[Contribution from the Chemical Laboratory of The Johns Hopkins University]

THE DIRECT INTRODUCTION OF SULFUR INTO AROMATIC HYDROCARBONS[1]

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Sulfur, in the presence of aluminum chloride, reacts with benzene to give thiophenol, diphenyl sulfide and diphenylene disulfide.[3] The same products are obtained by the dry distillation of the sodium salt of benzenesulfonic acid.[4] Since sulfur may be introduced into benzene by the use of a catalyst at low temperatures it was thought that at elevated temperatures this could be accomplished without the aid of a catalyst. Accordingly, the action of sulfur on benzene and ethylbenzene was investigated.

Results and Discussion.—Benzene and sulfur when heated together at 350° for twenty-four hours gave thiophenol, diphenyl sulfide, diphenyl disulfide, diphenylene disulfide (thianthrene) and hydrogen sulfide. It has been shown that diphenyl disulfide is obtained by heating thiophenol with sulfur,[5] and that this is decomposed on further heating to give diphenyl sulfide and free sulfur.[6] Diphenylene disulfide is formed by heating diphenyl sulfide with sulfur.[7] From the fact that thiophenol is obtained from sulfur and benzene, with the aid of a catalyst, it is probable that this is the first product formed at high temperatures without the aid of a catalyst. The formation of all other products isolated can be accounted for by the action of heat and sulfur on this one product.

The action of sulfur on ethylbenzene is quite different from that on benzene and much more rapid. When oxygen is passed into ethylbenzene, acetophenone is formed.[8] By analogy the action of sulfur should be such as to give thioacetophenone and hydrogen sulfide; no thio-ketone, however, was detected in the reaction mixture. Instead there was isolated a good quantity of 2,4-diphenylthiophene, this being the only sulfur-containing product, other than hydrogen sulfide. Baumann and Fromm[9] have shown that thioacetophenone polymerizes readily to give tri-thioacetophenone and that this is both depolymerized and decomposed on heating, anhydro-trithioacetophenone and 2,4-diphenylthiophene being

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[3] Friedel and Crafts, *Ann. chim. phys.*, [6] **14**, 438 (1888).

[4] Stenhouse, *Ann.*, **149**, 252 (1869).

[5] Holmberg, *ibid.*, **359**, 83 (1908).

[6] Graebe, *ibid.*, **174**, 189 (1874).

[7] Krafft and Vorster, *Ber.*, **26**, 2813 (1893).

[8] Stephens. This Journal, **48**, 2920 (1926).

[9] Baumann and Fromm, *Ber.*, **28**, 890, 895, 907 (1895).

formed. Further, they have shown that anhydro-trithioacetophenone decomposed on heating to give styrene and 2,4-diphenylthiophene, and that styrene may react in either of two ways to give ethylbenzene or 2,4-diphenylthiophene. Diphenylthiophene, being a comparatively stable compound, when once formed does not undergo further change, while the other above-mentioned compounds readily decompose on heating. It is for this reason that the only sulfur-containing compound obtained from the reaction was diphenylthiophene, the analogy, however, of sulfuration to oxidation being supported.

Experimental

Benzene and sulfur were heated in a steel bomb, of 100-cc. capacity, at 350° for twenty-four hours.[10] Upon opening the bomb much hydrogen sulfide escaped and within the bomb there was a brown oil having the odor of thiophenol. On distillation of this oil there was obtained a small fraction boiling between 76 and 90° and a smaller fraction boiling between 140 and 175°. These two fractions were redistilled several times, thus obtaining unchanged benzene and thiophenol. The latter was identified by its lead mercaptide (calcd., Pb, 48.7; found, Pb, 48.8). That portion of the reaction product boiling above 175° was distilled at a pressure of 5 mm., a mixture of an oil and a solid coming over between 120 and 210° which gave no clear-cut fractions. The residue was a hard, black, glass-like tar. Most of the distillate went into solution on treatment with cold, absolute alcohol but there remained a white solid, difficultly soluble in hot alcohol, which after several recrystallizations gave a melting point of 156.5°. With hot concentrated sulfuric acid this solid gave an intense purple coloration and was identified as diphenylene disulfide (thianthrene) by a mixed melting point with a known sample.

