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Benzyl Tosylates. I. Preparation and Properties

BY JAY K. KOCHI AND GEORGE S. HAMMOND

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Benzyl tosylate and several of its meta and para derivatives have been prepared. The compounds showed varying degrees of stability toward polymerization by self alkylation. *p*-Methoxybenzyl tosylate polymerizes slowly at −60° and very rapidly at room temperature.

Many of the derivatives of benzyl alcohol and its ring-substituted derivatives are well-characterized compounds. The benzyl halides, in particular, have been prepared and studied extensively.[1] The usual reagents for the conversion of alcohols to characteristic derivatives have, in some cases, been successfully applied to the benzyl alcohols.[2] As will become apparent in the next paper of this series, it was deemed interesting to study the solvolysis of benzyl *p*-toluenesulfonate and its congeners hereafter referred to as tosylates. We are reporting here the synthesis and some properties of a few of these compounds.

The methods of preparation of tosylate esters of phenols and aliphatic alcohols have been authoritatively studied by Tipson,[3] Drahowzal and Klamann,[4] and Gilman and Beaber[5] and reviewed by Suter.[6] Most of these procedures represent variations of the Schotten–Baumann reaction utilizing the parent hydroxylic component and *p*-toluenesulfonyl chloride in the presence of a base.

The instability of benzyl tosylate has been recognized.[7] Workers found that preparations of it could not be successfully stored for prolonged periods. Since it was thought that water may catalyze the decomposition of this compound, it was considered desirable to prepare it in an entirely anhydrous condition. The method consists of the tosylation of a suspension of the appropriate sodium benzylate, prepared by refluxing an ethereal solution of the alcohol with sodium hydride, with tosyl chloride at temperatures which vary with the reactivity of the alkoxide. In this manner yields of tosylate approximating 50–80% were obtained. Pure benzyl tosylate placed under ligroin and refrigerated has been preserved for periods of over three months without apparent degeneration.

A property which is characteristic of all the benzyl tosylates studied is the spontaneous transmutation of the white crystalline solids into colored, amorphous materials. The colors of the degradation products vary widely with the nature of the substituent and fade with time. Benzyl tosylate on decomposing first turns brown and then gradually becomes colorless. The colors of the amorphous materials derived from *p*-*β*-styryl,[8] *p*-methyl and *p*-methoxy are, respectively, blue, pink and deep red. The rate of this decomposition varies greatly with the nature of the aromatic substituent, and the purity of the tosylate. Whereas *p*-nitrobenzyl tosylate can be kept for prolonged periods without apparent decomposition, *p*-methoxybenzyl tosylate decomposes rapidly even at −60°. The order of stability of these tosylates appears to be roughly consistent with the expected nucleophilic reactivity of the aromatic ring and also with the stability of the derived benzyl carbonium ions, $ArCH_2^+$. Thus, *p*-methoxybenzyl tosylate is so reactive it could not be successfully isolated in pure form at room temperature. On the other hand, *m*-methoxybenzyl tosylate is a relatively well-behaved compound.

The constitution of the amorphous material resulting from the degeneration of benzyl tosylate has been studied by Drahowzal and Klamann.[9] They related the properties of this polymer with that obtained from the condensation of benzyl chloride under the influence of catalysts such as powdered silver or copper and stannic chloride, found by earlier workers. The empirical formula of this uncrystallizable material was $(C_7H_6)_x$. A similar substance with the same empirical formula and a molecular weight of 1100–1200 was obtained by Illari[10] from the reaction of benzyl alcohol with anhydrous aluminum chloride. The polybenzyl nature of this polymer was intimated by Monacelli and Hennion[11] who obtained a similar product from the cleavage of *n*-propyl benzyl ether with boron trifluoride. The pyrolysis of the polymer yielded, among other things, anthracene.

The tosylates were all characterized by duplicate quantitative sulfur analyses coupled with several determinations of solvolysis equivalents. The solvolysis equivalents were obtained by hydrolyzing weighed samples of pure tosylates in a medium of

TABLE I

PHYSICAL CONSTANTS OF SUBSTITUTED BENZYL TOSYLATES

Tosylate	Mol. wt.	Yield, %	M.p., °C.	Sulfur anal.[a] Calcd.	Sulfur anal.[a] Found	S.E.[b]
Benzyl	262.3	80	58.5– 58.9	...	...	262
p-Nitrobenzyl	307.3	70	105.0–105.5	10.43	10.39	308
p-Bromobenzyl	341.2	59	76.8– 77.5	9.40	9.41	340
m-Bromobenzyl	341.2	63	105.2–105.6	9.40	9.40	341
p-Methoxybenzyl	292.4	..	....	10.97	...	...
m-Methoxybenzyl	292.4	58	83.7– 84.0	10.97	11.07	293
p-Methylbenzyl	276.3	41	57.9– 58.5	11.60	...	276
m-Methylbenzyl	276.3	77	65.1– 65.5	11.60	11.51	276

[a] Parr Instrumental Manual No. 121, Parr Instrument Co., Moline, Ill. [b] Solvolysis equivalent.

