αβ-Unsaturated Aldehydes and Related Compounds. Part VII. Thermal Fission of* 1 : 1 : 3-*Trialkoxypropanes.*†

By R. H. Hall and E. S. Stern.

[Reprint Order No. 6308.]

Catalysed pyrolysis of 1 : 1 : 3-trialkoxypropanes in the liquid or the vapour phase gave mixtures of the acraldehyde dialkyl acetals and *cis*- and *trans*-1 : 3-dialkoxypropenes. 1 : 1 : 3-Triacetoxypropane behaved analogously, yielding acraldehyde diacetate (allylidene diacetate) and 1 : 3-diacetoxypropene.

For a series of 1 : 1 : 3-trialkoxypropanes the relative proportions of the products depended on the nature of the alkoxy-groups, and formation of the acetals was favoured by more drastic conditions, partly because the 1 : 3-dialkoxypropenes then isomerised.

Both fission products added alcohols in presence of acidic catalysts and regenerated the 1 : 1 : 3-trialkoxypropanes, the 1 : 3-dialkoxypropenes apparently doing so the more readily.

Hydrogenation of the 1 : 3-dialkoxypropenes and of 1 : 3-diacetoxypropene afforded trimethylene glycol diethers and diacetate, respectively.

The work reported here arose out of the desire to prepare simple acetals of acraldehyde (cf. Part V; *J.*, 1954, 3388). Since the usual laboratory methods, namely, reaction of acraldehyde with orthoformic esters (Fischer and Baer, *Helv. Chim. Acta*, 1935, **18**, 514; Schmidt, G.P. 553,177) or dehydrochlorination of 1 : 1-dialkoxy-3-chloropropanes (cf. Witzemann, Evans, Hass, and Schroeder, *Org. Synth.*, 1931, **11**, 1), were not entirely suitable for large-scale application, and since direct formation of the acetals from the aldehyde and alcohols proved unsatisfactory (cf. Part V), other methods were examined. The present paper describes the catalysed thermal fission of 1 : 1 : 3-trialkoxypropanes which yielded both the acetals and the isomeric 1 : 3-dialkoxypropenes. Since this work was completed (in 1950), Whetstone and Shell Development Co. (U.S.P. 2,626,283) and Myers, Magerlein, Staffen, and the Upjohn Co. (B.P. 713,088) have reported the direct conversion of acraldehyde into its lower dialkyl acetals, a porous calcined silica–alumina hydrogel being used as catalyst by the former authors, and sharply-defined trace amounts of certain specified acids by the latter.

The trialkoxy-compounds required as starting materials in the present investigation were accessible by direct acid-catalysed condensation of alcohols with acraldehyde, but the yields obtainable in this reaction, which has long been known (cf. Alsberg, *Jahresber.*, 1864, 495), were not always satisfactory (cf. Schulz and Wagner, *Angew. Chem.*, 1950, **62**, 105). However, removal of the water produced in the reaction by azeotropic distillation with an inert entrainer (Bellringer, Bewley, Hall, Jacobs, and Stern, *J. Appl. Chem.*, 1954, **4**, 679; cf. B.P. 713,833; B.P. Appln. 9158/52) gave very high yields (better than 90% in some cases) and the trialkoxy-compounds thus became readily available.

Trialkoxypropanes in which the alkoxy-groups were dissimilar, such as 3-butoxy-1 : 1-diethoxy- and 1 : 1-dibutoxy-3-ethoxy-propane, were not obtainable by the entrainment method and were prepared under mild conditions from the appropriate β-alkoxypropaldehyde and alcohol in the presence of an acid catalyst. The absence of any cross-etherification during the acetal formation was proved by mild acid hydrolysis of the trialkoxy-compound and characterisation of the derived β-alkoxypropaldehyde; in each case a homogeneous derivative of the original alkoxy-aldehyde was obtained.

The thermal fission of polyalkoxy-compounds is not new: acetals have been cracked to vinyl ethers with the loss of one molecule of alcohol in the liquid phase (Claisen, *Ber.*, 1898, **31**, 1006, 1019), in the vapour phase over a variety of solid catalysts (Sigmund *et al.*, *Monatsh.*, 1929, **51**, 234; 1927, **48**, 267; 1928, **49**, 271; Johanissian and Akunian, *Chem. Zentr.*, 1930, II, 552; Cabanac, *Compt. rend.*, 1930, **190**, 881; I.G. Farbenind., G.P. 525,836;

---

* Part VI, *J.*, 1954, 4303. † Part of this work is described in B.P. 695,789 and 709,913.

B.P. 345,253; Consortium für Electrochem. Ind., G.P. 560,354) and also in the vapour phase in presence of gaseous catalysts (Bramwyche, Mugdan, and the Distillers Co. Ltd., B.P. 603,471). Moreover, 1 : 1 : 3-trialkoxybutanes, the homologues of the compounds now studied, have been decomposed in the vapour and the liquid phase over solid catalysts, with the loss of two molecules of alcohol, to 1-alkoxybuta-1 : 3-dienes (Flaig, *Reichsamt f. Wirtschaftsausbau, Chem. Ber.*, 1942, 1073, abstracted in *Chem. Abs.*, 1947, **41**, 6190; see also *Annalen*, 1950, **568**, 1; Meier, *Ber.*, 1944, **77**, 108; Marion and Farmilo, *Canad. J. Res.*, 1947, **25**, *B*, 118; Farmilo and Nicholls, *ibid.*, 1950, **28**, *B*, 689); only traces of 1 : 3-dialkoxybut-1-enes are obtained in this reaction (Flaig, *locc. cit.*). Analogously, 1 : 3 : 3-trialkoxybutanes in the liquid phase over potassium hydrogen sulphate give 2-alkoxybuta-1 : 3-dienes (Dykstra, *J. Amer. Chem. Soc.*, 1935, **57**, 2255), whilst over alumina the corresponding 1 : 3-dialkoxybut-2-ene is obtained in good yield.

