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Mercuration of Monoallyl Ethers of Polyols[1]

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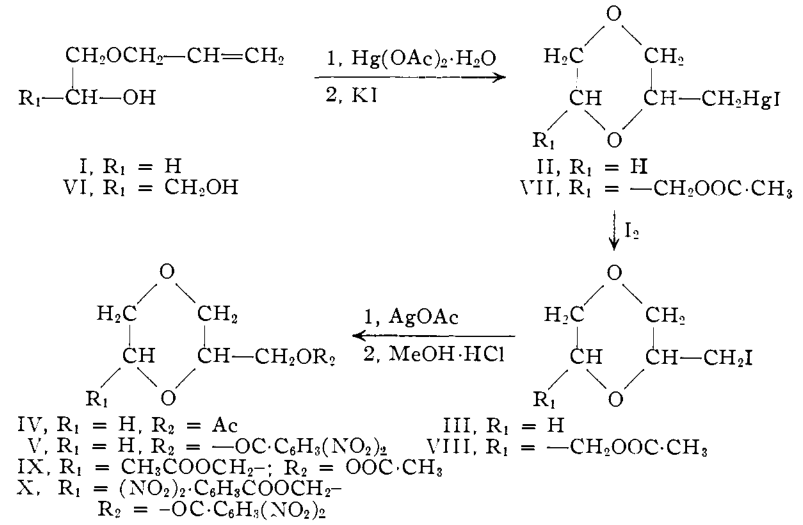
The mercuration of 2-allyloxyethanol, 3-allyloxy-1,2-propanediol and 3-allyl-D-mannitol is described. Degradative studies indicated that internal ether formation occurred, leading to substituted *p*-dioxane derivatives.

During the course of an investigation concerning the usefulness of various organic mercurials as diuretics, a series of monoallyl ethers of polyols was mercurated. The mercuration products of these allyl ethers represent a new type of mercurial diuretic of low toxicity. We were interested in determining their structure and especially whether internal ether formation occurred which would lead to substituted *p*-dioxane derivatives. The formation of cyclic ethers of the tetrahydropyran,[3-5] tetrahydrofuran[4] and dihydrobenzofuran[6] type by mercuration of suitably substituted olefins has been reported. Dioxane derivatives containing two mercury atoms also have been obtained by reaction of mercuric nitrate with allyl alcohol in the presence of nitric acid[3] or by treating allyl ether with mercuric acetate.[7,8] These reactions are special cases which lead to symmetrical compounds. Our investigation was concerned with the more general case of *p*-dioxane ring formation which was expected to occur on mercuration of allyl ethers with a hydroxyl group attached to the carbon next to the carbon atom bearing the allyloxy group. As examples we chose 2-allyloxyethanol,[9] 3-allyloxy-1,2-propanediol[10a] and 3-allyl-D-mannitol.[10b]

2-Allyloxyethanol (I) was mercurated in aqueous solution and the resulting acetoxymercuri compound converted directly to 2-iodomercurimethyl-*p*-dioxane (II) by reaction with one equivalent potassium iodide. Demercuration of the iodomercuri derivative II with iodine according to Sand and Singer[3] gave 2-iodomethyl-*p*-dioxane (III). Replacement of the iodine by the acetoxy group (IV), followed by hydrolysis of the acetate group and treatment with 3,5-dinitrobenzoyl chloride led to the 3,5-dinitrobenzoate of 2-*p*-dioxane-methanol (V) which was previously prepared by Kharasch and Nudenberg.[11] The identity of the two compounds was proof that the cyclic dioxane structure actually was present.

A similar sequence of reactions was carried out starting with 3-allyloxy-1,2-propanediol (VI). Mercuration of VI in aqueous solution followed by acetylation and treatment with potassium iodide gave 2-iodomercurimethyl-6-acetoxymethyl-*p*-dioxane (VII). Demercuration with iodine yielded the iodomethyl derivative VIII, which, without further purification, was converted to the diacetate of *p*-dioxane 2,6-dimethanol (IX). Hydrolysis of the acetate groups and treatment with 3,5-dinitrobenzoyl chloride gave the bis-3,5-dinitrobenzoate (X). The structure VII was assigned to the acetylated mercuration product because of the analogy to the mercuration product II of 2-allyloxyethanol (I) and because the demercurated compound IX gave only a bis-3,5-dinitrobenzoate after hydrolysis. A tris- or tetra-3,5-dinitrobenzoate would have been obtained if ring closure had not taken place.



