αβ-Unsaturated Aldehydes and Related Compounds. Part IV. The Homolytic Addition of Carbon Tetrachloride to Acraldehyde and its Acetals.*

By R. H. Hall and D. I. H. Jacobs.

[Reprint Order No. 5003.]

The homolytic addition of carbon tetrachloride to acraldehyde and to two of its acetals has been investigated. The free aldehyde gave no useful results, but the diethyl acetal under the influence of ultra-violet irradiation gave a poor yield of αγγγ-tetrachlorobutaldehyde diethyl acetal; a similar result was obtained with a cyclic acetal of acraldehyde, *viz.*, 4-methyl-2-vinyl-1 : 3-dioxan. In both cases higher-boiling compounds derived from 1 mol. of tetrahalide and 2 mols. of the acetal were also obtained.

The homolytic addition of polyhalogenomethanes to olefinic compounds under the influence of free-radical chain initiators of the diacyl peroxide type, or of ultra-violet irradiation, has been extensively investigated by Kharasch and his co-workers (*Science*, 1945, **102**, 128; *J. Amer. Chem. Soc.*, 1945, **67**, 1626, 1864; 1946, **68**, 154; 1947, **69**, 1100, 1105; *J. Org. Chem.*, 1948, **13**, 895; 1949, **14**, 79; see Hey, *Ann. Reports*, 1948, **45**, 139), and the probable mechanism of the reactions elucidated. The present paper describes homolytic addition of carbon tetrachloride to acraldehyde and its acetals, which, by analogy with Kharasch's work, would be expected to yield, as the 1 : 1 adducts, the compounds (I) and (II), respectively:

$$\text{(I)}\quad CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CHO \qquad\qquad CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CH(OR)_2\quad \text{(II)}$$

With acraldehyde itself, polymerisation would be expected to be a competing reaction, and in fact no simple adduct (I) could be isolated from reaction of the aldehyde with carbon

---

* Part III, *J.*, 1953, 1398.

tetrachloride in the presence of benzoyl peroxide or under ultra-violet irradiation. The products, white amorphous solids, always contained chlorine, but whether they were telomers or mixtures of telomers and aldehyde polymers was not ascertained. Experiments with carbon tetrabromide were no more promising, so attention was turned to acraldehyde acetals.

The peroxide-catalysed addition of acetaldehyde (Mondon, *Angew. Chem.*, 1952, **64**, 224) and butaldehyde (U.S. Rubber Co., B.P. 635,934) to acraldehyde diethyl acetal has been stated to yield the expected β-acyloxypropaldehyde diethyl acetals (III). There are, however, no reports of the addition of polyhalogenomethanes to acraldehyde acetals.

$$CH_2{:}CH{\cdot}CH(OEt)_2 + R{\cdot}CHO \longrightarrow R{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OEt)_2 \qquad (III)$$

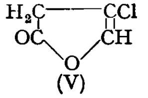
In the present work reaction of carbon tetrachloride with acraldehyde diethyl acetal under the influence of ultra-violet irradiation gave a rather complex mixture from which was isolated, in poor yield (maximum 18%, based on the acetal), a compound which was shown (see below) to be the 1 : 1-adduct, *viz.*, αγγγ-tetrachlorobutaldehyde diethyl acetal (II; R = Et). Similar results were obtained with a cyclic acetal of acraldehyde, 4-methyl-2-vinyl-1 : 3-dioxan, although the yield of 1 : 1 adduct was lower (8—9%). In both cases higher-boiling compounds derived from 1 mol. of carbon tetrachloride and 2 mols. of acetal were obtained; these compounds are considered briefly below.

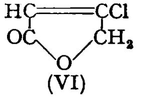
The acetals of αγγγ-tetrachlorobutaldehyde were very resistant to hydrolysis but boiling concentrated hydrochloric acid eventually furnished the free aldehyde which readily polymerised and also formed a solid hydrate; the infra-red spectrum of crystals of the latter contained a broad band with a maximum at 3250 cm.$^{-1}$ (hydroxyl group) but no bands due to a free aldehyde group. Attempted drying of the hydrate in a desiccator resulted in partial liberation of the aldehyde (weak band at 1745 cm.$^{-1}$, in CCl_4) which rapidly polymerised (set of strong bands between 970 and 1125 cm.$^{-1}$, indicative of polyaldehyde or acetal). The aldehyde (or hydrate) derived from either acetal yielded the same 2 : 4-dinitrophenylhydrazone, showing that the basic structure was the same in each case.

