At 200° the palmitic acid and the herring residue darkened slightly and each of the materials melted into a mass that solidified on cooling.

At 300° the palmitic acid darkened further in color and still solidified on cooling. The calcium palmitate and the herring residue remained apparently unchanged from the previous heat treatment.

Under the initial heat treatment at 350° for eighteen hours the palmitic acid yielded a still darker brownish product that remained fluid at ordinary room temperatures. The calcium palmitate and herring residue changed but slightly in color and gave but little appearance of having undergone any further decomposition.

In the further heating for seven days at 350° all the materials yielded a greenish fluorescent petroleum-like product. The yield was similar in each experiment and appeared relatively high compared to the quantity of original material taken. When the tube which had held the calcium palmitate was opened considerable pressure was shown. The odor resembled gasolene. The residue consisted of carbonaceous matter, a little napthenic-like oil, and calcium carbonate.

Summary

This paper describes the analysis of calcium and magnesium salts of fatty acids derived from herring buried under sea water, and discusses some geochemical possibilities related to the origin of petroleum in sedimentary deposits.

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The Preparation and Optical Resolution of Ammonium *dl*-Alpha-Bromocamphor-Pi-Sulfonate

BY A. W. INGERSOLL AND S. H. BABCOCK

The preparation of many asymmetric acids and bases is necessary for a comprehensive study of optically isomeric salts.[1] Obviously those acids and bases whose racemic forms are capable of resolution and whose active forms are useful resolving agents are especially valuable. Also the racemic forms are as necessary for this type of study as the active forms. Bases suitable for resolution work and available in both the racemic and active forms are fairly numerous, but there are relatively few acids of this description. Thus *d*-tartaric, *l*-malic, *d*-camphor-10-sulfonic and *d*-α-bromocamphor-π-sulfonic acids are the only ones that have been much used. The optical antipodes and the racemic forms of these, though known in

[1] (a) Ingersoll and White, THIS JOURNAL, **54**, 274 (1932); (b) Ingersoll and Burns, *ibid.*, **54**, 4712 (1932).

most cases, are comparatively uncommon. Satisfactory methods for preparing the rarer varieties of these and other suitable acids are therefore being studied. The preparation of *dl*-α-bromocamphor-π-sulfonic acid (as ammonium salt) and a simple method for resolving it into the pure *d*- and *l*-forms are described in this paper.

d-α-Bromocamphor-π-sulfonic acid has found extensive use as a resolving agent since its advantages for this purpose were pointed out by Pope and Peachey.[2] It is prepared by the sulfonation of *d*-α-bromocamphor derived from ordinary *d*-camphor[3,4] and is therefore readily accessible. The corresponding *l*-acid has been prepared similarly from *l*-camphor.[5] Since the latter is usually not entirely pure and is difficult to obtain, the *l*-acid is somewhat rare. The *dl*-acid and its simple salts appear not to have been completely described. It is said to be formed in traces when *d*-α-bromocamphor is sulfonated,[6] but in the few other instances in which this acid[7] or its derivatives[8,9] are mentioned in the literature, these appear to have been made only by mixing the active forms.

The method of preparation described in the present paper is based upon the direct sulfonation of *dl*-α-bromocamphor derived from commercial *dl*-camphor. This apparently simple method has not previously been described, doubtless because the necessary *dl*-α-bromocamphor has not been available in sufficient amounts. A method for obtaining this intermediate in good yields and large amounts was therefore first developed. It was found that *dl*-camphor reacts with one mole of bromine to form a semi-solid mass. This appears to contain chiefly *dl*-α-bromocamphor and the isomeric *dl*-α′-bromocamphor, together with *dl*-camphor and *dl*-α,α′-dibromocamphor. The separation of crystalline *dl*-α-bromocamphor was at first troublesome because of its excessive solubility and the presence of the even more soluble by-products. However, it was found that most of the α′-compound was converted to the α-compound by heating the mixture and then crystallizing the α-compound from slightly alkaline alcohol at −10°. This method of isomerizing the α′-compound was suggested by the experience of Marsh[10] and of Lowry[11] in the preparation of *d*-α-bromocamphor from *d*-camphor, though in this case the less soluble active compound crystallized readily. Haller[12] has described the bromination product

[2] Pope and Peachey, *J. Chem. Soc.*, **73**, 893 (1898).
[3] Kipping and Pope, *ibid.*, **67**, 356 (1895).
[4] Pope and Read, *ibid.*, **97**, 2199 (1910).
[5] Pope and Harvey, *ibid.*, **79**, 74 (1901).
[6] Kipping, *ibid.*, **79**, 370 (1901).
[7] Pope and Gibson, *ibid.*, **97**, 2207 (1910).
[8] Perkin and Robinson, *ibid.*, **99**, 788 (1911).
[9] Pope and Read, *ibid.*, **101**, 758 (1912).
[10] Marsh, *J. Chem. Soc.*, **59**, 968 (1891).
[11] Lowry, *ibid.*, **89**, 1033 (1906).
[12] Haller, *Compt. rend.*, **105**, 66 (1887).

