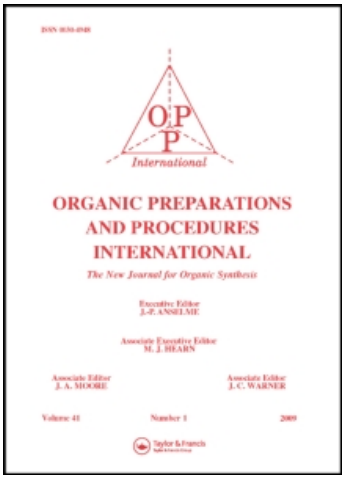

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IMPROVED SYNTHESIS OF 3-METHYL-2-NAPHTHOIC ACID

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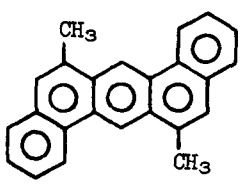
The Elbs pyrolysis of 2,3-dimethyl-1-naphthyl 3'-methyl-2'-naphthyl ketone (2) was considered as a possible route to 6,13-dimethyldibenz[a,h]-anthracene (1). For this purpose, the Friedel-Crafts reaction of 3-methyl-2-naphthoyl chloride with the readily available 2,3-dimethylnaphthalene (3) was considered as a good approach to the synthesis of 2. For this, a good route to 3-methyl-2-naphthoic acid (4) from 3 was needed as the three earlier reported syntheses of 4 did not seem good. In this paper, we describe an efficient synthesis of 4 from 3 which may in principle be applied to any symmetrically substituted dimethyl aromatic hydrocarbon.



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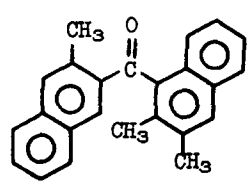

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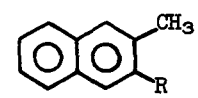

3 (R = CH_3)
4 (R = COOH)
5 (R = CH_2Br)
6 (R = CHO)

On treatment of 3 with NBS a mixture of products rich in 2-bromomethyl-3-methylnaphthalene (5)[7] was obtained. Rather than to try to obtain pure 5, the mixture was treated with hexamethylenetetramine to yield

2-methyl-3-naphthaldehyde (6)[8] and the latter was oxidized by silver nitrate under alkaline conditions to yield 4.[6] The overall yield from 3 to 4 was 69%.

When the acid chloride of 4 was condensed with 3 using aluminum chloride in o-dichlorobenzene a mixture of three isomeric ketones was obtained.[9] As this mixture was difficult to separate no further work with it was done. The desired ketone (2) was prepared by reaction of 2,3-dimethylnaphthylmagnesium bromide with 6 to yield 2,3-dimethyl-1-naphthyl 3'-methyl-2'-naphthyl carbinol (7) which was oxidized to 2. The attempted Elbs pyrolysis of 2 to 1 afforded a mixture of hydrocarbons.

EXPERIMENTAL

2-Methyl-3-naphthoic Acid (4). - A mixture of 156 g of 2,3-dimethylnaphthalene, 190 g of N-bromosuccinimide, and 5 g of benzoyl peroxide in 750 ml of carbon tetrachloride was refluxed for 1 hr. After cooling the solid was filtered and the solvent was removed from the filtrate on a rotary evaporator. The residue was heated at reflux with 300 g of hexamethylenetetramine in 800 ml of acetic acid and 400 ml of water for 3 hr. The mixture was cooled, treated slowly with 400 ml of concentrated hydrochloric acid, and heated at reflux for 1 hr. After cooling, an extract of the product in benzene-ether was washed with sodium carbonate and saturated salt solution. Removal of the solvent and crystallization of the residue from alcohol-water yielded 133 g (78%) of 6 as a colorless solid, mp 118-120°. This aldehyde (lit.[8] mp 124-125°) was sufficiently pure for oxidation to 4. The 2,4-dinitrophenylhydrazone, mp 238-239° was formed in high yield.

Anal. Calcd for $C_{18}H_{14}N_4O_4$: C, 61.7; H, 4.0; N, 16.0.

Found: C, 62.0; H, 4.0; N, 16.0.

In a typical oxidation, a solution of 50 g of sodium hydroxide in 250 ml of water and 750 ml of ethanol was added dropwise during 1 hr to a stirred solution under nitrogen of 51.0 g of 6 and 120 g of silver nitrate in 1500 ml of 80% alcohol. After a further 2 hr at room temperature the black precipitate of silver[10] was removed by suction filtration and washed further with aqueous alkali. The filtrate and washings were diluted with 500 ml of water and acidified with hydrochloric acid to yield 49.0 g (88%) of 4, mp 195-198°. Recrystallization from toluene afforded pure 4, mp 202-203° (lit.[5,6] mp 199°, 202-203°) with little loss.

2,3-Dimethyl-1-naphthyl 3'-Methyl-2'-naphthyl Carbinol (7). - To the Grignard reagent prepared from 85.0 g of 1-bromo-2,3-dimethylnaphthalene[11] and a small amount of ethylene dibromide[12] in 500 ml of ether and 200 ml of benzene was added a solution of 51.0 g of 6 in 500 ml of benzene and 250 ml of ether. After 8 hr at reflux the cooled mixture was added to cold dil. HCl. After a conventional workup, a concentrated benzene solution of the crude product was passed through a short column of neutral alumina. The benzene was removed on a rotary evaporator and the residue was crystallized from petroleum ether-absolute ethanol to yield 36.0 g (37%) of 7, mp 129-131°. The analytical sample, mp 133-134°, was obtained on crystallization from petroleum ether-benzene with little loss.

Anal. Calcd for $C_{24}H_{22}O$: C, 82.2; H, 6.8.

Found: C, 82.4; H, 6.8.

2,3-Dimethyl-1-naphthyl 3'-Methyl-2'-naphthyl Ketone (2). - A solution of 32.6 g of 7 in 200 ml of pyridine was added slowly to a solution of 35.0 g of chromic oxide in 500 ml of pyridine.[13] After stirring at room temperature for 2 hr the mixture was poured into dil. HCl. The organic product was isolated by extraction with ether-benzene. After removal

of solvents the residue was crystallized from ethanol-water to yield 29.1 g (90%) of 2, mp 167.0-169.5°. The analytical sample, mp 170-171°, was obtained with little loss by recrystallization from hexane.

Anal. Calcd for $C_{24}H_{20}O$: C, 88.9; H, 6.2.

Found: C, 88.8; H, 6.4.

Pyrolysis of 2. - After pyrolysis of 26.0 g of 2 at 450° for 30 min the mixture was distilled at 0.4 mm. After charcoal treatment followed by treatment with 2,4,7-trinitrofluorenone[14] 2.4 g of a red solid, mp 253-254° was obtained.

Anal. Calcd for $C_{37}H_{23}N_3O_7$: C, 71.5; H, 3.7; N, 6.8.

Found: C, 71.3; H, 3.9; N, 6.6.

Chromatography of this derivative over basic alumina followed by several recrystallization of the eluate residue from benzene-ethanol yielded 0.9 g of colorless solid, mp 204-210°. This material gave correct C and H analyses and mass spectrum for $C_{24}H_{18}$, expected for 1 but the nmr showed that the compound was still not pure. The nmr had methyl peaks at 7.30 τ (s) and 7.22 τ (s) in a ratio of 9:1 respectively. Hence the Elbs reaction is unsuitable for preparation of pure 1.

Anal. Calcd for $C_{24}H_{18}$: C, 94.1; H, 5.9.

Found: C, 94.0; H, 6.0.

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