I, $R_1 = H$
VI, $R_1 = CH_2OH$
II, $R_1 = H$
VII, $R_1 = —CH_2OOC·CH_3$
III, $R_1 = H$
VIII, $R_1 = —CH_2OOC·CH_3$
IV, $R_1 = H$, $R_2 = Ac$
V, $R_1 = H$, $R_2 = —OC·C_6H_3(NO_2)_2$
IX, $R_1 = CH_3COOCH_2—$; $R_2 = OOC·CH_3$
X, $R_1 = (NO_2)_2·C_6H_3COOCH_2—$
$R_2 = —OC·C_6H_3(NO_2)_2$

The mercuration of 3-allyl-D-mannitol (XI) in aqueous solution yielded an amorphous, very water-soluble mixture XII, from which two crystalline derivatives, a diisopropylidene compound XIIIa and a tetraacetate XIV were prepared, representing two distinctly different stereoisomers. Mercuration and ring closure of XI leads to the formation of a new asymmetric carbon atom at the 2-position of the dioxane ring. Degradation of XIIIa and XIV indicated that they are isomeric at this carbon atom.

Compound XIIIa, 2-acetoxymercurimethyl-5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-dioxane, was

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[3] Review article: J. Chatt, *Chem. Revs.*, **48**, 7 (1951).

[4] J. Sand and F. Singer, *Ann. Chem.*, **329**, 166 (1903).

[5] A. G. Brook, A. Rodgman and G. F Wright, *J. Org. Chem.*, **17**, 988 (1952).

[6] R. Adams, F. L. Roman and W. N. Sperry, THIS JOURNAL, **44**, 1781 (1922); L. E. Mills and R. Adams, *ibid.*, **45**, 1842 (1923).

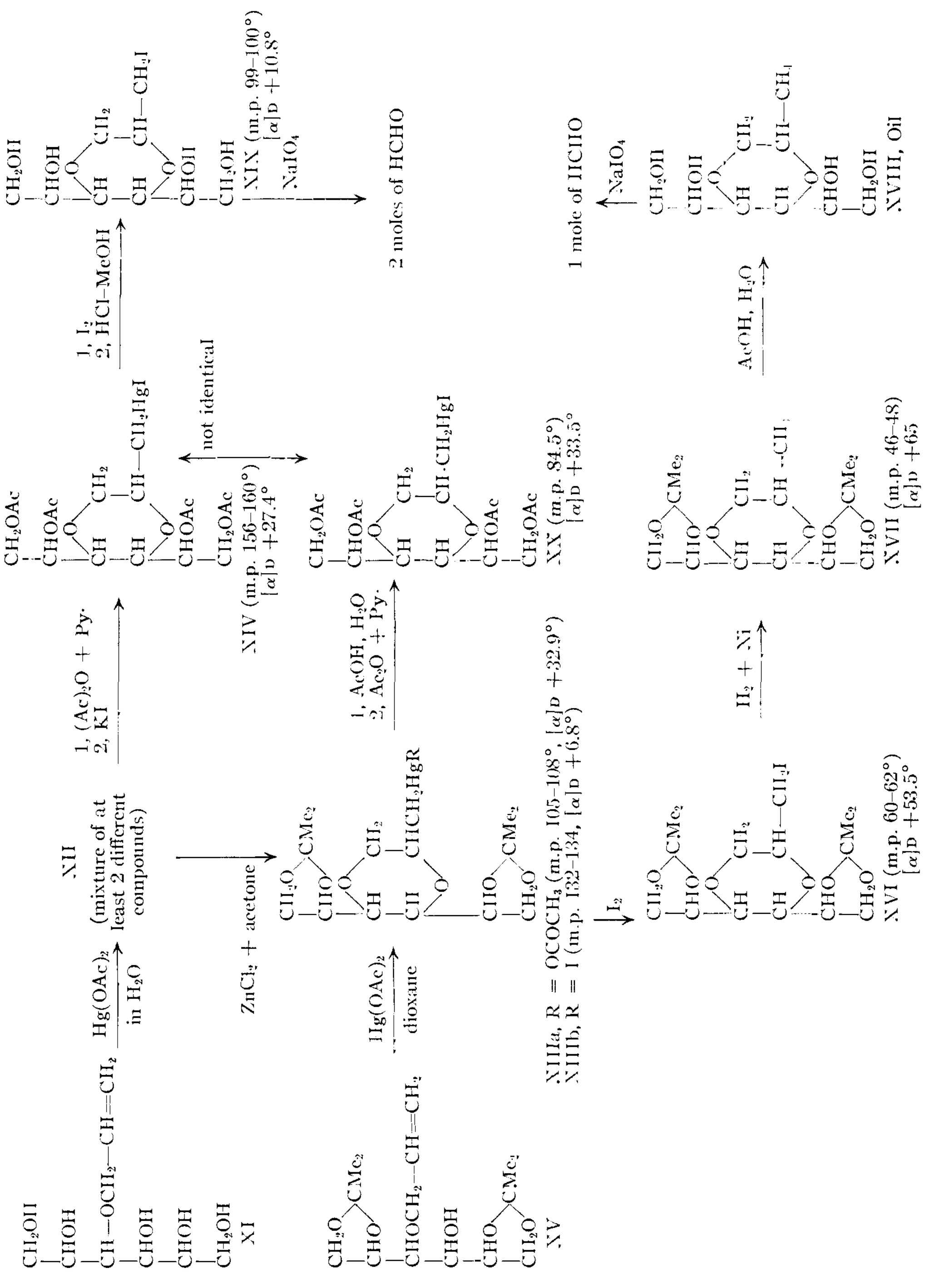
[7] A. N. Nesmeyanov and I. F. Lutsenko, *Bull. acad. sci., U.R.S.S., Classe sci. chim.*, 296 (1943).

