Behavior of Divinyl Glycol.—Two hundred g. of acrolein dissolved in one liter of water was treated during 96 hours with 150 g. of zinc copper couple,[12] 300 g. of acetic acid being added during the first 48 hours. The resulting product was treated with dry sodium carbonate, filtered and sufficient sodium hydroxide solution added to complete the neutralization. After filtration, the product was extracted with ether, the solution then saturated with potassium carbonate and further extracted. The combined ether extracts after drying over sodium sulfate yielded 68 g. (29%) of divinyl glycol; m. p., 97–104° (16 mm.). Forty-five g. of this glycol dissolved in 400 g. of 2% sulfuric acid was allowed to stand for two hours at 15° in contact with strips of lead. The product was then worked up as though it had resulted from a reduction. No product other than divinyl glycol could be isolated. The aqueous solution left after the extraction was steam distilled and the distillate extracted with ether. No product other than a trace of divinyl glycol was found.

Summary

1. Acrolein readily undergoes reduction in dil. sulfuric acid, lead electrodes being used, and the products formed are propionaldehyde, allyl and propyl alcohols, Δ'-cyclopentene aldehyde and probably traces of Δ'-cyclopentene carbinol.

2. Divinyl glycol under similar conditions does not undergo rearrangement to give any product resembling Δ'-cyclopentene aldehyde.

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THE ACTION OF ALKYL CHLOROCARBONATES ON HYDROXY-ARYLARSONIC ACIDS

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Recently, in making a study of the action of alkyl chlorocarbonates on amino-arylarsonic acids, it was shown that in the case of 3-amino-4-hydroxy-phenylarsonic acids, both the amino- and the hydroxyl- groups reacted with the chlorocarbonates.[1]

In this work the action of alkyl chlorocarbonates on hydroxy-arylarsonic acids was investigated more fully. Methyl, ethyl, propyl, *iso*propyl, butyl and *iso*butyl chlorocarbonates were condensed with *p*-hydroxy-phenylarsonic acid, *m*-hydroxy-phenylarsonic acid and 3-nitro-4-hydroxy-phenylarsonic acid. This was accomplished by adding the alkyl

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[12] Prepared by washing 80-mesh zinc dust thrice with a dilute copper sulfate solution sufficient to cover the zinc, and finally washing with water.

[1] Hamilton and Sly, This Journal, **47**, 435 (1925).

chlorocarbonate, drop by drop, during shaking, to a slightly alkaline solution of hydroxy-arylarsonic acid. In general, the products were colorless or slightly cream-colored crystals, soluble in hot water, alcohol and chloroform, but insoluble in ether and benzene. As a rule, when heated, they melted with effervescence, the decomposition point decreasing with increase in length of the carbon chain of the chlorocarbonate. The *iso*-compounds had higher decomposition points than the corresponding straight-chain compounds.

Experimental Part

Preparation of Hydroxy-Arylarsonic Acids

***p*-Hydroxy-phenylarsonic Acid.**—This compound was prepared by the direct arsonation of phenol according to the method of Christiansen and Norton,[2] modified in certain respects. It was thought that the presence of a solvent or suspending medium might increase the yield and make the preparation easier by lessening the amount of solidification due to tar formation. Xylene was chosen as the medium because its boiling point is near the desired reaction temperature, and it was thought it might hold the tar in solution even though more water were removed. Since the arsonation is a reversible reaction, removal of the water freed in the reaction should increase the yield.

One hundred and fifty g. of phenol, 300 g. of arsenic acid (b. p., 150°) and 600 g. of xylene were placed in a 1.5-liter flask fitted with a return hot-water condenser through which a stirrer was run. The mixture was refluxed on an oil bath for eight hours during which time it required practically no attention. It was then poured into about 1.5 liters of water during stirring. Finely ground barium hydroxide was added until the mixture was slightly alkaline and the whole was then filtered. The united filtrate and washings were separated in a large separatory funnel and the xylene was washed with a little water. The water solution was then freed from barium and sulfate ions and the filtrate from barium sulfate evaporated to about 1.5 liters on the steam-bath, neutralized to litmus with sodium hydroxide and filtered. It was then further evaporated until crystallization was well started and about 2.5 volumes of alcohol added, and the crystals were filtered out and washed with a little alcohol; maximum yield of anhydrous salt, 126 g.[3]

3-Nitro-4-hydroxy-phenylarsonic Acid.—This compound was prepared by the nitration of sodium *p*-hydroxy-phenylarsonate, according to the method of Benda and Bertheim;[4] yield 48 g., from 72 g. of sodium *p*-hydroxy-phenylarsonate.

