The Reaction of Epoxides with Carboxylic Acids.

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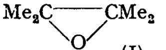
The reactions of 2 : 3-epoxy-2 : 3-dimethylbutane with formic, acetic, and trichloroacetic acid have been studied. For comparison, the behaviour of 1 : 2-epoxyoctane and 1 : 2-epoxy-1-phenylethane has been examined.

THIS paper records a qualitative examination of the reaction of some epoxides with carboxylic acids as a preliminary to an accurate kinetic study.

2 : 3-Epoxy-2 : 3-dimethylbutane (I) and formic acid rapidly give a moderate yield (~50%) of the expected glycol monoformate (II; R = H). The remainder of the product consists of 3 : 3-dimethylbutan-2-one (17%) (III), the monoformate (IV; R = H) (22%), and more complex material. With trichloroacetic acid, the monoester (II; R = CCl_3) is

accompanied by 2 : 3-dimethylbutadiene and 2 : 3-dimethylbut-3-en-2-ol (V), and the yield of ketone (III) is higher (25%). Acetic acid reacts relatively slowly and gives the glycol monoacetate (II; R = Me) as the main product with small amounts of 2 : 3-dimethylbutadiene, 2 : 3-dimethylbut-3-en-2-ol (V) and its acetate, 2 : 3-dimethylbut-2-en-1-ol (VI), and some more complex material not precisely identified : the yield of 3 : 3-dimethylbutan-2-one was quite small. Propionic acid reacts very slowly; after 6½ days in anhydrous propionic acid 60% of the epoxide was recovered unchanged. The remainder had been converted into the monopropionate (II; R = Et) with a small amount of unsaturated material.


(I)

$HO{\cdot}CMe_2{\cdot}CMe_2{\cdot}O{\cdot}COR$ (II)

$Me_3C{\cdot}COMe$ (III)

$R{\cdot}CO{\cdot}O{\cdot}CMe_2{\cdot}CMe_2{\cdot}O{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH$ (IV)

$HO{\cdot}CMe_2{\cdot}CMe{:}CH_2$ (V)

$CMe_2{:}CMe{\cdot}CH_2{\cdot}OH$ (VI)

$HO{\cdot}CHR{\cdot}CH_2{\cdot}O{\cdot}COMe$ (VII)

For comparison, the behaviour of 1 : 2-epoxyoctane and of 1 : 2-epoxy-1-phenylethane towards carboxylic acids was examined. With acetic acid each gives the glycol monoacetate (VII) as the main product. A small yield (7%) of phenylacetaldehyde was obtained from 1 : 2-epoxy-1-phenylethane; there was no clear evidence of rearrangement of 1 : 2-epoxyoctane to carbonyl compounds, but part of the product consisted of the acetate of a dihydroxydioctyl ether. Formic acid gave only a trace of octanal and formic esters of octanediol and of hydroxydioctyl ether.

Although it is generally recognised that epoxides can rearrange to ketones or aldehydes when heated alone or with a suitable catalyst or when treated with zinc chloride or magnesium halides in ether, there appears to be no well-authenticated example of rearrangement promoted by carboxylic acids (cf. Winstein and Henderson in Elderfield's " Heterocyclic Compounds," Wiley and Sons, Inc., New York, 1950, pp. 47—52). The phenomenon is essentially a reaction of the epoxide since 2 : 3-dimethylbutane-2 : 3-diol and its monoesters are unchanged by contact with even strong carboxylic acis such as trichloroacetic acid.

These observations support the view that the reaction of an epoxide with a carboxylic acid occurs in two phases. The first is the addition of a proton to the oxygen and opening of the epoxide ring to give $R_2C^+{\cdot}CR{\cdot}OH$, a type of structure similar to that postulated for the intermediate phase of the rearrangement of 1 : 2-glycols (cf. Wheland, " Advanced Organic Chemistry," Wiley and Sons, Inc., New York, 1949, p. 479). In the subsequent phase rearrangement may occur in the same way, its extent being governed by the rate of addition of anion to the positive centre. The formation of unsaturated alcohols and of dienes, such as occurs with 2 : 3-epoxy-2 : 3-dimethylbutane, is simply explained on this basis by assuming the expulsion of a proton from the carbon atom adjacent to the positive centre. The extension of this hypothesis to the reaction of epoxides with mineral acids accounts for the formation of carbonyl compounds from some epoxides under the influence of aqueous mineral acids. Among such examples are camphene oxide and di*neo*pentylethylene oxide, both of which rearrange to the corresponding aldehyde under the action of dilute mineral acids without an appreciable amount of glycol (Hickinbottom and Wood, *J.*, 1951, 1600; 1953, 1906). 1 : 2-Epoxy-2-phenylpropane also rearranges extremely easily under the influence of dilute mineral acids (Danilov and Venus-Danilova, *Ber.*, 1927, **60**, 1059).