A preliminary investigation of the homogeneous gas-phase decomposition of the 1 : 1 : 3-trialkoxypropanes under conditions similar to those of Bramwyche and Mugdan (*loc. cit.*) revealed that these compounds readily lost one molecule of alcohol, giving a mixture of the two theoretically possible structural isomers, the 1 : 3-dialkoxypropene (*A*) and the acraldehyde dialkyl acetal (*B*), which were separable by fractional distillation.

$$(B)\ \mathrm{CH_2{:}CH{\cdot}CH(OR)_2} \longleftarrow \mathrm{RO{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OR)_2} \longrightarrow \mathrm{RO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}OR}\ (A)$$

The structures were readily established by mild hydrolysis with very dilute aqueous acid, the lower-boiling acetals giving acraldehyde, whilst the 1 : 3-dialkoxypropenes afforded the β-alkoxypropaldehydes, characterised as 2 : 4-dinitrophenylhydrazones. Further, the diethyl acetal was compared with that prepared by the unequivocal method of Fischer and Baer (*Helv. Chim. Acta*, 1935, **18**, 514), and the hydrogenation product of 1 : 3-dimethoxypropene with synthetic 1 : 3-dimethoxypropane (Baker and Field, *J.*, 1932, 86).

Each of the 1 : 3-dialkoxypropenes, a new class of compound, can exist in two geometrically isomeric forms, and *cis*- and *trans*-1 : 3-dichloropropenes are, in fact, well known (cf. Hatch and Roberts, *J. Amer. Chem. Soc.*, 1946, **68**, 1196; Hatch, Gordon, and Russ, *ibid.*, 1948, **70**, 1093). In the present work, it was possible to separate partly *cis*- and *trans*-1 : 3-diethoxypropene by careful fractional distillation of the cracking product. The isomers, and, in particular, the *trans*-compound, were, however, not very stable to the prolonged heat treatment involved in a lengthy fractional distillation, and, although pure *cis*-isomer was obtained, the best sample of the higher-boiling *trans*-isomer isolated still contained about 25% of the *cis*-compound. The isomers were differentiated by infrared spectroscopy; the *cis*-isomer gave a characteristic broad peak at 746 cm.$^{-1}$, and the *trans*-isomer a sharp maximum at 939 cm.$^{-1}$ [cf. *cis*- and *trans*-but-1-enyl butyl ether (Hall, Philpotts, Stern, and Thain, *J.*, 1951, 3341)]. Both isomers showed a striking absorption band in the region 1660—1665 cm.$^{-1}$ by which they could readily be differentiated from the acraldehyde acetals whose spectra lacked a band in this region although they all had a characteristic maximum at 938 cm.$^{-1}$ (cf. Part V). The infrared spectra of all the 1 : 3-dialkoxypropenes prepared were remarkably similar and resembled that of a mixture of *cis*- and *trans*-1 : 3-diethoxypropene, so that it may be assumed that an equilibrium mixture of the isomers was generally produced in the thermal fission.

The 1 : 3-dialkoxypropenes had a pleasant odour, very different from that of the acraldehyde acetals, and were slightly water-soluble (about 5% v/v in the case of 1 : 3-diethoxypropene). As αβ-unsaturated ethers they very readily added alcohols in presence of acidic catalysts and regenerated 1 : 1 : 3-trialkoxypropanes; on hydrogenation over Raney nickel in neutral (ethanolic) solution they gave almost quantitatively the 1 : 3-dialkoxypropanes. 1 : 3-Dimethoxy- and 1 : 3-diethoxy-propane have previously been prepared in very poor yield by alkylation of propane-1 : 3-diol or its monoethers (Noyes, *Amer. Chem. J.*, 1897, **19**, 768; Baker and Field, *loc. cit.*) or by the reaction of 3-chloropropanol with sodium alkoxide (Rojahn and Lemme, *Arch. Pharm.*, 1925, **263**, 617); they may also be obtained by high-pressure hydrogenation of 1 : 1 : 3-trialkoxypropanes in alcohol over Raney nickel at 195° (Schulz and Wagner, *Angew. Chem.*, 1950, **62**, 105; see also FD 2464/49, G.P. Appl. D 78,864 IVd/12o; PB 70,309, Frame 7649; and PB 73,333, Frames 4297 and 4521), but this method is not attractive because of the vigorous conditions required and because the great reactivity of Raney nickel towards the solvent under these conditions introduces explosion hazards (personal communication from Mr. I. K. M. Robson).

Of the acraldehyde dialkyl acetals obtained in this investigation, the dimethyl and diethyl compounds were well known (cf., *e.g.*, Wohl and Momber, *Ber.*, 1914, **47**, 3348) and the di-*n*-propyl and di-*n*-butyl homologues had been isolated previously (cf. Part V). The di*iso*propyl acetal, however, was not accessible by the earlier methods, and was obtained for the first time; an alternative method of preparation was subsequently recorded by Myers, Magerlein, Staffen, and the Upjohn Chemical Co. (*loc. cit.*).

One notable feature of the fission described here was that both products, the acraldehyde acetal and the 1 : 3-dialkoxypropene, could be reconverted almost quantitatively into 1 : 1 : 3-trialkoxypropane simply by treatment with the appropriate alcohol in the cold in the presence of an acidic catalyst : the process was thus capable of adaptation to the preparation of either of the reaction products, the unwanted product being converted into starting material and recycled with no significant loss of material.

Owing to this ready addition of alcohol to both the unsaturated acetal and the ether, it was necessary to neutralise the acid catalyst in the fission products before they were cooled, either by adding a base to the hot gaseous mixture, or by feeding a tertiary heterocyclic base with the starting materials (cf. Bramwyche and Mugdan, *loc. cit.*) : the latter procedure was adopted, quinoline being employed in place of the pyridine advocated by Bramwyche and Mugdan (*loc. cit.*) as the latter was too low-boiling for the present experiments and in some cases, after distillation of the reaction products, contaminated the desired fractions.

The effects of changes of reaction conditions (particularly contact time, temperature, and catalyst concentration) were studied briefly with 1 : 1 : 3-triethoxypropane. Variation of the contact time at 350° or of the reaction temperature between 250° and 450° (Table 1) gave rather inconclusive results but it appeared that the production of 1 : 3-diethoxypropene was favoured, at the expense of the acetal, when the conversion of 1 : 1 : 3-triethoxypropane was reduced (*i.e.*, when the recovery of unchanged starting material was increased), irrespective of furnace temperature. This effect was ascribed to the relatively high thermal instability of 1 : 3-diethoxypropene; thus it was found (Table 2) that, under

TABLE 1. *Effect of variation of contact time and temperature on thermal fission of* 1 : 1 : 3-*triethoxypropane.*

Catalyst : di*iso*propyl sulphate (0·1 mole-%) in presence of quinoline (3·0 mole-%).

