[Communication from the Department of Industrial and Cellulose Chemistry,
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SYMMETRICAL TETRABROMO-ETHYL ETHER AND "SO-CALLED" TETRABROMOBUTYRALDEHYDE

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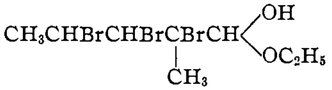
Freundler,[3] in the preparation of bromo-acetaldehyde by the bromination of paracetaldehyde isolated a crystalline product which from the analysis he was led to believe was tetrabromobutyraldehyde ($CH_2BrCHBrCBr_2CHO$), although as specifically pointed out by him, the compound possessed none of the usual aldehydic properties. He assumed that it was formed by the crotonization of the bromo-acetaldehyde, followed by addition of a second mole of bromine

$$2CH_2BrCHO \longrightarrow CH_2BrCH{=}CBrCHO + H_2O$$
$$CH_2BrCH{=}CBrCHO + Br_2{=}CH_2BrCHBrCBr_2CHO$$

The same type of reaction is indicated in the work of Kramer and Pinner[4] and of Freundler[5] on the chlorination of acetaldehyde. The trichlorobutyraldehyde isolated by these workers is presumably formed from the primary monochloro-acetaldehyde by condensation of this with acetaldehyde, followed by crotonization and subsequent addition of chlorine:

$$CH_3CHO + Cl_2 = CH_2ClCHO + HCl$$
$$CH_3CHO + CH_2ClCHO = CH_3CH{=}CClCHO + H_2O$$
$$CH_3CH{=}CClCHO + Cl_2 = CH_3CHClCCl_2CHO$$

More recently, Dworzak and Pfifferling,[6] by brominating parapropionaldehyde and treating the reaction mixture with alcohol, obtained a compound, the analysis and molecular weight of which corresponded to the half acetal



$$CH_3CHBrCHBr\underset{\displaystyle CH_3}{\underset{|}{C}}BrCH\begin{matrix}\diagup OH\\ \diagdown OC_2H_5\end{matrix}$$

apparently formed by a series of reactions similar to those above. This type of reaction, therefore, appears to be a general one.

However, while the other halogenated aldehydes referred to above possess characteristic aldehydic properties, and there would seem to be no

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[3] Freundler, *Compt. rend.*, **140**, 794, 1693 (1905); *Bull. soc. chim.*, [4] **1**, 71 (1907).

[4] Kramer and Pinner, *Ber.*, **3**, 383 (1870); *ibid.*, **8**, 1561 (1875).

[5] Freundler, *Bull. soc. chim.*, [4] **1**, 68, 201, 203 (1907).

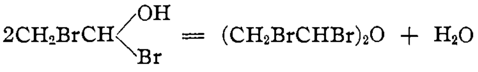
[6] Dworzak and Pfifferling, *Monatsh.*, **48**, 255 (1927).

reason to doubt the structures assigned to them, these same properties are entirely absent in the case of the tetrabromobutyraldehyde isolated by Freundler.

From a consideration of the polarities of the groups present, and of the effect of strongly negative groups, such as Br, on the reactivity of the carbonyl group,[7] it is to be expected that a compound such as Freundler's tetrabromobutyraldehyde would show a remarkable degree of reactivity, especially with regard to properties associated with the aldehyde group.

Further evidence against the aldehydic formula is available from Freundler's data. Heating with alcohol gave ethyl bromide, bromo-acetaldehyde and bromo-acetal. Cold fuming nitric acid oxidized it, giving bromo-acetic acid and hydrobromic acid but no tetrabromobutyric acid. These are not the reaction products one would expect from tetrabromobutyric aldehyde.

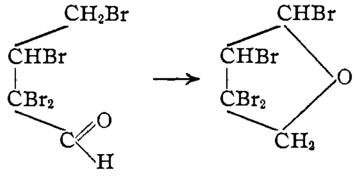
Stepanov, Preobrashenski and Shchukina,[8] in continuing the work of Hibbert and Hill[9] on the bromination of paracetaldehyde, pointed out that the tetrabromo compound of Freundler might possibly be tetrabromoethyl ether, formed by the loss of water from two moles of bromo-acetaldehyde bromohydrin



$$\underset{\text{A}}{2CH_2BrCH\langle{}^{OH}_{Br}} = \underset{\text{B}}{(CH_2BrCHBr)_2O} + H_2O$$

the intermediate addition compound (A) actually being isolated by them. This reaction is thus similar to the formation of dichloro-ethyl ether by the action of hydrochloric acid on acetaldehyde.[10]

There is, however, still a third possibility, namely, the formation of a butylene oxide ring derivative (III) obtained by ring closure due to wandering of a hydrogen atom



I III

This compound would be analogous to the *oxide ring form of a tetrose.*

It was to distinguish among these three formulas (designated below as I, II and III) that the present investigation was undertaken.

