in the Organic Chemistry Symposium at Bloomington, Ind., 1961.

(5) For the sake of clarity the reactions are written as proceeding through open primary carbonium ions.

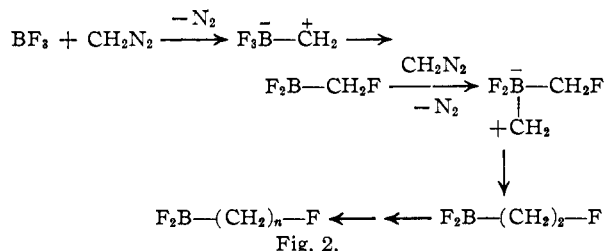
(6) That the reactions were carried out under heterogeneous conditions (see, however, ethyl diazoacetate) and that the trityl cation would be extensively solvated<sup>7</sup> by the ether solvent are ignored for the present discussion.

(7) W. B. Smith and P. S. Rao, *J. Org. Chem.*, **26**, 254 (1961).

assuming that the reaction proceeds through the 1,1,2-triphenylethyl carbonium ion (6). This ion may either lose a proton, forming triphenylethylene (7), or react with a second molecule of diazomethane. After rearrangement and proton loss the product then will be 1,2,3-triphenylpropene (10). Isolation of 10 is undoubtedly a reflection on the stability to be associated with the benzhydryl carbonium ion 6. Evidence for the proposed mechanism is the observation that the decomposition of 2,2,2-triphenylethylammonium nitrite in aqueous solution affords a good yield of triphenylethylene,<sup>8</sup> the reaction presumably proceeding *via* 5 and 6. The mechanism by which 6 and 9 lose protons to form their respective products is unknown at the present time, although the presence of unreacted diazomethane at the end of the reaction suggests that little free perchloric acid is present in the reaction mixture. A possible explanation is that the cations are present as oxonium salts which decompose on workup to afford the observed products.

The above mechanism bears a close similarity to the currently accepted mechanism for the boron trifluoride-catalyzed polymerization of diazomethane<sup>9,10</sup> (Fig. 2).

The complete lack of polymethylene formation in the reaction of trityl perchlorate with diazomethane can be ascribed to the greater migratory aptitude of phenyl than benzyl (e.g., 8→9), combined with a facile chain termination which is not available to the boron trifluoride-diazomethane polymerization intermediates.



The reaction between phenyldiazomethane, a monosubstituted diazoalkane, and trityl perchlorate was investigated. Dropwise addition of an ethereal solution of phenyldiazomethane to a stirred slurry of an equimolar amount of trityl perchlorate in ether led to a rapid reaction. Although the theoretical amount of nitrogen was collected, an 86% yield of trityl perchlorate was recovered unchanged. From the reaction mixture there was isolated an 11% yield of *trans*-stilbene, a 6% yield of tetraphenylethylene, a small quantity of triphenylmethane,<sup>11</sup> and a relatively large amount of unidentified dark oils. The reaction between phenyldiazomethane and one-tenth of an equivalent of trityl perchlorate afforded a 15%

(8) L. Hellerman, M. L. Cohn and R. E. Hoen, *J. Am. Chem. Soc.*, **50**, 1716 (1928).

(9) C. E. H. Bawn, A. Ledwith and P. Matthies, *J. Polymer. Sci.*, **34**, 93 (1959).

(10) A. G. Davies, D. G. Hare, O. R. Kahn and J. Sikora, *Proc. Chem. Soc.*, 172 (1961).

(11) Presumably by hydride abstraction from ether by the trityl cation.<sup>12</sup>

(12) M. Gomberg, *J. Am. Chem. Soc.*, **35**, 200 (1913).



azine. In our hands there was isolated a 91% yield of the azine and no tetraphenylethylene was detected. Aluminum chloride in ether also catalyzed the decomposition of diphenyldiazomethane. The product was an equimolar mixture of tetraphenylethylene and benzophenone azine.

