αβ-*Unsaturated Aldehydes and Related Compounds. Part V.* Reaction of Acraldehyde with Simple Aliphatic Alcohols. Formation of Acraldehyde Dialkyl Acetals and of β-Alkoxypropaldehydes and their Acetals.*

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A re-examination of the acid-catalysed reaction of acraldehyde with restricted amounts of alcohols showed that simple acetals could not be obtained directly in this way in good yield. In particular, Pingert's claims (*Org. Synth.*, 1945, **25**, 1) could not be substantiated (cf. Hall and Stern, *Chem. and Ind.*, 1950, 775), the low-boiling product being β-ethoxypropaldehyde and not acraldehyde diethyl acetal. The use of neutral salts as catalyst was also examined briefly and found unsatisfactory.

Several new acraldehyde acetals, β-alkoxypropaldehydes, and 1 : 1 : 3-trialkoxypropanes were isolated and characterised together with a number of compounds previously imperfectly described.

The work now reported was undertaken primarily to find an easy method of preparing simple dialkyl acetals of acraldehyde; other, broader, aims were the examination of any differences in reactivity of the aldehyde towards different alcohols and of the nature of the products obtained. A preliminary account of one aspect of this work has already been published (Hall and Stern, *Chem. and Ind.*, 1950, 775).

Of the simple dialkyl acetals of acraldehyde only the dimethyl and the diethyl have been described previously. They were accessible by two routes: the reaction of acraldehyde with ethyl orthoformate (Fischer and Baer, *Helv. Chim. Acta*, 1935, **18**, 514), and the dehydrohalogenation of β-halogenopropaldehyde acetals (*e.g.*, Witzemann, Evans, Hass, and Schroeder, *Org., Synth.*, 1931, **11**, 1, 26), neither of which was readily adaptable to large-scale work. More recently, Pingert (*Org. Synth.*, 1945, **25**, 1) claimed that reaction of acraldehyde with a limited amount of ethanol in the presence of hydrogen chloride gave a mixture of acraldehyde diethyl acetal (24—30% yield) and 1 : 1 : 3-triethoxypropane (21—26% yield), separable by fractional distillation. There was no other record, however, of the formation of acraldehyde acetals by the simple, acid-catalysed reaction of acraldehyde and alcohols, a reaction which had earlier been shown to give, with an excess of the alcohol, products such as β-alkoxypropaldehydes, and 1 : 1 : 3-trialkoxypropanes, and, in the presence of sufficient hydrogen chloride, 1 : 1-dialkoxy-3-chloropropanes and 1-alkoxy-1 : 3-dichloropropanes (cf. Alsberg, *Jahresber.*, 1864, 495; Fischer and Giebe, *Ber.*, 1897, **30**, 3056; Wohl, *ibid.*, 1898, **31**, 1797; Witzemann *et al.*, *loc. cit.*; Duliere, *Bull. Soc. chim.*, 1923, [4], **33**, 1650; Voet, *ibid.*, 1927, [4], **41**, 1308; Brabant, *Z. physiol. Chem.*, 1913, **83**, 208; Schulz, U.S.P. 2,288,211).

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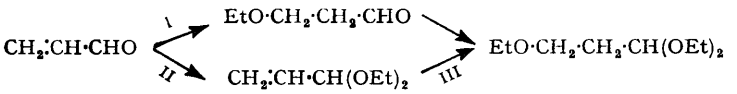
Interest centered initially therefore on a re-examination of Pingert's process, in the hope of obtaining the desired acetal, or an equilibrium mixture of acetal, β-ethoxypropaldehyde, and 1 : 1 : 3-triethoxypropane from which the acetal might be separated. The failure of such experiments to substantiate Pingert's claims has already been reported briefly (Hall and Stern, *loc. cit.*; see also Experimental section) : the products were β-ethoxypropaldehyde and 1 : 1 : 3-triethoxypropane. The former, which was mistaken by Pingert for the desired acetal, was an artefact produced from the triethoxy-compound during the distillation, since none was obtained when the reaction mixture was neutralised before distillation.

