employing methyl propionate instead of methyl benzoate. The copper chelate (m.p. 292° dec.) was acidified to give after recrystallization from benzene, 1.5 g. (13%) of β-diketone IX, m.p. 132–134°. One more recrystallization raised the melting point of IX to 135–136.5°.

Anal. Calcd. for $C_{13}H_{15}O_3N$: C, 66.93; H, 6.48; N, 6.01. Found: C, 66.76; H, 6.36; N, 5.92.

Benzoylation of p-hydroxyacetophenone to form β-diketone X. To a stirred suspension of 0.19 mole of sodium amide in 300 ml. of liquid ammonia[11] was added through a powder funnel 8.65 g. (0.063 mole) of *p*-hydroxyacetophenone. After 1 hr., 17.3 g. (0.127 mole) of methyl benzoate in an equal volume of dry ether was added over 15 min., and the liquid ammonia replaced by dry ether. The resulting ether suspension was stirred and refluxed for 2.5 hr. Dry benzene (250 ml.) was then added, and most of the ether distilled off. The resulting benzene suspension was refluxed for 24 hr. The mixture was added to crushed ice. After the ice had melted, the water layer was separated and filtered through Amend hyflo supercell (on a filter paper in a Büchner funnel) and then acidified with iced 6*N* hydrochloric acid. The precipitated oil was taken up in ether and dried over magnesium sulfate. The solvent was removed to give 13.3 g. of golden oil which gave, on recrystallization from benzene, 3.30 g. of 1-*p*-hydroxyphenyl-3-phenylpropane-1,3-dione (X), m.p. 146–153°. More (2.3 g.) of β-diketone X was isolated from the mother liquor through the copper chelate; total yield, 37%. Two recrystallizations from benzene raised the melting point of X to 154–156°.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.33; H, 5.05.

DURHAM, N. C.

[CONTRIBUTION FROM THE RADIUM INSTITUTE OF THE UNIVERSITY OF PARIS]

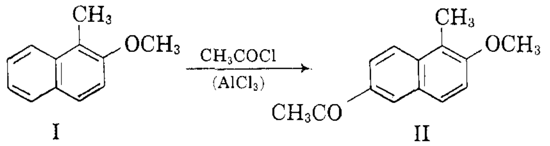
Orientation in Friedel-Crafts Reactions with 2-Methoxy-1-methylnaphthalene

NG. PH. BUU-HOÏ AND DENISE LAVIT

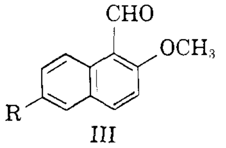
Received February 1, 1957

The acyl group in the Friedel-Crafts acetylation product (II) of 2-methoxy-1-methylnaphthalene in nitrobenzene is shown to enter position 6. The proof is based on the identity of the Kishner-Wolff reduction product of II and that of 1-formyl-2-methoxy-6-ethylnaphthalene, prepared by formylation of 2-methoxy-6-ethylnaphthalene. In the course of this work, a number of new homologs of 6-substituted naphthols, naphthaldehydes, naphthalene ketones, and their derivatives were prepared.

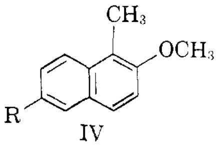
2-Methoxynaphthalene is known to undergo Friedel-Crafts acylations with aliphatic acid chlorides in nitrobenzene medium to give, as the isolated products, primarily the 6-acyl derivative, and some of the 8-acyl isomer; with carbon disulfide as solvent, substitution takes place predominantly in position 1.[1] It was of interest to investigate the behavior of 1-alkyl-2-naphthols in similar Friedel-Crafts reactions.



