1,8-Diacetylnaphthalene and its Cyclisation to 3-Methyl-1*H*-Phenalen-1-one

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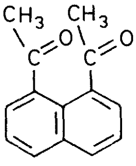
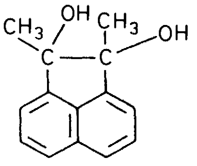
A single isomer of 1,8-diacetylnaphthalene (I) was formed on oxidation of *cis*- or *trans*-1,2-dimethylacenaphthene-1,2-diols (II). The dipole moment of diketone (I) (2.37 D) corresponds precisely to that calculated (CNDO/2) for the *trans*-isomer. Cyclisation of (I) to 3-methyl-1*H*-phenalen-1-one was achieved in 45 : 55 (v/v) ethanol–water solution on acid or alkali catalysis, or on electrochemical reduction. The rates of these reactions were measured, the cyclisation with alkali proceeding at *ca.* 50 000 times the rate of the reaction with acid. An explanation for the cyclisation on electrochemical reduction was obtained from calculations (INDO) of electron-densities of the radical anion of (I).

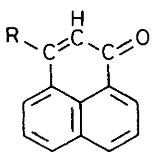
1,8-DIACETYLNAPHTHALENE (I) has been obtained by oxidation with chromic acid[1] or lead(IV) acetate[2,3] of 1,2-dimethylacenaphthene-1,2-diol (II). Only a single isomer of ketone (I) has been reported, although both *cis*- and *trans*-isomers of glycol (II) are known, their orientation following from their physical properties and rates of oxidative cleavage.[2] The diketone (I) undergoes cyclisation to 3-methylphenalenone (III; R = Me) in the presence of piperidine,[2] or of chromic acid–acetic acid,[1] but this reaction has not been studied further.



(I)



(II)



(III)

In our hands, oxidation (*cf.* ref. 1) of a mixture of *cis*- and *trans*-diols (II), or of each diol separately, led to the isolation of a single compound (I), m.p. 171—172 °C. The crude product was light brown, and melted at *ca.* 157—162 °C; careful crystallisation, and t.l.c. analysis, suggested the presence of a single isomer of diketone (I) with ketone (III; R = Me) as the coloured impurity.

The configuration in solution of 1,8-diacetylnaphthalene was considered next. For the related diketone, 1,8-dipropionylnaphthalene a rotational energy barrier of <34 kJ mol^{-1} was adduced from ^{1}H n.m.r. measurements.[4] This low value would suggest that *cis*- and *trans*-forms of this type would be rapidly interconvertible.[5]

We have measured the dipole moment of ketone (I), in tetrachloromethane solution at 30 °C, to be 7.91×10^{-30} C m (2.37 D). This value was compared with calculated[6] dipole moments for structures having cisoid and transoid configurations, with each acetyl group being orthogonal to the naphthalene ring system. Such a highly twisted arrangement of the side-chains was considered probable, in view of a conformational angle of *ca.* 45° for 1-acetylnaphthalene,[7] and the certainty of a widening of this angle when an acetyl group is confronted by another such group at the *peri*-position. The cisoid structure has a calculated dipole moment of 18.3×10^{-30} C m (5.49 D), and the transoid structure 7.87×10^{-30} C m (2.36 D). We believe that this provides good evidence that ketone (I) exists in solution nearly exclusively in the transoid configuration, in which form the horizontal components of the strong carbonyl dipoles can cancel each other out.

With a view to obtaining further structural information[8] attempts were made to produce the radical anion of diketone (I) by electrochemical reduction. The radical generated, however, proved to be that of 3-methylphenalen-1-one (III; R = Me). The spectrum obtained was identical with that generated from ketone (III; R = Me) under the same experimental conditions, and it could be analysed, together with the spectrum of the parent phenalen-1-one (III; R = H), with the help of hyperfine coupling constants for the ion radicals calculated by an MO method (see Experimental section). The experimental and calculated coupling constants are compared in Table 1.

TABLE 1

Experimental and calculated coupling constants (mT) for the anion radical of phenalen-1-one and 3-methylphenalen-1-one

Hydrogen atom	Phenalen-1-one		3-Methylphenalen-1-one	
	Expt.	Calc.	Exp.	Calc.
2-H	0.030	(+)0.013	<0.010	(+)0.052
3-H	0.435	(−)0.401		
4-H	0.540	(−)0.562	0.517	(−)0.582
5-H	0.130	(+)0.310	0.119	(+)0.315
6-H	0.540	(−)0.651	0.531	(−)0.670
7-H	0.540	(+)0.577	0.531	(−)0.580
8-H	0.100	(+)0.258	0.119	(+)0.250
9-H	0.500	(−)0.477	0.517	(+)0.472
CH_3			0.369	(+)0.452 *

* Average value for 3 methyl protons.