			Yield of products (%), based on starting material consumed		
Temp.	Contact time (sec. at operating temp.)	Unchanged material recovered (%)	EtOH	$CH_2{:}CH{\cdot}CH(OEt)_2$	$EtO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}OEt$
350° ± 5°	28	25	97	47·5	40
,,	56	17	94	44	42
,,	98	17	93	42	42
265	160	58	100	36·5	47
350	56	17	94	44	42
ca. 450	*ca.* 4·3	32	102	28·5	51·5

TABLE 2. *Behaviour of reaction products under conditions for thermal fission.*

In each run 0·1 mole-% of di*iso*propyl sulphate and 1 mole-% of a base were added.

					Yield of products (%), based on starting material consumed		
Substance	Base	Temp.	Contact time (sec. at operating temp.)	Unchanged material recovered (%)	EtOH	$CH_2{:}CH{\cdot}CH(OEt)_2$	$EtO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}OEt$
Acraldehyde diethyl acetal	Pyridine	360°	65	90	—	85—90% recovery	—
1 : 3-Diethoxypropene	Quinoline	350	53	58	Not detd.	37	58—60% recovery

similar conditions at 350°, acraldehyde acetal passed through the reaction tube substantially unchanged; 1 : 3-diethoxypropene was partly split and isomerised, giving ethanol and acraldehyde diethyl acetal—the probability that one of the geometrical isomers was less stable than the other was not investigated experimentally. The partial isomerisation of 1 : 3-diethoxypropene to the acetal was surprising, in view of the reverse isomerisation under acid conditions of 3 : 3-diacetoxy- (cf. Smith, Norton, and Shell Development Co., B.P. 638,763; Smith, Norton, and Ballard, *J. Amer. Chem. Soc.*, 1951, **73**, 5282), 3 : 3-dichloro-, and 3 : 3-dibromo-prop-1-ene (cf. Romburgh, *Bull. Soc. chim. France*, 1881, **36**, 550; 1882, **37**, 103; Stitz, *Oesterr. chem. Ztg.*, 1947, **48**, 186).

Further evidence of the lower stability, under the conditions of the reaction, of 1 : 3-diethoxypropene compared with the acetal was obtained from varying the concentration and proportion of catalyst (see Table 3) : the relative amount of 1 : 3-diethoxypropene formed was greatest under mild reaction conditions, when the product presumably underwent little further change. Thus catalyst concentrations of 0·06 and 0·1 mole-% (at a catalyst to neutraliser molar ratio of 1 : 10) gave about twice as much acraldehyde acetal as 1 : 3-diethoxypropene, but with 0·2 mole-% catalyst this proportion rose to 12. An increase in the amount of quinoline (used as neutralising base) greatly increased the amount of 1 : 3-diethoxypropene isolated, and the base may thus have acted as stabiliser for the diether as well as subsequently fulfilling its role of neutralising the catalyst and preventing recombination of the unsaturated ether with alcohol. Moreover, an increase in the amount of neutraliser used (from a 10- to a 30-fold excess) reduced the amount of starting material recovered, and it therefore seemed possible that the smaller excess was insufficient for the complete prevention of addition of ethanol to the enolic ether; this addition thus appeared to proceed much more readily than that of ethanol to acraldehyde acetal. A catalyst to neutraliser molar ratio of 1 : 30 was therefore desirable to ensure a reproducible, good yield of 1 : 3-diethoxypropene, but a greater excess of neutraliser conferred no further advantage.

TABLE 3. *Effect of variation in catalyst concentration and in catalyst to neutraliser ratio* (temp. 350°).

$Pr^i_2SO_4$ concn. (mole-%)	Quinoline concn. (mole-%)	Ratio, catalyst : neutraliser	Contact time (sec.)	Unchanged material recovered (%)	Yield of products (%), based on starting material consumed		
					EtOH	$CH_2{:}CH\cdot CH(OEt)_2$	$EtO\cdot CH_2\cdot CH{:}CH\cdot OEt$
0·1	0	—	90	18	98	50	15
0	3	—	53	83	15 *	5 *	37 *
0·06	0·6	1 : 10	54	26	100	49·5	25
0·1	1·0	1 : 10	57	33	90	58	24
0·2	2·0	1 : 10	42	29	97	65	6
0·1	3·0	1 : 30	56	17	94	44	42
0·1	6·0	1 : 60	45	16	94	48	40

* Low recoveries of products are probably due to a combination of distillation losses and very low conversion (<17%).

TABLE 4. *Thermal fission of* 1 : 1 : 3-*triethoxypropane.*

Catalyst and concn. (mole-%)		Neutraliser and concn. (mole-%)		Temp.	Contact time (sec.)	Unchanged material recovered (%)	Yield of products (%), based on consumed starting material		
							EtOH	$CH_2{:}CH\cdot CH(OEt)_2$	$EtO\cdot CH_2\cdot CH{:}CH\cdot OEt$
Me_2SO_4	1	Pyridine	3	370°	85	18	104	35	17
H_2SO_4	0·5	—*	—	360	84	10	107	37	5
—	—	—	—	360	64	>90	—	—	—
—	—	Quinoline	3	355	53	83	15	5	37

* Quinoline (3 mole-%) in receiver to neutralise catalyst.

Use of quinoline alone (in absence of acidic catalyst) resulted in little decomposition (cf. Table 4) : the useful cracking product, however, contained much more 1 : 3-diethoxypropene than acraldehyde diethyl acetal.

For the study of the effects of changes in starting material on the relative proportions and yields of the products, conditions were chosen under which reproducible results were obtained in the decomposition of 1 : 1 : 3-triethoxypropane (see Table 5). Similar conversions were attained for the five trialkoxypropanes examined, but it was found that trimethoxy- and tri*iso*propoxy-propane on fission gave the 1 : 3-dialkoxypropene preferentially, whilst triethoxy-, tri-*n*-propoxy-, and tri-*n*-butoxy-propane gave about equal amounts of the two structural isomers. There is no obvious explanation for these differences.

TABLE 5. *Effect of variation of starting material* [di*iso*propyl sulphate (0·1 mole-%); quinoline (3·0 mole-%); temp., 350°].

Starting material	Contact time (sec.)	Unchanged material recovered (%)	Yield of products (%), based on starting material consumed		
			ROH	$CH_2{:}CH{\cdot}CH(OR)_2$	$RO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}OR$
1 : 1 : 3-Trimethoxypropane ...	48	20	90	38	56
1 : 1 : 3-Triethoxypropane	56	17	94	44	42
1 : 1 : 3-Tri-*n*-propoxypropane...	52	18·5	83	43	45
1 : 1 : 3-Tri*iso*propoxypropane *	52·5	8·5	100	33	56
1 : 1 : 3-Tri-*n*-butoxypropane ...	49	16	98	40	41·5
1 : 1 : 3-Triethoxy-2-methylpropane	51	12·5	90	48·5	34
1 : 1 : 3-Triethoxybutane	50	0		Extensive decomp.	
1 : 1 : 3-Triacetoxypropane † ...	55	38	88	42	14

* Quinoline concn.: 2 mole-%. † Quinoline concn.: 1 mole-%.