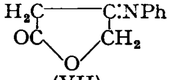
Proof of the structure of the tetrachloro-aldehyde was obtained in the following way. Oxidation of the hydrate, or of the acetals themselves, with concentrated nitric acid furnished in good yield a tetrachlorobutyric acid, which with concentrated sulphuric acid gave fumaric acid in 87% yield (based on the tetrachloro-acid). Clearly, the 1 : 1 adducts were of the type $CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CH(OR)_2$ and not $CH_2Cl{\cdot}CH(CCl_3){\cdot}CH(OR)_2$, and the derived carboxylic acid was αγγγ-tetrachlorobutyric acid (IV). The acetal structures were

$$\underset{(I)}{CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CHO} \xrightarrow{HNO_3} \underset{(IV)}{CCl_3{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2H} \xrightarrow{H_2SO_4} CO_2H{\cdot}CH{:}CH{\cdot}CO_2H$$

confirmed by treatment with concentrated sulphuric acid at 130° for 10 min. In each case a neutral chloro-compound, m. p. 54°, $C_4H_3O_2Cl$, was obtained. This was tentatively formulated as β-chlorobut-β-enolide (V); the isomer (VI), although a possibility in view of the results of Swain, Todd, and Waring (*J.*, 1944, 548) who obtained but-α-enolides by


(V)


(VI)


(VII)

cyclisation of β-formylpropionic acids, is known (Hill and Cornelison, *Amer. Chem. J.*, 1894, **16**, 288) as a solid of m. p. 25—26°.

The monochloro-compound showed only end-absorption below 2200 Å in the ultra-violet region (ϵ_{2200} 8300 in EtOH) (cf. data for unsaturated lactones; Haynes and Jones, *J.*, 1946, 954; Cocker and Hornsby, *J.*, 1947, 1157; Jones and Whiting, *J.*, 1949, 1423; Young, *J. Amer. Chem. Soc.*, 1949, **71**, 1346). An infra-red band at 1794 cm.$^{-1}$ was clearly the main carbonyl band, its position indicating a but-β-enolide ring system (cf. Grove and Willis, *J.*, 1951, 877, who give 1800 and 1750 cm.$^{-1}$ for the carbonyl stretching frequency in but-β- and -α-enolides, respectively, but point out that the positions of these maxima may be shifted considerably by substituents). A band at 1618 cm.$^{-1}$ was the main C:C band, comparable with that given by C:C in C:C·C·O– groups (cf. Nat. Bur. Stand. Catalog of Spectra, No. 143).

With 2 mols. of aniline the chloro-lactone furnished a small yield of a crystalline, chlorine-free compound which, though first formulated as β-anilinobut-β-enolide was shown (mixed m. p.; ultra-violet and infra-red absorption spectra) to be the anilinotetronic acid described as the Δ^{α}-compound by Wolff and Schimpff (*Annalen*, 1901, **315**, 156). The anilino-compound had an absorption maximum at 2860 Å (ε 25,100), analogous to that given by β-anilino-αα-dimethyl- (2810 Å; ε 24,000) and β-anilino-αα-pentamethylene-but-α-enolide (2810 and 2880 Å; 27,000 and 24,000, respectively) (Jones and Whiting, *loc. cit.*), but this did not definitely exclude the Δ^{β}-formulation as this compound would also be expected to absorb in this region. It did, however, eliminate a third possibility, namely, the anil (VII), whose C:NPh chromophoric system would absorb at shorter wave-lengths [Et_2C:NPh has $\lambda_{max.}$ 2500 Å, ε 12,000 (Braude, *Ann. Reports*, 1945, **42**, 126)]. As, however, Δ^{β}-lactones are known to be isomerised to the Δ^{α}-compounds on treatment with bases (Thiele, Tischbein, and Lossow, *Annalen*, 1901, **319**, 180; Lukes, *Coll. Czech. Chem. Comm.*, 1929, **1**, 461; Pauly, Gilmour, and Will, *Annalen*, 1914, **403**, 152), it seems probable that the anilino-compound was indeed the Δ^{α}-isomer.