The 1 : 1 : 3-triethoxypropane obtained could obviously have arisen by two different, possibly reversible, series of reactions (see diagram), but as neither of the intermediates was isolated in significant amounts when the reaction mixture was neutralised before distillation no evidence was forthcoming as to whether one or both of the reaction sequences had operated.

In an attempt to favour reaction II, neutral catalysts for acetal formation (calcium chloride or ammonium chloride) were used, together with a lower concentration of acid catalyst and a reduced ratio (1·5 to 1 molar) of ethanol to aldehyde. Small quantities of acraldehyde acetal were isolated, besides much 1 : 1 : 3-triethoxypropane, despite the fact that reaction III was shown to occur quite readily and almost quantitatively (by treating the acetal with ethanol containing hydrogen chloride). Evidently, in the presence of neutral catalysts and little acid, the rate of acetal formation (reaction II) was somewhat greater than that of its consumption (reaction III) and, at the low conversions attained, some of it remained unattacked.



Catalysis by neutral salts in the absence of acid gave no useful products, possibly because of hydrolysis of any acetal formed in the cold on distillation in the presence of the catalyst. However, azeotropic removal of water from the ammonium chloride-catalysed reaction excluded all possibility of a reversal of the reaction and pure acraldehyde diethyl acetal and 1 : 1 : 3-triethoxypropane (molar ratio 1 to 4) were isolated from the product, although the conversion was poor. Evidently the ammonium chloride was sufficiently acidic to function also as a catalyst for reaction III.

Some evidence for a reaction of type I was obtained by treating acraldehyde with *iso*propanol and sulphuric acid, the product containing β-*iso*propoxypropaldehyde as well as much high-boiling material from which a trace of 1 : 1 : 3-tri*iso*propoxypropane was isolated. No di*iso*propyl acetal of acraldehyde could be detected in the intermediate fractions; this was not altogether surprising as it was known (cf. Adkins and Adams, *J. Amer. Chem. Soc.*, 1925, **47**, 1368) that secondary alcohols formed acetals only with difficulty.

Apart from the use of neutral catalysts, which had already been found unsatisfactory, the potentially most promising ways of favouring reaction II at the expense of I and III involved the use of a higher alcohol [cf. addition of alcohols to acrylic esters (Rehberg, *J. Amer. Chem. Soc.*, 1946, **68**, 544; 1947, **69**, 2966)] and a lower ratio alcohol : acraldehyde. *n*-Propanol and acraldehyde in the presence of sulphuric acid gave a trace of pure dipropyl acetal but the main product was 1 : 1 : 3-tripropoxypropane, and some β-propoxypropaldehyde was also formed. With *n*-butanol and acraldehyde, however, over sulphuric acid and calcium chloride, acraldehyde dibutyl acetal and 1 : 1 : 3-tributoxypropane were obtained in a molar ratio of 4 to 5.

The foregoing qualitative results showed that variation in the experimental conditions and choice of alcohol influenced considerably the course of the reaction. For the preparation of acraldehyde acetals the use of higher alcohols seemed to be particularly advantageous, and this led to an investigation of the reaction of acraldehyde with polyhydric alcohols (to be reported).

The reactivity of α-methylacraldehyde towards ethanol under conditions favouring the formation of the acetal (ammonium chloride catalyst; azeotropic removal of water of reaction) was also examined briefly: the products contained equimolar amounts of α-methylacraldehyde diethyl acetal and 1 : 1 : 3-triethoxy-2-methylpropane. As the ratio was 1 to 4 for acraldehyde, substitution of α-methylacraldehyde had favoured acetal formation (reaction II) at the expense of alcohol addition (reactions I and III); addition of ethanol across the conjugated system of α-methylacraldehyde thus occurred less readily than across that of acraldehyde.

The acraldehyde acetals all showed a characteristic infra-red absorption band at 938 cm.$^{-1}$ and they all readily yielded acraldehyde 2 : 4-dinitrophenylhydrazone; they could thus be differentiated from isomeric structures. Furthermore, the dibutyl acetal on hydrogenation gave propaldehyde dibutyl acetal, identical with an authentic specimen.

