[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BUFFALO]

THE PREPARATION OF METHYL, ETHYL, PROPYL, AND BUTYL ORTHOCARBONATES[1]

HOWARD TIECKELMANN AND HOWARD W. POST

Received November 6, 1947

INTRODUCTION

The primary purpose of this investigation was to prepare certain esters of orthocarbonic acid for use in a projected study of their chemical reactions.

Interaction of carbon tetrachloride and sodium ethoxide does not form ethyl orthocarbonate, as many other investigators have testified (2, 8, 9, 10). Chloropicrin, however, is an excellent substitute for carbon tetrachloride (1, 2, 3, 4, 6, 7).

In 1937, Connolly and Dyson (5) prepared ethyl orthocarbonate in 40% yield by the action of sodium ethoxide on thiocarbonyl perchloride, Cl_3CSCl.

PREPARATION OF THE ESTERS

Most of the orthocarbonates used in later work in this laboratory were prepared in accordance with the method of Connolly and Dyson (5). The reaction was unique but the yields were good. It was noted that, after removal of the ester layer from the reaction mixture and acidification of the aqueous residue with dilute hydrochloric acid, hydrogen sulfide was evolved and sulfur was precipitated. This fact seemed to indicate the presence of a polysulfide, presumably of sodium, in the mixture after the reaction had been completed. In order to obtain further evidence on this point, sodium ethoxide was refluxed with sulfur whereupon a coffee colored solution was formed similar to that obtained after interaction of sodium ethoxide and thiocarbonyl perchloride. This solution also evolved hydrogen sulfide and precipitated free sulfur on treatment with dilute hydrochloric acid. The reactions concerned in this synthesis can therefore be represented as follows:

$$\text{(I)} \qquad C_2H_5ONa + Cl_3CSCl \rightarrow C_2H_5OSCCl_3 + NaCl$$

$$\text{(II)} \qquad 3\ C_2H_5ONa + C_2H_5OSCCl_3 \rightarrow C_2H_5OSC(OC_2H_5)_3 + 3\ NaCl$$

$$C_2H_5OSC(OC_2H_5)_3 \rightarrow C(OC_2H_5)_4 + S$$

$$2\ C_2H_5ONa + xS \rightarrow Na_2S_x + ?$$

$$Na_2S_x + 2\ HCl \rightarrow 2\ NaCl + HSH + S_{x-1}$$

Neither $C_2H_5OSCCl_3$ nor $C_2H_5OSC(OC_2H_5)_3$ was isolated in the course of this work, but the presence of the former had been demonstrated by Connolly and Dyson (5). As will be seen from Table I, the use of thiocarbonyl perchloride proved much more satisfactory than chloropicrin. Methyl, ethyl, propyl, and butyl orthocarbonates have here been prepared by this method. Only ethyl

---

[1] A portion of the thesis submitted by the first author in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Buffalo.

and i-butyl orthocarbonates had been prepared previously by others (5) using the thiocarbonyl perchloride reaction. Several attempts to prepare i-propyl orthocarbonate were made but these were unsuccessful.

TABLE I

PER CENT YIELDS OF ORTHOCARBONATES

ESTER	A(3)	B(4)	C(5)	D(6)	E(7)	F	G
CH_3		60			97	48	71
C_2H_5	30		40	41	80	57	78
C_3H_7						49	70
C_4H_9					46	39	66

F this work, Cl_3CNO_2
G this work, Cl_3CSCl

EXPERIMENTAL PART

Thiocarbonyl perchloride, Cl_3CSCl, was prepared by the method of Connolly and Dyson (5), Rathke (11), and Dyson (12). The authors are indebted to Mr. John Barone for much of the experimental work in this connection.

Methyl orthocarbonate from chloropicrin. Using the method described below for the ethyl homolog, 50 g. of chloropicrin (0.3 mole) and 35 g. of sodium (1.5 mole) in dry methyl alcohol gave 19.5 g. of methyl orthocarbonate, yield 48%. Physical constants: b.p. 113.5°, literature 114° (4); n_D^{20} 1.3858, literature n_D^{16} 1.3864 (4); d_4^{20} 1.020, literature $d_{18.5}^{18.5}$ 1.0232 (4).

Methyl orthocarbonate from thiocarbonyl perchloride. Using the method described below for the ethyl homolog, 56 g. (0.3 mole) of thiocarbonyl perchloride gave 29 g. of methyl orthocarbonate, yield 71%. Physical properties agreed with the product prepared from chloropicrin.

