graphite and from the 700 and 1000° Edenborn cokes.

The effect of the carbonization temperature of the coke on the yield of mellitic acid was studied. From Edenborn coal, little mellitic acid was obtained. With increasing carbonization temperature the yield increased rapidly up to 700°. With the 1000° coke about the same quantity was recovered as with the 700° coke. With high temperature cokes the interpretation of our results becomes difficult. There is at present no satisfactory explanation for the uniformity of mellitic acid yields from such widely different carbons as 700 and 1000° cokes, artificial and natural graphites.

Cokes with the same final carbonization temperatures but widely different heating rates show small differences in the mellitic acid yield, which probably does not have important significance.

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

# Some Ethers of 3-Butyn-1-ol[1]

BY P. A. MCCUSKER AND J. W. KROEGER

In view of the commercial availability of certain derivatives of ethylene glycol commonly known as Cellosolves and Carbitols, it was proposed to investigate the preparation and properties of acetylenic compounds derived from these starting materials. This group of compounds, the 1-alkoxy-3-butynes, provides not only a new type of acetylene for investigation but also furnishes a starting point for further syntheses since the terminal hydrogen of the chain is quite labile, being attached to a triply bonded carbon atom.

Various types of acetylenic ethers are reported in the literature[2] the majority of which are ethers of propargyl alcohol. Of the group of compounds described herein, all are new with the exception of 1-methoxy-3-butyne which was prepared by Lespieau[3] by dehydrohalogenation.

The technique of the preparation of acetylenic compounds as originally described by Picon,[4] who treated sodium acetylide in liquid ammonia with alkyl iodides, has been modified in this Laboratory to apply to alkyl bromides. The Cellosolves and Carbitols were converted to the corresponding bromides by the method of Palomaa and Kenetti.[5] Of these, 2,2′-dibromodiethyl ether and ethyl 2-bromoethyl glycol ether, the bromides derived from diethylene glycol and diethylene glycol monoethyl ether, respectively, are new compounds. The acetylenes were obtained from these various bromides in yields of 60 to 75% according to the type reaction

$$\mathrm{R{-}O{-}CH_2{-}CH_2Br + NaC{\equiv}CH \longrightarrow R{-}O{-}CH_2{-}CH_2{-}C{\equiv}CH + NaBr}$$

These acetylenes are quite stable to light and air. Carefully purified samples were water-white after standing for three months. The characteristic odor of the 1-alkynes is unusually powerful in these acetylenic ethers.

Sodium acetylide does not react appreciably with 2,2′-dichlorodiethyl ether, under the experimental conditions used. Ethylene bromohydrin when treated with sodium acetylide is converted to acetaldehyde, principally.

## Experimental

**Preparation of Bromides.**—Commercial samples of the various glycol derivatives were treated with phosphorus tribromide in the presence of pyridine.[4] Redistillation of the glycol ethers was usually unnecessary. The physical constants for 2,2′-dibromodiethyl ether, which has not previously been reported, are: b. p. 115° (32 mm.); $n^{27}\mathrm{D}$ 1.5131; $d^{27}_{4}$ 1.8222. The constants for ethyl, 2-bromoethyl glycol ether are: b. p. 100–101° (33 mm.); $n^{24}\mathrm{D}$ 1.4580; $d^{24}_{4}$ 1.3340.

**Preparation of Acetylenes.**—One liter of liquid ammonia was placed in a 3-liter three-necked flask and stirred vigorously while a rapid stream of acetylene was bubbled through. To this, 1.2 moles (excess) of sodium dissolved in liquid ammonia was added slowly. When all the sodium had been converted to sodium acetylide, one mole of bromide was slowly dropped in and the mixture was stirred for two to four hours. Five hundred milliliters of water was then added and the organic layer which separated was washed with dilute hydrochloric acid, then with saturated

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(1) Eighteenth paper on the chemistry of the alkyl acetylenes and their addition products; previous paper, THIS JOURNAL, **58**, 1861 (1936).

(2) Lespieau, *Compt. rend.*, **194**, 287 (1932); Yvon, *ibid.*, **180**, 748 (1925); Grard, *Ann. chim.*, **13**, 336 (1930); Liebermann, *Ann.*, **135**, 266 (1865).

(3) Lespieau, *Compt. rend.*, **144**, 116 (1907).

(4) Picon, *ibid.*, **158**, 1346 (1914); **169**, 32 (1919).

(5) Palomaa and Kenetti, *Ber.*, **64B**, 797 (1931); Tallmann, THIS JOURNAL, **56**, 127 (1934).