For comparison, 1 : 1 : 3-triethoxy-2-methylpropane (from α-methylacraldehyde) and 1 : 1 : 3-triethoxybutane (from crotonaldehyde) were also submitted to the "standard" reaction conditions. Triethoxy-2-methylpropane behaved normally, except that it gave the acetal of α-methylacraldehyde preferentially (48·5% yield) and less 1 : 3-diethoxy-2-methylpropene (34%), but 1 : 1 : 3-triethoxybutane decomposed extensively and gave much 1-ethoxybuta-1 : 3-diene (also obtained by Flaig, *Chem. Abs.*, 1947, **41**, 6190; *Annalen*, 1950, **568**, 1; Meier, *Ber.*, 1944, **77**, 108) and little, if any, of the desired fission products. Much milder conditions appeared to be necessary, therefore, for the successful preparation of 1 : 3-diethoxybut-1-ene or of crotonaldehyde diethyl acetal from 1 : 1 : 3-triethoxybutane, but these were not investigated.

With two "unsymmetrical" trialkoxypropanes, 3-butoxy-1 : 1-diethoxy- and 3 : 3-dibutoxy-1-ethoxy-propane, the lower alcohol tended to be split out preferentially (see Table 6).

TABLE 6. *Thermal fission of "unsymmetrical" 1 : 1 : 3-trialkoxypropanes* (0·1 mole-% of di*iso*propyl sulphate; temp., 350°).

Starting material	Quinoline concn. (mole-%)	Contact time (sec.)	Starting material recovered (%)	Yield of products (%), based on starting material consumed			
				EtOH	BuOH	Acetal	1 : 3-Dialkoxy-cmpd.
1 : 1-Dibutoxy-3-ethoxypropane	3	50	24%	51	48	45	38
3-Butoxy-1 : 1-diethoxypropane	1	71	14%	80	13	7	71

1 : 1 : 3-Triacetoxypropane, which was less accessible than the ethers and had to be prepared by the method of Smith and Shell Development Co. (U.S.P. 2,471,391; cf. Smith, Norton, and Ballard, *loc. cit.*), was also cracked under similar conditions (except that the catalyst to neutraliser ratio was 1 : 10) (see Table 5). The product contained more unchanged starting material than that from triethoxypropane, and three times as much acraldehyde diacetate was obtained as 1 : 3-diacetoxypropene.

In order to demonstrate the wide variety of conditions suitable for the acid-catalysed fission of 1 : 1 : 3-trialkoxypropanes, experiments were carried out with different catalysts: thus sulphuric acid (vapour phase and liquid phase), methyl sulphate (vapour phase), ammonium sulphate (liquid phase), and fuller's earth (heterogeneous solid–liquid phases) induced decomposition of triethoxypropane under the drastic reaction conditions used, giving in each case both the acetal and 1 : 3-diethoxypropene.

In conclusion, two microfilmed reports [FD 16/48 (Frames 3—4) and PB 73,507 (Frames 5066—5073)] of German war-time work (by Brendlein), which became available during this investigation, must be mentioned. These stated that pyrolysis of gaseous 1 : 1 : 3-trimethoxy- or 1 : 1 : 3-triethoxy-propane over alumina and other solid catalysts at 250—350° gave, besides alcohol, acraldehyde, and unchanged starting material, compounds designated as 1 : 3-dialkoxypropenes. Comparison of the physical constants recorded with data obtained in the present work (see Table 7), together with their reported

TABLE 7.

	German report		Present work			
			1 : 3-Dialkoxypropene		Acetal	
Alkyl	B. p.	n_D^{20}	B. p.	n_D^{20}	B. p.	n_D^{20}
Me	87—88°	1·3961	63·5°/98 mm.	1·4200	87·5—88°/750 mm.	1·3962
Et	123—124°	1·4020	82°/60 mm.	1·4238	57°/76 mm.	1·4012

ready hydrolysis to acraldehyde and alcohol, indicated, however, that they were really acraldehyde dialkyl acetals and that authentic 1 : 3-dialkoxypropenes had either not been obtained or not isolated. Repetition (by Mr. I. K. M. Robson) of the German work with trimethoxypropane gave, as expected, some acraldehyde and much methanol, together with a poor yield of acraldehyde dimethyl acetal; a little (1·5% w/w) of the higher-boiling 1 : 3-dimethoxypropene was, however, also isolated; in Brendlein's experiments this must have been present, if at all, in the distillation residues (*i.e.*, with the unchanged trimethoxypropane).

EXPERIMENTAL

Di*iso*propyl sulphate was prepared essentially by the method of Dorris and Sowa (*J. Amer. Chem. Soc.*, 1938, **60**, 358; cf. Crittenden, U.S.P. 2,504,807). Gaseous propylene was passed into concentrated sulphuric acid (98 g.) at −5° (or, initially at as low a temperature as could be attained without inducing solidification); when 80 g. had been absorbed the liquid was poured into ice-water and immediately extracted with ether. The extracts were washed with sodium carbonate solution until no acid remained, dried, and fractionated. The pure di*iso*propyl sulphate (91·5 g.) had b. p. 50°/0·2 mm., n_D^{20} 1·4080 (Dorris and Sowa, *loc. cit.*, give b. p. 98°/2 mm.).

Starting Materials.—1 : 1 : 3-Trimethoxypropane was kindly supplied by Mr. I. K. M. Robson; after fractional distillation the pure material had b. p. 94—95°/142 mm., n_D^{20} 1·4003.

1 : 1 : 3-Triethoxy-, 1 : 1 : 3-tripropoxy-, 1 : 1 : 3-tri*iso*propoxy-, and 1 : 1 : 3-tributoxypropane, and 1 : 1 : 3-triethoxy-2-methylpropane were prepared essentially by the method of Bellringer, Bewley, Hall, Jacobs, and Stern (*J. Appl. Chem.*, 1954, **4**, 679; cf. B.P. 713,833).