### Experimental

**Triphenylmethyl Perchlorate and Diazomethane.**—A dry solution of 10.0 mmoles of diazomethane in 100 ml. of ether was added dropwise to a stirred slurry of 3.46 g. (10.1 mmoles) of trityl perchlorate<sup>23</sup> in 50 ml. of dry ether at 0°. The trityl perchlorate dissolved rapidly, accompanied by nitrogen evolution, and on completion of the addition of diazomethane (10 min.) there was only a small amount of the salt undissolved. A further 10 ml. of the diazomethane solution was added, the clear yellow reaction mixture was kept at 0° for 15 min., and the unreacted diazomethane was then destroyed by the dropwise addition of acetic acid. The ethereal solution was washed with saturated sodium bicarbonate solution and saturated salt solution, dried over anhydrous sodium sulfate and evaporated to afford 2.67 g. of a brownish oil. Percolation of a hexane solution of this oil through a column of alumina (25 g.) afforded 2.25 g. of pasty crystals, m.p. 30–55°. Crystallization from hexane followed by chromatography of the mother liquors in hexane on silica gel afforded a total of 1.60 g. (62% yield) of triphenylethylene as clumps of needles, m.p. 66–67.5°, m.m.p. 67–68°, whose infrared spectrum (carbon tetrachloride) was identical with that of an authentic sample.

**Triphenylmethyl Perchlorate and Excess Diazomethane.**—In one portion, 3.17 g. (9.25 mmoles) of trityl perchlorate was added to a dry stirred solution of 18.0 mmoles of diazomethane in 150 ml. of ether at 0°. A vigorous reaction occurred, the salt dissolving with nitrogen evolution. After stirring at 0° for 15 min., acetic acid was added cautiously to destroy the unreacted diazomethane. The resulting colorless solution was washed with saturated sodium bicarbonate solution and saturated salt solution, dried over anhydrous sodium sulfate and evaporated. The residue, 2.57 g. of a green oil, was dissolved in hexane and percolated through a column of alumina (30 g.). Evaporation of the eluant afforded 2.38 g. of a pale yellow mobile oil which did not crystallize on seeding with a sample of triphenylethylene. Its infrared spectrum exhibited a medium intensity aliphatic carbon–hydrogen stretching band at 3.4  $\mu$ . This oil was adsorbed on silica gel (150 g.) and eluted with 1% chloroform in hexane to afford 805 mg. (34% yield) of triphenylethylene as clumps of needles, m.p. 66.5–68.0°, m.m.p. 67.2–68.1°, whose infrared spectrum was identical with that of an authentic sample. Continued elution with 1% chloroform in hexane afforded 667 mg. (27% yield) of pasty 1,2,3-triphenylpropene. Two recrystallizations from hexane gave 142 mg. of rosettes, m.p. 52.5–53°. The analytical sample had m.p. 52.5–54°.

*Anal.* Calcd. for C<sub>21</sub>H<sub>15</sub>: C, 93.29; H, 6.71; mol. wt., 270. Found: C, 93.39, 93.27; H, 6.64, 6.68; mol. wt. (Rast), 302.

Continued elution afforded only oils which resisted crystallization and were not investigated further.

The dehydration of dibenzylphenylcarbinol,<sup>24</sup> employing *p*-toluenesulfonic acid in refluxing benzene, afforded a 65% yield of authentic 1,2,3-triphenylpropene as stout needles, m.p. 62–63° (lit.<sup>25</sup> m.p. 62–63°). That the 53° melting sample was a polymorphic modification of 1,2,3-triphenylpropene was shown by comparison of the infrared spectra (carbon tetrachloride) of the two samples, by cross seeding experiments, and by a mixed melting point. A mixture of the two samples partially melted at 53°, resolidified, and remelted sharply at 62–63°. The ultraviolet spectrum of 1,2,3-triphenylpropene,  $\lambda_{\text{max}}^{\text{CH}_2\text{OH}}$  271 m $\mu$  (19,000), indicates a *trans*-stilbene chromophore.

**Triphenylmethyl Perchlorate and Phenyl diazomethane.**—A solution of 2.15 g. (18.2 mmoles) of phenyldiazomethane<sup>26</sup>

in 10 ml. of dry ether was added dropwise to a stirred slurry of 6.79 g. (19.8 mmoles) of trityl perchlorate in 50 ml. of dry ether at 0°. After nitrogen evolution had ceased (360 ml., 15 min.), the reaction mixture was filtered from unreacted trityl perchlorate. The filtrate was diluted with benzene and washed with saturated sodium bicarbonate solution and saturated salt solution, dried over anhydrous sodium sulfate and evaporated. Chromatography of the dark residual oil on alumina followed by silica gel afforded 174 mg. (11% yield) of *trans*-stilbene, m.p. after one recrystallization, 123.8–124.5°, identified by mixed melting point and infrared; 91 mg. of triphenylmethane, m.p. after two recrystallizations from hexane, 91–92°; 359 mg. (5.9% yield) of tetraphenylethylene, m.p. 220–224°, identified by mixed melting point and infrared; and 239 mg. of a dark green oil whose ultraviolet spectrum exhibited only end absorption and which was not investigated further.