The alcoholic solution from above was concentrated by boiling and cooled to $-10°$, a white solid separating out which was filtered while still cold. This solid, after recrystallization several times from alcohol, melted at 60°, and on treatment with dilute hydrochloric acid and zinc dust gave at once the odor of thiophenol; sulfur analysis gave 29.5% of sulfur (calcd. sulfur for diphenyl disulfide, 29.4%). It was thus identified as diphenyl disulfide. Vacuum fractionation of the residue from the above alcoholic solution gave an orange-colored liquid having a boiling-point range of 180–185° at 5 mm. This substance was identified as diphenyl sulfide by oxidation to the sulfone, melting point 127.5–128°.

The bomb leaked to some extent as shown by the fact that a piece of paper soaked in lead acetate solution placed above it during heating turned very black. From 50 g. of sulfur and 39 g. of benzene there were obtained: 6.3 g. of hydrogen sulfide (absorbed in lead acetate solution and weighed as the sulfide); 8.6 g. of unchanged benzene; 1.8 g. of thiophenol; 27.8 g. of a mixture of diphenyl sulfide, diphenyl disulfide and diphenylene disulfide; 22.1 g. of tar; a total of 66.6 g. The loss was 22.4 g.

The sulfide and disulfide seem to be formed in about equal quantities (molal) while the amounts of thiophenol and diphenylene disulfide are about equal and are about half as great as those of the sulfide and disulfide.

It was thought possible that the iron of the bomb was acting as a catalyst for the reaction. A mixture of benzene and sulfur, in the same proportions as used in the bomb, was sealed in a glass tube and this placed in the bomb, surrounding it with ben-

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[10] For a description of the bomb and method of temperature control, see the paper by Herndon and Reid, THIS JOURNAL, **50**, 3066 (1928).

zene to equalize the pressure. The identical reaction took place in the glass that had taken place in the steel.

Sulfur and Ethylbenzene.—For this reaction a much larger bomb, of a capacity of 800 cc., was employed than that used for benzene. Ethylbenzene (4.1 moles) and sulfur (6.2 moles) were placed in the bomb and heated at 340–350° for forty minutes, at which time a small leak in the bomb head developed and heating had to be stopped. When the bomb had cooled down to room temperature there remained a pressure of 1200 lb. per sq. in. in it. The bleeder valve was opened and 78 g. of hydrogen sulfide was removed. The leak was repaired and the bomb again heated at 340–350°, this time for four hours, at the end of which time a serious leak developed in the brass bleeder valve and heating had to be stopped. Hydrogen sulfide at high pressures seems to attack the brass threads of the valve very rapidly. This second leak caused a large loss in material.

There was removed from the bomb 378 g. of liquid containing a small amount of solid. The solid was filtered off and the liquid distilled, about 5 cc. coming over between 30 and 40°, at which point the temperature of the distilling vapors jumped rapidly to 130°. There was obtained 126 g. of liquid boiling between 130 and 145°, at which point the vapors became slightly yellow and the distillation was stopped. This liquid consisted chiefly of ethylbenzene, but contained a small amount of styrene in as much as it decolorized a small amount of bromine very rapidly. The residue in the distilling flask, along with the solid filtered from the original reaction mixture, was extracted with hot alcohol; this solution on cooling deposited 86.5 g. of a light yellow crystalline substance, which on recrystallization gave a melting point of 119.5–120.5°. On analysis it was found to contain 13.4% of sulfur; with concentrated sulfuric acid and isatin it gave an intense green-blue coloration. It was thus identified as 2,4-diphenylthiophene (calcd. sulfur, 13.56%).

Summary

Benzene reacts with sulfur at 350° to give thiophenol, diphenyl sulfide, diphenyl disulfide, diphenylene disulfide and hydrogen sulfide. In the case of ethylbenzene the side chain is the point of attack and 2,4-diphenylthiophene is the final product.

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