[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

Ketene Acetals. XXII. Diethoxymethylketene Diethylacetal

By S. M. McElvain and Leo R. Morris

Abstract.—An attempt to prepare carbon suboxide tetraethylacetal by the dehydrobromination of dibromomalonaldehyde diethylacetal (IV) was unsuccessful because one of the bromine substituents was removed as a positive halogen to form the monobromoacetal III, which then underwent dehydrohalogenation to yield diethoxymethylketene diethylacetal (V). This ketene acetal was converted by ethanol to ethyl ortho-β,β-diethoxypropionate (VI) and by bromine to ethyl α-bromo-β,β-diethoxypropionate (VII).

As part of the general study of ketene acetals in this Laboratory the preparation of the bis-ketene acetal, carbon suboxide tetraethylacetal ($(C_2H_5O)_2C{=}C{=}C(OC_2H_5)_2$), was undertaken. Although the preparation of this compound has not been achieved, the results obtained in the attempt seem of sufficient interest to report.

The proposed synthesis involved the double dehydrohalogenation of dibromomalonaldehyde tetraethylacetal (IV), which was obtained by the following sequence of reactions

$$CH_2{=}CHCHO \xrightarrow{Br_2} CH_2BrCHBrCHO \xrightarrow[HCl]{C_2H_5OH}$$

$$\underset{I}{C_2H_5OCH_2CHBrCH(OC_2H_5)_2} \longrightarrow \xrightarrow[(C_2H_5OH)]{KOH}$$

$$\underset{II}{C_2H_5OCH{=}CHCH(OC_2H_5)_2} \xrightarrow{Br_2}$$

$$[C_2H_5OCHBrCHBrCH(OC_2H_5)_2] \xrightarrow{C_2H_5OH}$$

$$\underset{III}{(C_2H_5O)_2CHCHBrCH(OC_2H_5)_2} \xrightarrow{C_5H_5N\cdot Br_2}$$

$$\underset{IV}{(C_2H_5O)_2CHCBr_2CH(OC_2H_5)_2}$$

The dibromoacetal (IV) did not lose both halogens as hydrogen bromide when treated with two equivalents of potassium *t*-butoxide. Instead, a mixture of the monobromoacetal (III) and diethoxymethylketene diethylacetal (V) was obtained. This result indicated that one of the bromine substituents of IV reacted as a positive halogen to be replaced by hydrogen and reverted to III, which then underwent dehydrohalogenation to V. This reaction course was confirmed when IV with one equivalent of potassium *t*-butoxide gave III in 44% yield; III, obtained in this manner or from II, was converted by potassium *t*-butoxide into V in 46–59% yield.

$$IV \xrightarrow[t\text{-}C_4H_9OH]{KOC_4H_9\text{-}t} III \xrightarrow{KOC_4H_9\text{-}t} \underset{V}{(C_2H_5O)_2CHCH{=}C(OC_2H_5)_2}$$

The reaction of one of the bromine substituents of IV as a positive halogen with potassium *t*-butoxide parallels the behavior of ethyl orthobromoacetate and ethyl orthodibromoacetate with sodium ethoxide.[1] In these cases it was shown that three ethoxyl groups on an adjacent carbon was necessary to cause a carbon-to-bromine bond to polarize as a positive bromine. In IV the bromine is activated by four ethoxyl groups, equally divided between two adjacent carbons; however, it appears that the electron-attracting contribution of one of the bromine substituents of IV is necessary to cause the separation of the other as a positive halogen, inasmuch as III undergoes dehydrohalogenation in spite of the four adjacent ethoxyl substituents.

The ketene acetal V reacts with ethanol to yield ethyl ortho-β,β-diethoxypropionate (VI) and with bromine to yield ethyl bromide and ethyl α-bromo-β,β-diethoxypropionate (VII).

$$V \xrightarrow[H^+]{C_2H_5OH} \underset{VI}{(C_2H_5O)_2CHCH_2C(OC_2H_5)_3}$$

$$V \xrightarrow{Br_2} C_2H_5Br + \underset{VII}{(C_2H_5O)_2CHCHBrCOOC_2H_5}$$

In the sequence of reactions used for the preparation of IV, the bromoethoxyacetal (I) was obtained in a 36% over-all yield from acrolein and was converted to II in 74% yield. The bromination of II, followed by the conversion of the intermediate dibromo derivative, to III was accomplished in 64% yield. Considerable difficulty was encountered in the bromination of III and a variety of procedures were tried without success. It is essential that the hydrogen bromide formed in this reaction be removed to prevent its destructive effect on the acetal groups. This cannot be accomplished by treating III with bromine in the presence of pyridine as the temperature of bromination is higher than that required for the oxidative-condensation of the amine by the bromine.[2] However, the use of preformed pyridine perbromide[2] as the brominating agent gave reproducible yields of 66% of the dibromoacetal (IV).