The 1 : 1 : 3-trialkoxypropanes were characterised by conversion, under controlled conditions, into the 2 : 4-dinitrophenylhydrazones of the corresponding β-alkoxypropaldehydes, reference samples of which were synthesised where required by the method of Heyse (G.P. 554,949).

The investigation was stopped when an attractive route to the acraldehyde acetals by thermal fission of the 1 : 1 : 3-trialkoxypropanes was discovered (to be reported).

Experimental

Materials.—Acraldehyde was redistilled material of *ca.* 95% purity (determined by analysis for unsaturation by the bromide–bromate method); it contained *ca.* 5% w/w of water and 0·1% w/w of quinol, unless otherwise specified. The quantities of acraldehyde given below all refer to the actual acraldehyde content of the material used.

Acraldehyde Diethyl Acetal (cf. Fischer and Baer, *loc. cit.*).—A mixture of ammonium nitrate (3 g.), ethanol (30 ml.), acraldehyde (1 mole), and ethyl orthoformate (144 g.) was boiled for 8 min., filtered cold, diluted with ether, and washed several times with 2N-ammonia and then with water. The organic layer was dried (K_2CO_3) and fractionated to give acraldehyde diethyl acetal (75 g.), b. p. 63°/91 mm., 59°/75 mm., 55°/65 mm., 26°/13 mm., n_D^{20} 1·4014 (Found: C, 64·95; H, 10·75. Calc. for $C_7H_{14}O_2$: C, 64·6; H, 10·85%). Fischer and Baer (*loc. cit.*) and Witzemann *et al.* (*Org. Synth.*, 1931, **11**, 1) give b. p. 122—125°, but Pingert (*loc. cit.*) gives b. p. 40°/18 mm., 52°/36 mm.; these last b. p.s appear to be too high for the acetal.

β-*Ethoxypropaldehyde* (cf. Heyse, *loc. cit.*).—Acraldehyde (2 moles) was added dropwise to stirred ethanol (500 ml.) containing 50% w/v aqueous sodium hydroxide (2 ml.) at −5° to −10°. The mixture was acidified with acetic acid (5 ml.) and then with phosphoric acid (1·0 g.), and fractionated, giving β-ethoxypropaldehyde (79·5 g., 40%), b. p. 66—66·5°/67 mm., n_D^{20} 1·4026 (Heyse, *loc. cit.*, gives no physical constants; Schulz and Wagner, *Angew. Chem.*, 1950, **62**, 105, give b. p. 133°; Schulz, U.S.P. 2,288,211, gives b. p. 134°/760 mm., 60°/40 mm.). The *semicarbazone* crystallised from ethyl acetate as needles, m. p. 117° (Found: C, 45·35; H, 8·3; N, 26·5. $C_6H_{13}O_2N_3$ requires C, 45·3; H, 8·25; N, 26·4%), and the 2 : 4-dinitrophenylhydrazone from 60% aqueous ethanol as fine plates, m. p. 85° (Found: C, 46·95; H, 4·9; N, 19·7. Calc. for $C_{11}H_{14}O_5N_4$: C, 46·8; H, 5·0; N, 19·85%). Both derivatives were unknown when first prepared in the course of the work reported here, but subsequently Feazel and Berl (*J. Amer. Chem. Soc.*, 1950, **72**, 2278) found m. p. 84·5—85° (corr.) for the 2 : 4-dinitrophenylhydrazone; they did not succeed in isolating the semicarbazone.

