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The Hydroxylation of Unsaturated Substances. VI. The Catalytic Hydroxylation of Cyclopentadiene[1]

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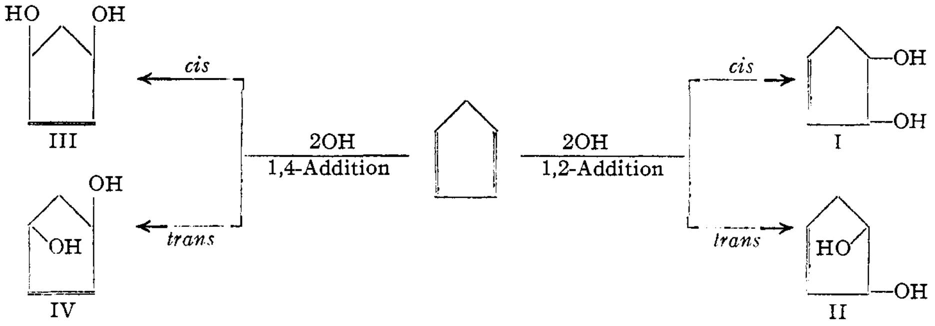
The addition of halogens and other related substances to conjugated systems is well known, and rules governing the type of addition are well established. However, no study has heretofore been reported on the addition of hydroxyl groups to conjugated systems. A study was therefore undertaken to ascertain the type of addition when two as well as four hydroxyl groups are added to a substance containing a conjugated system.

Most of our work was done with cyclopentadiene, which is known to have typical diene properties.[3] Moreover, its polymerization is essentially unaffected, at low temperatures, by light, oxygen or peroxides,[4] and it has the advantage of not losing the conjugation even if a shift of one of the double bonds is effected during the reaction.

There are four possible diols that could be produced by the addition of two hydroxyl groups to cyclopentadiene.



Not all of these diols are known. Criegee[5] obtained cyclopentene-3-diol-1,2(*cis*) (I) by the action of lead tetraacetate on cyclopentadiene and cyclopentene-3-diol-1,2(*trans*) (II) by the action of lead tetrabenzoate on the same diene. Dane and co-workers[6] obtained cyclopentene-2-diol-1,4 (IV?) by the oxidation of cyclopentene with selenium dioxide. The properties of our diol, prepared by the action of hydrogen peroxide on cyclopentadiene in the presence of osmium tetroxide, were not in agreement with those of the known diols. Furthermore, catalytic hydrogenation of our product yielded a cyclopentanediol which was different from any of the three known cyclopentane diols. Table I gives a summary of the properties and some of the derivatives of the known cyclopentanediols together with those of our diol.

It is well known that 1,2-diols are easily oxidized by lead tetraacetate,[5] the rate of oxidation being greater for the *cis* isomer. When our saturated diol was allowed to stand at room temperature for twenty-four hours with lead tetraacetate very little change in the concentration of the latter was detected. This observation indicates that the hydroxyl groups are not on the adjacent carbon atoms and our glycol cannot be a 1,2-diol. It is quite evident therefore that it must be a 1,4-diol. Moreover, since its derivatives differ in properties from those of the 1,4-diol described by Dane and co-workers, it must be a different isomer.

From previous observations, our reagent has been found to produce *cis* isomers when only one double bond is hydroxylated. It is therefore reasonable to assume that our product may be the *cis* isomer, while that described by Dane and co-workers is the *trans* isomer. This is borne out by the fact that a benzylidene derivative was obtained by the condensation of our unsaturated glycol with benzaldehyde in accordance with the

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(1) Contribution No. V, THIS JOURNAL, **61**, 1844 (1939).

(2) Abstracted from a portion of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry, M. I. T., August, 1939.

(3) Thiele, *Ann.*, **314**, 296 (1901); Farmer and Scott, *J. Chem. Soc.*, 172 (1929).

(4) Stobbe and Reuss, *Ann.*, **391**, 151 (1912); Staudinger and Lautenschlager, *ibid.*, **488**, 6 (1931); Schultze, THIS JOURNAL, **56**, 1552 (1934).

(5) Criegee, *Ann.*, **481**, 263 (1930).

(6) Dane, *et al.*, *ibid.*, **532**, 29 (1937).

TABLE I

SUMMARY OF PROPERTIES OF CYCLOPENTANEDIOLS

Diol	B. p., °C.	Mm.	M. p., °C.	
			Diphenylurethan	Di-*p*-nitrobenzoate
Cyclopentanediol-1,2(*cis*)[7,8,9]	106	10	205	117–118
Cyclopentanediol-1,2(*trans*)[7,8,9]	126.5–127.5	12	221	152
Cyclopentanediol-1,4[6]	....	..	195	.....
Our product	120–125	12	179–180	168–171

method of Platt and Hibbert.[10] This reaction has been used previously by a number of investigators[7,8,9] to determine the configuration of glycols.

When the hydroxylation of cyclopentadiene is carried out in the presence of excess hydrogen peroxide, cyclopentanetetrol is obtained to the extent of about 61% yield.