[8] R. K. Summerbell and J. R. Stephens, THIS JOURNAL **76**, 731 (1954).

[9] M. H. Palomaa, *Ber.*, **42**, 3873 (1909).

[10] (a) L. W. C. Miles and L. N. Owen, *J. Chem. Soc.*, 2934 (1950); (b) P. Bladon and L. N. Owen, *ibid.*, 591 (1950).

[11] M. S. Kharasch and W. Nudenberg, *J. Org. Chem.*, **8**, 189 (1943).



obtained from the mercuration mixture XII by acetonization according to Baer's[12] procedure and isolated as the iodide XIIIb. The same compound was also prepared by mercuration of 3-allyl-1,2;5,6-diisopropylidene-D-mannitol (XV) under anhydrous conditions in dioxane or 1,2-dimethoxyethane as described by Wright, *et al.*[4] Analysis and infrared spectroscopy of the iodomercuri compound XIIIb indicated that ring closure had occurred and that no free hydroxy group was present. The isopropylidene groups occupy the 1,2- and 5,6-positions, therefore the dioxane ring must incorporate the 3- and 4-positions of the mannitol chain. Demercuration of the iodomercuri compound XIIIb with iodine gave 2-iodomethyl-5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-dioxane (XVI).

Reductive removal of the iodine, using the method of Haskins, *et al.*,[13] gave 2-methyl-5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-dioxane (XVII). Hydrolysis of (XVII) with dilute acetic acid yielded 2-methyl-5,6-bis-(1,2-ethanediol)-*p*-dioxane (XVIII) as a sirup which could not be crystallized. To further establish its structure,

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(12) E. Baer, This Journal, **67**, 338 (1945).

(13) W. T. Haskins, R. M. Hann and C. S. Hudson, *ibid.*, **68**, 628 (1946).

the tetrol (XVIII) was oxidized with periodic acid.

Contrary to what might be expected, only 1 mole of periodate per mole of tetrol was consumed rapidly, even after 21 hours only 1.68 moles was taken up and only one mole of formaldehyde was formed after one hour, using Jeanloz's[14] method. A similar behavior was reported by Greville and Northcote[15] for 3,4-dimethylglucose which, due to the formation of a hemiacetal, is resistant to further periodate oxidation after removal of one carbon atom. Similar results were obtained, when we subjected 3,4-diallyl-D-mannitol[16] and 3,4-dimethyl-D-mannitol to periodate oxidation. With both compounds only one mole of periodate was consumed rapidly and one mole of formaldehyde produced. Under similar conditions 3-allyl-D-mannitol behaves normally, consumes 3 moles of periodate and gives 2 moles of formaldehyde.

Further it was found that hydrolysis of the crystalline iodomercuri compound XIIIb followed by acetylation gave a 2-iodomercurimethyl-*p*-dioxane-5,6-bis-ethanediol tetraacetate (XX), which differed from the tetraacetate obtained by direct acetylation of the mercuration mixture XII.

As was previously mentioned, the mercuration mixture XII, on acetylation and subsequently treatment with potassium iodide also yielded 2-iodomercurimethyl-*p*-dioxane-5,6-bis-ethanediol tetraacetate (XIV), which differs greatly in melting point and solubility from the tetraacetate XX. Demercuration of XIV followed by hydrolysis of the acetate groups gave 2-iodomethyl-*p*-dioxane-5,6-bis-ethanediol (XIX). Periodate oxidation of XIX gave after one hour, results approaching a consumption of 2 moles periodate and a yield of 2 moles formaldehyde. It is interesting to note the difference in the rate of oxidation between the two tetrols XVIII and XIX. The iodine containing tetrol XIX was used as the corresponding deiodinated tetrol was not obtained in sufficiently pure form. Structure XIV was assigned to the tetraacetate based on the analytical results which indicated that ring closure had taken place and because of the formation of two moles of formaldehyde on periodate oxidation.

