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

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

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

number of carbon atoms. These esters are solids which all melt below 65° yet are easily purified by recrystallization from petroleum ether and seem to be of promise as derivatives for identification.

A few experiments demonstrated the usefulness of the higher esters as alkylating agents. Lauryl and cetyl *p*-toluenesulfonates alkylated *n*-butylamine quite readily to give a mixture of the expected secondary and tertiary amines in yields which were almost identical with those obtained from *n*-butyl *p*-toluenesulfonate in a similar reaction. Cetyl cyanide was obtained in 85% yield from cetyl *p*-toluenesulfonate and potassium cyanide whereas the butyl ester gave only a 46% yield of cyanide. Lauryl *p*-toluenesulfonate combined with pyridine to give a crystalline quaternary ammonium salt in excellent yields when the two reagents were warmed together.

In order to compare the esters of aliphatic and aromatic sulfonic acids as alkylating agents, the reactions of *n*-butyl methanesulfonate and *n*-butyl *p*-toluenesulfonate with sodium phenolate, sodium acetate and aniline were studied. The yields of ether, ester and secondary amine, respectively, were practically the same with these two reagents. These experiments showed that the esters of the aliphatic sulfonic acids offer no advantage over the more readily available aromatic sulfonic acid esters.

Experimental

_n_-Butyl Methanesulfonate.—A mixture of 14.8 g. of *n*-butyl alcohol and 22.9 g. of methanesulfonyl chloride was placed in a 500-cc., three-necked flask, equipped with a mechanical stirrer and a separatory funnel and cooled in an ice-salt bath to 0°. The stirrer was started and 31.6 g. of pyridine was added slowly over a period of three to four hours. An excess of dilute hydrochloric acid was added to the cold solution to remove the pyridine and the aqueous solution was extracted with ether. The ether solution was dried over anhydrous potassium carbonate, filtered and evaporated. The ester was distilled under reduced pressure. The yield was 24.2 g. (79.5% of the theoretical amount) of a product boiling at 105–106° (6 mm.); d_4^{20} 1.1074; n_D^{20} 1.4319.

Anal. Calcd. for $C_5H_{12}O_3S$: S, 21.07. Found: S, 20.86.

_n_-Butyl _p_-Toluenesulfonate.—This ester was prepared in the same manner from 14.8 g. of *n*-butyl alcohol, 41.9 g. of *p*-toluenesulfonyl chloride and 31.6 g. of pyridine. The yield was 39.3 g. (86% of the theoretical amount) of a product boiling at 169° (4 mm.); d_4^{20} 1.1319; n_D^{20} 1.5085.

Higher Alkyl _p_-Toluenesulfonates and _p_-Bromobenzenesulfonates.—The esters of the alcohols with ten or more carbons were solids and their preparation varied slightly from the above procedure.

A solution of one equivalent of the alcohol in four equivalents of pyridine was cooled to below 20° and with stirring 1.1 equivalents of pure arylsulfonyl chloride was added in portions. The reaction mixture was stirred for about three hours after the addition was complete. The temperature of the reaction mixture was always held below 20°. The reaction mixture was treated with a fairly large excess of cold dilute hydrochloric acid and the ester which separated was collected on a Büchner funnel. After drying in the air the ester was recrystallized from alcohol or better from petroleum-ether. Usually one recrystallization gave a constant melting product. The esters were prepared in 12–25 g. lots.

The esters prepared and the yields and melting points of the purified products are listed in Tables I and II.

TABLE I

SOME ALKYL ESTERS OF *p*-TOLUENESULFONIC ACID

Alkyl group	Yield, %	M. p., °C.	Analysis, % S Calcd.	Found
Lauryl	75	30	9.42	9.22
Myristyl	66	35	8.70	8.49
Cetyl	67	49	8.11	7.94
Stearyl	57	56	7.55	7.59

TABLE II

SOME ALKYL ESTERS OF *p*-BROMOBENZENESULFONIC ACID

Alkyl group	Yield, %	M. p., °C.	Analysis, % Br Calcd.	Found
Decyl	78	43–44	21.2	21.1
Lauryl	66	49	19.7	20.0
Myristyl	68	51.5	18.4	18.4
Cetyl	60	60	17.3	17.3
Stearyl	62	64–65	16.3	16.2

Alkylation Experiments. (a) Pyridine

n-Butyl Pyridinium p-Toluenesulfonate.—A mixture of 22.8 g. of *n*-butyl *p*-toluenesulfonate and 7.9 g. of pyridine was heated in an oil-bath at 130–140° for two hours. On cooling the mixture solidified and was recrystallized from a mixture of ethyl acetate and acetone. The yield of product was 27 g. (88% of the theoretical amount); m. p. 114°.

