

bottle was then heated to 56° and hydrogen at 50 lb. pressure admitted, whereupon three molecular equivalents of hydrogen were absorbed in 7.6 minutes. The solution, after filtration from the catalyst and decolorization with charcoal, was allowed to crystallize; an additional crop of crystals being obtained after concentration of the mother liquor. The crops were combined and recrystallized from ethanol. The product melted sharply at 129° (cor.) and the yield was 19 g. (90%).

DEPARTMENT OF RESEARCH AND CONTROL  
UNITED DRUG COMPANY  
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## American Musk. II. A Preliminary Note on the Scent Glands of the Beaver

BY PHILIP G. STEVENS

The recent discovery<sup>1</sup> that cyclopentadecanol and cycloheptadecanol can be obtained in good yields from the scent glands of the common muskrat has prompted an investigation of the scent glands of the beaver. These glands, similar to those of the muskrat in function and shape, but considerably larger in size, have been used for years in the preparation of perfumes. While their odor is not musk-like, the presence of large ring carbinols has not been excluded, and a search for these compounds has now been made.

Walbaum and Rosental<sup>2</sup> studied the steam-distillable fraction of the glandular extract, and obtained therefrom benzyl alcohol, acetophenone, *p*-ethyl and other phenols, benzoic acid and *l*-borneol. St. Pfau<sup>3</sup> confirmed these results in part, but isolated as well an odoriferous lactone of unknown structure, and more recently Yost<sup>4</sup> obtained besides a resin, castorin, cholesterol and an unidentified volatile oil. None of these workers described any large ring compounds, but, since the extracts apparently were not saponified except possibly by Yost, these carbinols may have been overlooked, especially if present, as seems to be the case with 98% of the large ring compounds of the muskrat, as non-volatile esters. The results of saponification experiments described in this note indicate that no large ring carbinols or ketones are present in beaver scent glands. To be sure, the neutral, unsaponifiable fraction yielded a small amount of a viscous yellow oil on distillation with about the correct boiling point of a musk carbinol or ketone, but this oil had the composition C<sub>11</sub>H<sub>18</sub>O<sub>2</sub> and had a spicy odor, quite unlike musk. On oxidation with chromic acid, the oil gave a product with a cedar-like odor, with, however, no reminiscence of musk.

The acid fraction yielded benzoic acid, various phenolic substances, small amounts of anisic acid,<sup>5</sup> and in addition an amorphous acid, insoluble in benzene and ether, tentatively called

(1) Stevens and Erickson, *THIS JOURNAL*, **64**, 144 (1942).

(2) Walbaum and Rosental, *J. prakt. Chem.*, **117**, 225 (1927).

(3) St. Pfau, *Perfumery and Essent. Oil Record*, **18**, 205 (1927).

(4) Yost, *C. A.*, **26**, 4131 (1932).

(5) I am indebted to Professor Werner Bergmann for help in the identification of the anisic acid.

castoric acid. Oddly there seemed to be few long chain fatty acids present. This fact coupled with the absence of musk bodies is in sharp contrast to the abundance of fatty acids in the glands of the musk-deer, the civet cat and the muskrat.

### Experimental Part

Dried beaver castors (113 g., Fritsche Bros.) were sliced and extracted with ether, and insoluble tarry material was extracted with acetone (1.9 g. of yellow-brown crystalline material which separated from the acetone was not investigated). The solvents were removed from the combined extracts, the dark colored tarry residue (70 g.) was saponified with boiling 10% ethanolic potassium hydroxide, and the neutral products were separated from the acidic. The neutral, red oil (6.3 g.) yielded, after three fractional distillations, 1.5 ml. of a viscous, yellow, unsaturated (rapid bromine absorption from acetic acid) oil, b. p. 147–155° (1 mm.) with a spicy odor. *Anal.* Calcd. for C<sub>11</sub>H<sub>18</sub>O<sub>2</sub>: C, 72.5; H, 9.9. Found: C, 72.4; H, 9.9. An oil (36.2 g.) similarly prepared from 913 g. of glands (Firmenich & Co.), yielded, after separation of a considerable amount of cholesterol, a distillate, b. p. 86–195° (10–1 mm.), which, combined with similar fractions, was distilled through an efficient column. No pure product was obtained in the range 111–146° (1 mm.) (both boiling point and viscosity increased gradually). The fraction, b. p. 132–141° (1 mm.), had a fine spicy odor, did not react with 2,4-dinitrophenylhydrazine, and on oxidation with chromic acid, gave a product with a strong cedar, but no musk, odor.