EXPERIMENTAL

Reaction of 2 : 3-*Epoxy*-2 : 3-*dimethylbutane with Carboxylic Acids.*—2 : 3-Epoxy-2 : 3-dimethylbutane, b. p. 90—93°, n_D^{20} 1·3986, was prepared in 68—75% yield by the action of perbenzoic acid in ether on 2 : 3-dimethylbut-2-ene. The epoxide is reduced by lithium aluminium hydride in ether to 2 : 3-dimethylbutan-2-ol (82% yield) (3 : 5-dinitrobenzoate, m. p.

and mixed m. p. 110—111°) and with 2 : 4-dinitrophenylhydrazine in 20% aqueous sulphuric acid gives 3 : 3-dimethylbutan-2-one 2 : 4-dinitrophenylhydrazone.

2 : 3-Dimethylbut-2-ene was prepared by heating 2 : 3-dimethylbutan-2-ol with four times its weight of anhydrous oxalic acid for 8 hr. under reflux. The olefins thus formed were separated by distillation into 2 : 3-dimethylbut-2-ene, b. p. 72·6—73·4°, n_D^{20} 1·4120, and -1-ene, b. p. 54—55·8°, n_D^{20} 1·3902. The best yield of mixed olefin was 388 g. from 505 g. of alcohol; an average yield of 85% was obtained from smaller amounts of alcohol. The ratio of 2 : 3-dimethylbut-2-ene to its isomer was 4 : 1 as determined by the amounts separated by distillation.

2 : 3-Dimethylbutan-2-ol, prepared by the reaction of methylmagnesium bromide in ether with (*a*) ethyl *iso*butyrate (76% yield) and (*b*) methyl *iso*propyl ketone (85% yield), had b. p. 116—117°, n_D^{20} 1·4161—1·4169 (3 : 5-dinitrobenzoate, m. p. 110—111°).

(a) *With acetic acid; formation of* 3-*acetoxy*-2 : 3-*dimethylbutan*-2-*ol*. A mixture of 2 : 3-epoxy-2 : 3-dimethylbutane (13 g.) and anhydrous acetic acid (42·5 g.) was kept at room temperature for 14 days and then distilled at 4 mm. Acetic acid and the volatile products (A) of the reaction were collected in cold traps, the main product (B) at 34—47° (12·9 g.), and fraction (C) at 93—105° (1·2 g.).

2 : 3-Dimethylbutadiene (0·4 g.) (maleic anhydride adduct, m. p. and mixed m. p. 78°; dibromide, m. p. and mixed m. p. 137°) and a small amount of 2 : 3-dimethylbut-2-en-1-ol (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 107°) were isolated from fraction A.

The main product (B) consisted largely (9·8 g.) of 3-*acetxoy*-2 : 3-*dimethylbutan*-2-*ol*, b. p. 53—54°/5 mm., n_D^{20} 1·4328 (Found : C, 60·3; H, 10·0; Ac, 25·3. $C_8H_{16}O_3$ requires C, 60·0; H, 10·1; Ac, 26·8%). It was hydrolysed by aqueous alkali to 2 : 3-dimethylbutane-2 : 3-diol hydrate, m. p. and mixed m. p. 45—47°, and acetic acid (*p*-bromophenacyl ester, m. p. and mixed m. p. 83—85°). There was also present in B a lower-boiling unsaturated component which could not be separated in a pure state. Accordingly the combined lower-boiling fractions of B were hydrolysed by alkali to give 2 : 3-dimethylbutane-2 : 3-diol hydrate and 2 : 3-dimethylbut-3-en-2-ol, which was identified as its 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 127°.

