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POLYPHOSPHORIC ACID-CATALYSED CYCLISATIONS OF ARYL STYRYL KETONES

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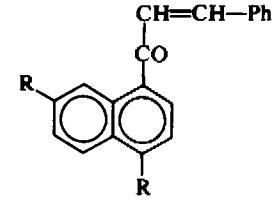
Abstract – Reaction of a number of aryl styryl ketones with polyphosphoric acid has been investigated and, with the exception of 9-anthryl styryl ketone, each undergoes smooth cyclisation to give an isomeric 5-membered ring ketone. The polyphosphoric acid- and aluminium chloride-catalysed cyclisations of 1-naphthyl styryl ketone, which give 3-phenyl-2,3-dihydrobenz(e)inden-1-one and phenalen-1-one respectively, are discussed and a general interpretation of the cyclisation modes of 1-naphthyl substituted ketones and carboxylic acids in terms of the HSAB theory is offered.

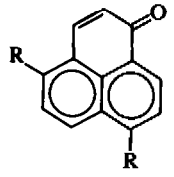
The aluminium chloride-catalysed cyclisation of 1-naphthyl styryl ketone (**1a**) and certain of its ring substituted derivatives to the corresponding derivatives of phenalen-1-one (**2a**) has long been known.[1-3] Recently, Jarcho[4] has prepared 4,7-dimethoxy-3-phenyl-2,3-dihydrophenalen-1-one (**3a**) by warming 4,7-dimethoxy-1-naphthyl styryl ketone (**1b**) in polyphosphoric acid. On subsequent treatment with aluminium chloride in refluxing benzene **3a** gave 4,7-dihydroxyphenalen-1-one (**2b**), which was also prepared directly from **1b** by treatment with aluminium chloride, although in very poor yield.

This raised the question of how 1-naphthyl styryl ketone reacts when treated with polyphosphoric acid (PPA), and it is now reported that cyclisation under these conditions takes place at the 2-position, to yield 3-phenyl-2,3-dihydro-1H-benz(e)inden-1-one (**4a**), rather than at the 8-position which would have given either phenalen-1-one or 3-phenyl-2,3-dihydrophenalen-1-one (**3b**). Compound **4a** has previously been prepared by the aluminium chloride-catalysed cyclisation of 3-(2-naphthyl)-3-phenylacrylic acid (**5**)[5] and its identity was confirmed by oxidation to 2-benzoyl-1-naphthoic acid.

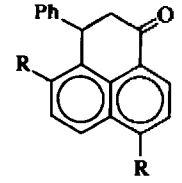
Attack at the 2-position of the naphthalene ring is the normal mode of cyclisation of $\alpha\beta$-unsaturated 1-naphthyl ketones in which no other ring substituents are present. Thus, aluminium chloride- and sulphuric acid-catalysed cyclisations of 1-naphthyl vinyl ketone[6] and 2-1-naphthoylacrylic acid[7] have been reported to yield exclusively the corresponding derivatives of 2,3-dihydro-1H-benz(e)inden-1-one (**4b**). On the other hand, cyclisation of 2-1-naphthyl derivatives of simple saturated carboxylic acids or their acid halides takes place chiefly at the 8-position, to give the corresponding phenalenone or dihydrophenalenone derivative, although a small yield of the dihydrobenzindenone is usually formed as a by-product.[8-11] The direction of cyclisation is, however, strongly influenced by substituents in the ring with, for example, OMe groups in the 5- or 7-positions of β-1-naphthylpropionic acid leading to cyclisation at the 8-position while a OMe group in the 6-position leads to



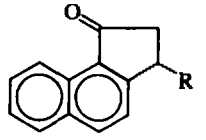
1a: R = H
b: R = OMe



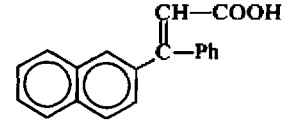
2a: R = H
b: R = OH



3a: R = OMe
b: R = H



4a: R = Ph
b: R = H



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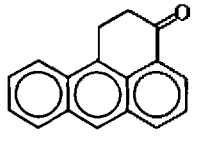

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cyclisation at the 2-position.[12,13] Jarcho's cyclisation of **1b** at the 8- instead of the 2-position may similarly be interpreted in terms of the electronic influence of the ring substituted OMe groups.[4]