It could thus be shown that in the three instances examined, internal ether formation with the formation of a *p*-dioxane ring proceeds readily, even in aqueous solution.

Experimental[17]

Mercuration of 2-Allyloxyethanol. 2-Iodomercurimethyl-*p*-dioxane (II).—A solution of 6.36 g. of mercuric acetate in 15 cc. of water was added to 2.04 g. of 2-allyloxyethanol.[9] After heating for 15 minutes on the steam-bath and allowing to stand for 18 hours at room temperature, 10 cc. of 2 *N* sodium hydroxide followed by a solution of 3.32 g. of potassium iodide in 4 cc. of water, was added. A precipitate formed which quickly crystallized. It was filtered off and recrystallized from a mixture of methanol and water; yield 7.7 g., m.p. 78–80°.

Anal. Calcd. for $C_5H_9HgIO_2$: Hg, 46.8. Found: Hg, 46.4.

Demercuration. 2-Iodomethyl-*p*-dioxane (III).—To 4.3 g. of iodomercuri methyl-*p*-dioxane dissolved in 25 cc. of chloroform a solution of 2.54 g. of iodine in 60 cc. of chloroform was added. After standing for 16 hours the mercuric iodide was filtered off, the solution washed with sodium thiosulfate, dried and evaporated to dryness. The residue was distilled twice *in vacuo* (bath temperature 90°, 15 mm.). On cooling the distillate crystallized, m.p. 30°.

Anal. Calcd. for $C_5H_9IO_2$: C, 26.3; H, 4.0. Found: C, 26.8; H, 4.3.

2-*p*-Dioxanemethanol (IV, V).—By refluxing 1.50 g. of 2-iodomethyl-*p*-dioxane with 8 cc. of acetic acid and 5 g. of silver acetate for 4 hours and distilling the reaction product, 0.55 g. of 2-acetoxymethyl-*p*-dioxane, m.p. 35–37°, was obtained.

Hydrolysis was carried out by refluxing for 30 min. 0.35 g. of the acetate with 3.5 cc. of methanol containing 1% anhydrous hydrogen chloride. The reaction mixture was evaporated to dryness, the residue was dissolved in 1 cc. of pyridine and treated with 0.4 g. of 3,5-dinitrobenzoyl chloride. The dinitrobenzoate V was recrystallized three times from methanol and melted at 107–109°. It gave no depression with a sample of the dinitrobenzoate of 2-*p*-dioxanemethanol.[11]

Anal. Calcd. for $C_{12}H_{12}N_2O_8$: N, 9.0. Found: N, 8.8.

Mercuration of 3-Allyloxy-1,2-propanediol. 2-Iodomercurimethyl-6-acetoxymethyl-*p*-dioxane (VII).—A solution of 19.1 g. of mercuric acetate in 40 cc. of water was added to 8.0 g. of 1-allyloxy-1,2-propanediol.[10a] The reaction mixture was heated for 1 hour on the steam-bath, then allowed to stand for 16 hours at room temperature. The solution was then filtered and evaporated to dryness, residue 22.8 g. The residue was acetylated at room temperature with 23 cc. of acetic anhydride and 46 cc. of pyridine. The acetylated sirupy product was dissolved in 15 cc. of methanol and a solution of 10.4 g. of potassium iodide in 10 cc. of water added. A heavy, oily precipitate formed. The supernatant solution was decanted and the product taken up in chloroform and washed with water. Evaporation of the chloroform gave a residue which, on standing, crystallized. The iodomercuri compound VII was recrystallized from ethyl acetate–hexane and melted at 71–72°; yield 13.0 g. (42% of theory).

Anal. Calcd. for $C_8H_{13}HgIO_4$: Hg, 39.9, acetyl 8.6. Found: Hg, 39.5; acetyl, 8.6, 8.9.