Anal. Calcd. for $C_{16}H_{21}O_3NS$: S, 10.44. Found: S, 10.36.

Lauryl Pyridinium p-Toluenesulfonate.—This quaternary ammonium salt was obtained in the same manner from 8 g. of lauryl *p*-toluenesulfonate and 1.9 g. of pyridine. The yield was 8.5 g. (86% of the theoretical amount) of a product melting at 135–136° after recrystallization from acetone.

Anal. Calcd. for $C_{24}H_{37}O_3NS$: S, 7.65. Found: S, 7.38.

(b) n-Butylamine

n-Butyllaurylamine and n-Butyldilaurylamine.—A solution of 7.3 g. of *n*-butylamine and 34.1 g. of lauryl *p*-toluenesulfonate in 50 cc. of dry toluene was refluxed for about six hours. The mixture was treated with a concentrated solution of aqueous sodium hydroxide and distilled with steam to remove the toluene and any remaining butylamine. The residue in the distilling flask was extracted with ether, and the ether solution was dried over anhydrous potassium carbonate, filtered and evaporated. The residue was distilled under reduced pressure. There was thus obtained 11.9 g. (49% of the theoretical amount) of *n*-butyllaurylamine, b. p. 138–140° (6 mm.); d_4^{20} 0.8174; n_D^{20} 1.4491; and 6.9 g. (44% of the theoretical amount) of *n*-butyldilaurylamine, b. p. 224–226° (6 mm.); d_4^{20} 0.8281; n_D^{20} 1.4582.

Anal.[3] Calcd. for $C_{16}H_{35}N$: N, 5.81. Found: N, 5.77. Calcd. for $C_{28}H_{59}N$: N, 3.42. Found: N, 3.62.

n-Butylcetylamine and n-Butyldicetylamine.—In exactly the same manner, 7.3 g. of *n*-butylamine and 39.4 g. of cetyl *p*-toluenesulfonate gave 15.1 g. (51% of the theoretical amount) of *n*-butylcetylamine, b. p. 193–197° (6 mm.); m. p. 31–32°; and 8.7 g.

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[3] These analyses were made by Mr. K. Eder.

(33% of the theoretical amount) of *n*-butyldicetylamine, b. p. 295–297° (6 mm.); m. p. 44–46°.

Anal.[3] Calcd. for $C_{20}H_{43}N$: N, 4.71. Found: N, 4.58. Calcd. for $C_{38}H_{75}N$: N, 2.69. Found: N, 2.58.

(c) Potassium Cyanide

Cetyl Cyanide.—To a solution of 13 g. of potassium cyanide in 150 cc. of water was added 39.6 g. of cetyl *p*-toluenesulfonate. The solution was boiled under a reflux condenser for about six hours, and then cooled and extracted with ether. The ether was evaporated and the residue was distilled under reduced pressure. The yield was 21.5 g. (86% of the theoretical amount) of cetyl cyanide which melted at 26–29°. The melting point of pure cetyl cyanide is given as 29.5–30°.[4]

***n*-Butyl Cyanide.**—The reaction between *n*-butyl *p*-toluenesulfonate and potassium cyanide under similar conditions gave only 46% of the theoretical amount of *n*-butyl cyanide; b. p. 136–140°.

Comparison of *n*-Butyl Methanesulfonate with *n*-Butyl *p*-Toluenesulfonate as a Butylating Reagent. (a) Phenol.—To a solution of 9.4 g. of phenol in 40 cc. of 10% sodium hydroxide was added 22.8 g. of *n*-butyl *p*-toluenesulfonate. The mixture was gently refluxed for about three hours, cooled and extracted with ether. The ether solution was dried over potassium carbonate, filtered and evaporated. On distillation of the residue under reduced pressure, a yield of 11 g. (73% of the theoretical amount) of *n*-butyl phenyl ether was obtained, b. p. 72–73° (6 mm.); d_4^{20} 0.9515; n_D^{20} 1.5049.

When 15.2 g. of *n*-butyl methanesulfonate was substituted for the *n*-butyl *p*-toluenesulfonate in a similar experiment, the yield of ether was 12.2 g. (81% of the theoretical amount); b. p. 72–73° (6 mm.); d_4^{20} 0.9516; n_D^{20} 1.5046.