Unreacted trityl perchlorate which was removed by filtration weighed 5.86 g. (86% recovery) and was identified by hydrolysis to triphenylcarbinol, m.p. 160.5–161.5°, m.m.p. 160.5–162°. Calculated on the basis of trityl perchlorate consumed, the yield of tetraphenylethylene was 39%.

**Triphenylmethyl Perchlorate and Excess Phenyl diazomethane.**—A solution of 2.04 g. (17.2 mmoles) of phenyldiazomethane in 10 ml. of dry ether was added dropwise to a stirred slurry of 592 mg. (1.73 mmoles) of trityl perchlorate in 10 ml. of dry ether at 0°. After stirring at 0° for 45 min., nitrogen evolution (322 ml.) was complete and excess saturated sodium bicarbonate solution was added to the yellowish reaction mixture. The ether layer was separated and the aqueous layer was extracted with benzene. The combined organic layers were washed with saturated salt solution, dried over anhydrous sodium sulfate, concentrated, percolated through a column of Florisil<sup>27</sup> and evaporated to afford 1.78 g. of a yellow semi-crystalline material. Adsorption of this on silica gel (200 g.) followed by successive elution with hexane, 5% chloroform in hexane, and 40% chloroform in hexane afforded 235 mg. (15% yield) of *trans*-stilbene, m.p. after two recrystallizations from hexane, 123.9–124.4°, identified by mixed melting point and infrared; 65 mg. (11% yield based on trityl perchlorate) of tetraphenylethylene, m.p. 221–223°, m.m.p. 222–224°; 510 mg. of a yellow gum whose ultraviolet spectrum exhibited only end absorption; and 215 mg. of triphenylcarbinol, m.p. after three recrystallizations from hexane, 160.4–161.3° identified by mixed melting point and infrared.

**Triphenylmethylperchlorate and Ethyl Diazoacetate.**—To a solution of 3.43 (10 mmoles) of trityl perchlorate in 25 ml. of dry acetonitrile at 0° was added dropwise 2.10 ml. (2.27 g., 20 mmoles) of ethyl diazoacetate, nitrogen being rapidly evolved. The resulting clear light yellow solution was poured into water (500 ml.) and the aqueous layer was extracted with chloroform. The combined chloroform extracts were washed with saturated sodium bicarbonate solution and saturated salt solution, dried over anhydrous sodium sulfate and adsorbed on a column of alumina. Elution with hexane afforded 2.66 g. (81% yield) of fine needles, m.p. 111–119°. One crystallization from ethyl acetate–hexane afforded 2.35 g. (72% yield) of ethyl triphenylacrylate as fine needles, m.p. 221–222° (lit.<sup>16</sup> m.p. 116–119°). The analytical sample was prepared by repeated recrystallization from ethyl acetate as needles or rhombs, m.p. 223.5–224°.

*Anal.* Calcd. for C<sub>23</sub>H<sub>20</sub>O<sub>2</sub>: C, 84.12; H, 6.14. Found: C, 83.99; H, 5.88.

**Triphenylmethyl Perchlorate and Diphenyldiazomethane.**—A solution of 1.91 g. (9.84 mmoles) of diphenyldiazomethane<sup>28</sup> (m.p. 29°) in 20 ml. of dry ether was added dropwise to a stirred slurry of 3.01 g. (8.77 mmoles) of trityl perchlorate in 25 ml. of ether at 0°. The purple color of the diazo compound disappeared immediately on contact with the slurry of trityl perchlorate. After completion of addition of the diazo compound, saturated sodium bicarbonate solution was added to hydrolyze the unreacted trityl perchlorate. The ether layer was separated and the aqueous layer was extracted with benzene. The combined organic layers were washed with saturated salt solution, dried over anhydrous sodium sulfate and evaporated to

(27) Floridin Co., Tallahassee, Fla.