Hydrogenation of the chloro-lactone in an attempt to prepare the corresponding saturated lactone, β-chloro-γ-butyrolactone, resulted in extensive hydrogenolysis and some butyric acid was formed. This degradation of a βγ-unsaturated γ-lactone to the deoxy-acid was reminiscent of the results obtained by Jacobs and Scott (*J. Biol. Chem.*, 1930, **87**, 601; cf. Cocker and Hornsby, *loc. cit.*; Eisner, Elvidge, and Linstead, *J.*, 1950, 2223) for a number of unsaturated lactones; in the present case the β-chlorine atom was also hydrogenolysed. The isolation of butyric acid was further evidence for an unbranched-carbon skeleton in the original tetrachloro-aldehyde.

Dehydrochlorination of the diethyl acetal of αγγγ-tetrachlorobutaldehyde with alkali led to a trichloro-aldehyde acetal which, on the basis of spectroscopic evidence (absence of band due to *trans*-CH:CH· at about 965 cm.$^{-1}$) and its resistance to further alkaline hydrolysis, was probably the acetal of 2 : 4 : 4-trichlorobut-3-enal; the inertness of CCl_2:C groups towards attack by alkali is well known. By alternate hydrogenation and dehydrochlorination, this acetal was converted into a mixture containing butaldehyde diethyl acetal; this provided further evidence for the straight-chain nature of the original tetrachlorobutaldehyde, although the yield of butaldehyde 2 : 4-dinitrophenylhydrazone finally isolated was not very high.

The high-boiling products obtained in the addition of carbon tetrachloride to acraldehyde diethyl acetal were examined only briefly. They contained the adduct derived from 1 mol. of the tetrahalide and 2 mols. of the acetal but this material could not be isolated in a pure state. It readily lost ethanol, forming a thermolabile unsaturated compound whose absorption spectrum contained bands at 711 and 1675 cm.$^{-1}$; these, by analogy with the bands at 733 and 1660 cm.$^{-1}$ given by *cis*-but-1-enyl butyl ether (Hall, Philpotts, Stern and Thain, *J.*, 1951, 3341), indicated the presence of a substituted *cis*-αβ-unsaturated ether grouping. The 1 : 2 adduct derived from the cyclic acetal of acraldehyde was more stable than that from the diethyl acetal and was obtained reasonably pure.

An attempt to use initiation by benzoyl peroxide for the reaction between carbon tetrachloride and acraldehyde diethyl acetal was unsuccessful, the only identifiable product being 1 : 1 : 3-triethoxypropane.

EXPERIMENTAL

Reaction of Carbon Tetrachloride with Acraldehyde.—(*a*) Refluxing a mixture of acraldehyde (65 g.), carbon tetrachloride (1200 g.), and benzoyl peroxide (5 g.) for 19 hr. afforded only an amorphous solid (27 g.) containing 10% of chlorine.

(*b*) Addition of acraldehyde (56 g.) in carbon tetrachloride (250 ml.) during 18 hr. to benzoyl peroxide (5 g.) in refluxing carbon tetrachloride (500 ml.), followed by a further 8 hours' boiling, filtration, and further refluxing of the filtrate after addition of more peroxide, yielded polymer (39 g.) containing 23% of chlorine.

(*c*) Refluxing acraldehyde (56 g.) in carbon tetrachloride (750 ml.) for 24 hr. under ultra-violet irradiation gave only a solid polymer (2 g.) containing 8% of chlorine.

Reaction of Carbon Tetrabromide with Acraldehyde.—Refluxing carbon tetrabromide (166 g.), carbon tetrachloride (600 ml.), and acraldehyde (28 g.) for 48 hr., with addition of benzoyl peroxide (2·5-g. portions) after 0, 7, and 24 hr., or refluxing a mixture of carbon tetrabromide (200 g.), acraldehyde (10·1 g.), and carbon tetrachloride (200 g.) for 5 hr. under ultra-violet irradiation afforded in each case only dark residues.