Formation of the cyclic ketone (III; R = Me) did not take place simply on standing in the solvent; therefore cyclisation of diketone (I) occurs subsequent to the electrochemical reduction. This may be the first recorded instance of such a cyclisation. The u.v.–visible spectrum of the solution undergoing reduction, gradually changed to that of the product (III; R = Me), *ca.* 50% being formed after 45 min. The rate constant of cyclisation k_1 at 25 °C was *ca.* 4×10^{-4} s^{-1}. No attempt was made to measure the rate accurately, since this must be a composite of pseudo-first-order cyclisation and diffusion processes, and being at least in part heterogeneous.

No previous kinetic measurements have been reported for the cyclisation of 1,8-diacetylnaphthalene (I). We here report that the cyclisation occurs quantitatively, by passage of a solution of the diketone through a short column of chromatographic (*viz.* alkaline) alumina, as well as in ethanol–water mixtures, using either acid or alkali as catalyst. Computed rate constants, and derived activation parameters, for the cyclisations of 1,8-diacetylnaphthalene (I) in acid or alkali media, are summarised in Table 2. The rate of cyclisation is seen to be *ca.* 5 × 10^4 as fast in the alkaline medium as in a solution containing the corresponding concentration of hydrochloric acid. The alkaline reaction is characterised by low values both of the enthalpy of activation ($\Delta H^‡$) and of the entropy of activation ($\Delta S^‡$).

TABLE 2

Computed rate constants at 298.15 K and activation parameters for the cyclisation of *trans*-1,8-diacetylnaphthalene, in 45 : 55 (v/v) ethanol–water, catalysed by hydrochloric acid or sodium hydroxide

	Medium	
	Acid	Alkali
Concentration (mol dm^{-3})	5.4×10^{-1}	5.4×10^{-5}
k_1(298.15 K)(computed)/s^{-1}	6.37×10^{-5}	2.74×10^{-4}
$\Delta H^‡$/kJ mol^{-1}	109	40
$\Delta S^‡$/J K^{-1} mol^{-1}	+42	−179
$\Delta G^‡$/kJ mol^{-1}	97	93
Correlation coefficient	0.997	0.992
k_2 (298.15 K)[a] /dm^3 mol^{-1} s^{-1}	1.18×10^{-4}	5.08

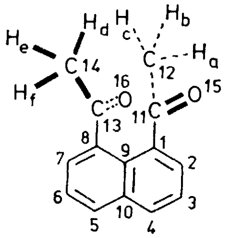
[a] Normalised, *i.e.* bimolecular, rate constant: $k_2 = k_1$/[catalyst].

The cyclisation in acidic solution, is characterised by an unusually high value of $\Delta S^‡$. Therefore the low observed rate in this medium is due to the high value of $\Delta H^‡$.

It proved instructive to explore the mechanism of the free radical cyclisation process by appropriate calculations on the radical anion of *trans*-1,8-diacetylnaphthalene (I). These showed that the MO containing the unpaired electron is essentially localised on one of the carbonyl groups, and that there is very little delocalisation of this electron onto other parts of the molecule, as anticipated from the orthogonal orientation of the acetyl functions. The energy of the spin-orbital concerned was calculated as −2.08 eV, whereas the lowest energy π^* orbital, associated with the naphthalene ring system, lies directly above the former orbital at an energy of 4.4 eV. The charge distribution and total unpaired electron spin density of the radical anion are given in Table 3.

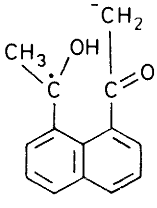
TABLE 3

Total unpaired electron spin densities and net electronic charges of the anion radical from *trans*-1,8-diacetylnaphthalene calculated using the INDO approximation

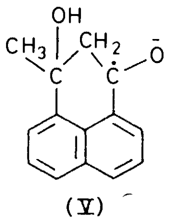


Atom	Unpaired spin densities (e)	Net charges (e)	Atom	Unpaired spin densities (e)	Net charges (e)
C-1	−0.0089	−0.026	O-15	0.1542	−0.606
C-2	0.0052	−0.108	O-16	0.2571	−0.708
C-3	−0.0025	−0.068	H-2	−0.0003	0.061
C-4	0.0037	−0.132	H-3	0.0003	0.047
C-5	0.0045	−0.146	H-4	0.0000	0.055
C-6	−0.0018	−0.061	H-5	−0.0002	0.053
C-7	0.0231	−0.121	H-6	0.0017	0.043
C-8	−0.0361	0.015	H-7	−0.0015	0.067
C-9	0.0303	0.019	H-12a	0.0025	0.098
C-10	−0.0003	0.061	H-12b	0.0000	0.090
C-11	0.0611	0.430	H-12c	0.0051	0.209
C-12	−0.0067	−0.389	H-14d	0.0336	0.069
C-13	0.4935	0.174	H-14e	0.0015	0.062
C-14	−0.0525	−0.330	H-14f	0.0342	0.140

