Lewis Acid-catalysed Cyclisations of 1-Anthryl Styryl Ketone; Benz[*de*]-anthracen-3-one

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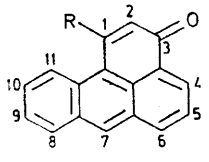
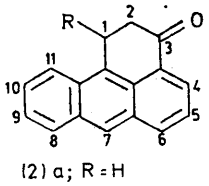
Cyclisation of 1-anthryl styryl ketone with aluminium chloride gave a small yield of the unstable base benz[*de*]anthracen-3-one (1a), whereas cyclisation with polyphosphoric acid gave a mixture of 2,3-dihydro-3-phenylcyclopent[*a*]anthracen-1-one and a stable analogue of (1a), 1-phenylbenz[*de*]anthracen-3-one. Comparison is made with reactions of 9-anthryl styryl ketone and 1-naphthryl styryl ketone under similar conditions and it is concluded that 1-anthryl styryl ketone is not an intermediate in the disproportionation of 9-anthryl styryl ketone to anthracene and anthracene-9,10-diyl bis(styryl ketone).

CAMERON *et al.*[1] have reported the synthesis of benz[*de*]-anthracen-3-one (1a) by two methods: the Lewis acid-catalysed cyclisation of 3-(9-anthryl)acrylic acid and the aerial oxidation of 1,2-dihydrobenz[*de*]anthracen-3-one



(1) a; R = H
b; R = Ph



(2) a; R = H
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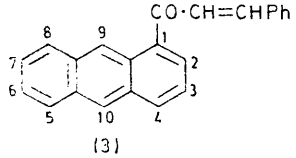

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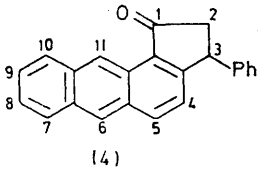

(4)

(2a), itself synthesised by the cyclisation of 3-(9-anthryl)-propionic acid.[2] The ketone (1a) was described as a deep red solid, unstable in light and in air, which dissolved in mineral acids to give a green solution.[1]

The cyclisation of 1-naphthyl styryl ketone with aluminium chloride to give phenalen-1-one [3,4] suggested that cyclisation of 1-anthryl styryl ketone (3) might yield the ketone (1a). It has been observed, however, that treatment of 9-anthryl styryl ketone under the conditions required for the cyclisation of 1-naphthyl styryl ketone to phenalenone gives anthracene and anthracene-9,10-diyl bis(styryl ketone).[4] No trace of the basic analogue of phenalenone, benz[*de*]anthracen-1-one, was detected and neither were the products of simple rearrangement, 1-anthryl styryl ketone and 2-anthryl styryl ketone.[4] Clearly the formation of anthracene-9,10-diyl bis(styryl ketone) follows migration of the styrylcarbonyl group, although from simple kinetic considerations 1-anthryl styryl ketone and, to a lesser extent, 2-anthryl styryl ketone should have been formed preferentially.[5] Normally formation of 1- and 2-acylanthracenes from rearrangement of the corresponding 9-acylanthracene is found not to be reversible.[5] However, it is possible that the formation of 1-anthryl styryl ketone from 9-anthryl styryl ketone is exceptionally reversible and that these compounds are intermediates in the formation of the thermodynamically

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[2] H. Dannenberg and H.-J. Kessler, *Annalen*, 1957, **606**, 184.
[3] C. F. Koelsch and J. A. Anthes, *J. Org. Chem.*, 1941, **6**, 558.
[4] A. T. Dlamini, H. J. Williams, and R. G. Shotter, *Tetrahedron*, 1973, **29**, 1327.
[5] (*a*) P. H. Gore, *J. Org. Chem.*, 1957, **22**, 135; (*b*) P. H. Gore and C. K. Thadani, *J. Chem. Soc.* (*C*), 1966, 1729.

controlled end-product anthracene-9,10-diyl bis(styryl ketone). If this were the case, independent synthesis of 1-anthryl styryl ketone and its treatment with aluminium chloride would be expected to yield anthracene and anthracene-9,10-diyl bis(styryl ketone).

