

## Autoxidation of 3,4-Dihydro-1-methylnaphthalen-2(1H)-one

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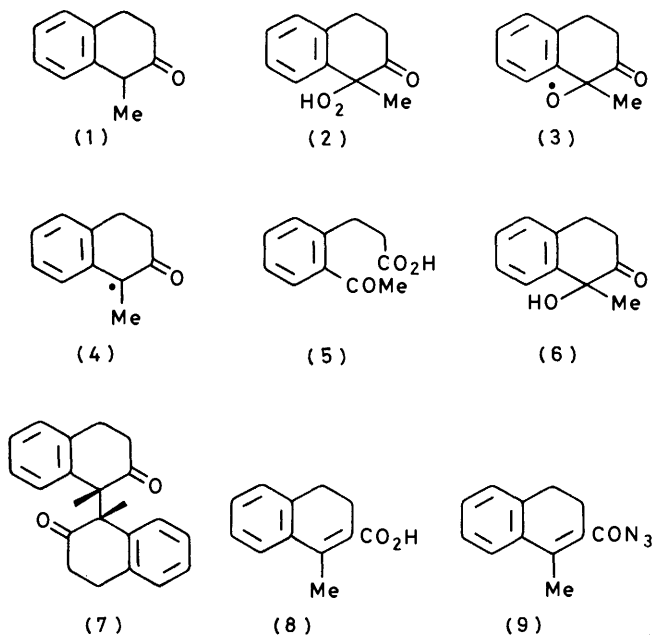
3,4-Dihydro-1-methylnaphthalen-2(1H)-one (1) is found to undergo autoxidation giving at least three distinct crystalline products, namely, 3-(2-acetylphenyl)propionic acid (5), 1,1'-bi-[3,4-dihydro-1-methylnaphthalen-2(1H)-one] (7), and 3,4-dihydro-1-hydroxy-1-methylnaphthalen-2(1H)-one (6). A new synthesis of the ketone (1) is described using a modified Curtius reaction with 3,4-dihydro-1-methyl-2-naphthoic acid (8) which excludes the use of any oxidising agent.

3,4-DIHYDRO-1-METHYLNAPHTHALEN-2(1H)-ONE (1) and its benzo-fused analogues have been extensively used for the synthesis of terpenoid and steroidal systems. Two methods are available for their preparation: (i) methylation of the corresponding 3,4-dihydronaphthalen-2(1H)-ones (2-tetralones),<sup>1</sup> preferably *via* enamines<sup>2</sup> and (ii) peracid oxidation of 3,4-dihydro-1-methylnaphthalenes<sup>3</sup> [easily accessible from 3,4-dihydro-naphthalen-1(2H)-ones (1-tetralones) by reaction with

ketones [as (1)] with a tertiary benzylic proton are prone to autoxidation but in spite of a great deal of work done with these ketones, no such report has yet been made. We record here our observation on autoxidation of the ketone (1) which affords at least three distinct crystalline products.

When the ketone (1) was left exposed to air for a prolonged period or when air was bubbled through it for a few days at room temperature or below, crystals started to separate out leaving the liquid slightly yellowish. The change occurred equally well in the dark and in diffused or direct sun light. The major component (*ca.* 30%) was an acid identified as 3-(2-acetylphenyl)propionic acid (5).<sup>5</sup> The crystalline solid separating from the liquid was found to be a dimeric product (7) isolated in 10–15% yield. The structure was established by spectral data: i.r. showed a saturated ketonic band at 1705 cm<sup>-1</sup>, n.m.r. had the methyl protons as a singlet at  $\tau$  8.15, and the mass spectra showed up a very weak parent peak at 318 (supported by molecularweight determination by Rast method), the major *m/e* peak being at 160 (same as the original ketone) which was conceivably due to the weak pivot bond joining two stable benzyl radicals and a ready McLafferty rearrangement as shown below. Chromatography of the residual liquid afforded yet another new compound identified as the keto-alcohol (6) isolated in 2–5% yield. The rest of the material consisted of the unchanged ketone (*ca.* 30%) and an unidentified gum. A trace amount of phenolic compound, probably 1-methyl-2-naphthol was also detected but not identified.

The reaction presumably goes through a number of intermediates, *e.g.* the hydroperoxide (2),<sup>6</sup> and the radicals (3) and (4), which are transformed into the products (5), (6), and (7) respectively. The hydroperoxide (2) was, however, not isolated. The ketone (1) used in the



methylmagnesium iodide] and the esters of 3,4-dihydro-1-methyl-2-naphthoic acids (as 8)<sup>4</sup> followed by acidic hydrolysis of the resultant epoxides in each case. The

<sup>1</sup> J. W. Cornforth, R. H. Cornforth, and R. Robinson, *J. Chem. Soc.*, 1942, 689.

