

properties of *sym*-diethoxypropanol did not agree well with those reported by Berthelot¹² for this compound; likewise data listed by Zunino⁹ for the dimethoxy-, di-*n*-propoxy-, di-*s*-propoxy- and diisoamoxy derivatives did not check closely with the values determined for these compounds in this investigation. However, excellent agreement was found with the data listed by Fairbourne, Gibson and Stephens^{10,11} for boiling points, densities and indices of refraction of the dimethoxy-, diethoxy-, di-*n*-propoxy- and di-*s*-propoxypropanols.

Preparation of *sym*-Dialkoxyacetones.—The *sym*-dialkoxypropanols were converted into the *sym*-dialkoxyacetones by using a procedure adapted from "Organic Syntheses."¹³ The calculated amounts of commercial grade sodium dichromate and *sym*-dialkoxypropanol were placed in a flask provided with a mechanical stirrer and maintained by cooling at 15–20° during the time of reaction. The required amount of concd. sulfuric acid, diluted one to five with water, was added slowly over a period of about four hours, but the stirring was continued for sixteen to eighteen hours. In cases in which marked thickening of the oxidation mixture was noted, water was added until the mixture could be stirred more easily. Finally, enough water was added to dissolve any chromium salt that had separated from solution; then the solution was extracted with three 75-cc. portions of ether. The ethereal extracts were treated with 25 cc. of 0.1 *N* sodium hydroxide solution and washed with three 50-cc. portions of water. The ether was removed and the ketones fractionated through efficient indented columns. The data for physical properties and analyses of the nine *sym*-dialkoxyacetones prepared are listed in Table III. Semi-

(12) Berthelot, *Ann.*, **92**, 303 (1854), recorded b. p. 190–191°; *d*₄²⁰ 0.920.

(13) Conant and Quayle, "Organic Syntheses," John Wiley & Sons, Inc., New York, N. Y., Vol. II, 1922, p. 13.

carbazones were prepared from the diethoxy-, di-*n*-propoxy-, and di-*n*-butoxyacetones; certain data for their physical characteristics and for the analyses for their nitrogen content appear in Table IV. Failure to obtain a semicarbazone from dimethoxyacetone may be attributed to its solubility; the 2,4-dinitrophenylhydrazone was employed to aid in characterization of this ketone. However, failure to obtain solid derivatives from the ketones of branched alkyl structure may be attributed to steric hindrance.

TABLE IV
SEMICARBAZONES OF *sym*-DIALKOXYACETONES,

—R	M. p., °C. (corr.)	Nitrogen, %	
		Calcd.	Found
CH ₃ ^a	119.5–120.5	18.79	18.64
C ₂ H ₅	90.0–91.0	20.69	20.59
<i>n</i> -C ₃ H ₇	85.5–87.0	18.18	18.26
<i>n</i> -C ₄ H ₉	82.5–83.5	16.22	16.50

^a These data are for the 2,4-dinitrophenylhydrazone of *sym*-dimethoxyacetone.

Summary

1. The synthesis of *sym*-dialkoxyacetones by conversion of *sym*-glycerol dichlorohydrin into *sym*-dialkoxypropanols and subsequent oxidation of the latter is very much less tedious and productive of better yields than is their preparation from alkyl alkoxyacetates by means of the Claisen condensation.

2. Nine *sym*-dialkoxyacetones have been prepared and adequately characterized.

AUSTIN, TEXAS

RECEIVED DECEMBER 9, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE COLLEGE]

Bromotrichloromethane and Iodotrichloromethane

By J. H. SIMONS, T. K. SLOAT AND A. C. MEUNIER

Compounds of the halogens with carbon are of increasing interest, but in regard to some of them very little information is available in the literature. A new method of synthesis of bromo- and iodotrichloromethane has been found and studied, and attempts have been made to cause these compounds to perform the Grignard reaction. A new method of making trichloroacetyl bromide has been employed, and a way has been found of preparing anhydrous sodium trichloroacetate that has not been reported previously.

The published methods of preparing bromotrichloromethane are: a sealed tube reaction of

chloroform with bromine,¹ by the reaction of carbon tetrachloride with aluminum tribromide,² by the action of sodium hypobromite with chloroform,³ and by the reaction of potassium trichloroacetate with bromine in a sealed tube.⁴ Iodotrichloromethane has been made previously by similar methods.^{3,5}

(1) Paternò, *Jahr.*, 300 (1872); Friedel and Silva, *Bull. soc. chim.*, **17**, 538 (1872); Lecompte, Volklinger and Tchakirian, *Compt. rend.*, **204**, 1927 (1937).

(2) Vesper and Rollefson, *THIS JOURNAL*, **56**, 1455 (1934).

(3) Dehn, *ibid.*, **31**, 1225 (1909).

(4) Van't Hoff, *Ber.*, **10**, 678 (1877); Wouters, *Bull. sci. acad. roy. Belg.*, **20**, 782 (1934).