In the parent diketone (I) molecule the mutual electrostatic interactions between the charges on the polar acetyl groups balance out exactly on symmetry grounds. As can be seen from Table 3 this situation no longer obtains in the ketyl radical, generated by reduction of the C(13)=O(16) group. The O(16) atom now carries a larger net negative charge than the O(15) atom of the other acyl group. Moreover, this O(16) atom is now opposite a methyl group, one of whose hydrogen atoms carries an appreciable positive charge. This atom, H(12c), is also the atom closest to the negative oxygen atom. The calculated distance, for strictly orthogonal acetyl groups within the radical, is *ca.* 170 pm. It is therefore plausible to suggest that an internal proton abstraction may take place, subsequent to a small disrotatory motion of the side chains, to give the radical (IV). An internal nucleophilic attack would then result in the radical (V), in which the electron is now delocalised over the naphthalene rings, and which on dehydration would lead to the conjugated unsaturated ketonic product (III; R = Me) of cyclisation.



(IV)



(V)

EXPERIMENTAL

M.p.s are uncorrected. Abbreviations used are: br = broad, dd = doublet of doublets, m = multiplet, md = medium, s = singlet, sh = shoulder, st = strong, t = triplet.

1,2-*Dihydroxy*-1,2-*dimethyl*-1,2-*dihydroacenaphthylene* (II).—The literature method [1] was used. *cis*-1,2-Dihydroxy-1,2-dimethyl-1,2-dihydroacenaphthylene had m.p. 189—

191 °C (acetone) (lit.,[9] 187—189 °C), τ($CDCl_3$) (*cf.* ref. 10) 2.15—2.7 (m, ArH), 6.97br (OH, exchangeable with D_2O), and 8.39 (s, CH_3); $\nu_{max.}$ (KBr) 1 370—1 380 st (C–CH_3) and 3 320 and 3 030br cm^{-1} (OH).[11] The *trans*-isomer had m.p. 183—184.5 °C ($CHCl_3$) (lit.,[9] 182—183 °C), mixed m.p. with the *cis*-isomer 158—170 °C; τ($CDCl_3$) 2.32—2.82 (m, ArH), 8.1 (s, OH, exchangeable with D_2O), and 8.34 (s, CH_3); $\nu_{max.}$ (KBr) 1 370—1 380 (C–CH_3) and 3 320 and 3 030md cm^{-1} (OH).[11]

1,8-*Diacetylnaphthalene* (I).—A mixture of *cis*- and *trans*-diols (II) was oxidised [1] to give ketone (I) (54%), m.p. 170—171 °C (lit.,[2,3] 171—172 °C); τ($CDCl_3$) 2.04 (dd, 4- and 5-H), 2.24 (dd, 2- and 7-H), 2.6 (t, 3- and 6-H), and 7.32 (s, CH_3), $J_{2,3} = J_{6,7} = 6.8$, $J_{2,4} = J_{5,7} = 1.6$ and $J_{3,4} = J_{5,6} = 7.6$ Hz; $\nu_{max.}$ (KBr) 1 680 cm^{-1} (lit.,[1] 1 683 cm^{-1}); $\lambda_{max.}$ ($CHCl_3$) 244 and 295 nm (ε 810 and 980 m^2 mol^{-1}).

Oxidation [1] of the *cis*-diol (II) gave a crude product, m.p. *ca.* 155 °C, which gave ketone (I) on crystallisation (ethanol). The *trans*-diol (II) similarly gave virtually pure ketone (I), m.p. 167 °C, after one crystallisation. The ketones were identical (mixed m.p., i.r. spectra).

3-*Methyl*-1H-*phenalen*-1-*one* (III; R = Me).—This compound was obtained by (i) oxidation of the diols (II) with an excess of chromic acid–acetic acid [1] above 25 °C, or (ii) treatment of ketone (I) with dilute alkali, or (iii) passage of the diketone (I) in benzene through a column of alumina (type H), as bright yellow crystals, m.p. 154 °C (lit.,[1,2] 155—156 °C); $\nu_{max.}$ (KBr) 1 640 (C=O) and 1 620 cm^{-1} (C=C) (lit.,[1] 1 640 cm^{-1}); $\lambda_{max.}$ ($CHCl_3$) 248, 255, 323, 355, and 365 nm (ε 1 600, 1 500, 550, 900, and 800 m^2 mol^{-1}).