No homogeneous product could be isolated from fraction C. It gave 3 : 3-dimethylbut-2-one 2 : 4-dinitrophenylhydrazone when heated with 2 : 4-dinitrophenylhydrazine in alcoholic sulphuric acid, and may therefore contain a 1 : 4- or 1 : 3-dioxan or an ester of an ether derived from a glycol.

When the epoxide was boiled in acetic acid, the same products were obtained.

(b) *With propionic acid*. The epoxide (19 g.) and propionic acid (70 g.) were mixed and kept at room temperature for 6½ days. The product, treated as above, gave unchanged epoxide (10·7 g.; n_D^{20} 1·3981—1·3990) and 2 : 3-*dimethyl*-3-*propionoxybutan*-2-*ol*, b. p. 60°/4 mm., n_D^{20} 1·4334 (3·8 g.) (Found : C, 62·0; H, 10·5. $C_9H_{18}O_3$ requires C, 62·0; H, 10·4%). It was identified by alkaline hydrolysis to 2 : 3-dimethylbutane-2 : 3-diol hydrate and propionic acid.

There were also in the product a small amount of lower-boiling, unidentified unsaturated material and 0·1 g. of higher-boiling residue with the characteristics of a dioxan.

(c) *With trichloroacetic acid*. 2 : 3-Epoxy-2 : 3-dimethylbutane (20 g.) was added to a solution of trichloroacetic acid (98 g.) in 1 : 2-dichloroethane (120 ml.). Heat was evolved during mixing, and after 36 hr. at room temperature the solution had become red. It was extracted with ice-water (2 × 200 c.c.) and then 10% sodium hydrogen carbonate solution (2 × 100 c.c.). Distillation of the dried solution gave fractions (*a*) b. p. up to 30°/4 mm., (*b*) b. p. 90—103°/4 mm., and (*c*) b. p. 103°/4 mm.

Fraction (*a*) consisted largely of dichloroethane but the lower-boiling parts were markedly unsaturated and contained some 2 : 3-dimethylbutadiene (maleic anhydride adduct, m. p. and mixed m. p. 77—78°; tetrabromide m. p. and mixed m. p. 139—140°). The amount of this present is difficult to estimate accurately but it appears to be less than 1 g. The higher-boiling material present in this fraction was concentrated into the boiling range 92—108° (4·0 g.) and it was identified as 3 : 3-dimethylbutan-2-one by its semicarbazone and 2 : 4-dinitrophenylhydrazone as well as by reduction to 3 : 3-dimethylbutan-2-ol.

Fractions (*b*) and (*c*) consisted largely of the trichloroacetate of 2 : 3-dimethylbutane-2 : 3-diol. Alkaline hydrolysis gave the glycol hydrate and chloroform. Attempts to obtain the ester pure were only partially successful; the purest samples were colourless oils, b. p. 92°/2·5 mm., n_D^{20} 1·4732—1·4736, which became yellow and then red even in sealed vessels (Found : C, 39·6; H, 5·4; Cl, 37·6. $C_8H_{13}O_3Cl_3$ requires C, 36·5; H, 5·0; Cl, 40·3%). The higher-boiling fractions were dark and deposited crystals of trichloroacetic acid.

(d) *With formic acid*. Anhydrous formic acid (34 g.) was mixed with 2 : 3-dimethyl-2 : 3-

epoxybutane (15 g.) with external cooling. Next morning the excess of formic acid and the volatile products were distilled off at 16 mm. into cold traps (product A). The remainder was freed from traces of formic acid by washing of its ethereal soution with sodium carbonate and separated into two main fractions, (B) b. p. 78—83°/16 mm., n_D^{20} 1·4411—1·4419 (5·2 g.), and (C) b. p. 141—143°/16 mm., n_D^{20} 1·4479 (3·4 g.), by distillation through a 12″ Fenske-packed column. Intermediate fractions amounting to 2·7 g. were also obtained, with a residue (0·5 g.) (D).

Fraction A was freed from formic acid by aqueous alkali and distilled to give 2·1 g. of crude 3 : 3-dimethylbutan-2-one, b. p. 90°, n_D^{20} 1·3999—1·3982 (semicarbazone, m. p. and mixed m. p. 158°).

