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.

MONTREAL, CANADA

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

---

[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

---

[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]

		Analysis (Dumas), %	
	M. p., °C.	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

		Analysis (Dumas), %	
	M. p., °C.	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.

CONTRIBUTION FROM THE
COLLEGE OF PHARMACY OF THE
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

F. F. BLICKE
F. D. SMITH

RECEIVED JANUARY 31, 1929
PUBLISHED JUNE 5, 1929

Esters of Dimethylethylacetic Acid.—In the course of an investigation being carried on in this Laboratory we had occasion to synthesize several esters of dimethylethylacetic acid. This acid was prepared by treating *tert.*-amylmagnesium chloride with carbon dioxide; esterification was brought about by refluxing the acid and the required alcohol with sulfuric acid as catalyst.

Tert.-amyl chloride was prepared in the following manner. Four thousand cc. of concentrated hydrochloric acid was added, during fifteen to twenty minutes, with mechanical stirring, to 2500 g. of *tert.*-amyl alcohol[1] contained in a 12-liter earthenware crock. The mixture warmed up to 45°; stirring was continued for four hours. The upper layer, *tert.*-amyl chloride containing some unchanged alcohol, was transferred to a 12-liter flask and saturated with dry hydrogen chloride in the presence of anhydrous calcium chloride, the mixture being mechanically stirred throughout the process. Saturation required one and one-half hours; the mixture warmed up to 50°. The calcium chloride was then removed and the *tert.*-amyl chloride mixture was refluxed for an hour. After standing over anhydrous sodium carbonate for twenty-four hours the product was filtered. Twenty cc. of dimethylaniline was then added and the product distilled through a 50-cm. fractionating column. There is continuous evolution of hydrogen chloride during distillation if dimethylaniline is not added. The *tert.*-amyl chloride boiled at 84–86°; the yield was 1960 g., or 65% of the theoretical amount.

Dimethylethylacetic acid was prepared in 60% yield by treating *tert.*-amylmagnesium chloride with carbon dioxide. Our procedure was patterned after that of Puntambeker and Zoellner[2] for the preparation of trimethylacetic acid. The ether from which the dimethylethylacetic acid had been extracted by means of sodium hydroxide solution, by the above directions, contained two by-products—*tert.*-amyl alcohol (b. p. 99–103°, n_D^{23}, 1.4035) and a camphoraceous smelling liquid (b. p. 164–167.5°; n_D^{22}, 1.4335; molecular weight in acetone, 183) which we have not yet investigated.

The esters are colorless liquids. The methyl, ethyl and *n*-propyl esters have menthol–peppermint odors; the *n*-butyl, *n*- and *iso*-amyl esters have but little odor. The refractive indices were determined at 25.0 ± 0.1° by means of an Abbé refractometer; the densities were determined at 25.00 ± 0.02° by means of a pycnometer of about 8-cc. capacity. The weights used in the density calculations were corrected for buoyancy. The boiling points were determined by means of Anschütz thermometers (stem wholly immersed in vapor) which had been standardized by the U. S. Bureau

---

[1] Kindly furnished by the Sharples Solvents Corporation.

[2] Puntambeker and Zoellner, "Organic Syntheses," John Wiley and Sons, Inc., New York, **8**, 104 (1928).

of Standards. The molecular weights were calculated using the Lorentz–Lorenz formula. Considerable difficulty was experienced in analyzing these esters, especially the lower ones, low results being obtained repeatedly. Correct results were finally obtained in all cases except that of the methyl ester by using a quartz combustion tube and high temperature.