Reaction of Acraldehyde and Ethanol.—Under Pingert's Conditions. In a typical experiment, a solution of hydrogen chloride (2 g.) in ethanol (30 ml.) was added to a mixture of acraldehyde (97% purity; 3 moles) and ethanol (292 ml.) cooled to 0° in an ice-bath. The temperature thereupon rose to 10°; when the ice had melted the mixture was kept for 60 hr. at room temperature. It was then cooled to 5°, partly neutralised with a solution (10—15 ml.) [from sodium (1 g.) in ethanol (25 ml.)], and copper carbonate (1·0 g.) was added. The solution, which was still acid to litmus, was fractionated, giving fractions: (i) ethanol containing about 6% of acraldehyde (77 g.), (ii) b. p. 40—55°/40 mm., n_D^{20} 1·4054 (15—20 g.), (iii) b. p. 30—40°/10 mm., n_D^{20} 1·4026—1·4036 (48 g.), (iv) 1 : 1 : 3-triethoxypropane, b. p. 70°/13 mm., n_D^{20} 1·4070 (91 g.), and a residue (145 g.). A small intermediate fraction (15 g.), b. p. 40—60°/10 mm., n_D^{20} 1·4140—1·4201, was disregarded. In some experiments the sodium ethoxide was omitted and copper carbonate (1·0 g.) only was added. The results were very similar.

Analysis of fraction (i) for acraldehyde by ultra-violet spectrophotometry and for acraldehyde

and its diethyl acetal by oximation and by bromine absorption (bromide–bromate method) showed that no acetal was present.

Dilution of fraction (ii) with carbon tetrachloride caused separation of a very small amount of aqueous phase. This was removed when shaken with anhydrous sodium sulphate. Infra-red examination of the dried solution indicated the presence of β-ethoxypropaldehyde and 1 : 1 : 3-triethoxypropane and the absence of acraldehyde diethyl acetal.

Fraction (iii) was shown to be β-ethoxypropaldehyde by comparison of its infra-red absorption spectrum with that of authentic material; acraldehyde diethyl acetal was absent (no band at 938 cm.$^{-1}$). In confirmation, fraction (iii) gave a 2 : 4-dinitrophenylhydrazone, m. p. 85°, and a semicarbazone, m. p. 117°, identical with the authentic derivatives of β-ethoxypropaldehyde prepared above.

Neutralisation of reaction product. In several experiments sufficient ethanolic sodium ethoxide was added to make phenolphthalein indicator just pink. A small piece (about 0·5 g.) of solid carbon dioxide was then added to bring the solution approximately to neutrality, and the filtered product was fractionally distilled without previous addition of copper carbonate.

In a typical experiment distillation gave: (i) ethanol containing about 0·2% of acraldehyde (101 g.), (ii) a small fraction (2·1 g.), b. p. 48°/200 mm—30°/70 mm., n_D^{20} 1·3660, (iii) a two-phase intermediate fraction (11 g.) b. p. 15—70°/11 mm., (iv) 1 : 1 : 3-triethoxypropane (130 g.), b. p. 70—72°/11 mm., n_D^{20} 1·4065—1·4080, and a residue (181 g.).

Fraction (ii) smelt of acraldehyde acetal, a trace of which (not more than 0·3 g.) may have distilled with the last few drops of ethanol. Fraction (iii) may have contained the water–1 : 1 : 3-triethoxypropane azeotrope.

Catalysis by hydrogen chloride and calcium chloride. Acraldehyde (2 moles) was added rapidly to stirred ethanol (170 ml.), containing hydrogen chloride (0·62 g.) and calcium chloride (15 g.), cooled to 0°. The mixture was stirred at 0° for 0·5 hr., at room temperature for 0·5 hr., and at 50° for 2 hr., and then kept overnight at room temperature. After addition of calcium carbonate (1·7 g.) and filtration, the mixture was rapidly distilled under reduced pressure (loss of acraldehyde and ethanol), and the distillate was fractionated, giving: (i) ethanol (11·5 g.), (ii) impure acraldehyde diethyl acetal (12·7 g.), b. p. 50—55°/70 mm., n_D^{20} 1·4057, and (iii) 1 : 1 : 3-triethoxypropane (101 g.), b. p. 72°/12 mm., n_D^{20} 1·4064.

Catalysis by salts in absence of acid. (*a*) Acraldehyde (1 mole), ethanol (128 ml.), and calcium chloride (5 g.) were stirred at room temperature for 1 hr., at 40° for 2 hr., and then at room temperature overnight. After addition of potassium carbonate (5 g.) the mixture was filtered and rapidly distilled. The distillate contained only acraldehyde and ethanol.

