

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 159]

## The Hydroxylation of Unsaturated Substances. IV. The Catalytic Hydroxylation of Unsaturated Hydrocarbons<sup>1</sup>

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It already has been shown that under the influence of osmium tetroxide,<sup>2</sup> vanadium pentoxide,<sup>3</sup> chromium trioxide<sup>3</sup> and even ultraviolet light<sup>4</sup> hydrogen peroxide behaves as though it dissociates into two hydroxyl radicals which subsequently add on to carbon-carbon double bonds to form glycols which may or may not oxidize further depending upon the experimental conditions employed. The present investigation deals with the hydroxylation of several unsaturated hydrocarbons using the method originally developed by the authors.<sup>2</sup> The compounds were chosen to give a varied arrangement of groups about the double bond, and in all cases, with the exception of benzene, the corresponding glycol was obtained.

In hydroxylations via the hypochlorous acid addition to the double bond or the formation of epoxy compounds by means of peracids, the glycols produced have, as a rule, the *trans* configuration, whereas the present method seems to result almost invariably in glycols which have the *cis* configuration. This fact increases the value of this method since several of the *cis* glycols are not well characterized and many of them not even synthesized. Table I summarizes the results obtained in the present investigation.

TABLE I  
SUMMARY OF HYDROCARBON HYDROXYLATIONS

Hydrocarbon	Glycol	Yield, %
Ethylene	Ethylene glycol	88 93 97
Propylene	Propylene glycol	68
Cetene	Cetene glycol	77 82
Styrene	Phenyl glycol	50
Pentene-2	Pentanediol-2,3	26 29 30
Isobutylene	Isobutylene glycol	38 <sup>2</sup>
2-Methylbutene-1	2-Methylbutanediol-1,2	45 51
Trimethylethylene	Trimethylethylene glycol	40 <sup>2</sup>
Hexene-3	Hexanediol-3,4	36
Cyclohexene	<i>cis</i> -Cyclohexanediol-1,2	58
Diallyl	Hexanetetrol-1,2,5,6	45
<i>d</i> -Limonene	<i>p</i> -Menthanetetrol-1,2,8,9	35

Aldehydes, ketones and organic acids are also formed as by-products when the glycols are

(1) Presented before the Organic Division of the American Chemical Society at Chapel Hill, N. C., April 12, 1937.

(2) Milas and Sussman, *THIS JOURNAL*, **68**, 1302 (1936).

(3) Milas, *ibid.*, **59**, 2342 (1937).

(4) Milas, Kurz and Anslow, Jr., *ibid.*, **59**, 543 (1937).

oxidized further. The glycol formed from stilbene, for example, was found to be completely oxidized to benzaldehyde which was produced in almost quantitative yield.

The hydroxylation of benzene<sup>3</sup> yielded about 23% of phenol, which is not a glycol but is presumably formed as the result of dehydration of the initial glycol, 1,2-dihydroxycyclohexadiene-3,5.

### Experimental

**Ethylene Glycol from Ethylene.**—In some early experiments an apparatus was used consisting of a flask mounted on a shaking machine and connected to a reservoir of ethylene by means of a flexible steel tubing. By determining the amount of ethylene consumed and that of glycol formed the yield of the latter could easily be computed. Although the yields were as high as 88% the results were not satisfactory because of the evolution of small amounts of oxygen due to a slight decomposition of the peroxide reagent during the reaction. In order to correct for this, the apparatus illustrated by Fig. 1 was adopted and used with all gaseous unsaturated hydrocarbons.

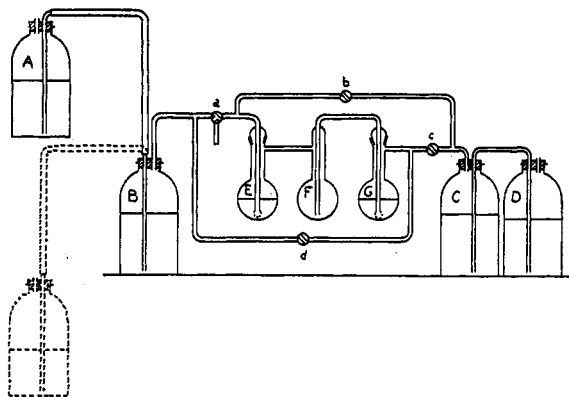


Fig. 1.—Apparatus for catalytic hydroxylations of gaseous unsaturated substances.