The alkaline solution from the saponification was acidified, the precipitated black-red oil extracted with ether, the ether extracted with sodium bicarbonate,<sup>6</sup> the alkaline solution acidified, the liberated acids extracted with ether, and, after removal of the solvent, steam-distilled, yielding 21.5 g. of benzoic acid. The non-volatile residue was dissolved in a large excess of hot sodium carbonate, the cooled solution, after saturation with carbon dioxide, was filtered, and the acidified filtrate deposited a dark-colored precipitate which, centrifuged from benzene twice, yielded 36 g. of air-dried castoric acid as a light chocolate powder, insoluble in ether and benzene, but soluble in methanol.

The aqueous solution separated from the castoric acid was extracted with chloroform, the organic solvent removed, the residue steam-distilled, and the cooled aqueous solution of the non-volatile products deposited crystals which after treatment with norite and crystallization from benzene yielded anisic acid, m. p. 178–180° (a mixture with an authentic sample, m. p. 180–181°, melted at 178–180.5°).

(6) The separations were made difficult by the deposition of tars. There was however no troublesome frothing of any of the alkaline solutions, indicating the absence of any long chain fatty acids.

STERLING CHEMISTRY LABORATORY  
YALE UNIVERSITY  
NEW HAVEN, CONN.

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### Preparation of Malononitrile

BY ALEXANDER R. SURREY

Malononitrile can be prepared by the dehydration of cyanoacetamide with phosphorus pentachloride, by the fusion of the dry materials.<sup>1</sup> This method is not satisfactory for the preparation of large quantities of malononitrile inasmuch as very careful manipulation is needed to prevent the violent decomposition of the product during or before its distillation. The following more convenient method has now been perfected.

(1) Corson, Scott and Vose. "Organic Syntheses," **10**, 66 (1930).

A mixture of 1260 g. (15 moles) of cyanoacetamide, 800 ml. of phosphorus oxychloride, 1000 g. of sodium chloride, and 5 liters of ethylene dichloride in a 12-liter, 3-necked, round-bottomed flask, is refluxed with stirring for eight hours. After cooling and filtration, the precipitate is washed with 500 cc. of solvent. The filtrates are combined and the ethylene dichloride distilled under reduced pressure. The residue, crude malononitrile, 790 g., is decanted and distilled in a vacuum. The colorless product, b. p. 113–118° (25 mm.), solidifies on cooling; yield, 700–720 g. (70–72%).

The reaction as carried out above proceeds smoothly and the malononitrile can be distilled without difficulty. The addition of sodium chloride<sup>2</sup> to the reaction mixture increases the yield considerably. Without it, a red viscous mass separates from the reaction mixture which can then be filtered only with difficulty. The use of sodium chloride gives lighter colored, granular precipitates which easily can be removed by filtration and washed.

(2) Kao, Yen and Chien, *J. Chinese Chem. Soc.*, **2**, 240 (1934).

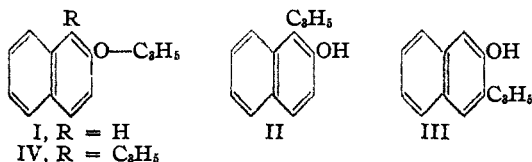
WINTHROP CHEMICAL COMPANY

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### The Pyrolysis of 1-Allyl-2-allyloxy-3-naphthoic Acid

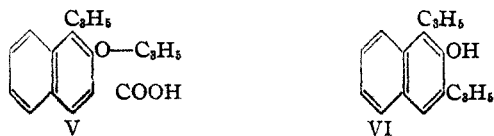
By V. P. WYSTRACH AND D. S. TARBELL

In his early work, Claisen<sup>1</sup> showed that 2-allyloxynaphthalene (I) rearranged smoothly into 1-allyl-2-naphthol (II), no 3-allyl-2-naphthol (III) being obtained.



