The infrared spectrum of suberoin was similar to that of sebacoin[3] showing strong absorption at 2.92 and 5.90 μ, OH and CO stretching, respectively.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.55, 67.39; H, 9.88, 10.01.

Suberoin semicarbazone, m.p. 179.5–180°, was obtained in 70% yield after two recrystallizations from ethanol.

Anal. Calcd. for $C_9H_{17}O_2N_3$: C, 54.25; H, 8.60; N, 21.09. Found: C, 54.23, 54.50; H, 8.53, 8.62; N, 21.02, 21.06.

Suberoin *p*-phenylazobenzoate after purification by chromatographing and recrystallizing showed m.p. 128.5–129°.

Anal. Calcd. for $C_{21}H_{22}O_3N_2$: C, 71.99; H, 6.33; N, 7.99. Found: C, 72.01, 72.03; H, 6.36, 6.40; N, 8.08, 8.10.

Suberil (1,2-Cycloöctanedione).—This α-diketone was obtained in approximately the same yield by the oxidation of suberoin using either of two reagents. Oxidation of 21.3 g. (0.15 mole) of suberoin using 60 g. (0.30 mole) of cupric acetate monohydrate in 10 ml. of methanol and 150 ml. of 50% acetic acid[8] gave 64–70% of crude suberil showing b.p. 65.5–77° (3 mm.). Oxidation of 21.3 g. (0.15 mole) of suberoin using 28 g. (0.06 mole) of bismuth oxide in 75 ml. of acetic acid[9] gave a 62% yield of suberil. Upon redistillation the pure diketone showed b.p. 68.8–69.5° (3 mm.). Freezing point determinations of the solid diketone after four redistillations were unsatisfactory.

The infrared spectrum of suberil was similar to those of sebacil[3] and 1,2-cyclononanedione[1] showing very strong absorption at 5.86 μ, CO stretching, and weak absorption at 2.90–2.98 μ, OH stretching.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.65, 68.85; H, 8.65, 8.78.

The quinoxaline derivative of suberil was prepared by the method of Leonard and Mader.[10] It was obtained in 75% yield after recrystallizations from ethanol; m.p. 120.2–120.7°.

Anal. Calcd. for $C_{14}H_{16}N_2$: C, 79.20; H, 7.60; N, 13.20. Found: C, 79.06, 79.00; H, 7.62, 7.60; N, 13.20.

Oxidation of suberil with periodic acid afforded suberic acid, m.p. 140–141°, in 59% yield. A mixed m.p. determination with an authentic specimen of suberic acid showed no depression.

The dihydrazone of suberil was prepared following the method described for sebacil dihydrazone.[3] The crude dihydrazone, m.p. 103–104.5°, was obtained in 93% yield. Careful recrystallization from benzene, keeping the temperature below 60°, gave the pure hydrazone (69%), m.p. 105–106°.

Anal. Calcd. for $C_8H_{16}N_4$: C, 57.11; H, 9.59; N, 33.30. Found: C, 57.40, 57.12; H, 9.46, 9.58; N, 33.00.

Cycloöctyne.—The preparation and purification procedures were similar to those for cyclononyne[1] with the following modifications. The reaction mixture was heated at 80° with a water-bath, length of heating was reduced to 5–8 hr. depending upon cessation of evolution of nitrogen, and all distillations were carried out under nitrogen.

The impure distilled acetylene was obtained in 9.3% yield. After purification by chromatographing, the pure acetylene showed b.p. 157.5–158° (740 mm.) (micro method), $n^{20}\text{D}$ 1.4850 and d^{20}_4 0.868 (micro method).

The infrared spectrum of cycloöctyne was similar to those of cyclononyne and cyclodecyne[6] showing weak absorption at 4.53 μ characteristic of C≡C stretching.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.83, 89.00; H, 10.93, 11.09.

Quantitative reduction in acetic acid using Adams catalyst required 102% of two molar equivalents of hydrogen.

Ozonolysis of 0.4 g. of cycloöctyne following the procedure used for cyclononyne[1] gave 0.43 g. of an acidic product which showed a m.p. of 138.5–140° after two recrystallizations. When this acidic product was mixed with an authentic specimen of suberic acid the m.p. was not depressed.

Hydration of 0.2 g. of cycloöctyne using the procedure described for cyclononyne[1] gave 0.2 g. of an oil of camphor-like odor. This oil was converted to a semicarbazone having m.p. 170–171°. The m.p. of a mixture of this semicarbazone and authentic cycloöctanone semicarbazone was not depressed.

When treated with phenyl azide, according to the procedure of Ziegler and Wilms,[6] cycloöctyne reacted explosively forming a viscous liquid product which was not characterized.

ITHACA, N. Y.

---

[8] P. Ruggli and P. Zeller, *Helv. Chim. Acta*, **28**, 741 (1945).

[9] W. Rigby, *J. Chem. Soc.*, 793 (1951).

[10] N. J. Leonard and P. M. Mader, THIS JOURNAL, **72**, 5388 (1950).

