under 0.5 mm. This method was modified for the preparation of 1-methylthio-3-chloropropanol-2 in that the mixture was diluted with 150 ml. of dioxane. This was necessitated by the extensive decomposition that resulted when the unmodified procedure was used.

1-Ethylsulfonyl-3-chloropropanol-2 (II).—Five ml. of 30% perhydrol was added slowly to a mixture of 1.0 g. of 1-ethylthio-3-chloropropanol-2 in 10 ml. of glacial acetic acid. After the initial reaction had subsided, the solvent was removed at water-bath temperature, and the residue placed in a refrigerator for recrystallization. The yield of product, m. p. 47° was 1.0 g. or 83%.

1-Butylsulfonyl-2,3-epoxypropane (III).—A 1.0-g. sample of 1-butylsulfonyl-3-chloropropanol-2 was dissolved in 5 ml. of 50% ethanol and 2 g. of sodium hydroxide in 10 ml. of 50% ethanol was slowly added. After an hour, the solid which had formed was removed by filtration and crystallized from acetone. The yield of crystals m. p. 170° was 0.75 g. or 90% of theory (mol. wt. calcd., 176; found, 179 (Rast)). The lower members of this series were prepared similarly except that water, instead of 50% ethanol, was used as a solvent.

1-Ethylthio-2,3-epoxypropane (IV).—This compound was prepared by dehydrohalogenation of 1-ethylthio-3-chloropropanol-2 as well as by the action of potassium ethyl mercaptide on epichlorohydrin. Either procedure was a repetition of the directions of Nenitzescu and Scarlatescu[4] except that the potassium ethyl mercaptide was added to the epichlorohydrin, rather than the reverse.

1,3-Bis-(butylthio)-propanol-2 (V).—A mixture of 13 g. of 1-butylthio-2,3-epoxypropane and 10 g. of *n*-butyl mercaptan was heated to reflux, whereupon 0.2 g. of zinc chloride was added. Heating was continued until a sudden rise to 200° indicated that reaction had occurred. The product was washed with water, dried with Drierite, and distilled at 1 mm. The yield of product boiling at 133° was 11.5 g. or 55%, based upon 1-butylthio-2,3-epoxypropane.

1,3-Bis-(ethylsulfonyl)-propanol-2 (VI).—Ten ml. of 30% perhydrol was added slowly to a mixture of 2 g. of 1,3-bis-(ethylthio)-propanol-2 in 10 ml. of glacial acetic acid. After the initial reaction had subsided, the solvent was removed at water-bath temperature, and the residue crystallized from 95% ethanol. The yield was 1.9 g. of product melting at 113° (70%).

Hydrolysis of Bis-(alkylsulfonyl)-propanols.—About 0.25 g. of the bis-(alkylsulfonyl)-propanol was suspended in 25.00 ml. of 0.1038 *N* NaOH and refluxed for eight hours. The unreacted sodium hydroxide was then determined by titration with 0.1134 *N* hydrochloric acid. Based upon the following equation, the decomposition ranged from 0% (1,3-bis-(hexylsulfonyl)-propanol-2) to 16% (1,3-bis-(ethylsulfonyl)-propanol-2).

$$(RSO_2CH_2)_2CHOH + NaOH \longrightarrow RSO_2Na + CH_2OHCHOHCH_2SO_2R$$

Hydrolysis of 1-Ethylthio-2,3-epoxypropane and Periodic Acid Oxidation of the Glycol.—A 10-g. sample of 1-ethylthio-2,3-epoxypropane was refluxed with 50 ml. of 0.4 *N* sulfuric acid for three hours. The resulting solution was then treated with potassium periodate according to the directions of Hatch and Nesbitt.[12] The filtrate from this treatment gave the usual aldehyde tests and on treatment with methone, gave methylene bis-methone, m. p. 188–189°, in 60% yield.

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Summary

1. Mercaptans react with epichlorohydrin to produce secondary alcohols.

2. Data concerning the first six members of six homologous series are presented. With the following exceptions these are new to the literature: 1,3-bis-(ethylthio)-propanol-2, 1,3-bis-(ethylsulfonyl)-propanol-2, 1-ethylthio-3-chloropropanol-2, 1-propylthio-3-chloropropanol-2, 1-ethylthio-2,3-epoxypropane, and 1-ethylsulfonyl-3-chloropropanol-2.

