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

The Ethyl Orthohalogenoacetates and their Reaction with Zinc and Magnesium

BY FREDERICK BEYERSTEDT AND S. M. MCELVAIN

When the problem involving the preparation of ketene diethylacetal was undertaken it seemed that the two most obvious routes to this structure were (1) the removal of halogen acid from a halogenated acetal

$$XCH_2CH(OC_2H_5)_2 \longrightarrow CH_2{=}C(OC_2H_5)_2 + HX$$

and (2) the application of Boord's reaction[1] for the preparation of olefins to orthohalogenoacetic esters

$$XCH_2C(OC_2H_5)_3 + Zn \longrightarrow CH_2{=}C(OC_2H_5)_2 + C_2H_5OZnX$$

The first of these reactions proved to be quite satisfactory for the preparation of this acetal and details of its application were reported in a previous paper.[2] The present paper deals with the results of a study of the second reaction. While it has not been possible to realize the preparation of ketene acetal from this reaction, the preparation and behavior of these halogeno esters with the metals zinc and magnesium, seem to be of sufficient interest to report.

Ethyl orthochloroacetate was prepared by the alcoholysis of the imino ether hydrochloride obtained from chloroacetonitrile according to the procedure of Sah.[3] The yield was quite low (15%). All attempts to prepare the corresponding bromo ester by this method were unsuccessful. It was finally found that this ester could be prepared quite readily and in good yields by the direct bromination of ethyl orthoacetate in the presence of pyridine. From the bromo ester the iodo ester was prepared by heating the former with an alcoholic solution of sodium iodide.

$$CH_3C(OC_2H_5)_3 \xrightarrow[\text{pyridine}]{Br_2} BrCH_2(OC_2H_5)_3 \xrightarrow{NaI} ICH_2(OC_2H_5)_3$$

Ethyl orthochloroacetate was found to be so inert that it could not be made to react with either zinc or magnesium at temperatures as high as 160°. The halogen of ethyl orthobromoacetate is sufficiently reactive to allow this ester to react with zinc at 160° and with magnesium at 130°. In the former case, however, it appeared that the temperature necessary to initiate the reaction was so high that it had caused the decomposition of the orthoester into ether and the bromo ester

$$BrCH_2C(OC_2H_5)_3 \longrightarrow (C_2H_5)_2O + BrCH_2COOC_2H_5$$

and that it was this latter compound that really had reacted with the metal. The reaction between the bromo ester and the magnesium was carried out in di-*n*-butyl ether and could not be made to take place at a temperature lower than 130°. Under these conditions considerable (29%) ethyl bromide distilled from the reaction mixture. The product remaining in the reaction flask yielded, when worked up, small amounts of ethyl alcohol and ethyl acetate, but mainly a non-distillable residue from which nothing definite could be isolated. The first reaction product was undoubtedly $BrMgCH_2C(OC_2H_5)_3$, but instead of this compound simply decomposing intramolecularly into ketene acetal and C_2H_5O-MgBr, it appeared to undergo a variety of intermolecular condensations, some of which yielded ethyl bromide instead of magnesium ethoxybromide.

Compared to the other orthohalogeno esters, the ethyl orthoiodoacetate is extremely reactive. It reacted with zinc at 35° and with magnesium at temperatures as low as 5°. In the case of zinc, however, a protective coating of the reaction product stopped the reaction when only about one-half of the metal had been used. The products obtained when the reaction mixture was worked up were quite similar to those obtained from the bromo ester. The yield of ethyl iodide from the decomposition of the $IMgCH_2C(OC_2H_5)_3$ amounted to about 22% of the theoretical. When an excess of the iodo ester was treated with magnesium without a solvent the reaction started at room temperature and proceeded until the metal disappeared. Under these conditions a 43% yield of ethyl iodide was obtained when the reaction mixture was distilled.

In an attempt to diminish the amount of intermolecular condensation the iodo ester in ether solution was allowed to react with magnesium at 5°. At this temperature, which is the lowest at which any visible reaction appears, fifteen hours

---

[1] Boord, *et al.*, THIS JOURNAL, **52**, 3396 (1930); **53**, 1505 (1931); **54**, 751 (1932); **55**, 3293. 4930 (1933).

[2] Beyerstedt and McElvain, *ibid.*, **58**, 529 (1936).

[3] Sah, *ibid.*, **50**, 516 (1928).

are required to dissolve the metal completely. Although the intermolecular condensation yielding ethyl iodide did not occur under these conditions, the main reaction product was again a non-distillable mixture. The only products that were identified were ethyl acetate and diethyl succinate and these were found only in very small amounts.

It appears, therefore, that about all that can be said concerning the behavior of these orthohalogenoacetic esters with the metals, zinc and magnesium, is that the organo-metallic halides, which are first formed, enter into poly-intermolecular condensation at the temperatures which are necessary for their formation. None of them gives any indication of decomposing intramolecularly into ketene diethylacetal and the ethoxymetallic halide.