The nature of the catalytic reagent may influence the yields of the products obtained, but no evidence has hitherto been presented for its governing the direction of cyclisation of 1-naphthyl derivatives. Green and Hey[12] studied PPA, sulphuric acid, tin(IV) chloride and aluminium chloride as catalysts for the cyclisation of a number of 1-naphthyl substituted carboxylic acids but in no case did the use of any one lead to a different direction of cyclisation from the others. However, the conditions do seem to be important in determining whether cyclisation at the 8-position leads to the dihydrophenalenone or whether dehydrogenation also takes place to give the corresponding phenalenone. Thus, cyclisation of β-1-naphthylpropionic acid has been reported to give phenalen-1-one with aluminium chloride[5,8] and tin(IV) chloride,[9] whereas use of anhydrous hydrogen fluoride as catalyst gives 2,3-dihydrophenalen-1-one.[8] Careful studies of the hydrogen fluoride-catalysed cyclisation of a number of β-1-naphthylcarboxylic acids[11] showed that, while the major product was the dihydrophenalenone in each case, small yields of the phenalenone and the dihydrobenzindenone were also formed. Aerial oxidation of the dihydrophenalenone to the phenalenone during the work up of the products was demonstrated and, from this, it was concluded that the principal route to the phenalenone was by dehydrogenation of the dihydrophenalenone initially formed. Nonetheless the conditions under which this takes place are not clearly established, since no derivatives of phenalenone have been reported as products by independent workers investigating the cyclisation of other, ring substituted β-1-naphthylpropionic acids.[12,14]

The cyclisation of 1-naphthyl styryl ketone differs from established trends, therefore, in two important respects. First, the aluminium chloride-catalysed cyclisation of 1-naphthyl styryl ketone occurs at the 8-position, and not the more usual 2-position of αβ-unsaturated 1-naphthyl-ketones, and, second, the direction of the aluminium chloride-catalysed cyclisation is the reverse of that observed with PPA catalysis. A concerted mechanism for the former reaction has been proposed,[2] in which the driving forces are seen as the formation of the highly conjugated phenalenone system and the formation of benzene. The latter factor distinguishes the cyclisation of 1-naphthyl styryl ketone from those of other 1-naphthyl αβ-unsaturated ketones and is presumably critical in changing the normal reaction path. If the aluminium chloride-catalysed cyclisation took place as an earlier, separate step before the loss of benzene there would have been no reason to suppose the direction of cyclisation to be different from that of the PPA-catalysed reaction. The ability of aluminium chloride and the inability of PPA to remove benzene from this type of system is clearly shown by Jarcho's synthesis of **2b** from **1b**, via **3a**.[4] Certainly the formation of phenalenone, in this case at least, does not proceed via a dehydrogenation step, and an early claim by Kalischer[15] that the aluminium chloride catalysed cyclisation of 1-naphthyl styryl ketone gives **3b** must be regarded as erroneous.

In contrast to 1-naphthyl styryl ketone, attempts to cyclise 9-anthryl styryl ketone in PPA failed. Under 140° no reaction took place and above this temperature anthracene was the only product detected. Cyclisation also fails when 9-anthryl styryl ketone is refluxed with aluminium chloride in carbon disulphide, conditions under which 1-naphthyl styryl ketone gives phenalenone but under which 9-anthryl styryl ketone disproportionates to anthracene and 9,10-anthryl bis-(styryl ketone).[2] The failure of aluminium chloride to catalyse cyclisation of 9-anthryl styryl ketone has been attributed to steric hindrance to the formation of the cyclic transition state by the second *peri* hydrogen[2] but a similar explanation for the failure of PPA to induce cyclisation is less sound in view of the ready cyclisation with this catalyst of 1-naphthyl styryl ketone in which steric interference by the *peri* hydrogen would also be expected. The answer may lie in the different steric requirements for the formation of a 6- as opposed to a 5-membered ring, but until more is known about the role of PPA in these reactions,[16] no firm conclusion can be drawn.

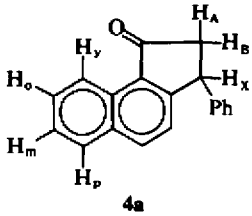
A possible interpretation of the general preference of 1-naphthyl αβ-unsaturated ketones to cyclise at the 2-position, and of 1-naphthyl substituted carboxylic acids and their acid halides to cyclise at the 8-position, requires that the 8-position of the naphthalene ring be a harder donor than the 2-position. Thus, cyclisation of 1-naphthyl αβ-unsaturated ketones involves attack on the ring by the C-4 carbon of the conjugated ketone, which is regarded as softer than the C-2 carbon,[17] while cyclisation of 1-naphthyl substituted carboxylic acids involves attack by a species approximating to an acylium ion, which is known to be hard.[18] A similar assumption that the *peri*- positions of 9-anthryl derivatives are hard further rationalises not only the failure to induce cyclisation of 9-anthryl styryl ketone but also the successful cyclisation of β-9-anthrylpropionic acid with tin(IV) chloride to give a good yield of 1,2-dihydro-3H-benz(de)anthacene-3-one (**6**).[19]