Experimental

Hydroxylation of Cyclopentadiene to Cyclopentene-2-diol-1,4.—The cyclopentadiene was obtained by the thermal decomposition of the technical grade of dicyclopentadiene. It was fractionated through an efficient column and the fraction boiling under a total reflux at 40–43° collected and used in our experiments.

In a typical experiment 0.85 mole of hydrogen peroxide in 560 cc. of anhydrous *t*-butyl alcohol was cooled to about 2° then mixed with 51 g. (0.773 mole) of freshly distilled cyclopentadiene and 5 cc. of a 0.5% osmium tetroxide solution likewise in *t*-butyl alcohol. The reaction was complete at 0° in three days. The solvent was then removed under reduced pressure in an atmosphere of nitrogen and the dark-brown, viscous residue extracted a number of times first with petroleum ether, then with ethyl ether. Finally, the residual liquid was fractionated under reduced pressure and the fraction, 23.7 g., boiling at 80–83° (1 mm.) collected.

Anal. Calcd. for $C_5H_8O_2$: C, 60.0; H, 8.00. Found: C, 60.1; H, 7.70.

This glycol is a pale yellow, highly viscous liquid, soluble in water, alcohol and ethyl acetate; insoluble in ether, benzene and other hydrocarbon solvents. It reduces rapidly ammoniacal silver nitrate in the cold, and decolorizes bromine water instantly. It is not a ketonic substance since all attempts to form the conventional derivatives were unsuccessful.

Considerable difficulty also was encountered in the preparation of esters. After a number of trials, the di-(3,5-dinitrobenzoate) was obtained by treating the glycol (0.5 g.) with 3,5-dinitrobenzoyl chloride (0.5 g.) in 10 cc. of anhydrous pyridine. Upon removal of the pyridine and 3,5-dinitrobenzoic acid, a viscous product was obtained from anhydrous benzene which was induced to crystallize by stirring with an alcohol–acetone solution. It was further recrystallized from alcohol, m. p. 185.5–186°.

Anal. Calcd. for $C_{19}H_{12}O_{12}N_4$: C, 46.72; H, 2.46. Found: C, 47.35; H, 2.84.

The benzylidene derivative of the glycol was prepared by heating at 120° for twenty minutes a mixture of glycol (1 g.), benzaldehyde (1 g.) and six drops of 40% sulfuric acid. The dark-brown resinous product formed was extracted with hot benzene from which the benzylidene derivative was precipitated by the addition of petroleum ether. It was then recrystallized from a 50–50 mixture of ligroin–petroleum ether, m. p. 115–117°.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.7; H, 6.38. Found: C, 77.4; H, 6.16.

Catalytic Reduction of Cyclopentene-2-diol-1,4.—Cyclopentene-2-diol-1,4 (0.1348 g.) in 15 cc. of ethyl alcohol was reduced catalytically in the presence of 0.02 g. of platinum oxide catalyst. The volume of hydrogen absorbed was 29.6 cc. as compared with the calculated volume of 30.2 cc. A large amount of the diol was then reduced catalytically and upon purification and fractionation the cyclopentanediol-1,4 boiled at 120–125° (12 mm.).

The di-(*p*-nitrobenzoate) of cyclopentanediol-1,4 was prepared by heating, for a few minutes, the diol (0.45 g.) with *p*-nitrobenzoyl chloride (1.65 g.) and 10 cc. of anhydrous pyridine. The mixture was then poured into cold water and the ester extracted with ethyl acetate, from which it was precipitated by the addition of methyl alcohol. After a number of crystallizations from ethyl alcohol, the ester melted at 179–181°.

Anal. Calcd. for $C_{19}H_{16}O_8N_2$: C, 57.0; H, 4.40. Found: C, 57.11; H, 4.37.

The diphenylurethan of the saturated diol was prepared by mixing the diol (0.5 g.) with 3 cc. of phenyl isocyanate and the mixture brought to boiling. After a few minutes, the mixture was cooled and washed with a small volume of anhydrous benzene, then dissolved in hot glacial acetic acid to which had been added a small amount of petroleum ether. On cooling a white crystalline precipitate separated out which was recrystallized from ligroin; m. p. 168–171°.

Anal. Calcd. for $C_{19}H_{20}O_4N_2$: C, 67.1; H, 5.89. Found: C, 67.51, 67.46; H, 6.28, 6.32.

The Effect of Lead Tetraacetate on Cyclopentanediol-1,4.—A solution of cyclopentanediol-1,4 (0.0919 g.) in 25 cc. of aldehyde-free acetic acid was mixed at constant temperature (25°) with 25 cc. of a solution of lead tetraacetate. Aliquot parts of this mixture were removed from time to time, allowed to react with excess potassium iodide solution and the iodine liberated titrated against standard sodium thiosulfate solution. It was found that the concentration of lead tetraacetate in the mixture remained constant after eighteen hours and changed only slightly after twenty-four hours.

