in benzene gives 0.08 g. of isobutyl 3,5-dinitrobenzoate, m.p. 84–85°, not depressed by an authentic sample.

O-*s*-Butylhydroxylamine Hydrochloride.—A similar preparation from *s*-butyl iodide and hydroxyurethan gives a substance very difficult to crystallize. The yield after two vacuum sublimations was 1.3 g. from 18.4 g. of the iodide. This substance is extremely hygroscopic, and the melting point is changed by warming *in vacuo*. It gives a strongly acid solution in water. Treatment with nitrous acid gives 0.8 cc. of an oil identified by the formation of 0.23 g. of *s*-butyl 3,5-dinitrobenzoate, m.p. 73–75°, not depressed by an authentic sample.

O-Tritylbenzohydroxamic Acid.—A mixture of 8 g. of potassium benzohydroxamate, 12.5 g. of trityl chloride and 100 cc. of anhydrous pyridine is refluxed for one hour. Dilution with water followed by extraction with ether, washing of the ether layer with water, drying over $MgSO_4$, and concentration gives 11 g. of a white solid, m.p. 123–150°. Crystallization from alcohol and from benzene–petroleum ether eventually raises the melting point to 150–152°.

Anal.[9] Theory for $C_{26}H_{21}O_2N$: C, 82.3; H, 5.58; N, 3.70. Found: C, 82.32, 82.33; H, 5.59, 5.65; N, 3.92, 3.82.

Various attempts at alkaline hydrolysis gave back this substance unchanged. Refluxing with alcoholic KOH gives Tschichibabin's hydrocarbon, *p*-tritylphenyldiphenylmethane, m.p. 230–232°, identified as its bromo derivative, m.p. 238–241°, and by a mixed melting point with an authentic sample of the hydrocarbon.[11]

Tracer Experiment

Sodium Nitrite-N^{15}.—Sodium nitrate-N^{15} was reduced with metallic lead, by the procedure described elsewhere.[12]

Preparation of Nitrous Oxide-N^{15}.—Solutions of 125 mg. of O-*n*-butylhydroxylamine hydrochloride in 1.0 ml. of water and 69 mg. of sodium nitrite-N^{15} in 1.0 ml. of water were placed in the legs of a two-legged flask. The flask was connected to a vacuum manifold, and after the solutions had been frozen with an acetone-Dry Ice-bath, the air was pumped off. The solutions were then thawed and mixed. Nitrous oxide was evolved vigorously, and was led through a trap held at −80° and condensed in a storage bulb cooled by a liquid nitrogen bath. A mass spectroscopic examination of the sample seemed to indicate the presence of some carbon dioxide. It was therefore transferred to a second storage bulb partly filled with dry sodium hydroxide pellets and stored for 24 hours.

Analysis of the Sample.—A sample of the purified gas was analyzed in a Consolidated Nier Isotope Ratio mass spectrometer, using the number two collector and scanning the mass spectrum magnetically. The pertinent ion intensities observed are recorded in Table I.

TABLE I

M/e	Intensity
45	133.5
44	273.3
31	21.9
30	51.1

Acknowledgment.—We wish to express our appreciation to Dr. L. Friedman of Brookhaven National Laboratory for the performance of the mass spectral analysis.

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(11) F. Ullmann and W. Borsum, *Ber.*, **35**, 2878 (1902).

(12) A. Bothner-By and L. Friedman, THIS JOURNAL, **73**, 5391 (1951).

DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA, AND THE
DEPARTMENT OF CHEMISTRY
BROOKHAVEN NATIONAL LABORATORY
UPTON, LONG ISLAND, NEW YORK
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The Coupling of Phenol Alcohols with Benzene Diazonium Chloride

BY E. MARDER AND I. W. RUDERMAN

In the study of the intermediates produced in the phenol–formaldehyde resinification, it is desirable