2,6-*p*-Dioxanedimethanol (IX, X).—A solution of 6.6 g. of iodine in 200 cc. of chloroform was added to 13 g. of the iodomercuri compound VII and allowed to stand at room temperature for four hours. The mercuric iodide was filtered off, the solution washed with thiosulfate, dried and evaporated to dryness. The residue was distilled *in vacuo* (bath temp. 135–145°, 0.04 mm.) and yielded 6.56 g. of crude 2-iodomethyl-6-acetoxymethyl-*p*-dioxane (VIII). The 2,6-diacetoxymethyl-*p*-dioxane was obtained by refluxing 6.5 g. (VIII) with 25 cc. of acetic acid and 15 g. of silver acetate for 4 hours. The silver salts were filtered off, washed with ethyl acetate and the filtrates evaporated to dryness. The residue was distilled *in vacuo* (bath temp. 115–120°, 0.02 mm.) to give 3.8 g. of the 2,6-diacetoxymethyl-*p*-dioxane (IX). Without further purification 3.8 g. of this diacetate was hydrolyzed by refluxing for 30 min. with 38 cc. of methanol containing 1% anhyd. hydrogen chloride. Evaporation of the solvent gave 2.4 g. of crude 2,6-*p*-dioxanedimethanol. This was converted directly into the bis-3,5-dinitrobenzoate by warming 1.0 g. with 6.5 cc. of pyridine and 3.33 g. of 3,5-dinitrobenzoyl chloride to 80° for 15 min., allowing to stand at room temperature for 1 hour, and pouring into 25 cc. of water. The crystalline precipitate was washed with sodium carbonate solution, water and alcohol and recrystallized from dioxane–ethanol; yield 3.4 g. of bis-dinitrobenzoate (X), m.p. 180–182°.

Anal. Calcd. for $C_{20}H_{16}N_4O_{14}$: C, 44.8; H, 3.0; N, 10.5. Found: C, 45.0; H, 3.1; N, 10.6.

Mercuration Product of 3-Allyl-D-mannitol (XII).—A solution of 9.54 g. of mercuric acetate in 45 cc. of water containing 0.1 cc. of acetic acid was added to 6.66 g. of 3-allylmannitol[10b] dissolved in 30 cc. of water. The reaction mixture was warmed to 60° for 1 hour then allowed to stand at room temperature for 16 hours. A sample of the solution when tested with sodium hydroxide or dilute potassium iodide solution did not show any ionic mercury. The solu-

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[14] R. Jeanloz, *Helv. Chim. Acta*, **27**, 1509 (1944).

[15] G. D. Greville and D. H. Northcote, *J. Chem. Soc.*, 1945 (1952).

[16] A. N. Wrigley and E. Yanovsky, THIS JOURNAL, **70**, 2194 (1948).

[17] All melting points are uncorrected and were taken by the capillary tube method in an aluminum block.

tion was evaporated to dryness and the amorphous residue dried *in vacuo*.

Introduction of Isopropylidene Groups. Formation of XIIIb.—The reaction mixture which contained 10 g. of mercurated 3-allylmannitol (XII) and 10 g. of fused zinc chloride sticks dissolved in 60 cc. of acetone, was stirred for 4 hours at room temperature. It was then poured into a mixture of 13 g. of potassium carbonate dissolved in 13 cc. of water and 60 cc. of ether. The precipitated zinc salts were filtered off, the filtrate dried with anhyd. potassium carbonate and evaporated to dryness. The residue, 9.3 g., was dissolved in 20 cc. of methanol, a solution of 2.75 g. of potassium iodide in 5 cc. of water was added and the product extracted into chloroform. After washing, drying and concentrating the chloroform solution, 9.5 g. of residue was obtained. Chromatography of 6.0 g. of the residue on 125 g. of alumina gave, from the eluates with benzene–ether (4:1) 3.27 g. of material which after recrystallization from ethyl acetate–hexane melted at 132–134° and showed no depression in mixture with a sample of 2-iodomercurimethyl-5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-dioxane (XIIIb), prepared from 3-allyl-1,2,5,6-diisopropylidene-D-mannitol[10b] (see below).

Mercuration of 3-Allyl-1,2,5,6-diisopropylidene-D-mannitol. 2-Acetoxymercurimethyl-5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-dioxane (XIIIa).—Finely powdered mercuric acetate (96 g.) was stirred with a solution of 90.6 g. of 3-allyl-1,2,5,6-diisopropylidenemannitol[10b] (XV) in 750 cc. of anhydrous dioxane for 4 hours at 60° and 16 hours at room temperature. The reaction mixture was filtered and concentrated *in vacuo*. The residue was taken up in chloroform and washed with water. After drying, the solution was concentrated *in vacuo*. On standing the residue crystallized; after recrystallization from ethyl acetate–hexane or isopropyl ether, the product XIIIa melted at 105–108°.

Anal. Calcd. for $C_{17}H_{28}HgO_8$: Hg, 35.8. Found: Hg, 35.9; $[\alpha]^{25}_{D}$ +32.9° (2% in ethanol).

