Summary

When pure n-heptane is refluxed with aluminum chloride, low-boiling fractions can be isolated for which the boiling points, refractive indices and C. T. S. in aniline indicate the presence of three hexanes, together with at least three, and probably five, of the eight branched-chain heptanes. The total amount of these hydrocarbons formed is about 6 and 5%, respectively, of the reacted n-heptane.

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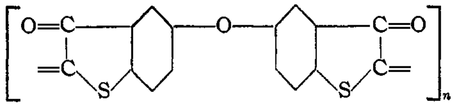
[Contribution from the Chemical Laboratory of Northwestern University]

Studies in the Phenyl Ether Series. IV. Phenoxybenzene-4,4'-dithiol and Related Compounds

By C. M. Suter and Paul H. Scrutchfield

It was found some time ago[1] that the action of chlorosulfonic acid upon phenyl ether in the cold produced the 4,4'-disulfonyl chloride. It was believed to be of interest to prepare from this, through the intermediate dithiol and dithioglycolic acid, the polymeric thioindigo dye having the formula indicated.



Although attempts to obtain this were not successful it seems desirable to report the preparation and properties of the intermediates.

Reduction of the disulfonyl chloride to the dithiol was found to be more difficult than had been anticipated, zinc and sulfuric acid or aluminum amalgam in alcohol and ether[2] yielding chiefly polymeric products. However, the use of stannous chloride and hydrogen chloride in glacial acetic acid, a method previously employed by Bogert and Bartlett[3] to reduce a nitronaphthalenesulfonyl chloride, gave good yields of the dithiol. At the same time a trace of hydrogen sulfide was formed as indicated by the stannic sulfide present in the reaction product.

The action of chlorosulfonic acid or fuming sulfuric acid of various concentrations upon the dithioglycolic acid either gave no ring closure or yielded water-soluble products evidently containing sulfonic acid groups. These latter were not investigated. Attempts to convert the acid chloride of the dithioglycolic acid into the cyclic compound by treatment with aluminum chloride were also unsuccessful. It seemed likely that ring closure would be facilitated by the presence of a bromine para to the hydrogen through which this must occur but preliminary experiments upon the bromination of the dithioglycolic acid were not successful.

Experimental

Phenoxybenzene-4,4'-dithiol.—Hydrogen chloride was passed into a suspension of 80 g. (0.36 mole) of stannous chloride in 300 cc. of glacial acetic acid until the mixture became homogeneous. To this was added 11 g. (0.03 mole) of phenoxybenzene-4,4'-disulfonyl chloride and the mixture shaken for fifteen minutes. Reduction occurred readily with the evolution of heat. After filtering, the reaction mixture was poured into 300 cc. of concentrated hydrochloric acid to decompose the stannic salt of the dithiol. After recrystallizing from petroleum ether there was obtained 5 g. or 71% of the theoretical amount of product melting at 103–104°. The crude material was slightly yellow due to the stannic sulfide present. This was readily removed by boiling with concentrated hydrochloric acid, leaving a colorless product.

Although the purity of the dithiol was evident from its neutral equivalent, analyses for sulfur by the Parr bomb method gave slightly erratic results. These ranged from 26.39 to 27.36% with an average of 26.92% for seven determinations. Corresponding anomalies were not noted for the sulfides prepared from the dithiol.

Anal. Calcd. for $C_{12}H_{10}S_2O$: S, 27.34. Found: S, 26.92.

Phenoxybenzene-4,4'-dithioglycolic Acid.—Four and five-tenths grams (0.019 mole) of the dithiol and 7 g. (0.074 mole) of chloroacetic acid were dissolved in a slight excess of 5% potassium hydroxide and the solution allowed to stand overnight. The potassium salt which separated was dissolved in water and the solution acidified with hydrochloric acid. Crystallization from xylene gave 5.5 g. or 83% of the theoretical amount of the acid melting at 165–166°.

Anal. Calcd. for $C_{16}H_{14}S_2O_5$: S, 18.31; neut. eq., 175. Found: S, 18.37, 18.39; neut. eq., 174.

Various amounts of chlorosulfonic acid in acetic anhydride or in sulfuric acid either did not affect the dithio-

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[1] Suter, This Journal, 53, 1112 (1931).

