containing chlorine atoms attached to adjacent carbon atoms. Substitution of sodium formate for potassium acetate led to the same result. It was found, however, that the desired diacetate could be obtained (although in low yields) by heating 20.4 g. of glycerol-α,β-di-chlorohydrin-α'-methyl ether with 29 g. of fused potassium acetate and 30 cc. of glacial acetic acid under pressure at 165° for sixteen hours. The crude reaction product had a dark brown color. It was filtered from the solid material, the filtrate neutralized with solid potassium carbonate, again filtered and the filtrate concentrated under reduced pressure to a small volume. Further filtration and fractionation of the filtrate yielded 4.2 g. of a clear colorless liquid, b. p. 215–225°. Three grams of this material was hydrolyzed by refluxing for one hour with 25 cc. of 75% aqueous ethyl alcohol containing 3% of hydrochloric acid. After neutralization with lead carbonate, filtration and concentration, the residual oil on distillation yielded 1.2 g. of glycerol-α-methyl ether; b. p. 111–112° (13 mm.); $d_4^{17} = 1.1189$; $n_D^{17} = 1.4445$. Its identity as pure glycerol-α-methyl ether was further established by its conversion into the di-phenyl carbamate, m. p. 117° C.[9] A mixed melting point of this material with a known sample showed no lowering, while a mixed melting point with the di-phenyl carbamate of glycerol-β-methyl ether melted indefinitely at 93°.

Summary

1. Glycerol-α,α'-di-chlorohydrin on methylation and conversion of the α,α'-dichloro-β-methyl ether into the acetate, followed by saponification, yields only glycerol-β-methyl-ether.
2. Glycerol-α,β-di-chlorohydrin-α'-methyl ether on conversion into its acetate, followed by saponification, yields only glycerol-α-methyl ether.
3. Previous work in this field, pointing to the probability of the migration of a methyl radical in the conversion of glycerol-α,α'-di-chlorohydrin-β-methyl ether into the acetate and subsequent hydrolysis of the latter is based on the mistaken identity of the resulting product as glycerol-α-methyl ether.
4. The bearing of these results on the methylation of glycerol and carbohydrate derivatives is pointed out and the importance of the pure α- and β-glycerol methyl ethers as "type substances" further confirmed.

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NOTES

The Identification of Ortho-, Meta- and Para-Hydroxybenzoic Acids.—It was found necessary, recently, to isolate, purify and identify small amounts of *o*-, *m*- and *p*-hydroxybenzoic acids.

Lyman and Reid[1] have recommended the *p*-nitrobenzyl esters as suitable compounds by means of which these hydroxy acids can be identified. These investigators converted the acids into their sodium salts and heated these, dissolved in a mixture of water and alcohol, with *p*-nitrobenzyl bromide. We obtained unsatisfactory results by the use of this method since it was found that the esters, as soon as they are formed, react to some extent with *p*-nitrobenzyl bromide to form the *p*-nitrobenzyl

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[1] Lyman and Reid, THIS JOURNAL, **39,** 704 (1917).

ethers, that is, the dinitrobenzyl derivatives of the hydroxy acids. In fact the substance described by Lyman and Reid as the *p*-nitrobenzyl ester of *p*-hydroxybenzoic acid was, in reality, the dinitrobenzyl compound.

The esters, or mononitrobenzyl compounds, are very soluble in organic solvents and hence are difficult to purify, but the dinitrobenzyl derivatives are much less soluble and can be recrystallized readily from acetone. The method was now modified in such a way that the formation of the dinitrobenzyl products was favored. As a result not only were compounds formed which could be recrystallized with less loss of material, but since the molecular weight of the dinitrobenzyl derivative is considerably higher than that of the mononitrobenzyl compound, a larger amount of material, in the case of the former substance, could be obtained from a given weight of the hydroxy acid. Furthermore, by the use of the dinitrobenzyl derivatives, it is possible to separate a mixture of two isomeric hydroxybenzoic acids; the derivative of the *p*-hydroxy acid is quite insoluble in acetone, that of the meta acid more soluble while the ortho isomer is fairly soluble.