Treatment of 1-anthryl styryl ketone with aluminium chloride in refluxing carbon disulphide in fact gave a low yield of the cyclic ketone (1a), which was the only product identified. It appears therefore that 1-anthryl styryl ketone and, by implication, 2-anthryl styryl ketone are not intermediates in the disproportionation of 9-anthryl styryl ketone to anthracene and 9,10-anthracene-9,10-diyl bis(styryl ketone), although the problem of why they are not intermediates remains.[6]

The ketone (1a) is an unstable red compound which decomposes rapidly in air to give a resinous, non-basic product. Its mass spectrum showed *m/e* 230 and 202 as reported,[1] but in other respects our observations differed. Our compound did not exhibit an i.r. band at 1 520 cm^{-1} and did not give a violet colouration when warmed with chloroform and aqueous alkali.

1-Anthryl styryl ketone was also treated with polyphosphoric acid. It has been observed that treatment of 1-naphthyl styryl ketone with polyphosphoric acid leads to cyclisation at the 2- rather than the 8- (*peri*) position to yield its isomer, 2,3-dihydro-3-phenylbenz[*e*]inden-1-one,[7] and a similar mode of cyclisation was expected for 1-anthryl styryl ketone. Two major products were obtained, however. The first was a cyclic isomer of 1-anthryl styryl ketone, 2,3-dihydro-3-phenylcyclopent[*a*]anthracen-1-one (4), formed by cyclisation at the 2-position in direct analogy with the cyclisation of 1-naphthyl styryl ketone under similar conditions.[7] The second was a stable compound, identified as 1-phenylbenz[*de*]anthracen-3-one (1b).

The deep red colour of the latter suggested a chromophore similar to that of ketone (1a) and its basic nature was shown by some solubility in concentrated hydrochloric acid to give a green solution. Its i.r. spectrum shows the exceptionally low-frequency carbonyl absorption which characterises both phenalenone and the cyclic ketone (1a),[1] and further support for its structure is given by its n.m.r. spectrum (see Experimental section). It appears that cyclisation takes place to give first 1-phenyl-1,2-dihydrobenz[*de*]anthracen-3-one (2b), which is oxidised to give the ketone (1b). We note the failure of attempts to synthesise and isolate the naphthalene analogue of the ketone (2b), 3-phenyl-2,3-dihydrophenalen-1-one,[3] and the retention of the phenyl group is consistent with previous experience with polyphosphoric acid- as opposed to aluminium chloride-catalysed cyclisations of aryl styryl ketones.[7,8] Cyclisation at the *peri*-position, to give 3-phenylphenalen-1-one, is not observed when 1-naphthyl styryl ketone is treated with polyphosphoric acid under similar conditions, and an explanation for this has been offered in terms of the relative ' hardness ' of the positions *ortho* and *peri* to the carbonyl group in the naphthalene ring.[7] It appears therefore that this difference is less marked in 1-anthryl styryl ketone than in 1-naphthyl styryl ketone and that the *peri*-H-8 in 1-anthryl styryl ketone does not seriously hinder the formation of the suggested intermediate (2b).

The evidence supporting the structures of the ketones (1a and b) is strong but the stability of ketone (1b) compared with (1a) invites further comment. While there appears to be no steric strain in structure (1a), Courtauld atomic models show that accommodation of the phenyl group in ketone (1b) involves severe distortion of the molecule, with the phenyl group twisted *ca.* 60° from the plane of the anthracene ring, and some distortion from planarity of C-1, C-2, and C-3 as well as of the anthracene ring itself is also probable. Certainly the phenyl group cannot contribute significantly to the resonance stabilisation of the ketone (1b) and a possible explanation for its stability relative to (1a) may be that, whereas the first step in the breakdown of the ketone (1a) in air is the addition of oxygen across the *meso*-positions of the anthracene ring, steric distortion makes such a reaction less favourable with the ketone (1b). This is supported by the instability of ketone (1a) in comparison with phenalenone. Compound (2b) would not, incidentally, be expected to show steric strain.

