

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Ethers of *p*-Hydroxybenzoic Acid as Derivatives for the Identification of Alkyl Halides

BY W. M. LAUER, P. A. SANDERS, R. M. LEEKLEY AND H. E. UNGNADE

The authors have had occasion to prepare a number of ethers of *p*-hydroxybenzoic acid during the last few years. These derivatives have much to recommend them for identification purposes, even though there are already several different types of derivatives which are useful for the identification of alkyl halides.¹

A procedure which is suitable for the preparation of small amounts of the ethers follows. A solution of metallic sodium (0.2 g.) in absolute alcohol (5 ml.) is prepared in a 25-cc. Erlenmeyer flask fitted with a reflux condenser. Ethyl *p*-hydrobenzoate (1 g.) is dissolved in the alcoholic solution of sodium ethoxide and then the alkyl halide (1 ml.) is added. After refluxing for one-half to one hour, a considerable portion of the alcohol is removed by distillation and the residue is treated with water to dissolve the precipitated sodium halide. The aqueous solution is then extracted with ether and the ether extract is shaken with three portions (5 ml. each) of aqueous sodium hydroxide (10%). The ether solution is concentrated and a saturated solution (5 m.) of potassium hydroxide in methyl alcohol is added. The reaction mixture is heated for approximately ten minutes. The precipitated potassium salt is then dissolved in water and the solution acidified (congo red) with dilute sulfuric acid. Extraction with ether yields the *p*-alkoxybenzoic acid, which is crystallized from a suitable solvent. In a number of cases benzene or mixtures of benzene and petroleum ether were used.

Several substituted *p*-alkoxybenzoic acids are included in the following table. It is a well-known fact that certain substituted allyl halides undergo the α,γ -transposition upon ether formation, yielding mixtures of isomeric products. Several mixtures of this kind were separated, but usually such separations are quite difficult. This, of course, is not true in the case of allyl chloride and α,γ -dimethylallyl chloride, which give *p*-alkoxybenzoic acid and *p*-(α,γ -dimethylallyloxy)-benzoic acid, respectively.

Unfortunately several of the *p*-alkoxybenzoic acids possess melting points which show only a slight difference. The same situation exists in the case of some of the other types of derivatives in common use for characterization purposes. A mixed melting point determination renders identification certain, however. It should be noted that *p*-(*n*-alkoxy)-benzoic acids exhibit mesomorphism.² Thus

(1) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1935; Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1932; see also Merritt, Levey and Cutter, *THIS JOURNAL*, **61**, 15 (1939).

(2) Jones, *J. Chem. Soc.*, 2660 (1929); 1874 (1935); Bennett and Jones, *ibid.*, 420 (1939).

p-(*n*-butoxy)-benzoic acid, upon melting at 147–148° changes to a cloudy viscous liquid which exists over a definite temperature range. The cloudy liquid clears sharply at 160° and this temperature appears to be as characteristic of the substance as the transition at 147–148°.

TABLE I

MELTING POINTS OF ETHERS OF *p*-HYDROXYBENZOIC ACID

Ether	M. p., °C.
Methyl	180–182 ^a ; 184 ^b
Ethyl	195 ^b
<i>n</i> -Propyl	145.5–147 ^a ; 145 ^b (154 ^b)
Isopropyl	160–163 ^a
<i>n</i> -Butyl	147–148 ^a ; 147 ^b (160 ^b)
Isobutyl	140–141 ^{a,d}
<i>s</i> -Butyl	121–123 ^c
<i>n</i> -Amyl	123–124 ^c ; 124 ^b (151 ^b)
Isoamyl	141–142 ^a
<i>n</i> -Hexyl	105.5–107 ^c ; 106 ^b (153 ^b)
<i>n</i> -Heptyl	92 ^b , (95 ^b , 148 ^b)
<i>n</i> -Octyl	100 ^b (104 ^b , 148 ^b)
<i>n</i> -Nonyl	92 ^b (99 ^b , 141 ^b)
<i>n</i> -Decyl	92 ^b (120 ^b , 149 ^b)
<i>n</i> -Dodecyl	95 ^b (129 ^b , 137 ^b)
Cetyl	100 ^b (131 ^b , 133 ^b)
Benzyl	188–190 ^a
Allyl	160–162 ^a ; 162–163 ^c
α -Methylallyl	155–156 ^c
γ -Methylallyl	176.5–178 ^c
α -Ethylallyl	108–109 ^c
γ -Ethylallyl	156.5–158 ^c
α,γ -Dimethylallyl	131–132 ^c
α -Propylallyl	74.5–75.5 ^c
γ -Propylallyl	139.5–140 ^c

^a Cohen and Dudley, *J. Chem. Soc.*, **97**, 1737 (1910). Uncorrected values. ^b Bennett and Jones, *ibid.*, 424 (1939). Values in parentheses refer to liquid-liquid transition temperatures. All values are corrected. ^c Present work. Uncorrected values. ^d *Anal.* Calcd. for C₁₁H₁₄O₃: C, 68.04; H, 7.27. Found: C, 67.94; H, 7.32.

Summary

The use of ethers of *p*-hydroxybenzoic acid as derivatives for the identification of alkyl halides is suggested. A number of such ethers have been prepared and a convenient procedure is described.

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