(b) Aniline.—A mixture of 9.3 g. of aniline and 22.8 g. of *n*-butyl *p*-toluenesulfonate was heated in an oil-bath at 130–140° for about two hours. On cooling the mixture a white solid was obtained. Addition of excess concentrated aqueous sodium hydroxide solution liberated the mixed amines. The amines were collected in ether, dried over potassium carbonate and distilled under reduced pressure. The yield of *n*-butylaniline was 9.6 g. (64% of the theoretical amount); b. p. 115–120° (15 mm.); d_4^{20} 0.9358; n_D^{20} 1.5381.

Repetition of the experiment with the substitution of 15.2 g. of *n*-butyl methanesulfonate for the *p*-toluenesulfonate gave 10.1 g. (68% of the theoretical amount) of *n*-butylaniline; b. p. 112–114° (9 mm.); d_4^{20} 0.9362; n_D^{20} 1.5373.

(c) Sodium Acetate.—A mixture of 13.6 g. of powdered sodium acetate ($CH_3CO_2Na \cdot 2H_2O$) and 22.8 g. of *n*-butyl *p*-toluenesulfonate was thoroughly mixed and heated to 130–140° in an oil-bath for about five hours. The mixture was then cooled, treated with 100 cc. of water and extracted with ether. On distillation 7 g. (60% of the theoretical amount) of *n*-butyl acetate was obtained; b. p. 123–125°; d_4^{20} 0.8797; n_D^{20} 1.3989.

In a similar run 15.2 g. of *n*-butyl methanesulfonate gave 7.3 g. (63% of the theoretical amount) of *n*-butyl acetate; b. p. 123–125°; d_4^{20} 0.8799; n_D^{20} 1.3990.

Summary

1. Some higher alkyl (C_{10} and above) esters of *p*-toluenesulfonic acid and *p*-bromobenzenesulfonic acid have been prepared.

2. These esters have been found to be useful alkylating agents in such typical reactions as alkylation of an amine or the preparation of an alkyl

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[4] Shriner, Fulton and Burks, THIS JOURNAL, 55 (1933).

cyanide. The yields of product are approximately the same or better than can be obtained from lower alkyl sulfonates in the same reaction.

3. Comparison of *n*-butyl methanesulfonate with *n*-butyl *p*-toluenesulfonate has shown that there is no advantage of an ester of an aliphatic sulfonic acid over an ester of an aromatic sulfonic acid for alkylation reactions.

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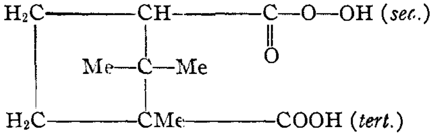
Studies in Organic Peroxides. I. Peroxides in the Camphoric Acid Series

BY NICHOLAS A. MILAS AND AMBROSE MCALEVY

Introduction

In connection with our general studies in auto-oxidation reactions[1] and especially the catalytic effects produced by organic peroxides on these and other related reactions, we had occasion to synthesize and study the properties of several new peroxides. The present communication describes the successful synthesis of some peroxides and peracids which are structurally related to camphoric acid.

A careful search of the literature revealed that up to the present time no definite peroxides of the camphoric acid series have been prepared.[2] We have obtained from camphoric anhydride and sodium peroxide a camphoric acid peracid which has the peracid group attached to the secondary carbon atom.



We have also prepared the methyl ester of this peracid by converting the tertiary monomethyl ester of camphoric acid to the acid chloride, to the ester peroxide and finally to the ester peracid.[3] The possibility of making the isomeric acid peracid through its ester derivative was precluded by the fact that the secondary monomethyl ester yields the tertiary ester secondary acid chloride[4] which gives the same ester peracid obtained from the tertiary monomethyl ester of camphoric acid. This conclusion was

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(1) Milas, THIS JOURNAL, **52**, 739 (1930); **53**, 221 (1931); *Chem. Rev.*, **10**, 295 (1932).

(2) (a) Brodie, *Proc. Roy. Soc.*, (London) **9**, 361 (1858); **12**, 655 (1863); *J. Chem. Soc.*, **17**, 263 (1864); *Ann.* (Supplement), **3**, 217 (1864); (b) Kingzett, *J. Chem. Soc.*, **45**, 93 (1884); (c) Vanino and Thiele, *Ber.*, **29**, 1724 (1896).

(3) Von Baeyer and Villiger, *Ber.*, **33**, 1575 (1900).

(4) Quadrat-J-Khunda, *J. Chem. Soc.*, 208 (1930); Bredt, *J. prakt. Chem.*, **133**, 87 (1932).