Experimental

α-Bromo-β-ethoxypropionaldehyde diethylacetal (I) was prepared in 41% yield by the method of Fischer[3] from acrolein dibromide. It boiled at 105–115° (19 mm.); $n^{25}D$ 1.4593. I was converted to β-ethoxyacrolein diethylacetal (II), b.p. 99–104° (25 mm.), $n^{25}D$ 1.4220, d^{25}_4 0.905, in 74% yield by the procedure of Price and Moos.[4]

Bromomalonaldehyde Tetraethylacetal (III).—The procedure used was a modification of that previously reported by Pailthorpe.[5] To 87.6 g. (0.50 mole) of β-ethoxyacrolein diethylacetal (II) in 150 ml. of carbon tetrachloride, 70.2 g. (0.44 mole) of bromine in 80 ml. of carbon tetrachloride was added dropwise until a red color persisted; a temperature of 0–10° was maintained during the addition. Then 40 g. of precipitated calcium carbonate was added, followed by 270 ml. (4.6 mole) of absolute ethanol. The mixture was stirred and refluxed for thirty minutes, after which it was cooled and filtered to remove suspended solids. The filtrate was neutralized rapidly with sodium bicarbonate solution,

---

(1) McElvain and Walters, This Journal, **64**, 1963 (1942).

(2) McElvain and Goese, *ibid.*, **65**, 2227 (1943).

(3) Fischer, *Ber.*, **30**, 3056 (1897).

(4) Price and Moos, This Journal, **67**, 207 (1945).

(5) Pailthorpe, M.S. Thesis, University of Wisconsin, 1947.

the carbon tetrachloride layer separated, and the aqueous layer washed twice with ether. The ether washings and the organic layer were combined and dried over anhydrous sodium sulfate for one hour, after which solvents were removed at water-pump pressure. Distillation through an eight-inch Vigreux column gave 95 g. (64%) of III, b.p. 95–102° (0.4 mm.), $n^{25}\text{D}$ 1.4448, d^{25}_4 1.208.

Anal. Calcd. for $C_{11}H_{23}O_4Br$: Br, 26.8; C_2H_5O, 60.2. Found: Br, 25.5; C_2H_2O, 59.8.

Dibromomalonaldehyde Tetramethylacetal (IV).—To 107 g. (0.36 mole) of III was added 90 g. (0.38 mole) of pyridine perbromide, prepared by mixing equimolecular quantities of pyridine and bromine, each dissolved in carbon tetrachloride, followed by separating, washing and drying the precipitate. The mixture was stirred and heated to 90° for 2.5 hours, during which the red color of the perbromide gradually turned to brown hydrobromide. After cooling and decanting the thick liquid, ether washes of the residue were added to the decantate and the solution dried over anhydrous sodium sulfate. Solvents were removed under diminished pressure and the residue fractionated through an eight-inch Vigreux column to give two main fractions: (a) 10.3 g., b.p. 90–115° (0.5 mm.), $n^{25}\text{D}$ 1.4737, and (b) 81.2 g., b.p. 115–125° (0.5 mm.), $n^{25}\text{D}$ 1.4764. Fraction (b) represented a 60% yield of IV. By adding fraction (a) to the next run, an additional 6% of IV could be recovered.

Anal. Calcd. for $C_{11}H_{22}O_4Br_2$: Br, 42.3. Found: Br, 42.6.

Reaction of IV with Potassium *t*-Butoxide.—Potassium *t*-butoxide was prepared by dissolving metallic potassium in excess *t*-butyl alcohol, and then evaporating the excess alcohol at diminished pressure. A white powder with about 65% theoretical basicity was obtained, indicating that a mole of alcohol was still present with each mole of base. This product was used in the subsequent experiments.

When the dibromoacetal (IV) was caused to react with two equivalents of this base, the major product isolated was the monobromoacetal III (29%), together with a small quantity (10%) of the ketene acetal (V) described below. In the hope of improving the recovery of dehalogenated material, the reaction of IV with the base was carried out in two steps. In a 100-ml. three-necked flask fitted with thermometer, stirrer and reflux condenser protected by a calcium chloride tube, 19.0 g. (0.05 mole) of the dibromoacetal (IV) was added to 9.1 g. (0.05 mole of base) of potassium *t*-butoxide. Upon warming and stirring an exothermic reaction occurred; the temperature was kept at 75–85° for about nine hours, during which time a finely divided precipitate of potassium bromide appeared in the brown reaction mixture. This suspension was cooled, diluted with 100 ml. of anhydrous ether, and centrifuged. The decantate was concentrated at water-pump pressure and then fractionated through an eight-inch Vigreux column to give the following fractions: (a) 1.7 g., b.p. 60–85° (0.2 mm.), $n^{25}\text{D}$ 1.4320; (b) 6.6 g., b.p. 85–95° (0.2 mm.), $n^{25}\text{D}$ 1.4463; (c) 2.5 g., b.p. 95–120° (0.2 mm.), $n^{25}\text{D}$ 1.4693. A residue of about 2 g. of tar remained in the flask.

