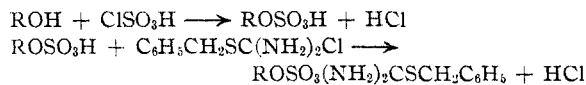


NOTES

Identification of Alcohols and Alkyl Hydrogen Sulfates with S-Benzylthiuronium Chloride

BY ROBERT K. BAIR AND C. M. SUTER

The sodium salts of many acids including sulfonic acids¹ react with S-benzylthiuronium chloride to form derivatives which are of value in the identification of the original materials. The reagent is produced in nearly quantitative yield by the action of benzyl chloride with thiourea.^{1,2} It has now been found that most alcohols are easily identified by this same reagent through first converting them to the corresponding alkyl hydrogen sulfates by warming in dioxane solution with chlorosulfonic acid. The benzylthiuronium salts of



methyl and ethyl hydrogen sulfate are too soluble in water to be isolated readily and the *n*-octyl compound showed an anomalous melting point

TABLE I
S-BENZYLTHIURONIUM DERIVATIVES

Alcohol	M. p., °C. (cor.)	Nitrogen, %	
		Calcd.	Found
<i>n</i> -Propyl	111.5-112.5	9.15	9.16
<i>i</i> -Propyl	142-143	9.15	9.07
<i>n</i> -Butyl	100-101	8.75	8.83
<i>s</i> -Butyl	117-119	8.75	8.73
<i>i</i> -Butyl	136-137	8.75	8.91
<i>n</i> -Amyl	85-86 ^e	8.38	8.25
<i>n</i> -Hexyl	85-86 ^e	8.04	7.87
<i>n</i> -Heptyl	77-79	7.74	7.33
<i>n</i> -Octyl	42-70	7.45	7.91
<i>n</i> -Decyl	73-75 ^a	6.93	6.88
Lauryl ^b	74-76	6.48	6.55
Myristyl ^b	87-88	6.08	6.02
Cyclohexyl ^{c,d}	163-164	8.10	8.05
Bornyl ^f	174-175	7.01	7.12
Menthyl ^f	149-150	6.98	6.97
Ethylene glycol	180-181	10.10	10.39

^a Nitrogen analyses by Dr. T. S. Ma, University of Chicago.

^b Chlorosulfonic acid added to solid alcohols dissolved in dioxane.

^c Thiuronium derivatives made from alkyl hydrogen sulfates.

^d We are indebted to Dr. Sydney Archer for purifying samples of the last four compounds.

^e Mixed melting points were taken: *n*-amyl and *n*-hexyl, 77-82°; *n*-heptyl and *n*-decyl, 53-71°.

(1) Chambers and Watt, *J. Org. Chem.*, **6**, 376 (1941).

(2) Donleavy, *This Journal*, **58**, 1004 (1936).

behavior although the analysis was satisfactory. Ethylene glycol was identified as the bis-(hydrogen sulfate) but the behavior of other glycols was not studied.

Obviously this method of identification is applicable to sodium alkyl sulfates as such and this is of considerable interest because of the varied commercial uses of these compounds. However, the difference in melting point for the decyl and lauryl compounds is small.

Procedure.—About 5 drops of the alcohol is added to a mixture of 4 drops of chlorosulfonic acid and 5 drops of dioxane. If hydrogen chloride is not immediately evolved, the resulting mixture is warmed with shaking and allowed to stand for five or ten minutes. Then after the addition of 1 ml. of water, 1 ml. of a saturated aqueous solution (or 15% alcohol solution) of S-benzylthiuronium chloride is added. If crystals do not form in a few minutes the solution is chilled in an ice-bath. The derivatives of the lower molecular weight alcohols (to *n*-hexyl inclusive) can be recrystallized from 10% ethyl alcohol, and derivatives of higher alcohols from 50% alcohol. In preparing samples for analyses the quantities used in this procedure were multiplied by five.

The corresponding *p*-chlorobenzylthiuronium derivatives were also made from about eight alcohols; however, several of these were waxy, difficult to filter and to obtain in a pure state. Also five of them melted between 80 and 90°. No derivatives of methanol and ethanol were obtained by using either the *p*-chloro-S-benzyl- or S-benzylthiuronium chloride.

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

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The Dehydration of 1,5-Hexadiene-3-ol to 1,3,5-Hexatriene and 1,3-Cyclohexadiene¹

BY LEWIS W. BUTZ

That the dehydration of 1,5-hexadiene-3-ol under the conditions recently described² yields about 70% of 1,3,5-hexatriene was demonstrated by conversion of part of the products to 1-vinylanthraquinone. At the same time it appeared that 1,3-cyclohexadiene was formed in about 30% yield, since reaction of the hydrocarbon products with 1,4-naphthoquinone gave a 1,4-ethano adduct. The alternative explanation would be that hexatriene is converted to cyclohexadiene when

(1) Not subject to copyright.

(2) L. Butz, E. Butz and Gaddis, *J. Org. Chem.*, **5**, 178 (1940).