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

Some Reactions of 1,2-Diethoxyethylene and its Bromo Derivatives

BY S. M. McELVAIN AND CHARLES H. STAMMER[1]

RECEIVED JANUARY 12, 1953

The bromination product (II) of 1,2-diethoxyethylene (I) has been converted to bromodiethoxyethylene (III), which is found to add either ethanol or water in both possible directions. The intermediate addition product (IV), identical with the product from the addition of hydrogen bromide to ethoxyketene acetal, is found to be too unstable to isolate. III may be reconverted to I *via* the lithium derivative or to the dibromo derivative (VIII) of I. The distinctive pyrolysis behaviors of II, III and VIII are described. Acyl halides and phthalic anhydride promote the polymerization of I, but maleic anhydride produces a 1:1 copolymer which retains the functional groups of the monomers. Benzoyl peroxide adds stoichiometrically to I to yield the two stereoisomeric 1,2-dibenzoyloxy-1,2-diethoxyethanes (XI).

In an earlier paper[2] describing the preparation and properties of 1,2-diethoxyethylene (I), a few of the reactions that were used to establish its structure were indicated. The present paper reports a further study of the reactions of this compound, particularly the preparation and properties of its bromo derivatives.

The addition of bromine to I was found in the earlier experiments to occur rapidly at 0–10°, but attempts to isolate the dibromo compound (II) were unsuccessful because of its rapid decomposition into hydrogen bromide and an intractable tar; however, II could be immediately hydrolyzed to glyoxal in high yield.[2] A further study of this bromination reaction has shown that II separates as a white solid when a petroleum ether solution of I is treated with bromine at −20°. This product is unstable at room temperature and attempts to purify it by recrystallization gave material of variable melting point. II reacts with ethanol to yield glyoxal tetraethylacetal[3] (92%); with potas-

---

[1] Wisconsin Alumni Research Foundation Research Assistant, 1951–1952.

[2] S. M. McElvain and C. H. Stammer, THIS JOURNAL, **73**, 915 (1951).

[3] *Cf.* R. C. Schreyer, *ibid.*, **73**, 2962 (1951).

sium *t*-butoxide at 0° it is converted to bromodiethoxyethylene (III) in 80% yield.

$$\underset{\text{I}}{C_2H_5OCH{=}CHOC_2H_5} \xrightarrow{Br_2} \underset{\text{II}}{C_2H_5OCHBrCHBrOC_2H_5} \xrightarrow{KOC_4H_9(t)} \underset{\text{III}}{C_2H_5OCH{=}CBrOC_2H_5}$$

The bromo compound III was resistant to further dehydrobromination by potassium *t*-butoxide and other strong bases. The reaction of III with ethanol was of considerable interest because one of the possible addition products (IV) would have the structure of an intermediate postulated for the addition of hydrogen bromide to an ethoxyketene acetal. It was found that ethanol containing a trace of acid added to III in both possible directions (a) to form ethyl ethoxyacetate (V) and (b) to form the bromoether acetal (VI). Compared to I the reaction of III with ethanol is quite slow, requiring about 3 hours for completion. If the reaction mixture were titrated to neutrality with alcoholic sodium ethoxide after the alcohol addition was complete, the ethoxy ester (V) and glyoxal tetraethylacetal (VII) were obtained in 61 and 35% yields, respectively. Apparently the intermediate (IV), in contrast to VI, which may be separated from the reaction mixture if the sodium ethoxide is not used, does not exist for sufficient time to react with the sodium ethoxide to form the expected orthoester. This observation indicates that an unstable intermediate of the type of IV could be formed when hydrogen bromide adds to a ketone acetal.[4]

$$\text{III} \xrightarrow[H^+]{C_2H_5OH} \begin{cases} \xrightarrow[61\%]{(a)} \underset{\text{IV}}{[C_2H_5OCH_2C(OC_2H_5)_2Br]} \longrightarrow \underset{\text{V}}{C_2H_5OCH_2COOC_2H_5} + C_2H_5Br \\ \xrightarrow[35\%]{(b)} \underset{\text{VI}}{(C_2H_5O)_2CHCHBrOC_2H_5} \xrightarrow{NaOC_2H_5} \underset{\text{VII}}{(C_2H_5O)_2CHCH(OC_2H_5)_2} \end{cases}$$

By more indirect evidence it was shown that water was added to III in a manner similar to ethanol. After refluxing III with water for an hour, titration of the homogeneous solution for both acidity and bromide ion showed the presence of two moles of acid for each bromide ion. From a similar run a 17% yield of glyoxal 2,4-dinitrophenylhydrazone was isolated from the aqueous solution. It appears therefore that water adds to III mainly *via* (a) to yield ethoxyacetic acid, ethanol and hydrogen bromide and to a small extent *via* (b) to yield glyoxal, which titrates as glycolic acid with base, ethanol and hydrogen bromide.

