

The isomeric products, β -diketone XV and the ketone enol benzoate XVI, from the benzylation of diisobutyl ketone (see Table I) boiled 32 to 35° apart at 1.6 mm. and gave satisfactory analyses (see Table II). The higher boiling product gave an enol test and a copper chelate which are characteristic of β -diketones, whereas the lower boiling product failed to produce a distinct enol test³³ or to form a

copper chelate. Moreover, only the latter isomer XVI gave a positive test for unsaturation with bromine in carbon tetrachloride as should be expected for the ketone enol benzoate.

may be ascribed to the presence of a trace of the isomeric β -diketone XV.

(33) The slight enol test recorded in Table II for this product XVI

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Methyl and Ethyl Trichloromethyl Ethers^{1,2}

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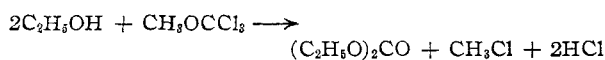
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Methyl and ethyl trichloromethyl ethers, ROCCl_3 , have been prepared by the action of anhydrous chlorine on the corresponding alkoxydichloromethanesulfonyl chloride or bis-[alkoxythiocarbonyl] disulfide. Methyl trichloromethyl ether reacts readily with water, benzoic acid, sodium phenate, ethanol, methanethiol and aniline to form methyl chloroformate, benzoyl chloride and methyl chloroformate, methyl phenyl carbonate, diethyl carbonate, dimethyl dithiocarbonate, and diphenylurea, respectively. Ethyl trichloromethyl ether appears to be somewhat less reactive.

Douglass and Marascia³ have reported that methoxydichloromethanesulfonyl chloride, $\text{CH}_3\text{OC}-\text{Cl}_2\text{SOCl}$, reacts with anhydrous chlorine to form methyl trichloromethyl ether, CH_3OCCl_3 , I. The present study has revealed that the latter compound can also be prepared by the direct chlorination at 0–25° of crude bis-(methoxythiocarbonyl) disulfide, $(\text{CH}_3\text{OCS})_2\text{S}_2$. Sulfur mono- and dichlorides are also formed in the reaction, but these can be separated from the reaction mixture by distillation and by reaction with cyclohexene to produce higher boiling compounds which remain behind when the ether is distilled. In a similar manner ethyl trichloromethyl ether (II) can be prepared from bis-(ethoxythiocarbonyl) disulfide.

Methyl trichloromethyl ether is a highly reactive compound. In some of its reactions it behaves in a manner analogous to benzotrichloride, undergoing hydrolysis to the acid chloride $\text{CH}_3\text{OCOC}_2\text{H}_5$ and reacting with benzoic acid to form benzoyl chloride and methyl chloroformate. The reaction with sodium phenoxide shows a similar type of reaction in forming methyl phenyl carbonate.

With alcohols the reaction of I follows an unexpected course. Treatment with methyl alcohol leads to the formation of dimethyl carbonate. With ethyl alcohol the methyl group was eliminated from the ether as methyl chloride and a 61% yield of diethyl carbonate was obtained. A similar reaction was observed with methyl mercaptan in that dimethyl dithiocarbonate was the only product isolated.



With aniline Marascia⁴ found that compound I reacted to give a nearly quantitative yield of di-

phenylurea, although no other products were isolated.

All attempts to prepare methyl orthocarbonate from I were unsuccessful. There was also no evidence of reaction between hydrogen sulfide and I.

Ethyl trichloromethyl ether (II) was not investigated extensively but it does not appear to be as reactive as I. It failed to react with benzoic acid, but with methylaniline it formed N,N'-dimethylcarbanilide.

Experimental

The Preparation of Bis-(methoxythiocarbonyl) Disulfide.—To a stirred solution of 160 g. of sodium hydroxide, 600 ml. of water and 800 ml. of methanol, cooled by means of an ice-bath, was added dropwise over a 1-hour period 240 ml. of carbon disulfide.

After the addition was complete, 0.1 g. of potassium iodide was added and chlorine was bubbled through the mixture until the color of free iodine indicated that the end-point had been reached. The iodine color was discharged with 10% sodium bisulfite and the xanthate disulfide was separated, washed repeatedly with water, and dried over calcium chloride. The crude disulfide was used for later experiments because it cannot be distilled, even at reduced pressure, without decomposition.

The Preparation of Methyl Trichloromethyl Ether (I).—In a chlorination flask fitted with a mechanical stirrer was placed 212 g. of crude bis-(methoxythiocarbonyl) disulfide. While the flask and its contents were cooled in an ice-salt-bath a stream of anhydrous chlorine was passed in at such a rate that the temperature did not rise above 10° except at night when chlorination was discontinued. Chlorination was continued until the weight had increased 420 g., and required 58 hours including two overnight periods.

