through a 25-cm. Podbielniak column yielded 7.2 g. (17%), of 2,3-dibromobutane, b.p. (no decomposition) 153–155° (741 mm.), n^{25}_D 1.5094; reported[22] b.p. of mixture of *dl* and *meso*, 157–158°. For comparison, a sample of dibromoisobutylene prepared from isobutylene showed a boiling point of 145–147° (738 mm.) with decomposition.

Removal of the volatile material from the reaction vessel at 0.5 mm. pressure yielded 66.3 g. of distillate and 3.7 g. of dark residue. Distillation of the volatile material through an efficient true-bore annular space column yielded, in addition to recovered *n*-butyl bromide, 2.8 g. (15%) of *n*-butyl chloride, 3.6 g. (18%) of methyl isobutyrate, and 23.4 g. (74%) of methyl α,α-dimethylcaproate, the major portion of which boiled at 164–167° (742 mm.), n^{25}_D 1.4121. Refractionation through a 25-cm. Heli-Pak column yielded an analytical sample of **methyl α,α-dimethylcaproate** (XIV), b.p. 168.5° (740 mm.), n^{25}_D 1.4124, d^{25}_4 0.8707.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.46; OCH_3, 19.6; MR_D, 44.73. Found: C, 68.25; H, 11.41; OCH_3, 16.1; MR_D, 45.22.

Overnight saponification of 5.5 g. of XIV in alcoholic potassium hydroxide yielded 3.0 g. (60%) of α,α-dimethylcaproic acid, b.p. 216–220° (726 mm.), n^{25}_D 1.4240; reported[23a] b.p. 210–218°. Upon successive treatments with thionyl chloride and ammonium hydroxide 2.7 g. of this acid yielded 1.8 g. (66%) of α,α-dimethylcaproamide, m.p. 77–85°. One recrystallization from pentane raised the melting point to 92–93°; reported[23a,b] m.p. 88–89°, 92°.

The other butylations of I, which are listed in Table II, were carried out and worked up in a manner similar to that described in (c).

(d) **2-Bromoöctane and $ZnCl_2$**.—A mixture of 22.3 g. (0.192 mole) of I, 92.5 g. (0.480 mole) of 2-bromoöctane, b.p. 65.2–66.0° (11 mm.), n^{25}_D 1.4482, and 1.92 g. (7.3 mole per cent.) of fused zinc chloride was refluxed for five hours. At this time 19.7 g. (108%) of methyl bromide, b.p. 1–7° (739 mm.), had collected in the cold trap, and all the catalyst had dissolved.

Distillation of the volatile material under reduced pressure gave 91.6 g. of distillate, which fumed from hydrogen bromide, and 3.8 g. of black residue. Distillation through an efficient true-bore annular space column of the material boiling below 137° and of the higher boiling material through a 25-cm. Vigreux column yielded: (a) 8.15 g. (42%) of methyl isobutyrate, b.p. 88–95°; (b) 6.00 g. of intermediate fraction, b.p. 95–119.5°, containing, on the basis of refractive index, 3.9 g. (20%) of methyl isobutyrate and 2.1 g. (10%) of octylene, (c) 19.10 g. (89%) of a mixture of 1-octene and 2-octene the properties of which indicate a predominance of the latter, b.p. 119.5–122.1° (739 mm.), mainly at 121.0–122.1° (739 mm.), n^{25}_D 1.4099, d^{20}_4 0.735; reported[24] for 2-octene, b.p. 124.1–124.7 (745 mm.) (123–123.5°), n^{20}_D 1.4149, d^{20}_4 0.7248; (d) 8.70 g. of intermediate fraction, b.p. 47–63° (11 mm.), (e) 33.60 g. of recovered 2-bromoöctane, b.p. 63–70° (11 mm.), (f) 2.30 g. of intermediate fraction, b.p. 66–123° (11 mm.); (g) 1.90 g. of an unsaturated hydrocarbon, b.p. 123–125° (11 mm.), n^{25}_D 1.4439, d^{25}_4 0.7975; and (h) 1.6 g. of residue. Extraction of fraction (d) with base yielded 1.7 g. (10%) of isobutyric acid, n^{25}_D 1.3928; neut. equiv., 92 (calcd. 88).