[12] Hatch and Nesbitt, THIS JOURNAL, **67**, 39 (1945).

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Steric Hindrance: Some Reactions of Mesitylacetylene

BY MELVIN S. NEWMAN AND HARRY E. CONNOR[1]

The steric hindrance to addition reactions provided by two methyl groups ortho to an unsaturated function has been recognized for some time.[2] Kadesch[3] has contributed to the understanding of this phenomenon by making the hypotheses that (1) addition to a carbonyl function must occur by approach of the reagent more or less in a plane perpendicular to the plane defined by the carbonyl group and the two contiguous atoms; and (2) the carbonyl group in acetomesitylene, and similar hindered compounds, cannot be coplanar with the ring because of repulsive interaction between the hydrogens in the methyl group of the acetyl group and the ortho methyls. Thus the two ortho methyl groups prevent reaction by (A) restricting the free rotation of the acetyl group so that it can never be planar with the ring (thus allowing for an unhindered perpendicular approach of any reactants) at reasonable temperatures[4]; and (3) by hindering perpendicular approach of reagents to the non-planar acetyl group.

If these hypotheses are correct, it occurred to us that if a linear function were diortho substituted, addition reactions should occur until an angular function were formed and that this should then be resistant to further addition reactions. Accordingly we prepared mesitylacetylene[5,6] and

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[1] The material presented herein was taken from the M.S. thesis of Harry E. Connor, The Ohio State University, 1949.

[2] For a review see A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 318 ff.

[3] R. G. Kadesch, THIS JOURNAL, **66**, 1207 (1944).

[4] Acetomesitylene can react with hydroxylamine at higher temperatures, *e. g.*, E. Feith and S. H. Davies, *Ber.*, **24**, 3546 (1891), and communication from Dr. P. A. S. Smith, Univ. of Michigan.

[5] T. H. Vaughn and J. A. Nieuwland, THIS JOURNAL, **56**, 1207 (1934).

[6] R. C. Fuson and J. S. Meek, *J. Org. Chem.*, **10**, 551 (1945).

compared its reactivity to that of phenylacetylene.

Under similar conditions mesitylacetylene adds only one molecule of bromine to form 1,2-dibromo-1-mesitylethylene whereas phenylacetylene adds two molecules of bromine to form the expected tetrabromide. Attempts to add more bromine to the above dibromide resulted only in nuclear bromination. Similarly, mesitylacetylene did not add two molecules of methanol to yield the expected acetal of acetomesitylene under conditions where phenylacetylene readily did so. Evidence for the addition of one molecule of methanol to form the enol ether of acetomesitylene was obtained, although this compound was not isolated in a pure state. It was possible to hydrate mesitylacetylene to acetomesitylene. However, it is necessary to add only one molecule of water to the triple bond to effect this transformation. Thus, we have obtained evidence which provides support for Kadesch's theoretical considerations[3] and extends them to functions other than the carbonyl group.

Experimental

Mesitylacetylene.—1-Chloro-1-mesitylethylene, b. p. 99–105° at 1 mm., prepared in 65% yield from acetomesitylene, was converted in 76% yield into mesitylacetylene, b. p. 63–68° at 2 mm., $n^{25}\text{D}$ 1.5422, in agreement with the recent literature.[5,7] The known mercury derivative,[8] m. p. 238–240° uncor., was obtained.

Reactions of Mesitylacetylene and Phenylacetylene.—To an ice-cold solution of 10 g. of mesitylacetylene in 15 cc. of chloroform was added slowly a solution of pure bromine in chloroform until the bromine color persisted. The chloroform was then removed and the residue distilled and redistilled to yield 2 g. (44%) of 1,2-dibromo-1-mesitylethylene, b. p. 132–134° at 4–5 mm. Attempts to add bromine to this product were unsuccessful. At higher temperatures bromine was taken up but copious evolution of hydrogen bromide occurred.