The reaction mixture was distilled using a 12-in. column packed with glass beads. The first fraction boiling 57–60° (760 mm.) consisted chiefly of sulfur dichloride. The second, a pale yellow liquid, boiled 48–51° (100 mm.) and contained the major part of the I. The residue consisted chiefly of sulfur monochloride and intermediate products from the reaction.

The second crude fraction was cooled in an ice-salt-bath while anhydrous cyclohexene was added dropwise with stirring until the yellow color had been discharged. The resulting mixture was then distilled through a 12-in. packed column and yielded 110 g. of nearly colorless I. Sometimes the last traces of yellow color were hard to eliminate but careful redistillation usually gave a colorless, pure product in 30% yield or better with the properties: b.p. 109.5–110° (760 mm.), d_{20}^{20} 1.4349 and n_D^{20} 1.4520.

Anal. Calcd. for CH_3OCCl_3 : C, 16.08; H, 2.02; Cl,

(1) This work was supported by the Office of Naval Research under contract Nonr 647(00) with the University of Maine.

(2) Taken in part from the Master's Thesis of Glenn H. Warner.

(3) I. B. Douglass and Frank J. Marascia, *THIS JOURNAL*, **77**, 1899 (1955).

(4) Frank J. Marascia, Master's Thesis, University of Maine, 1954.

71.21; mol. wt., 149.4; MR_D , 28.08.⁵ Found: C, 16.38; H, 1.98; Cl, 71.27; mol. wt., 147.8; MR_D , 28.09.

The Preparation of Ethyl Trichloromethyl Ether (II).—By the use of procedures similar to those just described bis-(ethoxythiocarbonyl) disulfide was prepared and chlorinated. The chlorination of 243 g. of crude disulfide yielded 63.4 g. (25%) of purified ethyl trichloromethyl ether which boiled 122–125° (760 mm.) and had d_{20}^{20} 1.2696 and n_D^{20} 1.4457.

Anal. Calcd. for $C_2H_5OCCl_3$: Cl, 65.08; mol. wt., 163.4; MR_D , 32.29. Found: Cl, 65.62; mol. wt., 163.6; MR_D , 32.11.

The Reaction of I with Water.—A mixture of 8 g. of I and 0.94 g. (0.053 mole) of water was heated on the steam-bath and a colorless liquid slowly distilled into the ice-cooled receiver at 55–67°. The distillate was dried over $CaCl_2$ and on redistillation yielded 3.5 g. of methyl chloroformate (65% of theory) which was identical in boiling point, refractive index and density with an authentic sample. The *p*-nitrophenyl derivatives of experimental and authentic samples both melted 109–111° and the melting points were unchanged on mixing.

The Reaction of I with Aqueous Sodium Phenoxide.—To 14.3 g. of phenol and 8 g. of sodium hydroxide dissolved in 200 ml. of water was added slowly, with stirring, 7.5 g. of I. The oil that separated was extracted with ether, washed with 1 *N* potassium hydroxide, dried, and distilled. After removing the ether 4.9 g. of colorless liquid boiling 212–215° (760 mm.) and having d_{20}^{20} 1.5214 and n_D^{20} 1.4975 was obtained. Methyl phenyl carbonate prepared from an authentic sample of methyl chloroformate and phenol had comparable properties. The yield of methyl phenyl carbonate was 64.5% based on the quantity of I used.

Anal. Calcd. for $CH_3OCOOC_6H_5$: MR_D , 28.98. Found: experimental product, MR_D , 29.50; authentic sample, MR_D , 29.40.

Reaction of I with Methyl Mercaptan.—Into a large test-tube, cooled to the temperature of solid carbon dioxide, were placed 16 g. of methyl mercaptan and 15 g. of I. There was no apparent immediate reaction and the mixture was allowed to stand overnight in the Dry Ice-bath and then at room temperature for several days. On distilling the mixture through a 12-inch Vigreux column there was obtained 4.9 g. of pale yellow liquid boiling 67–69° (20 mm.) and having d_{20}^{20} 1.1838 and n_D^{20} 1.5487. An authentic sample of *S,S'*-dimethyl dithiocarbonate, $(CH_3S)_2CO$, prepared by the reaction of phosgene with methyl mercaptan had identical properties. An authentic sample of the isomeric methyl methylxanthate, $CH_3OCSSCH_3$, also boiled 67–69° (20 mm.) but had d_{20}^{20} 1.1807 and n_D^{20} 1.5629. The yield was 40% based on the weight of I.

Anal. Calcd. for $(CH_3S)_2CO$: MR_D , 32.34. Found: for experimental product, MR_D , 32.70; for authentic sample, MR_D , 32.70.