***m*-Hydroxy-phenylarsonic Acid.**—This was made in four steps. Phenylarsonic acid was prepared by the method of Palmer and Adams;[5] yield, 50%. The phenylarsonic acid was nitrated using a slightly modified

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[2] Christiansen and Norton, THIS JOURNAL, **45,** 2188 (1923).

[3] This yield is practically the same as obtained by Christiansen and Norton, Ref. 2.

[4] Benda and Bertheim, *Ber.*, **44,** 3446 (1911).

[5] Palmer and Adams, THIS JOURNAL, **44,** 1361 (1922).

method of Michaelis;[6] yield, 80–85%. The reduction of the 3-nitrophenylarsonic acid to *m*-arsanilic acid was effected by the method of Johnson and Adams;[7] yield, 45–50%. Finally the *m*-arsanilic acid was converted into *m*-hydroxy-phenylarsonic acid by following the procedure of Jacobs and Heidelberger;[8] yield, 50%.

Alkyl Chlorocarbonates.—Methyl, ethyl, propyl, *iso*propyl, butyl and *iso*butyl chlorocarbonates were prepared by the method of Rose,[9] by passing phosgene into the chilled alcohol.

Preparation of Carbo-alkoxy-hydroxy-arylarsonic Acids.—In the preparation of 4-carbo-alkoxy-hydroxy-phenylarsonic acids one molecular equivalent of sodium *p*-hydroxy-phenylarsonate was dissolved in water and enough normal sodium carbonate solution added to make the liquid slightly alkaline. One and one-half molecular equivalents of the chlorocarbonate were then added, drop by drop, during shaking. The reaction was carried out at room temperature, except in the case of the butyl chlorocarbonates,