Fraction B was essentially the 3-formyloxy-2 : 3-dimethylbutan-2-ol, b. p. 82°/15 mm., n_D^{20} 1·4416 [Found : C, 57·9; H, 9·8; $H{\cdot}CO_2$, 24·9%; *M* (Rast), 180. Calc. for $C_7H_{14}O_3$: C, 57·5; H, 9·7; $H{\cdot}CO_2$, 30·8%; *M*, 146]. The analytical figures and an abnormally high active-hydrogen content (0·96. Reqd. : 0·69%) indicate the presence of some glycol but no separation could be effected by chromatography. The ester was hydrolysed by aqueous alkali to the glycol hydrate and formic acid (reducing properties and α-naphthalide, m. p. and mixed m. p. 138—139°).

Fraction C was not homogeneous and after several distillations no completely pure compound was isolated. Analyses of successive fractions suggest a mixture of the mono- and di-formates of di-(2-hydroxy-1 : 1 : 2-trimethylpropyl) ether : (*a*) b. p. 144—146°/15 mm., n_D^{20} 1·4473 [Found : C, 61·8; H, 10·0%; *M*, (Rast) 207]; (*b*) b. p. 146—147°/15 mm., n_D^{20} 1·4478 [Found : C, 62·7; H, 10·0%; *M*, 217] (Calc. for monoformate, $C_{13}H_{26}O_4$: C, 63·4; H, 10·6%; *M*, 246. Calc. for diformate, $C_{14}H_{26}O_5$: C, 61·3; H, 9·55%; *M*, 274). Chromatography on alumina gave, as the more elutable material, the approximately pure diformate, b. p. 92°/0·5 mm., n_D^{20} 1·4472 (Found : C, 61·85; H, 10·1%). Alkaline hydrolysis gave formic acid and an oil which was not homogeneous since it deposited a small amount of crystalline material. Acid hydrolysis with a solution of 2 : 4-dinitrophenylhydrazine in alcoholic hydrochloric acid gave 3 : 3-dimethylbutan-2-one 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 126°.

Fraction D and the higher-boiling parts of C were combined and chromatographed on alumina. A rapidly elutable solid was obtained (0·5 g.), having m. p. 147—148° after crystallisation from light petroleum (b. p. 60—80°). This is a saturated ester; it is non-carbonylic. From analyses of different specimens, it appears to be a mixture of the diformate of 1 : 2-di-(2-hydroxy-1 : 1 : 2-trimethylpropoxy)-1 : 1 : 2-trimethylpropane, with some of the monoformate (Found: C, 65·6, 64·7; H, 10·0, 10·6; active H, 0·08, 0·09; $H{\cdot}CO_2$, 19·7, 20·2. Calc. for $C_{20}H_{38}O_6$: C, 64·1; H, 10·2; active H, 0; $H{\cdot}CO_2$, 24·0. Calc. for $C_{19}H_{38}O_5$: C, 65·9; H, 11·05; active H, 0·29; $H{\cdot}CO_2$, 13·0%).

Reaction of 1 : 2-*Epoxyoctane with Carboxylic Acids.*—1 : 2-Epoxyoctane, b. p. 62·5—63·0°/17 mm., n_D^{20} 1·4193—1·4198, was obtained in 80—85% yield by reaction of oct-1-ene with perbenzoic acid in chloroform. It is reduced by lithium aluminium hydride in ether to octan-2-ol (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 32—32·5°; α-naphthylamine adduct, m. p. and mixed m. p. 67—67·5°).

(a) *With acetic acid.* 1 : 2-Epoxyoctane (32 g.) and acetic acid (75 g.) were mixed and kept at room temperature for 7 days. Distillation at 16 mm. removed excess of acetic acid and unchanged 1 : 2-epoxyoctane (16 g.). The remaining reaction product (16·6 g.) was separated into two main fractions : (*a*) b. p. 106—111°/4 mm., n_D^{20} 1·4369—1·4373 (10 g.), and (*b*) b. p. 166—176°/4 mm. Fraction (*a*) was essentially 1-acetoxyoctan-2-ol, b. p. 77°/0·4 mm., n_D^{20} 1·4370 [Found : C, 64·1; H, 10·85; Ac, 21·6; active H, 0·42%; *M* (Rast), 176. Calc. for $C_{10}H_{20}O_3$: C, 63·8; H, 10·7; active H, 0·53; Ac, 22·9%; *M*, 188]. Alkaline hydroysis gave acetic acid and octane-1 : 2-diol (di-3 : 5-dinitrobenzoate; α-naphthylamine adduct, m. p. and mixed m. p. 113°). Oxidation with *tert.*-butyl chromate as described below gave 1-acetoxyoctan-2-one, m. p. and mixed m. p. 41—42°. From fraction (*b*) 2-2′-*hydroxyoctyloxyoctyl acetate* was isolated, having b. p. 145—152°/0·5 mm., n_D^{20} 1·4471 [Found : C, 68·0; H 11·45; Ac, 12·4; active H, 0·35%; *M* (Rast), 279. $C_{18}H_{36}O_4$ requires C, 68·3; H, 11·5; Ac, 13·6; active H, 0·32%; *M*, 316].