(*b*) A mixture of acraldehyde (2 moles), ethanol (330 ml.; 4 moles), methylene dichloride (100 ml.), and ammonium chloride (6 g.) was refluxed up a 3-ft. Vigreux column fitted with a phase-separating still-head, which removed the upper (aqueous) layer of the distillate and continuously returned the lower layer to the column. After 2 days no more water collected (total volume of aqueous layer, 45 ml.), and the still residues were rapidly distilled. The distillate on fractionation gave pure acraldehyde diethyl acetal (17 g.), b. p. 60°/79 mm., n_D^{20} 1·4012, and 1 : 1 : 3-triethoxypropane (135 g.), b. p. 75°/19 mm., n_D^{20} 1·4067.

Reaction of Acraldehyde Diethyl Acetal with Ethanol.—The acetal (38 g.) was dissolved in ethanol (50 g.), and the solution treated below 3° with ethanol (50 g.) containing hydrogen chloride (1 g.). After several days at room temperature, the solution was made just alkaline with ethanolic sodium ethoxide and the excess of alkali neutralised with solid carbon dioxide. On fractional distillation of the product pure 1 : 1 : 3-triethoxypropane (47 g., 93%) was obtained.

Characterisation of Reaction Products.—(*a*) Acraldehyde diethyl acetal (1 g.) was shaken with 2N-hydrochloric acid (10 ml.) until the solution was homogeneous; addition of a dilute solution of 2 : 4-dinitrophenylhydrazine sulphate in methanol precipitated acraldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 164—165°.

(*b*) 1 : 1 : 3-Triethoxypropane (1·5 g.), b. p. 74°/15 mm., n_D^{20} 1·4068 (Found: C, 61·4; H, 11·2. Calc. for $C_9H_{20}O_3$: C, 61·4; H, 11·45%), was suspended in water (10 ml.) Concentrated hydrochloric acid (3 drops) was added, and the mixture shaken until homogeneous and then treated with a solution of 2 : 4-dinitrophenylhydrazine (2 g.) and sulphuric acid (0·5 ml.) in methanol (25 ml.). The precipitate, on recrystallisation from 60% aqueous ethanol, gave β-ethoxypropaldehyde 2 : 4-dinitrophenylhydrazone as fine plates, m. p. 85°, identical with authentic material (see above). Unless the above procedure was followed closely the derivative was sometimes contaminated with acraldehyde 2 : 4-dinitrophenylhydrazone.

Reaction of Acraldehyde with n-*Propanol.*—In a typical experiment, a mixture of *n*-propanol (300 ml.; 4 moles), acraldehyde (2 moles), and concentrated sulphuric acid (2 g.) was kept over-

night and then neutralised (phenolphthalein) with 5N-sodium hydroxide. Sodium acetate (2 g.) was added and the mixture rapidly distilled under reduced pressure; two major fractions were then obtained, *viz.*, one boiling below 50°/200 mm., the other above 60°/200 mm. The latter on fractional distillation gave, besides unchanged *n*-propanol, a fraction (13 g.), b. p. 52—55°/10 mm., n_D^{20} 1·4145, and pure 1 : 1 : 3-*tri*-n-*propoxypropane* (45 g.), b. p. 113°/15 mm., n_D^{20} 1·4179 (Found: C, 66·3; H, 11·85. $C_{12}H_{26}O_3$ requires C, 66·05; H, 12·0%). The smaller fraction, on repeated refractionation, gave *acraldehyde di*-n-*propyl acetal* (2·4 g.), b. p. 93°/92 mm., n_D^{20} 1·4120 (Found: C, 68·2; H, 11·75. $C_9H_{18}O_2$ requires C, 68·3; H, 11·45%), together with some material which contained β-propoxypropaldehyde (detected by infra-red spectroscopy; for preparation of authentic aldehyde, see Hall and Stern, *J.*, 1952, 4083).

