quinones were then oxidized by dissolving in cold acetic acid and treating with chromic oxide dissolved in a little water. Strong dilution with water precipitated the quinones which were fractionally crystallized from alcohol.

2. **Potential Determination.**—(a) The relative potentials in benzene were measured according to the directions previously outlined.[7] (b) The potentiometric determinations were made by titrating a solution of the phenyl hydroquinone in the 70% alcoholic solution with tetrabromo-*o*-benzoquinone. The reaction cell was connected to a hydrogen electrode by a bridge containing the same solvent. Good agreement was observed among the titration curves for each substance.

The author wishes to express his sincere appreciation for the interest and advice of Professor L. F. Fieser during the course of this research.

Summary

An investigation was made of the reaction between a series of quinones and aromatic diazonium compounds to give arylquinones. The reaction can be utilized to give polyarylquinones. Potential measurements were made with a number of the quinone–hydroquinone systems and the effects of substitution and solvent upon the potentials have been discussed.

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[CONTRIBUTION FROM KENT AND JONES CHEMICAL LABORATORIES, UNIVERSITY OF CHICAGO]

The Preparation of Aldonic and Saccharinic Acid Amides in Liquid Ammonia

BY J. W. E. GLATTFELD AND DUNCAN MACMILLAN*

The desirability of obtaining erythrose in its optically active as well as inactive forms has been mentioned recently.[1] These tetroses are needed in order to make possible certain plans for a study of the conversion of the tetroses into the C_4-saccharinic acids. At the present time these sugars are not available in pure condition and efforts are being made in this Laboratory to produce *dl*-erythrose by the reduction of *dl*-erythronic lactone. The methods of reduction so far tried, when applied to *dl*-erythronic lactone, have not produced the tetrose. These experiments were carried out practically entirely in aqueous solution. It seemed desirable to try the reduction of the lactone also in other media, and liquid ammonia was therefore used. These reduction experiments in liquid ammonia led at once to the new procedure for the preparation of the amides that is reported below.

Very little work has been done so far with the carbohydrates or their derivatives in liquid ammonia. The most recent work reported in the literature along this line is that of Muskat.[2] This author apparently did not work with the sugar acids, however, and was interested especially in the alkylation of the sugars.

Amides of aldonic and saccharinic acids have been prepared in a number of ways, such as the solution of the lactones in aqueous ammonia,[3] the treatment of alcoholic solutions with ammonia gas,[4] and the hydrolysis of nitriles.[5] As amide formation in liquid ammonia proceeds rapidly, and requires little apparatus, the new method has some advantages over those previously employed. Thus several attempts to obtain *dl*-erythronamide by the procedure described by Weerman[4] were made. In each case the product was a gum which would not crystallize even when subjected to scratching, cooling, evacuation or trituration. The liquid ammonia technique was then used, and the resulting gum crystallized on standing in a vacuum desiccator. Also in the preparation of certain amides, in which it is otherwise necessary to work with absolute alcohol in anhydrous systems, the liquid ammonia technique is far more convenient.

While all aldonic and saccharinic acid lactones used so far have yielded amides at liquid ammonia temperatures, this is not true of some other lactones. For example, it is found that coumarin may be recovered from liquid ammonia unchanged. The lactone of γ-hydroxybutyric acid is not affected by liquid ammonia at its boiling point, although it is ammonolyzed at room temperature when sealed in a bomb with liquid ammonia. An extended study of ammonolysis of lactones is under way, and it is hoped that it may lead to a further understanding of the lactone bond.

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*The material n this article will be used by Duncan Macmillan as part of his dissertation for the degree of Doctor of Philosophy in the University of Chicago.

[1] Glattfeld and Forbrich, THIS JOURNAL, **56**, 1209 (1934).

[2] Muskat, *ibid.*, **56**, 693 (1934).

[3] Hudson and Komatsu, *ibid.*, **41**, 1141 (1919).

[4] Weerman, *Rec. trav. chim.*, **37**, 24 (1918).

[5] Kiliani, *Ber.*, **19**, 3033 (1886).

