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.

quite slowly in butylacetylene at room temperature, quantities of the acid sufficient to permit its isolation are not conveniently obtained. Consequently, recourse was had to the fact that the formation of the peroxide in butylacetylene is greatly accelerated by heating to 35–45° in the presence of oxygen. One and one-half moles of butylacetylene was maintained under these conditions for three months. The peroxide concentration at first increased very rapidly, but within a few weeks it had reached a value which was roughly constant thereafter. The concentration of the acid, on the other hand, increased steadily throughout the duration of the experiment. These results indicate that after a few weeks the rate of formation of the peroxide was approximately equal to the rate at which the peroxide oxidized butylacetylene, the peroxide being destroyed in the latter process. At the end of the three-month period of heating, the concentration of the acid in the butylacetylene, as determined with standard alcoholic potassium hydroxide using phenolphthalein as the indicator, was 2.12 normal. In the meantime the color of the butylacetylene had gone through the changes water white to yellow to reddish-brown.

The acid was separated from the butylacetylene by means of aqueous sodium carbonate. The aqueous layer was neutralized with hydrochloric acid and extracted with ether. From the ether extract there was isolated 8 g. of valeric acid. There were also obtained a complex mixture of other compounds in quantities too small to isolate and a large amount of polymer, which ranged from a light brown, viscous liquid to a dark brown tar. The butylacetylene layer from the sodium carbonate extraction also contained much dark brown, viscous polymer.

In an effort to isolate the peroxide a quantity of old butylacetylene was distilled through an efficient column. When most of the butylacetylene had been removed, the residue suddenly began to fume and darken, and much heat was evolved. After a few minutes the reaction subsided, and there remained in the distilling flask an acidic, viscous, dark brown, strongly lachrymatory liquid. Evidently the peroxide is highly unstable when in a concentrated form.

Experimental

Butylacetylene.—The butylacetylene, b. p. 70.5–70.7° corr. (747 mm.), was prepared from butyl bromide and sodium acetylide in liquid ammonia by a modification of the method described by Lebeau and Picon.[4]

Special Purification of Butylacetylene.—To a solution of 41 g. (0.5 mole) of butylacetylene in 160 cc. of 95% ethyl alcohol there was added slowly and with stirring a solution of 170 g. (1 mole) of silver nitrate in 250 cc. of water. The white precipitate of $C_4H_9C{\equiv}CAg{\cdot}AgNO_3$ was filtered, washed with water, and recrystallized from 1800 cc. of 95% ethyl alcohol. The crystals were thoroughly washed with water, and then refluxed for three hours with a solution of 115 g. of sodium cyanide in 250 cc. of water. The regenerated butylacetylene was dried with calcium chloride and distilled. In this way 30 g. of butylacetylene was recovered. Since olefins are not precipitated by silver nitrate under these conditions, any trace of olefin present would be removed by this process.

Isolation of Valeric Acid.—One and one-half moles of butylacetylene was maintained at 35–45° for three months in the presence of oxygen. At the end of this time the solution was refluxed and stirred for two hours with 200 cc. of a saturated aqueous solution of sodium carbonate. The aqueous layer was neutralized with 12 normal hydrochloric acid, which produced more than enough sodium chloride to saturate the solution. The fatty acid was removed by extracting with three 50-cc. portions of ether. Upon distilling the ether extract there was obtained 8 g. of valeric acid, which had the following properties: b. p. 185–186° (744 mm.), reported b. p. 187° (760 mm.); neutralization equivalent 105,[5] theoretical 102.

DUCLAUX VALUES

	Obtained	Reported
First 10 cc.	26.0	24.5
Second 10 cc.	20.0	20.6
Third 10 cc.	16.4	17.0

Summary

1. Butylacetylene which has been carefully purified to remove olefin impurities forms a peroxide readily.

2. Evidence is presented which indicates that the peroxide is not formed by a polymer or allene form of the acetylene hydrocarbon.

3. Valeric acid has been identified as one of the decomposition products of the peroxide formed in butylacetylene.

4. The peroxide in butylacetylene is quite unstable when in a concentrated form.

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[4] Lebeau and Picon, *Compt. rend.*, **156**, 1077 (1913); Picon, *ibid.*, **158**, 1346 (1914); *ibid.*, **169**, 32 (1919).

[5] The valeric acid was not completely dry.