Cyclisation of several other aryl styryl ketones in PPA has been investigated. 2-Naphthyl styryl ketone gave a fair yield of 1-phenyl-1,2-dihydro-3H-benz(e)inden-3-one (**7**), whose structure was confirmed by oxidation to 1-benzoyl-2-naphthoic acid. All previously recorded cyclisations of 2-naphthyl derivatives have taken place at the 1- rather than the 3-position, as is consistent with the greater stabilisation of the transition state leading to the former.[5,7,20]

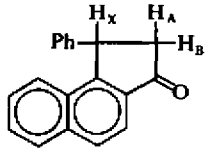
2-Phenanthryl styryl ketone gave a compound which was assigned 15-phenyl-15,16-dihydro-17H-cyclopenta(a)phenanthren-17-one (**8**) rather than the alternative 10-phenyl-9,10-dihydro-8H-cyclopenta(b)phenanthren-8-one (**9**) on the strength of its infrared spectrum, in which no peak characteristic of absorbtion by an isolated ring proton was present, and by analogy with 2-naphthyl styryl ketone. Distinction between the two possibilities from the compound's NMR spectrum was not found possible.

6-Chrysyl styryl ketone gave 7-phenyl-6,7-dihydro-5H-cyclopenta(g)chrysen-5-one (**10**), and 3-pyryl styryl ketone gave 1-phenyl-1,2-dihydro-3H-cyclopenta(c)pyren-3-one (**11**), the structures of both compounds being supported by their NMR spectra.

The NMR spectra of the cyclised products **4a**, **7**, **8**, **10** and **11** all showed the characteristic three quartets of an ABX system. In addition, **4a**, **10** and **11** gave absorbtions downfield from the main aromatic band which were attributed to the deshielding effect of the carbonyl group on the neighbouring *peri* hydrogen (H_Y). The downfield absorptions were not given by **7** or **8**, in which no *peri* hydrogen adjacent to the CO group is present (they would also not be given by structure **9**). The downfield absorbtion by **11** was a clean doublet, which is assigned to coupling of H_Y with the *ortho*- hydrogen H_O. However, the downfield absorbtions of **4a** and **10** are more complex, due to coupling of H_Y not only with H_O but with H_M and H_P, protons which are not present in **11**.



4a



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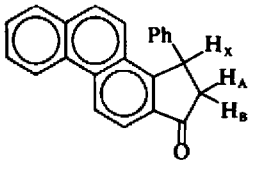

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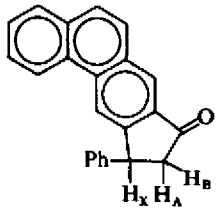

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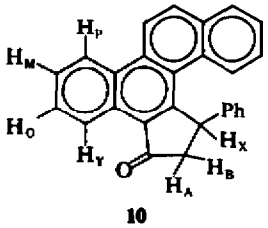

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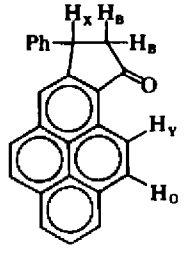

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EXPERIMENTAL

Chromatography was on alumina (Brockmann Activity No. 1). Infrared spectra were determined for Nujol mulls or KBr discs and were recorded on a Unicam SP 200 G spectrometer. NMR spectra were determined for solns in $CDCl_3$ with TMS as internal reference and were recorded on a Perkin Elmer R 10 instrument.

Preparation of aryl styryl ketones. 9-Anthryl styryl ketone (m.p. 202°) was prepared by direct cinnamoylation of anthracene as described by Dlamini *et al.*[2] All other aryl styryl ketones were prepared by alkali-catalysed condensation of benzaldehyde with the appropriate aryl methyl ketone.

1-Acetylnaphthalene was prepared and purified by Baddeley's method,[21] b.p. 120–124°/2 mm, (lit,[21] 163°/15 mm). 1-Naphthyl styryl ketone was obtained as a yellow oil (81%), b.p. 240–242°/0·5 mm, (lit,[22] 220°/6 mm), dibromide m.p. 166–167° (lit,[22] 166–167°).