1 : 1-*Dibutoxy*-3-*ethoxypropane.* A mixture of β-ethoxypropaldehyde (124 g.) (prepared by the method of Heyse and I.G. Farbenind., G.P. 554,949; cf. Part V) and *n*-butanol (500 ml.) containing concentrated sulphuric acid (1 ml.) and calcium chloride (5 g.) was kept for 10 days at room temperature, treated with calcium oxide (10 g.), and kept for 2 days with occasional agitation. After addition of calcium chloride (15 g.) the mixture was filtered and fractionated, giving, besides unchanged starting materials, pure 1 : 1-*dibutoxy*-3-*ethoxypropane* (195 g., 70%), b. p. 122°/11 mm., 96°/0·5 mm., n_D^{20} 1·4207 (Found : C, 67·2; H, 12·15. $C_{13}H_{28}O_3$ requires C, 67·2; H, 12·15%).

Hydrolysis of this acetal (2·5 g.) with water (25 ml.) containing concentrated hydrochloric acid (10 drops) at room temperature (10 min.; shaking) and subsequent addition of 2 : 4-dinitrophenylhydrazine (2 g.) in dilute methanolic sulphuric acid gave β-ethoxypropaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 85° (identical with authentic material). This proved that no cross-etherification occurred under the mild conditions used for the preparation of the acetal.

3-*Butoxy*-1 : 1-*diethoxypropane.* A solution of β-butoxypropaldehyde (92 g.; cf. Part V) in ethanol (450 ml.) containing anhydrous hydrogen chloride (1 g.) and calcium chloride (5 g.) was kept at room temperature for 72 hr., then neutralised (sodium ethoxide in ethanol), and rapidly distilled. Fractionation of the high-boiling portion of the distillate gave, besides starting materials, 3-*butoxy*-1 : 1-*diethoxypropane* (100 g., 70%), b. p. 100°/10 mm., n_D^{20} 1·4141 (Found : C, 65·0; H, 11·55. $C_{11}H_{24}O_3$ requires C, 64·7; H, 11·85%).

Hydrolysis of this acetal with dilute hydrochloric acid and treatment of the hydrolysate with 2 : 4-dinitrophenylhydrazine reagent as described above gave β-butoxypropaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 72°, identical with that described in Part V.

1 : 1 : 3-*Triacetoxypropane* (cf. Smith and Shell Development Co., U.S.P. 2,471,391). Acraldehyde (4 moles; containing 4—5% w/w of water) was added below 40° during 30 min. to a stirred solution of sulphuric acid (0·5 g.) in acetic anhydride (500 g.). When addition was complete the mixture was kept at 40° for 4 hr., diluted with acetic acid (1820 g.), and kept at 50° overnight. After treatment with sodium acetate (1 g.) the mixture was rapidly distilled at progressively reduced pressure, three main cuts being taken : the first, b. p. below 60°/60 mm. was acetic acid; the second cut, b. p. 65°/60 mm. to 82°/9 mm., on fractionation gave acraldehyde diacetate (3 : 3-diacetoxyprop-1-ene) (47%), b. p. 71°/10·5 mm., n_D^{20} 1·4204 (Evans and Shell Development Co., B.P. 596,620, give b. p. 85—88°/20 mm.); the third cut, b. p. 82°/9 mm. to 160°/0·2 mm., on fractionation gave pure 1 : 3-diacetoxypropene (9%), b. p. 56°/0·3 mm., n_D^{20} 1·4422 (Found : C, 53·55; H, 6·6. Calc. for $C_7H_{10}O_4$: C, 53·15; H, 6·35%), and pure 1 : 1 : 3-triacetoxypropane (9·5%), b. p. 90°/0·3 mm., n_D^{20} 1·4270. Smith, Norton, and Shell Development Co. (B.P. 638,763) gave b. p. 82°/5 mm., and 91—92°/10 mm., n_D^{20} 1·4384, for the 1 : 3-diacetoxypropene (the lower n_D^{20} might be due to the presence of different proportions of geometrical isomers or to contamination); and Smith, Norton, and Shell Development Co. (B.P. 655,040) gave b. p. 90—98°/0·6 mm., 100—101°/0·8 mm., n_D^{20} 1·4270, for 1 : 1 : 3-triacetoxypropane. [Some of these constants were also recorded by Smith, Norton, and Ballard (*J. Amer. Chem. Soc.*, 1951, **73**, 5282) after the present work had been completed.] The occurrence of the 1 : 3-diacetoxypropene in the products was, perhaps, surprising as no 1 : 3-dialkoxypropene was formed in the analogous preparation of trialkoxypropanes; the same observation was, however, subsequently made by Smith *et al.* (*loc. cit.*).

Hydrolysis of the 1 : 1 : 3-triacetoxypropane (1 g.) with water (15 ml.) containing concentrated hydrochloric acid (1 ml.) at room temperature (10 min.; shaking) and subsequent addition of 2 : 4-dinitrophenylhydrazine (1 g.) dissolved in methanol (30 ml.) containing sulphuric acid (1·5 ml.) gave, after 30 min. at room temperature, β-acetoxypropaldehyde 2 : 4-dinitrophenylhydrazone, which, crystallised from methanol, had m. p. 124—124·5° (Ballard, Geyer, Mortimer, and Shell Development Co., U.S.P. 2,467,876, give m. p. 124·5—125·5°). Smith *et al.* (*loc. cit.*) subsequently reported that the triacetoxy-compound gave acraldehyde 2 : 4-dinitrophenylhydrazone on treatment with acid and 2 : 4-dinitrophenylhydrazine.

Similar hydrolysis of 1 : 3-diacetoxypropene, n_D^{20} 1·4422, except that less hydrochloric acid was used (3 drops) gave the same 2 : 4-dinitrophenylhydrazone, m. p. 123·5—124°, and a trace of acraldehyde 2 : 4-dinitrophenylhydrazone, m. p. 166—166·5°.

*Homogeneous Vapour-phase Reactions Catalysed by Di*iso*propyl Sulphate.—Apparatus.* The apparatus consisted of a Pyrex glass tube, inclined to the horizontal at an angle of about 15° and heated by a tubular furnace, 2·5 ft. in length, the ends of which were plugged with asbestos wool. The furnace temperature was measured by means of a calibrated thermocouple inserted in the annular space between the reaction tube and the furnace. Several glass tubes were available and their different diameters (from 3/16 to 1 in.) provided one means of varying the contact time of the reactants. The glass tube was provided at the feed end with a gas inlet and with a side-arm for the liquid feed. The liquid was actually vapourised in the hot zone of the tube as no pre-heater was used. The feed-rate was controlled and kept constant by a modified Mariotte feed, and the flow-rate of the diluent gas (nitrogen) was measured by means of a directly calibrated capillary flowmeter and adjusted and kept constant by needle-valves. From the known feed rates and the volume of the hot zone, the contact time was calculated.