(28) J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

(23) H. J. Dauben, Jr., L. R. Honnen and M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

(24) A. Klages and S. Heilmann, *Ber.*, **37**, 1447 (1904).

(25) A. Orechoff, *ibid.*, **47**, 89 (1914).

(26) H. Staudinger and A. Gaulé, *ibid.*, **49**, 1897 (1916); distilled at 35–40° (bath temp.) at 0.4 mm. Gasometric analysis indicated a purity of ca. 90%.

afford 3.83 g. of a white solid, m.p. 125–190°. Repeated recrystallization of this material and chromatography of the mother liquors on alumina and silica gel afforded 1.24 g. (76% yield) of tetraphenylethylene, m.p. and m.m.p. 223–224°; 220 mg. of dibenzhydryl ether, m.p. 100–103°, identified by mixed melting point and infrared; and 2.12 g. (93% yield) of triphenylcarbinol, m.p. 155–158°, m.m.p. 158–160°.

**Catalytic Dimerization of Diphenyldiazomethane.**—A solution of 12.5 g. (64.5 mmoles) of diphenyldiazomethane (m.p. 29°) in 100 ml. of dry ether was added over a 10-min. period to a stirred slurry of 1.15 g. (3.35 mmoles) of trityl perchlorate in 100 ml. of ether at 0°. The purple color was discharged rapidly on addition. After stirring at 0° for an additional 10 min., saturated sodium bicarbonate solution was added, the ether layer was separated, and the aqueous layer was extracted with benzene. The combined organic layers were washed with saturated salt solution, dried over anhydrous sodium sulfate and evaporated. Repeated recrystallization of the residue and chromatography of the mother liquors on alumina and silica gel afforded 10.36 g. (97% yield) of tetraphenylethylene, identified by m.p., m.m.p., and infrared; 932 mg. (96% yield) of triphenylcarbinol, m.p. and m.m.p. 160.5–161.5°; and 206 mg. (1.8% yield) of dibenzhydryl ether as needles, m.p. 105–107.5°, m.m.p. 107–108°.

*Anal.* Calcd. for  $C_{26}H_{22}O$ : C, 89.11; H, 6.33. Found: C, 88.98, 88.89; H, 6.35, 6.38.

Hydrolysis of a 135-mg. sample of the dibenzhydryl ether in refluxing aqueous dioxane-sulfuric acid for 12 hr. gave, on chromatography, 32 mg. of recovered ether and 95 mg. (89% yield) of benzhydrol, m.p. 64.5–65.5°, m.m.p. 65.5–66.0°.

**Tetra-(*p*-anisyl)-ethylene.**—A solution of 2.56 g. (10.1 mmoles) of di-(*p*-anisyl)-diazomethane<sup>29</sup> (m.p. 110°) in 100 ml. of dry ether was added dropwise to a stirred slurry of 273 mg. (0.80 mmole) of trityl perchlorate in 25 ml. of dry ether at 0°. A rapid evolution of nitrogen accompanied by discharge of the blue-purple color of the diazo compound occurred. After completion of addition of the diazo compound the unreacted trityl perchlorate was hydrolyzed by the addition of saturated sodium bicarbonate solution.

(29) R. Baltzly, N. B. Mehta, P. B. Russell, R. E. Brooks, E. M. Grivsky and A. M. Steinberg, *J. Org. Chem.*, **26**, 3669 (1961).

The ether layer was separated and the aqueous layer was extracted with benzene. The combined organic layers were washed with saturated salt solution, dried over anhydrous sodium sulfate and evaporated. One crystallization of the white residue from ethyl acetate gave 1.91 g. (84% yield) of tetra-(*p*-anisyl)-ethylene as rods, m.p. 184–185° (lit.<sup>30</sup> m.p. 181–182°).

*Anal.* Calcd. for  $C_{38}H_{28}O_4$ : C, 79.62; H, 6.24. Found: C, 79.93; H, 5.95.