(5) Besson, *Bull. soc. chim.*, [3] **9**, 175 (1880).

Preparation of Bromo- and Iodotrichloromethane.—The former was obtained by passing trichloroacetyl bromide at atmospheric pressure through a glass tube heated electrically to 400°. Two passages of the same material through the furnace yielded about 10% bromotrichloromethane and about 5% hexachloroethane. Most of the original material was recovered. A gas evolved was identified by analysis as carbon monoxide.

Unpurified trichloroacetyl iodide distilled at atmospheric pressure produced about 75% iodotrichloromethane and 5% hexachloroethane. It was prepared by the method reported by Gustus and Stevens⁶ of passing hydrogen iodide through trichloroacetyl chloride and permitting the hydrogen chloride to escape. They obtained trichloroacetyl iodide by low pressure distillation.

Preparation of Trichloroacetyl Bromide.—This compound was prepared in a similar manner by passing hydrogen bromide through liquid trichloroacetyl chloride kept in a salt-ice bath. Distillation at atmospheric pressure yielded about 70% of the acid bromide, none of bromotrichloromethane and some unconverted acid chloride.

Decomposition of Trichloroacetyl Chloride.—Several passages of this material through the furnace at 600° caused about one-third to react. Carbon tetrachloride and hexachloroethane were formed in the ratio of about ten to one. Carbon monoxide and some phosgene were also produced.

Identification.—Bromotrichloromethane was identified by its boiling point 103 to 105°, reported 104°; liquid density 1.994 g./cc. at 20°, reported 1.959; molecular weight by vapor density (Dumas) 200, theory 198; and total halogen analysis as silver halides. Iodotrichloromethane was identified by its boiling point, 135 to 140°, reported 142°, and by total halogen analysis as silver salts.

Reaction of Salts of Trichloroacetic Acid with Bromine.—Attempts were made to prepare bromotrichloromethane by passing bromine through anhydrous mercurous or sodium trichloroacetate in a furnace. With the mercurous salt no reaction was found up to the temperature at which it sublimed. The sodium salt neither reacted nor decomposed at 500°. This was unexpected as both Van't Hoff⁴ and Wouters⁴ reported the reaction of the potassium salt in sealed tubes. We tried the anhydrous sodium salt with bromine in a sealed tube and obtained no reaction.

We believe, therefore, that the reaction taking place in sealed tubes is not between bromine and the salt but the well-known reaction between bromine and chloroform resulting from the haloform reaction of the hydrated salt.

Preparation of Anhydrous Sodium Trichloroacetate.—This compound has previously been made⁷ in small quantities by drying the hydrate in a vacuum desiccator over

phosphorus pentoxide. We prepared it easily by neutralizing the acid with sodium ethylate in absolute alcohol. Removal of the alcohol at room temperature produced the anhydrous salt in crystalline form.

Grignard Reactions.—Bromotrichloromethane in dilute solution in ether was added to magnesium in ether in which there was a small amount of a hydrocarbon Grignard compound. The mixture was stirred for seven hours. The resultant gave a negative Gilman test and did not produce an anilide with phenyl isocyanate. Silver nitrate produced a copious white precipitate with an aqueous solution. No isolatable compounds were found. Similar experiments with iodotrichloromethane produced only hexachloroethane.

Discussion.—The thermal decomposition of the acid halides indicates that the carbon-carbon bond is broken readily in these compounds, and the resulting CCl_3 fragment can then add the halogen present in the gas mixture. This is also indicated from the fact that C_2Cl_6 is also formed, probably from a union of two CCl_3 fragments. Senderens⁸ obtained chiefly chloroform but also some hexachloroethane, tetrachloroethylene, carbon monoxide, carbon dioxide, and hydrogen chloride by the thermal decomposition of trichloroacetic acid. The main reaction in this case seems analogous to those taking place with the acid halides.

Summary

Carbon tetrachloride, bromotrichloromethane, and iodotrichloromethane have been prepared by the thermal decomposition of trichloroacetyl chloride at 600°, bromide at 400°, and iodide below 140°. Hexachloroethane is also formed in these reactions.

Trichloroacetyl bromide has been made by passing hydrogen bromide through trichloroacetyl chloride.

Anhydrous sodium trichloroacetate has been made by neutralizing trichloroacetic acid with sodium ethylate in absolute alcohol and evaporating the alcohol.

Bromotrichloromethane and iodotrichloromethane both failed to form a Grignard compound. The latter coupled to form hexachloroethane.

STATE COLLEGE, PENNSYLVANIA

RECEIVED NOVEMBER 16, 1938

(6) Gustus and Stevens, *THIS JOURNAL*, **55**, 374 (1933).

(7) Verhoek, *ibid.*, **56**, 571 (1934).

(8) Senderens, *Compt. rend.*, **172**, 155 (1921).