(b) *With formic acid.* Anhydrous formic acid reacts with 1 : 2-epoxyoctane with the development of heat. After the oxide (20 g.) and formic acid (36 g.) had been kept for 2 days, the mixture was diluted with ether and the unchanged acid removed by 10% aqueous sodium carbonate. Distillation of the dried ethereal solution gave fractions : (*a*) b. p. 75—78°/0·6 mm., n_D^{20} 1·4328—1·4329 (14·6 g.), a saturated viscous liquid with a pleasant odour; (*b*) b. p. 78—146°/1 mm., n_D^{20} 1·4410 (0·1 g.); (*c*) b. p. 146—177°/1·0 mm., n_D^{20} 1·440—1·4450 (6·2 g.); (*d*) b. p.

177—190°/1·2 mm., n_D^{20} 1·4493 (1·4 g.) ; and in the cold traps 0·4 g. from which a small amount of the octanone 2 : 4-dinitrophenylhydrazone, m. p and mixed m. p. 99—101°, was obtained. Fraction (*a*) consisted mainly of the diformate of octane-1 : 2-diol with some of the monoformate (Found, for redistilled material, b. p. 73°/0·5 mm., n_D^{20} 1·4329 : C, 59·7; H, 9·1; $H{\cdot}CO_2$, 36. Calc. for monoformate, $C_9H_{18}O_3$: C, 62·0; H, 10·4; $H{\cdot}CO_2$, 25·8. Calc. for diformate, $C_{10}H_{18}O_4$: C, 59·4; H, 9·0; $H{\cdot}CO_2$, 44·5%). By chromatography on silica with light petroleum–ether for elution, the later portions gave nearly pure monoformate (0·4 g.), b. p. 84°/0·6 mm., n_D^{20} 1·4388 (Found : C, 62·3; H, 10·3; active H, 0·30; $H{\cdot}CO_2$, 27·2%). Oxidation by *tert.*-butyl chromate and chromatography on silica gave a product from which the 1-hydroxyoctan-2-one 4-phenylsemicarbazone was obtained, with m. p. and mixed m. p. 135° (Found : C, 64·8; H, 8·3; N, 14·7. Calc. for $C_{15}H_{23}O_2N_3$: C, 65·0; H, 8·4; N, 15·1%).

Fraction C consisted of the mono- and di-formate of 2-2′-hydroxyoctyloxyoctan-1-ol. No appreciable separation could be achieved by further distillation or chromatography. The main bulk of this fraction boiled at 152—161°/1 mm. and had n_D^{20} 1·4442, and samples for analysis were taken after further distillation (b. p. 137°/0·5 mm.) [Found : C, 66·3; H, 10·8; active H, 0·09%; *M* (Rast), 282. Calc. for monoformate, $C_{17}H_{34}O_4$: C, 67·5; H, 11·3; active H, 0·34%; *M*, 302. Calc. for diformate, $C_{18}H_{34}O_5$: C, 65·4; H, 10·4%; *M*, 330]. Alkaline hydrolysis gave formic acid and an oil which deposited crystals of 2-2′-hydroxyoctyloxyoctan-1-ol, m. p. and mixed m. p. 77·5°.

No homogeneous material could be isolated from fraction (*d*).