Anal. Calcd. for $C_{11}H_{12}Br_2$: C, 43.5; H, 4.0; Br, 52.6. Found[9]: C, 44.8; H, 3.9; Br, 51.8.

In a comparable experiment phenylacetylene[10] was converted into 1,1,2,2-tetrabromophenylethane, m. p. 74–74.5°, in 92% yield. This compound had been described as a liquid.[11] For analysis the compound was recrystallized from alcohol.

Anal. Calcd. for $C_8H_6Br_4$: C, 22.8; H, 1.4; Br, 75.8. Found[9]: C, 22.8; H, 1.7; Br, 75.7.

Under anhydrous conditions a solution of 7.2 g. of mesitylacetylene, 5.2 cc. of absolute methanol, 0.5 g. of red mercuric oxide, and 0.2 cc. of boron trifluoride etherate was allowed to stand at room temperature for two days.[12] After suitable procedure 5 g. of a colorless liquid, b. p. 75–77° at 2 mm. was obtained. This compound was not pure, but its infrared spectrum indicated the presence of the ether linkage and carbon–carbon unsaturation. The low methoxyl value obtained on analysis (8.5%[9] as compared with a theoretical value of 17.6% for the methyl enol ether of acetomesitylene) makes it unlikely that any acetal was present. An attempt to add methanol in the presence of sodium methylate was unsuccessful, starting material being recovered (81%). Under similar conditions, phenylacetylene yielded 67% of acetophenone dimethylacetal,[13] b. p. 74–76° at 8 mm.

The hydration of mesitylacetylene to acetomesitylene was accomplished in 54% yield essentially according to the hydration method used for benzylphenylacetylene.[14] The acetomesitylene was characterized as its dinitro derivative, m. p. 137–139°, mixed m. p. with authentic sample[15] not depressed.

Summary

Mesitylacetylene adds one molecule of bromine. The dibromide thus formed does not add bromine. The theoretical implications of these findings are discussed.

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[7] R. C. Fuson and J. S. Meek, *J. Org. Chem.*, **10**, 551 (1945).

[8] T. H. Vaughn, THIS JOURNAL, **55**, 3453 (1933).

[9] Microanalysis by H. S. Clark Analytical Laboratory, Evanston, Ill.

[10] Prepared according to J. C. Hessler, *Org. Syn.* Coll. Vol. I, p. 438 (1943).

[11] L. P. Kinnicutt and G. M. Palmer, *Am. Chem. J.*, **5**, 387 (1883).

[12] Compare G. F. Hennion, D. B. Killian, T. H. Vaughn and J. A. Nieuwland, THIS JOURNAL, **56**, 1130 (1934).

[13] M. T. Bogert and P. P. Herrera, *ibid.*, **45**, 243 (1923).

[14] J. R. Johnson, T. L. Jacobs and A. M. Schwartz, *ibid.*, **60**, 1885 (1938).

[15] R. C. Fuson and J. T. Walker, *ibid.*, **52**, 3273 (1930).

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[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

Kinetics of the Iodination of Aniline

BY ERNST BERLINER

From a study of the kinetics of the iodination of phenol in water Painter and Soper concluded that the reaction takes place either between phenol and hypoiodous acid, or between the phenoxide ion and the positive iodine ion (I^+).[1] Since the aromatic rings of both phenol and the phenoxide ion are very reactive toward electrophilic reagents, a distinction between these two reaction schemes could not be made on chemical grounds, but the authors preferred the latter of the two possibilities. If the iodination of aniline is similar to the iodination of phenol, a more clear-cut distinction between the positive iodine ion and hypoiodous acid as the iodinating species might be possible, because the two aromatic compounds, aniline and the anilinium ion, behave very differently in electrophilic aromatic substitution reactions. Wistar and Bartlett have on the same basis shown that the diazo coupling reaction of aromatic amines takes place between free aniline and the diazonium cation, whereas the kinetic data for the diazo coupling of phenols did not make such

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[1] Painter and Soper, *J. Chem. Soc.*, 342 (1947); Soper and Smith, *ibid.*, 2757 (1927).