Bromodiethoxyethylene (III) reacts with lithium butyl to give a lithium compound that is converted by ethanol to a diethoxyethylene with essentially the same physical properties as those of the original sample of I from which III was prepared. This series of reactions, I → II → III → I, should have produced the other stereoisomer of I if the original sample of I was a single compound,[5] and *trans* addition and *trans* elimination in the first and second reactions of the series is assumed. The identity of these two samples of I indicates either that the properties of the *cis* and *trans* forms of I are essentially the same or that I as produced from the dealcoholation of ethoxyacetal is a mixture of approximately equal parts of these stereoisomers.[6]

Bromodiethoxyethylene (III) absorbs bromine quantitatively at −20° to yield the tribromo compound (VIII), which, in contrast to the dibromo compound (II), gave no evidence of decomposition at room temperature. Potassium *t*-butoxide converted VIII to dibromodiethoxyethylene (IX) in 74% yield. The structure of IX was shown by hydrolysis to ethyl glyoxalate (X), a reaction requiring somewhat more strenuous conditions than the hydrolysis of III.

$$\text{III} \xrightarrow{Br_2} \underset{\text{VIII}}{C_2H_5OCHBrCBr_2OC_2H_5} \xrightarrow{KOC_4H_9} \underset{\text{IX}}{C_2H_5OCBr{=}CBrOC_2H_5} \xrightarrow{H_2O} \underset{\text{X}}{OCHCOOC_2H_5}$$

Both III and IX are enol ethers of acyl bromides and as such bear a formal relationship to the ketene acetals, which are enol ethers of esters. The addition reactions of III and IX with ethanol and water, while similar, differ in degree. In the case of the unsymmetrical structure (III) the bromo substituent is not able to completely control the direction of addition as does the ethoxyl substituent of a ketene acetal.

The bromo compounds II, III and IX showed distinctive behaviors when subjected to pyrolysis. The most unstable compound (II) rapidly pyrolyzed at 150° although decomposition began much below that temperature. The reaction products were hydrogen bromide (45%), ethyl bromide (77%) and V (18%). The relatively high yield of hydrogen bromide indicates the intermediate formation of III. The pyrolysis of the latter compound occurred at 150–170° and yielded ethylene (15%), ethyl bromide (74%), V (26%) and a large amount of polymeric tar. The presence of ethylene among the pyrolysis products indicates a pyrolysis of III in the manner of vinyl ethyl ether[7] into ethylene

---

[4] An alternative intermediate in the reactions of hydrogen bromide with the ketene acetal is the onium ion $C_2H_5OCH_2\overset{\oplus}{C}(OC_2H_5)_2 \leftrightarrow C_2H_5OCH_2C(OC_2H_5){=}\overset{\oplus}{O}C_2H_5$, which would be converted by Br^- to V and ethyl bromide. A comparable intermediate could conceivably be formed in the reaction of III with acidic ethanol, *e.g.*, $C_2H_5OCH_2\overset{\oplus}{C}BrOC_2H_5 \leftrightarrow C_2H_5OCH_2C(Br){=}\overset{\oplus}{O}C_2H_5$, but the reaction of this onium ion with ethanol should yield either IV or diethyl ether, neither of which was observed.

[5] *Cf.* D. Y. Curtin and E. E. Harris, THIS JOURNAL, **73**, 4519 (1951).

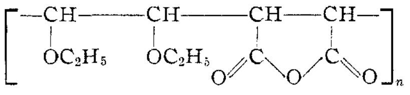
[6] Samples of I from the dealcoholation of ethoxyacetal had a b.p. 130–133° and $n^{25}D$ 1.4195–1.4210. The inconstancy of these properties indicated a mixture of *cis* and *trans* isomers. A sample $n^{25}D$ 1.4209 was fractionated through an all-glass 92-plate concentric tube column and two fractions boiling within the range 132–133° collected; the $n^{25}D$ of these fractions were 1.4172 and 1.4219. The infrared spectra of these fractions showed significant differences in the 11 and 13.6 μ regions. Jones (THIS JOURNAL, **72**, 5322 (1950)) points out that *trans*-ethylene structures characteristically absorb in the 10.4 μ region while the *cis* structures absorb in the 14.8 μ region.

[7] A. T. Blades and G. W. Murphy, THIS JOURNAL, **74**, 1039 (1952), report data to indicate that the pyrolysis of this ether into ethylene and acetaldehyde is an intramolecular decomposition.

and ethoxyacetyl bromide. This acyl halide then promotes the polymerization of III as other acyl halides cause the polymerization of I (see below); the ethanol eliminated from the polymer converts the ethoxyacetyl bromide to the ester V. The dibromodiethoxyethylene (IX) underwent pyrolysis at 170–180° to yield ethylene (31%), bromoethoxyacetyl bromide ($C_2H_5OCHBrCOBr$) (53%) and ethyl bromide (50%). The first two products result from the same type of decomposition noted above for III. The yield of ethyl bromide indicates that about half of IX must have decomposed into this halide and bromoethoxyketene $C_2H_5OCBr{=}C{=}O$, the polymerization of which would account for the tarry residue from this pyrolysis.

