Summary

1. A study of the reaction of sulfur on various halogenated derivatives of diphenyl sulfide was made. It was found that the reactions were quite different from those involving unsubstituted aryl sulfides. The products were halogenated benzenes and complex sulfides and polysulfides.

2. It was found that a halogen substituted aryl sulfoxide or a halogen substituted aryl ether gave products similar to those in 1 due to a preliminary reduction to the sulfides.

3. A mechanism has been proposed to account for the course of the reaction.

4. Experiments, using halogen substitution products of diphenylamine and diphenylmethane, showed that these compounds, when acted upon by sulfur, do not yield halogenated benzenes.

PRINCETON, N. J. RECEIVED OCTOBER 28, 1938

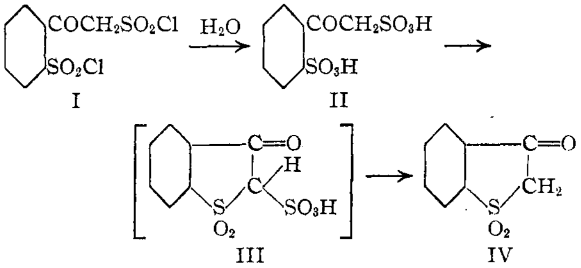
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

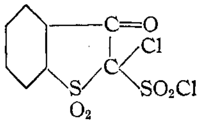
The Reaction of Chlorosulfonic Acid with Acetophenone. New Synthesis of a Cyclic Ketosulfone

BY ARTHUR W. WESTON AND C. M. SUTER

It was reported by Riesz and Frankfurter[1] that the action of chlorosulfonic acid upon acetophenone yields a disulfonyl chloride. Since the dithiol obtained by reduction of this, unlike o-thiolacetophenone,[2] did not oxidize in alkaline solution to a thioindigo dye, they concluded that the sulfonyl groups must occupy the 3,4- or 3,5-positions. Further, sulfonation of acetophenone-4-sulfonic acid gave a disulfonyl chloride differing from the compound obtained directly from acetophenone and still not containing an ortho sulfonyl group. The product from acetophenone was therefore assigned the 3,5-structure.

It has now been found that this assignment is in error. The disulfonyl chloride does not give the haloform reaction. When it is hydrolyzed and the resulting potassium sulfonate fused with alkali the sole product identified is salicylic acid. Titration of the solution obtained by hydrolysis of the disulfonyl chloride with boiling water requires four equivalents of alkali. When the hydrolysis solution is evaporated to dryness without neutralization, sulfuric acid and a crystalline solid only slightly soluble in water are produced. This solid when hydrolyzed with strong alkali gives *o*-methanesulfonylbenzoic acid[3] and therefore must be 3(2)-thianaphthenone-1-dioxide[3,4] (IV), a conclusion confirmed by its physical properties. The reactions are indicated by the accompanying equations.





V

That the disulfonyl chloride did not correspond to structure V was shown by its lack of oxidizing action toward aqueous potassium iodide. Although there seems to be no exactly parallel case known, the loss of sulfuric acid from the intermediate III is accounted for by the accumulation of activating groups.

The question arises as to the mechanism by which I is formed. Feist[5] has assumed that in the preparation of 2-carbethoxy-3(2)-thionaphthenone-1-dioxide by the action of fuming sulfuric acid upon ethyl benzoylacetate the first step is ortho sulfonation followed by ring closure. Krekeler[6] has shown that acetophenone may be monosulfonated by pyrosulfuric acid but the position assumed by the substituent was not determined. Repetition of Krekeler's experiment and fusion of the resulting barium sulfonates with potassium hydroxide gave a mixture in which

---

(1) Riesz and Frankfurter, *Monatsh.*, **50**, 68 (1928).

(2) Farbw. vorm. Meister Lucius and Brüning, German Patent 198,509, *Chem. Zentr.*, **79**, I, 2118 (1908).

(3) Arndt, Kirsch and Nachtwey, *Ber.*, **59B**, 1079 (1929).

(4) Lanfry, *Compt. rend.*, **155**, 1518 (1912).

(5) Feist, *Ber.*, **58B**, 2311 (1925).

(6) Krekeler, *ibid.*, **19**, 678, 2626 (1886).

salicylic and *m*-hydroxybenzoic acids were identified. Assuming that chlorosulfonic acid might first affect the side chain of acetophenone, it was of interest to determine the action of this reagent upon acetophenone-ω-sulfonic acid. Actually a 15% yield of the disulfonyl chloride I was obtained so that ortho sulfonation may occur either before or after the introduction of the sulfo substituent in the side chain.

It was considered not impossible that the ketosulfone (IV) might be an intermediate in the formation of I, as it might arise from ring closure of acetophenone-ω-sulfonic acid or the acid chloride. However, the action of chlorosulfonic acid upon the ketosulfone gave no detectable amount of the disulfonyl chloride (I).

