# α-Naphthol Synthesis *via* Knoevenagel Condensation in the Presence of Molecular Sieves

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Diphenylethanal condenses with diethyl malonate, ethyl acetoacetate, and ethyl benzoylacetate under Knoevenagel conditions in the presence of molecular sieves to give the 1-naphthols (2), (5), and (6). Glass wool is a less effective catalyst for formation of (2). 3,3-Diethoxycarbonyl-1,1-diphenylpropene (4) is converted into the naphthol (2) in high yield by heating with molecular sieves but its saturated analogue (3) is unaffected.

DURING the course of work concerned with the synthesis of derivatives of 1,1-diphenylpropane, an attempt was made to synthesise the unsaturated malonic ester (1) by condensing diphenylacetaldehyde with diethyl malonate. The Knoevenagel condensation is known to be affected by steric factors,[1] and it was hoped to improve the yield of (1) by removal of the water formed during the reaction. A small-scale preparation was attempted in boiling benzene using piperidinium benzoate as catalyst and a substantial quantity of molecular sieves was added to the mixture to absorb water. From this reaction a solid compound, $C_{19}H_{16}O_3$, was isolated whose spectroscopic properties indicated structure (2). The ^1H n.m.r. spectrum showed the presence of only one ethoxy-group and one low-field singlet (δ 12.8) disappearing on treatment with D_2O. The remaining signals were in the aromatic region of the spectrum. The i.r. spectrum
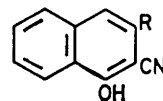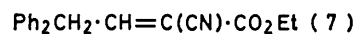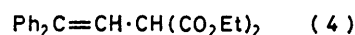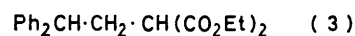
$$Ph_2CH \cdot CH = C(CO_2Et)_2 \quad (1)$$
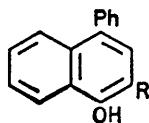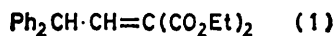
(2) R = CO_2Et
(5) R = Ac
(6) R = Bz

showed an absorption at 1 660 cm^{-1} but no hydroxy-absorption was apparent in spectra measured with pastes in paraffin or hexachlorobutadiene. The ^{13}C n.m.r. spectrum showed absorptions characteristic of a carbon atom in an ester carbonyl group and the hydroxy-bearing carbon atom of a phenol. The compound gave a dark green colour with ethanolic ferric chloride. All these observations are consistent with the structure (2), the low carbonyl absorption in the i.r. spectrum being characteristic of hydrogen-bonded carboxy-functions. The u.v. spectrum is also consistent with the presence of a naphthalene chromophore.
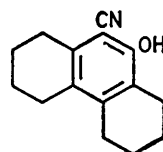
The yield of (2) was considerably improved by using boiling toluene as the reaction solvent, and the importance of the molecular sieves was established by a series of experiments. In the absence of the zeolite but with the piperidinium benzoate catalyst, prolonged reaction led to formation of only a trace of compound (2), detected by t.l.c. using its intense fluorescence in u.v. light. With molecular sieves present in an otherwise identical experiment (2) was formed in over 50% yield. In the

absence of piperidinium benzoate, the molecular sieves alone procured the formation of (2) in significantly lower yield.
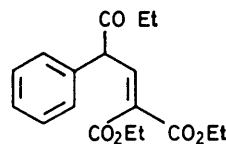
An obvious route for the formation of (2) involves the initial formation of (1) followed by an intramolecular cyclisation of the highly delocalised enolate anion. The failure of (3) to undergo cyclisation under identical

$$Ph_2CH \cdot CH_2 \cdot CH(CO_2Et)_2 \quad (3)$$

$$Ph_2C = CH \cdot CH(CO_2Et)_2 \quad (4)$$

$$Ph_2CH_2 \cdot CH = C(CN) \cdot CO_2Et \quad (7)$$

(8) R = H

(9)

(10)
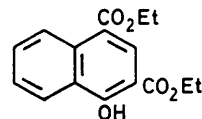
(11)

reaction conditions is consistent with this proposal and supports the importance of delocalisation of the negative charge into the aromatic rings, which will be activated thereby towards acylation by an ester group. In an attempt to isolate compound (1), the product of reaction between diphenylacetaldehyde and diethyl malonate with piperidinium benzoate but in the absence of molecular sieves was examined. H.p.l.c. separated a trace of

compound (2) and a small quantity of an oil which appeared from spectroscopic properties to be either (1) or (4). Neither ^{1}H nor [13]C n.m.r. spectra were sufficiently conclusive to assign the structure with certainty, and the i.r. spectrum showed carbonyl absorptions at 1 734 and 1 750 cm^{-1}, which are at somewhat high frequency for $\alpha\beta$-unsaturated esters. The u.v. spectrum is, however, closely similar to that of 1,1-diphenylethene,[2] strongly favouring structure (4). Heating this ester (4) in toluene with molecular sieves alone converted it in high yield into (2).