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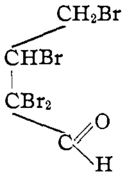
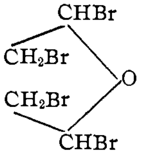
[7] A. Michael, "Ueber einige Gesetze und deren Anwendung in der organischen Chemie," *J. prakt. Chem.*, **60**, 291 (1899).

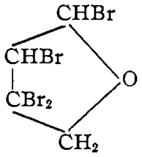
[8] Stepanov, Preobrashenski and Shchukina, *Ber.*, **59B**, 2533 (1926).

[9] Hibbert and Hill, THIS JOURNAL, **45**, 734 (1923).

[10] Lieben, *Ann.*, **106**, 336 (1858).


I


II


III

The substance (II) ($C_4H_6OBr_4$) contains two more hydrogen atoms than I and III ($C_4H_4OBr_4$). Analysis of the tetrabromo compound, prepared by Freundler's procedure, gave: C, 12.74; H, 1.60; Br, 82.2; calcd. for $C_4H_4Br_4O$: C, 12.36; H, 1.03; Br, 82.4; calcd. for $C_4H_6Br_4O$: C, 12.31; H, 1.54; Br, 82.0. The analysis thus favors the ether formula, II.

Further evidence for the ether formula, II, was obtained by condensing the compound with ethylene glycol; bromo-ethylidene glycol being obtained in 57.2% yield.

Final definite proof of the symmetrical tetrabromodiethyl ether formula II, was obtained by its direct synthesis and comparison with Freundler's compound. The product was obtained by the addition of bromine to divinyl ether, the latter being prepared by the action of powdered caustic potash on β,β'-dichloro-ethyl ether.

$$(CH_2ClCH_2)_2O + 2KOH = (CH_2{=\!=}CH)_2O + 2KCl$$
$$(CH_2{=\!=}CH)_2O + 2Br_2 = (CH_2BrCHBr)_2O$$

The melting points of symmetrical tetrabromo-ethyl ether prepared in this way, of Freundler's compound, and of a mixture of equal parts of the two, were found to be identical. The analyses were also in agreement, thus definitely establishing the identification of Freundler's compound as symmetrical tetrabromo-ethyl ether. It seems probable that *both* this and tetrabromobutyraldehyde are present in the reaction mixture obtained in the bromination of paracetaldehyde, but that the latter has not, as yet, been isolated.

The preparation of divinyl ether from dichloro-ethyl ether constitutes a new synthesis of this product and makes it easily available for investigation. It readily undergoes polymerization on warming, more rapidly in presence of a trace of benzoyl peroxide. These properties are being further investigated in connection with a general study on the nature of polymerization.

Experimental

Preparation of Freundler's Tetrabromo Compound.—The procedure followed was essentially that of Freundler:[3] 200 g. of bromine was added slowly from a dropping funnel to 70 g. of paracetaldehyde contained in a three-necked flask fitted with a stirrer and mercury seal and protected from moisture by a calcium chloride tube. The flask was surrounded by a freezing mixture of ice and salt and the temperature during addition was kept at −5 to −10° by adjusting the rate of addition of bromine. This required one and one-half to two hours. An additional 120 g. of bromine was then added at −5° during the course of about fifteen minutes. The temperature was allowed to rise gradually to 15°,[11] was held at this temperature for fifteen minutes, then allowed to rise to 20° and kept there until the red color of the bromine disappeared. The reaction product was then poured on a mixture of ice and finely ground sodium carbonate crystals, and the whole well stirred until all the hydrobromic acid was neutralized. The tetrabromo compound was deposited in white crystals. These were separated by filtration, dried between filter papers and recrystallized from ether; yield, 35%; m. p. 63–65°.

Anal. Subs., 0.2414, 0.2040, 0.2008: CO_2, 0.1110, 0.0955, 0.0951; H_2O, 0.0370, 0.0278, 0.0298. Subs., 0.1385, 0.1017; AgBr, 0.2680, 0.1963. Calcd. for $C_4H_6Br_4O$: C, 12.31; H, 1.54; Br, 82.0. Calcd. for $C_4H_4Br_4O$: C, 12.36; H, 1.03; Br, 82.4. Found: C, 12.54, 12.76, 12.91; H, 1.70, 1.51, 1.60; Br, 82.3, 82.1. Subs., 0.8415; benzene, 21.96 g.; Δt, 0.510°. Calcd. for $C_4H_6Br_4O$: mol. wt., 389.7. Found: 375.9.