Kinetic Measurements.—Solutions of ketone (I) (*ca.* 1.4 × 10^{-3} mol dm^{-3}) and of hydrochloric acid (1.00 mol dm^{-3}) or sodium hydroxide (1.00 × 10^{-3} mol dm^{-3}) at the appropriate temperature were mixed thoroughly in a volumetric flask, so as to give a final solvent composition of 45 : 55 (v/v) ethanol–water. A portion of the mixture was transferred to the solution cell (quartz; 1 cm) of a thermostatted cell-holder of a Perkin-Elmer 402 spectrophotometer, and readings were taken either continuously, or at chosen intervals, at 359 nm.

Rate constants for the pseudo-first-order reactions were calculated by the iterative procedure described before.[12] Normally *ca.* 50 data points were taken for each kinetic run, up to *ca.* 85% reaction. Experimental rate constants for the cyclisation in acid or alkali media are given in Table 4, and derived activation parameters in Table 2.

TABLE 4

First-order rate constants for the cyclisation of ketone (I) in 45 : 55 (v/v) ethanol–water [a]

[Catalyst]/mol dm^{-3}	10^4 k_1/s^{-1} (t/°C)
HCl, 5.4 × 10^{-1}	0.621 (25.4), 1.02 (27.5),[b] 2.53 (34.3),[b] 5.41 (40.0) [b]
NaOH, 5.4 × 10^{-5}	2.35 (22.0), 2.37 (22.2), 2.65 (24.9), 2.71 (25.3), 3.08 (26.7), 3.69 (29.9), 3.37 (31.7), 4.88 (34.7) [c]

[a] Reactions were followed at 359 nm. [b] Runs in duplicate. [c] Mean error 2.8%.

E.s.r. Measurements.—Solutions of ketone (I) (*ca.* 10^{-3} mol dm^{-3}) in dimethylformamide, containing tetra-n-butylammonium perchlorate as supporting electrolyte, were reduced at the mercury pool surface in a standard electrochemical cell of a Varian E3 e.s.r. spectrometer, working at 9.5 GHz. No anion radical was visible up to potentials of 1.8 V. Above this voltage an orange-yellow solution was formed, which gave an e.s.r. signal. The radical spectrum was not analysable in terms of the expected ketyl radical of the parent compound (I), but was identified as, and identical with, the radical anion from 3-methyl-1*H*-phenalen-1-one (III; R = Me).

Ketone (I) was stable, *i.e.* no yellow compound was formed, until electrolytic reduction was carried out. The rate of formation of ketone (III; R = Me) on reduction was estimated using the absorption maximum of the product at 355 nm.

Measurement of Dipole Moments.—Dielectric constants, densities, and refractive indices were measured, for solutions of ketone (I) in pure tetrachloromethane,[13] as previously described.[14] The results used are given in Table 5. The methods of Hedestrand,[15] and of Guggenheim,[16] were then used, together with the data of Table 5, to calculate the dipole moment of ketone (I). By each procedure the dipole moment obtained was 7.91 × 10^{-30} C m (2.37 D).

TABLE 5

Data used for the determination of the apparent dipole moment of 1,8-diacetylnaphthalene (I) in tetrachloromethane solution at 30 °C

Weight fraction (w_2)	Dielectric constant (ϵ_{12})	Density (kg m^{-3}) (d_{12})	Refractive index (D) (n_{12})	$10^6(r_{12})_D$ (m^3)	$10^6(r_2)_D$ (m^3)
0	2.2176	1 574.8	1.4545	0.172 12	
8.0 × 10^{-4}	2.2235	1 574.2	1.4547	0.172 25	0.3364
1.2 × 10^{-3}	2.2268	1 573.9	1.4548	0.172 32	0.3388
2.3 × 10^{-3}	2.2353	1 572.9	1.4551	0.172 50	0.3384
2.7 × 10^{-3}	2.2384	1 572.6	1.4552	0.172 56	0.3351
3.5 × 10^{-3}	2.2444	1 571.9	1.4554	0.172 69	0.3350

Calculation of Dipole Moments.—The dipole moments of the cisoid and transoid forms of ketone (I) were estimated theoretically, using the semiempirical CNDO/2 LCAO MO method.[6] For this purpose the standard geometrical parameters listed by Pople and Beveridge [17] were employed. It was assumed that the planes of the acetyl groups in these molecules are perpendicular (orthogonal) to the plane of the naphthalene moiety. Dipole moments thus obtained are quoted in the Discussion section.

Calculations on Free Radicals.—Total unpaired electron spin densities, hyperfine coupling constants, and charge distributions were calculated for the radical anions of ketones (I), (III; R = Me), and (III; R = H). The method used was a semiempirical unrestricted Hartree–Fock MO calculation using the INDO approximation; [17] standard geometric parameters were employed. For ketone (I) the two acetyl groups were considered to have the transoid configuration, and to be at right angles to the plane of the naphthalene moiety. For the ketyl radical of diketone (I) a C–O bond length of 129 pm was assumed, corresponding to a bond order of 1.5.

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