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The Use of Triiodophenyl Ethers for the Identification of Alkyl Halides

BY ROBERT D. DREW AND JULIAN M. STURTEVANT

In a recent paper proposing the use of sodium saccharin as a reagent for the preparation of derivatives of alkyl halides, Merritt, Levey and Cutter¹ have pointed out that the types of derivatives for these compounds previously investigated are relatively difficult to prepare. Another convenient type of derivative is suggested by the work of Brenans² and Daniels and Lyons,³ who found certain ethers of 2,4,6-triiodophenol to be nicely crystalline substances. In the present work a convenient standardized method of preparation has been devised using the sodium salt of triiodophenol and the alkyl halide dissolved in absolute alcohol, and several new ethers have been

utes, or until a precipitate of sodium halide has formed. After filtering, the solution is cooled and diluted with water, the precipitate filtered and recrystallized from alcohol or dilute alcohol. About 1 g. of product is obtained after three or four successive recrystallizations. Some of the lower melting ethers separate from the cooled reaction mixture as liquids. In these cases the mixture is allowed to settle, the supernatant liquid decanted, and the product recrystallized from alcohol. One such recrystallization is usually sufficient to produce a solid product. A slightly longer period of reflux is found to give better results in these cases.

TABLE I
2,4,6-TRIIODOPHENYL ETHERS

Halide used	M. p., °C. (corr.)	Empirical formula	Calcd.	% iodine	
				Found	Found
Methyl iodide ^a	98.5	C ₇ H ₅ I ₃ O
Ethyl bromide ^a	83.5	C ₈ H ₇ I ₃ O	76.16	76.49	76.12
<i>n</i> -Propyl bromide ^a	82.0	C ₉ H ₉ I ₃ O	74.11	73.94	73.77
Isopropyl bromide	43.0	C ₉ H ₉ I ₃ O	74.11	73.82	73.89
<i>n</i> -Butyl bromide	66.0	C ₁₀ H ₁₁ I ₃ O	72.13	71.83	71.55
Isobutyl bromide	48.0	C ₁₀ H ₁₁ I ₃ O	72.13	71.91	71.63
<i>n</i> -Amyl bromide	47.0	C ₁₁ H ₁₃ I ₃ O	70.25	70.03	69.70
<i>n</i> -Hexyl bromide	44.5	C ₁₂ H ₁₅ I ₃ O	68.49	68.37	68.34
Benzyl chloride ^a	122.5	C ₁₃ H ₉ I ₃ O	67.76	67.51	67.73
β -Phenylethyl bromide	88.0	C ₁₄ H ₁₁ I ₃ O	66.12	66.16	65.59
γ -Phenyl- <i>n</i> -propyl bromide	63.5	C ₁₅ H ₁₃ I ₃ O	64.54	64.57	64.46
<i>p</i> -Nitrobenzyl bromide	207.5	C ₁₃ H ₉ I ₃ NO ₂	62.73	63.10	62.65
Ethylene bromohydrin	137.5	C ₈ H ₇ I ₃ O ₂	73.81	73.82	73.94
Ethyl bromoacetate ^b	124.0	C ₁₀ H ₉ I ₃ O ₂	68.25	67.94	67.92
Ethyl α -bromopropionate	80.5	C ₁₁ H ₁₁ I ₃ O ₂	66.58	66.65	66.30

^a Ethers previously prepared by Brenans.² Brenans also prepared the allyl ether, melting at 113–114°, from allyl iodide. ^b Previously prepared by Daniels and Lyons,³ who found the melting point to be 128.5°.

prepared. As found by Merritt, Levey and Cutter¹ in the case of sodium saccharin, most alkyl chlorides react very slowly with sodium triiodophenolate.

Experimental

Five grams of 2,4,6-triiodophenol and an equivalent amount of the alkyl halide are added to 22 cc. of a solution of sodium ethylate (12.3 g. of sodium dissolved in 1 liter of absolute ethyl alcohol), and the solution is refluxed for thirty min-

In Table I are listed the corrected melting points and the analyses (by the Parr bomb method) of the various ethers prepared by this method. It was found in all cases where the melting points are close together that a mixed melting point shows a large depression.

Summary

The use of 2,4,6-triiodophenol as a reagent for the identification of alkyl halides has been found to be satisfactory. Several new alkyl triiodophenyl ethers have been prepared, and their melting points determined.

(1) Merritt, Levey and Cutter, *THIS JOURNAL*, **61**, 15 (1939).

(2) Brenans, *Bull. soc. chim.*, **25**, 819 (1901).

(3) Daniels and Lyons, *THIS JOURNAL*, **58**, 2646 (1936).