<sup>2</sup> G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, 1963, **85**, 207.

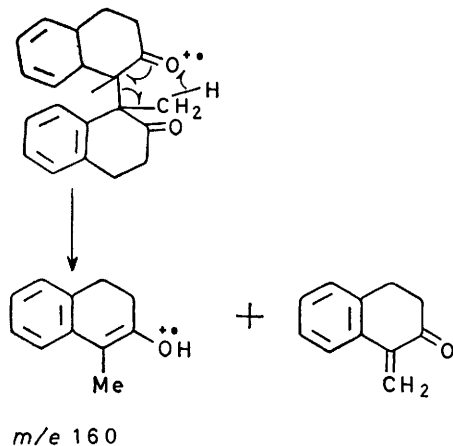
<sup>3</sup> R. Ghosh and R. Robinson, *J. Chem. Soc.*, 1944, 506; F. H. Howell and D. A. H. Taylor, *ibid.*, 1958, 1248; D. A. H. Taylor, *ibid.*, 1961, 3319; G. Stork, A. Meisels, and J. E. Davies, *J. Amer. Chem. Soc.*, 1963, **85**, 3419, and references cited therein.

<sup>4</sup> E. Wenkert and S. A. Greenfield, *Chem. and Ind.*, 1967, 1252.

<sup>5</sup> Y. Odaira and S. Tsutsumi, *Technol. Rept. Osaka Univ.*, 1958, **8**, 455 (*Chem. Abs.*, 1959, **53**, 18,921b).

<sup>6</sup> E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt, Rinehart, Winston, New York, 1959, p. 705, and references cited therein.

above experiments was prepared by perbenzoic acid oxidation of 3,4-dihydro-1-methylnaphthalene<sup>3</sup> and so the possibility of peroxide impurity which might trigger the autoxidation could not be wholly ignored. An alternative method of its preparation was, therefore, devised which excluded the use of any oxidising agent.



It consisted of cyclodehydration of ethyl  $\alpha$ -phenethylacetylacetate<sup>7</sup> followed by a modified Curtius reaction<sup>8,9</sup> on the resultant 3,4-dihydro-1-methyl-2-naphthoic acid (8). The ketone (1) obtained in 45% yield through the intermediate acid azide (9) underwent autoxidation in a similar fashion.

#### EXPERIMENTAL

<sup>1</sup>H N.m.r. spectra were measured with a Varian T60 60 MHz spectrometer for solutions in [<sup>2</sup>H]chloroform with tetramethylsilane as internal standard. Mass spectra were determined with a Hitachi RMU-6L spectrometer by using the direct inlet system. M.p.s were taken for samples in open capillaries in a sulphuric acid bath. The homogeneity of compounds was checked by t.l.c. on silica gel.

**3,4-Dihydro-1-methyl-2-naphthoic Acid (8).**—Ethyl  $\alpha$ -phenethylacetoacetate was cyclized with concentrated sulphuric acid according to known procedure<sup>7</sup> to afford 3,4-dihydro-1-methyl-2-naphthoic acid (8), m.p. 131–132 °C (methanol) in 50% yield.

**3,4-Dihydro-1-methylnaphthalen-2(1H)-one (1).**—The foregoing acid (5 g, 0.026 mol) was dissolved in dry acetone (80 ml), chilled to –5 °C, and triethylamine (4.62 g, 0.046 mol) was added dropwise with stirring under nitrogen. Ethyl chloroformate (5.0 g, 0.046 mol) was then introduced and the mixture was stirred in the cold for 30 min. A solution of sodium azide (3.9 g, 0.06 mol) in water (10 ml) was added dropwise and the stirring continued for 1 h more at 0 °C. The mixture was poured into ice-water, the precipitated azide (9) was filtered off, taken up in toluene (50 ml), and the solution heated on a steam-bath until gas evolution ceased (1 h). Toluene was removed under reduced pressure and the crude isocyanate was refluxed with a mixture of hydrochloric acid (25 ml), acetic acid (25 ml), and water (25 ml) for 24 h under nitrogen. The cooled solution was diluted with water, the organic matter extracted with ether, and the ethereal layer was washed with aqueous sodium hydrogen carbonate. The residue after

removal of ether was distilled to give 3,4-dihydro-1-methylnaphthalen-2(1H)-one (1) as an oil (1.93 g, 45%), b.p. 130 °C at 15 mmHg,  $n_D^{30}$  1.5516; semicarbazone, m.p. 202 °C (lit.,<sup>7</sup> m.p. 202 °C).

