N-(p-nitrobenzyl)-carbamates are summarized in Table II.

Alkyl N-(p-Aminobenzyl)-carbamates.—A solution of 5 g. of the alkyl N-(p-nitrobenzyl)-carbamate in 100 cc. of absolute ethanol was shaken with 0.2 g. of platinum oxide-platinum black and hydrogen at 3 atm. pressure. The reductions were complete in three to ten minutes. The platinum was removed by filtration and the filtrate saturated with dry hydrogen chloride. An equal volume of absolute ether was added to facilitate the separation of the hydrochloride. The hydrochloride salts were removed by filtration. The yields varied from 50 to 90%, most of the loss being due to the difficulties in causing complete separation of the hydrochlorides. Evaporation of the alcohol-ether mother liquor gave colored impure products which could not be obtained in a colorless condition by recrystallization. The data are summarized in Table III.

Summary

A series of alkyl N-(p-nitrobenzyl)-carbamates was prepared by the action of the alcohols from methyl to octyl on the azide of p-nitrophenylacetic acid. Catalytic reduction of these nitro compounds and subsequent treatment with hydrogen chloride produced the corresponding hydrochlorides of alkyl N-(p-aminobenzyl)-carbamates. Solutions of these hydrochlorides produced intracutaneous anesthesia but only a few caused surface anesthesia. All were quite irritating to the tissues.

URBANA, ILLINOIS RECEIVED JULY 15, 1938

[CONTRIBUTION OF THE G & A LABORATORIES, INC., SAVANNAH, GEORGIA]

Reactions Involved in the Sulfonation of Heat Treated Abietic Acid

BY TORSTEN HASSELSTROM AND JOHN D. MCPHERSON

Recent work of Fieser and Campbell[1] on dehydroabietic acid together with the investigations of Fleck and Palkin[2] and Littman[3] has produced evidence that α-pyroabietic acid heretofore regarded as an isomeric abietic acid is actually a mixture of dehydroabietic acid and hydrogenated abietic acids produced through the reactions of dehydrogenation and disproportionation of abietic acid.

In a previous communication[4] we reported that the sulfonation of heat treated abietic acid yields a crystalline sulfonic acid and as a by-product a lactone belonging to the tetrahydroabietic acid series of compounds. We have obtained evidence that the sulfonic acid[5] has the composition of $C_{20}H_{28}O_5S \cdot 3H_2O$ and hence may be established as a dehydroabietic acid sulfonate. This identity is established further by the preparation of the dimethyl ester, diethyl ester and diamide of this sulfonic acid. Since the lactone is saponified only with difficulty and easily regenerated,[4] it is apparently a γ-lactone formed from a $\Delta^{9,10}$-dihydroabietic acid as a result of hydration due to the sulfuric acid employed. Hence it is likely that the corresponding hydroxytetrahydroabietic acid has the hydroxyl in position 10. It is worthy of note that the addition of two atoms of hydrogen to abietic acid by catalytic means produces an easily lactonized dihydroabietic acid.[6] This lactone formation in the abietic acid series points to the fact that on saturation of one double bond of the original abietic acid, the remaining double bond moves to a position more favorable for hydration and lactonization.

The results obtained by us on the sulfonation of heat treated abietic acid do not agree with those previously recorded in the literature. On sulfonation of α-pyroabietic acid Fanica[7] obtained a crystalline monosulfonic acid for which the formula $C_{20}H_{30}O_5S$ was designated. He also reports as a residue a non-crystalline sulfur containing material.

Our findings that the sulfonation of heat treated rosin yields a dehydroabietic acid sulfonate and a lactone belonging to the tetrahydroabietic series of compounds are additional proof that the dehydrogenation and disproportionation of abietic acid occur on heat treatment.

Experimental

Dehydroabietic Acid Sulfonate.—The sulfonic acid was prepared from partially refined pseudopimaric acid according to Hasselstrom.[5a] It was recrystallized from water, glacial acetic acid and water; m. p. 223–224° (dec.). It was dried at 100° under vacuum.

Anal. Calcd. for $C_{20}H_{28}O_5S \cdot 3H_2O$: C, 55.29; H, 7.83;

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[1] Fieser and Campbell, THIS JOURNAL, **60**, 159 (1938).

[2] Fleck and Palkin, *ibid.*, **60**, 921 (1938).

[3] Littman, *ibid.*, **60**, 1419 (1938).

[4] Hasselstrom, Brennan and McPherson, *ibid.*, **60**, 67 (1938).

[5] (a) Hasselstrom, U. S. Patent 2,121,032 (1938); (b) Hasselstrom, U. S. Patent 2,121,033 (1938).

[6] (a) Ruzicka and Meyer, *Helv. Chim. Acta*, **5**, 333 (1922); (b) Ruzicka, Waldman, Meier and Hösli, *ibid.*, **16**, 139 (1933).