I II

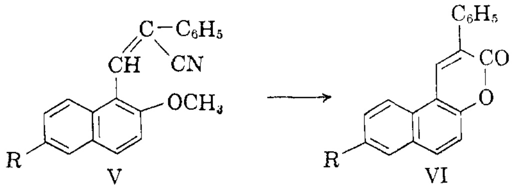


III



IV

A convenient intermediate was 2-methoxy-1-methylnaphthalene (I), readily prepared by Kishner-Wolff reduction of 2-methoxy-1-naphthaldehyde. Acetylation of compound I, effected in nitrobenzene medium by Robinson and Weygand,[2] afforded a reaction product which, without proof of constitution, they considered to be 6-methoxy-5-methylacetonaphthone (II). Such a proof was now provided, by Kishner-Wolff reduction of this ketone to 6-ethyl-2-methoxy-1-methylnaphthalene (IV; R = C_2H_5), which was found to be identical with a sample prepared by Kishner-Wolff reduction of 6-ethyl-2-methoxy-1-naphthaldehyde (III; R = C_2H_5). The latter aldehyde was readily prepared by formylation[3] of 6-ethyl-2-methoxynaphthalene with dimethylformamide in the presence of phosphorus oxychloride. The position taken by the formyl group in this reaction was ascertained by condensation of the aldehyde (III; R = C_2H_5) with benzyl cyanide to give the diarylacrylonitrile (V; R = C_2H_5), which yielded on demethylation with pyridine hydrochloride 3′-



V VI

---

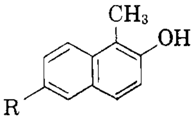
(1) L. Gattermann, R. Ehrhardt, and H. Maisch, *Ber.*, **23**, 1199 (1890); M. L. Rousset, *Bull. soc. chim. Belges*, [3] **15**, 633 (1896); R. R. Galle, *J. Gen. Chem. U.S.S.R.*, **8**, 402 (1938).

(2) R. Robinson and F. Weygand, *J. Chem. Soc.*, 389 (1941).

(3) For similar formylations of naphthol ethers with dimethylformamide, see N. P. Buu-Hoï and D. Lavit, *J. Chem. Soc.*, 2776 (1955).

ethyl-3-phenyl-5,6-benzocoumarin (VI; R = C_2H_5); this coumarin cyclization of diarylacrylonitriles derived from methoxy aldehydes has often been used as proof of the position *ortho* to a methoxy radical occupied by the formyl group.[4] 6-*n*-Propyl-2-methoxynaphthalene was similarly formylated to 2-methoxy-6-*n*-propyl-1-naphthaldehyde (III; R = n-C_3H_7), which underwent condensation with benzyl cyanide to a diarylacrylonitrile (V; R = n-C_3H_7), and this in turn was demethylated to 3-phenyl-3′-*n*-propyl-5,6-benzocoumarin (VI; R = n-C_3H_7). Kishner-Wolff reduction of the aldehyde (III; R = n-C_3H_7) yielded 2-methoxy-1-methyl-6-*n*-propylnaphthalene (IV; R = C_3H_7), a product identical with that obtained by similar reduction of the propionylation product of 2-methoxy-1-methylnaphthalene.

The ready accessibility of 6-alkyl-2-methoxy-1-methylnaphthalenes provided a convenient route to 6-alkyl-1-methyl-2-naphthols, which were obtained by demethylation with pyridine hydrochloride; 6-ethyl-1-methyl-2-naphthol (VII; R = C_2H_5) and 1-methyl-6-*n*-propyl-2-naphthol (VII; R = n-C_3H_7) were thus prepared in excellent yield.



(VII, R = C_2H_5 or n-C_3H_7)

The fact that the Friedel-Crafts acetylation of 2-methoxy-1-methylnaphthalene occurred only at position 6, whereas under the same experimental conditions 2-methoxynaphthalene would yield a mixture of the 6- and 8-acetyl derivatives, could possibly be explained on the grounds of steric hindrance exerted on position 8 by the *peri*-methyl group.

In the course of this work, a number of further new derivatives, including several chalcones, in the naphthalene series were prepared, and are reported below.

EXPERIMENTAL[5]

Preparation of 6-ethyl-2-methoxynaphthalene. The following method, which was found more satisfactory than Lévy's procedure,[6] gave a much purer product: A solution of 66.5 g. of recrystallized 2-methoxy-6-acetonaphthone (m.p. 111°) and 67 g. of 98% hydrazine hydrate in 400 ml. of diethylene glycol was heated at 120° for a few minutes to allow the hydrazone to form. After cooling, 55 g. of potassium hydroxide was added, and the mixture refluxed for 90 min., with removal of water. Water was added on cooling, the reduction product taken up in benzene, the benzene solution washed first with dilute hydrochloric acid, then with water, dried over calcium chloride, and the solvent distilled. Fractionation of the residue *in vacuo* yielded 50 g. of 6-ethyl-2-methoxynaphthalene, b.p. 160–161°/14 mm., crystallizing from ethanol in lustrous leaflets, m.p. 62°; Lévy[6] gave m.p. 58° for a less pure product.