2-Acetylnaphthalene (Koch-Light) was recrystallised from EtOH, m.p. 53–54°, (lit,[21] 55°). 2-Naphthyl styryl ketone (90%) was obtained as pale yellow needles (EtOH), m.p. 105–106°, (lit,[22] 105–106°).

2-Acetylphenanthrene was prepared by Kloetzel and Pandit's method.[23] After recrystallising from EtOH (white needles) it had m.p. 142°, lit,[24] 142–143°). *2-Phenanthryl styryl ketone* (91%) was obtained as pale yellow needles (acetone), red-brown with H_2SO_4. (Found: C, 89·7; H, 5·35; M, 273. $C_{23}H_{16}O$ requires: C, 89·6; H, 5·2%; M, 308), ν_{max} 1674 cm^{-1} (C=O).

6-Acetylchrysene was prepared by Carruther's method.[25] After recrystallisation (white needles, benzene-EtOH) it had m.p. 142°, (lit,[25] 142–143°. *6-Chrysyl styryl ketone* (95%) was obtained as pale yellow elongated hexagons (toluene) violet with HSO_4. (Found: C, 90·45; H, 5·10; M, 368. $C_{27}H_{18}O$ requires: C, 90·5; H, 5·05%; M, 358), ν_{max} 1670 cm^{-1} (C=O).

3-Acetylpyrene was prepared by a modification of the Vollmann *et al.* method.[26] Pyrene (10·1 g, 0·05 mol) was dissolved in an equal mixture (w/w) of $ZnCl_2$, AcOH and Ac_2O (50 ml). The soln was heated for 4 hr on a water bath and then poured into ice-dil HCl. The ppt was recrystallised twice from EtOH to give yellow crystals of 3-acetylpyrene (5·7 g, 45%), m.p. 92° (lit,[26] 90°), yellow in UV light. 3-Pyryl styryl ketone (91%) had m.p. 120° (lit,[27] 119·5–120·5°), deep purple with H_2SO_4, yellow-green fluorescence in UV light, ν_{max} 1661 cm^{-1} (C=O).

Reactions in polyphosphoric acid

General method. The aryl styryl ketone (0·01 mol) was added with stirring to PPA (60 ml) at 136° (ethylbenzene bath) and the mixture was maintained at this temp with stirring for ½ hr. The products were then poured into water (350 ml) and the ppt, if any, was collected, washed well with water and dried. If no ppt was formed the aqueous mixture was extracted with chloroform, the extracts dried (Na_2SO_4) and the solvent removed by distillation. The crude product was in each case taken up in acetone and boiled for 5 min with a little decolourising charcoal. The soln was then filtered through paper and the acetone removed by distillation.

(a) 1-*Naphthyl styryl ketone* (2·60 g) gave a solid which

after recrystallising twice from EtOH gave white crystals of 3-phenyl-2,3-dihydro-1H-benz(e)inden-1-one (1·35 g, 52%), m.p. 118–119°, (lit,[5] 118°), yellow with H_2SO_4, ν_{max} 1685s (C=O), 833s cm^{-1} (2 adjacent Ar-H). (Found: C, 87·88; H, 5·62. Calc. for $C_{19}H_{14}O$: C, 88·34; H, 5·46%), NMR τ 0·78 (m, Ar, 1H), 2·1–2·65 (m, Ar, 5H), 2·91 (s, Ph), 5·59 (q, CH), 6·6–7·65 (two quas, CH_2), $J_{CH\text{-}CH_2 trans}$ 7·4 Hz, $J_{CH\text{-}CH_2 cis}$ 3·8 Hz, $J_{CH_2 gem}$ 18·6 Hz.

(b) *2-Naphthyl styryl ketone* (2·60 g) gave white crystals of *1-phenyl-1,2-dihydro-3H-benz(e)inden-3-one* (1·57 g, 60·5%), m.p. 111°, yellow with H_2SO_4, ν_{max} 1719s (C=O), 833s cm^{-1} (two adjacent Ar-H). (Found: C, 88·12; H, 5·51; M, 234. $C_{19}H_{14}O$ requires: C, 88·34; H, 5·46%; M, 258), NMR τ 2·2–3·2 (m, Ar, 11H), 5·28 (q, CH), 6·64–7·78 (two quas, CH_2), $J_{CH-CH_2 trans}$ 7·6 Hz, $J_{CH-CH_2 cis}$ 2·9 Hz, $J_{CH_2 gem}$ 19·3 Hz.