When 1-allyl-2-allyloxynaphthalene (IV), in which the alpha position is blocked, is heated, no reaction occurs and IV remains unchanged. These findings constitute a proof that the 1,2-bond in naphthalene has more double bond character than the 2,3-bond and that the alpha position is more reactive than the beta position.<sup>1,2</sup>

Since allyl phenyl ethers containing an ortho carboxyl group rearrange much more readily with the elimination of carbon dioxide than do those without the carboxyl,<sup>3</sup> it was thought that 1-allyl-2-allyloxy-3-naphthoic acid (V) might rearrange via decarboxylation to give 1,3-diallyl-2-naphthol (VI). However, heating V at 214° for forty-eight minutes resulted in the formation of an intractable tar, although 25% of the theoretical amount of carbon dioxide was evolved. Little reaction was observed at temperatures below 200°.



(1) Claisen, *Ber.*, **45**, 3167 (1912).

(2) Fieser and Lothrop, *This Journal*, **57**, 1459 (1935).

(3) Claisen and Eisleb, *Ann.*, **401**, 21 (1912); Tarbell and Wilson, *This Journal*, **64**, 607 (1942).

This result substantiates the observations that the 2,3-bond in naphthalene has much less double bond character than the 1,2-bond and less than any bond in benzene. It is of interest to note that in a Kolbe reaction at high temperatures,  $\beta$ -naphthol gives 2-hydroxy-3-naphthoic acid rather than the 1-isomer,<sup>4</sup> indicating some reactivity at the 3-position.

### Experimental<sup>5</sup>

**Methyl 2-Hydroxy-3-naphthoate.**—The procedure of Cohen and Dudley<sup>6</sup> gave an 83% yield of this ester as pale yellow needles after one recrystallization from dilute ethanol, m. p. 74–74.5°.

**Methyl 1-Allyl-2-hydroxy-3-naphthoate.**—A solution containing 6.48 g. of sodium hydroxide in 10 ml. of water was slowly added to a refluxing mixture of 30 g. of methyl 2-hydroxy-3-naphthoate and 27.6 g. of allyl bromide in 100 ml. of methyl ethyl ketone. After six hours the solvent was distilled off, water added and the product taken up in ether. The ether was evaporated and the product subjected to a vacuum distillation during which process the allyl group rearranges to the 1-position. A fraction amounting to 31.0 g. (86.3%) was obtained at 160–162° (1 mm.).

**1-Allyl-2-allyloxy-3-naphthoic Acid (V).**—The preparation of this compound is essentially the same as that previously described for methyl 1-allyl-2-hydroxy-3-naphthoate. Ten grams of methyl 1-allyl-2-hydroxy-3-naphthoate and 7.9 g. of allyl bromide yielded 2.9 g. (26%) of the desired ether-acid, m. p. 112–113°. The intermediate methyl ester was not isolated. Saponification of the crude reaction product gave a mixture of the 2-hydroxy- and 2-allyloxy acids. They were partially separated by extraction with petroleum ether (b. p. 60–70°) in a Soxhlet apparatus and further by fractional recrystallization from dilute methanol. One more recrystallization from dilute methanol gave an analytically pure sample, m. p. 112.5–113°, as very faintly yellow prisms.

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{18}\text{O}_3$ : C, 76.10; H, 6.01; neut. equiv., 268.3. Found: C, 76.30; H, 6.0; neut. equiv., 268.5.

**Pyrolysis of 1-Allyl-2-allyloxy-3-naphthoic Acid.**—No decomposition was observed when this substance was heated at 150° for thirty minutes. At 200° slight gas evolution began after twenty minutes and the reaction product was a tar after thirty minutes. Twenty-five per cent of the theoretical amount of carbon dioxide was evolved in forty-eight minutes at 214° (refluxing methyl salicylate), but the product was an intractable tar.

(4) Fieser, in Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1943, 2nd ed., Chap. 3, p. 201.

(5) All melting points are corrected; analysis by Robert Bauman.

(6) Cohen and Dudley, *J. Chem. Soc.*, **97**, 1748 (1910), report m. p. 73–74°.

(7) Bergman and Berlin, *J. Org. Chem.*, **3**, 249 (1938).

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF ROCHESTER  
ROCHESTER, NEW YORK

RECEIVED JULY 23, 1943

## NEW COMPOUND

### 4-Methylthiazolo-(2,3-b)-tetrahydropyrimidine Hydrobromide

This substance was prepared from 2-amino-4-methylthiazole and trimethylene dibromide.