(e) ***t*-Amyl Bromide**.—A mixture of 11.6 g. (0.1 mole) of I and 15.1 g. (0.1 mole) of *t*-amyl bromide was refluxed for 11 days. After this time, 10.3 g. of a mixture of methyl bromide and amylenes had collected in the cold trap. Distillation of this cold trap material through a 25-cm. Podbielniak column yielded 6.1 g. of material in the cold trap and 1.5 g. (21%) of a mixture of amylenes, b.p. 31–34° (740 mm.), n^{25}_D 1.3765. The material caught in the cold trap absorbed 3.6 g. of bromine, corresponding to an additional 1.5 g. (21%) of amylene. Distillation of the bromination mixture gave the dibromo derivative, b.p. 58–62° (16 mm.), n^{25}_D 1.5071, d^{20}_4 1.6642; reported[25] for 1,2-dibromo-2-methylbutane, b.p. 47.2–48.0° (9 mm.), n^{20}_D 1.5088, d^{20}_4 1.6711. Subtraction of the 3.0 g. of amylene from the 10.3 g. of volatile material leaves 7.3 g. (77%) of methyl bromide.

Distillation of the remaining reaction mixture through a 25-cm. Heli-Pak column yielded: (a) 9.20 g. of an azeotrope of methyl isobutyrate and *t*-amyl bromide, b.p. 88–91° (739 mm.), n^{25}_D 1.3990; (b) 4.95 g. of a mixture of methyl isobutyrate, *t*-amyl bromide and I, b.p. 91–108°; and (c) 1.7 g. of liquid residue, b.p. 108–230°. The amount of I in fractions (a) and (b) was estimated by titration with bromine. The *t*-amyl bromide content was obtained by extraction of the other components with 85% phosphoric acid. On this basis the yields of products were estimated as: recovered I (18%), recovered *t*-amyl bromide (30%), and methyl isobutyrate (71%).

---

(22) G. T. Morgan and W. J. Hickinbottom, *J. Chem. Soc.*, **123**, 99 (1923); the boiling point of the 1,2-dibromobutane is reported as 166° (Lepingle, *Bull. soc. chim.*, **39**, 741 (1926)).

(23) (a) C. L. Carter and S. N. Slater, *J. Chem. Soc.*, 130 (1946); (b) R. Locquin and L. Leers, *Compt. rend.*, **178**, 2095 (1924).

(24) F. C. Whitmore and J. M. Herndon, THIS JOURNAL, **55**, 3429 (1933).

(25) M. L. Sherrill and G. F. Walter, *ibid.*, **58**, 742 (1936).

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. XXXI. Dimethylketene Ethyleneacetal

BY S. M. MCELVAIN AND CLYDE L. ALDRIDGE[1]

RECEIVED MARCH 13, 1953

Dimethylketene ethyleneacetal (IV), prepared by the dealcoholation of methyl ethylene orthoisobutyrate (II), has extraordinary reactivity for a disubstituted ketene acetal. It reacts exothermically with benzyl bromide at room temperature to yield the benzylated ester V, and spontaneously with oxygen to form polymeric material containing one atom of oxygen per ketene acetal unit; smaller amounts of the cyclic dimer IX, acetone and ethylene carbonate are the other products of this autoxidation.

The unusual reactivities of ketene cyclic acetals (2-methylene-1,3-dioxolanes and 1,3-dioxanes) and certain of their halogen derivatives, which may be prepared by the dehydrohalogenation of the corresponding α-haloacetals, were reported[2] in paper XIX of this series. It seemed of interest to prepare a cyclic analog of dimethylketene dimethylacetal[3] and compare its properties with those of the latter compound as well as with those of the previously reported[2] ketene cyclic acetals. This paper describes the preparation and some of the remarkable properties of dimethylketene ethyleneacetal (IV).