The four one-gallon (4-liter) bottles A, B, C and D contained saturated brine. In operation with bottle A in the elevated position and stopcocks a and c opened while stopcocks b and d were closed, the gas which was stored in bottle B was bubbled through flask E containing the peroxide reagent together with the osmium tetroxide catalyst, then passed through trap F and bubbled through flask G containing strong alkaline pyrogallol solution to absorb the oxygen present in the gas, and finally collected in bottle C. When all the gas in bottle B was displaced with brine, stopcocks a and c were closed while b and d

were opened and bottle A was lowered to a second position. The gas passed through the peroxide reagent, through the pyrogallol solution and collected again in bottle B. This circulation of the gas was continued until the reagent changed from colorless to dark brown, indicating the completion of the reaction. The gas finally was collected in bottle B which was graduated and the amount consumed measured and reduced to standard conditions, taking into account its solubility in the *t*-butyl alcohol reagent and the vapor pressure of the saturated brine.

At the end of two days 58.6 cc. (0.1 mole) of a 5.8% solution of hydrogen peroxide in *t*-butyl alcohol and in the presence of 4 cc. of a 0.5% solution of osmium tetroxide in the same solvent<sup>5</sup> consumed 1046 cc. (N. T. P.) of ethylene. The reaction mixture was then fractionated and the fraction boiling at 93–95° (13 mm.) collected; yield, 2.8 g. or 97%. An earlier experiment with this apparatus gave a yield of 93%. The boiling point of ethylene glycol has been reported by Karvonen<sup>6</sup> as 93° (13 mm.) and by Moureu and Dode<sup>7</sup> as 96.5° (14 mm.). For further identification our product was benzoylated and the benzoyl derivative purified; m. p. 70°. An authentic sample of ethylene glycol dibenzoate melted at 70.5°, and a mixed melting point showed no depression.

**Propylene Glycol from Propylene.**—The apparatus illustrated in Fig. 1 was also used for the hydroxylation of propylene. Pure propylene (furnished through the courtesy of Dr. Robert T. Armstrong) was bubbled through 59.5 cc. of the peroxide reagent containing 1 cc. of the osmium tetroxide catalyst until the yellow color of the solution disappeared completely. This took nine hours. The mixture was then fractionated and the fraction boiling at 90–91° (14 mm.) collected; yield 2.3 g. Levene and Walti<sup>8</sup> have reported the boiling point of propylene glycol as 88–90° (12 mm.). Since the volume of propylene consumed to form 2.3 g. of propylene glycol amounted to 1015 cc. (N. T. P.), the yield of the latter was computed as 68%. Our propylene glycol was identified further by oxidizing a few drops of it with bromine water on the water-bath. The resulting solution was found to reduce Fehling's solution showing the presence of acetol.<sup>9</sup>

**Cetene Glycol from Cetene.**—Nine grams of cetene (b. p. 120–126° at 2–3 mm.) was mixed with an equimolecular quantity of the peroxide reagent containing 0.5 cc. of the osmium tetroxide catalyst. At the beginning of the reaction, the solution was orange and, after one hour, it turned colorless with the peroxide completely consumed. When the mixture was freed from the solvent and the residue fractionated, 0.4 g. of unreacted cetene and 8.1 g. of a yellowish white waxy solid were obtained. The latter was recrystallized several times from ligroin to a constant m. p. of 75°. The m. p. recorded in the literature<sup>10</sup> for cetene glycol is 75–76°. In this experiment the yield of cetene glycol was 82%, while in another experi-

ment in which the amount of catalyst was doubled, the yield was only 77%.

**Phenyl Glycol from Styrene.**—Four and fifty-five hundredths grams of freshly prepared and distilled styrene, b. p. 43° (34 mm.), was mixed with an equimolecular quantity of the peroxide reagent and the mixture cooled to 0° in an ice-bath. To the cold solution was then added 0.5 cc. of the osmium tetroxide catalyst. At this temperature the peroxide was consumed entirely at the end of two days. The solvent and a small amount (0.3 g.) of unused styrene were removed by distillation at the temperature of the water-bath and the residue was extracted several times with 10-cc. portions of hot water. When the aqueous extract was evaporated to dryness under reduced pressure, a solid residue, 2.9 g., was obtained. This was recrystallized from benzene and petroleum ether into white needles, m. p. 65–66°. Balla<sup>11</sup> has reported the m. p. of phenyl glycol as 66°. As a further identification of our product, the benzoyl derivative was prepared and recrystallized from ethyl alcohol; m. p. 92–93°. Balla<sup>11</sup> gave 95° as the m. p. of this derivative. The yield of phenyl glycol, calculated on the basis of the styrene used, amounted to 50% of the theoretical.