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[1] See C. G. Swain and W. Langsdorf, THIS JOURNAL, **73**, 2813 (1951), for leading references.

[2] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948.

[3] J. Tipson, *J. Org. Chem.*, **9**, 239 (1944).

[4] F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 452, 460 (1951).

[5] H. Gilman and N. J. Beaber, THIS JOURNAL, **47**, 518 (1925).

[6] C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 514.

[7] C. M. Suter, *ibid.*, pp. 525, 527.

[8] J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3452 (1953).

[9] F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 468 (1951).

[10] G. Illari, *Ann. chim.*, **40**, 483 (1950) [*C. A.*, **46**, 3978 (1952)].

[11] W. J. Monacelli and G. F. Hennion, THIS JOURNAL, **63**, 1722 (1941).

50 volume per cent. aqueous acetone at reflux temperatures. The liberated *p*-toluenesulfonic acid was then titrated with standard triethylamine solution (also in 50% aqueous acetone solution). The alcohols produced in the solvolysis of *p*-methoxybenzyl tosylate and *p*-bromobenzyl tosylate were isolated and subjected to infrared analyses. The spectra were the same as those of the original alcohols.

The properties of the tosylates which were prepared are summarized in Table I.

Experimental

Benzyl alcohol (Eastman Kodak, Co. chlorine-free) was redistilled *in vacuo;* b.p. 86.8–88.0° at 7 mm.

***p*-Nitrobenzyl alcohol** was prepared by the hydrolysis of *p*-nitrobenzyl chloride according to the method of Soderbaum and Widman[12]; yield 27%, m.p. 96.0–97.0°.

***m*-Bromobenzyl alcohol** was obtained by the lithium aluminum hydride reduction of *m*-bromobenzoic acid[13]; b.p. 255–257° at 738 mm., yield 76%.

***p*-Methoxybenzyl alcohol** also was obtained by the lithium aluminum hydride reduction using *p*-methoxybenzaldehyde; b.p. 106° at 22 mm., yield 40%.

***p*-Methylbenzyl alcohol** was obtained from *p*-methylbenzoic acid *via* the lithium aluminum hydride reduction. The oil on crystallization from water yielded fine white crystals melting at 61.0–62.1°; yield 89%. In a previous attempt to prepare this compound, *p*-methylbenzaldehyde (Matheson, reagent grade) was reduced with lithium aluminum hydride. The oil resulting from this synthesis did not crystallize after repeated freezings. It showed a wide range in melting from −13 to −4°, although the liquid distilled at a constant temperature range of 216–217° at 721 mm. Attempts to prepare a derivative of the parent aldehyde by treatment with *p*-nitrophenylhydrazine and oxidation of the aldehyde to the corresponding methylbenzoic acid indicated that the aldehyde was a mixture of the *ortho* and *para* isomers.

***p*-Bromobenzyl alcohol** was prepared by a procedure similar to that used for the preparation of *p*-nitrobenzyl alcohol, starting with *p*-bromobenzyl bromide; m.p. 76.5–77.0°, yield, 41%.

***m*-Methylbenzyl alcohol** was prepared by the reduction of *m*-toluic acid; b.p. 217.5–219.5° at 743 mm., yield 78%.

***m*-Methoxybenzyl alcohol** was obtained from the lithium aluminum hydride reduction of the corresponding acid; b.p. 243–244° at 734 mm., yield 74%.

***p*-Toluenesulfonyl chloride** (Eastman Kodak Co., reagent grade) was redistilled *in vacuo;* b.p. 123–124° at 7–8 mm., m.p. 69.5–70.5°.

Preparation of Substituted Benzyl Tosylates. General Procedures. Method A.—To 10 ml. (0.097 mole) of benzyl alcohol, dissolved in 100 ml. of anhydrous ether, was added 2.4 g. (0.10 mole) of sodium hydride. The mixture was stirred and refluxed for 12 hours. The use of 6-mm. glass beads in conjunction with a paddle-type stirrer was found to be helpful in crushing the sodium hydride *in situ.* The suspension of the sodium alcoholate was cooled to −20° with a Dry Ice-bath and a solution of 19.5 g. (0.097 mole) of *p*-toluenesulfonyl chloride in 100 ml. of anhydrous ether was then added dropwise to the suspension. In all operations caution was exercised to exclude moist air from the solutions. After the tosyl chloride solution was added, the reaction mixture was stirred for two hours at −10° and then at room temperature for one additional hour. The suspension was then filtered repeatedly with a minimum exposure to air until a clear solution was obtained. It was found helpful to use a medium grade sintered glass funnel for the last filtration. When the clear ethereal solution was cooled in Dry Ice-bath, a copious precipitate of fine white needles was obtained. The crystals were quickly filtered and recrystallized several times from dry petroleum ether, yield 20 g. (80%).