McNall[4] in this Laboratory prepared some alkyl ethylene orthoesters, $RC(OR')OCH_2CH_2O$, in the acetate and propionate series by the alcoholysis of the appropriate iminoester hydrochloride with one equivalent of ethylene glycol in the absence of a

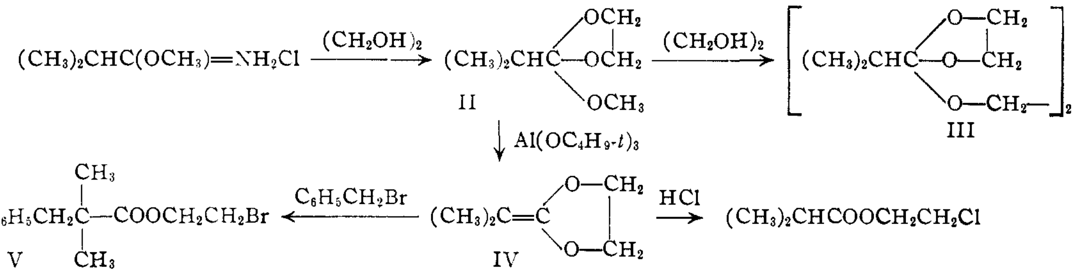
---

(1) U. S. Rubber Company Fellow 1951–1952; du Pont Summer Research Assistant, 1951 and 1952.

(2) S. M. McElvain and M. J. Curry, THIS JOURNAL, **70**, 3781 (1948).

(3) S. M. McElvain and W. R. Davie, *ibid.*, **73**, 1400 (1951).

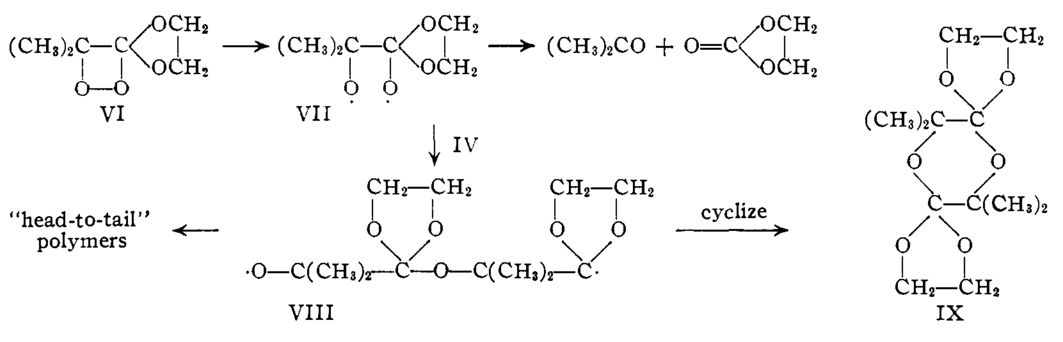
(4) L. N. McNall, B.S. Thesis, University of Wisconsin, 1950.



solvent. The application of this procedure to methyl iminoisobutyrate hydrochloride (I) in the present work produced methyl ethylene orthoisobutyrate (II) in 30–55% yields together with about 10% yield of the diorthoester III. The latter compound was doubtless formed from the interaction of II during its distillation with unreacted ethylene glycol, as it was possible to prepare III by heating II with ethylene glycol in the presence of a trace of acid. However, the use of the extraction technique, which proved so effective for increasing the yields of methyl orthoisobutyrate,[5] raised the yield of II to 65%.

The dealcoholation of II with aluminum *t*-butoxide produced dimethylketene ethyleneacetal (IV) in 28% yield along with methyl isobutyrate (32%) and *t*-butyl isobutyrate (28%). The formation of small amounts of the latter ester was observed in the dealcoholation of methyl orthoisobutyrate[5]; its appearance as a major reaction product in the dealcoholation of II is doubtless due to the more rapid conversion of the methyl ester to the *t*-butyl ester by the aluminum *t*-butoxide at the higher reaction temperatures which prevail in this dealcoholation.