Iodide (XIIIb).—To a solution of 16.8 g. of XIIIa in 40 cc. of methanol, 4.98 g. of potassium iodide dissolved in 10 cc. of water was added. The iodide crystallized from the solution, it was filtered off and recrystallized from ethyl acetate–hexane, m.p. 132–134°.

Anal. Calcd. for $C_{15}H_{25}HgIO_6$: Hg, 31.9. Found: Hg, 31.2; $[\alpha]^{25}_{D}$ +6.8° (2% in ethanol).

2-Iodomethyl-5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-dioxane (XVI).—The iodomercuri compound XIIIb (17.0 g.) was dissolved in 50 cc. of chloroform. A solution of 6.9 g. of iodine in 150 cc. of chloroform was added and the reaction mixture warmed to 60° for 30 min., then allowed to stand for 16 hours at room temperature. The mercuric iodide was filtered off, the solution was washed with sodium thiosulfate, dried and concentrated *in vacuo*. The residue XVI crystallized on standing and was recrystallized from hexane, m.p. 60–62°.

Anal. Calcd. for $C_{15}H_{25}IO_6$: C, 42.1; H, 5.9. Found: C, 42.1; H, 5.7; $[\alpha]^{26}_{D}$ +53.5° (1% in ethanol).

2-Methyl-5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-dioxane (XVII).—To a solution of 6.4 g. of iodomethyl derivative XVI in 90 cc. of methanol were added 2.20 g. of diethylamine and $^1/_4$ teaspoon of Raney nickel. On hydrogenation 435 cc. of H_2 (0° (760 mm.)), calcd. 336 cc. H_2, was taken up. The reaction mixture was filtered, evaporated to dryness and the residue taken up in ether. The solution was washed with water to remove diethylamine hydroiodide, dried and taken to dryness. On standing, the residue crystallized. The product XVII was recrystallized from hexane, m.p. 46–48°.

Anal. Calcd. for $C_{15}H_{26}O_6$: C, 59.6; H, 8.7. Found: C, 59.8; H, 9.0; $[\alpha]^{24}_{D}$ +65.0 (2% in ethanol).

2-Methyl-5,6-bis-(1,2-ethanediol)-*p*-dioxane (XVIII).—To obtain the tetrol, 1.5 g. of diisopropylidene derivative XVII was warmed to 60° with 20 cc. of 50% aqueous acetic acid for 3 hr. The solution was then evaporated to dryness. The sirupy residue representing the tetrol (XVIII) could not be crystallized; dried 4 hours at 90°, 1 mm.

Anal. Calcd. for $C_9H_{18}O_6$: C, 48.6; H, 8.2. Found: C, 48.6; H, 8.2; $[\alpha]^{28}_{D}$ +58° (1% in ethanol).

3,4-Dimethyl-D-mannitol.—To a solution of 15.7 g. of 1,2;5,6-diisopropylidene-D-mannitol[12] in 65 cc. of acetone and 15 cc. of water, a solution of 24 g. of sodium hydroxide dissolved in 24 cc. of water was added. Dimethyl sulfate (30.2 g.) in 30 cc. of acetone was added dropwise with stirring over a period of 1.75 hours while gently refluxing. Stirring was continued for an additional 90 min. The acetone was distilled off, 140 cc. of water and 19.1 cc. of concd. sulfuric acid diluted with 115 cc. of water was added. The reaction mixture was cooled and extracted with ether. The ether extract yielded 14.1 g. of crude 1,2;5,6-diisopropylidene-3,4-dimethyl-D-mannitol which was directly hydrolyzed by warming to 60° for 2 hours with 200 cc. of 50% aqueous acetic acid. The solution was concentrated *in vacuo* and the 3,4-dimethyl-D-mannitol recrystallized from ethanol; yield 5.4 g., m.p. 144–146°.

Anal. Calcd. for $C_8H_{18}O_6$: C, 45.7; H, 8.6; $-OCH_3$, 29.5 (2). Found: C, 45.9; H, 8.6; $-OCH_3$, 29.6; $[\alpha]^{25}_{D}$ +40.8 (1% in water).

Periodate Oxidations. (a) **3,4-Dimethyl-D-mannitol.**—To a solution of 107.2 mg. of 3,4-dimethylmannitol in 10 cc. of water, 10 cc. of 0.1440 molar sodium periodate and water to a total volume of 50 cc. were added. Samples were withdrawn at intervals and the consumption determined according to the standard procedure using 0.1 *N* sodium arsenite and 0.1 *N* iodine solution.

Consumption after min.	Moles $NaIO_4$/mole
15	1.1
120	1.13
19 hr.	1.32

Formation of formaldehyde[14]: 20.92 mg. of 3,4-dimethylmannitol gave 30.4 and 30.8 mg. of dimedon derivative; calcd. for 1 mole HCHO, 29.1 mg.