Experimental

Sulfonation of Acetophenone.—The procedure of Riesz and Frankfurter[1] was modified as follows. To 900 g. (7.8 moles) of chlorosulfonic acid cooled in ice was added with mechanical stirring during two hours 90 g. (0.75 mole) of acetophenone dissolved in 90 g. of carbon tetrachloride. The mixture was allowed to come to room temperature and finally was heated at 110° for forty-five minutes. The cooled reaction mixture was poured on four liters of crushed ice and the precipitate filtered off and washed with petroleum ether and then with ether. The yield was 44 g. or 20% of the theoretical amount. Contrary to the report of Riesz and Frankfurter, the product was not appreciably soluble in ether. Crystals obtained from decalin melted at 194–195°, in agreement with the value reported earlier (195–196°). It did not give the haloform reaction and no derivative was obtained with dinitrophenylhydrazine. The analysis agreed with the empirical formula suggested previously.[1] *Anal.* Calcd. for $C_8H_6O_5S_2Cl_2$: Cl, 22.36. Found: Cl, 22.42. Hydrolysis of a sample with water and titration of the solution with standard alkali showed the formation of four acid hydrogens per mole corresponding to a disulfonyl chloride. *Anal.* Calcd. for 0.1249 g. of $C_8H_6O_5S_2Cl_2$: 42.08 ml. of 0.03744 *N* NaOH. Found: 42.99 ml. of NaOH.

Structure of the Disulfonyl Chloride. A. Fusion with Alkali.—A sample of the acid chloride was hydrolyzed by boiling with water, the solution was neutralized with sodium hydroxide and evaporated to dryness. Two grams of the dry salt was fused with 5 g. of potassium hydroxide for one hour at 250–300°. The melt was dissolved in water, acidified with hydrochloric acid and the solution extracted with ether. From the ether was obtained a solid which gave the ferric chloride test, the oil of wintergreen test and the nitro derivative characteristic of salicylic acid.

B. Conversion to 3(2)-Thianaphthenone-1-dioxide.—When 0.5 g. of the acid chloride was hydrolyzed by boiling with 10 ml. of distilled water the solution gave no test for sulfate ion. Upon concentration to 2 ml. the test was still negative. Further heating until hydrogen chloride was evolved was accompanied by the separation of a white solid which increased in amount when water was added; the aqueous solution now gave a test for sulfate ion. When the hydrolysis and evaporation were carried out with 8.5 g. of the acid chloride the yield of dioxide was 3.9 g. or 81% of the theoretical amount of material melting at 133.5–134°. The melting point of 3(2)-thianaphthenone-1-dioxide has been reported as 136[3] and 139°.[4] It was soluble in sodium bicarbonate,[4] did not add bromine, decolorized potassium permanganate in sodium carbonate solution and gave no evidence of reaction with benzaldehyde in alkaline solution. The absence of a color with ferric chloride in alcohol and the lack of reaction with acetyl chloride or phenyl isocyanate showed the absence of a hydroxyl group. With 2,4-dinitrophenylhydrazine a derivative with m. p. 298–299° was obtained. Identification was made by hydrolysis with 20% sodium hydroxide by boiling for two hours[3] which gave a 90% yield of *o*-methanesulfonylbenzoic acid which after drying to remove water of hydration and crystallizing from toluene melted at 137–138.5°. The reported m. p. is 138–140°. *Anal.* Calcd. for $C_8H_8O_4S$: neut. equiv., 200.1. Found: neut. equiv., 200.8. As a further check the acid was converted into its methyl ester, m. p. 60°, a value slightly lower than that previously reported.[3]

Sulfonation of Acetophenone.—From 30 g. (0.25 mole) of acetophenone treated with 45% oleum according to Krekeler[6] was obtained 42 g. (63%) of a mixture of barium sulfonates. An attempt to isolate the sulfonation product by adding the reaction mixture to sodium chloride solution gave no precipitate. Extraction of the dry sodium salts from the sulfonation reaction by liquid ammonia[7] or absolute alcohol did not serve to separate the sulfonates from inorganic material.

To 15 g. of fused potassium hydroxide in a nickel crucible was added gradually 5 g. of the barium sulfonates mixture. The temperature of the fusion mixture was slowly raised to 300° and maintained there for forty-five minutes. The melt was treated with water, the mixture filtered and acidified, and extracted with ether. This gave 1.2 g. (46%) of mixed hydroxybenzoic acids. An aqueous solution of a portion of this mixture gave a purplish-red color with ferric chloride. A positive "oil of wintergreen" test also was obtained. The presence of the *m*-hydroxybenzoic acid was indicated by the formation of an orange-red solution upon boiling a portion of the solid with concentrated sulfuric acid. Three crystallizations of 0.5 g. of the mixture from water gave nearly pure *m*-hydroxybenzoic acid, m. p. 197°, showing no depression with a known sample. At least 60% of the mixture consisted of the meta acid. No *p*-hydroxy acid was noted.

Sulfonation of Sodium Acetophenone-ω-sulfonate.—The sulfonate was prepared from phenacyl bromide and sodium sulfite essentially according to the method of Parkes and Tinsley.[8] Five grams of the dry sodium sulfonate was added in small portions to 50 g. of chlorosulfonic acid with stirring and the mixture heated at 110° for one hour. After cooling and pouring on ice and triturating the precipitate with ether 1.0 g. of brownish solid was obtained which upon crystallization twice from decalin melted at 190° and gave no depression with the disulfonyl

---

(7) Billman and Audrieth, THIS JOURNAL, **60**, 1945 (1938).