The ketene acetal IV was characterized by its reaction (highly exothermic) with hydrogen chloride to produce β-chloroethyl isobutyrate in 92% yield; the unsubstituted and monohaloketene cyclic acetals, in contrast, are rapidly polymerized by traces of acid.[2] The behavior of IV with benzyl bromide is most remarkable in that it reacts with this halide exothermically at room temperature to yield β-bromoethyl α,α-dimethylhydrocinnamate (V) in 80% yield. In contrast, dimethylketene dimethylacetal requires a temperature of about 110° to initiate a reaction with benzyl bromide.[5]



The first samples of IV that were prepared soon became cloudy and in the course of a few days had gelled completely. In view of the strong tendency of other ketene cyclic acetals to polymerize,[2] it was presumed that IV was showing a similar behavior. However, it was found that IV could be recovered in good yield by distillation from catalytic amounts of either aluminum chloride or benzoyl peroxide, although it did react vigorously with a stoichiometric amount of the latter reagent. It became apparent from analytical data that the polymerization of IV is associated with the absorption of oxygen. Samples of IV stored under nitrogen or carbon dioxide were unchanged after 24 hours, while a sample stored under oxygen rapidly became cloudy and completely gelled in this time.

The absorption of oxygen by IV was followed volumetrically and found to be 46% of one molecular equivalent. From this autoxidation acetone (11%), ethylene carbonate[6] (3.7%) and unchanged IV (19%) were obtained as volatile products. Of the remainder of the reaction mixture (61% by weight) about two-thirds was ether soluble and from this portion was separated 2,2,5,5-tetramethyl-3,3,6,6-bis-dioxyethylene-1,4-dioxane (IX), m.p. 165–166°, in 7% yield. The structure of IX was shown by its molecular weight, the absence of carbonyl bands in its infrared spectrum, and its hydrolysis to α-hydroxyisobutyric acid is 94% yield. The ether-insoluble portion was a white solid, which melted at 220–225° and gave analyses approximating the addition of one oxygen per ketene acetal unit. It was not sufficiently soluble in ordinary solvents for recrystallization or in camphor for a molecular weight determination. This solid was doubtless a polymer of the diradical VIII, as it reacted vigorously with immediate solution in dilute acid; from this solution α-hydroxyisobutyric acid was isolated in 33% yield.

The nature of these autoxidation products indicates that an intermediate peroxide VI is first

---

[5] S. M. McElvain and C. L. Aldridge, This Journal, **75**, 3987 (1953).

[6] The autoxidation of phenylketene dimethylacetal yields benzaldehyde (38%), dimethyl carbonate (40%) and dimethyl α,α'-diphenylsuccinate (37%) (S. M. McElvain and W. R. Davie, *ibid.*, **74**, 1816 (1952).

formed from the action of oxygen on IV. VI opens to the diradical VII which breaks down to a small extent into acetone and ethylene carbonate, but mainly combines with IV to yield the diradical VIII. Cyclization of this diradical produces the dioxane IX while linear polymerization yields species of higher molecular weight, the larger of which are high melting and ether-insoluble.

It should be noted that the boiling point (153°) and refractive index ($n^{25}_{\rm D}$ 1.4540) of IV are considerably higher than those of dimethylketene dimethylacetal (b.p. 107°, $n^{25}_{\rm D}$ 1.4096), indicating a higher degree of polarization and polarizability of the double bond of IV. A similar difference was observed between the other ketene cyclic acetals and the related dimethylacetals.[2]

Experimental

Methyl Ethylene Orthoisobutyrate (II). (i).—In a 1-liter 3-neck round-bottom flask fitted with a Hershberg stirrer and calcium chloride tube, 244.5 g. (1.78 moles) of methyl iminoisobutyrate hydrochloride[5] was mixed with 112 g. (1.80 moles) of ethylene glycol. The mixture was stirred rapidly for 2.3 hours at room temperature and then allowed to stand for 15 hr. After this time it was heated with stirring at 55° for 1.5 hr. The liquid product was extracted from the solid ammonium chloride with absolute ether and filtered. Most of the ether was distilled off and then a small amount of precipitated amide removed from the remaining liquid by filtration. Extraction of the crude ammonium chloride with ethyl acetate yielded isobutyramide which, when combined with that obtained by filtration, amounted to 13.3 g. (8.5%). The ammonium chloride remaining weighed 85.3 g. (89%). The filtrate was then distilled to give 156 g. of material boiling from 68–74° (31 mm.). A liquid residue amounting to 66.2 g. remained in the pot.