As a further comparison of the properties of diethoxyethylene (I) with those of its unsymmetrical isomer, ketene diethylacetal, the reaction of I with certain acyl halides and acid anhydrides was studied. Benzoyl chloride, which was found[8] to react with ketene acetal at 100°, does not react with I below the reflux temperature of the mixture. The reaction products from a 1:1 reaction mixture were ethyl benzoate (79%), ethyl chloride (43%), hydrogen chloride (9%) and benzoic acid (4%). The remainder of the reaction mixture was a polymeric tar. The course of reaction appears to be a catalytic polymerization of I by the acyl chloride followed by the reaction of the main portion of the acyl chloride with the ethanol eliminated from the polymer. The hydrogen chloride formed in this reaction then converts a portion of the ethoxyl groups of the polymer or of I to ethyl chloride. This reaction course is substantiated by the products obtained from the reaction of I and benzoyl chloride in a 20:1 ratio: I (40%), ethanol (6%), ethoxyacetal (9%), and polymer representing unrecovered I. Acetyl chloride showed a similar reaction pattern with I. Only ethanol and tar were produced from the reaction of phthalic anhydride with I; in this case the ethanol evolved from the polymer yields a non-volatile acid ester with the anhydride.

Maleic anhydride, which yields 3,5-diethoxy-1,6-dihydrophthalic anhydride with ketene acetal,[9] reacts with I in ether solution to form an amorphous solid polymer in 82% yield. This polymer was slowly soluble in 0.1 *N* alkali; ethoxyl content indicated that it contained a 1:1 ratio of I and maleic anhydride as in XI, but the saponification equivalent indicated only 1.5 carboxyl groups per polymer unit, which suggests a more complex structure than XI. The molecular weight (Rast), of this polymer was approximately 1500.



XI

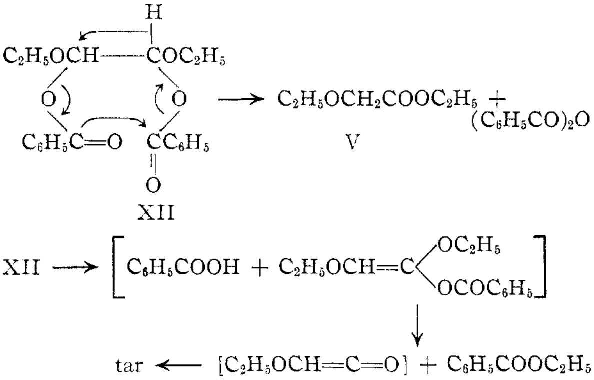
The polymerization of I by acyl halides prompted a study of its reaction with benzoyl peroxide. When I was heated with catalytic amounts of this reagent, there was no evidence of polymerization. However, when equimolecular quantities of these reactants were mixed in benzene solution, an exothermic reaction occurred. From this reaction was isolated the two stereoisomeric forms of XII. One of these forms, a solid, m.p. 65–68°, was obtained in 67% yield, while the other was an oil and amounted to a 22% yield. Each of these compounds had the same ethoxyl content and yielded approximately the same amounts of benzoic acid and glyoxal on hydrolysis.

$$I + (C_6H_5COO)_2 \longrightarrow$$

$$\underset{\text{XII}}{C_2H_5OCH(OCOC_6H_5)CH(OC_2H_5)OCOC_6H_5} \xrightarrow{H_3O^+}$$

$$2C_2H_5OH + 2C_6H_5COOH + OCHCHO$$

The solid isomer could be distilled without decomposition at 171–176° (0.2 mm.). However, when heated at atmospheric pressure, it pyrolyzed at 275–300° to ethyl ethoxyacetate (71%), benzoic anhydride (67%), ethyl benzoate (22%) and benzoic acid (27%). The formation of these products may be rationalized by the reactions



In contrast to the solid isomer the liquid isomer of XII decomposed when heated to 100°. The only products separated from this decomposition in sufficient quantities to identify were benzoic acid (37%) and 14% of the solid form of XII, which probably was dissolved in the liquid isomer before its pyrolysis.

Experimental

1,2-Dibromo-1,2-diethoxyethane (II).—A solution of 2 g. of diethoxyethylene[2] (I) in 10 ml. of petroleum ether (b.p. 40–60°) was placed in a 6″ sample tube fitted with a rubber stopper holding a microburet and calcium chloride tube. The solution was cooled in a Dry Ice–acetone-bath maintained at −20° and one equivalent of bromine was added slowly from the buret. After removal of the supernatant liquid through a filter stick, the extremely hygroscopic white crystalline dibromide weighed 4.12 g. (86.8%), m.p. 32–40° (melting points were taken in rapidly filled and sealed capillaries). After three recrystallizations from 5:2 petroleum ether (b.p. 40–60°)–ether, it weighed 0.97 g., m.p. 43–48°.

Anal. Calcd. for $C_6H_{12}O_2Br_2$: Br, 57.9. Found: Br, 56.7.

Other attempts at purification of this compound led to material melting in the range of 37–56°.

Reactions of II. (a) Ethanolysis.—To a solution of 10 g. (0.086 mole) of I in 75 ml. of dry ether stirred in a 250-ml. 3-necked round-bottomed flask fitted with a condenser (attached to a 30-cm. calcium chloride tube at the top) and microburet and cooled to −20° in a Dry Ice–acetone-bath was added 4.2 ml. (95%) of bromine. The Dry Ice–acetone-bath was replaced by an ice-bath and 20 ml. (0.34 mole) of dry ethanol was added over a period of 20 minutes to the reaction mixture. After 25 minutes at 0°, the solution was refluxed 10 minutes and, after cooling, was neutralized to

---

[8] S. M. McElvain and D. Kundiger, This Journal, **64**, 254 (1942).