(c) *With trichloroacetic acid.* A solution of trichloroacetic acid (98 g.) in 1 : 2-dichloroethane (120 ml.) was mixed with 1 : 2-epoxyoctane (26 g.). A vigorous exothermic reaction occurred, and thereafter the solution was kept at room temperature for 7 days. The excess of trichloroacetic acid was removed by saturated aqueous sodium carbonate, and the neutral product distilled to remove the solvent. It was not possible to distil the reaction product even at 0·5 mm. without decomposition. It was accordingly hydrolysed by aqueous alkali to chloroform and a neutral oil which was separated by distillation into octane-1 : 2-diol (19·5 g.), m. p. 28—31°, and a fraction, b. p. 152—158°/0·6 mm., n_D^{20} 1·4550—1·4560. The latter slowly deposited 2-2′-hydroxyoctyloxyoctan-1-ol, m. p. and mixed m. p. 75·5°. The liquid portion of this fraction also contained a considerable amount of this ether (Found : C, 70·9; H, 12·5; active H, 0·74%; *M*, 233. Calc. for $C_{16}H_{34}O_3$: C, 70·0; H, 12·5; active H, 0·74%; *M*, 274). It gave a di-3 : 5-dinitrobenzoate, characterised as the di-α-naphthylamine adduct, m. p. and mixed m. p. 83·5—84° (Found : C, 63·95; H, 6·15; N, 8·65. Calc. for $C_{50}H_{56}O_{13}N_6$: C, 63·3; H, 5·95; H, 8·85%).

Reaction of Octane-1 : 2-*diol with* 1 : 2-*Epoxyoctane*.—(a) *Preparation of* 2-2′-*hydroxyoctyloxyoctan*-1-*ol*. The epoxide (7 g.) and the glycol (5·5 g.) were heated together for 24 hr. at 130—140° (bath-temp.) with acetic acid (5 ml.). Distillation gave unchanged glycol and its monoacetate, and a fraction, b. p. 154—165/1·2 mm. (1·0 g.), which deposited 2-2′-hydroxyoctyloxyoctan-1-ol, m. p. 75° (from light petroleum) (Found : C, 70·0; H, 12·2; active H, 0·68. Calc. for $C_{16}H_{34}O_3$: C, 70·0; H, 12·5; active H, 0·73%), characterised as the α-naphthylamine adduct of its di-3 : 5-dinitrobenzoate, m. p. 84°.

(b) *Preparation of* 1-*acetoxyoctan*-2-*one*. A solution of 1-diazo-octan-2-one was prepared by adding *n*-heptanoyl chloride (70 g.) in benzene (50 ml.) to well-stirred ice-cold ethereal diazomethane (from 120 g. of α-nitrosomethylurea). The solution was kept at 0° for 36 hr., then freed from ether. To three-quarters of the residue was added acetic acid (60 g.) and the reaction completed by heating at 60—80°. The mixture was then diluted with ether, washed free from acid with aqueous sodium carbonate, dried, and distilled. 1-*Chloro-octan*-2-*one* was collected at 101—102°/18 mm. (n_D^{20} 1·4440—1·4443; 16 g.) (Found : C, 59·6; H, 9·6; Cl, 21·1. Calc. for $C_8H_{15}OCl$: C, 59·1; H, 9·3; Cl, 21·8%) and 1-*acetoxyoctan*-2-*one* at 98—104°/5 mm. (m. p. 41—42°; 11·8 g.). The latter crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 42° (Found : C, 64·3; H, 9·5. $C_{10}H_{18}O_3$ requires C, 64·5; H, 9·7%). There were also a small preliminary fraction (? methyl heptanoate), and about 7 g. of residue.

1-Acetoxyoctan-2-one was also prepared by heating 1-chloro-octan-2-one (25 g.) with anhydrous potassium acetate (20 g.) in dry alcohol (38 g.) for 14 hr. (yield 8 g.; m. p. 40—42°), and by the oxidation of octanediol monoacetate, as follows. 1-Acetoxyoctan-2-ol (4·5 g.) in light petroleum (b. p. 40—60°; 30 ml.) was added dropwise to a solution of chromium trioxide (4 g.) in *tert.*-butyl alcohol (14 ml.) diluted with light petroleum (b. p. 40—60°; 50 ml.). After 36 hr., there were added water (50 ml.), ether (50 ml.), and powdered oxalic acid till there was no further action. The product, in ether, was washed successively with 10% sulphuric acid, 5N-acetic acid, and 10% aqueous sodium carbonate, and distilled. Crude 1-acetoxyoctan-2-one was collected at 68—73°/0·5 mm. (3·0 g.); purified by chromatography on alumina, it had m. p. and mixed m. p. 41—42°. It was characterised as its *semicarbazone*, m. p. 40—41° (Found : C, 54·3; H, 8·7; N, 17·0. $C_{11}H_{21}O_3N_3$ requires C, 54·3; H, 8·7; N, 17·3%). Reaction with 2 : 4-dinitrophenylhydrazine gave a red solid which on chromatography and crystallisation from benzene and then acetic acid melted at 159°, being 2-*oxo-octanal bis*-2 : 4-*dinitrophenylhydrazone* (Found : C, 48·1; H, 4·5; N, 21·7. $C_{20}H_{22}O_8N_8$ requires C, 47·8; H, 4·4; N, 22·3%).