Reaction of Carbon Tetrachloride with Acraldehyde Diethyl Acetal.—In a typical experiment, the acetal (65 g., 0·5 mole) and carbon tetrachloride (1200 g.) were refluxed in a Pyrex flask under ultra-violet irradiation for 22 hr., then washed with dilute sodium hydrogen carbonate solution; the excess of carbon tetrachloride was distilled off at atmospheric pressure, followed by unchanged acetal (approx. 17 g.) at 70 mm., and the residue then fractionated at 0·5—1·0 mm., the lower-boiling product being taken off through a helices-packed column (35 × 1 cm.) and the higher-boiling material through a short Vigreux column. The main fractions were: (i) b. p. 100—106°/1 mm. (25·7 g.), n_D^{20} 1·4654—1·4668, and (ii) b. p. 142—143°/0·5—1·0 mm. (12·8 g.), n_D^{20} 1·471—1·473.

A middle cut of fraction (i) had b. p. 105°/1 mm., n_D^{20} 1·4668 (Found: C, 33·95; H, 5·55; Cl, 49·9. $C_8H_{14}O_2Cl_4$ requires C, 33·85; H, 4·95; Cl, 49·95%); this was *αγγγ-tetrachlorobutaldehyde diethyl acetal.* Fraction (ii) could not be purified; on redistillation it gradually decomposed with the production of an αβ-unsaturated ether; *e.g.*, a fraction of b. p. 131°/0·4 mm., n_D^{20} 1·4717, thus obtained was found (by infra-red examination) to contain about 10% of the unsaturated ether. Repeated fractionation increased this amount.

In an experiment in which the washing with sodium hydrogen carbonate was omitted, a slow decomposition of the contents of the distilling-flask took place after the tetrachlorobutaldehyde had been collected, the volatile products of the decomposition being condensed in a trap at −80°, and in place of fraction (ii) above there was obtained a liquid, b. p. 145—150°/0·5—1·0 mm., n_D^{20} 1·4917—1·4930, which was largely the αβ-unsaturated ether derived from the adduct of 1 mol. of carbon tetrachloride and 2 mols. of acraldehyde diethyl acetal by elimination of 1 mol. of ethanol (Found: C, 42·05; H, 5·75; Cl, 40·2. Calc. for $C_{13}H_{22}O_3Cl_4$: C, 42·4; H, 6·05; Cl, 38·55%). Attempts to purify this by refractionation were unsuccessful.

The trap contents obtained above contained ethanol and hydrogen chloride, and afforded a 2 : 4-dinitrophenylhydrazone which, recrystallised from ethanol, formed needles, m. p. 122° alone or mixed with authentic *β-chloropropaldehyde 2 : 4-dinitrophenylhydrazone*, m. p. 122° (Found: C, 40·2; H, 3·5; N, 20·6; Cl, 12·8. $C_9H_9O_4N_4Cl$ requires C, 39·6; H, 3·35; N, 20·6; Cl, 13·0%), obtained from β-chloropropaldehyde diethyl acetal prepared by Crawford and Kenyon's method (*J.*, 1927, 396).

αγγγ-Tetrachlorobutaldehyde.—The above diethyl acetal (10 g.) was added to aqueous hydrochloric acid (50 ml.; 15% w/v), and the mixture refluxed for 18 hr. Steam-distillation afforded a pale yellow oil which solidified almost completely in contact with water. The solid was triturated with light petroleum (b. p. 40—60°), filtered off, and washed with more of the solvent. A crystalline white solid (4 g.), m. p. 50—51°, was obtained, which liquefied in a vacuum-desiccator. The crystalline *hydrate* was dried for analysis in the following manner; a sample was kept at room temperature at 0·2 mm. for about 2 hr., washed with light petroleum (b. p. 40—60°) to remove traces of free aldehyde, and re-dried at room temperature at 0·2 mm. for 10 min. (Found: C, 21·5; H, 2·8; Cl, 62·0. $C_4H_4OCl_4,H_2O$ requires C, 21·1; H, 2·65; Cl, 62·25%). In a later experiment the free aldehyde was isolated (by ether-extraction of the steam-distillate) and found to have b. p. 83—85°/12 mm., n_D^{20} 1·4982; it polymerised before it could be analysed.