[9] S. M. McElvain and H. Cohen, *ibid.*, **64**, 260 (1942).

phenolphthalein by adding a dilute sodium ethoxide solution. Distillation of this solution through a 25-cm. Podbielniak column afforded 15.9 g. (0.077 mole, 92.2%) of the tetraethylacetal of glyoxal, b.p. 71–73° (7 mm.), n^{25}D 1.4040.

(b) **Pyrolysis.**—After bromination of 10 g. of I at −20° in 35 ml. of dry ether, the solution was transferred to a 25-ml. pear-shaped flask and the solvent removed under a mild vacuum. The white crystalline residue was then heated for one hour at 125–145° in an oil-bath under a reflux condenser attached through a Dry Ice–acetone cold trap to a water trap. After this heating period, the reflux condenser was replaced by a 25-cm. Podbielniak column attached through a still head to the same cold trap-water trap system. Distillation afforded 6.86 g. (77.2%) of ethyl bromide, 1.96 g. (18.1%) of ethyl ethoxyacetate and tar. Titration of the water trap solution showed the presence of 2.98 g. (45.3%) of hydrogen bromide.

1-Bromo-1,2-diethoxyethylene (III).—In a 3-necked 500 ml. round-bottomed flask fitted with stirrer, condenser holding a calcium chloride tube, and 50-ml. buret was placed a solution of 80 g. of I in 60 ml. of dry ether. After cooling the stirred solution in a Dry Ice–acetone-bath maintained at −25°, 32.1 ml. (91%) of bromine was added over a period of 1.5 hours. Under these conditions a considerable amount of the product precipitated as a white solid. The mixture became homogeneous when 100 ml. of dry benzene was added and the temperature was allowed to rise to 0° by placing it in an ice-bath. This solution was then drawn by reduced pressure into a stirred slurry of 107.5 g. (0.96 mole) of vacuum-dried potassium *t*-butoxide in 300 ml. of benzene over a period of 1 hour. The reaction mixture was then allowed to stand for 1.5 hours at 0°. The solution was then concentrated under diminished pressure at 40–50° to approximately 350 ml. and transferred to a 500-ml. round-bottomed flask without removal of the precipitated potassium bromide. After removal of the remaining solvent the product was distilled through a 25-cm. Podbielniak column. The product III boiled at 56–58° (7 mm.), n^{25}D 1.4609, d^{24}_{4} 1.278, and weighed 98.5 g. (80.9%); M_r calcd. 40.492, M_r found 41.781.

Anal. Calcd. for $C_6H_{11}O_2Br$: C_2H_5O, 46.3; Br, 40.6. Found: C_2H_5O, 47.2; Br, 40.1.

Reactions of III. (a) **With Ethanol.**—In a flame-dried 100-ml. round-bottomed flask fitted with a coil condenser (attached at the top to a 30-cm. calcium chloride tube) and having two side arms, one containing a thermometer and the other an inlet tube for hydrogen chloride, was placed exactly 30 ml. of anhydrous ethanol. Hydrogen chloride was passed into the ethanol until it contained 0.13 g. as determined by the removal and titration of a 1-ml. aliquot. Addition of 35 g. (0.18 mole) of III to this solution caused no increase in the temperature until 1.5 hours later when it rose abruptly to 60° and was prevented from increasing further only by cooling the flask in an ice-bath. When the reaction mixture had cooled spontaneously to room temperature (total time, 2.3 hours), it was neutralized to a phenolphthalein end-point by addition of 30.2 ml. of 2.22 *N* sodium ethoxide–ethanol solution (68 meq., 37.2%). Distillation of this solution through a 25-cm. Helipak column afforded 10.32 g. (52.7%) of ethyl bromide, 14.84 g. (61.5%) of ethyl ethoxyacetate and 13.04 g. (35.6%) of glyoxal tetraethylacetal, b.p. 71–73° (7 mm.), n^{25}D 1.4034.

(b) **With Water** (i).—When 0.137 g. of III was refluxed with 15 ml. of distilled water for one hour, titration of the solution to a phenolphthalein end-point required 11.2 ml. of 0.0958 *N* sodium hydroxide solution (152% of one equivalent). Titration by the Volhard method showed the presence of 0.54 meq. (76%) of bromide ion. (ii) After refluxing a mixture of 0.5 g. of III with 10 ml. of distilled water for 2 hours, the cooled solution was added to a boiling solution of 1.0 g. of 2,4-dinitrophenylhydrazine and 2 ml. of concentrated hydrochloric acid in 20 ml. of absolute ethanol. The mixture was refluxed for 45 minutes and cooled, whereupon 0.18 g. (16.7%) of glyoxal bis-2,4-dinitrophenylhydrazone, m.p. 306–308°, separated and was collected on a filter. After recrystallization from pyridine, it melted at 315–316°.