[2] Gebauer-Fuelnegg, *ibid.*, 49, 1387 (1927).

[3] Bogert and Bartlett, *ibid.*, 53, 4046 (1931).

glycolic acid or produced water-soluble derivatives. Similar results were obtained with oleum. With phosphorus pentoxide in xylene a small amount of red material was obtained which was soluble in 5% sodium hydroxide but not in water. Reducing agents did not affect this, however.

By the action of thionyl chloride upon the acid there resulted an oily material which could not be distilled. Analysis for halogen indicated the majority of the product to be the acid chloride.

Anal. Calcd. for $C_{16}H_{12}S_2O_3Cl_2$: Cl, 18.32. Found: Cl, 15.75, 15.90.

Treatment of this crude material with aluminum chloride gave a red tar from which nothing definite was obtained.

4,4′-Dimethylthioldiphenyl Ether.—To a solution of 5 g. (0.021 mole) of phenoxybenzene-4,4′-dithiol in 3.5 g. of sodium hydroxide in 175 cc. of water was added with vigorous stirring 10.6 g. (0.084 mole) of methyl sulfate. After a few minutes a white precipitate formed which was filtered, washed with dilute alkali, then with water and dried. The yield of sulfide was 5 g. or 89% of the theoretical amount of material melting at 81–81.5°.

Anal. Calcd. for $C_{14}H_{14}S_2O$: S, 24.45. Found: S, 24.47, 24.52.

Summary

1. Phenoxybenzene-4,4′-dithiol and the corresponding dithioglycolic acid and dimethyl sulfide were prepared.

2. Attempts to prepare a polymeric thioindigo dye were unsuccessful.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Reaction of Butylacetylene with Oxygen

BY CHARLES A. YOUNG, R. R. VOGT AND J. A. NIEUWLAND

Although the peroxides of a large number of organic compounds have been studied, members of the acetylene series have received but little attention. Bodenstein[1] has postulated the intermediate formation of a peroxide in the thermal reaction between acetylene and oxygen. Young, Vogt and Nieuwland[2] have shown the existence of substances possessing oxidizing power in a number of standard preparations of acetylenic hydrocarbons which had been exposed to air. The oxidizing properties of these substances are in all respects similar to those ascribed to peroxides in the case of olefins which have been similarly treated. The authors have found that the oxidizing power in acetylene hydrocarbon preparations can be rather precisely compared, and that the reactivity of the sample in many processes is a function of the oxidizing power.[3]

Before the publication of data which shows that the presence of a peroxide compound is the controlling factor in many of the reactions of acetylenes, it has appeared desirable to demonstrate that the oxidizing power of acetylene hydrocarbon samples is not due to extraneous impurities, but is probably due, at least at first, to an unstable oxygen compound of the acetylene hydrocarbon. It is quite possible, however, that peroxide compounds of oxidation products of the acetylene may also be present.

In order to show that the oxidizing properties of butylacetylene which has been exposed to oxygen are not derived from small amounts of olefin impurities, a quantity of butylacetylene has been subjected to a very rigorous process of purification. The butylacetylene so obtained forms the peroxide with the same readiness and to the same extent as does butylacetylene purified in the customary manner. As was shown in a previous communication,[2] a dialkylacetylene forms compounds of a peroxide nature as readily as a monoalkylacetylene does. It is not likely, therefore, that the peroxide is produced by some polymer of the acetylene hydrocarbon. If an alkyl acetylene exists in equilibrium with the isomeric allene derivative, it is conceivable that it is the latter which forms the peroxide. However, phenylacetylene, in which no allene modification is possible, forms a peroxide readily.

Butylacetylene which has been exposed to the air for six months or so gives a good aldehyde test with Schiff's reagent and has a pronounced acid reaction. When a small amount of butylacetylene is allowed to evaporate at room temperature, the residue has an odor strongly resembling that of valeric acid. However, since the acid forms

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[1] Bodenstein, *Z. physik. Chem.*, **12B**, 155 (1931).

[2] Young, Vogt and Nieuwland, THIS JOURNAL, **56**, 1822 (1934); *J. Chem. Soc.*, 115 (1935).

[3] Unpublished work of Young, Vogt and Nieuwland.