Fraction (a) showed considerable unsaturation to bromine, while fraction (b) showed only a slight test for unsaturation. Fraction (b) was refractionated to give a middle-cut, b.p. 85–86° (0.2 mm.), $n^{25}\text{D}$ 1.4442, corresponding to bromomalonaldehyde tetraethylacetal (III).

Anal. Calcd. for $C_{11}H_{23}O_4Br$: C_2H_5O, 60.2; Br, 26.7. Found: C_2H_5O, 59.0; Br, 24.3.

The crude fractions represented a 44% yield of III, based on the refractive indices and bromine absorption.

Diethoxymethylketene Diethylacetal (V).—A slurry was made from 32.3 g. (0.11 mole) of the crude product of III (isolated from the reaction of IV with one equivalent of base) and 29.0 g. (0.17 mole of base) of potassium *t*-butoxide. This mixture was stirred for seven hours while being heated at 95–100°. After cooling, 200 ml. of anhydrous ether was added, the mixture centrifuged, and the decantate concentrated at reduced pressure. Distillation through an eight-inch Vigreux column gave these fractions: (a) 0.9 g., b.p. 70–80° (0.8 mm.), $n^{25}\text{D}$ 1.4200; (b) 11.5 g., b.p. 83–90° (0.8 mm.), $n^{25}\text{D}$ 1.4285; (c) 1.6 g., b.p. 90–108° (0.8 mm.), $n^{25}\text{D}$ 1.4329.

Fractions (b) and (c) represent a 46% yield of V. To ensure complete removal of halogen and to give a pure sample for analysis, the crude fractions above were combined with a small amount of potassium *t*-butoxide and fractionated through a ten-inch Fenske column. The major fraction was V, obtained as a colorless liquid, b.p. 104–105° (9.5 mm.), $n^{25}\text{D}$ 1.4269, d^{25}_4 0.941.

Anal. Calcd. for $C_{11}H_{22}O_4$: C, 60.50; H, 10.16; C_2H_5O, 82.6; *M*D, 59.1. Found: C, 60.13; H, 10.08; C_2H_5O, 81.7; *M*D, 59.6.

When the above dehydrohalogenation procedure was applied to a sample of III prepared from II, a 59% yield of V was obtained.

Ethyl Ortho-β,β-diethoxypropionate (VI).—A solution of 3.1 g. of diethoxymethylketene diethylacetal (V) and 10 ml. of absolute ethanol was prepared with no evidence of reaction, but when 0.5 ml. of ethanol containing a trace of hydrogen chloride was added, a temperature rise of about 6° followed. The mixture was warmed to about 50° for ten minutes and allowed to cool to room temperature for one hour. After the alcohol was removed at diminished pressure, the residue was distilled through an eight-inch Vigreux column to give 2.2 g. (60%) of VI as a colorless liquid, b.p. 103–106° (6 mm.), $n^{25}\text{D}$ 1.4140, d^{25}_4 0.944.

Anal. Calcd. for $C_{13}H_{28}O_5$: C, 59.06; H, 10.68; C_2H_5O, 85.2; *M*D, 70.5. Found: C, 59.23; H, 10.64; C_2H_5O, 84.7; *M*D, 70.0.

Ethyl α-Bromo-β,β-diethoxypropionate (VII).—A solution of 2.11 g. (0.0097 mole) of diethoxymethylketene diethylacetal (V) in 10 ml. of carbon tetrachloride was cooled in an ice-bath and treated with a solution of bromine in carbon tetrachloride; 1.20 g. (0.0075 mole) of bromine was absorbed before a yellow color persisted. The solution was then carefully distilled through an eight-inch Vigreux column to give 0.7 g. (66%) of ethyl bromide, b.p. 30–60°, $n^{25}\text{D}$ 1.4270. The remaining solvent was removed under diminished pressure, and the residue distilled to give as the major fraction 1.75 g. (67%) of VII, a colorless liquid, b.p. 108–115° (6.5 mm.), $n^{25}\text{D}$ 1.4471. The constants reported for this compound[6] are b.p. 113–114° (9 mm.), $n^{20}\text{D}$ 1.4458.

Anal. Calcd. for $C_9H_{17}O_4Br$: C_2H_5O, 50.2; Br, 29.7. Found: C_2H_5O, 48.5; Br, 29.6.

MADISON, WIS.

RECEIVED JUNE 29, 1950

---

[6] Oroshnik and Spoerri, THIS JOURNAL, **67**, 721 (1945).