**Pentenediol-2,3 from Pentene-2.**—Seven grams of pentene-2 (b. p. 36.7–36.8°) was mixed with an equimolecular quantity of the peroxide reagent, the mixture cooled to 0° and added to it 1 cc. of the catalyst. The solution became colored deep orange, and after three days at 0° the color disappeared and the reaction was complete. When the mixture was fractionally distilled through a Davis column, 2.9 g. of unused pentene-2 and a fraction, 1.8 g., boiling at 97–98° (17 mm.) were obtained in addition to the solvent. The literature<sup>12</sup> gives 96.5–97° (17 mm.) as the b. p. of pentenediol-2,3. The density of our product at 0° was found to be 1.005 as compared with a value of 0.995 reported by Wagner and Saizew.<sup>13</sup> The yield of the glycol, in this experiment, was 29.5%, while in two other experiments, carried out under the same conditions, yields of 26 and 30% were obtained.

**2-Methylbutenediol-1,2 from 2-Methylbutene-1.**—Seven grams of 2-methylbutene-1 (furnished through the courtesy of Dr. George Thomson) was mixed with an equimolecular quantity of the peroxide reagent, the mixture cooled to 0° and treated with 1 cc. of the catalyst. The solution colored orange, and after three days at 0° the color disappeared and the reaction was complete. By fractionating the mixture to remove the solvent and the unused 2-methylbutene-1 (1.8 g.), a fraction of 3.5 g. was obtained which had a b. p. of 111–114° (37 mm.) and 188° under atmospheric pressure. The b. p. of 2-methylbutenediol-1,2 has been reported by Henry<sup>14</sup> as 190°. The yield of our product in this experiment was 45%, while a second experiment yielded 52% of the theoretical.

For further identification of the glycol, its mono-3-nitrophthalic acid ester was prepared in accordance with the method of Monier.<sup>15</sup> After several recrystallizations from hot water, the ester melted sharply at 199.8° (corr.). Its neutralization equivalent was found to be 292 as com-

(5) To prevent the reduction of this catalyst in pure *t*-butyl alcohol by the presence of traces of isobutylene, one must add to the stock solution a few drops of the peroxide reagent.

(6) Karvonen, *Ann. Acad. Sci. Fennicae*, **A10**, No. 10, p. 9.

(7) Moureu and Dode, *Bull. soc. chim.*, [5] **4**, 640 (1937).

(8) Levene and Walti, *Org. Syntheses*, **10**, 85 (1930).

(9) Kling, *Compt. rend.*, **129**, 219 (1899); *Ann. chim.*, [8] **5**, 492 (1905).

(10) Kraft and Grosjean, *Ber.*, **23**, 2354 (1890).

(11) Balla, *Compt. rend.*, **198**, 947 (1934).

(12) Froebe and Hochstetter, *Monatsh.*, **28**, 1084 (1902).

(13) Wagner and Saizew, *Ann.*, **179**, 308 (1875).

(14) Henry, *Compt. rend.*, **144**, 1404 (1907).

(15) Monier, Ph.D. Thesis, M. I. T., 1932.

pared with the calculated values of 297 for the mono-3-nitrophthalate ester of 2-methylbutanediol-1,2.

**Hexanediol-3,4 from Hexene-3.**—A commercial sample of hexene-3 (furnished by du Pont Company through the courtesy of Professor James F. Norris) was fractionated and the fraction boiling at 65.5–67.5° collected and used for hydroxylation. Eight and four-tenths grams of hexene-3 was mixed with an equimolecular quantity of the peroxide reagent, the mixture cooled to 0° and to it added 1 cc. of the catalyst. The mixture developed an orange color, and after two days at 0°, this color disappeared and the reaction was complete.

Four grams of the unused hexene-3 was removed when the mixture was fractionated further under reduced pressure, the main fraction (2.2 g.) distilled at 108–112° (17 mm.). This b. p. is not wholly in agreement with that recorded in the literature<sup>16</sup> for the isomers of hexanediol-3,4. Lack of time prevented further investigation of this product. The yield, calculated as hexanediol, was 36% of the theoretical.