(c) **Pyrolysis.**—To a 50-ml. round-bottomed flask attached through a 25-cm. Podbielniak column and still head to a series of three 15-cm. test-tubes cooled in a water-bath to 10° and each containing about 2 ml. of bromine and 5 ml. of water was added 41.4 g. of III. The flask was heated in an oil-bath at 150–175° until distillation of ethyl bromide (18.0 g., 77.4%) stopped (3 hours). Fractionation of the residue through the column gave 7.49 g. (26.6%) of ethyl ethoxyacetate and a black intractable tar. When the bromine trap contents were washed with 10% sodium hydroxide solution, dried over anhydrous magnesium sulfate and distilled, 6.0 g. (15%) of ethylene dibromide, b.p. 129–131°, n^{25}D 1.5330, was obtained.

(d) **With *n*-Butyllithium.**—To an unfiltered solution of approximately 0.24 mole of *n*-butyllithium dissolved in 100 ml. of ether and stirred in a 250-ml. 3-necked round-bottomed flask fitted with calcium chloride tube and dropping funnel and cooled in a Dry Ice–acetone-bath to −35° was added a solution of 15 g. (0.077 mole) of III in 20 ml. of dry ether over a period of 20 minutes. After another 5 minutes, 10 ml. of dry ethanol was added slowly and the solution was allowed to come to room temperature. It was washed with two 50-ml. portions of water and the organic layer dried over anhydrous magnesium sulfate. After removal of the solvent, fractionation of the residue through a 25-cm. Podbielniak column afforded 5.1 g. (57%) of I, b.p. 130–131°, n^{25}D 1.4208.

(e) **With Bromine.**—A solution of 2.057 g. (10.6 millimoles) of III in 10 ml. of petroleum ether (b.p. 40–60°) was cooled to −20° in a Dry Ice–acetone-bath and 13.1 ml. of an 0.8 *M* bromine solution (99%) in carbon tetrachloride added over a period of 0.5 hour. The product did not precipitate from the solution. When the solution was allowed to come to room temperature there was no discoloration and no fuming.

1,2-Dibromo-1,2-diethoxyethylene (IX).—A solution of 42.1 g. (0.217 mole) of bromodiethoxyethylene (III) in 50 ml. of dry ether was prepared in a 250-ml. 3-necked round-bottomed flask fitted with condenser carrying a 10-cm. calcium chloride tube, stirrer and buret. After cooling the flask in a Dry Ice–acetone-bath maintained at −20°, 10.5 ml. (94.5%) of bromine was added from the buret to the solution over a period of 45 minutes. This solution was added to a slurry of 24.3 g. of potassium *t*-butoxide in 100 ml. of dry benzene over a 45-minute period. The mixture was warmed to 60° for 15 minutes and then the solvent was removed at 50–60° under diminished pressure. Distillation of the residue afforded 44 g. (74.5%) of IX, b.p. 80° (7 mm.), n^{25}D 1.4973, d^{25}_{4} 1.6313; M_r calcd. 48.257, M_r found 49.353.

Anal. Calcd. for $C_6H_{10}O_2Br_2$: Br, 58.6; C_2H_5O, 33.0. Found: Br, 58.2; C_2H_5O, 32.4.

Reactions of IX. (a) **Hydrolysis.**—A mixture of 1.0 g. of IX and 2 ml. of 2 *N* sulfuric acid was refluxed for 80 minutes. The homogeneous solution was added to a solution of 0.73 g. of 2,4-dinitrophenylhydrazine and 2 ml. of concentrated sulfuric acid in 15 ml. of absolute ethanol and, after refluxing for 30 minutes, the solution was concentrated to approximately 15 ml. and cooled. The yellow plates of ethyl glyoxylate 2,4-dinitrophenylhydrazone which precipitated were collected on a filter; yield 0.96 g. (92.8%), m.p. 115–120°. Two recrystallizations of this solid from ethanol containing two drops of concentrated sulfuric acid changed the melting point to 124.5–125.5° (lit.[10] 123–124°).

(b) **Pyrolysis.**—The pyrolysis system consisted of a 25-ml. pear-shaped flask containing a thermometer attached through a 25-cm. Podbielniak column, still-head and Dry Ice–acetone cold trap to a series of four 15-cm. test-tubes each containing approximately 2 ml. of bromine and 5 ml. of water. A 24.8-g. sample of IX was placed in the flask, which was heated in an oil-bath at 180–185° for two hours; during this time the material became black. The contents of the tubes containing bromine were combined and washed with four 25-ml. portions of 10% sodium hydroxide solution; distillation of the remaining organic layer afforded 5.28 g. (30.9%) of ethylene dibromide, b.p. 129–130°, n^{25}D 1.5331. About 2.5 g. (25.3%) of ethyl bromide was collected in the Dry Ice–acetone cold trap. Distillation of the residue through the 25-cm. Podbielniak column yielded 11.8 g. (52.7%) of α-bromo-α-ethoxyacetyl bromide, b.p. 70° (7 mm.), n^{25}D 1.5080, along with small amounts of lower and higher boiling liquids.

Anal. Calcd. for $C_4H_6O_2Br_2$: Br, 65.0; C_2H_5O, 18.3. Found: Br, 65.0; C_2H_5O, 19.0.