***p*-Methoxybenzyl Tosylate.**—The reactivity of *p*-methoxybenzyl tosylate is much greater than that of the unsubstituted compound. The preparation of this particular compound required very careful exclusion of moisture and rapid manipulation. The sodium salt of the alcohol was prepared in the usual manner, caution being taken to exclude all possibilities of moist air entering the flask. An anhydrous solution of tosyl chloride was added to the salt suspension maintained at −70° within five minutes. The temperature of the reaction mixture was then allowed to rise to −30° in one-half hour. A siphon arrangement was quickly attached to the system, and a vacuum applied at lower end. The filtration was carried out through a pressure filter into a filter flask maintained at −70° in a Dry Ice-bath. It was necessary to execute this process in a few minutes. After several minutes the *p*-methoxybenzyl tosylate began to crystallize as fine white needles. Subsequently the rate of solvolysis[8] of this compound was measured directly with the crude material. Its isolation involved filtration in the absence of moist air on a sintered glass plate and rapid removal to the solvolysis cell. The polymerization of this tosylate proceeds even at −70°. Various attempts to recrystallize the material in a variety of solvents were futile. Even attempts to determine melting points were unsuccessful. In every case the fine crystals polymerized into a red mass below room temperature. A partial confirmation of the identity of this tosylate was made by analyzing the hydrolysis product. Approximately 200 mg. of tosylate was quickly transferred to a flask containing 100 ml. of the solvolysis medium. The solution was then refluxed for approximately one-half hour, cooled, and the acetone removed by distillation *in vacuo.* The resulting liquid was repeatedly extracted with ether (100 ml.). The ethereal solution was washed once with water and then dried over Drierite. The solution was then inspissated and the small amount of residual liquid was submitted to infrared analysis. The spectrogram proved to be the same as that of an authentic sample of *p*-methoxybenzyl alcohol.

Method B. *p*-Nitrobenzyl Tosylate.—Method A was found to be not applicable to *p*-nitrobenzyl tosylate. This compound was made by the method of Tipson.[3] Five grams of tosyl chloride was dissolved in dry pyridine (25 ml.) and cooled to −10°. To this solution was added 3.7 g. of *p*-nitrobenzyl alcohol and the temperature maintained. After 20 minutes fine crystals began to appear. Ten minutes later 60 ml. of 5 *N* sulfuric acid at −10° was added. The temperature rose to 25° and the solid was removed by filtration. The hard crystals were washed three times with 50-ml. portions of ligroin. The crude tosylate was recrystallized five times from ligroin, yielding white leaflets melting at 103–104°.

With the exception of *p*-nitrobenzyl tosylates all the alcohols were treated by method A. The variations in experimental conditions for the preparation of the various tosylates were: length of time of heating the alcohol with sodium hydride, temperature and length of time in which the alkoxide was mixed with tosyl chloride and the temperature and length of time in which the two were stirred. For convenience these experimental conditions are listed in Table II. Every tosylate, with the exception of *p*-methoxybenzyl tosylate was recrystallized from ligroin. It was found that the temperature of the recrystallizing solvent should never be raised above 60°. Higher temperatures led to the rapid polymerization of the majority of the tosylates, especially the more reactive ones.

TABLE II

PREPARATION OF SUBSTITUTED BENZYL TOSYLATES

		Reaction TsCl with alkoxide				
		Mix		Stir		
Alcohol	Time reaction with NaH, hr.	Temp., °C.	Time, hr.	Temp., °C.	Time, hr.	Wt. alcohol, g.
Benzyl	12	−30	0.5	−10	2	10.5
p-Bromobenzyl	36	0	.5	10	3	7.6
m-Bromobenzyl	16	−30	1	25	3.4	9.4
p-Methylbenzyl	12	−30	0.5	−20	2	4.1
m-Methylbenzyl	17	−30	.5	0	2	4.1
p-Methoxybenzyl	8	−70	.2	−30	0.5	6.7
m-Methoxybenzyl	10	−20	1	15	2.5	4.4

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(12) H. G. Soderbaum and O. Widman, *Ber.*, **25**, 3290 (1892).

(13) W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469.