Experimental

Ethyl Orthochloroacetate.—This ester was prepared in yields of 15% of the theoretical from chloroacetonitrile[4] by the procedure of Sah.[3] The product obtained boiled at 74–75° (13 mm.); $n^{25}\text{D}$ 1.4199; d^{25}_{25} 1.0349.

Anal. Calcd. for $C_8H_{17}O_3Cl$: Cl, 18.03. Found: Cl, 17.95.

Ethyl Orthobromoacetate.—To a stirred mixture of 40.5 g. (0.25 mol.) of ethyl orthoacetate[5] and 20.8 g. (0.25 mol.) of pyridine was added dropwise 40 g. (0.25 mole) of bromine over a period of thirty minutes. The reaction mixture was kept at 10° during the bromination. When all of the bromine had been added the color of the reaction mixture was a dark red but after three hours of stirring, with the temperature maintained at 10°, it had changed to a pale yellow. The brominated ester was then separated from the precipitated pyridine hydrobromide and this salt thoroughly washed by triturating it several times with anhydrous ether. These washings were combined with the bromo ester filtrate and distilled. The yield of ethyl orthobromoacetate was 44 g. (74%), b. p. 77–79° (9 mm.); $n^{25}\text{D}$ 1.4393; d^{25}_{25} 1.2639.

Anal. Calcd. for $C_8H_{17}O_3Br$: Br, 33.15. Found: Br, 33.02.

From some of the brominations a small amount of a higher boiling material remained after the ethyl orthobromoacetate distilled. This material proved to be ethyl orthodibromoacetate which boiled at 102–104° (8 mm.); $n^{25}\text{D}$ 1.4691; d^{25}_{25} 1.5272.

Anal. Calcd. for $C_8H_{16}O_3Br_2$: Br, 49.95. Found: Br, 49.88.

Ethyl Orthoiodoacetate.—A solution of 27 g. (0.18 mol.) of anhydrous sodium iodide (dried by heating for twelve hours at 100° and 10 mm. pressure) in 110 cc. of absolute alcohol (distilled from magnesium ethoxide) together with 30 g. (0.125 mole) of ethyl orthobromoacetate was sealed in a Pyrex bomb tube and heated at 110° for sixteen hours. The liquid contents of the bomb tube were then distilled under diminished pressure in order to separate them from the sodium bromide and excess sodium iodide. The resulting distillate was then fractionated. The yield of ethyl orthoiodoacetate was 22 g. (60%), b. p. 96–98° (10 mm.); $n^{25}\text{D}$ 1.4660; d^{25}_{25} 1.4200.

Anal. Calcd. for $C_8H_{17}O_3I$: I, 44.06. Found: I, 44.20.

The preparation of ethyl orthoiodoacetate by the action of potassium ethoxide on di-iodoacetylene has been reported by Nef.[6] He reported the boiling point of the compound to be 93° (14 mm.).

The Reaction of Ethyl Orthobromoacetate with Magnesium.—A solution of 24.1 g. (0.1 mole) of the bromo ester in 25 g. of di-*n*-butyl ether is heated with 2.4 g. (0.1 atom) of magnesium until reaction begins. This occurs at about 130° and the reaction is allowed to continue until the metal disappears (about four hours). The solvent ether was removed from the reaction mixture under diminished pressure from a steam-bath. Fractionation of the distillate so obtained yielded 3.2 g. (29%) of ethyl bromide, b. p. 36–40°, and 22.5 g. of di-*n*-butyl ether, b. p. 134–138°. The solid product remaining in the reaction flask was treated with 65 cc. of a 10% aqueous solution of acetic acid and the resultant solution extracted three times with 50-cc. portions of ether. The ether extract, after washing with 5% sodium bicarbonate solution, drying, and distilling, yielded the following fractions: (a) 2.5 g., b. p. 75–79°; (b) 2.5 g., b. p. 25–75° (8 mm.); (c) 1.0 g., b. p. 75 (8 mm.) – 175 (0.5 mm.); (d) non-distillable residue, 5 g.

Fraction (a) was shown by saponification to be 60% ethyl acetate and 40% ethyl alcohol; (b) refractionated at atmospheric pressure yielded about 1 g. of di-*n*-butyl ether and 0.8 g. of acetoacetic ester, b. p. 175–185°. Fractions (c) and (d) were not investigated further.

This bromo ester was allowed to react with zinc in the absence of any solvent. No reaction occurred until the temperature was raised to 160°. The reaction was allowed to run over a three-hour period during which time considerable material distilled from the reaction mixture. This distillate was mainly diethyl ether and ethyl bromoacetate together with a small amount of ethyl bromide. The first two of these products indicated that the temperature necessary for the reaction had caused pyrolysis of the orthobromo ester and that the reaction had then proceeded with the ethyl bromoacetate. The product in the reaction flask, when worked up, yielded small amounts of alcohol and ethyl acetate, but mainly non-distillable material.

