[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OKLAHOMA]

The Use of Ethyl Sulfone-bis-acetate in the Identification of Aliphatic Amines[1]

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It has been reported by Lovén[2] in 1884 that the amide of sulfone-bis-acetic acid was formed in high yield by the action of ammonium hydroxide on the ethyl ester in the course of a few minutes. During the course of other work in this Laboratory, this observation was checked and the melting point of the amide, 226°, reported for the first time.[3]

It was thought that the lower primary and secondary amines might behave in a similar manner. Such substituted amides, possessing an unusual combination of reactive groups, should merit further study, and might also serve as suitable derivatives in the identification of the amines. Ten such derivatives have been made and identified by nitrogen analysis, and their melting points established.

The yields from isopropyl and from cyclohexyl amine are notably lower than the others reported and no reaction at all could be obtained when the ester was treated with 2-aminobutane, the only other compound tried in which the amino group was attached to a secondary carbon.

Similarly no reaction could be had even on prolonged refluxing between the ester and dimethylamine, diethylamine and dipropylamine, respectively. These were the only secondary amines tried.

The anilide, *o*-toluidide, and the *p*-toluidide of this ester have been prepared previously[4] by prolonged refluxing of the ester with the amine in alcoholic solution. Preliminary tests indicate, however, that the aryl substituted amides may also be prepared by direct interaction of the amine with the ester and work on this topic will be done in this Laboratory soon.

Experimental Part

Sulfone-bis-acetic Acid.—The method described by Loven[2] was materially improved by C. A. Forrest,[5] and has been modified still further by the present workers. 94.5 g. of chloroacetic acid was dissolved in 75 cc. of water and neutralized with a saturated solution of sodium carbonate. A solution of 142 g. of hydrated sodium sulfide in 100 cc. of water was slowly added with stirring. Considerable heat was evolved but the boiling point of the solution was not reached. This was then allowed to stand for three hours. A small amount of a dark green flocculent precipitate was filtered off, the solution placed in a large beaker equipped with a mechanical stirrer and 70 g. of magnesium chloride hexahydrate was added. Finely powdered potassium permanganate was then added, 1–2 g. at a time, until a drop on a test plate indicated an excess. During this oxidation the temperature rose to about 40°. The precipitated manganese dioxide and magnesium hydroxide together with unused undissolved permanganate was filtered off and the filtrate warmed with a few cc. of ethyl alcohol to remove the excess permanganate in solution. The solution was again filtered and 145 g. of $BaCl_2 \cdot 2H_2O$ added with stirring. After a few hours the precipitated barium sulfone-bis-acetate was filtered off. It was then digested for an hour and a half with 27 cc. of concd. sulfuric acid in 250 cc. of water. The barium sulfate was removed by filtration and the filtrate evaporated until crystallization started. On cooling the sulfone-bis-acetic acid crystallized. It was sucked as dry as could be by means of a water pump, washed first with *n*-butyl alcohol and then with ether and dried in a vacuum desiccator for one hour. A further crop of crystals was obtained by careful evaporation of the filtrate almost to dryness; yield, 58 g. or 64%; melting point 183–184°.

Ethyl Sulfone-bis-acetate.—The ester was prepared by slight modification of the method used by Lovén who, however, did not characterize the substance. It boiled between 164–167° at 2 mm.; density 1.210 at 28°, index of refraction 1.4464 at 28°.[6] For use as a reagent in the identification of amines it does not appear necessary to purify it by distillation.

Di-N-methyl sulfone-bis-acetamide and di-N-ethyl sulfone-bis-acetamide were prepared by warming 3–4 g. of the corresponding amine hydrochloride in a small distilling flask with an excess of concd. sodium hydroxide and the amine was passed directly into a test-tube containing 10 cc. of water and 2 g. of the ester. After shaking for two or three minutes the volume was reduced to about 6 cc. by evaporation and the substituted amide crystallized in an ice-bath. These substances could be crystallized from alcohol but washing with a little cold alcohol followed by ether gave a product apparently quite pure.

The other amine derivatives were all prepared by adding about 0.01 mole of the ester to 0.04–0.05 mole of amine and shaking for three to five minutes. The mixture was then poured into 20 cc. of water, and in most cases the substituted amide crystallized immediately. In the case of the isopropylamine derivative it was necessary to evapo-

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(1) Based on a thesis presented by John P. Alden to the Faculty of the Graduate School of the University of Oklahoma in partial fulfilment of the requirements for the degree of Master of Science, 1933.