Condensation with Ethylene Glycol.—One hundred and fifty-five g. of the tetrabromo compound and 300 g. of ethylene glycol were heated on the water-bath for six hours with constant stirring. The reaction mixture was extracted with ether, the ether extract first washed with saturated calcium chloride solution, then with saturated sodium bicarbonate, dried over calcium chloride and distilled under reduced pressure. The lower fractions (b. p. 65–80° at 27 mm.) still contained ethylene bromohydrin. They were redissolved in ether, the ether solution was thoroughly washed with water, dried over calcium chloride, redistilled and the distillate added to the main fraction; total yield, 75.5 g. (57.2%); b. p. 80–82° at 27 mm.

Anal. Subs., 0.1669, 0.1669, 0.1687: AgBr, 0.1867, 0.1911, 0.1909. Calcd. for $C_4H_7O_2Br$: Br, 47.83. Found: Br, 47.62, 48.28, 48.2.

Preparation of Divinyl Ether.—Two hundred grams of finely-powdered caustic potash contained in a small copper flask was strongly heated by a Bunsen burner and fifty grams of β,β'-dichloro-ethyl ether slowly dropped onto the heated alkali during the course of twelve hours. The flask was provided with a reflux water condenser kept at 40°, thus permitting the escape of the divinyl ether (b. p. 34–35°), but not of the intermediate product, vinyl chloro-ethyl ether (b. p. 106–108°). The first condenser was connected in turn to a second, and this with a well-cooled receiving flask. The refluxing was continued for about forty-eight hours; yield, 13.4 g. (54.9%); b. p. 34–35°.

Preparation of Symmetrical Tetrabromo-ethyl Ether.—One gram of divinyl ether was dissolved in 10 cc. of chloroform and a solution of 4.5 g. of bromine in 15 cc. of chloroform slowly added, the reaction flask being immersed in a freezing mixture during the addition.[12] On evaporation of the chloroform a product was left which crystallized on rubbing violently with a glass rod. It was recrystallized from ether; m. p. 63–64°. A mixture of equal parts of the compounds prepared by this, and by Freundler's method, respectively, melted at 62.5–64°.

Anal. Calcd. for $C_4H_6OBr_4$: Br, 82.03. Found: Br, 82.30, 81.75. Calcd. for $C_4H_6OBr_4$: C, 12.31; H, 1.54. Found: C, 12.68, 12.60; H, 1.77, 1.66.

Summary

1. The crystalline product obtained by Freundler in the bromination of paracetaldehyde and described by him as tetrabromobutyraldehyde is shown to be symmetrical tetrabromodiethyl ether.

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[11] If temperature is allowed to rise too rapidly, the reaction gets beyond control and an explosion may occur.

[12] When working on a large scale it is possible to add free bromine directly to the carefully cooled divinyl ether. The reaction product is then poured onto a mixture of powdered ice and sodium carbonate as in Freundler's preparation.

2. The latter has been synthesized from divinyl ether and found to be identical with Freundler's compound.
3. A new and simple synthesis of divinyl ether is described.

MONTREAL, CANADA

[CONTRIBUTION FROM THE DIVISION OF RESEARCH, DEPARTMENT OF PUBLIC WORKS, BUREAU OF STANDARDS, CITY OF BALTIMORE]

EMPLOYMENT OF PYRIDINE AS CATALYST IN PRODUCTION OF DIMETHYL-ALPHA-NAPHTHYLAMINE

BY FREDERICK G. GERMUTH

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Introduction

Subsequent experimentation carried on by the author with the view of ascertaining means of increasing the yield of terpineol from α-pinene and benzenesulfonic acid in acetic acid solution by inducing catalysis, developed the interesting fact that the presence of α-picoline ($NC_5H_4CH_3$) tended to increase the rate at which production occurred, accompanied by an increase in the actual yield of the product. This increase, however, is not greatly in excess of the quantity of terpineol obtained by the usual method.

It has been shown[1] that when an increase in the moisture content obtains the effect of such treatment upon the production of the substance sought is not proportional to the amount of water added at varying temperatures. It is believed that higher temperatures compensate for the decided increase in water content. The addition of α-picoline in minute and larger quantities increased the yields to an average of 2.35% in excess of those previously furnished. Unsuccessful attempts were made to enlarge this figure by the application of pyridine, (C_5H_5N), and related substances, but without avail.

It was considered advisable to test the effect of adding pyridine and certain of its homologs to reacting proportions of α-naphthylamine and methyl sulfate in alkaline solution to ascertain what effect, if any, the aromatic compound might have upon the mechanism of the reaction involved in the production of dimethyl-α-naphthylamine. The addition of α-picoline and that of the β-variety having been previously resorted to without the attainment of the sought-for objective, the contemplated step appeared feasible.

The discovery was made by the author that the yield of this methylated substitution product of naphthalene is greatly increased when the heterocyclic base is utilized as carrier. This compound has been used successfully as catalyst in Perkin's synthesis of cinnamic acid in this country[2] as well

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[1] Germuth, *Am. J. Pharm.*, **99**, 402 (1927).

[2] Bacharach and Brogan, THIS JOURNAL, **50**, 3333 (1928).