due (102 g.) was dissolved in pyridine (300 ml.) and the solution was cooled and placed in the refrigerator overnight. The crystals which separated were collected on a filter and redissolved in pyridine (300 ml.). This solution was filtered in order to remove slightly soluble polymerization products of formaldehyde which had separated. It was cooled and placed in the refrigerator. After twenty-four hours, the crystals which had formed were isolated by filtration and dried in vacuum over concentrated sulfuric acid for two days; weight of the sorbitol–pyridine compound, 106.3 g.; melting point 90°. When this compound was mixed with pure sorbitol–pyridine, the melting point of the mixture was 90°. The sorbitol–pyridine compound was converted into the triformal derivative which proved to be identical with triformal-*d*-sorbitol prepared from glucose.[1]

Summary

The fruits of several species of the family *Rosacae* are convenient sources of sorbitol. Small quantities of sorbitol have been isolated from the leaves of some of these plants. Sorbitol extracted from a variety of plant materials with alcohol is crystallized readily from pyridine.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. II. Bromoketene Diethylacetal. Observations on the Reactivity of Bromo- and Iodoethoxyacetal[1]

BY FREDERICK BEYERSTEDT AND S. M. MCELVAIN

The preparation of tetraethoxyethylene (IV) was the original object of this work. That compound is of particular interest on account of its alleged dissociation into the divalent carbon compound, carbon monoxide acetal. The latter substance is reported to have been isolated[2] in small yields from the reaction of sodium ethoxide with ethyl diethoxyacetate and in much larger yields from ethyl formate through the following series of reactions

$$HCOOC_2H_5 + NaOC_2H_5 \longrightarrow C_2H_5OH + C(ONa)OEt \xrightarrow{POCl_3} C(Cl)OC_2H_5 \xrightarrow{NaOC_2H_5} C(OC_2H_5)_2$$

Unsuccessful attempts to repeat the latter procedure have been reported[3] in the literature. The recent preparation of ketene diethylacetal[4] from iodoacetal and the demonstration that it had not been described previously would seem to invalidate the former procedure. In fact, it is doubtful if such an acetal, which is really an ether of the enolic form of an ester, has ever been prepared simply by the action of sodium ethoxide on the ester.

It seemed desirable, therefore, to undertake the preparation of tetraethoxyethylene (diethoxyketene diethylacetal) (IV) by a method related to that by which the ketene diethylacetal was obtained. The reactions involved in the projected synthesis were

$$BrCH_2CH(OC_2H_5)_2 \xrightarrow{Br_2} \underset{\text{I}}{Br_2CHCH(OC_2H_5)_2} \xrightarrow{KOC_2H_5} \underset{\text{II}}{(C_2H_5O)_2CHCH(OC_2H_5)_2} \xrightarrow{Br_2} \underset{\text{III}}{(C_2H_5O)_2CBrCH(OC_2H_5)_2} \longrightarrow \underset{\text{IV}}{(C_2H_5O)_2C{=}C(OC_2H_5)_2}$$

This synthesis failed at the transformation of dibromoacetal (I) to glyoxal tetraethylacetal[5] (II). The dibromoacetal (I) after fifteen hours of heating at 150° with an excess of saturated alcoholic solution of potassium ethoxide gave an incomplete reaction, as judged from the amount of precipitated potassium bromide. The product isolated still contained bromine and it was necessary to heat it for an additional ten hours at 150° to render it halogen-free. After these periods of heating the only products which could be isolated were small amounts of glyoxal and traces of the glyoxal tetraethylacetal. After several experiments it was found that one of the halogens of dibromoacetal was removed quite easily by the potassium ethoxide, but that the second one came out only with the greatest difficulty. Pinner[5] records a similar observation on the dichloroacetal.

The replacement of a single bromine of dibromoacetal by the ethoxyl group to form bromo-

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[2] Scheibler, *Ber.*, **59**, 1022 (1926).