Hydroxylation of Cyclopentadiene to Cyclopentanetetrol-1,2,3,4.—Cyclopentadiene (16 g.) was hydroxylated at 0° with hydrogen peroxide (0.533 mole) in 321 cc. of *t*-butyl alcohol and 2 cc. of osmium tetroxide catalyst.

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(7) Van Loon, Dissertation, Delft, 1919; *C. A*, **17**, 1956 (1923).

(8) Mann, *Rec. trav. chim.*, **48**, 332 (1929).

(9) Mousserou and Granger, *Compt. rend.*, **205**, 327 (1937).

(10) Platt and Hibbert, *Can. J. Res.*, **7**, 629 (1932).

After three days the reaction was complete and the alcohol removed under reduced pressure in an atmosphere of nitrogen, leaving a brownish, highly viscous residue of 24.9 g. This contained some diol which was estimated by catalytic hydrogenation and found to be 20.5%. On the basis of the cyclopentadiene used, the yield of the diol was 20.7% and that of the tetrol 60.9%.

To remove the diol, the mixture was extracted a number of times with anhydrous ethyl acetate in which the tetrol is insoluble. Finally, the tetrol was precipitated a number of times from ethyl alcohol by the addition of ethyl acetate. This procedure yielded an amorphous, slightly colored and extremely hygroscopic solid which could not be crystallized. It had no definite m. p., turning brown at 190° and black at 200°. It is very soluble in water and alcohol but insoluble in ether, ethyl acetate and hydrocarbon solvents. Attempts to distil it at a very high vacuum caused decomposition and the product formed was no longer soluble in water.

The tetrabenzoate was prepared by shaking a mixture of tetrol (0.5 g.) in water (5 cc.) with benzoyl chloride (3 cc.) and 10 cc. of 10% sodium hydroxide solution. The oil which separated was extracted with ether, the ethereal solution washed with dilute sodium hydroxide, dried with anhydrous magnesium sulfate and the ether removed. A viscous liquid was obtained which failed to crystallize.

Anal. Calcd. for $C_{33}H_{26}O_8$: C, 72.0; H, 4.72. Found: C, 71.95; H, 5.20.

Saponification equivalent calculated for the tetrabenzoate, 138.8; found, 133.4. Attempts to prepare crystalline derivatives of the tetrol were not successful.

Summary

1. The hydroxylation of cyclopentadiene led to the production of cyclopentene-2-diol-1,4 and cyclopentanetetrol-1,2,3,4.

2. It has been shown that in the hydroxylation of a conjugated system, like that of cyclopentadiene, the hydroxyl groups add on to 1,4-positions of the conjugated system, and the addition results in the production of the *cis* isomer.

3. The hydrogenation of cyclopentene-2-diol-1,4 led to the production of a hitherto unknown cyclopentanediol-1,4.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some Factors Affecting Halogen–Metal Interconversions

BY HENRY GILMAN AND FRED W. MOORE

This report describes the examination of some factors affecting the halogen–metal interconversion reaction between α-bromonaphthalene and some organolithium compounds.

$$\alpha\text{-}C_{10}H_7Br + RLi \longrightarrow \alpha\text{-}C_{10}H_7Li + RBr$$

Although we have found that α-naphthyllithium can be obtained in a 97% yield by this reaction, the procedure is not recommended for the preparation of this organolithium compound which is available in a 96% yield by the more direct synthesis.[1] It is probable, however, that some of the optimal conditions determined for the conversion of α-bromonaphthalene to α-naphthyllithium can be extended to other RX compounds which either do not react at all or react in an unsatisfactory manner with lithium or other metals.

Solvents.—The most effective solvent was di-*n*-butyl ether, and the order of decreasing effectiveness of the other solvents examined was: diethyl ether, dimethylaniline, benzene, cyclohexane and petroleum ether (b. p. 28–38°). Although reaction proceeds slowest in petroleum ether, this solvent is one of choice for some halogen–metal interconversions like those of β-bromostyrene and some poly-halogen compounds.[5a]

Time.—The reaction in diethyl ether proceeds with great speed, and optimal yields in this solvent at room temperature are obtained in less than one-half minute. Thereafter, the yield decreases with time, probably because of the secondary coupling reaction which is discussed later. Under corresponding conditions the maximum yield in di-*n*-butyl ether is obtained in five minutes, and in dimethylaniline in ten minutes.

Temperature.—Cooling to −80° by a solid carbon dioxide–acetone mixture not only slowed down the interconversion reaction but also gave a distinctly lower maximum yield than that observed at room or reflux temperature. It will be recalled that marked cooling is essential in halogen–metal interconversions with some compounds having other functional groups: for example, *o*-bromonitrobenzene, bromo- and iodobenzoic acids, and bromopyridines and bromoquinolines.[2]

Catalytic Effect of Some Finely Divided Metals.—It was shown earlier that copper bronze

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[1] Gilman, Zoellner and Selby, THIS JOURNAL, **55**, 1252 (1933).

[2] Gilman and Spatz, *ibid.*, **62**, 446 (1940), and unpublished studies.