The formation of traces of (2) even in the absence of the zeolite was surprising and it seemed possible that the surface of the glass reaction vessel might be the catalyst responsible. Performing the condensation reaction in the presence of a large amount of glass wool led to an enhanced yield of (2) but much less than that obtained with molecular sieves.

In order to examine the scope of the reaction, similar reactions in the presence of molecular sieves were performed with ethyl acetoacetate, ethyl benzoylacetate, and ethyl cyanoacetate in place of diethyl malonate. The first two of these gave compounds (5) and (6) respectively, but the reaction with ethyl cyanoacetate led to a dark tarry product from which no characterisable material has so far been isolated. The reaction of diethyl malonate with phenylacetaldehyde under similar conditions in the presence of molecular sieves also gave a complex mixture, whilst phenylpropan-2-one and 1,1-diphenylpropan-2-one failed to react.

A few cases are reported in the literature of Knoevenagel reactions giving aromatic products by reactions similar to those described above. In many of these cases the condensations involve cyanoacetic esters. Compound (7) (or its tautomer) cyclises to (8; R = H) during vacuum distillation[3] and a range of benzyl ketones react with ethyl cyanoacetate under the normal conditions of the Knoevenagel reaction to give products of general structure (8).[4] 2-Cyclohexylidenecyclohexanone likewise condenses with ethyl cyanoacetate to form (9).[5] A few examples are recorded of derivatives of (10) cyclising on heating to form derivatives of (11).[6] In none of these cases is catalysis by surfaces suggested, although all are probably assisted by adventitious base. The function of the molecular sieve in the work reported here is uncertain, although it may provide a surface which stabilises the adsorbed carbanion intermediate whilst holding it in a conformation favourable for cyclisation.

EXPERIMENTAL

N.m.r. spectrometers used in this work were: Perkin-Elmer R34 (^{1}H, 220 MHz), JEOL PFT-100 (^{13}C, 25 MHz) and Bruker WH400 (^{13}C, 100 MHz). I.r. spectra were measured with a Perkin-Elmer PE-180 spectrometer and u.v. spectra with a Perkin-Elmer 554 spectrometer. The molecular sieves used in this work were type 4A (4—8 mesh beads), made by the Davison Chemical Division of W. R. Grace and Co., and used without any pretreatment.

2-Ethoxycarbonyl-4-phenyl-1-naphthol (2).—A mixture of diphenylethanal (1.5 g), diethyl malonate (1.3 ml), piperidine (0.1 g), benzoic acid (0.15 g), toluene (2.5 ml), and molecular sieves (5 g) was heated at 140 °C in an oil-bath for $3\frac{1}{2}$ days. The mixture was diluted with dichloromethane, and the solution was washed with dilute hydrochloric acid and sodium hydrogencarbonate solution and dried (MgSO$_4$). Evaporation of the solvent left a thick oil which crystallised with time to give the title compound (1.3 g, 52%), m.p. 115—117 °C (from ethanol) (Found: C, 77.9; H, 5.7. $C_{19}H_{16}O_3$ requires C, 78.1; H, 5.5%), $\nu_{max.}$ (paste) 1 660 cm^{-1}; δ_H (CDCl$_3$) 1.23 (3 H, t, J 7 Hz), 4.37 (2 H, q, J 7 Hz), 7.2—7.6 (7 H, m), 7.69 (1 H, s), 7.7—7.8 (1 H, m), 8.4—8.5 (1 H, m), and 12.1 (1 H, s, removed by D$_2$O treatment); δ_C (CDCl$_3$) 14.3 (q), 61.4 (t), 105.3 (s), 124.1, 124.8, 125.8, 127.1, 128.3 129.3, 130.1, 131.1 (s), 140.1 (s), 160.3 (s), and 171.0 (s); $\lambda_{max.}$ (EtOH) 225, 250, 256 (s), 296, 306, 348, and 360 nm (log ε 4.51, 4.58, 4.56, 3.75, 3.75, 3.80, and 3.77).

Compound (2) was also isolated in much lower yield from an experiment performed under identical conditions except for the use of glass wool (3 g) in place of molecular sieves.

Alkaline hydrolysis of compound (2) gave the corresponding carboxylic acid m.p. 215—220 °C (decomp.) (Found: C, 77.2; H, 4.5. $C_{17}H_{12}O_3$ requires C, 77.3; H, 4.5%).