of *dl*-camphor as a "buttery mass." He was unable to crystallize this under any conditions, but did prepare a specimen of *dl*-α-bromocamphor, m. p. 51°, by mixing the active forms. His description of this compound was confirmed.

dl-α-Bromocamphor was sulfonated with chlorosulfonic acid and ammonium *dl*-α-bromocamphor-π-sulfonate isolated. Although the yield was somewhat low (30–35%) it was not difficult to prepare large amounts of the pure salt. The optical resolution was then carried out. In a recent paper[1b] it was shown that the active forms of α-*p*-tolylethylamine can easily be prepared in good yields by resolving the *dl*-base with *d*-camphoric acid. When ammonium *dl*-α-bromocamphor-π-sulfonate is combined with the *l*-form of this base in dilute acetic acid, the *l*B*l*A salt and, in smaller amounts, the *l*B*d*A salt can be gotten pure from the solution. The ammonium salts of the corresponding acids were obtained from these salts in good yields. This method of resolution appears to be more satisfactory than that of Pope and Gibson.[7] These workers resolved the *dl*-acid, whose source was not mentioned, by means of *d*-1,2-dihydropapaverine (*d*-pavine). This base had been obtained from synthetic *dl*-pavine by resolution with *d*-α-bromocamphor-π-sulfonic acid. Although the resolution was apparently not difficult, the base employed is too rare for general use.

Experimental

Preparation of *dl*-α-Bromocamphor.—*dl*-Camphor (152 g.) was placed in a three-necked flask on a steam-bath and bromine (163 g.) was slowly added while the mixture was stirred.[13] It gradually liquefied and hydrogen bromide was evolved. Including two hours for adding the bromine, the mixture was heated for ten hours. While still warm it was then poured with stirring into two liters of water containing a few grams of sodium sulfite. The waxy solid, when broken up, filtered, washed with fresh water and air-dried, weighed 220–235 g. and was slightly brown. Many unsuccessful attempts were made to crystallize the substance from the usual organic solvents, in which it is very soluble. Finally it was found that a filtered solution in 95% ethanol (1 cc. per gram), when held at −10° in the freezing chamber of an electric refrigerator and inoculated with crude or previously purified material, slowly deposited about half the material as a colorless, crystalline mass, m. p. 47–49°. Recrystallization under similar conditions gave back about 80% of the first crop, m. p. 49–50°. On concentration the mother liquors gave some crystalline material, but principally a reddish-brown oil. The initial yield of crystalline product was considerably increased when the alcoholic solution of the crude product or the oil was made slightly alkaline with sodium hydroxide and warmed for a few minutes before cooling. Also the oily material from several runs, when distilled at 4 mm., was separated into a small forerun (chiefly *dl*-camphor), a dark residue, and a main fraction boiling at 108°. This solidified, and then melted at 44–46°. It contained 34.2% of bromine instead of 34.6% calculated for monobromocamphor, and when crystallized from alkaline alcohol gave back about half its weight as crystals, m. p. 49–50°. By thus alternately distilling and crystallizing an average yield of 178 g. (77%) of crystals, melting at 49° or higher, was obtained in five runs.

Pure *dl*-α-bromocamphor separates from 95% ethanol in large, monoclinic hemimorphic crystals, melting at 50.5–51° (corr.), in agreement with Haller's value.

[13] Armstrong and Mathews, *Chem. News*, **37**, 4 (1878).

Anal. Calcd. for $C_{10}H_{15}OBr$: Br, 34.6. Found: Br, 34.4.

Ammonium-*dl*-α-Bromocamphor-π-sulfonate.—Pure *dl*-α-bromocamphor was sulfonated in 230-g. lots with chlorosulfonic acid and converted to a solution containing the ammonium sulfonate. The procedure used by Kipping and Pope[3] for the preparation of the corresponding dextro compound was followed. When the initially dark brown solution was concentrated in stages the crude ammonium salt separated and was systematically recrystallized. Much of the material remained as a sirupy residue and the yield of pure salt (100–115 g. or 30–35%) is considerably lower than claimed for the dextro salt.

The pure salt crystallizes from water as a dense crystalline mass or in thick transparent prisms and is anhydrous. It melts with decomposition at 250–254°. The solubility is 15.9 g. per 100 g. of water at 25°. This is smaller than that of the corresponding *d*-salt, which was found to be 20.6 g. at 25°. The crystal form is also different.

Anal. Calcd. for $C_{10}H_{15}O_4NSBr$: N, 4.27; Br, 24.36. Found: N, 4.25; Br, 24.69.