Preparation of 1-*Formyloxyoctan*-2-*one*.—Prepared from 1-diazo-octan-2-one (from 37 g. of *n*-heptanoyl chloride) and formic acid by the procedure described above, this *ester* had b. p. 120°/14 mm., m. p. 24—25°, n_D^{20} 1·4341 (Found : C, 63·1; H, 9·3. $C_9H_{16}O_3$ requires C, 62·8; H, 9·4%). Its 4-*phenylsemicarbazone* had m. p. 113·5° (from alcohol) (Found : 62·7; H, 7·5; N, 14·0. $C_{16}H_{23}O_3N_3$ requires C, 62·9; H, 7·6; N, 13·8%); it is partially hydrolysed by boiling aqueous alcohol and with barium hydroxide in boiling alcohol gives 1-*hydroxyoctan*-2-*one* 4-*phenylsemicarbazone*, m. p. 135° (Found : C, 64·8; H, 8·3; N, 14·7. $C_{15}H_{23}O_2N_3$ requires C, 65·0; H, 8·4; N, 15·1%). With semicarbazide the ester gives 1-*hydroxyoctan*-2-*one semicarbazone*, m. p. 124° (Found : C, 54·0; H, 9·3; N, 21·6. $C_9H_{19}O_2N_3$ requires C, 53·7; H, 9·5; N, 21·0%). 1-*Hydroxyoctan*-2-*one thiosemicarbazone*, prepared similarly, had m. p. 148·5° (Found : C, 49·8; H, 9·1; S, 14·9. $C_9H_{19}ON_3S$ requires C, 49·7; H, 8·8; S, 14·8%). 2 : 4-Dinitrophenylhydrazine in acid solution gave 2-oxo-octanal bis-2 : 4-dinitrophenylhydrazone, m. p. 158—159°, identical with that obtained from 1-acetoxyoctan-2-one.

1 : 2-*Epoxy*-1-*phenylethane* (*Styrene Oxide*)—The epoxide prepared by the action of perbenzoic acid on styrene in chloroform contained benzaldehyde as a persistent impurity. It was shaken with aqueous semicarbazide hydrochloride and sodium acetate for 4 hr. and kept overnight. Distillation of the dried organic layer gave 1 : 2-epoxy-1-phenylethane, b. p. 77·2°/11 mm., n_D^{20} 1·5362—1·5360.

Styrene oxide (10·6 g.) and glacial acetic acid (53 g.) were mixed and kept at room temperature for 2 days. Distillation gave acetic acid and fractions, (*a*) b. p. 54—58°/6 mm. (0·7 g.), and (*b*) 120°/4 mm. to 129°/5 mm. (10·3 g.), n_D^{20} 1·5170—1·5191. Fraction (*a*) contained some acetic acid and gave the phenylacetaldehyde semicarbazone (0·8 g.), m. p. and mixed m. p. 158—159°. The greater part of fraction (*b*) boiled at 120°/4 mm., had n_D^{20} 1·5190—1·5191, and consisted essentially of 2-acetoxy-1-phenylethan-1-ol. Alkaline hydrolysis gave phenylethane-1 : 2-diol, m. p. 65—66°, and acetic acid. Oxidation by *tert*.-butyl chromate yielded ω-acetoxyacetophenone (2 : 4-dinitrophenylhydrazone, orange needles, m. p. 185—186°). ω-Acetoxyacetophenone, prepared from phenacyl bromide (Stoermer, *Ber.*, 1906, **39**, 2294), melted at 39—40° and gave a 2 : 4-dinitrophenylhydrazone identical with that just described.

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