(b) **3,4-Diallyl-D-mannitol.**—To a solution of 249.8 mg. of 3,4-diallyl-D-mannitol in 10 cc. of water, 15 cc. of 0.1450 molar sodium periodate and water to 50 cc. were added.

Consumption after min.	Moles $NaIO_4$/mole
30	1.14
60	1.03

Formation of formaldehyde on periodate oxidation according to Jeanloz[14]: 18.1 mg. of 3,4-diallylmannitol gave 16.2 and 15.5 mg. of dimedon derivative; calcd. for 1 HCHO, 19.6 mg.

(c) **Tetrol (XVIII).**—To a solution of 86.0 mg. of tetrol (XVIII) in 10 cc. of water were added 10 cc. of 0.1920 molar periodic acid and water to 50 cc. Samples (10 cc.) were withdrawn at intervals.

Consumption after min.	Moles $NaIO_4$/mole
30	1.0
75	1.02
5 hr.	1.23
21 hr.	1.68

Formation of formaldehyde[14]: oxidation time 1 hr., 22.1 mg. of tetrol (XVIII) gave 27.7 and 29.3 mg. of dimedon derivative, calcd. for 1 mole formaldehyde: 29.0 mg.

(d) **3-Allyl-D-mannitol (XI).**—To a solution of 80.4 mg. of 3-allylmannitol[10] dissolved in 10 cc. of methanol were added 10 cc. of 0.1480 molar sodium periodate and water to 25 cc.; 5-cc. samples were titrated at intervals.

Consumption after min.	Moles $NaIO_4$/mole
2	2.52
5	2.72
15	3.10
30	3.14

Formation of formaldehyde[14]: 15.7 mg. of XI gave 38.1 mg. of dimedon derivative; oxidation time 30 min.; calcd. for 2 moles HCHO, 39.4 mg.

Acetylation of XII, 2-Iodomercurimethyl-*p*-dioxane-5,6-bis-ethanediol Tetraacetate (XIV).—The mercuration mixture XII obtained from 13.32 g. of 3-allyl-D-mannitol and 19.10 g. of mercuric acetate was warmed with 75 cc. of acetic anhydride and 120 cc. of pyridine until a clear solution was obtained. The acetylation mixture was allowed to stand 16 hours at room temperature, then evaporated to dryness. The residue was dissolved in chloroform and washed with water. After drying, the chloroform was removed *in vacuo* and the residue dissolved in methanol. A solution of 10 g. of potassium iodide in 15 cc. of water was added, and the product precipitated as a heavy oil by addition of water. The supernatant solution was decanted and the product dissolved in chloroform, washed with water and isolated again by evaporation of the solvent. The residue was dissolved in ethyl acetate, on standing, crystals deposited, which were filtered off and recrystallized from methanol, yield 3.5 g., m.p. 150–154°. Further recrystallization raised the melting point of the tetraacetate to 156–160°.

Anal. Calcd. for $C_{17}H_{25}HgIO_{10}$: Hg, 28.0; I, 17.7; acetyl, 24.0. Found: Hg, 27.6; I, 17.6; acetyl, 24.0; $[\alpha]^{25}D$ +27.4° (1% in chloroform).

Tetrol (XIX), 2-Iodomethyl-*p*-dioxane-5,6-bis-ethanediol.—Demercuration: 3.6 g. of iodomercuri derivative XIV was dissolved in 20 cc. of chloroform. A solution of 1.27 g. of iodine in 30 cc. of chloroform was added and the mixture warmed to 60° for 5 min., then allowed to stand at room temperature for 16 hr. The mercuric iodide was filtered off and excess iodine removed from the filtrate by washing with sodium thiosulfate solution. Evaporation of the chloroform gave 2.80 g. of residue.

Hydrolysis.—The residue (2.80 g.) was refluxed with 100 cc. of methanol containing 1% anhydrous hydrogen chloride for 45 min., the solution was then evaporated to dryness leaving a residue of 1.73 g. which crystallized partly on standing. Recrystallization from ethyl acetate–hexane gave crystals of the tetrol (XIX) melting at 99–100°.

Anal. Calcd. for $C_9H_{17}IO_6$: C, 31.1; H, 4.9. Found: C, 31.4; H, 5.0; $[\alpha]^{26}D$ +10.8° (2% in ethanol).

Periodate oxidation: 87.7 mg. of tetrol (XIX) was dissolved in 10 cc. of methanol and 4 cc. of 0.1580 molar sodium periodate, water to 25 cc. was added.