Alcoholysis of 1.0 g. of this acyl bromide in the presence of 1.0 g. of 2,4-dinitrophenylhydrazine gave 1.10 g. (71.5%) of the ethyl glyoxylate 2,4-dinitrophenylhydrazone, m.p.

---

(10) C. W. Crane, *et al.*, *J. Chem. Soc.*, 827 (1946).

124–125° after recrystallization from ethanol. A mixed melting point of this derivative with that formed from the hydrolysis product of IX showed no depression.

Reactions of I with Acyl Halides and Acid Anhydrides. (a) Benzoyl Chloride.—(i) A mixture of 10 g. (0.086 mole) of I and 12.26 g. (0.086 mole) of benzoyl chloride was heated to reflux for 4.5 hours under a condenser attached through a Dry Ice–acetone cold trap to a water trap. At the end of this time, 2.39 g. (43%) of ethyl chloride had collected in the cold trap and 0.28 g. (9%) of hydrogen chloride had collected in the water trap. When distilled, the reaction mixture afforded 10.2 g. (79%) of ethyl benzoate, b.p. 113–117° (30 mm.), n^{25}D 1.4988, and 1.7 g. of a fraction, b.p. 106–135° (10 mm.), which crystallized. A black tarry residue (3.8 g.) remained. When the solid fraction was recrystallized from petroleum ether (b.p. 40–60°), 0.40 g. (3.8%) of benzoic acid, m.p. 121–122°, was obtained. (ii) When a mixture of 20 g. (0.172 mole) of I and 1.21 g. (0.0086 mole) of benzoyl chloride was refluxed in the same apparatus as used above for 4.5 hours, about 0.1 g. of ethyl chloride appeared in the cold trap and no hydrogen chloride was collected in the water trap. The black solution was distilled through a 25-cm. Podbielniak column to afford 8.0 g. (40%) of unchanged I, together with lower and higher boiling fractions. These fractions on redistillation yielded 0.28 g. (5.9%) of ethanol, 1.59 g. (9.5%) of ethoxyacetal, b.p. 164–168°, and a residue smelling strongly of ethyl benzoate. From the reaction residue weighing 3.95 g. was distilled 0.97 g., b.p. 150–167° (9 mm.), of a yellow viscous oil containing 58.9% ethoxyl.

(b) With Acetyl Chloride.—When 10 g. (0.086 mole) of I and 6.75 g. (0.086 mole) of acetyl chloride were refluxed for 4.5 hours in the same apparatus as used above, no ethyl chloride or hydrogen chloride was evolved. Distillation of the black reaction mixture through a 25-cm. Podbielniak column gave 3.2 g. (47%) of unchanged acetyl chloride and 4.03 g. (53.1%) of ethyl acetate. The residue was tar weighing 8.27 g.

(c) With Phthalic Anhydride.—In a 25-ml. distilling flask were placed 8.0 g. (0.068 mole) of I and 10.0 g. (0.068 mole) of powdered phthalic anhydride. After heating in an oil-bath at 110–120° for 1 hour, distillation of the mixture yielded 3.86 g. of distillate, b.p. 80–129°, and 14.12 g. of a black tarry residue from which no phthalic anhydride was obtained when heated under diminished pressure. Redistillation of the distillate gave the following fractions: (a) 1.66 g., b.p. 69–79°, n^{25}D 1.3641; (b) 1.17 g., b.p. 79–150°, n^{25}D 1.4062. When 0.25 g. of fraction (a) was treated with 0.65 g. of phenyl isocyanate, heat was evolved and 0.5 g. (55.5%) of ethyl N-phenylcarbamate, m.p. 45–48°, was extracted from the mixture with boiling petroleum ether (b.p. 90–100°). After recrystallization from 50% ethanol, it melted 50–51°; a mixed melting point with an authentic sample showed no depression. Three drops of fraction (b) absorbed about one-third as much bromine as did a similar amount of I, indicating that fraction was a mixture of ethanol and I.

(d) With Maleic Anhydride.—To a stirred solution of 8.44 g. (0.086 mole) of maleic anhydride in 100 ml. of dry ether was added 10 g. (0.086 mole) of I. A yellow color appeared immediately and a white precipitate began to form in 25 minutes. After 16 hours at room temperature, 15.2 g. (82.4%) of the white solid was collected on a filter and washed with ether. The filtrate when distilled afforded only ether and 3.05 g. of dark semi-solid residue. The white product had the following properties: it changed to a brown translucent solid at 175–185° without melting; it showed a molecular weight (Rast) of 1500; it gave a saponification equivalent of 163 (calcd. for the polymer unit X, 107); acidification of the titrated solution from the saponification equivalent determination gave an acid which had a neutral equivalent of 210 and a molecular weight (Rast) of 2000.

Anal. Calcd. for $C_{10}H_{14}O_5$ (polymeric anhydride): C_2H_5O, 42.0. Found: C_2H_5O, 40.2. Calcd. for $C_{10}H_{16}O_6$ (polymeric acid): C_2H_5O, 38.18. Found: C_2H_5O, 37.3.