(c) *8-Anthryl styryl ketone* (3·08 g) gave unchanged starting material (2·42 g, 78·5%) as the only crystalline product. In a second experiment the temp was raised to 185° (diethyl oxalate bath) and the reaction time increased to 1 hr. A sublimate of anthracene was formed and careful chromatography of the tarry products extracted from the aqueous mixture gave anthracene (total yield 0·68 g, 38%) as the only identified product.

(d) *2-Phenanthryl styryl ketone* (3·08 g) gave a gum which was solidified by dissolving a little warm propanol and allowing the soln to stand at −80°. Recrystallisation from MeOH gave white needles of *15-phenyl-15,16-dihydro-17H-cyclopenta(a)-phenanthren-17-one* (1·45 g, 47%), m.p. 222°, orange-yellow with H_2SO_4, ν_{max} 1704s (C=O), 830s cm^{-1} (two adjacent Ar-H). (Found: C, 88·97; H, 5·2; M, 266. $C_{23}H_{16}O$ requires: C, 89·61; H, 5·2%; M, 308), NMR τ 1·25–3·10 (m, Ar, 13H), 5·05 (q, CH), 6·46–7·57 (two quas, CH_2), $J_{CH-CH_2 trans}$ 7·7 Hz, $H_{CH-CH_2 cis}$ 2·6 Hz, $J_{CH_2 gem}$ 19·2 Hz.

(e) *6-Chrysyl styryl ketone* (3·58 g) gave *7-phenyl-6,7-dihydro-5H-cyclopenta(g)chrysen-5-one* (2·2 g, 61%), pale yellow needles (n-propanol-toluene), golden-yellow with H_2SO_4, ν_{max} 1715 cm^{-1} (C=O). (Found: C, 90·7; H, 5·2; M, 328. $C_{27}H_{18}O$ requires: C, 90·5; H, 5·05%; M, 358), NMR τ 0·35 (m, Ar, 1H), 1·13–3·0 (m, Ar, 14H), 4·26 (q, CH), 6·27–7·42 (two quas, CH_2), $J_{CH-CH_2 trans}$ 7·7 Hz, $J_{CH-CH_2 cis}$ 2·0 Hz, $J_{CH_2 gem}$ 18·6 Hz.

(f) *3-Pyryl styryl ketone* (3·32 g). Chromatography of the crude product gave first pyrene (0·28 g, 14%), m.p. and mixed m.p. 150°, and then *1-phenyl-1,2-dihydro-3H-cyclopenta(c)pyren-3-one* (1·89 g, 57%), m.p. 199–200°, pale yellow needles (benzene), blood red with H_2SO_4, green fluorescence in UV light, ν_{max} 1698 cm^{-1} (C=O). (Found: C, 89·95; H, 4·90; M, 325. $C_{25}H_{16}O$ requires: C, 90·35; H, 4·85%; M, 332), NMR τ 0·52 (d, Ar, 1H), 1·65–2·95 (m, Ar, 12H), 5·27 (q, CH), 6·36–7·37 (two quas, CH_2), $J_{CH-CH_2 trans}$ 7·8 Hz, $J_{CH-CH_2 cis}$ 4·7 Hz, $J_{CH_2 gem}$ 18·9 Hz.

Oxidations

(a) *3-Phenyl-2,3-dihydro-1H-benz(e)inden-1-one* (0·516 g, 0·002 mol) was added to a mixture of $KMnO_4$ (1·054 g, 0·0067 mol) and 1M NaOH (50 ml). The mixture was boiled under reflux until the supernatant soln was colourless (2 hr) and was then filtered hot through paper. SO_2 was allowed to bubble through the cooled soln for 10 min, and the soln was again filtered and added to an excess of conc HCl. The resultant white ppt was washed well with water and recrystallised from a 60:40 n-propanol-water mixture to give white needles of 2-benzoyl-1-naphthoic acid (0·11 g, 20%), m.p. 140–141° (lit, 141·8–142·8°,[28] 139–141°[29]). 8-Benzoyl-1-naphthoic acid has been reported to have m.p. 129–130°.[30]

(b) *1-Phenyl-1,2-dihydro-3H-benz(e)inden-3-one* (0·516 g, 0·002 mol) was oxidised similarly and gave 1-benzoyl-2-naphthoic acid (0·17 g, 31%), m.p. 223–224° (lit, 223·5–224·5,[28] 223–225°[29]). 3-Benzoyl-2-naphthoic acid has been reported to have m.p. 200–205°.[31]

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