[3] Arbusow, *ibid.*, **64**, 698 (1931); Wood and Bergstrom, THIS JOURNAL, **55**, 3314 (1933); *cf.* also Adickes, *Ber.*, **60**, 272 (1927); **63**, 3012 (1930).

[4] Beyerstedt and McElvain, THIS JOURNAL, **58**, 529 (1936).

[5] The preparation of this acetal in very low yields from glyoxal has been described by Harris and Temme [*Ber.*, **40**, 171 (1907)] and from dichloroacetal by Pinner [*ibid.*, **5**, 151 (1872)].

ethoxyacetal (V) was then attempted in an alcoholic solution of potassium ethoxide. The calculated quantity of potassium bromide was obtained readily, but on working up the product it was found to have a boiling range of 10–12° at 7 mm. Repeated fractionation through a 35-cm. Widmer column separated the product into two components: (a) bromoethoxyacetal (V), b. p. 77–78° (12 mm.); and (b) the isomeric ethyl orthobromoacetate (VII), b. p. 84–85° (12 mm.). The latter compound obviously had resulted from the elimination of hydrogen bromide from the dibromoacetal to form bromoketene acetal (VI) which then had added a molecule of alcohol to form the ortho ester.

$$\begin{tikzcd}
Br_2CHCH(OC_2H_5)_2 \arrow[r, "KOC_2H_5"] \arrow[dr] & \underset{\text{V}}{Br(C_2H_5O)CHCH(OC_2H_5)_2} & \\
 & \underset{\text{VI}}{BrCH{=}C(OC_2H_5)_2} \arrow[r, "C_2H_5OH"] & \underset{\text{VII}}{BrCH_2C(OC_2H_5)_3}
\end{tikzcd}$$

The isolation of ethyl orthobromoacetate from this reaction mixture suggested the elimination of hydrogen bromide from the dibromoacetal by means of potassium *t*-butoxide.[4] With this reagent and the dibromoacetal a reaction took place immediately and a yield of bromoketene diethylacetal (VI) amounting to 82% of the theoretical was obtained. This acetal boils at 72–74° (9 mm.) and, like the unsubstituted ketene acetal,[4] reacts vigorously with water and ethyl alcohol to give ethyl bromoacetate and ethyl orthobromoacetate, respectively.

THE BOILING POINTS OF KNOWN KETENE ACETALS AND THE CORRESPONDING ESTERS

Compound	Formula	B. p. °C.	Mm.	Difference, °C.
Ketene acetal[a]	$CH_2{=}C(OC_2H_5)_2$	124		
Ethyl acetate	$CH_3COOC_2H_5$	77		47
Carbethoxyketene acetal[b]	$C_2H_5OOCCH{=}C(OC_2H_5)_2$	128	12	
Diethyl malonate	$CH_2(COOC_2H_5)_2$	88	12	40
Phenylketene acetal[c]	$C_6H_5CH{=}C(OC_2H_5)_2$	136	12	
Ethyl phenyl acetate	$C_6H_5CH_2COOC_2H_5$	109	12	27
Bromoketene acetal	$BrCH{=}C(OC_2H_5)_2$	73	9	
Ethyl bromoacetate	$BrCH_2COOC_2H_5$	47	9	26

[a] Ref. 4. [b] Reiter and Weindel, *Ber.*, **40**, 3358 (1907). [c] Staudinger and Rathsam, *Helv. Chim. Acta*, **5**, 646 (1922).

Since the second bromine atom of dibromoacetal was removed with such difficulty, it seemed desirable to replace the bromine of bromoethoxyacetal (V) by iodine and attempt the formation of triethoxyethylene (ethoxyketene diethylacetal) (IX) from the iodo compound (VIII).

$$Br(C_2H_5O)CHCH(OC_2H_5)_2 \longrightarrow \underset{\text{VIII}}{I(C_2H_5O)CHCH(OC_2H_5)_2} \longrightarrow \underset{\text{IX}}{C_2H_5OCH{=}C(OC_2H_5)_2}$$

The iodoethoxyacetal (VIII) was prepared from the bromo compound by treating the latter with an alcoholic solution of sodium iodide. This iodo compound, however, proved to be too inert to allow for the formation and isolation of the acetal (IX). It showed only a relatively small amount of reaction after being heated for three hours with potassium *t*-butoxide in *t*-butyl alcohol at the boiling point of the alcohol. More complete reaction was obtained at higher temperatures in sealed tubes but the only product isolated was a resinous material which could not be made to depolymerize.[4] Evidently the temperature and time necessary for the elimination of the halogen acid irreversibly polymerized the triethoxyethylene as it was formed.