**Autoxidation of 3,4-Dihydro-1-methylnaphthalen-2(1H)-one (1).**—Air was bubbled through the ketone (1) (9.0 g) for 10–14 days when the colour of the liquid turned yellow and a crystalline solid separated out. This was filtered and washed successively with light petroleum (b.p. 40–60 °C) and a little of ether. The 1,1'-bi[3,4-dihydro-1-methylnaphthalen-2(1H)-one] (7) thus obtained crystallised from ethyl acetate as white needles (1.0–1.30 g), m.p. 146–147 °C (Found: C, 82.9; H, 7.25. C<sub>22</sub>H<sub>22</sub>O<sub>2</sub> requires C, 83.0; H, 6.9%);  $\nu_{\max}$  (Nujol) 1705 cm<sup>-1</sup>;  $\tau$ (CDCl<sub>3</sub>) 2.70–3.20 (8 H, m, ArH), 7.70–8.10 (8 H, m, 4 × CH<sub>2</sub>), and 8.15 (6 H, s, 2 × Me);  $m/e$  318 (M<sup>+</sup>, 0.04%), 160 (100), 158 (24), 145 (9), 131 (45), 118 (77), 117 (76), 115 (46), and 91 (18).

**3-(2-Acetylphenyl)propionic Acid (5).**—The residual liquid in the above experiment was taken up in ether and the ethereal solution extracted with aqueous sodium hydrogen carbonate. The alkaline solution on acidification afforded 3-(2-acetylphenyl)propionic acid (3.1 g), m.p. 72–73 °C (benzene-petroleum) (Found: C, 68.5; H, 6.4%; M<sup>+</sup> 192. Calc. for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>: C, 68.75; H, 6.25%; M<sup>+</sup> 192). (CHCl<sub>3</sub>) 1710 and 1680 cm<sup>-1</sup>;  $\nu_{\max}$  (CHCl<sub>3</sub> + Et<sub>3</sub>N) 1680 cm<sup>-1</sup>;  $\tau$ (CDCl<sub>3</sub>) 2.27 (1 H, m, ArH), 2.63 (3 H, m, ArH), 6.80 (2 H, t, J 7 Hz, ArCH<sub>2</sub>), 7.30 (2 H, t, J 7 Hz, CH<sub>2</sub>CO<sub>2</sub>H), and 7.40 (3 H, s, COMe).

**3,4-Dihydro-1-hydroxy-1-methylnaphthalen-2(1H)-one (6).**—The ethereal solution from the foregoing experiment was washed with aqueous sodium hydroxide. The alkaline extract on acidification furnished some phenolic matter (ca. 50–60 mg) (diazo-coupling test) which could not be solidified. The ethereal solution on evaporation and subsequent distillation afforded a colourless oil (3.0 g), b.p. 115–125 °C at 5 mmHg, leaving a viscous residue (ca. 1.5 g). The distilled oil was chromatographed on neutral alumina (benzene-light petroleum) to furnish, in order of elution, the unconverted ketone (1) (2.2 g), some binaphthyl derivative (7), and a very low-melting solid (400 mg). The last fraction was sublimed to give 3,4-dihydro-1-hydroxy-1-methylnaphthalen-2(1H)-one (6) (200 mg) as a low-melting solid, m.p. 32–35 °C (Found: C, 76.9; H, 6.95. C<sub>11</sub>H<sub>12</sub>O<sub>2</sub> requires C, 75.0; H, 6.8%);  $\nu_{\max}$  (CHCl<sub>3</sub>) 3500 and 1710 cm<sup>-1</sup>;  $\tau$ (CDCl<sub>3</sub>) 2.26–2.90 (4 H, m, ArH), 6.30 (1 H, br, s, OH, exchangeable with D<sub>2</sub>O), 6.85 (2 H, m, ArCH<sub>2</sub>), 7.25 (2 H, m, CH<sub>2</sub>CO), and 8.44 (3 H, s, Me);  $m/e$  176 (M<sup>+</sup>, 28%), 158 (50), 133 (72), 118 (100), 105 (36), 90 (64), and 77 (30).

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<sup>8</sup> J. Weinstock, *J. Org. Chem.*, 1961, **26**, 3511; M. Fetizon and M. Golfier, *Bull. Soc. chim. France*, 1966, 870.

<sup>9</sup> D. Nasipuri and S. K. Ghosh, *J.C.S. Perkin I*, 1974, 2720.