The di-*p*-nitrobenzyl compounds were obtained in the following manner: 1.25 g. of *p*-nitrobenzyl bromide was dissolved in 10 cc. of pure acetone and a solution prepared from 0.35 g. of the hydroxy acid, 0.3 g. of sodium hydroxide crystals ($NaOH + H_2O$)[2] and 4 cc. of water was added. The mixture was refluxed for two hours. In the case of the *p*-hydroxy acid the dinitrobenzyl derivative separated in crystalline form from the hot reaction mixture; from the *m*- and *o*-hydroxy acids oils were obtained which solidified when cooled. The products were treated with 5 cc. of 10% sodium hydroxide and then filtered. The dinitrobenzyl compounds remained undissolved while the alkaline filtrate yielded, upon acidification, a small amount of the ether-acid. After three recrystallizations from acetone the derivatives were obtained in a nearly colorless state.

TABLE I

DI-*p*-NITROBENZYL DERIVATIVES OF HYDROXYBENZOIC ACIDS

	M. p., °C.	Analysis (Dumas), % Calcd. for $C_{21}H_{16}O_7N_2$	Found
o-Hydroxy[a]	137–139	N 6.86	6.50
m-Hydroxy[b]	142–144	N 6.86	6.86
p-Hydroxy[c]	196–197	N 6.86	6.83

[a] Readily soluble in hot acetone and somewhat soluble in the cold solvent, insoluble in ether and soluble in hot benzene.

[b] The solubilities are intermediate between those of the ortho and para isomers.

[c] Quite insoluble in hot acetone, ether and benzene.

The mononitrobenzyl derivatives, that is, the *p*-nitrobenzyl esters, were prepared as follows: 1.4 g. of the hydroxy acid and 0.55 g. of sodium hydroxide crystals were dissolved in 5 cc. of water. After the addition of 15 cc. of pure acetone, 2.15 g. of *p*-nitrobenzyl bromide was added in

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[2] An equivalent amount of potassium carbonate may be used instead.

small portions during the course of one-half hour, the material having been refluxed during this period. The mixture was heated for an hour longer, then cooled, diluted with water, acidified with hydrochloric acid and the precipitated material filtered. The latter was treated with 5% sodium hydroxide and filtered to remove the dinitrobenzyl derivative and other alkali-insoluble compounds. The alkaline filtrate was acidified and the precipitate filtered. The product was dried and then dissolved in a very small amount of hot acetone. Water was added until the solution became turbid. When cooled the mononitrobenzyl derivative separated in crystalline form.

TABLE II

p-NITROBENZYL ESTERS OF HYDROXYBENZOIC ACIDS[a]

	M. p., °C.	Analysis (Dumas), %	
		Calcd. for $C_{14}H_{11}O_5N$	Found
o-Hydroxy[b]	97– 98	N 5.12	5.15
m-Hydroxy[c]	106–108	N 5.12	5.23
p-Hydroxy[d]	180–182	N 5.12	5.22

[a] These compounds are all very soluble in cold acetone and alcohol.

[b] Lyman and Reid, THIS JOURNAL, **39**, 710 (1917), obtained this substance but published no analytical results.

[c] Lyman and Reid, *ibid.*, **39**, 710 (1917).

[d] Lyman and Reid, *ibid.*, **39**, 711 (1917), obtained a compound which they supposed to be the *p*-nitrobenzyl ester of *p*-hydroxybenzoic acid; the substance melted at 198.5°. This compound was undoubtedly the dinitrobenzyl derivative.

The *p*-nitrobenzyl ethers of the hydroxy acids were obtained as follows: 0.5 g. of the dinitrobenzyl derivative was hydrolyzed with 3 g. of potassium carbonate dissolved in 30 cc. of 50% alcohol. The alcohol was evaporated on a steam-bath and the aqueous mixture filtered from *p*-nitrobenzyl alcohol. The alkaline filtrate was acidified and the precipitated material recrystallized from a small amount of acetone.

TABLE III

p-NITROBENZYL ETHERS OF HYDROXYBENZOIC ACIDS

	M. p., °C.	Analysis (Dumas), %	
		Calcd. for $C_{14}H_{11}O_5N$	Found
o-Hydroxy[a]	166–168	N 5.12	5.20
m-Hydroxy[b]	193–196	N 5.12	5.25
p-Hydroxy[c]	259–261	N 5.12	5.05

[a] This compound is soluble in hot acetone and alcohol.

[b] This substance is somewhat soluble in hot acetone and alcohol.

[c] Inasmuch as the dinitrobenzyl derivative of the *p*-hydroxy acid is insoluble in dilute alcohol, it is hydrolyzed into the ether much more slowly than the other isomeric dinitrobenzyl compounds. The ether is practically insoluble in hot acetone and hot alcohol.

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