Addition of a methanolic solution of the free aldehyde, or its hydrate, to a saturated solution of 2 : 4-dinitrophenylhydrazine in aqueous 2N-hydrochloric acid gave the *2 : 4-dinitrophenylhydrazone*, which separated from methanol as yellow needles, m. p. 124—125° (Found: C, 30·6; H, 2·2; N, 14·4; Cl, 36·2. $C_{10}H_8O_4N_4Cl_4$ requires C, 30·8; H, 2·05; N, 14·35; Cl, 36·3%). Attempts to prepare this derivative by treating the diethyl acetal directly with ethanolic sulphuric acid or aqueous hydrochloric acid solutions of 2 : 4-dinitrophenylhydrazine gave only unstable uncrystallisable gums. Although the crystalline derivative was stable in the solid state it decomposed slowly in methanol at room temperature.

αγγγ-Tetrachlorobutyric Acid.—αγγγ-Tetrachlorobutaldehyde diethyl acetal (10 g.) was added dropwise to nitric acid (70 ml.; 70% w/v) at 50—60° during 3 hr. The mixture was then heated at 100° for 30 min., poured into cold water (500 ml.), and extracted with ether. A strong smell of chloropicrin was noticed. The ether extract was shaken with sodium hydrogen carbonate solution, and the aqueous alkaline solution separated, acidified, and extracted with ether. The ether extract was dried (Na_2SO_4), the solvent distilled off, and the residual liquid fractionated through a small Vigreux column. A colourless oil (5·8 g., 73%), b. p. 117—120°/0·5 mm., n_D^{20} 1·4992, was obtained, which solidified at −40°. Recrystallisation from light petroleum (b. p. 40—60°) at −50° afforded *αγγγ-tetrachlorobutyric acid*, m. p. 27—29° (Found: C, 21·4; H, 1·8; Cl, 62·3. $C_4H_4O_2Cl_4$ requires C, 21·25; H, 1·8; Cl, 62·75%). Its *p-phenylphenacyl* ester had m. p. 96° after recrystallisation from ethanol (Found: C, 51·3; H, 3·55. $C_{18}H_{14}O_3Cl_4$ requires C, 51·45; H, 3·35%). The *anilide*, prepared by way of the acid chloride (thionyl chloride under reflux), separated from aqueous ethanol (50%) in colourless needles, m. p. 124° (Found: C, 39·85; H, 3·05; N, 4·95; Cl, 46·9. $C_{10}H_9ONCl_4$ requires C, 39·9; H, 3·0; N, 4·65; Cl, 47·1%).

Reaction of αγγγ-Tetrachlorobutyric Acid with Concentrated Sulphuric Acid.—(*a*) A solution of the butyric acid (2 g.) in concentrated sulphuric acid (10 g.) was heated at 130° for 10 min., cooled, and poured on crushed ice. The mixture obtained was extracted continuously with ether, the dried (Na_2SO_4) ether extract evaporated on the steam-bath, and the residue (0·5 g.) recrystallised from water. The product did not melt in an open tube but gradually sublimed above 200°. A sample purified by sublimation was shown by infra-red spectroscopic examination to be mainly (more than 90%) fumaric acid. The di-*p*-nitrobenzyl ester prepared from it had m. p. 147—149°, and the mixed m. p. with authentic fumaric ester (m. p. 150—152°) was 149—151°.

(*b*) A solution of αγγγ-tetrachlorobutyric acid (4·37 g.) in concentrated sulphuric acid (25 ml.) was heated at 130° until evolution of hydrogen chloride ceased (approx. 1 hr.), cooled, and poured on crushed ice (100 g.). The mixture obtained was extracted continuously with ether, and the extract evaporated on the steam-bath. The residue was dissolved in water (50 ml.), thiourea (0·2 g.) added, and the solution refluxed for 24 hr. to isomerise any maleic acid to fumaric acid. The cooled product was filtered, and the precipitate washed with cold water (5 ml.) and dried to constant weight in a vacuum-desiccator. The fumaric acid thus obtained weighed 1·95 g. (87%) and had m. p. 292° in a sealed tube (recorded m. p.s range from 287° to 295°).

