

903. *Some Derivatives of cis-1 : 2 : 3 : 6-Tetrahydrophthalic Anhydride.*

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The preparation and properties of the chlorohydrin and epoxide from *cis*-1 : 2 : 3 : 6-tetrahydrophthalic anhydride and several of its dialkyl esters are described. Reactions of the anhydride with chlorine and bromine, and preparation of the imide are reported.

LITTLE has been reported about *cis*-1 : 2 : 3 : 6-tetrahydrophthalic anhydride (*Annalen*, 1928, 460, 98; *Ber.*, 1929, 62, 2087) or its derivatives. Some reactions involving the ethylenic linkage are now reported.

Hydrogenation with Raney nickel in dry ethyl acetate gives *cis*-hexahydrophthalic anhydride, which cannot be obtained by direct hydrogenation of phthalic anhydride (Adkins, Wojcik, and Covert, *J. Amer. Chem. Soc.*, 1933, 55, 1669). The alkyl esters of the unsaturated anhydride are similarly reduced.

Bromination in chloroform gives 4 : 5-dibromohexahydrophthalic acid and a polymeric syrup. Chlorination results in immediate liberation of hydrogen chloride, and an unstable polymeric resin containing chlorine is formed.

Reaction with aqueous ammonia gives the imide.

Preparation of 4 : 5-epoxyhexahydrophthalic anhydride is possible only under anhydrous conditions in which rupture of the anhydride ring does not occur. Peracetic acid in glacial acetic acid below 30° gives it in 56% yield as a colourless, crystalline compound. It is soluble in several organic solvents and on warming with water it dissolves to give, presumably, the dibasic acid, which then interpolymerises; a syrupy acidic resin is isolated on concentration. Alkalis form salts and alcohols form half-esters which then polymerise. The polymers produced are all water-sensitive.

4-Chloro-5-hydroxyhexahydrophthalic anhydride is formed by reaction of the epoxy-anhydride in ethyl acetate with hydrogen chloride in ether.

The epoxides of dialkyl 1 : 2 : 3 : 6-tetrahydrophthalates are prepared in good yields directly by oxidation with peracetic acid or by reaction with hypochlorous acid and then dehydrochlorination with alcoholic sodium hydroxide (sodium hypochlorite solution causes hydrolysis of the ester groups). Compounds containing the epoxide ring polymerise when heated with acid catalysts, *e.g.*, boron trifluoride or perchloric acid, and allyl compounds do so when heated with peroxide catalysts. It is thus possible partially to polymerise such compounds as diallyl and allyl ethyl 4 : 5-epoxyhexahydrophthalate with boron trifluoride to soft, solvent-soluble, viscous resins which can be rendered insoluble by further heating with benzoyl peroxide.

EXPERIMENTAL

cis-4 : 5-Epoxyhexahydrophthalic Anhydride.—*cis*-1 : 2 : 3 : 6-Tetrahydrophthalic anhydride (40 g.) was added with stirring at <30° (cooling, as necessary) to peracetic acid solution (315 g.) (prepared by the method of Findlay *et al.*, *J. Amer. Chem. Soc.*, 1945, 67, 412), containing 8.4 g. of per-acid per 100 g. of acetic acid. The anhydride dissolved momentarily with only slight evolution of heat and crystals of epoxide were deposited immediately. Next morning

the supernatant liquid contained no peracetic acid. The cis-4 : 5-epoxy-anhydride, collected and dried *in vacuo* over sodium hydroxide, recrystallised from ethyl acetate as rods (25.0 g.), m. p. 204—205° (Found : C, 57.5; H, 4.9. C₈H₈O₄ requires C, 57.1; H, 4.8%).

A clear syrup was obtained on removal of the acetic acid from the residual liquor and gave an acidic solution on dissolving in water. The epoxide was soluble in ethyl acetate, acetic acid, benzene, acetone, or dioxan and was insoluble, or slightly soluble, in ligroin, ether, chloroform, or carbon tetrachloride.

4-Chloro-5-hydroxyhexahydrophthalic Anhydride.—The epoxy-anhydride in ethyl acetate with hydrogen chloride in ether at room temperature gave 4-chloro-5-hydroxyhexahydrophthalic anhydride, rods (from ethyl acetate), m. p. 164—165° (Found : C, 47.0; H, 4.5; Cl, 17.3. C₈H₈O₄Cl requires C, 46.95; H, 4.4; Cl, 17.4%).

cis-1 : 2 : 3 : 6-Tetrahydrophthalimide.—The cis-anhydride (50 g.) was heated with 28% aqueous ammonia (45 ml.). Water was boiled off during 1 hour and the temperature raised to 300° during the next 45 minutes. Distillation gave the imide (36 g.), b. p. 157°/1 mm., which crystallised from chloroform as rods, m. p. 136—138° (Found : C, 63.5; H, 6.0; N, 9.3. C₈H₈O₂N requires C, 63.6; H, 6.0; N, 9.3%), very soluble in water, alcohol, or chloroform, slightly soluble in ether, insoluble in light petroleum.