The product was condensed in a water-cooled coil condenser to which was attached a two-necked flask containing about 0·1—0·5 g. of quinol; the exit, from the other neck of this receiver, led through another condenser into a trap cooled by solid carbon dioxide–acetone. Loss of volatile reaction product was thus avoided.

Method and working-up. In a typical run quinoline (7·2 g., 3 mole-%) and then di*iso*propyl sulphate (0·34 g., 0·1 mole-%) were added to 1 : 1 : 3-triethoxypropane (327 g., 1·86 moles). This feed material was dropped at a constant rate (about 45 ml. per hr.) into a reaction tube (vol. of heated zone : 350 ml.) kept at 350° ± 5°. The flow of diluent nitrogen was 4·9 l. per hr. (measured at room temperature; *i.e.*, 10·8 l. per hr. at 350°). The contact (or residence) time was, therefore, about 56 sec. at the operating temperature.

The run was interrupted after 7·5 hr., when 330 ml. (295 g.) of feed had been added. The product (containing 0·5 g. of quinol) was fractionally distilled under reduced pressure in an atmosphere of nitrogen, through a glass column (40 cm. long × 2·5 cm. int. diam.) packed with glass helices and provided with a heated jacket and a total-reflux, variable take-off head. In some distillations a column (48 cm. long × 3 cm. int. diam.) packed with stainless-steel gauze Lessing rings (1/8 × 1/8 in.) was used.

This fractionation gave : (i) ethanol (58 g.), b. p. 26°/68 mm., n_D^{20} 1·364—1·365 (lit., 1·362; therefore slightly impure) ; (ii) acraldehyde diethyl acetal (76·5 g.), b. p. 55°/61 mm., n_D^{20} 1·4015 ; (iii) 1 : 3-diethoxypropene (73·5 g.), b. p. 47—48°/12 mm., n_D^{20} 1·4230; (iv) unchanged 1 : 1 : 3-triethoxypropane (50 g., 17%), b. p. 68°/11 mm., n_D^{20} 1·4068, and a residue (18 g.) ; distillation loss thus amounted to 19 g. (hold-up; loss of low-boiling materials). The molar efficiency of formation of products, based on the amount of starting material consumed, was : ethanol 94%, acetal 44%, and 1 : 3-diethoxypropene 42%.

Results.—The unsaturated products derived from the various 1 : 1 : 3-trialkoxypropanes are shown in Table 8.

TABLE 8. *Pyrolysis of* 1 : 1 : 3-*trialkoxypropanes.*

			Starting material		Products			
			$R^1O\cdot CH_2\cdot CHR^2\cdot CH(OR^3)_2$		$CH_2{:}CR^2\cdot CH(OR^3)_2$		$R^1O\cdot CH_2\cdot CR^2{:}CH\cdot OR^3$ [g]	
R^1	R^2	R^3	B. p./mm.	n_D^{20}	B. p./mm.	n_D^{20}	B. p./mm.	n_D^{20}
Me	H	Me	94—95°/142	1·4003	87·5—88°/750 [c]	1·3962 [c]	64°/98	1·4202
Et	H	Et	69—70°/10 [a, b]	1·4066 [a, b]	55°/67 [b]	1·4012 [b]	55°/18 mm.	1·4238
Pr^n	H	Pr^n	109°/12 [a, b]	1·4175 [a, b]	52—53°/12·5 [b]	1·4120 [b]	73°/12	1·4287
Pr^i	H	Pr^i	89—91°/11 [a, b]	1·4096 [a, b]	38·5°/12 [d]	1·4053	62·5°/12	1·4225
Bu^n	H	Bu^n	123°/4 [a, b]	1·4257 [a, b]	83°/9 [b]	1·4204 [b]	110°/16	1·4348
Et	H	Bu^n	122°/11	1·4207	85—86°/10 [e]	1·4210 [e]	80—80·5°/10 [e]	1·4286
Bu^n	H	Et	100°/10	1·4141	— [f]	—	72·5—74°/10 [f]	1·4296
Et	Me	Et	75°/11·5 [a, b]	1·4083 [a, b]	32°/12 [b]	1·4083 [b]	54°/14	1·4259

[a] Cf. Bellringer *et al.*, *J. Appl. Chem.*, 1954, **4**, 679. [b] Cf. Part V; *J.*, 1954, 3388. [c] The acraldehyde dimethyl acetal was obtained initially as a methanol azeotrope, b. p. 31°/180 mm., n_D^{20} 1·3618, approx. 1 : 1 (acetal determined by oximation). Refractionation of the azeotrope at 1 atm. gave a lower-boiling mixture of methanol and acetal, b. p. 63°/750 mm., n_D^{20} 1·3580, and some pure acetal (for constants, see Table; Wohl and Momber, *Ber.*, 1914, **47**, 3349, give b. p. 86°/760 mm.). Alternatively, the original azeotrope was diluted with saturated aqueous sodium chloride and the upper layer separated, dried, and fractionated; it consisted largely of the acetal. [d] Myers, Magerlein, Staffen, and the Upjohn Co. (B.P. 713,088) subsequently gave b. p. 68·5—69·5°/50 mm. [e] The fractionation of the pyrolysis products gave : (i) somewhat impure ethanol, b. p. below 50°/67 mm., n_D^{20} 1·364—1·368, (ii) impure butanol (containing some ethanol), b. p. 57°/67 mm., n_D^{20} 1·391—1·398, (iii) 1-butoxy-3-ethoxyprop-1-ene (see Table), (iv) acraldehyde dibutyl acetal (see Table), and (v) unchanged starting material. Intermediate fractions are neglected; quinoline distilled between fractions (iv) and (v). [f] The fractionation of the pyrolysis products gave : (i) slightly impure ethanol, b. p. 26—30°/65 mm., n_D^{20} 1·368, (ii) a small fraction containing butanol and acraldehyde diethyl acetal, b. p. *ca.* 35°/17 mm., n_D^{20} 1·399—1·403, (iii) 3-butoxy-1-ethoxyprop-1-ene (see Table), and (iv) unchanged starting material. [g] Mixed stereoisomers.