TABLE I

CARBO-ALKOXY-HYDROXY-ARYLARSONIC ACIDS

Phenylarsonic acids	Formula	Yield %	M. p. °C. uncorr.	Analysis Subs. G.	Analysis 0.0506*N*I₂	As, % Calcd.	As, % Found
4-Carbomethoxy-hydroxy-	$CH_3OCO_2C_6H_4AsO_3H_2$	74	> 250	0.2043	29.33	27.15	27.25
4-Carbethoxy-hydroxy-	$C_2H_5OCO_2C_6H_4AsO_3H_2$	67	> 250	.1715	23.27	23.84	23.75
4-Carbopropoxy-hydroxy-	$C_3H_7OCO_2C_6H_4AsO_3H_2$	75	> 250	.1984	25.69	24.64	24.58
4-Carbo-*iso*propoxy-hydroxy-	$(CH_3)_2CHOCO_2C_6H_4AsO_3H_2$	76	> 250	.2070	26.89	24.64	24.65
4-Carbobutoxy-hydroxy-	$C_4H_9OCO_2C_6H_4AsO_3H_2$	89	> 250	.1725	21.51	23.56	23.66
4-Carbo-*iso*butoxy-hydroxy-	$(CH_3)_2CHCH_2OCO_2C_6H_4AsO_3H_2$	53	> 250	.1600	19.96	23.56	23.68
3-Nitro-4-carbomethoxy-hydroxy-	$CH_3OCO_2C_6H_3(NO_2)AsO_3H_2$	65	> 250	.2043	25.44	23.35	23.64
3-Nitro-4-carbethoxy-hydroxy-	$C_2H_5OCO_2C_6H_3(NO_2)AsO_3H_2$	68	154	.2045	24.35	22.37	22.59
3-Nitro-4-carbopropoxy-hydroxy-	$C_3H_7OCO_2C_6H_3(NO_2)AsO_3H_2$	75	133	.2037	23.00	21.47	21.43
3-Nitro-4-carbo-*iso*propoxy-hydroxy-	$(CH_3)_2CHOCO_2C_6H_3(NO_2)AsO_3H_2$	55	168	.2029	23.01	21.47	21.51
3-Nitro-4-carbobutoxy-hydroxy-	$C_4H_9OCO_2C_6H_3(NO_2)AsO_3H_2$	30	137	.2034	22.27	20.64	20.78
3-Nitro-4-carbo-*iso*butoxy-hydroxy-	$(CH_3)_2CHCH_2OCO_2C_6H_3(NO_2)AsO_3H_2$	50	141	.1544	16.96	20.64	20.86
3-Carbomethoxy-hydroxy-	$CH_3OCO_2C_6H_4AsO_3H_2$	67	143	.1558	22.33	27.15	27.21
3-Carbethoxy-hydroxy-	$C_2H_5OCO_2C_6H_4AsO_3H_2$	50	128	.1054	14.41	25.84	25.96
3-Carbopropoxy-hydroxy-	$C_3H_7OCO_2C_6H_4AsO_3H_2$	34	115.5	.1907	24.69	24.64	24.57
3-Carbo-*iso*propoxy-hydroxy-	$(CH_3)_2CHOCO_2C_6H_4AsO_3H_2$	40	154	.1539	20.07	24.64	24.75
3-Carbobutoxy-hydroxy-	$C_4H_9OCO_2C_6H_4AsO_3H_2$	40	87	.1528	18.85	23.56	23.41
3-Carbo-*iso*butoxy-hydroxy-	$(CH_2)_2CHCH_2OCO_2C_6H_4AsO_3H_2$	52	100	.1988	23.89	23.56	23.89

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[6] Hamilton and Sly, THIS JOURNAL, **47,** 436 (1925). Michaelis and Loesner, *Ber.,* **27,** 265 (1894).

[7] Johnson and Adams, THIS JOURNAL, **45,** 1307 (1923).

[8] Jacobs and Heidelberger, *ibid.,* **41,** 1445 (1919).

[9] Rose, *Ann.,* **205,** 229 (1880).

with which 65° was used. After the odor of the chlorocarbonate could no longer be detected dil. hydrochloric acid was added until the mixture was acid to congo-red. When the acid was added a drop at a time during shaking and the mixture allowed to stand between additions of the acid, the product was obtained in well-defined, colorless crystals.

The 3-nitro-4-carbo-alkoxy-hydroxy-phenylarsonic acids were prepared as above except that the free acid was dissolved in a slight excess of normal sodium carbonate solution.

In the case of the 3-carbo-alkoxy-hydroxy-phenylarsonic acids one equivalent of the alkyl chlorocarbonate was added. The higher members of this series formed oils readily and it was necessary to avoid a large excess of the chlorocarbonate as this seemed to favor formation of the oil. If an oil were formed it could usually be crystallized by separating it from the aqueous layer and leaving for some time in the desiccator. The crystalline mass was then dissolved in hot water and the solution allowed to stand for a considerable time during shaking and if necessary concentrated in a vacuum. The lower members showed an extreme tendency to form supersaturated solutions in which it was very difficult to start crystallization. Scratching the container and seeding failed to start crystallization in solutions which on simply standing for several days would suddenly start to form crystals. Slow evaporation also sometimes started crystallization.

Summary

The action of the alkyl chlorocarbonates on hydroxy-arylarsonic acids has been studied.

The methyl, ethyl, propyl, *iso*propyl, butyl and *iso*butyl chlorocarbonates were condensed with sodium *p*-hydroxy-phenylarsonate, *m*-hydroxy-phenylarsonic acid and with 3-nitro-4-hydroxy-phenylarsonic acid and the products isolated and identified.

The products with the *p*-hydroxy-phenylarsonic acid were colorless crystals not melting below 250°. The other products were light yellow powders or crystals decomposing at temperatures which decreased with increasing molecular weight, the *iso* compounds having somewhat higher melting points.

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