(2) Lovén, *Ber.*, **17**, 2818 (1884).

(3) A. A. Alberts, M.S. Thesis, University of Oklahoma, 1930.

(4) Props, unpublished M.S. Thesis, University of Oklahoma, 1926.

(5) C. A. Forrest, unpublished M.S. Thesis, University of Oklahoma, 1928.

(6) The last two constants were determined by C. A. Forrest, unpublished M.S. Thesis, University of Oklahoma, 1927.

rate to a small volume and chill. The precipitated amide was filtered, washed with a small amount of alcohol and then with ether and dried. Crystallization from alcohol did not change the melting points.

The following table indicates the substituted amides that have been prepared, together with melting points, nitrogen analyses and approximate yields based on the ester.

N-SUBSTITUTED AMIDES OF SULFONE-BIS-ACETIC ACID
$SO_2(CH_2CONHR)_2$

Amine	M. p., °C.	Yield, %	N, % Calcd.	N, % Found
Methyl	186	85	13.45	13.45
Ethyl	178	78	11.86	11.57
n-Propyl	184	85	10.60	10.52
Isopropyl	148	50	10.60	10.80
n-Butyl	192	80	9.58	9.50
Isobutyl	155	65	9.58	9.60
n-Amyl	174	80	8.74	8.75
Isoamyl	152	80	8.74	8.90
n-Heptyl	182	95	7.44	7.40
Cyclohexyl	170	40	8.13	8.09

Summary

1. Ten substituted amides of sulfone-bis-acetic acid have been prepared by the interaction of the ester with primary aliphatic amines.

2. These reactions go quickly, the amides are formed in good yields and in pure condition, and appear to be convenient derivatives for the identification of these amines.

3. No reaction could be obtained under similar or more drastic conditions with 2-aminobutane, dimethylamine, diethylamine or di-*n*-propylamine.

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Concerning Selectivity as Exhibited by Certain Osmotic Diaphragms

BY LAURIE L. BURGESS

In the course of his experience with alginic acid and products arising from it, the author observed that osmotic diaphragms could be prepared by precipitating a solution of sodium alginate with a solution of a suitable metallic salt, such as a salt of calcium, aluminum, zinc, etc. This precipitate was a colloidal jelly-like mass, which during filtration formed a continuous layer over the surface of the cloth or other medium used as a filter. When such a layer had formed, it appeared to be semi-permeable, and generally behaved like an osmotic diaphragm, so that unless this membrane was broken up by stirring, the further course of the filtration was extremely slow.

It was further observed, when a solution of complex ionic composition, such as sea water, was used to effect the precipitation of the alginate, that the filtrate appeared to show differences in the concentrations of some of its ionic constituents as compared to those in the original solution. In this particular case, the concentration of potassium in the filtrate appeared to be noticeably greater than its concentration in the original sea water. This casual observation seemed to be worthy of more extensive investigation, the results of which are embodied in this article.

The establishment of a selective action by the agency of such diaphragms would have interesting chemical and probably biological significance. Some of the marine algae, particularly the Valoniaceae, accumulate potassium chloride in preference to other salts present in the sea water. The mechanism of this accumulation has been studied extensively by Osterhout and his co-workers, who have built up an interesting theory with respect to it.[1]

Using the methods suggested earlier in this paper, it would not of course be possible to prepare diaphragms which would duplicate the performance of the living plasma membranes. Nevertheless, a study of their behavior, since they accomplish a somewhat similar result, might yield information of value in dealing with the chemical aspects of this biological problem.

Purpose of this Investigation.—The present investigation was undertaken for the purpose of determining whether or not osmotic diaphragms prepared from alginates and other materials did exert a selective action upon the substances dissolved in the solutions bathing them, and, if so, to learn which ions were favored, which were retarded and which were unaffected. It was also hoped that some further light on the theoretical explanation of selectivity might be secured.

Apparatus.—The apparatus consisted of a wooden ring, 1.3 cm. thick, with an inner diameter of 11.4 cm., and an outer diameter of 14 cm., through which two holes had been bored, as shown in the diagram, Fig. 1. The wood

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[1] For a list of papers up to 1931, see Osterhout, *Biol. Reviews*, **6**, 369 (1931). Also see Osterhout and Stanley, *J. Gen. Physiol.*, **15**, 667 (1932); Osterhout, *ibid.*, **16**, 157, 529 (1933).