TABLE I

ESTERS OF DIMETHYLETHYLACETIC ACID

Ester	B. p., °C. (746 mm., corr.)	n^{25}_{D}	d^{25}_{4}	Mol. wt. Calcd.	Mol. wt. Found	Analyses Calcd. C, %	Analyses Calcd. H, %	Analyses Found C, %	Analyses Found H, %
Methyl	125 –125.5	1.3991	0.8943	130	134	64.6	10.8	61.0	10.7
								62.8	7.7
Ethyl[a]	141.8–142.2	1.3989	.8601	144	145	66.6	11.2	66.4	11.1
n-Propyl	164 –164.4	1.4040	.8575	158	159	68.4	11.5	68.1	11.4
n-Butyl	184 –184.7	1.4098	.8566	172	173	69.7	11.7	71.0	11.5
n-Amyl	202.5–203.5	1.4140	.8544	186	187	70.9	11.9	71.0	11.8
Iso-Amyl	192.5–196.5	1.4128	.8533	186	187	70.9	11.9	70.6	11.7

[a] Bouveault and Blanc, *Bull. soc. chim.*, [3] **31**, 749 (1904), report boiling point as 141–142° and d^{0}_{4} as 0.883.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
MIDDLEBURY COLLEGE
MIDDLEBURY, VERMONT

B. B. CORSON
J. S. THOMAS
D. D. WAUGH

RECEIVED FEBRUARY 11, 1929
PUBLISHED JUNE 5, 1929

Reaction of Alizarin and Mercuric Acetate.—The observation here reported was made some six years ago. Since the work is not to be continued, the facts obtained are presented as being of possible interest in anthraquinone chemistry.

Alizarin when heated with excess mercuric acetate gave large amounts of mercurous acetate, indicating an oxidation of the alizarin. The product contained organic mercury. Five runs with varying concentrations and times of heating varying from 30 to 100 hours gave almost identical results. The organic product appeared to be acetoxymercurydihydroxyalizarin. The following average analyses were obtained on the products from the five runs.

Anal. Calcd. for $C_{16}H_{10}O_8Hg$: Hg, 49.8. Found: 49.5, 50.0, 49.8, 49.7, 49.7.

Treatment of the product with hydrochloric acid gave a yellow-red dye with properties similar to those of alizarin.

The mercury compound when treated with the amount of standard sodium hydroxide corresponding to the four hydroxyls gave a bluish-red solution. The solution at 20° then contained 0.2 g. per 100 cc. Warming the solution changed the color to red and precipitated some material which dissolved again on cooling. Both the cold and hot solutions were neutral to litmus.

The positions of the groups in the mercurated product were not determined. The results of other oxidation and substitution reactions on alizarin would make it appear probable that the product was 1,2,5,8-tetrahydroxy-4-acetoxymercuri-anthraquinone. Treatment of this product with halogens should give interesting halogenated tetrahydroxyanthraquinones.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

FRANK C. WHITMORE
G. J. LEUCK

RECEIVED MARCH 4, 1929
PUBLISHED JUNE 5, 1929

The Reaction of Mercuric Acetate with *p*-Bromodiethylaniline.—The present observations are published because of their wide divergence from the results obtained with closely analogous substances. Dialkylanilines, including dimethyl, diethyl, di-*n*-propyl, di-*n*-butyl, methylethyl, and ethylbenzyl, react readily with mercuric acetate to give products containing acetoxymercuri groups in the para position.[1] If the para position is occupied, mercuration would be expected to take place in one of the free ortho positions. This proved to be the case with *p*-bromodimethylaniline, which gave an excellent yield of the ortho mercurated product.[2] At the time that work was done, attempts were made to extend it to the homologous dialkylanilines. Contrary to expectations, this proved to be impossible. The experiments have been repeated many times since under a great variety of conditions, but the results have been consistently negative. No organic mercury compound has been obtained.

The attempts at mercuration of *p*-bromodiethylaniline were carried out in 95% alcohol, 50% alcohol, glacial acetic acid, 50% acetic acid, ether, water and without a solvent. The temperature was varied from 0° to the boiling point of the solvent used and the times from a few hours to weeks. The concentrations of the reactants were varied over a wide range. In all experiments similar results were obtained; the products were unchanged material, mercurous acetate and unmanageable oxidation products.

UNIVERSITY OF MINNESOTA AND
NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS

FRANK C. WHITMORE
A. R. CADE
G. J. LEUCK

RECEIVED MARCH 6, 1929
PUBLISHED JUNE 5, 1929

---

[1] Whitmore, Hanson and Carnahan, THIS JOURNAL, **51**, 894 (1929).

[2] Whitmore, *ibid.*, **41**, 1841 (1919).