The acraldehyde acetals were each characterised by hydrolysis and preparation of the 2 : 4-dinitrophenylhydrazone of the parent acraldehyde (m. p. and mixed m. p.). They all showed a characteristic infrared absorption peak at about 938 cm.$^{-1}$. *Acraldehyde diisopropyl acetal* was a new compound when prepared (Found : C, 68·0; H, 11·65. $C_9H_{18}O_2$ requires C, 68·3; H, 11·45%) ; it was subsequently described (b. p. 68·5—69·5°/50 mm.), but not analysed, by Myers, Magerlein, Staffen, and the Upjohn Co. (B.P. 713,088). On hydrogenation in ethanol (60 ml.) over Raney nickel (7·5 g. of " paste ") it (15·8 g.) gave propaldehyde di*iso*propyl acetal, b. p. 144°/752 mm., n_D^{20} 1·3995 (Adams and Adkins, *J. Amer. Chem. Soc.*, 1925, **47**, 1358, give b. p. 146·5°).

The 1 : 3-dialkoxypropenes were all new compounds (see Table 9). They had characteristic infrared absorption peaks at about 746, 938, and 1660—1665 cm.$^{-1}$. On hydrolysis with dilute acid (cf. analogous reaction of 1 : 3-diacetoxypropene) and treatment of the hydrolysate with 2 : 4-dinitrophenylhydrazine reagent they gave the corresponding β-alkoxypropaldehyde 2 : 4-dinitrophenylhydrazone (see Table 9). Hydrogenation over Raney nickel at atmospheric temperature and pressure (for conditions see Table 10) resulted in the absorption of 1 mol. of hydrogen and formation of the corresponding 1 : 3-dialkoxypropanes which are listed in Table 11.

Reaction of 1 : 3-*Diethoxypropene with Ethanol*.—Addition of 1 : 3-diethoxypropene (13 g.) in ethanol (13 g.) to ethanol (10 g.) containing anhydrous hydrogen chloride (1 g.) resulted in spontaneous warming; the mixture was kept at room temperature overnight, made just alkaline (litmus) with sodium ethoxide in ethanol, filtered, and distilled, giving 1 : 1 : 3-triethoxypropane (16 g., 91%), b. p. 177°/755 mm., n_D^{20} 1·4068.

Reaction of Acraldehyde Diethyl Acetal with Ethanol.—This was described in Part V.

Pyrolysis of 1 : 1 : 3-*Triacetoxypropane* (see Table 5).—Besides acetic acid, b. p. 22—30°/12 mm., n_D^{20} 1·372—1·380, there were obtained : (i) allylidene diacetate (3 : 3-diacetoxyprop-1-ene) [this had b. p. 29°/0·3 mm., n_D^{20} 1·4195, and on hydrolysis with 2N-hydrochloric acid gave acraldehyde (smell), characterised as 2 : 4-dinitrophenylhydrazone, m. p. 166°]; and (ii) 1 : 3-diacetoxypropene, which, as obtained from the first fractionation, had b. p. 56°/0·3 mm., n_D^{20} 1·4444 and probably contained a trace of quinoline; on re-fractionation it had n_D^{20} 1·4420, identical with the material obtained in the course of preparing 1 : 1 : 3-triacetoxypropane.

TABLE 9. 1 : 3-*Dialkoxypropenes.*

		Found (%)		Required (%)		2 : 4-Dinitrophenyl-hydrazone, m. p.*
1 : 3-Dialkoxypropene	Formula	C	H	C	H	
1 : 3-*Dimethoxypropene*	$C_5H_{10}O_2$	58·85, 58·5	9·8, 9·8	58·8	9·85	—
1 : 3-*Diethoxypropene*	$C_7H_{14}O_2$	64·45	10·8	64·6	10·85	84—85° [a]
1 : 3-*Dipropoxypropene*	$C_9H_{18}O_2$	68·4	11·75	68·3	11·45	99—100° [b]
1 : 3-*Diisopropoxypropene*	$C_9H_{18}O_2$	68·4	11·55	68·3	11·45	98—99° [c]
1 : 3-*Dibutoxypropene*	$C_{11}H_{22}O_2$	70·7	11·6	70·9	10·9	71—72° [d]
1-*Butoxy*-3-*ethoxypropene*	$C_9H_{18}O_2$	68·7	11·6	68·3	11·45	85° [a]
3-*Butoxy*-1-*ethoxypropene*	$C_9H_{18}O_2$	68·45	11·35	68·3	11·45	72° [d]
1 : 3-*Diethoxy*-2-*methylpropene*	$C_8H_{16}O_2$	66·45	11·35	66·6	11·2	—

* Identities confirmed by mixed m. p.s with authentic β-alkoxypropaldehyde 2 : 4-dinitrophenylhydrazones: [a] Hall and Stern, *Chem. and Ind.*, 1950, 775 (cf. Part V; Feazel and Berl, *J. Amer. Chem. Soc.*, 1950, **72**, 2278), m. p. 85°. [b] Hall and Stern, *J.*, 1952, 4083, m. p. 100·5°. [c] Part V, m. p. 99°. [d] Part V, m. p. 72—73°.

† Precise fractionation afforded the *cis*-isomer, b. p. 45—46°/10 mm., n_D^{20} 1·4230, free from the *trans*-isomer (infrared), together with fractions enriched in the latter. The purest sample, b. p. b. p. 47—48°/10 mm., n_D^{20} 1·4239, of the *trans*-compound obtained, however, still contained about 25% of the *cis*-isomer.

TABLE 10. *Hydrogenation of* 1 : 3-*dialkoxypropenes.*

$R^1O{\cdot}CH_2{\cdot}CR^2{:}CH{\cdot}OR^3$								
R^1	R^2	R^3	(g.)	Solvent and wt. (g.)		Raney nickel " paste " (g.)	H_2 absorbed (mols.)	Pure product (g.)
Me	H	Me	8·0	MeOH	32	4	1·02	*ca.* 5 [c]
Et	H	Et	48	EtOH	280	35	0·99	46·5
Pr^n	H	Pr^n	— [a]	EtOH	—	—	—	—
Pr^i	H	Pr^i	12·8	EtOH	44	6·5	0·97	11·0
Bu^n	H	Bu^n	6·9	EtOH	40	5	1·01	6·5
Et	H	Bu^n	7·0	EtOAc	40	5	0·98	6·3 [b]
Bu^n	H	Et	8·6	EtOH	40	5	0·99	6·5 [b]
Et	Me	Et	18·6	EtOH	48	5	0·94	17·1

[a] Quantitative data not available (starting material slightly impure). [b] These hydrogenations afforded the same product, 1-butoxy-3-ethoxypropane. [c] Ether-extraction necessary to obtain pure material.