Reaction of Ethyl Orthoiodoacetate with Zinc and Magnesium.—This iodo ester in an ether solution reacts with zinc at 35°. The reaction, however, is incomplete because of the insolubility of the resulting organo-metallic compound which coats the metal and prevents further reaction. Removal of the volatile products under diminished pressure from the reaction mixture after reaction had ceased gave a distillate from which fractionation produced ethyl iodide (22%) and the unreacted orthoiodoester.

---

(4) Bauer, *Ann.*, **229**, 165 (1885).

(5) This material was prepared by the procedure of Sah.[3] It was found, however, that stirring the mixture of the imino ether hydrochloride and absolute alcohol reduced the reaction time to one-third of that required by the original procedure and raised the yield of ethyl orthoacetate from 36 to 51% of the theoretical.

(6) Nef, *Ann.*, **298**, 352 (1897).

The non-volatile portion of the reaction mixture, when worked up, yielded a small amount of ethyl acetate but mainly a non-distillable condensation product.

With magnesium the iodo ester reacted without a solvent at room temperature. Removal of the volatile portion of the reaction mixture gave a considerable amount (43%) of ethyl iodide. The non-volatile portion of the reaction mixture in this case also was found to consist mainly of non-distillable material.

In ether solution ethyl orthoiodoacetate reacted with magnesium at temperatures as low as 5°, but even at this low temperature polyintermolecular condensation could not be avoided. While no ethyl iodide was produced, the main reaction product appeared to be the same type of non-distillable material which had been obtained in the other runs. In addition to this indefinite product small amounts of ethyl acetate and diethyl succinate were isolated by distillation.

The authors wish to express their gratitude to the Wisconsin Alumni Research Foundation for a grant that made this work possible.

Summary

Procedures for the preparation of ethyl ortho-chloro-, -bromo-, and -iodoacetates are described. Of these orthohalogeno esters the chloro compound is too inert to react with either zinc or magnesium. Both the bromo and iodo esters react with these metals to form organo-metallic halides which then undergo poly-intermolecular condensation to give indefinite, non-volatile products. There was no evidence that these organo-metallic halides decomposed intramolecularly into ketene acetal and an ethoxymetallic halide.

MADISON, WISCONSIN RECEIVED APRIL 30, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Nature of Calomel Vapor[1]

BY FRANK T. GUCKER, JR., AND RALPH H. MUNCH

Introduction

Calomel vapor has been studied by numerous investigators for more than a century, yet its exact composition is still in doubt. A good critical discussion of the earlier work is contained in an article by Alexander Smith and Menzies.[2] In 1833, E. Mitscherlich[3] determined its vapor density and found that it corresponded to the formula HgCl. This conclusion was confirmed by the later work of Deville and Troost,[4] Rieth,[5] and Harris and Victor Meyer.[6] All of these results were obtained at temperatures from 450° to somewhat above 500°. In 1864, W. Odling[7] discovered that a piece of gold leaf exposed to calomel vapor became amalgamated. He concluded that calomel vapor is decomposed to some extent at least, presumably into mercuric chloride and mercury, and this conclusion was confirmed by others. In 1894, W. Harris and Victor Meyer[6] attempted to find the extent of the dissociation by separating the mercury and mercuric chloride vapors by diffusion through a porous clay tube. Since they obtained a large amount of free mercury in this way, they argued that the dissociation is nearly complete. This conclusion, however, is not justified, since the removal of the mercury would cause increased dissociation, even if the original dissociation had been slight. No method which changes the concentration of any constituent in the equilibrium will give a reliable estimate of its extent.

Smith and Menzies,[2] realizing that no qualitative experiments could solve the problem, devised a quantitative method based on a study of the vapor pressures of mercury, calomel, and a mixture of the two, at temperatures from 360 to 400°. If calomel and mercury are immiscible and their vapors neither react nor have a common component, the vapor pressure of the mixture would be the sum of the vapor pressures of the constituents. On the other hand, if calomel and mercury are immiscible and the calomel vapor is completely dissociated into mercuric chloride and mercury, the vapor pressure of the mixture would be less than the sum of the vapor pressures of the constituents. They found experimentally that calomel is slightly soluble in mercury, and that the vapor pressure of the mixture corresponds to that calculated for the case of complete dis-

---

(1) Parts of this paper were presented at the Midwest Sectional meeting of the American Chemical Society at Louisville, November, 1935.

(2) Smith and Menzies, THIS JOURNAL, **32**, 1541 (1910).

(3) E. Mitscherlich, *Pogg. Ann.*, **29**, 193 (1833).

(4) Deville and Troost, *Compt. rend.*, **45**, 821 (1857).

(5) R. Rieth, *Ber.*, **3**, 666 (1870).

(6) W. Harris and Victor Meyer, *ibid.*, **27**, 1482 (1894).

(7) W. Odling, in private communication cited by Williamson, *J. Chem. Soc.*, **17**, 211 (1864).