As mentioned above, ketene acetals are ethers of the enolic forms of esters. A comparison of the boiling points of those ketene acetals, which are known with certainty, with the corresponding esters is shown in the table below. It is seen that, even though there is a progressive decrease in the difference between the boiling points of the ester and the corresponding acetal as the molecular weight of the ester increases, a considerable difference between the boiling points of the two types of compound persists.

If a similar comparison is made between Scheibler's other ketene acetals[6] and the corresponding esters, the conclusion that he did not have the acetals which he reported is inescapable.

Experimental

Dibromoacetal.—The apparatus and procedure were the same as described in the preparation of the bromoacetal[4] except for the size of the run and temperature conditions. Four moles of bromoacetal was brominated at a temperature of 10–15°. At the end of the bromination the reaction mixture was allowed to come to room temperature for 5 to 6 hours or it was stirred overnight without affecting

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(6) Scheibler, *et. al*, *Ann.*, **458**, 21 (1927).

the yield. The reaction mixture was worked up in the same manner as before. The yield of dibromoacetal boiling at 94–97° (12 mm.), was 550 g. (50%); $n^{25}D$ 1.4790; d^{25}_{25} 1.6200.

Anal. Calcd. for $C_6H_{12}O_2Br_2$: Br, 57.93. Found: Br, 57.75.

Bromoethoxyacetal.—To a stirred mixture of 138 g. (0.5 mole) of dibromoacetal and 100 cc. of absolute alcohol in a 1-liter three-necked flask, fitted with a dropping funnel and reflux condenser was added slowly a 300-cc. alcoholic solution of 20 g. (0.5 atom) of potassium. The flask was heated on a steam-bath during the addition and for two hours after the last of the alcoholic alkali had been added. The condenser was then set for downward distillation and 300 cc. of alcohol removed from the reaction mixture, after which the precipitated potassium bromide was filtered off. The filtered salt was washed thoroughly with anhydrous ether and the washings combined with the filtrate. The combined filtrates were distilled completely from an oil-bath under reduced pressure to remove the product from the dissolved salt. In this manner 96 g. of material boiling at 75–85° (12 mm.) was obtained. Upon careful fractionation through a 35-cm. Widmer column 82 g. of bromoethoxyacetal, b. p. 76–79° (12 mm.), and 14.0 g. of higher boiling product were obtained. Refractionation of the bromoethoxyacetal gave 75 g. (62.5%) of pure compound, b. p. 77–78° (12 mm.). The 14.0 g. of higher boiling material upon careful fractionation was separated into 5 g. of ethyl orthobromoacetate, b. p. 84–85° (12 mm.) and 8.0 g. of an intermediate mixture. The bromoethoxyacetal thus obtained has the following constants $n^{25}D$ 1.4596; d^{25}_{25} 1.3202.

Anal. Calcd. for $C_8H_{17}O_3Br$: Br, 33.15. Found: Br, 33.01.

If the addition of the reagents in the above procedure was reversed, a much larger amount of the high boiling fraction was obtained with a corresponding decrease in the fraction containing the bromoethoxyacetal.

