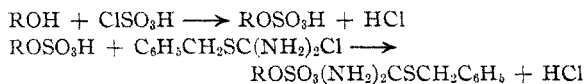


## NOTES

### 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 acids<sup>1</sup> 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.<sup>1,2</sup> 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.<br>(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 <sup>e</sup>   | 8.38        | 8.25  |
| <i>n</i> -Hexyl           | 85-86 <sup>e</sup>   | 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 <sup>e</sup>   | 6.93        | 6.88  |
| Lauryl <sup>b</sup>       | 74-76                | 6.48        | 6.55  |
| Myristyl <sup>b</sup>     | 87-88                | 6.08        | 6.02  |
| Cyclohexyl <sup>c,d</sup> | 163-164              | 8.10        | 8.05  |
| Bornyl <sup>e</sup>       | 174-175              | 7.01        | 7.12  |
| Menthyl <sup>e</sup>      | 149-150              | 6.98        | 6.97  |
| Ethylene glycol           | 180-181              | 10.10       | 10.39 |

<sup>a</sup> Nitrogen analyses by Dr. T. S. Ma, University of Chicago.

<sup>b</sup> Chlorosulfonic acid added to solid alcohols dissolved in dioxane.

<sup>c</sup> Thiuronium derivatives made from alkyl hydrogen sulfates.

<sup>d</sup> We are indebted to Dr. Sydney Archer for purifying samples of the last four compounds.

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

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.

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### The Dehydration of 1,5-Hexadiene-3-ol to 1,3,5-Hexatriene and 1,3-Cyclohexadiene<sup>1</sup>

BY LEWIS W. BUTZ

That the dehydration of 1,5-hexadiene-3-ol under the conditions recently described<sup>2</sup> 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) Chambers and Watt, *J. Org. Chem.*, **6**, 376 (1941).

(2) Donleavy, *THIS JOURNAL*, **58**, 1004 (1936).

(1) Not subject to copyright.

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

heated with naphthoquinone at 50°, a result hardly to be expected.

In contact with maleic anhydride at 30°, the hydrocarbon products gave a crystalline compound which was different from the adduct obtained by Farmer and Warren<sup>3</sup> from hexatriene and maleic anhydride at 100°. Since Farmer and Warren considered their compound to be an ethylenetetrahydrophthalic anhydride, it appeared likely that the new isomer was the vinyltetrahydrophthalic anhydride, the normal adduct, and this view was expressed publicly.<sup>4</sup>

This has now been shown not to be the case. The substance, m. p. 147°, does not depress the m. p. of the ethanetetrahydrophthalic anhydride prepared<sup>5</sup> from cyclohexadiene and maleic anhydride. This is further evidence that the hydrocarbon obtained by the dehydration of the hexadienol contained cyclohexadiene. While the possibility of a direct hexatriene → cyclohexadiene transformation is still not excluded, it must be supposed that it occurs, if at all, during the dehydration of the hexadienol rather than during the reaction with naphthoquinone or maleic anhydride at 50 or 30°. However, it appears that the hexatriene prepared by this method is not always contaminated with so much cyclohexadiene, and the formation of the latter must depend on small variations in procedure, because the hydrocarbon has been found<sup>6</sup> not to yield, upon reaction with 5-acetoxy-1,4-toluquinone, any of the adducts obtained from cyclohexadiene and this quinone.

(3) Farmer and Warren, *J. Chem. Soc.*, 897 (1929).

(4) *J. Wash. Acad. Sci.*, 29, 548 (1939).

(5) I. G. Farbenindustrie A.-G., *Chem. Zentr.*, 100, II, 2502 (1929).

(6) E. Butz and L. Butz, *J. Org. Chem.*, 7, 199 (1942).

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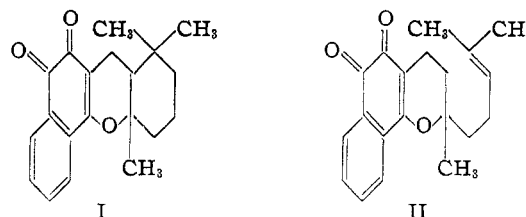
### The Condensation of $\beta$ -Cyclogeraniol with Leucoisonaphthazarin

BY MARSHALL D. GATES AND FERNANDA MISANI

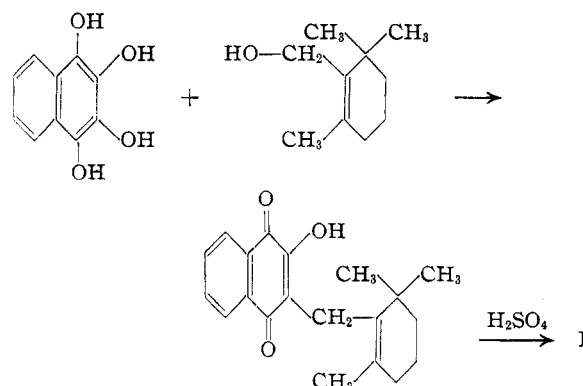
In a recent paper Fieser and Gates<sup>1</sup> described the preparation of  $\beta$ -geranolapachone, a member of the  $\beta$ -lapachone series, by cyclization of 2-hydroxy-3-geranyl-1,4-naphthoquinone with concentrated sulfuric acid. The high melting point of this compound (234°) suggests that further cyclization of the side chain may have taken

(1) Fieser and Gates, *THIS JOURNAL*, 63, 2948 (1941).

place to give structure I rather than the supposed structure II.



A choice between these two structures was readily made by synthesizing structure I by application of the general scheme employed by Fieser and Gates.<sup>1</sup>



The  $\beta$ -cyclogeraniol employed (m. p. 44°) was prepared by Meerwein-Ponndorf reduction of  $\beta$ -cyclocitral according to Kuhn and Hoffer.<sup>2</sup> Condensation with leucoisonaphthazarin gave the desired 2-hydroxy-3-( $\beta$ -cyclogeranyl)-1,4-naphthoquinone in rather poor yield, but in easily isolated form. On cyclization with sulfuric acid,  $\beta$ -cyclogeranolapachone (I) was obtained. It proved to be identical with  $\beta$ -geranolapachone prepared according to Fieser and Gates, and their  $\beta$ -geranolapachone must therefore be regarded as  $\beta$ -cyclogeranolapachone (I).

The conditions used in the condensation of allylic alcohols with hydroxyhydroquinones in these syntheses are not sufficiently acidic (oxalic acid) to bring about cyclization of the geranyl group during the condensation. This is shown by the non-identity of the products obtained by the condensation of geraniol and  $\beta$ -cyclogeraniol with leucoisonaphthazarin.

#### Experimental Part<sup>3</sup>

**Isonaphthazarin.**—The following procedure represents an improvement over that reported by Fieser and Gates.<sup>1</sup> A solution of 8.9 g. of 2-hydroxy-1,4-naphthoquinone

(2) Kuhn and Hoffer, *Ber.*, 67, 357 (1934).

(3) All melting points are corrected.