A sharp one-proton absorption at τ 8.74 in the n.m.r. spectrum of the ketone (1b) is assigned to H-11, which would be expected to be strongly shielded by the phenyl group. Our assignments of the spectra of the ketones (1a and b) are based on analogy with the spectrum of phenalenone, which has been fully analysed.[9]

A single-crystal *X*-ray diffraction study of the ketone (1b) is in progress to determine the geometry of the molecule with particular reference to the H-11–Ph interaction. Although crystals suitable for data collection have not yet been obtained, the crystal data with approximate unit cell parameters have been determined from rotation and Weissenberg photographs. The crystals are orthorhombic, probably $P2_12_12_1$, with $a = 15.12$, $b = 17.95$, $c = 5.67$ Å, and $Z = 4$.

As expected, the n.m.r. spectrum of the cyclic ketone (4) shows the characteristic three quartets of an ABX system [7] and, as does the spectrum of 1-anthryl styryl ketone, shows two sharp singlets downfield of the main aromatic band due to the *meso* protons of the anthracene system. This deshielding is compounded for H-9 (1-anthryl styryl ketone) and H-11 [ketone (4)] by the presence of the *peri*-carbonyl group.[7,10]

EXPERIMENTAL

Chromatography was carried out on neutral alumina (Brockmann activity I). I.r. spectra were measured for Nujol mulls and recorded on a Unicam SP 200 G or a

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[7] R. G. Shotter, K. M. Johnston, and H. J. Williams, *Tetrahedron*, 1973, **29**, 2163.

[8] M. Jarcho, *J. Amer. Chem. Soc.*, 1968, **90**, 4644.

[9] H. Prinzbach, V. Freudenberger, and U. Scheidegger, *Helv. Chim. Acta*, 1967, **50**, 1087.

[10] R. H. Martin, N. Defay, and F. Geerts-Evrard, *Tetrahedron*, 1964, **20**, 1505; F. Gobert and S. Combrisson, *ibid.*, 1974, **30**, 2919.

Perkin-Elmer 157 G spectrometer. N.m.r. spectra were recorded on a Varian HA-100 instrument for solutions in deuteriochloroform with tetramethylsilane as internal reference. Mass spectra were recorded on an A.E.I. MS 12 instrument. All cyclisations were carried out under nitrogen.

1-Acetylanthracene [11] had m.p. 109.5° (lit.,[5b] 110.5—111°), $\nu_{max.}$ 1 665 cm^{-1} (C=O).

Phenalen-1-one [4] showed $\nu_{max.}$ 1 638 cm^{-1} (C=O), *m/e* 180 (M^+) and 152 ($M^+ - CO$).

1-*Anthryl Styryl Ketone*.—This was prepared by an alkali-catalysed condensation of 1-acetylanthracene (11.0 g, 0.05 mol) and benzaldehyde (5.3 g, 0.05 mol). Trituration of the resultant oil with ether yielded a solid which gave pale yellow crystals (12.1 g, 78%), m.p. 89—90° (from ethanol) (deep grey turning to brown-purple with sulphuric acid), $\nu_{max.}$ 1 668s (C=O) and 1 598s cm^{-1} (C=C) (Found: C, 89.55; H, 5.4. $C_{23}H_{16}O$ requires C, 89.6; H, 5.2%), τ 0.97 (1H, s, H-9), 1.56 (1H, s, H-10), and 1.86—2.78 (14H, m).