Reaction of I with Methanol.—In a flask fitted with sealed stirrer, dropping funnel and reflux condenser attached to a Dry Ice-trap was placed 200 ml. of absolute methanol. Compound I, 15 g., was then added dropwise to the stirred methanol and when all had been added the reaction mixture was heated on a steam-bath and maintained at reflux temperature for one hour. After cooling and pouring the mixture into water, the reaction product was recovered by extracting with ether, washing with sodium bicarbonate, drying and distilling. The product was a colorless liquid (3.9 g.) boiling 90–93° and having d_{20}^{20} 1.0687 and n_D^{20} 1.3680. Dimethyl carbonate is reported as boiling 90–91° and having d_{20}^{20} 1.0694 and n_D^{20} 1.3687.

Anal. Calcd. for $(CH_3O)_2CO$: MR_D , 18.53; mol. wt., 90.08. Found: MR_D , 18.97; mol. wt., 88.8.

(5) Atomic and group refractivities used are those of A. I. Vogel, *J. Chem. Soc.*, 1842 (1948).

The yield of dimethyl carbonate was 44% of the theoretical based on the methyl trichloromethyl ether used.

From the Dry Ice-trap there was recovered 5 ml. of colorless liquid which boiled below room temperature. A molecular weight of 50.9 was found which compares favorably with a calculated value of 50.49 for methyl chloride.

Reaction of I with Ethanol.—In a procedure similar to that just described, 15 g. of I was allowed to react with 19 g. of absolute ethanol. Upon distilling the resulting product through a 12-inch Vigreux column there was obtained 3.2 g. of colorless liquid boiling 119–122° and having d_{20}^{20} 0.9746 and n_D^{20} 1.3839. Diethyl carbonate is reported to boil 124–125° and to have d_{20}^{20} 0.9751 and n_D^{20} 1.3845. The yield of diethyl carbonate was 28.25%.

Anal. Calcd. for $(C_2H_5O)_2CO$: MR_D , 28.83; mol. wt., 118.13. Found: MR_D , 28.42; mol. wt., 116.9.

From the Dry Ice-trap there was recovered 2 ml. of a low boiling, colorless liquid with molecular weight of 51.0. Methyl chloride has a calculated molecular weight of 50.49.

In the repetition of this experiment, using pyridine in the ethanol, a yield of 61% of diethyl carbonate was obtained.

Reaction of I with Benzoic Acid.—A mixture of 12.2 g. of benzoic acid and 15 g. of I was maintained at reflux temperature until the evolution of hydrogen chloride had ceased.

Two fractions were obtained on distilling the black reaction mixture. The first, boiling 72–76° (760 mm.), was identified as methyl chloroformate by density and refractive index and by forming methyl *p*-nitrophenyl carbonate. This derivative melted 108–109° after recrystallization from alcohol and melted unchanged when mixed with an authentic sample. The yield of methyl chloroformate was 37.6%.

The second fraction, consisting of 6.5 g. of liquid with the characteristic odor of benzoyl chloride, was identified by boiling point, refractive index, density and the formation of benzanilide. The melting point of the latter derivative was unchanged when mixed with an authentic sample. The yield of benzoyl chloride was 46%.

Reaction of I with Aniline.—A 1.0-g. sample of I was treated with a benzene solution of aniline and pyridine. A vigorous reaction took place immediately. The resulting white solid was washed, first with 10% hydrochloric acid and then with water. After two recrystallizations from alcohol the solid melted at 239° (uncor.) and when mixed with authentic diphenylurea melted unchanged.

Other Attempted Reactions of I.—Several attempts were made to prepare methyl orthocarbonate by the reaction of I with sodium methoxide in absolute methanol. In one experiment a trace of liquid having approximately the expected properties was obtained, but the yield could not be improved.

I, 15.0 g., was refluxed gently at atmospheric pressure while hydrogen sulfide was bubbled slowly in for three hours. Upon distilling the reaction mixture the only product obtained was 12 g. of unchanged I.

Reaction of II with Methylaniline.—When 16.5 g. of ethyl trichloromethyl ether was added dropwise to 42.8 g. of ice-cold methylaniline there was immediate reaction and a white solid separated. The mixture was heated in the steam-bath for one hour and the resulting solid was extracted repeatedly with dilute hydrochloric acid and finally with water. Recrystallization from aqueous alcohol gave 20.4 g. (85%) of white crystals melting 121–123° (uncor.). A mixed melting point with authentic *N,N'*-dimethyl carbanilide prepared from phosgene and dimethylaniline was unchanged.

Attempted Reaction of II with Benzoic Acid.—Benzoic acid, 12.2 g., was mixed with 16.5 g. of ethyl trichloromethyl ether and refluxed gently for three hours. Distillation of the reaction mixture through a 12-inch Vigreux column yielded only unchanged II.

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