Acraldehyde di-*n*-propyl acetal (0·5 g.) was converted on hydrolysis, in the usual manner, into acraldehyde (characterised as 2 : 4-dinitrophenylhydrazone, m. p. 164—165°). Similarly 1 : 1 : 3-tri-*n*-propoxypropane gave β-*n*-propoxypropaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 100—100·5°, identical with the authentic derivative (*idem*, *loc. cit.*).

Reaction of Acraldehyde with n-*Butanol.*—On mixing of cold *n*-butanol (148 g.; 2 moles) containing concentrated sulphuric acid (0·3 ml.) and calcium chloride (15 g.) with acraldehyde (2 moles), a temperature rise to 40° was observed. The mixture was then kept overnight, dried by addition of calcium chloride (25 g.) and of potassium carbonate (5 g.), filtered, and rapidly distilled under reduced presure. Two fractions were collected, one boiling below and the other above 60°/90 mm. The higher-boiling material on fractional distillation gave, besides a little unchanged *n*-butanol, *acraldehyde di*-n-*butyl acetal* (36 g.), b. p. 84°/13 mm., n_D^{20} 1·4204 (Found: C, 70·9; H, 12·1. $C_{11}H_{22}O_2$ requires C, 70·9; H, 11·9%), and 1 : 1 : 3-*tri*-n-*butoxypropane* (67·2 g.), b. p. 78—80°/0·2 mm., n_D^{20} 1·4258 (Found: C, 69·55; H, 12·15. $C_{15}H_{32}O_3$ requires C, 69·15; H, 12·4%).

Hydrogenation of acraldehyde di-*n*-butyl acetal (5 g.) over 5% palladium–charcoal catalyst (1·0 g.) in ethyl acetate (50 ml.) at room temperature and pressure resulted in the very rapid uptake of hydrogen (97% of theory); fractional distillation of the product gave *propaldehyde di*-n-*butyl acetal* (4·1 g.), b. p. 94°/14 mm., n_D^{20} 1·4128 (Found: C, 70·5; H, 12·75. $C_{11}H_{24}O_2$ requires C, 70·15; H, 12·8%). This was also obtained (40% yield) by keeping overnight a mixture of propaldehyde (58 g.) and *n*-butanol (150 g.) containing concentrated sulphuric acid (0·5 ml.), separating the lower (aqueous) layer, and neutralising, drying, and fractionally distilling the upper layer.

Shaking 1 : 1 : 3-tri-*n*-butoxypropane (1 g.) with water (10 ml.) containing concentrated hydrochloric acid (5 drops) and ethanol (1 ml.) and treating the resulting homogeneous solution with 2 : 4-dinitrophenylhydrazine sulphate in methanol gave β-n-*butoxypropaldehyde* 2 : 4-*dinitrophenylhydrazone* (see below), which crystallised from aqueous ethanol in shiny plates, m. p. 72—73° (Found: C, 50·65; H, 5·75; N, 17·9. $C_{13}H_{18}O_5N_4$ requires C, 50·3; H, 5·85; N, 18·05%).

β-*Butoxypropaldehyde.*—A solution of acraldehyde (2 moles) in *n*-butanol (150 g.) was slowly added to a stirred solution of 50% w/v aqueous sodium hydroxide (2 g.) in *n*-butanol (590 g.) kept at −5° to −10° (acetone–solid carbon dioxide). When addition was complete, the mixture was stirred at −7° for 20 min., acidified with acetic acid (5 ml.) and phosphoric acid (0·56 ml.), and then rapidly distilled. The fraction boiling above 45°/10 mm. on refractionation gave β-butoxypropaldehyde (105 g.; about 48%), b. p. 60°/15 mm., n_D^{20} 1·4156 (Found: C, 64·65; H, 10·7. Calc. for $C_7H_{14}O_2$: C, 64·6; H, 10·85%) (Schulz and Wagner, *Angew Chem.*, 1950, **62**, 105, gave b. p. 146—148°/760 mm. but neither analysed nor characterised the aldehyde).