Resolution of Ammonium *dl*-α-Bromocamphor-π-sulfonate.—The ammonium salt (49.2 g.) was dissolved in 400 cc. of boiling water and 20.3 g. of *l*-α-*p*-tolylethylamine and 13 g. of glacial acetic acid were added. Upon cooling most of the salt separated as a colorless oil and then solidified. This was redissolved and the solution inoculated with a sample of the solid. The first fraction of crystals then obtained on cooling was levorotatory, but successive fractions were alternately dextro- and levorotatory. After some experimentation it was found that the less soluble *l*B*l*A salt tends to form large prisms on the bottom of the vessel while the *l*B*d*A salt forms needles filling the solution. Also the salts differ more in solubility at 50–80° than at lower temperatures. Hence when levorotatory fractions were recrystallized at 80 to 50° from about seven parts of water, after inoculation with the prisms, principally the *l*B*l*A salt separated. The warm mother liquor, when decanted and cooled, then gave strongly dextrorotatory deposits. By judicious combination of fractions similar in appearance and rotation and inoculation with the appropriate crystals, there was soon obtained about 75% of the *l*B*l*A salt and 55% of the *l*B*d*A. The intermediate fractions could be further separated but it was better to combine them with similar fractions from following runs. The total yields of the salts in three runs were then 92 g. (89%) and 80 g. (76%), respectively.

***l*-α-*p*-Tolylethylamine-*l*-α-bromocamphor-π-sulfonate** forms coarse, hydrated prisms, solubility 2.10 g. per 100 g. of water at 25°. The anhydrous salt melts at 165° (corr.).

Anal. Calcd. for $C_{19}H_{28}O_4NSBr \cdot H_2O$: H_2O, 3.87. Found: H_2O, 3.97.

Rotation. Hydrated salt, 0.8445 g. made up to 50 cc. in water gave α_D^{25} −2.12 in 2 dm.; $[\alpha]_D^{25}$ −62.7°; M_D −291° (10^2).

***l*-α-*p*-Tolylethylamine-*d*-α-bromocamphor-π-sulfonate** crystallizes initially in needles or narrow prisms. These change to irregular masses on standing in the solution for several days; both forms are the monohydrate. The needles lose their water on exposure to air for several days, and then melt at 232° (corr.). The solubility (hydrated needles) is 2.96 g. per 100 g. of water at 25°.

Anal. Calcd. for $C_{19}H_{28}O_4NSBr \cdot H_2O$: H_2O, 3.87. Found: H_2O, 3.80.

Rotation. Subs., 1.2297 g. (anhydrous) made up to 50 cc. in water gave α_D^{25} +3.09° in 2 dm.; $[\alpha]_D^{25}$ +59.4°; M_D +265° (10^2).

Ammonium *l*-α-Bromocamphor-π-sulfonate.—The *l*B*l*A salt described above was treated with a slight excess of dilute barium hydroxide and the base distilled with steam. The barium was completely removed with ammonium carbonate and the filtered solution evaporated to obtain the *l*-ammonium salt. This resembled the familiar *d*-salt, and its rotation, $[\alpha]_D^{25}$ −86.6°, agrees with the value of Pope and Harvey.[5] The yields of recovered base and ammonium salt were nearly quantitative.

Ammonium *d*-α-Bromocamphor-π-sulfonate was similarly obtained from the *l*B*d*A salt. The specific rotation was +85.8°.

Summary

1. A satisfactory method for preparing *dl*-α-bromocamphor from *dl*-camphor is described.

2. Ammonium *dl*-α-bromocamphor-π-sulfonate was prepared from *dl*-α-bromocamphor, and this salt and its optical resolution by means of *l*-α-*p*-tolylethylamine are described.

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Higher Alkyl Sulfonates

BY VLADIMIR C. SEKERA AND C. S. MARVEL

Although alkyl esters of the aromatic sulfonic acids have long been known as alkylating agents, the real development of these reagents has been more recent and even now they are used only for the unusual alkylation reactions. The alkyl halides and sulfates are the common reagents for introducing alkyl groups and are unquestionably the most useful reagents for the lower molecular weight radicals. However, the higher alkyl halides (ten carbons or more) are somewhat sluggish in their alkylation reactions and the higher sulfates are not easily obtained. The work which is reported in this paper was undertaken in order to find a satisfactory method of preparing the higher aliphatic esters of the aromatic sulfonic acids, to study these esters as alkylating agents, and to compare the corresponding esters of aliphatic sulfonic acids and aromatic sulfonic acids in simple alkylation reactions.

It has been found that the method of preparing sulfonic acid esters from an alcohol, a sulfonyl chloride and pyridine can be extended to the alkyl esters of both aliphatic and aromatic sulfonic acids. Patterson and Frew[1] were apparently the first to use this general method. Ferns and Lapworth[2] pointed out the difficulty of obtaining ethyl and benzyl esters of sulfonic acids because they readily combined with pyridine to give water-soluble products which were evidently quaternary ammonium salts. However, this side reaction has not been found to be serious with the higher alkyl esters when they were prepared at 0°. The yields of esters which were obtained varied from 60–80% of the theoretical amounts.

Two series of esters, the *p*-toluenesulfonates and the *p*-bromobenzenesulfonates, were prepared from the higher normal alcohols with an even

[1] Patterson and Frew, *J. Chem. Soc.*, **89**, 332 (1906).

[2] Ferns and Lapworth, *ibid.*, **101**, 273 (1912).