Bromination.—Bromine (11 g.) in chloroform (25 ml.) was added slowly, with stirring, to the tetrahydrophthalic anhydride (10 g.) in chloroform (100 ml.). The temperature rose to 35—40° after about half the bromine solution had been added and then liberation of hydrogen bromide began. The mixture was then cooled to 0°, and the rest of the bromine solution added. Concentration gave a mixture of crystals and a syrup. The latter was leached out in cold glacial acetic acid. The 4 : 5-dibromohexahydrophthalic acid (6.4 g.; m. p. 220°) was soluble in hot glacial acetic acid, alcohol, acetone, or hot water, but insoluble in benzene, butyl acetate, or chloroform. Recrystallisation from alcohol-chloroform (1 : 1) gave rods, m. p. 222—223° (Found : C, 29.5; H, 3.2; Br, 48.1. C₈H₁₀O₄Br₂ requires C, 29.1; H, 3.0; Br, 48.5%). The acetic acid-soluble fraction (13 g.) was obtained as a water-insoluble yellowish-brown, tacky polymer which contained bromine.

Chlorination.—The cis-tetrahydrophthalic anhydride, when treated with chlorine in chloroform or carbon tetrachloride at -20° to 10°, immediately evolved hydrogen chloride. The products were chlorinated polymeric resins and liquid fractions of variable composition, soluble in alcohol and containing labile chlorine (they gave sodium chloride on addition of sodium hydroxide). Addition of a drop of aqueous sodium hydroxide to alcoholic solutions of the liquid fractions evoked a bright red colour, but this disappeared as the alkali was neutralised; the material acted as an indicator until the solution was neutral (phenolphthalein). On storage the liquids became insoluble in alcohol.

The polymeric resinous fractions were also unstable; acidity developed and they were sensitive to atmospheric moisture.

Dialkyl 4 : 5-Epoxyhexahydrophthalates (see Tables) from Tetrahydrophthalates.—(a) By

4-Chloro-5-hydroxyhexahydrophthalates.

No.	Ester	Yield, %	B. p. (°/mm.)	Formula	Found (%) :			Required (%) :		
					C	H	Cl	C	H	Cl
1.	Me ₂	86	152—154/0.5	C ₁₀ H ₁₅ O ₅ Cl	47.3	5.4	13.6	47.1	5.9	14.2
2.	Et ₂	77	146/0.5	C ₁₂ H ₁₉ O ₅ Cl	51.8	6.6	13.95	51.7	6.8	12.75
3.	Bu ⁿ ₂	75	160/1	C ₁₆ H ₂₇ O ₅ Cl	—	—	—	—	—	—
4.	Diallyl ...	65	186—188/0.4	C ₁₄ H ₁₉ O ₅ Cl	55.4	6.2	11.7	55.5	6.3	11.7
5.	Allyl Et	—	—	—	—	—	—	—	—	—

4 : 5-Epoxyhexahydrophthalates.

No.	Yields (%)		B. p. (°/mm.)	Formula	Found (%) :		Required (%) :	
	Method a	Method b			C	H	C	H
1.	—	85	112/0.6	C ₁₀ H ₁₄ O ₅	56.8	6.55	56.1	6.5
2.	74	90	120/0.3	C ₁₂ H ₁₈ O ₅	59.3	7.35	59.5	7.4
3.	47	82	160—164/0.8	C ₁₆ H ₂₆ O ₅	64.1	8.0	64.4	8.7
4.	0*	42	133—136/0.3	C ₁₄ H ₁₈ O ₅	62.1	6.6	63.2	6.8
5.	44	—	141—144/1	C ₁₃ H ₁₈ O ₅	62.0	6.2	61.4	7.1

* Polymers formed.

peracetic acid. The ester (1 mol.) was dissolved in acetic acid containing peracetic acid (1.01 mols.) and kept for 20 hours at 20—25°. Acetic acid was removed *in vacuo* below 50° and the dialkyl 4 : 5-epoxyhexahydrophthalate was distilled *in vacuo*.

(b) *By hypochlorite.* A solution of hypochlorous acid was prepared by passing chlorine into a stirred suspension of calcium carbonate (1 part) in ice-water (25 parts) below 3° and added at <10° during 20 minutes to a vigorously stirred mixture of the ester with twice its weight of water. Stirring was continued for 30 minutes, and the temperature allowed to rise to room temperature. Excess of hypochlorous acid was destroyed by sodium sulphite and, after decantation of the supernatant liquid, the chlorohydrin was extracted from admixed calcium salts with ether. The chlorohydrin was converted into the epoxide by addition of the equivalent amount of alcoholic sodium hydroxide. After filtration the epoxide purified by distillation.

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