6-Ethyl-2-methoxy-1-naphthaldehyde (III; R = C_2H_5). To 48.5 g. of the foregoing ether and 22.8 g. of dimethylformamide, 48.5 g. of phosphorus oxychloride was carefully added, and the mixture refluxed for 5 hr. on the water bath. To the reaction product, a saturated aqueous solution of sodium acetate was added, and refluxing was resumed for a further 30 min. The aldehyde formed was taken up in benzene, the benzene layer washed with dilute hydrochloric acid, then with water, dried over calcium chloride, and the solvent removed. Vacuum fractionation of the residue yielded 47 g. of a product, b.p. 210–211°/12 mm., crystallizing from ethanol in shiny colorless needles, m.p. 61°. The halochromy in sulfuric acid was deep yellow.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.5; H, 6.6. Found: C, 78.4; H, 6.6.

6-Ethyl-2-methoxy-1-methylnaphthalene (IV; R = C_2H_5). (a) Forty-four grams of the foregoing aldehyde dissolved in 260 ml. of diethylene glycol was reduced with 44 g. of hydrazine hydrate and 39 g. of potassium hydroxide in the usual way. Yield: 32.5 g. of a product, b.p. 178–180°/17 mm., crystallizing from ethanol in lustrous colorless leaflets, m.p. 41°.

Anal. Calcd. for $C_{14}H_{16}O$: C, 84.0; H, 8.1. Found: C, 83.7; H, 8.2.

(b) A similar reduction, performed with 20 g. of the acetylation product of 2-methoxy-1-methylnaphthalene (m.p. 97–98°, prepared according to Robinson and Weygand[2]), yielded 16 g. of the same product.

6-Ethyl-1-methyl-2-naphthol (VII; R = C_2H_5). A mixture of 5 g. of 6-ethyl-2-methoxy-1-methylnaphthalene and 20 g. of redistilled pyridine hydrochloride was refluxed for 20 min.; after cooling, dilute hydrochloric acid was added, and the solid formed taken up in chloroform. The chloroform solution was then washed with water and dried over sodium sulfate, and the solvent removed. Recrystallization of the residue from cyclohexane yielded 3.5 g. of colorless prisms, m.p. 102°.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.8; H, 7.6. Found: C, 83.6; H, 7.6.

1-Phenyl-2-(6-ethyl-2-methoxy-1-naphthyl)acrylonitrile (V; R = C_2H_5). A solution of 0.8 g. of 6-ethyl-2-methoxy-1-naphthaldehyde and 0.48 g. of benzyl cyanide in warm ethanol was treated with a few drops of a 20% aqueous solution of sodium hydroxide. The solid precipitate which formed almost immediately, crystallized from ethanol in yellowish needles (0.7 g.), m.p. 136°. The solutions in sulfuric acid were yellow.

Anal. Calcd. for $C_{22}H_{19}NO$: C, 84.3; H, 6.1. Found: C, 84.0; H, 6.2.

3′-Ethyl-3-phenyl-5,6-benzocoumarin (VI, R = C_2H_5). A mixture of 0.5 g. of the foregoing acrylonitrile and 5 g. of pyridine hydrochloride was refluxed for 10 min.; on cooling, dilute hydrochloric acid was added, the mixture then boiled, and the precipitate collected after cooling. Recrystallization from ethanol afforded 0.3 g. of pale yellow needles, m.p. 141°; the ethanol solutions gave a violet-blue fluorescence.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.4. Found: C, 83.9; H, 5.5.

2-Methoxy-6-n-propylnaphthalene. This ether[7] was prepared from 100 g. of 2-methoxy-6-propionaphthone (m.p. 111°), 100 g. of hydrazine hydrate, and 83 g. of potassium hydroxide in 600 ml. of diethylene glycol. Yield: 79 g. of a product, b.p. 171–172°/13 mm., which crystallized from ethanol in lustrous colorless leaflets, m.p. 56°.

Anal. Calcd. for $C_{14}H_{16}O$: C, 84.0; H, 8.1. Found: C, 84.0; H, 8.0.

---

(4) N. P. Buu-Hoï, B. Eckert, and R. Royer, *J. Org. Chem.*, **19**, 1548 (1954); N. P. Buu-Hoï and D. Lavit, *J. Org. Chem.*, **21**, 21 (1956); *J. Chem. Soc.*, 1743 (1956).