Reaction of αγγγ-Tetrachlorobutaldehyde Diethyl Acetal with Concentrated Sulphuric Acid.—A solution of the acetal (10 g.) in concentrated sulphuric acid (50 ml.) was heated at 130° for 10 min. Considerable charring occurred. The product was poured on crushed ice (100 g.) and extracted continuously with ether. The ethereal solution was dried and evaporated to dryness, and the residue recrystallised from light petroleum (b. p. 60—80°). White, needle-like crystals (1·1 g.) of *β-chlorobut-β-enolide* were obtained, which, after two further recrystallisations from the same solvent, had m. p. 54° (Found: C, 40·95; H, 2·8; Cl, 29·3. $C_4H_3O_2Cl$ requires C, 40·55; H, 2·55; Cl, 29·95%). Ultra-violet absorption in ethanol: increasing absorption down to 2200 Å (ε 8300); no maxima.

A solution of the lactone (1 mol.) in aniline (2 mols.) solidified overnight. The solid was dissolved in ethanol, the solution poured into a large volume of dilute hydrochloric acid, and the precipitate filtered off and washed with water, then with dilute ammonia, and finally with water. Recrystallisation from ethanol gave creamy-white nodules, m. p. 222° (Found: C, 68·3; H, 5·5; N, 8·15; Cl, absent. Calc. for $C_{10}H_9O_2N$: C, 68·55; H, 5·2; N, 8·0%). Ultra-violet absorption in ethanol: max. 2860 Å (ε 25,100). The m. p. was undepressed on admixture of the crystals with authentic anilinotetronic acid (β-anilinobut-α-enolide) of m. p. 220—221°, prepared by the method of Wolff and Schimpff (*loc. cit.*), which had identical ultra-violet and infra-red absorption spectra.

Hydrogenation of β-Chlorobut-β-enolide.—Hydrogenation of the chloro-lactone (0·4 g.) in dry ether (25 ml.) over Adams's catalyst (0·05 g.) resulted in absorption of 161 ml. (N.T.P.) of hydrogen and formation of 1·05 equiv. of acid (titre = 3·60 ml. of N-NaOH). The sodium salt of the acid produced was isolated and converted by way of the acid chloride into the anilide which, crystallised from water, had m. p. 96°, undepressed on admixture with authentic *n*-butyranilide, m. p. 97°.

Dehydrochlorination of αγγγ-Tetrachlorobutaldehyde Diethyl Acetal.—A mixture of the acetal (10 g.) and a solution of potassium hydroxide (2·5 g., 1·25 equivs.) in absolute ethanol (70 ml.) was refluxed for 4 hr. The potassium chloride which separated was filtered off, the filtrate concentrated on the steam-bath to remove ethanol, and the residue diluted with ether. The ether solution was washed with water and dried, the solvent distilled off, and the residual liquid fractionated, giving a colourless liquid (7·2 g.), b. p. 110—112°/13 mm., n_D^{20} 1·4683, which on the basis of infra-red spectroscopic analysis was probably 2 : 4 : 4-trichlorobut-3-enal diethyl acetal (Found: C, 39·3; H, 5·45; Cl, 42·3. Calc. for $C_8H_{13}O_2Cl_3$: C, 38·8; H, 5·3; Cl, 42·9%). Attempts to prepare a 2 : 4-dinitrophenylhydrazone from it were unsuccessful.

The trichloro-compound was hydrogenated in ethanol solution over Adams's catalyst until absorption of gas ceased, treated with ethanolic potassium hydroxide solution, and re-hydrogenated alternately until three dehydrochlorinations and three hydrogenations had been performed. No purification was attempted at any stage except to remove solid material. The final ethanolic solution obtained was poured into a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. Fractional crystallisation of the product afforded butaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 118—119°; mixed m. p. with authentic material (m. p. 120—120·5°) 119—120°.