(8) Parkes and Tinsley, *J. Chem. Soc.*, 1861 (1934).

chloride obtained from acetophenone. The dianilide was prepared and its m. p. and mixed m. p. were identical with those of the acetophenonedisulfonyl chloride (209–210°).

Summary

1. The action of chlorosulfonic acid upon acetophenone yields the 2,ω-disulfonyl chloride.
2. Sulfonation of acetophenone with 45% oleum yields a mixture of the ortho and meta sulfonic acids.
3. By evaporating its aqueous solution to dryness, acetophenone-2,ω-disulfonic acid is converted into the cyclic ketosulfone, 3(2)-thianaphthenone-1-dioxide.

EVANSTON, ILLINOIS RECEIVED NOVEMBER 3, 1938

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Thermal Hydrogen–Chlorine Reaction.[1] I. Experimental Kinetics

BY J. C. MORRIS[2] AND R. N. PEASE

The thermal reaction between hydrogen and chlorine has received a surprisingly small amount of attention, considering the fundamental theoretical importance of this combination. Older results of Sirk,[3] Melander,[4] and Sachtleben[5] are of little value, except in a qualitative way. The more recent results of Christiansen[6] and of Kornfeld and Khodschaian[7] have been obtained almost entirely for mixtures containing oxygen. Initial concentrations in these two cases were not varied sufficiently to specify a kinetic equation for the pure gases, and an extrapolation to zero oxygen of the equations found for oxygen-containing mixtures yields quite different expressions. Only in the work of Pease[8] were the starting compositions widely varied, but in this instance the results were only approximate. A thorough investigation of the kinetics of this reaction in order to clear up the discrepancies and to establish the mechanism of the process in the pure gaseous mixture seemed indicated, and was the object of the present research.

Experimental Details.—Experiments were carried out in a static system, the Pyrex reaction vessel being about 3.5 cm. in diameter and 22 cm. long, giving a volume of about 200 cc. Since the qualitative results of Pease[8] had shown that the reaction started and ended on the walls of the reaction bulb, it was expected that different types or treatment of surface would influence the rate, and therefore particular attention was paid to the construction of the bulbs used. Five different ones were employed, four of clean Pyrex, and the other of Pyrex coated with potassium chloride. The Pyrex bulbs were cleaned by boiling them in concentrated hydrochloric acid solution for several days, rinsing with distilled water, and were dried by evacuation at 200°. The potassium chloride-coated bulb was prepared by soaking in a concentrated solution of potassium chloride for some days, draining thoroughly, and drying. The deposited potassium chloride was then fused on the surface to ensure a continuous layer. All the bulbs were wrapped in metal foil to exclude light, and all leads were painted with black enamel.

The hydrogen used was prepared by electrolysis of 30% potassium hydroxide on nickel electrodes, purified by passage over heated platinized asbestos, and dried with either calcium chloride or liquid air. It was made fresh for each run and stored in a measuring buret. The chlorine was taken from a tank and led directly into a 1-liter storage bulb. For some experiments this was simply a reservoir from which a desired pressure of chlorine could be obtained in the reaction chamber. In others the chlorine was condensed in this bulb and further purification was attempted by distilling off about a quarter of this at −80°. No difference in the rate of reaction could be traced to this source.

The problem of stopcock grease was a serious one, but it was found that if the stopcocks were protected from light, Apiezon was attacked very slowly and so was satisfactory. None of the peculiar results found could be attributed to the effect of the stopcock grease.

The procedure for making a run was the following. After flushing and evacuating thoroughly, a measured volume of hydrogen was introduced into the reaction bulb from the measuring buret to the desired pressure as given by a quartz spiral manometer, which was used as a null point instrument. Then chlorine was admitted rapidly from the storage vessel up to the desired total pressure, which was again recorded by means of the manometer. After the reaction had proceeded the desired length of time, the gas mixture was admitted successively to two liquid air traps and then to a large Toepler pump. These traps condensed the chlorine and the hydrogen chloride completely as shown by tests. The unreacted and uncondensed hydrogen was pumped by the Toepler back into the measuring buret, where its volume was again meas-

---

(1) Submitted in partial fulfillment of the degree of Doctor of Philosophy.

(2) Present address: Mallinckrodt Laboratory, Harvard University, Cambridge, Mass.

(3) Sirk, *Z. physik. Chem.*, **61**, 545 (1908).

(4) Melander, *Arkiv Kemi, Mineralogi, Geologi*, **5**, no. 12 (1913–1915).

(5) Sachtleben, Dissertation, Hanover, 1914; see Christiansen, ref. 6.

(6) Christiansen, *Z. physik. Chem.*, **B2**, 405 (1929).

(7) Kornfeld and Khodschaian, *ibid.*, **B35**, 403 (1937).

(8) Pease, THIS JOURNAL, **56**, 2368 (1934).