**cis-Cyclohexanediol-1,2 from Cyclohexene.**—Cyclohexene (Eastman Kodak Company) was freed from peroxides by treating with a saturated solution of sodium bisulfite, separating, drying with calcium chloride and fractionating and the fraction boiling at 83–85° collected and used for hydroxylation. Two and six-tenths grams of cyclohexene was mixed with an equimolecular quantity of the peroxide reagent, the mixture cooled to 0° and added to it 0.5 cc. of the catalyst. The orange coloration of the solution disappeared overnight on standing at 0° and the reaction was complete. The solvent and unused cyclohexene (0.77 g. determined as the dibromide) were removed by distillation, the residue subjected to fractionation under reduced pressure and the fraction (1.5 g.) boiling at 117° (14 mm.) collected and recrystallized several times from ethyl acetate into white platelets which melted sharply at 98°. Rothstein<sup>17</sup> reported the m. p. of *cis*-cyclohexanediol-1,2 as 98°. The yield of this product was 58% of the theoretical.

If the hydroxylation of cyclohexene is carried out at room temperature with no attempt to control it, very little or none of the dihydroxy compound can be isolated; instead the reaction goes beyond the glycol stage with the production of adipic aldehyde and acid.

**Hexanetetrol-1,2,5,6 from Diallyl.**—Four and one-tenth grams of diallyl (b. p. 55–60°) was mixed with 58.4 cc. of the peroxide reagent, the mixture cooled to 0° and added to it 1 cc. of the catalyst. The solution lost its orange color on standing overnight at 0° and the reaction was found to be complete. When it was fractionated to remove the solvent, 0.8 g. of the unused diallyl was recovered leaving a highly viscous residue (2.7 g.) which failed to crystallize. However, after several months of standing, the residue crystallized and was further

recrystallized from alcohol and ether; m. p. 95°. Wagner<sup>18</sup> reported the m. p. of hexanetetrol-1,2,5,6 as 95.5°. The yield of our tetrol was 45% of the theoretical.

**p-Menthanetetrol-1,2,8,9 from d-Limonene.**—Six and eight-tenths grams of *d*-limonene (Eastman Kodak Company) was mixed with 59.5 cc. of the peroxide reagent, the mixture cooled to 10–15° and added to it 5 cc. of the catalyst. The orange color of the solution disappeared on standing overnight at this temperature and the peroxide had been consumed completely. After removal of the solvent by distillation, 0.3 g. of the unused limonene was recovered by vacuum distillation, and the residual sirup (3.4 g.) recrystallized first from ethyl acetate and again from ethyl alcohol and ether; m. p. 188–189° [192–193° (corr.)]. Wagner<sup>19</sup> reported the m. p. of *p*-menthanetetrol-1,2,8,9 as 191.5–192°. The yield obtained in the above experiment was 35% of the theoretical.

**Phenol from Benzene.**—Seven and eight-tenths grams of benzene (thiophene-free) was mixed with an equimolecular quantity of the peroxide reagent, and to the mixture was added 5 cc. of the catalyst. After ten days of standing at room temperature, the reaction was complete and the solution acquired a dark-brown coloration. It was then fractionated to remove the solvent and the unused benzene (5.2 g.), and the residue (strong phenolic odor) was dissolved in water and treated with a slight excess of bromine. The precipitated tribromophenol was removed and recrystallized from dilute alcohol; m. p. 93°. An authentic sample of symmetrical tribromophenol was prepared and found to have a m. p. of 92°, and mixed m. p. with our product showed no depression. The yield of phenol amounted to 23% of the theoretical.

### Summary

1. Hydrogen peroxide in anhydrous *t*-butyl alcohol and in the presence of osmium tetroxide effects the hydroxylation of several unsaturated hydrocarbons.

2. An apparatus has been devised for the quantitative hydroxylation of unsaturated gaseous hydrocarbons.

3. Ethylene glycol has been obtained from ethylene; propylene glycol from propylene; cetene glycol from cetene; phenyl glycol from styrene; pentanediol-2,3 from pentene-2; 2-methylbutanediol-1,2 from 2-methylbutene-1; hexanediol-3,4 from hexene-3; *cis*-cyclohexanediol-1,2 from cyclohexene; hexanetetrol-1,2,5,6 from diallyl; *p*-menthanetetrol-1,2,8,9 from *d*-limonene; and phenol from benzene.

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RECEIVED AUGUST 30, 1937

(16) Farmer, Larois, Switz and Thorpe, *J. Chem. Soc.*, 2946 (1927); Kuhn and Rebel, *Ber.*, **60**, 1570 (1927).

(17) Rothstein, *Ann. chim.*, [10] **14**, 461 (1930).

(18) Wagner, *Ber.*, **21**, 3344 (1888).

(19) Wagner, *ibid.*, **23**, 2315 (1890).