The main product was refluxed over sodium hydride for three hours and fractionated through a 25-cm. column packed with wire saddles to give 140 g. (55%) of **methyl ethylene orthoisobutyrate** (II), b.p. 160–160.5° (744 mm.), $n^{25}_{\rm D}$ 1.4188, d^{25}_4 1.007.

Anal. Calcd. for $C_7H_{14}O_3$: C, 57.51; H, 9.65; $Mr_{\rm D}$, 37.25. Found: C, 57.24; H, 9.43; $Mr_{\rm D}$, 36.64.

The 66.2 g. of viscous residue was distilled through a 7-cm. Vigreux column to yield: (a) 30.3 g. of intermediate fraction, b.p. 49–110° (5.5–0.5 mm.) and (b) 25.8 g. (10%) of **ethylene glycol di-(ethylene orthoisobutyrate)** (III), b.p. 110–123° (0.5 mm.). Redistillation yielded an analytical sample, b.p. 110–112° (0.2 mm.), $n^{25}_{\rm D}$ 1.4451, d^{25}_4 1.0823.

Anal. Calcd. for $C_{14}H_{26}O_6$: C, 57.91; H, 9.03; $Mr_{\rm D}$, 72.3. Found: C, 57.76, 57.87; H, 9.16, 9.13; $Mr_{\rm D}$, 71,5.

(ii).—A mixture of 87.5 g. (0.636 mole) of methyl iminoisobutyrate hydrochloride and 39.1 g. (0.630 mole) of ethylene glycol was stirred for 10 minutes in a 500-ml. round bottom flask fitted with a Hershberg stirrer and spiral condenser. Then 200 ml. of dry petroleum ether (b.p. 35°) was added and rapid stirring continued for 63 hr. Filtration of the reaction mixture followed by washing of the precipitate with two 25-ml. portions of pentane yielded 39.5 g. of crude ammonium chloride. The combined filtrate and washings were made basic to phenolphthalein by addition of 1 g. of sodium methoxide. Filtration, removal of the solvent at atmospheric pressure, and distillation of the product at reduced pressure yielded: (a) 60.7 g. (65.5%) of II, b.p. 60–66.5° (22 mm.), $n^{25}_{\rm D}$ 1.4188; (b) 1.4 g., b.p. 100–120° (22 mm.), $n^{25}_{\rm D}$ 1.4314; and (c) 9.4 g. of partly solidified residue.

Extraction of the crude ammonium chloride with two 25-ml. portions of hot ethyl acetate yielded 28.5 g. (84%) of ammonium chloride. Upon reduction in volume the ethyl acetate extracts yielded 4.2 g. (7.3%) of isobutyramide, m.p. 121–124°.

Analytically pure II, b.p. 160.4° (744 mm.), $n^{25}_{\rm D}$ 1.4188, was obtained by distillation from sodium hydride.

Conversion of II to III.—A mixture of 14.60 g. (0.1 mole) of methyl ethylene orthoisobutyrate (II), 3.10 g. (0.05 mole) of ethylene glycol and 0.1 g. of methyl iminoisobutyrate hydrochloride was placed in a 25-ml. round-bottom flask attached to a 7-cm. Vigreux column leading to a stillhead. The system was protected from moisture by a calcium chloride tube. The mixture was heated at 135° and methanol collected. After 3.25 hours 1.1 g. had been collected and evolution had ceased. At this point an additional 0.1 g. of methyl iminoisobutyrate hydrochloride was added and heating continued for an additional hour during which time 0.3 g. of methanol was collected to make a total of 1.4 g. (43%), b.p. 64–66° (740 mm.), $n^{25}_{\rm D}$ 1.3282.