Cyclisations of 1-*Anthryl Styryl Ketone*.—(a) *In polyphosphoric acid*. The general method described in a previous paper was followed with 3.08 g (0.01 mol) of 1-anthryl styryl ketone,[7] and the crude products, obtained as a black solid, were extracted with benzene. The solvent was removed, and the residue chromatographed. Elution with benzene gave yellow crystals of 2,3-*dihydro*-3-*phenylcyclopent*[a]*anthracen*-1-*one* (0.65 g, 21%), m.p. 165—166° (from ethanol) (crimson with sulphuric acid, turquoise fluorescence in chloroform solution); $\nu_{max.}$ 1 692 cm^{-1} (C=O) (Found: C, 89.4; H, 5.25. $C_{23}H_{16}O$ requires C, 89.6; H, 5.2%), τ 0.27 (1H, s, H-11), 1.69 (1H, s, H-6), 1.84—2.97 (11H, m, ArH), 5.55 (1H, dd, H-3), and 6.59—7.37 (2H, 2 dd, CH_2) ($J_{CH,CH_2\text{-}trans}$ 7.2, $J_{CH,CH_2\text{-}cis}$ 3.4, $J_{CH_2\text{-}gem}$ 19.0 Hz).

Further elution with chloroform gave a sharp band which yielded a deep carmine solid, 1-*phenylbenz*[de]*anthracen*-3-*one* (0.34 g, 11%), m.p. 163—164° (from benzene) (intense blue-green with sulphuric acid, sparingly soluble in concentrated hydrochloric acid to give a green solution); $\nu_{max.}$ 1 632s (C=O), 1 601m, and 1 552s cm^{-1} (Found: C, 89.85; H, 4.65. $C_{23}H_{14}O$ requires C, 90.2; H, 4.55%), *m/e* 306 (M^+) and 276 ($M^+ - CH_2O$); τ 1.17 (1H, d, H-4, $J_{4,5}$ 7.0 Hz, showing splitting $J_{4,6}$ 1.4 Hz), 1.35 (1H, s, H-7), 1.61 (1H, d, H-6, $J_{5,6}$ 8.2 Hz, showing splitting $J_{4,6}$ 1.4 Hz), 1.98—2.99 (9H, m, ArH), 3.22 (1H, s, H-2), and 8.74 (1H, s, H-11). The solid was stable in air and gave no colour in the aqueous phase when warmed and shaken with chloroform–aqueous alkali.

Further elution with chloroform gave a series of green compounds which were not further investigated.

(b) *With an excess of aluminium chloride in carbon disulphide*. The method was similar to that used [4] for the cyclisation of 1-naphthyl styryl ketone to phenalen-1-one. 1-Anthryl styryl ketone (3.08 g, 0.01 mol) gave a dark red residue which was dissolved in benzene and quickly chromatographed. Elution with chloroform gave a deep carmine solid which was recrystallised from benzene–light petroleum (2 : 1) to yield benz[*de*]anthracen-3-one (0.185 g, 8%) (deep olive-green with sulphuric acid, soluble in concentrated hydrochloric acid to give a green solution); $\nu_{max.}$ 1 636s (C=O), 1 601m, and 1 551s cm^{-1} (no peak at 1 520 cm^{-1}); *m/e* 230 (M^+) and 202 ($M^+ - CO$). The n.m.r. spectrum showed that some of the compound had decomposed, but clear peaks were observed at τ 1.27 (1H, d, H-4, $J_{4,5}$ 7.0 Hz, showing splitting $J_{4,6}$ 1.5 Hz), 1.46 (1H, s, H-7), and 3.17 (1H, d, H-2, $J_{1,2}$ 10.4 Hz, no splitting). Cameron *et al.*[1] did not record an n.m.r. spectrum. The compound gave no colour in the aqueous layer when warmed with chloroform–aqueous alkali. The isolated compound quickly decomposed; elution of the crude products through alumina with chloroform gave a pale red resinous solid, $\nu_{max.}$ 1 687 cm^{-1} (C=O) (insoluble and no colour in concentrated hydrochloric acid).

One of us (H. J. W.) thanks Professor R. C. Cookson and the technical staff of the Chemistry Department, Southampton University, for facilities and assistance in carrying out much of this work.

[4/2588 *Received*, 11*th December*, 1974]

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