CCCCXXIV.—*The Partial Esterification of Polyhydric Alcohols. Part IV. The Oxidation of Allyl Esters to α-Monoglycerides.*

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ALLYL alcohol and its homologues have been oxidised to the corresponding glycerols by potassium permanganate (Wagner, *Ber.*, 1888, **21**, 1231, 3351; 1890, **23**, 2313), and sodium chlorate solution, activated by a trace of osmium tetroxide (Hofmann, *Ber.*, 1912, **45**, 3335; Hofmann, Ehrhart, and Schneider, *Ber.*, 1913, **46**, 1657), has also been used in similar reactions. The nearest approach to the direct oxidation of an allyl ester to an α-monoglyceride

$$CH_2{:}CH{\cdot}CH_2{\cdot}O{\cdot}COX \xrightarrow{H_2O + O_2} OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}COX$$

so far recorded, however, is Bailly's synthesis of α-monoglycerophosphoric acid from allylphosphoric acid (*Compt. rend.*, 1915, **160**, 663).

The failure of the previous attempts (J., 1921, **119**, 1038) to oxidise allyl esters directly to α-monoglycerides has now been traced to the difficulty of finding a suitable solvent, allyl esters being practically insoluble in water and most organic solvents being themselves attacked by oxidising agents of the kind required.

Allyl *p*-nitrobenzoate and 3 : 5-dinitrobenzoate have been oxidised, by suitably treating solutions in acetone with aqueous potassium permanganate, to the corresponding α-monoglycerides, which have been proved identical with authentic specimens prepared from *iso*propylidene glycerol (Fischer, *Ber.*, 1920, **53**, 1596) or monosodium glyceroxide (J., 1925, **127**, 2759). Glycerol α-2 : 4-dinitrophenyl ether (*loc. cit.*, J., 1921) also has been obtained by oxidising allyl 2 : 4-dinitrophenyl ether. The yields are not good, but the method is capable of producing α-monoglycerides of a high degree of purity.

Aqueous sodium chlorate activated by osmium tetroxide (Hofmann, Ehrhart, and Schneider, *loc. cit.*), and also hydrogen peroxide, were unsuccessfully tried as oxidising agents; the latter had no action on the allyl esters in acetone solution, and the former oxidised them apparently to compounds other than glycerides.

Allyl picrate (allyl 2 : 4 : 6-trinitrophenyl ether) resisted oxidation to the corresponding glyceride and attempts to prepare this substance from monosodium glyceroxide and from α-monochlorohydrin failed.

The allyl esters prepared during this investigation were characterised each by the preparation of the dibromo-derivative.

EXPERIMENTAL.

Allyl p-*Nitrobenzoate.*—4 G. of quinoline were added to 5·6 g. of *p*-nitrobenzoyl chloride, the product was dissolved in 10—15 c.c. of chloroform, 2 c.c. of allyl alcohol were added, and the whole was kept for 2 days. Ether was then added in excess and the mixture was shaken with water, dilute sulphuric acid, sodium bicarbonate solution, and again with water. After the ethereal solution had been dried with fused sodium sulphate, the solvent was removed; the residual oil solidified on cooling and crystallised from alcohol in needles, m. p. 30° (yield, 4·3 g.) (Found : C, 58·5; H, 4·4. Calc. : C, 58·0; H, 4·35%). This compound has been described as an oil (A.P. 1360994) and as a solid of m. p. 28° (Meisenheimer, *Ber.*, 1919, **52**, 1675).

Dibromo-derivative. Allyl *p*-nitrobenzoate and bromine in slight excess were kept in chloroform. After ½ hour, the solvent was removed, and the excess of bromine volatilised on a water-bath; the oily residue, which solidified, crystallised from alcohol in plates, m. p. 57—58° (yield, nearly theoretical) (Found : Br, 43·7. $C_{10}H_9O_4NBr_2$ requires Br, 43·6%).

Oxidation of Allyl p-*Nitrobenzoate to Glycerol α-Mono*-p-*nitrobenzoate.*—A solution of 0·5 g. of allyl *p*-nitrobenzoate in 100 c.c. of acetone was treated with 79 c.c. of 1% aqueous potassium permanganate. After some hours, the manganese dioxide was removed, the filtrate neutralised with dilute hydrochloric acid, the acetone distilled off, and the residue evaporated to 40—50 c.c. on a water-bath. The hot filtered solution deposited over-night 0·25 g. of pure, crystalline glycerol α-mono-*p*-nitrobenzoate which, alone or mixed with authentic specimens prepared from monosodium glyceroxide or *iso*propylidene glycerol (J., 1925, **127**, 2763), melted at 107°.

Allyl 3 : 5-*dinitrobenzoate* was prepared, in the same way as the *p*-nitrobenzoate, from 4 g. of quinoline, 6·6 g. of 3 : 5-dinitrobenzoyl chloride in 15 c.c. of dry chloroform, and 2 c.c. of allyl alcohol. The crude product (5·4 g.), on crystallisation from alcohol, yielded long needles, m. p. 50° (compare A. P. 1360994) (Found : C, 47·6; H, 3·5. Calc. : C, 47·6; H, 3·2%).

The *dibromo*-derivative, prepared in the same way as the preceding one (yield, theoretical), crystallised from alcohol in plates, m. p. 85° (Found : Br, 38·5. $C_{10}H_8O_6N_2Br_2$ requires Br, 38·8%).

Oxidation of Allyl 3 : 5-*Dinitrobenzoate to Glycerol α-Mono*-3 : 5-*dinitrobenzoate.*—The glyceride was prepared (65 c.c. of 1% aqueous potassium permanganate were used) and isolated in the same way as the *p*-nitrobenzoate. The product, after being dried in a vacuum over sulphuric acid, crystallised from chloroform in needles which, alone or mixed with an authentic specimen (J., 1925, **127**, 2763), melted at 118°. The yield was 0·25 g. from 0·5 g. of allyl 3 : 5-dinitrobenzoate.

Oxidation of Allyl 2 : 4-Dinitrophenyl Ether to Glycerol α-Mono-2 : 4-dinitrophenyl Ether.—A solution of 0·96 g. of allyl 2 : 4-dinitrophenyl ether (J., 1921, **119**, 1038) in 130 c.c. of acetone was treated with the equivalent quantity of 1% aqueous potassium permanganate and kept for 12 hours. The glycerol ether was isolated as in the other cases, but the final solution was evaporated to 100 c.c. before being left over-night to crystallise. The product was dried in a vacuum over sulphuric acid and recrystallised from benzene; it then melted at 85°, alone or mixed with an authentic specimen of glycerol α-mono-2 : 4-dinitrophenyl ether (*ibid.*, p. 1037). The yield was 20—30%.

Allyl 2 : 4 : 6-Trinitrophenyl Ether.—Picryl chloride (4·9 g.), dissolved in 25 c.c. of allyl alcohol, was added to a cold solution of 1·14 g. of potassium hydroxide in the same solvent (10 c.c.). After ½ hour, the mixture was warmed and poured into 200 c.c. of water; the *ether* then separated. It crystallised from alcohol in long needles (yield, 2—3 g.), m. p. 90° (Found : N, 15·75. $C_9H_7O_7N_3$ requires N, 15·6%).

This reaction is erratic and the yield stated is the best obtained. In some experiments, no ether was produced, potassium picrate being the only substance isolated.

The *dibromo*-derivative was prepared and isolated as in the other two cases. It crystallised from alcohol in prisms, m. p. 106—107° (yield, theoretical) (Found : Br, 37·9. $C_9H_7O_7N_3Br_2$ requires Br, 37·3%).

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