**Boron Trifluoride Etherate and Diphenyldiazomethane.**—To a solution of 1.080 g. (5.56 mmoles) of diphenyldiazomethane (m.p. 29°) in 10 ml. of dry ether was added at 0° 1 drop of freshly distilled boron trifluoride etherate. Nitrogen was vigorously evolved. After standing at 0° for 0.5 hr. the solution was a pale yellow color, a white precipitate had appeared, and nitrogen evolution had ceased. Evaporation of the solvent afforded 992 mg. (99% yield) of slightly yellow rods, m.p. 150–160°. Percolation of a hexane solution of this material through a column of alumina afforded 911 mg. (91% yield) of benzophenone azine as pale yellow rods, m.p. 162–163° (lit.<sup>31</sup> m.p. 164°). The analytical sample was prepared by recrystallization from ethyl acetate as pale yellow rods, m.p. 163°.

*Anal.* Calcd. for  $C_{26}H_{20}N_2$ : C, 86.63; H, 5.59; N, 7.77. Found: C, 86.52; H, 5.59; N, 7.71.

**Aluminum Chloride and Diphenyldiazomethane.**—To a solution of 1.155 g. (5.95 mmoles) of diphenyldiazomethane (m.p. 29°) in 10 ml. of dry ether was added a solution of 55 mg. of freshly sublimed aluminum chloride in 1 ml. of ether. After being stirred at 25° for 8 hr. the now colorless solution was taken up in benzene, washed with saturated sodium bicarbonate solution and saturated salt solution, dried over anhydrous sodium sulfate and evaporated. The residue, 1.023 g. of yellow crystals, m.p. 140–190°, was chromatographed on silica gel (100 g.). Elution with 25% chloroform in hexane afforded directly 464 mg. (47% yield) of tetraphenylethylene, m.p. and m.m.p. 224–224.5°. Elution with 40% chloroform in hexane afforded 577 mg. (54% yield) of benzophenone azine, m.p. 161.5–163°. One recrystallization from ethyl acetate gave 414 mg. (38% yield) of rods, m.p. 163°, m.m.p. 162.5–163°.

(30) L. Gattermann, *Ber.*, **23**, 2874 (1895).

(31) A. Purgotti and G. Vigand, *Gazz. chim. ital.*, **31**, **II**, 560 (1902).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

## Peroxides. X. The Thermal Decomposition of 1-Hydroxyisobutyl-1-*d* Isobutyl-1,1-*d*<sub>2</sub> Peroxide and Related Compounds<sup>1</sup>

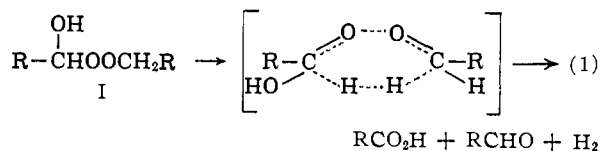
By LOIS J. DURHAM AND HARRY S. MOSHER

RECEIVED DECEMBER 18, 1961

A kinetic study has been made of the thermal decomposition reaction of 1-hydroxyisobutyl-1-*d* isobutyl-1,1-*d*<sub>2</sub> peroxide and related deuterium labeled compounds, which yield acid, aldehyde and isotopic hydrogen. A minimum isotope effect [ $k_H/k_D$ ] of between three and four was observed and has been interpreted as evidence for the proposed cyclic concerted mechanism. The introduction of deuterium into this peroxide has reduced the rate of the hydrogen evolution reaction to such an extent that competing side reactions now account for the major portion of the decomposition. For this reason strict quantitative interpretation of the results was not possible although approximate values for the enthalpy and entropy of activation have been reported for the reaction involving the evolution of deuterium from the trideuterated peroxide.

### Introduction

Previous research on the thermal decomposition of primary 1-hydroxyalkyl alkyl peroxides involving product analysis<sup>2</sup> and kinetic studies<sup>1</sup> gave



(1) Paper IX in this series, L. J. Durham and H. S. Mosher, *J. Am. Chem. Soc.*, **82**, 4537 (1960).

evidence which was interpreted in terms of a cyclic concerted mechanism (eq. 1) to explain the formation of acid, aldehyde and molecular hydrogen. The possibility of this reaction also being explained by a cage mechanism led to the present investigation. Presumably a radical cage-type mechanism would involve as a first step the homolytic cleavage of the O–O bond. Once formed, the radical fragments would be in a position to react either with each other or with solvent molecules within the solvent cage. From the principles of primary

(2) L. J. Durham, C. F. Wurster and H. S. Mosher, *J. Am. Chem. Soc.*, **80**, 332 (1958).