Table I

Properties of Compounds $R—O—C_2H_4—C\equiv CH$

| R— | B. p., °C. | Mm. | $n_D$ | Temp., °C. | $d_4$ | $MR_D$ Calcd. | $MR_D$ Found | Hg deriv., m. p., °C. |
|---|---|---|---|---|---|---|---|---|
| $CH—^3$ | 87.5 | 748 | 1.4117 | 22 | 0.8505 | 24.9 | 24.6 | 113.9 |
| $C_2H_5—$ | 104.0 | 747 | 1.4148 | 22 | .8273 | 29.6 | 29.7 | 98.6–99.0 |
| $C_4H_9—$ | 147–148 | 747 | 1.4191 | 27 | .8185 | 38.8 | 39.1 | 42.2–42.5 |
| $HC\equiv C—C_2H_4—CH_2—$ | 164–165 | 750 | 1.4519 | 26 | .8980 | 36.8 | 36.6 | [a] |
| $BrCH_2—CH_2—$ | 99–100 | 35 | 1.4788 | 25 | 1.3271 | 37.3 | 37.8 | 85.0–86.0 |
| $C_2H_5—O—C_2H_4$ | 84.5–85.5 | 34 | 1.4381 | 24 | 0.9267 | 40.23 | 40.25 | [a] |

[a] The mercury derivatives of these two compounds could not be crystallized and decomposed above 100°.

Table II

Analytical Data

| Compound | Calculated | Found |
|---|---|---|
| $C_2H_5OC_2H_4C\equiv CH$ | C, 73.5; H, 10.2 | 73.3; 10.1 |
| $C_4H_9OC_2H_4C\equiv CH$ | C, 76.1; H, 11.2 | 75.8; 10.1 |
| $C_2H_5OC_2H_4OC_2H_4C\equiv CH$ | C, 67.5; H, 9.9 | 67.2; 9.3 |
| $HC\equiv CC_2H_4OC_2H_4C\equiv CH$ | C, 78.7; H, 8.2 | 78.4; 8.0 |
| $BrC_2H_4OC_2H_4C\equiv CH$ | Br, 45.1 | 45.3 |
| $BrC_2H_4OC_2H_4Br$ | Br, 68.9 | 68.7 |
| $BrC_2H_4OC_2H_4OC_2H_5$ | Br, 40.6 | 40.6 |
| $(CH_3OC_2H_4C\equiv C)_2Hg$ | Hg, 54.4 | 54.0 |
| $(C_2H_5OC_2H_4C\equiv C)_2Hg$ | Hg, 50.8 | 50.5 |
| $(C_4H_9OC_2H_4C\equiv C)_2Hg$ | Hg, 44.6 | 44.6 |
| $(BrC_2H_4OC_2H_4C\equiv C)_2Hg$ | Hg, 36.3 | 41.1[a] |

[a] This derivative was apparently contaminated with a more highly mercurated compound.

sodium carbonate solution and finally was dried over sodium sulfate and fractionated. The properties of the acetylenes prepared in this manner are given in Table I. In the reaction of sodium acetylide with dibromodiethyl ether, some 2′-bromo-1-ethoxy-3-butyne was also obtained.

The mercury derivatives mentioned in Table I were prepared by the method of Johnson and McEwen[6] and were recrystallized from benzene.

## Summary

1. Some new acetylenic ethers have been described.

2. The physical constants of 2,2′-dibromodiethyl ether and ethyl 2-bromoethyl glycol ether are reported.

(6) Johnson and McEwen, This Journal, 48, 471 (1926).

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# NOTES

## Concerning the Alleged Absorption of Gaseous Nitrogen by Benzene Solutions of Rubber and Guttapercha Hydrocarbons

By Louis B. Howard[1] and Guido E. Hilbert

Experiments described by De Jong[2] have been interpreted as indicating that dilute benzene solutions of rubber or guttapercha hydrocarbon from sheet balata, when exposed to sunlight for a few days in either quartz or ordinary glass vessels, absorb gaseous nitrogen in appreciable amounts.[3] If such a photochemical combination of rubber and nitrogen actually occurs, one might reasonably expect other unsaturated hydrocarbons containing isoprene units such as carotene and xanthophyll to behave similarly. These substances which always are found closely associated with chlorophyll in green plants possess physiological functions which, as yet, remain quite obscure. It therefore seemed of very great importance from both a theoretical and a practical standpoint to attempt to confirm these results of De Jong.

In the present study the experimental procedure of the original investigation was followed as closely as the description of the work allowed. Several variable factors, such as temperature, barometric pressure, vapor pressure of the benzene solutions and the heating effect of sealing the tubes, were controlled. In one experiment Pyrex tubes of 150-cc. capacity were filled with

(1) Now employed at the Whittier, Calif., station of the Bureau of Entomology and Plant Quarantine.

(2) De Jong, *Rec. trav. chim.*, 51, 153 (1931).

(3) In one case a tube containing 54 cc. of a 1.05% solution of rubber in benzene under an atmosphere of nitrogen was found to draw in 11 cc. of water when opened under the surface of this liquid after six days of irradiation. This was considered to indicate an absorption of 12.8 mg. of nitrogen which according to his calculations represented 2.5% of the weight of the rubber.