[7] (a) Fanica, *Bull. inst. pin.*, **44**, 151 (1933); (b) *ibid.*, **45**, 181 (1933); (c) Greth, *Z. angew. Chem.*, **47**, 927 (1934).

mol. wt., 434. Found: C, 55.33; H, 8.15;[8] mol. wt. (by titration for a dibasic acid), 433.

When dried at 150° for six hours, it lost 3 molecules H_2O. Calcd. for $C_{20}H_{28}O_5S$: mol. wt., 381. Found: mol. wt. (by titration for a dibasic acid), 381, 379.5.

Dimethyl Ester of Dehydroabietic Acid Sulfonate.—Five grams of dehydroabietic acid sulfonate was neutralized to phenolphthalein with a dilute aqueous solution of sodium hydroxide and the whole was evaporated to dryness. The pale yellowish powdered residue was dried for two hours at 125° and then boiled for ten minutes with 30 g. of dimethyl sulfate. After cooling, the clear dark solution was poured into ice water and then the mixture boiled for about one hour. The separated solid was removed, washed with a hot dilute sodium bicarbonate solution and then with water; yield, about 3 g. of crude dimethyl ester. It was recrystallized from acetone and methanol, the white silky needles melting at 176.7–177.7° (corr.).

Anal. Calcd. for $C_{22}H_{32}O_5S$: C, 64.69; H, 7.86. Found: C, 64.87; H, 8.04.

Diethyl Ester of Dehydroabietic Acid Sulfonate.—This was obtained in the same manner as the dimethyl ester, from 5 g. of dehydroabietic acid sulfonate and 30 g. of diethyl sulfate. It was recrystallized from acetone and methanol, the white silky needles melting at 150.4–151.4° (corr.).

Anal. Calcd. for $C_{24}H_{36}O_5S$: C, 66.00; H, 8.32. Found: C, 66.18; H, 8.35.

Diamide of Dehydroabietic Acid Sulfonate.—Five grams of dehydroabietic acid sulfonate was mixed with about 15 g. of phosphorus pentachloride and heated for about one hour on the water-bath under reflux. After cooling, the liquid was poured drop by drop into strong aqueous ammonia cooled with ice. The precipitated solid material was removed and extracted with boiling water until free from sulfonic acid. The diamide was then crystallized from ethanol, the transparent prismatic plates melting at 254–255.5° (corr.) (with slight dec.).

Anal. Calcd. for $C_{20}H_{30}O_3N_2S$: C, 63.43; H, 7.99. Found: C, 63.22; H, 8.09.

Summary

1. A dehydroabietic acid sulfonic acid is formed on sulfonation of heat treated abietic acid. This was confirmed further by the preparation of the dimethyl ester, diethyl ester and the diamide of the sulfonic acid.

2. The fact that a dehydroabietic acid sulfonate and a lactone belonging to the tetrahydroabietic acid series are formed on sulfonation of heat treated abietic acid are additional evidence that dehydrogenation and disproportionation of abietic acid occurs on heat treatment.

SAVANNAH, GA.

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[8] All analyses by Mr. S. Gottlieb, Columbia University.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL, AND THE BIOLOGICAL LABORATORIES, HARVARD UNIVERSITY]

Alicyclic Amino Acids

BY J. P. GREENSTEIN AND J. WYMAN, JR.

I

A great amount of data is now available on the dielectric constants of solutions of various amino acids, peptides, betaines and related molecules, which exist as dipolar ions. Although an exact theory of the relation of dielectric constant to molecular properties is still lacking in the case of polar liquids, the picture which emerges from such data is fairly simple and convincing.[1] There is no question that the large positive dielectric increments of all these compounds are due to their very large moments as dipolar ions. But beyond this a correlation of these increments with the properties of the molecules, as well as other empirical considerations, has led to the conclusion that in the case of polar liquids there is an approximately linear relation between dielectric constant and volume polarization, a conclusion which has been justified to some degree by recent theoretical investigations of Onsager[2] and of Van Vleck.[3] On this basis the dielectric increments of highly polar molecules like dipolar ions should be very nearly proportional to their molar polarizations, or, in view of that part of Debye's theory relating polarization to moment, to the square of their moments. This interpretation of the dielectric increments has made it possible to assign relative values to the moments of molecules, and, in connection with further inductions from data on pure liquids, even to estimate absolute values which are not far different from those estimated on an entirely different basis. Its application in detail to the large body of data on dipolar ions containing one positive and one negative charge separated by an aliphatic chain shows that in these molecules the mean square distance between the charges is proportional to the length of the intervening chain.

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[1] J. Wyman, *Chem. Rev.*, **19**, 213 (1936).

[2] Onsager, THIS JOURNAL, **58**, 1486 (1936).

[3] Van Vleck, *J. Chem. Phys.*, **5**, 556 (1937).