Preparation of Bromoketene Diethylacetal.—Four grams (0.1 atom) of potassium was dissolved in 75 g. of *t*-butyl alcohol. To the boiling alcoholic solution 27.6 g. (0.1 mole) of dibromoacetal was added through a dropping funnel. Reaction took place immediately with the precipitation of potassium bromide. The mixture was heated for one hour to ensure complete reaction of the alkoxide. Upon cooling the precipitated salt was filtered off and the reaction product distilled under reduced pressure to remove it from the remaining salt. On fractionation of the resulting distillate 16 g. (82%) of bromoketene diethylacetal, b. p. 72–74° (9 mm.) was obtained: $n^{25}D$ 1.4610; d^{25}_{25} 1.3233.

Anal. Calcd. for $C_6H_{11}O_2Br$: Br, 44.64. Found: Br, 44.55.

Iodoethoxyacetal.—To 36.1 g. (0.15 mole) of bromoethoxyacetal in a Pyrex bomb tube was added a solution of 30 g. (0.20 mole) of sodium iodide in 100 cc. of absolute alcohol. The tube was sealed and heated in a bomb furnace at 140° for three hours. Four such tubes were opened and the contents filtered from the precipitated sodium bromide. The filtrate was distilled at a pressure of 100 mm. to remove the alcohol. The residue was then filtered from the remaining salt and distilled under reduced pressure. Upon fractionation, 95 g. of material, b. p. 75–94° (12 mm.), 62 g. of iodoethoxyacetal, b. p. 95–97° (12 mm.), and 13.5 g. of residue were obtained. The lower boiling fraction was again treated with sodium iodide and heated at 140° for another three hours. Upon working up the product from this reaction exactly as before an additional 85 g. of iodoethoxyacetal, b. p. 95–97° (12 mm.), was obtained, bringing the total yield to 147 g. (85% of the theoretical); $n^{25}D$ 1.4670; d^{25}_{25} 1.4285.

Anal. Calcd. for $C_8H_{17}O_3I$: I, 44.06. Found: I, 43.91.

Reaction of Iodoethoxyacetal with Potassium *t*-Butoxide.—A solution of 4 g. (0.1 atom) of potassium in 75 g. of *t*-butyl alcohol was heated to its boiling point and 28.8 g. (0.1 mole) of iodoethoxyacetal added. After the reaction mixture had refluxed for three hours, it was distilled at a pressure of 100 mm. to remove the *t*-butyl alcohol. The residue was distilled from the salt and unreacted alkoxide at a pressure of 12 mm. Upon fractionation of this distillate 2.3 g. of material, b. p. 38–40° (11 mm.), and 16.8 g. (59%) of unreacted iodoethoxyacetal, b. p. 93–95° (11 mm.) was obtained. Analysis of the mixture of potassium iodide and alkoxide remaining in the flask from which the product had been distilled indicated the extent of the reaction was 38%. The residue contained a semi-solid gum which was water insoluble. This gummy residue presumably was polymerized ethoxyketene acetal which resulted from the elimination of halogen acid from the iodoethoxyacetal. The lower boiling fraction upon investigation proved to be ethyl orthoacetate. On distillation at atmospheric pressure it boiled at 144–146° and when treated with water and shaken for about five minutes it hydrolyzed to give ethyl acetate. The origin of this ortho ester in the reaction product was most likely due to the fact that the iodoethoxyacetal contained small amounts of orthoiodo ester. This supposition is strengthened further by the fact that from eight experiments in which higher reaction temperatures were used the yield of this lower boiling product was always 2.3 to 2.5 g. even though in some cases 90% of the theoretical amount of potassium iodide was formed. The recovered iodoethoxyacetal showed an iodine content of 43.75% (calcd. 44.06%) and gave none of the ethyl orthoacetate when treated with potassium *t*-butoxide. The organic reaction product from the runs using higher reaction temperatures was the same type of resinous polymer mentioned above.

Summary

The preparation and properties of bromoketene diethylacetal, bromo-, and iodoethoxyacetal are described. The halogen of bromoethoxyacetal is very inert while that in iodoethoxyacetal may be removed without too great difficulty with potassium *t*-butoxide. However, the conditions for this reaction are sufficiently drastic that the expected triethoxyethylene (ethoxyketene diethylacetal) is apparently irreversibly polymerized.

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