Consumption after min.	Moles $NaIO_4$/mole
15	1.57
50	1.86

Formation of formaldehyde[14]: 36.0 mg. of tetrol (XIX) gave 49.3 mg. of dimedon derivative (oxidation time 30 min.) and 53.9 mg. of dimedon derivative (oxidation time 60 min.) corresponding to 1.63 and 1.79 moles HCHO/mole tetrol, respectively.

Hydrolysis and Acetylation of Iodomercuri Compound XIIIb. 2-Iodomercurimethyl-*p*-dioxane-5,6-bis-ethanediol Tetraacetate (XX).—A solution of 5.54 g. of the diisopropylidene–iodomercuri compound XIIIb in 70 cc. of 50% aqueous acetic acid was warmed 1.5 hr. to 60–70°, then concentrated *in vacuo*. A thick sirup remained which contained a small amount of mercuric iodide. The product was extracted with warm ethyl acetate and after concentrating the solution, acetylated with 12 cc. of acetic anhydride and 25 cc. of pyridine. The acetylation mixture was allowed to stand for 16 hours at room temperature and then worked up as usual. By cooling and stirring with isopropyl ether the acetylated product could be crystallized. The tetraacetate XX was recrystallized from ethyl acetate–hexane and melted at 84–85°.

Anal. Calcd. for $C_{17}H_{25}HgIO_{10}$: Hg, 28.0; acetyl, 24.0; Found: Hg, 27.9; acetyl, 24.5; $[\alpha]D$ +33.5° (1% in chloroform).

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SUMMIT, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XXI. 3-Chloro-2-phenyl-1-propene[1]

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3-Chloro-2-phenyl-1-propene has been prepared by the reaction between 2-phenyl-2-propen-1-ol and thionyl chloride. The allylic alcohol was prepared by the hydrolysis of the corresponding acetate made by selenium dioxide oxidation of 2-phenyl-1-propene and by the hydrolysis of the corresponding bromide (3-bromo-2-phenyl-1-propene) made by the reaction between 2-phenyl-1-propene and N-bromosuccinimide. The relative reactivities of 3-chloro-2-phenyl-1-propene with potassium iodide in acetone and sodium ethoxide in ethanol have been determined.

The study of the influence of various groups and atoms on the reactivity of the allylic chlorine atom of various substituted allylic chlorides has been extended to include 3-chloro-2-phenyl-1-propene (β-phenylallyl chloride). This chloride belongs to the type $CH_2{=}CYCH_2Cl$. Previously reported compounds of this type have had Y as H, Br, Cl and CH_3.[2,3]

The 3-chloro-2-phenyl-1-propene was prepared by two different routes from 2-phenyl-1-propene (α-methylstyrene) as indicated in Fig. 1.

The oxidation of 2-phenyl-1-propene by selenium dioxide in the presence of an acetic anhydride–acetic acid mixture to give 3-acetoxy-2-phenyl-1-propene has been reported by Butler.[4] Recovery of the product by steam distillation as prescribed by Butler led to extremely low yields. Much higher yields were obtained by low pressure distillation of the product. The ester was saponified to 2-phenyl-2-propen-1-ol (β-phenylallyl alcohol) which was characterized by its 3,5-dinitrobenzoate, α-naphthylurethan, infrared spectrum and by reduction of 2-phenylpropan-1-ol.

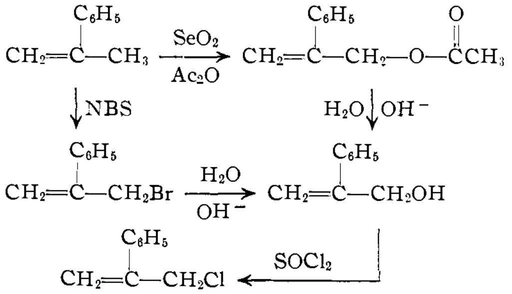

Fig. 1.—Preparation of 3-chloro-2-phenyl-1-propene from 2-phenyl-1-propene.

The same alcohol was obtained by the N-bromosuccinimide bromination of 2-phenyl-1-propene followed by hydrolysis of the 3-bromo-2-phenyl-1-propene. The fact that the bromination proceeded

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(1) For number XX of this series see L. F. Hatch and K. E. Harwell, THIS JOURNAL, **75**, 6002 (1953).

(2) L. F. Hatch, L. B. Gordon and J. J. Russ, *ibid.*, **70**, 1093 (1948).

(3) L. F. Hatch and H. E. Alexander, *ibid.*, **71**, 1037 (1949).

(4) J. M. Butler, U. S. Patent, 2,537,622 (Jan. 9, 1951); *C. A.*, **45**, 5723 (1951).