TABLE I

PROPERTIES OF AZO DYES PREPARED FROM SOME PHENOLS AND PHENOL ALCOHOLS

Coupler	Product	M.P., °C.	Crude yield, %	Carbon, % Calcd.	Carbon, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Visible light absorption $\lambda_{max.}$ in Å.	Visible light absorption $\epsilon_{max.}$ in liters/mole-cm.
2,4-Dimethylphenol	6-Phenylazo-2,4-dimethylphenol	90–91	84	74.38	74.36	12.40	12.95	6.26	5.95	4090	6390
2-Hydroxy-α^1-mesitylenol	6-Phenylazo-2,4-dimethylphenol	90–91	85	74.38	74.36	12.40	12.31	6.26	6.21	4090	6420
2,6-Dimethylphenol	4-Phenylazo-2,6-dimethylphenol	94–95	76	74.38	74.38	12.40	12.44	6.26	6.36	4380–4400	1070
4-Hydroxy-α^1-mesitylenol	4-Phenylazo-2,6-dimethylphenol	94–95	100	74.38	74.56	12.40	12.54	6.26	6.28	4380–4400	1070
p-Cresol	2-Phenylazo-*p*-cresol	107–108	55	73.56	73.36	13.22	13.72	5.70	5.65	3980–3990	8180
2-Hydroxy-α^1,α^3-mesitylenediol	2-Hydroxymethyl-6-phenylazo-*p*-cresol	118–119	53	69.46	69.31	11.57	11.54	5.83	5.90	3980–3990 4040	7150 7190
	Diurethan[a] derivative of 2-hydroxymethyl-6-phenylazo-*p*-cresol	158	. . .	69.97	69.24	11.67	11.49	5.04	5.46	. . .	. . .

[a] This derivative was prepared in order to establish more definitely that only one of the two hydroxymethyl groups is displaced during the coupling reaction.

to be able to determine the presence of unreacted positions ortho or para to the phenolic hydroxyl group. Thus, Niederl and McCoy[1] used the coupling reaction with a diazonium salt as a qualitative test for open end positions in a phenolic polymer. The general applicability of the coupling reaction to phenol–formaldehyde intermediates is, however, open to question because of the possible (or, indeed, probable) presence of hydroxymethyl groups. Thus, exploratory experiments carried out in 1944[2] showed that 2-hydroxy-α^1,α^3-mesitylenediol couples with benzenediazonium chloride even though this phenol contains no free ortho or para positions.

A more detailed study of this reaction was begun by the authors in 1949. Three alkylated phenols and three hydroxymethyl derivatives of these phenols were coupled with benzenediazonium chloride, and the reaction products were isolated, purified, and compared. After this work was completed there came to our attention a recent paper by Ziegler and Zigeuner[3] that contained essentially all of our results. It seems desirable, however, to record briefly our work, both for its confirmatory value and for the additional information that it provides.

We have found that 2-hydroxy-α^1-mesitylenol (I), 4-hydroxy-α^1-mesitylenol (II) and 2-hydroxy-α^1,α^3-mesitylenediol (III) couple with benzenediazonium chloride in alkaline solution with the liberation of formaldehyde, although these phenol alcohols contain no open positions ortho or para to the phenolic hydroxyl group. The purified azo dyes obtained from (I) and 2,4-dimethylphenol were found to be identical as were those obtained from (II) and 2,6-dimethylphenol. The product formed on coupling (III) differs from that obtained on coupling *p*-cresol in that the former still contains a single ortho hydroxymethyl group. The liberation of formaldehyde upon the coupling of phenol alcohols was confirmed by preparing methylenedi-β-naphthol, a derivative of formaldehyde, according to the procedure of Mulliken.[4]

Acknowledgment.—We wish to thank the U. S. Atomic Energy Commission whose support made this research possible.

[1] Niederl and McCoy. THIS JOURNAL, **65**, 629 (1943).

[2] I. W. Ruderman, M. S. Dissertation, New York University, 1944.

[3] Ziegler and Zigeuner, *Monatsh.*, **79**, 42 (1948); *C. A.*, **44**, 1929^g (1950).

[4] S. P. Mulliken. "A Method for the Identification of Pure Organic Compounds," Vol. I, John Wiley and Sons, Inc., New York. N. Y., 1904. p. 24.

