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[2] 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.

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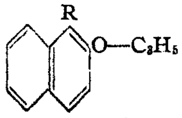
(2) Kao, Yen and Chien, *J. Chinese Chem. Soc.*, **2**, 240 (1934).

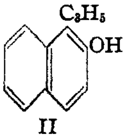
WINTHROP CHEMICAL COMPANY
RENSSELAER, NEW YORK
RECEIVED SEPTEMBER 17, 1943

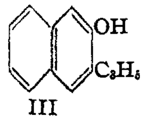
The Pyrolysis of 1-Allyl-2-allyloxy-3-naphthoic Acid

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

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

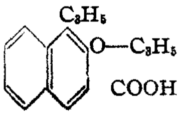

I, R = H
IV, R = C_3H_5

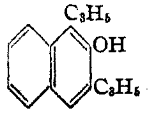

II


III

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.[1,2]

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,[3] 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°.


V


VI

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, β-naphthol gives 2-hydroxy-3-naphthoic acid rather than the 1-isomer,[4] indicating some reactivity at the 3-position.

Experimental[5]

Methyl 2-Hydroxy-3-naphthoate.—The procedure of Cohen and Dudley[6] 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.[7]—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 $C_{17}H_{16}O_3$: 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.

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(1) Claisen, *Ber.*, **45**, 3157 (1912).

(2) Fieser and Lothrop, THIS JOURNAL, **57**, 1459 (1935).

(3) Claisen and Eisleb, *Ann.*, **401**, 21 (1913); Tarbell and Wilson, THIS JOURNAL, **64**, 607 (1942).

(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.