Oxidation of Aryl Trityl Sulfides with Hydrogen Peroxide

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Received April 28, 1953

Recent attempts to characterize aryl trityl sulfides by preparation of sulfoxides and sulfones by means of oxidations in acidic media have been unsuccessful.[1,2] Apparently the sulfides were cleaved in the acidic media because partial oxidations produced significant amounts of the diaryl disulfides and triphenylcarbinol. Complete oxidations produced the arylsulfonic acids, or derivatives of these, and triphenylcarbinol.

Knoll[3] observed no reaction during an unsuccessful attempt to prepare phenyl trityl sulfone by oxidation of phenyl trityl sulfide with hydrogen peroxide in glacial acetic acid at room temperature for 12 hours.

During the present work, phenyl trityl sulfide (I) in glacial acetic acid was kept at 21–22° for 12 hours with the same mole ratio of hydrogen peroxide as was used by Knoll. There was isolated a 44% yield of benzophenone (II), and small amounts of phenol (III), diphenyl disulfide and trityl peroxide. The rate of oxidation of I was markedly increased by the addition of an equimolar quantity of sulfuric acid, and after ten minutes at 26–28° a 65% yield of II was obtained.

o-Tolyl trityl sulfide in acetone was oxidized very slightly, if at all, by an excess of hydrogen peroxide during six hours at room temperature. In the presence of mercuric chloride and much less peroxide, a 41% yield of II was obtained in ten minutes.

By using four moles of hydrogen peroxide per mole of I in acetic acid at an initial temperature of 80°, oxidation was complete within ten minutes. Good yields of II, III and benzenesulfonic acid (as its sodium salt) were obtained. At an initial temperature of 60° and the same reaction period, an 81% yield of II was obtained, and at 40°, not over 50% of I had reacted.

The experimental evidence appeared to indicate that the main reactions during the oxidation of an aryl trityl sulfide by hydrogen peroxide in acidic media were, (a) the oxidation of either free or incipient aryl thiol through the disulfide stage to arylsulfonic acid, and (b) the oxidation of either free or incipient trityl cation to II and III.

Acknowledgment.—This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation, New York, N. Y.

Experimental[4]

Preparation of Aryl Trityl Sulfides.—The sulfides were prepared by using the procedures previously reported.[5]

Oxidation of I at Room Temperature.—To 200 ml. of glacial acetic acid were added 4.2 g. (0.012 mole) of I and 0.024 mole of hydrogen peroxide, as Superoxol. The reaction mixture was kept at 21–22° for 12 hours and then poured into water. This mixture was extracted with ether, and the ethereal solution then extracted with 20% sodium hydroxide. A small amount of III was obtained from the alkaline extract. From the ethereal solution was obtained 0.15 g. (5%) of trityl peroxide, a 44% yield of II (1.9 g. of its 2,4-dinitrophenylhydrazone), and 0.1 g. (8%) of diphenyl disulfide.

Oxidation of I in Presence of Sulfuric Acid.—To 200 ml. of glacial acetic acid were added 9.6 g. (0.027 mole) of I and 1.52 ml. (0.027 mole) of concentrated sulfuric acid. To this solution was added 0.054 mole of hydrogen peroxide. By cooling, the solution was kept at 26–28° for ten minutes. The yields were: II (65%, 6.4 g. of the 2,4-dinitrophenylhydrazone); III, 0.9 g. (35%); 0.3 g. (4.5%) of trityl peroxide; and 0.6 g. (30%) of diphenyl disulfide.

Oxidation of *o*-Tolyl Trityl Sulfide in Presence of Mercuric Chloride.—To 100 ml. of acetone at 28° were added 5.15 g. (0.014 mole) of *o*-tolyl trityl sulfide and 0.028 mole of hydrogen peroxide. A solution containing 4.5 g. (0.016 mole) of mercuric chloride in 35 ml. of acetone was added dropwise for 12 minutes. After two minutes the mixture was cooled, and 0.8 g. of *o*-tolylmercaptomercuric chloride was obtained by filtration. After evaporation of the filtrate, the residue was found to contain 0.3 g. of the mercaptomercuric chloride, 14% of III, 41% of II and 10% of *o*-tolyl disulfide.

Oxidation of Sulfides at 80°.—To 120 ml. of glacial acetic acid was added 9.6 g. (0.027 mole) of I. The solution was heated to 80°, and 0.108 mole of hydrogen peroxide added dropwise within three minutes. The reaction was strongly exothermic, and after a total of ten minutes the solution was poured into 300 ml. of cold water. The aqueous suspension was extracted with ether, and 1.3 g. (50%) of III was obtained from the ethereal solution by alkaline extraction. From the ethereal solution was obtained 4.5 g. (91%) of II. The aqueous acetic acid was evaporated to dryness, and after addition of sodium hydroxide 3.3 g. (62%) of sodium benzenesulfonate was obtained. By using identical conditions, 10 g. of *p*-tolyl trityl sulfide was oxidized. The yields were: II, 4.5 g. (91%); III, 1.7 g. (68%); sodium *p*-toluenesulfonate, 2.6 g. (45%). A similar oxidation of *o*-tolyl trityl sulfide produced II (79%) and III (45%). An oxidation of *m*-tolyl trityl sulfide produced II (80%) and III (50%).

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(1) D. C. Gregg and C. A. Blood, Jr., *J. Org. Chem.*, **16**, 1255 (1951).

(2) D. C. Gregg, K. Hazleton and T. F. McKeon, Jr., *ibid.*, **18**, 36 (1953).

(3) R. Knoll, *J. prakt. Chem.*, **113**, 40 (1926).

(4) The Superoxol was Merck's 30% hydrogen peroxide. The identity of each oxidation product and each derivative was established, where possible, by mixed melting points with an authentic sample. The sodium arylsulfonates were characterized by preparing the corresponding arylsulfonamides and S-benzylthiuronium salts. All yields are based on complete cleavage of the sulfides. Temperatures are uncorrected.

(5) D. C. Gregg, H. A. Iddles and P. W. Stearns, Jr., *J. Org. Chem.*, **16**, 246 (1951).

Existence of Two Solid Forms of 2-Methylfuran

By James B. Hickman

Received April 1, 1953

In the course of continuation of earlier work[1] on the f.p.–composition behavior of the system, 2-methylfuran–methanol, it was found that 2-methylfuran upon cooling gives two distinct halts in the time–temperature curve, presumably corresponding to two different solid modifications. The higher-melting solid (I), f.p. −90.19°, obtained by rapid cooling, is evidently the one concerned in the f.p. data previously reported.[1,2] The lower-melting solid (II), f.p. −101.92°, can be obtained by slower cooling, ordinarily resulting in inception of freezing from a less highly supercooled liquid. (The f.p. values stated represent results reproduced three or more times within ±0.01°; however, if the shortness of equilibrium time, and the extent of extrapolation of the equilibrium curve involved are

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(1) J. B. Hickman and J. L. Hall, *Proc. W. Va. Acad. Sci.*, **22**, 72 (1950).

(2) E. I. du Pont de Nemours Corp., "New Products Bulletin," No. 24, May 4, 1948.