DEPARTMENT OF PHYSICS
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

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4-β-(β'-Hydroxy)-ethoxyethoxyphenylarsonic Acid and Some Acyl Derivatives[1,2]

BY ROBERT L. MCGEACHIN

In the search for an organic arsenical with a side chain to which a fat-solubilizing group might be added, we have studied the reaction of 4-hydroxyphenylarsonic acid with diglycolchlorohydrin (β-chloro-β'-hydroxy diethyl ether). This reaction gave 4-β-(β'-hydroxy)-ethoxyethoxyphenylarsonic acid,[3] a compound with an esterifiable hydroxyl group in the side chain.

Although the use of potassium iodide as a catalyst has been found to be essential in the reaction of some chloro compounds with 4-hydroxyphenylarsonic acid, in this case the reaction proceeded smoothly and in good yields without any catalyst.

In studying the esterification of the hydroxyl group of 4-β-(β'-hydroxy)-ethoxyethoxyphenylarsonic acid, we have found that the lower acyl chlorides will react but considerable decomposition accompanied the reactions. The same difficulty was encountered with acid anhydrides at elevated reaction temperatures so that the acylations were finally carried out at room temperature even though a prolonged reaction time was necessary at the lower temperature. Acetylation and butyrylation were accomplished by this method.

Attempts were made to prepare the stearyl derivative using stearyl chloride in pyridine but only the unreacted 4-β-(β'-hydroxy)-ethoxyethoxyphenylarsonic acid could be isolated from the reaction mixture. Attempts at benzoylation by the Schotten–Baumann method were likewise unsuccessful.

Experimental

Preparation of 4-β-(β'-Hydroxy)-ethoxyethoxyphenylarsonic Acid (I).—To a solution of 21.8 g. of 4-hydroxyphenylarsonic acid (prepared by decomposition of diazotized *p*-arsanilic acid) in 150 ml. of 2 *N* sodium hydroxide was added 24.9 g. of diglycolchlorohydrin and the mixture heated under reflux conditions for eight hours. The original insoluble layer of diglycolchlorohydrin gradually disappeared during the course of the reaction.

The hot reaction mixture was made just acid to congo red with concd. hydrochloric acid, filtered through a charcoal mat and placed in the ice-box overnight. On cooling the product, a white crystalline solid, separated from solution. This was filtered off, washed with ice-water and dried *in vacuo* over calcium chloride; yield 19.9 g. (65%); m.p. 127°.

Anal.[4] Calcd. for $C_{10}H_{15}O_6As$: As, 24.51. Found: As, 24.44, 24.48.

Preparation of 4-β-(β'-Acetoxy)-ethoxyethoxyphenylarsonic Acid.—Two grams of I was added to 10 ml. of acetic anhydride containing 4 drops of concd. sulfuric acid and the mixture shaken continuously for 20 hours, the arsonic acid gradually going into solution. Most of the acetic anhydride was then distilled off under reduced pressure and the product precipitated by addition of 15 ml. of ether. This white solid was filtered off, washed well with ether and finally a little water, then dried *in vacuo* at 80° for an hour and at room temperature for 24 hours; yield 1.0 g. (45%); m.p. 125°; mixed m.p. with I, 100–110°.

Anal. Calcd. for $C_{12}H_{17}O_7As$: As, 21.55. Found: As, 21.50, 21.35.

Preparation of 4-β-(β'-Butyroxy)-ethoxyethoxyphenylarsonic Acid.—Two grams of I was added to a mixture of 20 ml. of butyric anhydride and 5 ml. of dioxane containing 4 drops of pyridine. The arsonic acid went into solution slowly on shaking which was continued for 48 hours. Most of the dioxane and excess butyric anhydride were distilled off under reduced pressure, 10 ml. of ether added and the mixture placed in the ice-box overnight. A white solid crystallized out in the cold. This was filtered off, washed with cold ether and allowed to dry 24 hours in the air; yield 0.5 g. (20%); m.p. 69–70°.

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[1] This work was begun in the Avery Laboratory of Chemistry of the University of Nebraska under the direction of Dr. C. S. Hamilton.

[2] The portion of the work done in this Laboratory was aided by a grant to the University of Louisville from the Kentucky State Medical Research Commission.

[3] First synthesized by J. Parker.

[4] A modification of the method of F. E. Cislak and C. S. Hamilton, THIS JOURNAL, **52**, 638 (1930), was used in the arsenic analyses.