β-Butoxypropaldehyde gave a 2 : 4-dinitrophenylhydrazone, m. p. 72—73°, identical with that described above (mixed m. p.), and a *semicarbazone*, crystallising from ethyl acetate–light petroleum in long needles, m. p. 97° (Found: C, 51·45; H, 9·1; N, 22·2. $C_8H_{17}O_2N_3$ requires C, 51·35; H, 9·15; N, 22·45%).

Reaction of Acraldehyde and iso*Propanol.*—Acraldehyde (97% purity; 1 mole), *iso*propanol (120 g.; 2 moles), and concentrated sulphuric acid (1·1 ml.) were kept at room temperature for 48 hr. The mixture was then neutralised (phenolphthalein) with 5N-sodium hydroxide, made just acid with acetic acid, and rapidly distilled under reduced pressure; two main fractions were collected, boiling below and above 50°/180 mm., respectively. The higher-boiling material (*ca.* 75 g.) on fractionation gave: (i) β-iso*propoxypropaldehyde* (15—25 g.), b. p. 45°/15 mm., n_D^{20} 1·4048 (Found: C, 62·25; H, 10·65. $C_6H_{12}O_2$ requires C, 62·05; H, 10·4%), (ii) intermediate fractions (*ca.* 20 g.), b. p. 50—95°/15 mm., n_D^{20} 1·410—1·433, (iii) impure 1 : 1 : 3-tri*iso*propoxypropane (7 g.), b. p. 90—97°/11 mm., n_D^{20} 1·4127, and (iv) high-boiling substances (29 g.).

The β-*iso*propoxypropaldehyde [fraction (i)] gave a 2 : 4-*dinitrophenylhydrazone*, plates, m. p. 99° (from aqueous methanol) (Found : C, 48·5; H, 5·4; N, 19·0. $C_{12}H_{16}O_5N_4$ requires C, 48·65; H, 5·45; N, 18·9%), and a *semicarbazone*, needles, m. p. 127·5—128° (from 25% aqueous ethanol) (Found : C, 48·4; H, 8·75; N, 24·2. $C_7H_{15}O_2N_3$ requires C, 48·55; H, 8·75; N, 24·25%).

Refractionation of fraction (iii) gave material (1·5 g.), b. p. 87°/8 mm., n_D^{20} 1·4113, the properties of which approximated to those of authentic 1 : 1 : 3-tri*iso*propoxypropane, b. p. 89°/11 mm., n_D^{20} 1·4096 (Hall, Stern, and the Distillers Co., Ltd., B.P. 695,789; cf. Bellringer, Bewley, and the Distillers Co., Ltd., B.P. Appln. 9689/50). On hydrolysis with dilute hydrochloric acid and treatment with 2 : 4-dinitrophenylhydrazine reagent it furnished β-*iso*propoxypropaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 99°.

Reaction of α-Methylacraldehyde with Ethanol.—A mixture of α-methylacraldehyde (140 g.; 2 moles), ethanol (184 g.; 4 moles), ammonium chloride (6 g.), and methylene dichloride (150 ml.) was rapidly distilled through a 3-ft. Vigreux column fitted with a phase-separating still-head; the upper (aqueous) layer of the distillate was removed and the lower layer continuously returned as reflux. After 8 days, 35 ml. of water had been removed and no more appeared to be formed. The reaction mixture was rapidly distilled (the pressure being progressively reduced) and the material (129 g.) boiling above 80°/750 mm. was fractionated, giving α-methylacraldehyde diethyl acetal (71 g.), b. p. 52°/30 mm., 39°/10 mm., n_D^{20} 1·4081 (oximation equiv., 145. Calc. : equiv., 144), and 1 : 1 : 3-triethoxy-2-methylpropane (84·5 g.), b. p. 74°/10 mm., n_D^{20} 1·4089 (oximation equiv., 188. Calc. : equiv., 190) (cf. Bellringer *et al.*, *loc. cit.*).

Repetition of the above experiment, with hydrogen chloride (0·5 g.) in place of ammonium chloride, gave α-methylacraldehyde diethyl acetal (63 g.) and 1 : 1 : 3-triethoxy-2-methylpropane (76 g.).

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