sized and coupled to 3,3′-dimethoxymesitil and the corresponding *cis*-enediol. The *trans*-enediol has been obtained by hydrogenation of the benzil.

The corresponding enediol with methoxyl groups in the para positions, 2,2′,6,6′-tetramethyl-4,4′-dimethoxystilbenediol, has been shown to exist but is exceedingly sensitive to oxidation by the air.

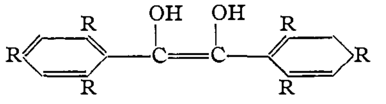
URBANA, ILLINOIS RECEIVED JUNE 19, 1941

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Enediols. IX.[1] Enediols in the Naphthalene Series

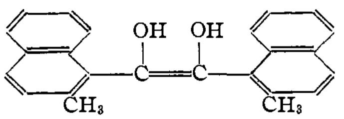
BY REYNOLD C. FUSON, C. H. MCKEEVER[2] AND LYELL C. BEHR

Enediols of type I have been prepared in which R = CH_3, C_2H_5 or $(CH_3)_2CH$. The evidence at hand with respect to these compounds suggests that their peculiar character is closely related to the aromatic nature of the rings involved. This point of view raises the question as to whether the benzene ring might not be replaced by some other aromatic nucleus. In the present work it has been shown that the naphthalene ring will serve.

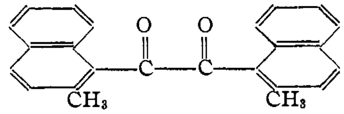


I

The enediols which have been made are the *cis* and *trans* di-(2-methyl-1-naphthyl)-acetylene glycols (II).

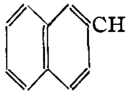


II

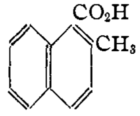


III

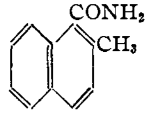
The starting point in the synthesis was 2-methylnaphthalene. Bromination of this hydrocarbon produced 2-methyl-1-bromonaphthalene[3] (IV). 2-Methyl-1-naphthoic acid (V) was made from the bromo compound by carbonation of the corresponding Grignard reagent. Several methods of carbonation were tried. The best of these involved addition of well-crushed dry-ice to the Grignard solution.[3] One of the methods studied consisted in making the nitrile from the bromo compound by the procedure of Newman.[4] The nitrile was obtained in good yield but the hydrolysis gave only traces of the desired acid. 2-Methyl-1-naphthamide (VI) was always the chief product.



IV



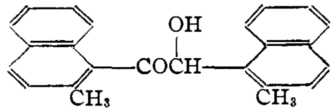
V



VI

Treatment of 2-methyl-1-naphthoyl chloride with the binary mixture, $Mg + MgI_2$,[5] gave a mixture of *cis*-di-(2-methyl-1-naphthyl)-acetylene glycol (II) and 2,2′-dimethyl-1,1′-naphthil (III). The diol was colorless and the diketone was orange-red. The use of a nitrogen atmosphere increased the quantity of the enediol at the expense of the naphthil. Hydrogenation of the naphthil could be used to obtain either the *cis* or *trans* enediol merely by changing the solvent. In methanol the *cis* compound was produced whereas in petroleum ether the *trans* isomer was the product.

The enediols could be transformed into the corresponding diacetates by heating with acetic anhydride. The keto form, 2,2′-dimethyl-1,1′-naphthoin (VII), was obtained by heating the *trans* compound with a mixture of methanol and hydrochloric acid. This change has not been observed to take place spontaneously.



VII

No satisfactory method has yet been discovered for determining the stability of enediols toward the air. It appears that the new enediols are about as stable as the hexaethylstilbenediols, less stable than the hexaisopropyl analogs and more stable than the enediols of the mesitylene series.

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(1) For the preceding communication in this series see Fuson, Corse and Welldon, THIS JOURNAL, 63, 2645 (1941).

(2) Röhm and Haas Research Assistant, 1938-1940.

(3) McGrew, Ph.D. Thesis, University of Illinois, 1938.

(4) Newman, THIS JOURNAL, 59, 2472 (1937).

(5) Gomberg and Bachmann, *ibid.*, 49, 236 (1927).

Experimental

2-Methyl-1-naphthoic Acid.—Bromination of 2-methylnaphthalene in carbon disulfide gave a 92% yield of 2-methyl-1-bromonaphthalene, boiling at 125–129° (5 mm.).

The 1-bromo compound was converted to the corresponding Grignard reagent in a mixture of ether and benzene, and dry-ice was added in portions to the solution. The acid obtained in this way was recrystallized from a mixture of acetic acid and water. It melted at 124–126°[6]; yield 72%.