The remainder of the mixture was distilled to give: (a) 6.40 g. (43%) of recovered II, b.p. 87–90° (64 mm.), $n^{25}_{\rm D}$ 1.4190; (b) 4.55 g. of intermediate fraction b.p. 74–127° (0.7 mm.), $n^{25}_{\rm D}$ 1.4418; and (c) 4.50 g. (54% on basis of unrecovered II) of III, b.p. 106–108° (0.2 mm.), $n^{25}_{\rm D}$ 1.4468.

Dimethylketene Ethyleneacetal (IV).—A mixture of 70.0 g. (0.48 mole) of methyl ethylene orthoisobutyrate (II) and 124.5 g. (0.506 mole) of aluminum *t*-butoxide was placed in a 250-ml. round-bottom flask attached to a 7-cm. Vigreux column leading to a 25-cm. Heli-Pak column. The opening to the air from the stillhead was through a Dry Ice–acetone trap followed by a calcium chloride tube. The pot was immersed in an oil-bath at 165–170°; after 30 minutes, takeoff was begun. After 4.5 hr. of distillation had yielded 25.85 g. of distillate, b.p. 81–90°, the oil-bath temperature was raised to 180° for 30 minutes and an additional 4.95 g. of distillate, b.p. 90–91°, was collected. The pressure was then reduced to 15 mm. and 37.23 g. of additional distillate obtained.

Refractionation of the volatile material through the 25-cm. Heli-Pak column yielded: (a) 22.75 g. of the azeotrope of *t*-butyl alcohol and methyl isobutyrate and intermediate fraction, b.p. 79.5–91.0° (741 mm.); (b) 9.05 g. (18.4%) of methyl isobutyrate, b.p. 91–92° (741 mm.), $n^{25}_{\rm D}$ 1.3808; (c) 2.25 g. of intermediate fraction, b.p. 92–125° (741 mm.), $n^{25}_{\rm D}$ 1.3852; and (d) 13.45 g. (19.5%) of *t*-butyl isobutyrate, b.p. 125–128° (741 mm.), $n^{25}_{\rm D}$ 1.3903; reported[7] b.p. 126.7° (760 mm.), $n^{20.1}_{\rm D}$ 1.3921; (e) 2.40 g. of intermediate fraction, b.p. 132–153.1° (741 mm.), $n^{25}_{\rm D}$ 1.4284; (f) 10.80 g. (19.8%) of dimethylketene ethyleneacetal (IV), b.p. 153.1–153.2° (741 mm.), $n^{25}_{\rm D}$ 1.4540, d^{25}_4 1.0023; and (g) 5.90 g. of less pure IV, $n^{25}_{\rm D}$ 1.4420; 0.30 g. of isobutylene, b.p. −5–0° was caught in the cold trap.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.13; H, 8.84; $Mr_{\rm D}$, 30.53. Found: C, 63.33; H, 9.18; $Mr_{\rm D}$, 30.84.

The methyl isobutyrate content of fraction (a) was determined by saponification with alcoholic potassium hydroxide. A 4.00-g. aliquot of fraction (a) yielded, after saponification, acidification and distillation, sufficient acid to neutralize 82.6 ml. of 0.1063 *N* sodium hydroxide; neut. equiv., 90 (calcd. for isobutyric acid, 88). This corresponds to 4.90 g. (10%) of methyl isobutyrate in the entire fraction. The remaining 17.8 g. corresponds to a 50% yield of *t*-butyl alcohol.

Proration of the intermediate and impure fractions on the basis of refractive indices and bromine titrations (of the ketene acetal) gives the following total yields: (1) IV (28%), (2) *t*-butyl isobutyrate (23%), methyl isobutyrate (32%), *t*-butyl alcohol (50%).

Reactions of IV. (i) **With Hydrogen Chloride.**—A 9.4-g. sample of IV was placed in a 25-ml. round-bottom flask with side arm and ground glass joint connected to a stillhead by means of a 7-cm. Vigreux column. The system was protected from moisture by a calcium chloride tube. Dry hydrogen chloride was passed in until 3.7 g. had been added. The reaction was highly exothermic and the temperature was controlled by periodic application of a Dry Ice–acetone bath. Distillation of the reaction mixture yielded 11.7 g. (92%) of **β-chloroethyl isobutyrate** (VI), b.p. 60–64° (15 mm.), $n^{25}_{\rm D}$ 1.4230. Redistillation yielded an analytical sample, b.p. 168.9° (737 mm.), $n^{25}_{\rm D}$ 1.4230, d^{25}_4 1.0541.