Reaction of I with Benzoyl Peroxide. (i) 5 Mole Per Cent.—When 5 g. of I and 0.5 g. of benzoyl peroxide were mixed in a 10-ml. flask, heat was evolved and the solution became cloudy. After heating the mixture at 100° for one hour, distillation gave 3.61 g. (72.2%) of unchanged I. The residue weighed 1.65 g. and was partially crystalline.

(ii) 1:1 Molar Quantities.—To a stirred solution of 104.2 g. of benzoyl peroxide in 500 ml. of dry benzene in a 2-l. 3-necked round-bottomed flask, fitted with a condenser (through which was suspended a thermometer dipping into the solution) and dropping funnel, was added 50 g. of I over a 1-hour period. The flask was cooled by a water-bath and the rate of addition of I was adjusted so that the inside temperature did not exceed 35°. After 5 hours at room temperature, the solution gave a negative peroxide test (acetic acid, iodide ion, starch mixture) and the solvent was removed at room temperature at water-pump pressure leaving a waxy residue. This residue was stirred with 150 ml. of petroleum ether (b.p. 40–60°) for 4 hours and the insoluble solid collected on a filter. The filtrate was evaporated in a jet of air. This procedure was repeated twice using 100-ml. portions of petroleum ether to extract the oil from the solid. Finally there remained 84 g. of solid 1,2-dibenzoyloxy-1,2-diethoxyethane (XII), m.p. 60.5–62°, and an oil–solid slurry which afforded another 21.91 g. of solid and 34.40 g. (22.3%) of oily XII. A mixture of oil and solid weighing 7.0 g. was not further separated. Thus the total yield of the solid XII was 105.9 g. (68.6%). Several recrystallizations of this solid from petroleum ether (b.p. 60–68°) changed its melting point to 65–68°.

Anal. Calcd. for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19; C_2H_5O, 25.1. Found: C, 67.25; H, 6.43; C_2H_5O, 27.6.

Reactions of 1,2-Dibenzoyloxy-1,2-diethoxyethane (XII). (a) Hydrolysis.—A mixture of 2.23 g. of 2,4-dinitrophenylhydrazine, 5 ml. of concentrated hydrochloric acid and 40 ml. of absolute ethanol was refluxed until homogeneous and 2.0 g. of XII, m.p. 65–68°, added. After the mixture was refluxed for 1 hour, 2.31 g. (98%) of glyoxal bis-2,4-dinitrophenylhydrazone, m.p. 310–311°, was filtered from the solution. Recrystallization of this solid from pyridine raised the melting point to 315–316°. A mixed melting point of this solid with an authentic sample of glyoxal bis-2,4-dinitrophenylhydrazone showed no depression. The hydrolysis filtrate was made basic with 20% sodium hydroxide solution and extracted with ether. The aqueous solution was then acidified with concentrated hydrochloric acid and 1.2 g. (87.8%) of benzoic acid, m.p. 112–115°, was collected on a filter. One recrystallization from water raised the melting point to 120–121°. The same procedure as used for the hydrolysis of the solid was used for the hydrolysis of 2 g. of the oil. Glyoxal-bis-2,4-dinitrophenylhydrazone was isolated in 85.7% yield and benzoic acid was found in 71% yield.

(b) Pyrolysis.—In a 125-ml. distilling flask attached through a water-cooled 50-ml. round-bottomed flask to a Dry Ice–acetone cold trap was added 63.0 g. of XII, m.p. 65–68°. The distilling flask was heated in a Woods metal-bath at 275–300° for one hour during which time 25.1 g. of distillate was collected leaving 35.7 g. of black residue. Nothing was collected in the cold trap. Fractionation of this distillate through a 25-cm. Podbielniak column yielded 16.6 g. (71.5%) of ethyl ethoxyacetate, b.p. 70–72° (30 mm.), n^{25}D 1.4012, and some higher boiling fractions, which, when dissolved in 25 ml. of petroleum ether (b.p. 60–68°) along with a fraction, b.p. 100–190° (30 mm.), obtained from distillation of the pyrolysis residue, yielded 5.8 g. (27%) of benzoic acid, m.p. 120–121°. Distillation of the mother liquor from this crystallization gave 5.84 g. (22.1%) of ethyl benzoate. The highest boiling fraction, 26.5 g. (66.7%), b.p. 133–135° (0.1 mm.), n^{25}D 1.5808, distilled from the pyrolysis residue, crystallized on seeding with benzoic anhydride, m.p. 42–43.5°. A mixed melting point with an authentic sample showed no depression.

In a 25-ml. distilling flask connected to a bell-shaped fraction cutter containing six 8-cm. test-tubes was placed 14.7 g. of liquid XII. At 0.2 mm. decomposition began at an oil-bath temperature of 95° and six fractions were collected ranging in boiling point from 52 to 170°. Two fractions boiling between 93 and 130° yielded 2.0 g. (37.2%) of benzoic acid, m.p. 120–121°, on crystallization. The highest boiling fraction yielded 1.94 g. (13.2%) of the solid XI on crystallization. A mixed melting point of this sample with an authentic sample showed no depression. The remaining fractions showed no constancy of physical properties and were too small to purify further.

Madison, Wisconsin