Attempts to make the acid by hydrolysis of the nitrile (see below) gave low yields. Ten grams of the nitrile was heated for nine hours with a mixture of 25 cc. of sulfuric acid and 25 cc. of acetic acid. The yield of 2-methyl-1-naphthoic acid was only 1.5 g. Six grams of the corresponding amide was obtained.[6]

2-Methyl-1-naphthonitrile.—A mixture of 20 g. of 2-methyl-1-bromonaphthalene, 11 g. of cuprous cyanide and 13 cc. of dry pyridine was heated for twenty-four hours at 200–220°. The reaction mixture while still warm was poured into a dilute solution of ammonia and stirred frequently over a period of two hours. The nitrile crystallized from high-boiling petroleum ether as thin needles melting at 87–88°; yield 14.8 g.

Reaction of the Acid Chloride with the Binary Mixture.—The acid chloride was made in 95% yield by treating the acid with thionyl chloride.[6] It boiled at 158–162° (8 mm.). The solution of the binary mixture was prepared as follows. Six grams of magnesium, 150 cc. of dry benzene, 80 cc. of dry ether and a small amount of iodine were heated to reflux. After the reaction had started more iodine was added, in small portions, until the total was 30 g. Stirring was continued for one and a half hours, during which time the reaction mixture became almost colorless. A solution of 18 g. of 2-methyl-1-naphthoyl chloride in 25 cc. of dry ether was added over a period of one hour. The mixture was heated and stirred for eight hours more and poured into a mixture of ice and glacial acetic acid. The organic layer was washed rapidly with water, with 5% potassium bicarbonate, twice with 5% sodium thiosulfate and again with water. After the solvents had been evaporated rapidly with the aid of a water pump, the residue was digested with 35 cc. of benzene and the enediol removed by filtration. The yield of diol was 4 g.; m. p. 186–188°.

Treatment with acetic anhydride converted the *cis*-enediol to the corresponding diacetate, melting at 198–199°.

The enediol was white when first obtained but turned yellow on exposure to the air. The change occurred much more rapidly when the enediol solution was allowed to come in contact with the air. The yield was increased when the preparation was carried out in an atmosphere of nitrogen. If the original reaction mixture was freed from benzene by evaporation and the residue crystallized from acetone (by spontaneous evaporation of the solvent) some 2,2′-dimethyl-1,1′-naphthil could be obtained. The remaining material was a dark sticky tar.

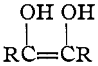
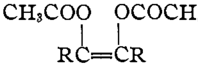
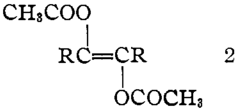
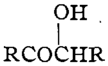
The diketone could be made in good yield by oxidation of the *cis*-enediol with hydrogen peroxide. It could also be prepared by shaking an alkaline solution of the enediol in the air. It was orange-red and melted at 160–160.5°.

Catalytic Hydrogenation of the Diketone.—A mixture of 2,2′-dimethyl-1,1′-naphthil with Adams platinum oxide catalyst was shaken on a low pressure hydrogenation machine for fourteen hours at the end of which time the solution had become colorless. The product was the *cis*-enediol, melting at 184–187°. When the solvent was high-boiling petroleum ether the product was the *trans*-enediol which did not melt sharply but gave the *trans* diacetate when treated with acetic anhydride.

Isomerization of the trans-Enediol to the Naphthoin.—A mixture of 0.2 g. of the *trans*-enediol, 3 cc. of methanol and 3 cc. of concentrated hydrochloric acid was heated under reflux for one hour and poured into 50 cc. of water. The naphthoin was obtained as white, fluffy needles, melting at 149–151.5°.

In the table are shown the important data regarding the various new compounds reported in this paper.

TABLE I

Compound	M. p., °C.	Analyses, %[a] Calcd. C	H	Found C	H
RCN[b]	87–88[c]	86.18	5.43	86.41	5.62
 $\overset{\text{OH}}{\text{RC}}=\overset{\text{OH}}{\text{CR}}$	186–188	84.68	5.92	84.69	6.00
RCOCOR	160–160.5	85.18	5.36	85.30	5.40
 $\overset{\text{CH}_3\text{COO}}{\text{RC}}=\overset{\text{OCOCH}_3}{\text{CR}}$	198–199	79.22	5.70	79.28	5.78
 $\overset{\text{CH}_3\text{COO}}{\text{RC}}=\underset{\text{OCOCH}_3}{\text{CR}}$	267–270	79.22	5.70	78.95	5.86
 $\text{RCO}\overset{\text{OH}}{\text{CH}}\text{R}$	149–151.5	84.66	5.93	84.56	6.02

[a] The microanalyses reported in this paper were carried out by Mr. L. G. Fauble and Miss Mary S. Kreger. [b] R = 2-Methyl-1-naphthyl. [c] All melting points are corrected.

Summary

2,2′-Dimethyl-1,1′-naphthil has been prepared and converted into the corresponding enediols. Only the *cis*-form was characterized. Its properties indicated that the naphthalene nucleus has about the same effect as that of benzene on the stability of the enediol group.

URBANA, ILLINOIS RECEIVED JULY 14 1941

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(6) Mayer and Sieglitz, *Ber.*, **55**, 1835 (1922).