Reaction of Carbon Tetrachloride with Acraldehyde Diethyl Acetal in the Presence of Benzoyl Peroxide.—A solution of the acetal (65 g.) in carbon tetrachloride (800 g.) was refluxed for 36 hr. with the addition of benzoyl peroxide (2·5 g. each time) at 0, 12, and 24 hr. Isolation of the product afforded a main fraction (30 g.), b. p. 39—40°/0·5 mm., which was largely 1 : 1 : 3-triethoxypropane (infra-red analysis; mixed m. p. of derived 2 : 4-dinitrophenylhydrazone with authentic β-ethoxypropaldehyde 2 : 4-dinitrophenylhydrazone); no other compounds were identified.

Addition of Carbon Tetrachloride to 4-*Methyl*-2-*vinyl*-1 : 3-*dioxan.*—A solution of the cyclic acetal (64 g.) in carbon tetrachloride (1200 g.) was refluxed for 24 hr. under ultra-violet irradiation. The excess of carbon tetrachloride was then removed on the water-bath, and the residual liquid distilled without fractionation at 1 mm. pressure. The distillate consisted of: (i) 20 g. (approx.), b. p. below 190°; (ii) 40—45 g., b. p. 190—200°; and (iii) residue (10 g.). Fraction (ii) on cooling became glassy, but could not be induced to crystallise. It was probably 1 : 5 : 5 : 5-*tetrachloro*-1 : 3-*di*-(4-*methyl*-1 : 3-*dioxan*-2-*yl*)*pentane* (Found: Cl, 34·3. $C_{15}H_{24}O_4Cl_4$ requires Cl, 34·55%).

A further experiment in which the reaction mixture was irradiated but not heated gave similar results. The crude reaction mixture in both cases was much less coloured than that obtained when using acraldehyde diethyl acetal, and the absence of decomposition during distillation was also in marked contrast to that which occurred on working up reaction mixtures from the latter acetal.

The low-boiling fractions from each experiment with the cyclic acetal were bulked and refractionated at about 0·5 mm.: no sharp separation into fractions was found over the range 33—115°/0·5 mm., but then a largely homogeneous fraction (24·2 g.), b. p. 115—120°/0·5 mm., was obtained, which on further fractionation afforded 4-*methyl*-2-1′ : 3′ : 3′ : 3′-*tetrachloropropyl*-1 : 3-*dioxan* (*i.e.*, the 1 : 1 adduct), b. p. 108—112°/0·3 mm., n_D^{20} 1·4926 (Found: C, 34·95; H, 4·2; Cl, 50·8. $C_8H_{12}O_2Cl_4$ requires C, 34·1; H, 4·3; Cl, 50·3%). Satisfactory analytical figures for carbon could not be obtained.

A portion of the pure material was refluxed for 8 hr. with concentrated hydrochloric acid, then steam-distilled, and the distillate was extracted with ether. Evaporation of the dried ether solution and distillation of the residual liquid *in vacuo* furnished approximately equal quantities of an aldehyde, b. p. 83—85°/12 mm., n_D^{20} 1·4982, and unchanged acetal, b. p. 145—150°/12 mm., n_D^{20} 1·4937. The 2 : 4-dinitrophenylhydrazone prepared from the former had m. p. 126° [mixed m. p. with αγγγ-tetrachlorobutaldehyde 2 : 4-dinitrophenylhydrazone (m. p. 124°, above) 123—125°].

Another portion of the 4-methyl-2-1′ : 3′ : 3′ : 3′-tetrachloropropyl-1 : 3-dioxan, on treatment with concentrated sulphuric acid at 130° as described on p. 2038 for tetrachlorobutaldehyde diethyl acetal, furnished the same chloro-lactone, β-chlorobut-β-enolide (m. p. and mixed m. p. 54°).

The authors are indebted to Dr. H. M. Stanley for his interest, to Mr. A. R. Philpotts and Mr. W. Thain for the determination and interpretation of infra-red and ultra-violet absorption data and for valuable discussions, to Mr. D. J. Annetts and Mr. D. A. Burch for assistance with the experimental work, and to the Directors of the Distillers Co., Ltd., for permission to publish this paper.

THE DISTILLERS CO., LTD., RESEARCH AND DEVELOPMENT DEPT.,
GREAT BURGH, EPSOM, SURREY.
[*Received, January 2nd,* 1954.]