Diethyl 3,3-Diphenylprop-2-ene-1,1-dicarboxylate (4).—The reaction of diphenylethanal with diethyl malonate under conditions identical with those described above, except for the absence of molecular sieves, gave an oily product from which h.p.l.c. separated a very small quantity of compound (2), identified by i.r. and [1]H n.m.r. comparison, and a low yield of compound (4) identified by its spectroscopic properties: $\nu_{max.}$ (film) 1 734 and 1 750 cm^{-1}, $\lambda_{max.}$ (EtOH) 252 nm (log ε 4.17); δ_H (CDCl$_3$) 1.24 (6 H, t, J 7 Hz), 4.17 (1 H, d, J 10 Hz), 4.20 (4 H, q, J 7 Hz), 6.35 (1 H, d, J 10 Hz) and 7.1—7.5 (10 H, m); δ_C (CDCl$_3$, 100 MHz) 14.0 (q), 53.1 (d), 61.6 (t), 119.9 (d), 127.7, 127.8, 128.2, 128.5, 129.8, 138.6 (s), 141.5 (s), 146.6 (s), and 168.3 (s).

Heating compound (4) (0.2 g) in toluene (1 ml) with molecular sieves (2 g) at 140° for $2\frac{1}{2}$ days converted it into compound (2) (0.15 g, 87%).

2-Acetyl-4-phenyl-1-naphthol (5).—This compound was obtained by the reaction of diphenylethanal with ethyl acetoacetate in the presence of piperidine, benzoic acid, and molecular sieves as described above; it formed yellow crystals (14%), m.p. 182—183 °C (from ethanol) (Found: C, 81.9; H, 5.3. $C_{18}H_{14}O_2$ requires C, 82.4; H, 5.3%), $\nu_{max.}$ (KBr) 1 620 cm^{-1}; $\lambda_{max.}$ (EtOH) 220, 259, 286s, 298s, 309 (s), and 374 nm (log ε 4.52, 4.54, 4.05, 4.03, 3.94, and 4.10); δ_H (CDCl$_3$) 2.65 (3 H, s), 7.2—7.6 (8 H, m), 7.7—7.8 (1 H, m), 8.5—8.6 (1 H, m), and 14 (1 H, broad, removed by D$_2$O treatment); δ_C (CDCl$_3$) 27.2, 113.0 (s), 125.0, 125.8, 126.1, 127.6, 128.7, 130.4, 131.2, 136.1 (s), 140.3 (s), and 162.1 (s).

2-Benzoyl-4-phenyl-1-naphthol (6).—This compound was obtained by the reaction of diphenylethanal with ethyl benzoylacetate in the presence of piperidine, benzoic acid, and molecular sieves as described above; it formed yellow needles (33%), m.p. 160—161 °C (from ethanol) (Found: C, 85.0; H, 4.8. $C_{23}H_{16}O_2$ requires C, 85.2; H, 4.9%), $\nu_{max.}$ (paste) 1 586 cm^{-1}; $\lambda_{max.}$ (EtOH) 223, 266, and 393 nm (log ε 4.47, 4.51, and 3.55); δ_H (CDCl$_3$) 7.3—7.6 (11 H, m), 7.65—7.9 (3 H, m), 8.5—8.7 (1 H, m), and 13.88 (1 H, s, removed by D$_2$O treatment).

Diethyl 3,3-Diphenylpropane-1,1-dicarboxylate (3).—Diethyl malonate (85 ml) was added to a stirred suspension

of sodium hydride powder (10 g) in dry dimethoxyethane (300 ml). After gas evolution had ceased, 2,2-diphenyl-ethyl toluene-*p*-sulphonate (69.8 g) was added and the mixture boiled under reflux for 48 h. The solvent was evaporated and the residue extracted with ether. Work-up of the ether solution gave an oil from which chromatography (silica gel with benzene and ether) and vacuum distillation separated *the ester* (3) (*ca.* 40 g), b.p. 150—152 °C/0.01 mmHg (Found: C, 73.9; H, 7.0. $C_{21}H_{24}O_4$ requires C, 74.1; H, 7.1%), $\nu_{max.}$ (film) 1 732 and 1 750 cm^{-1}; δ_H (CDCl$_3$) 1.20 (6 H, t, *J* 7 Hz), 2.66 (2 H, t, *J* 7 Hz), 3.23 (1 H, t, *J* 7 Hz), 3.98 (1 H, t, *J* 7 Hz), 4.13 (4 H, q, *J* 7 Hz), and 7.1—7.4 (10 H, m); δ_C (CDCl$_3$) 14.0 (q), 34.4 (t), 48.7 (d), 50.3 (d), 61.3 (t), 126.5, 127.8, 128.6, 143.4 (s), and 169.3 (s). This ester was recovered unchanged after being heated in toluene with molecular sieves at 140 °C for 3 days. T.l.c. and i.r. examination of the reaction product showed no sign of any product.

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