Ethyl orthocarbonate from chloropicrin. Ethyl alcohol, 95%, was refluxed with calcium oxide, then distilled and treated with magnesium ethoxide. The distillate from this treatment was used for the preparation of sodium ethoxide. Thirty-five grams (1.5 gr. atom) of sodium was added in small portions to about one liter of absolute alcohol. In this and in all previous steps, the system was protected from atmospheric moisture by calcium chloride tubes. The sodium ethoxide solution was warmed to 40–50° on the water-bath. The water-bath was then removed and 50 g. (0.3 mole) of chloropicrin was added at such a rate that the temperature of the reaction mixture remained at about 40° to 45°. Higher temperatures resulted in lower yields. Lower temperatures than 40° resulted in the accumulation of unreacted chloropicrin to a point where a sudden reaction took place with explosive violence. The addition of the chloropicrin took about one hour, at the end of which the solution was thick and light yellow in color. The precipitate was sodium chloride and sodium nitrite. At this point the mixture was allowed to stand overnight.

Alcohol was distilled off from the water-bath to avoid excessive overheating. The residue was taken up with water and extracted with ether. The ether extracts were combined and fractionated; yields 31 to 35 grams, b.p. 158–160°. Less stringent precautions in connection with the exclusion of moisture during the reaction resulted in the presence of varying amounts of diethyl carbonate with the product.

Ethyl orthocarbonate from thiocarbonyl perchloride. Details here were much the same as in the preceding method. The solution of sodium ethoxide was kept in an ice-bath during addition of thiocarbonyl perchloride (56 g. in 50 cc. of dry ether) to prevent the temperature from rising above room temperature during the reaction. The system was allowed to stand overnight. Alcohol was distilled off through a column as before and the residue extracted with water and ether. From the ether layer a fraction was isolated, b.p. 158–160°, ethyl orthocarbonate, yield 77%.

It was necessary to keep the system cool during addition of the halogen compound since otherwise the sulfur formed would react with sodium ethoxide and lower the yield considerably. The final color of the mixture was a light yellow. Interaction of sulfur and sodium ethoxide at higher temperatures produced a dark coffee color.

Propyl orthocarbonate from chloropicrin. With the method used for the ethyl compound, 50 g. of chloropicrin (0.3 mole) gave 37.1 g. of propyl orthocarbonate, yield 49%. Physical properties: b.p. 224°, literature 224.2° (3); n_D^{20} 1.4100; d_4^{20} 0.897, literature (8°) 0.911 (3).

Propyl orthocarbonate from thiocarbonyl perchloride. Using the same method as for the ethyl homolog, 56 g. (0.3 mole) of thiocarbonyl perchloride gave 53 g. of propyl orthocarbonate, 70% yield with physical properties in agreement with the above.

Butyl orthocarbonate from chloropicrin. In similar manner, 50 g. (0.3 mole) of chloropicrin gave 36.5 g. of butyl orthocarbonate, 39% yield. Physical properties, b.p. 273°; n_D^{20} 1.4216; d_4^{20} 0.8879.

Butyl orthocarbonate from thiocarbonyl perchloride. As before, 56 g. (0.3 mole) of thiocarbonyl perchloride gave 61.5 g. of butyl orthocarbonate, yield 66%. Physical properties agreed with the above.

SUMMARY

1. The preparation of methyl, ethyl, propyl, and butyl orthocarbonates by the action of the proper sodium alkoxide on chloropicrin has been repeated and data are presented on yields.

2. It has been shown that better yields may be obtained on substituting thiocarbonyl perchloride in the above syntheses.

BUFFALO, N. Y.

BIBLIOGRAPHY

(1) BASSETT, *Ann.*, **132**, 54 (1863).
(2) DEUTSCH, *Ber.*, **12**, 115 (1879).
(3) ROSE, *Ann.*, **205**, 249 (1880).
(4) VON HARTEL, *Ber.*, **60**, 1841 (1927).
(5) CONNOLLY AND DYSON, *J. Chem. Soc.*, 827 (1937).
(6) MCELVAIN AND MCBANE, M.S. Thesis, University of Wisconsin (1941).
(7) HILL, Unpublished
(8) PONZIO, *Gazz. chim. ital.*, **36** (II), 149 (1906).
(9) NEF, *Ann.*, **308**, 329 (1899).
(10) INGOLD AND POWELL, *J. Chem. Soc.*, **119**, 1228 (1921).
(11) RATHKE, *Ann.*, **167**, 195 (1873).
(12) DYSON, *Org. Syntheses*, Coll. Vol. I, 506 (1941).