Anal. Calcd. for $C_6H_{11}O_2Cl$: C, 47.84; H, 7.36; Cl, 23.54. Found: C, 47.90; H, 7.38; Cl, 23.94.

(ii) **With Benzyl Bromide.**—A mixture of 4.25 g. (0.037 mole) of IV and 6.37 g. (0.037 mole) of benzyl bromide was placed in a 25-ml. round-bottom flask attached to a stillhead. A dropper was fitted in the side arm for removal of samples, and the system was protected with a calcium chloride tube. The stillhead thermometer was immersed in the reaction mixture. Within 10 minutes after mixing, the temperature

---

(7) K. W. F. Kohlrausch and R. Skrabal, *Monatsh.*, **70**, 393 (1937).

of the reaction mixture had risen spontaneously to 40°; when the heat of the reaction began to diminish the temperature was maintained at this level by means of an oil-bath. The progress of the reaction was followed by periodically removing two drops of the solution and titrating, by use of another dropper, the unsaturation with dilute bromine in carbon tetrachloride. Half the unsaturation had disappeared after 1.75 hr.; 90% after 20 hr. The reaction was completed by heating at 100° for 30 minutes.

Distillation of the reaction mixture yielded: (a) 0.65 g., n^{25}_{D} 1.4914 in cold trap; (b) 0.58 g. of recovered benzyl bromide, b.p. 32° (0.1 mm.), n^{25}_{D} 1.5600; and (c) 8.48 g. (80%) of **β-bromoethyl α,α-dimethylhydrocinnamate (V)**, b.p. 105–106° (0.2 mm.), n^{25}_{D} 1.5175, d^{25}_{4} 1.2702.

Anal. Calcd. for $C_{13}H_{17}O_2Br$: C, 54.74; H, 6.01; Br, 28.02. Found: C, 54.76; H, 6.01; Br, 28.64.

(iii) **With Aluminum Chloride.**—A mixture of 0.040 g. (0.0003 mole) of anhydrous aluminum chloride and 4.8 g. (0.0426 mole) of IV, n^{25}_{D} 1.4537, in a 10-ml. distilling flask was placed in an oil-bath at 160°. The temperature was raised to 225° over a period of 20 minutes, whereupon 2.51 g. (52%) of IV, b.p. 152–153°, n^{25}_{D} 1.4522 distilled. A further 1.35 g. (29%) of IV, b.p. 71–72° (28 mm.), n^{25}_{D} 1.4521, was collected under reduced pressure. There remained 0.65 g. of tan residue in the pot.

(iv) **With Benzoyl Peroxide.**—To 1.020 g. of IV in a 10-ml. round-bottom flask was added 0.095 g. (4.4 mole per cent.) of benzoyl peroxide in small portions under a nitrogen atmosphere. Each addition was accompanied by a violent local reaction. When the addition was completed the solution was cooled and the nitrogen atmosphere replenished. After standing for 4 hr. at room temperature and 1.25 hr. at 85° the solution was still clear and colorless. The flask was attached to a side arm leading to a Dry Ice–acetone trap and the volatile material removed at 25° (0.1 mm.) for 2 hr. and at 130° (0.1 mm.) for 1 hr. Recovered IV, 0.90 g. (88%), n^{25}_{D} 1.4511, collected in the cold trap. There remained 0.155 g. of clear viscous oil in the reaction flask.

(v) **With Oxygen.**—A 10.22-g. (0.090 mole) sample of IV was placed in a 50-ml. flask with ground glass joint attached to a spiral condenser which was connected to a calibrated reservoir of oxygen equipped with a dibutyl phthalate pressure equalizer. The absorption of oxygen caused the flask to become warm to the touch. After 12 hr. the reaction mixture was completely gelled and the absorption of oxygen was proceeding at about one-tenth the initial rate. The flask then was heated at 60° for 48 hr. At the end of this time the absorption of oxygen was proceeding at 1% of its original rate. A total of 1048 ml. at 29° and 741 mm. (46% of one molecular equivalent) of oxygen was absorbed; the gain in weight of the flask amounted to 1.20 g. (41.7%).