(5) With Miss J. Collard.

(6) G. Lévy, *Compt. rend.*, **202**, 1679 (1936).

(7) R. D. Desai and W. S. Waravdekar [*Proc. Indian Acad. Sci.*, **24A**, 382 (1946)] gave m.p. 49–50° for an impure sample of this substance.

As a by-product of the reduction, the corresponding *azine* was obtained; it crystallized from benzene in silky yellow needles, m.p. 241°.

2-Methoxy-6-n-propyl-1-naphthaldehyde (III; R = n-C_3H_7). This was prepared from 78 g. of the foregoing ether, 37 g. of dimethylformamide, and 78 g. of phosphorus oxychloride in the usual way. Yield: 75 g. of an *aldehyde,* b.p. 216–218°/13 mm., crystallizing from ethanol in shiny colorless prisms, m.p. 49°.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.9; H, 7.1. Found: C, 78.7; H, 7.2.

The corresponding *thiosemicarbazone* crystallized from ethanol in shiny yellowish leaflets, melting with decomposition around 258°.

Anal. Calcd. for $C_{16}H_{19}N_3OS$: N, 14.0. Found: N, 13.7.

2-Methoxy-1-methyl-6-n-propylnaphthalene (IV; R = n-C_3H_7) was prepared from 67 g. of the foregoing aldehyde, 67 g. of hydrazine hydrate, and 60 g. of potassium hydroxide in 400 ml. of diethylene glycol. Yield, 56 g. of an *ether,* b.p. 183–185°/15 mm., crystallizing from ethanol in lustrous colorless leaflets, m.p. 35°.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.1; H, 8.5. Found: C, 84.0; H, 8.5.

1-Methyl-6-n-propyl-2-naphthol (VII; R = n-C_3H_7). Demethylation of 53 g. of the foregoing ether with 200 g. of pyridine hydrochloride yielded 44 g. of a *naphthol,* b.p. 194–195°/15 mm., crystallizing from cyclohexane in colorless leaflets, m.p. 99°.

Anal. Calcd. for $C_{14}H_{16}O$: C, 84.0; H, 8.1. Found: C, 83.7; H, 8.3.

1-Phenyl-2-(2-methoxy-6-n-propyl-1-naphthyl)acrylonitrile (V; R = n-C_3H_7) was obtained from 1 g. of 2-methoxy-6-n-propyl-1-naphthaldehyde and 0.56 g. of benzyl cyanide with a few drops of 20% aqueous sodium hydroxide. This *nitrile* crystallized from ethanol in silky yellowish needles (0.9 g.), m.p. 126°.

Anal. Calcd. for $C_{23}H_{21}NO$: C, 84.4; H, 6.5. Found: C, 84.1; H, 6.6.

3-Phenyl-3'-n-propyl-5,6-benzocoumarin (VI; R = n-C_3H_7). A mixture of 0.5 g. of the foregoing nitrile and 5 g. of pyridine hydrochloride was treated as for the lower homolog, to give 0.3 g. of a *coumarin,* crystallizing from ethanol in long yellowish needles, m.p. 136°. The solutions in ethanol or acetone showed a strong violet-blue fluorescence, and the halochromy in sulfuric acid was greenish-yellow.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.1; H, 5.8. Found: C, 84.0; H, 5.7.

Chalcones derived from 2-methoxy-6-acetonaphthone. These compounds were readily prepared by adding a few drops of a 20% aqueous solution of sodium hydroxide to a warm ethanolic solution of equimolar amounts of 2-methoxy-6-acetonaphthone and the appropriate aldehyde. The *2-furylidene derivative* crystallized from ethanol in fine yellowish needles, m.p. 112°, giving a crimson halochromy in sulfuric acid.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.7; H, 5.1. Found: C, 77.5; H, 5.4.

The *p-anisal derivative* crystallized from ethanol in shiny, pale yellow leaflets, m.p. 131°; deep red halochromy in sulfuric acid.

Anal. Calcd. for $C_{21}H_{18}O_3$: C, 79.2; H, 5.7. Found: C, 79.1; H, 5.9.

The *α-naphthylidene* derivative crystallized from a mixture of ethanol and benzene in pale yellow leaflets, m.p. 173°; violet halochromy in sulfuric acid.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.2; H, 5.4. Found: C, 84.9; H, 5.3.

PARIS (V^e), FRANCE