Experimental Part

The reaction may be carried out in the type of apparatus described by Fernelius and Johnson[6] in their review of the liquid ammonia system. It is not necessary, however, to use anhydrous conditions. The results are thoroughly satisfactory when an open Dewar flask is used or when the lactone is dissolved in the liquid ammonia in an open dish. Owing to the great solubility of carbohydrate derivatives in liquid ammonia, comparatively little ammonia is required. The authors' practice has been to dissolve between 15 and 30 g. of lactone in about 300 cc. of liquid ammonia in an open Dewar flask. The reaction is usually complete in a few hours. Completion may be hastened by pouring the solution into an evaporating dish. In general the amide crystallizes as soon as the liquid ammonia has evaporated. The yields of ammonia-free residue are quantitative. The following description is typical of the procedure.

The Preparation of *d*-Gluconamide.—Seventeen and eight-tenths grams (0.1 mole) of *d*-glucono-γ-lactone (m. p. 133°) was dissolved in 300 cc. of liquid ammonia in an evaporating dish. A stream of warm air was passed over the surface of the solution. Within an hour the ammonia had evaporated, leaving a residue which was pumped free of ammonia in a vacuum desiccator. The solid residue melted at 139–140°, and decomposed at 142°. The weight was 19.4 g., corresponding closely to that of 0.1 mole of gluconamide (19.5 g.). The amide was then recrystallized from 300 cc. of 90% alcohol. The recrystallized substance melted at 143–144° and weighed 15.5 g.

No difficulty was experienced in using this procedure in the preparation of all amides reported below except that it proved difficult to obtain the erythronamides in crystalline form from the residual gums at first. When crystal seeds were once available, however, this difficulty disappeared. All other residues from the evaporation of the ammonia crystallized easily.

The new compounds were analyzed for nitrogen. Only a small amount of *d*-erythronamide that had been used for rotations was available for the analysis. This may account for the low value.

TABLE OF THE CONSTANTS AND ANALYSES OF SOME OF THE AMIDES PREPARED IN THE COURSE OF THIS WORK

The specific rotations of the galactonamide and the mannonamide made by the new procedure were considerably different from those reported in the literature.[3] These amides were therefore made by the Weerman method also and the constants found to be the same as those of the amides made by the new procedure. New compounds are marked with asterisks. All rotations were taken in water solution at the concentration shown in the last column and at "room temperature" (approximately 20°).

Name	M. p., °C.	$[\alpha]^{20}_D$	Concn., %	Formula	Kjeldahl nitrogen, % Calcd.	Found	
**dl*-1,3-Dihydroxybutyramide[7]	118.5–119.5			$C_4H_9O_3N$	11.76	11.77	11.66
**dl*-2,3-Dihydroxybutyramide	90.7			$C_4H_9O_3N$	11.76	11.69	11.65
**dl*-Erythronamide	62.3			$C_4H_9O_4N$	10.37	10.28	10.30
**d*-Erythronamide	94.8	+28.2	4.8	$C_4H_9O_4N$	10.37	9.74	
**l*-Erythronamide	94.8	−28.0	5.1	$C_4H_9O_4N$	10.37	10.55	
d-Galactonamide	175.0	+31.5	3.8				
d-Galactonamide (Weerman method)	176.0	+31.8	1.8				
d-Gluconamide	145.0	+31.0	5.0				
d-Mannonamide (from γ-lactone)	176.0	−13.1	2.2				
d-Mannonamide (from δ-lactone)	177.0	−13.1	3.0				
d-Mannonamide (by Weerman method)	176.0	−13.2	2.7				

Summary

The authors have developed a simple method for the preparation of the amides of the aldonic and saccharinic acids which consists essentially of the solution of the lactones of the acids in liquid ammonia.

The preparation of *dl*-1,3-dihydroxybutyramide, *dl*-2,3-dihydroxybutyramide, *d*, *l* and *dl*-erythronamide is reported for the first time.

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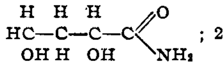
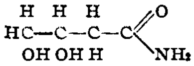
(6) Fernelius and Johnson, *J. Chem. Ed.*, **6**, 445 (1929).

(7) 1,3-Dihydroxybutyramide,  ; 2,3-dihydroxybutyramide,  .