At 0.2 mm. pressure, 3.25 g. of volatile liquid distilled from the reaction mixture and was caught in a cold trap; 7.14 g. of solid residue remained in the reaction flask. The volatile material was fractionated through a 25 cm. Podbielniak column to yield: (a) 0.444 g. (8.5%) of acetone, b.p. 56° (740 mm.), n^{25}_{D} 1.3562; (b) 0.322 g. of intermediate fraction, b.p. 70–151.5° (740 mm.), n^{25}_{D} 1.4088, containing 0.149 g. (2.8%) of acetone and 0.173 g. (1.7%) of recovered IV; (c) 1.475 g. (14.4%) of recovered IV, b.p. 151.5–152.5° (740 mm.), n^{25}_{D} 1.4506; (d) 0.262 g. (2.6%) of recovered IV, b.p. 82–84° (46 mm.), n^{25}_{D} 1.4490; and (e) 0.290 g. (3.7%) of ethylene carbonate, b.p. 157–160° (44 mm.), n^{25}_{D} 1.4330; reported[8] b.p. 152° (30 mm.).

Extraction of the solid residue with two 50-ml. portions of ether yielded 4.83 g. (42% of the weight of the reaction mixture) of ether soluble material and 2.00 g. (18% of the weight of the reaction mixture) of white powder, m.p. 220–225° with decomposition, which was insoluble in ether, acetone, alcohol and only partially soluble in chloroform. Distillation of the ether soluble material yielded 2.5 g. of material, b.p. 160–195° (46 mm.), which partially solidified on cooling. Crystallization from ether gave 0.80 g. of **2,2,5,5-tetramethyl-3,3,6,6-bis-(dioxyethylene)-1,4-dioxane** (IX), m.p. 147–158°. Two crystallizations from petroleum ether (b.p. 65°) gave an analytical sample, m.p. 165.5–166.0°; mol. wt. (Rast), 300 (calcd. for IX, 260).

Anal. Calcd. for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75. Found: C, 55.51; H, 7.91.

The infrared absorption curve showed no carbonyl peak and no hydroxyl peak, and strong absorption at 8.65 and 9.3 μ consistent with the multiplicity of ether linkages in IX. The polymer, m.p. 220–225°, was not sufficiently soluble in the ordinary organic solvents for recrystallization or in camphor for molecular weight determination.

Anal. Calcd. for $(C_{12}H_{20}O_6)x$: C, 55.37; H, 7.75. Found: C, 54.50; H, 7.87.

Hydrolysis of IX.—A 0.248-g. sample of IX was warmed on the steam-bath for 15 minutes with 0.25 ml. of 0.1222 *N* hydrochloric acid. The resultant homogeneous solution was refluxed for 1.5 hr. with 4.00 ml. of 0.768 *N* alcoholic potassium hydroxide. The excess base was titrated with 9.47 ml. of 0.1222 *N* hydrochloric acid; sapn. equiv., 131.5 (calcd. 130).

Evaporation of the neutral solution to dryness, trituration of the residue with ether containing dry hydrogen chloride, filtration and evaporation of the ether solution to dryness yielded 0.186 g. (94%) of α-hydroxyisobutyric acid, m.p. 65–71°. Sublimation raised the melting point to 76.5–78.3°; reported[9] m.p. 79°. A mixed melting point with an authentic sample showed no depression.

When the hydrolysis procedure described for IX was applied to 0.823 g. of the polymer, m.p. 220–225°, 0.22 g. (33%) of α-hydroxyisobutyric acid, m.p. 59–67° was obtained. Sublimation raised the melting point to 78.1–79.3°. A mixed melting point with an authentic sample showed no depression.

Madison, Wisconsin

---

(8) D. Vorländer, *Ann.*, **280**, 187 (1894).

(9) H. G. Rule and J. Harrower, *J. Chem. Soc.*, 2326 (1930).