TABLE 11. 1 : 3-*Dialkoxypropanes.*

				Found (%)		Required (%)	
1 : 3-Dialkoxypropane	B. p./mm.	n_D^{20}	Formula	C	H	C	H
1 : 3-Dimethoxypropane [a]	105—105·5°/756	1·3898	$C_5H_{12}O_2$	—	—	—	—
1 : 3-Diethoxypropane [b,c]	140—141°/750	1·3980	$C_7H_{16}O_2$	63·2	12·0	63·6	12·2
1 : 3-*Dipropoxypropane*	165°/750	1·4080	$C_9H_{20}O_2$	67·3	12·2	67·45	12·6
1 : 3-*Diisopropoxypropane*	159—160°/750	1·4015	$C_9H_{20}O_2$	67·65	12·55	67·45	12·6
1 : 3-*Dibutoxypropane*	213°/750, 97°/11	1·4170	$C_{11}H_{24}O_2$	69·8	12·95	70·15	12·85
1-*Butoxy*-3-*ethoxypropane*	182°/750	1·4100	$C_9H_{20}O_2$	67·9	12·75	67·45	12·6
1 : 3-*Diethoxy*-2-*methylpropane*	145°/750	1·4012	$C_8H_{18}O_2$	65·6	12·65	65·7	12·4

[a] Also obtained (b. p. 105°, n_D^{20} 1·3889), in poor yield, by Baker and Field's method (*J.*, 1932, 86) from 3-methoxypropan-1-ol (56 g.) containing sodium (4·3 g.) on methylation with methyl sulphate (60 g.) in ether (150 ml.). Baker and Field (*loc. cit.*) give b. p. 106°/753 mm. [b] d_4^{20} 0·834, $[R]_D^{20}$ 37·63 (calc. 37·81). [c] Noyes (*Amer. Chem. J.*, 1897, **19**, 768) gives b. p. 140—141°/760 mm., d_{25}^{25} 0·835; Rojahn and Lemme (*Arch. Pharm.*, 1925, **263**, 617) record b. p. 140°.

1 : 3-Diacetoxypropene (15 g.) in ethyl acetate (60 ml.) containing Raney nickel (7·5 g. of

" paste," under ethyl acetate) rapidly absorbed hydrogen (1·05 mol.), and gave 1 : 3-diacetoxypropane, b. p. 207°/748 mm., n_D^{20} 1·4200 (Smith, Norton, and Ballard, *J. Amer. Chem. Soc.*, 1951, **73**, 5282, subsequently recorded b. p. 88—90°/10 mm., n_D^{20} 1·4184 and 1·4192). The use of ethanol as solvent induced side-reactions, including the formation of some ethyl acetate.

Pyrolysis of 1 : 1 : 3-*Trimethoxypropane over Alumina* (by I. K. M. ROBSON).—The apparatus was similar to that for the homogeneous vapour-phase experiments except that the reaction tube (1-in. diameter) was horizontal and was packed with alumina (vol. of packed zone, 245 ml.). 1 : 1 : 3-Trimethoxypropane (358·5 g.) was fed into the reaction tube at a constant rate during 2 hr. together with nitrogen (17·55 l./hr. at N.T.P.), the average reaction temperature being 228°. The bulk (301·6 g.) of the product (318·1 g.) was fractionated to give the following main fractions : (i) a mixture (224·7 g.) of acraldehyde, methanol, and acraldehyde dimethyl acetal, boiling range 38°/752 mm. to 63°/748 mm. (mainly 60—63°/748 mm.), n_D^{20} 1·3773—1·3923; (ii) acraldehyde dimethyl acetal (11·3 g.), b. p. 32—52°/100 mm., n_D^{20} 1·3973; (iii) 1 : 3-dimethoxypropene (5·4 g.), b. p. 63·5—66°/98 mm., n_D^{20} 1·4201; and (iv) a residue (23·0 g.). Intermediate fractions are neglected in the above summary.

Other Catalysed Thermal Fissions.—(1) *Vapour phase.* Miscellaneous experiments with 1 : 1 : 3-triethoxypropane designed to examine the effect of (*a*) acidic (sulphuric acid, methyl sulphate) and basic catalysts (quinoline), on the course of the reaction, and (*b*) the reaction conditions on the two products (acetal or 1 : 3-dialkoxypropene) are summarised in Tables 4 and 2, respectively.

(2) *Liquid phase.* The following experiments were performed using liquid 1 : 1 : 3-triethoxypropane and either solid or liquid catalysts : (*a*) Ammonium sulphate. 1 : 1 : 3-Triethoxypropane (79·5 g.) and powdered ammonium sulphate (0·1 g.) were refluxed in a flask attached to a fractionating column, and the products were distilled out as formed. A further portion (0·1 g.) of the catalyst was added when the reaction slowed down, and heating was continued until no more liquid remained in the flask. The distillate on fractional distillation gave ethanol (12·7 g.), acraldehyde diethyl acetal (13·8 g.), 1 : 3-diethoxypropene (19·6 g.), and unchanged 1 : 1 : 3-triethoxypropane (22·75 g.). (*b*) Fuller's earth. Fuller's earth (5 g.; No. 249) was suspended in kerosene (50 g.) and vigorously stirred at 165°; 1 : 1 : 3-triethoxypropane (100 g.) was then added slowly. The temperature was raised to 220° when addition was complete, and the products were distilled out as they were formed. They were dried (K_2CO_3), and on fractional distillation gave ethanol (40·5 g.), acraldehyde diethyl acetal (12 g.), and 1 : 3-diethoxypropene (2 g.). (*c*) Sulphuric acid. 1 : 1 : 3-Triethoxypropane (100 g.) and concentrated sulphuric acid (0·185 g.) were refluxed in a flask attached to a fractionating column, and the products were distilled as they were formed. The product on fractional distillation gave ethanol (27·55 g.), acraldehyde diethyl acetal (29·5 g.), 1 : 3-diethoxypropene (11·9 g.), and unchanged 1 : 1 : 3-triethoxypropane (12·5 g.).

The authors thank Mr. I. K. M. Robson for collaboration on one aspect of this investigation, and Messrs. D. A. Burch, A. J. Clark, and R. Hayward for assistance with the experimental work. They are also indebted to Dr. H. M. Stanley and Dr. K. H. W. Turck for their interest and encouragement, to Mr. A. R. Philpotts and Mr. W. Thain for infrared absorption data and for valuable discussions, and to the Directors of the Distillers Co., Ltd., for permission to publish this paper.

THE DISTILLERS CO., LTD., RESEARCH AND DEVELOPMENT DEPARTMENT,
GREAT BURGH, EPSOM, SURREY.
[*Received, April 6th,* 1955.]