

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

PREPARATION OF TOSYLATES OF PHENOLS AND ACIDIC ALCOHOLS

Stanley E. Wentworth^a; Patrick L. Sciaraffa^b

^a Army Materials and Mechanics Research Center, Watertown, Massachusetts ^b Polaroid Corporation, Cambridge, Massachusetts

To cite this Article Wentworth, Stanley E. and Sciaraffa, Patrick L.(1969) 'PREPARATION OF TOSYLATES OF PHENOLS AND ACIDIC ALCOHOLS', *Organic Preparations and Procedures International*, 1: 4, 225 – 228

To link to this Article: DOI: 10.1080/00304946909458387

URL: <http://dx.doi.org/10.1080/00304946909458387>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

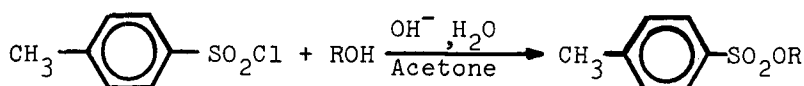
This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PREPARATION OF TOSYLATES OF PHENOLS AND ACIDIC ALCOHOLS

Stanley E. Wentworth
 Army Materials and Mechanics Research Center
 Watertown, Massachusetts 02172

Patrick L. Sciaraffa
 Polaroid Corporation
 Cambridge, Massachusetts 02139



Although there are many reports of the preparation of the title compounds,¹ each one differs somewhat from the next and the yields are variable.

We wish to report a simple preparation of tosylates of phenols and of acidic alcohols. The method involves stirring an acetone solution of tosyl chloride and the alcohol (or phenol) with an excess of aqueous base, removal of the solvent, and isolation of the product. Reaction time is conveniently overnight, but could be reduced to as little as 4 hrs in the case of phenol without effect on the yield. The yields in many cases were better than those reported and were generally above 90%, except when a non-acidic alcohol such as n-butanol was used.² The low yield in this case

TABLE

Compound	Yield (%)	m.p. (°C)	
		Found	Lit. (ref.)
n-BuOTos	50 ^a	-	-
C ₆ H ₅ OTos	98	94-96	94-95 (3)
p-ClC ₆ H ₄ OTos	91	70-72	79.6-80.6 (4)
p-BrC ₆ H ₄ OTos	95	78-80	93-95 (5)
p-IC ₆ H ₄ OTos	95	97-99	99 (6)
p-NO ₂ C ₆ H ₄ OTos	89	96-98	97-97.5 (7)
CF ₃ CH ₂ OTos	95	40-42	41 (8)
$\begin{array}{c} \text{CF}_3 \\ \\ \text{C}_6\text{H}_5\text{CHOTos} \end{array}$	94	113-116	113-116 (9)
$\begin{array}{c} \text{CF}_3 \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{CHOTos} \end{array}$	91	89-92	b, d
C ₇ F ₁₅ CH ₂ OTos	75	53-56	c, d
$\begin{array}{c} \text{CH}_2\text{OTos} \\ / \\ (\text{CF}_2)_3 \\ \backslash \\ \text{CH}_2\text{OTos} \end{array}$	99	96-98	92-94 (10)

a. Crude yield, not isolated.

b. New compound: Anal. Calcd. for C₁₆H₁₅F₃O₃S:
S, 9.31. Found S, 9.19.

c. New compound: Anal. Calcd. for C₁₅H₉F₁₅O₃S:
C, 32.5; H, 1.63. Found: C, 32.4; H, 1.58.

d. The ir spectra of the new tosylates closely resembled those of the known tosylates (see fig.)

TOSYLATES OF PHENOLS AND ACIDIC ALCOHOLS

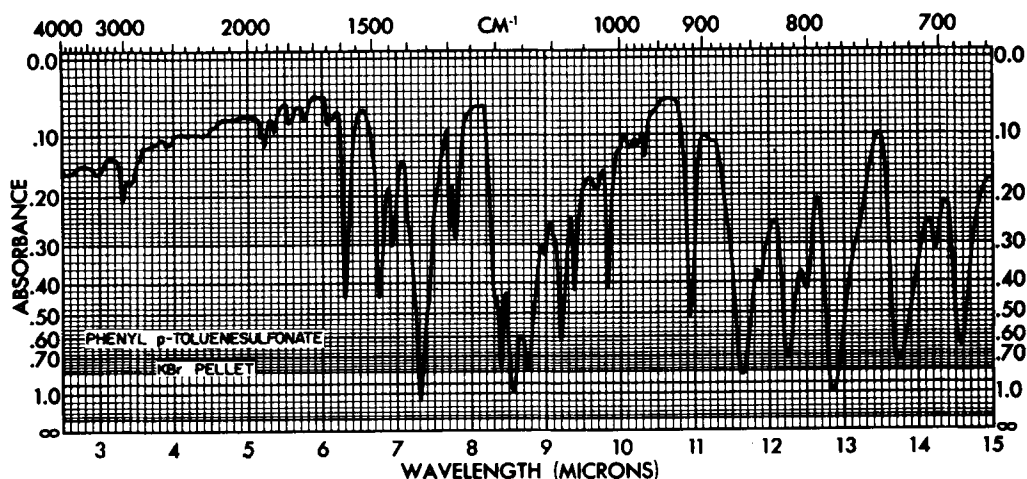


FIG. 1

may be due to further reaction of the tosylate with the excess base, or, as suggested by a referee, competitive hydrolysis of the tosyl chloride. Other compounds prepared by this method are reported in the Table.

EXPERIMENTAL

Phenyl tosylate. To a stirred solution of 5.0 g. of tosyl chloride and 2.5 g. of phenol in 20 ml. of acetone was added dropwise 1.28 g. of sodium hydroxide in 8 ml. of water. After having been stirred overnight, the solution was evaporated in vacuo. The resulting semi-solid was partitioned between ether and water. The layers were separated and the aqueous phase washed with a further portion of ether. The combined ethereal extracts were evaporated and the residue recrystallized from a mixture of hexane and acetone to give 6.45 g. (98%) of phenyl tosylate, m.p. 94-96°, lit.³ m.p. 94-95°.

REFERENCES

1. R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry", John Wiley and Sons, Inc., New York, N. Y., 1953, p. 823.
2. A. T. Roos, H. Gilman, and N. J. Beaber, "Organic Syntheses", Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 145.
3. R. Otto, Ber., 19, 1832 (1886).
4. M. Neeman, A. Modiano, and Y. Shor, J. Org. Chem., 21, 671 (1956).
5. S. E. Hazlet, J. Am. Chem. Soc., 59, 287 (1937).
6. D. Matheson and H. McCombie, J. Chem. Soc., 1103 (1931)
7. E. Bamberger and A. Rising, Ber., 34, 228 (1901).
8. G. Van Dyke Tiers, H. A. Brown, and T. S. Reid, J. Am. Chem. Soc., 75, 5978 (1953).
9. R. A. Shepard and S. E. Wentworth, J. Org. Chem., 32, 3197 (1967).
10. B. S. Marks and G. C. Schweiker, J. Am. Chem. Soc., 80, 5789 (1958)

(Received March 4, 1969)