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ANOMALOUS DISPROPORTIONATION OF 9-BENZOYLANTHRACENE AND 9-ANTHRYL STYRYL KETONE

A. T. DLAMINI and H. J. WILLIAMS*
Department of Chemistry, The University of Zambia, P.O. Box 2379, Lusaka, Zambia

and

R. G. SHOTTER
Chemical Laboratory, The Polytechnic of Central London, 115 New Cavendish Street, London, W1M 8JS

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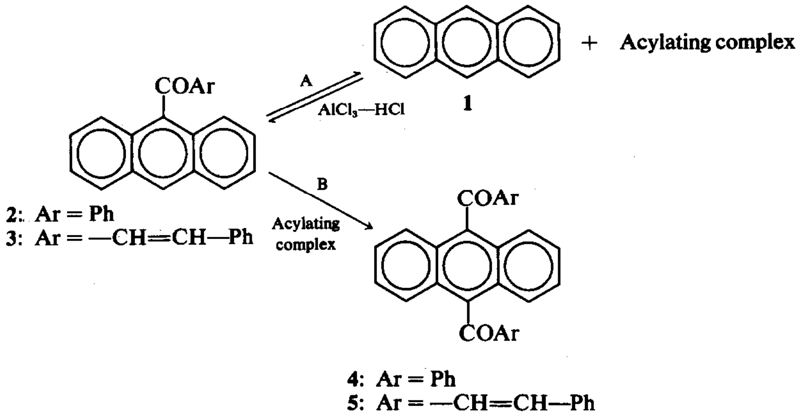
Abstract—9-Benzoylanthracene and 9-anthryl styryl ketone disproportionate to anthracene and the corresponding 9,10-diacylanthracene when warmed in carbon disulphide or nitrobenzene with an excess of aluminium chloride. The reactions are co-catalysed by hydrogen chloride. Comparison is made with other 9-anthryl ketones and with 1-naphthyl styryl ketone, which undergo different reactions under similar conditions. The results are interpreted in terms of steric requirements.

Under certain conditions Friedel-Crafts benzoylation and cinnamoylation of anthracene, using equimolecular quantities of acyl halide and hydrocarbon, has been reported to give the 9,10-diacylanthracene and unchanged anthracene rather than the expected 9-acyl derivative.[1,2] No explanation of these observations has been attempted and we have accordingly reinvestigated the aluminium chloride-catalysed reactions of benzoyl chloride and cinnamoyl chloride with anthracene in carbon disulphide and nitrobenzene.

We confirm that 9-benzoylanthracene (2), 9,10-dibenzoylanthracene (4), 9-anthryl styryl ketone (3) and 9,10-anthryl bis-(styryl ketone) (5) are formed under conditions similar to those described by Gore and Hoskins[1] and by earlier workers.[2-5] We have further shown that both 9-benzoylanthracene and 9-anthryl styryl ketone disproportionate when boiled under reflux in carbon disulphide with an excess of aluminium chloride to give anthracene and the corresponding 9,10-diacyl derivative in roughly equimolecular proportions. Both reactions were complete after about 5 hr, but when a stream of dry hydrogen chloride was introduced the reaction time needed was lowered to 30 min. This is approximately the time required for the preparation of 9,10-dibenzoylanthracene and 9,10-anthryl bis-(styryl ketone) from anthracene by refluxing with the appropriate acyl halide in carbon disulphide with an excess of aluminium chloride, conditions under which hydrogen chloride is formed *in situ*. At 20° disproportionation did not take place, both 9-benzoylanthracene and 9-anthryl styryl ketone yielding acid resistant compounds which contained aluminium on prolonged contact with aluminium chloride in carbon disulphide. Under these conditions both 9,10-dibenzoylanthracene and 9,10-anthryl bis-(styryl ketone) were shown not to react and thus were not formed from the corresponding monoacyl anthracenes. Under no conditions was rearrangement of 9-benzoylanthracene[1] or 9-anthryl styryl ketone to the corresponding 1- or 2-isomers observed. Disproportionation of 9-benzoylanthracene and 9-anthryl styryl ketone also took place in nitrobenzene at 45° and, as in carbon disulphide, the rate was accelerated by the introduction of hydrogen chloride.

From these data it was concluded that aluminium chloride catalysed reactions of anthracene with benzoyl chloride or cinnamoyl chloride give, in the first instance, the monoacyl derivative 9-benzoylanthracene or 9-anthryl styryl ketone, which may then undergo disproportionation under suitable conditions which include higher temperatures, the presence of an excess of aluminium chloride, and hydrogen chloride as co-catalyst. These conclusions are consistent with Gore and Hoskins' results.[1]

9,10-Dibenzoylanthracene and 9,10-anthryl bis-(styryl ketone) must have exceptional thermodynamic stability to be formed by disproportionation, since both the benzoyl and cinnamoyl groups in 9-benzoylanthracene and 9-anthryl styryl ketone deactivate the 10-position at which further electrophilic attack must take place. The role of hydrogen chloride lies almost certainly in promoting the rapid equilibrisation of reaction A (Scheme 1), which is necessary if accumulation of the kinetical-

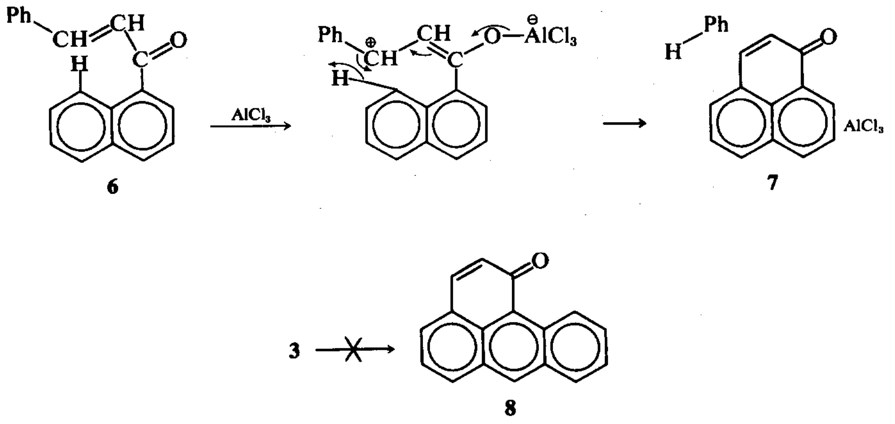


SCHEME 1

ly less favoured 9,10-diacyl derivatives is to take place at an appreciable rate. At lower temperatures the rate of reaction B is presumably too slow to compete successfully with other, more complex reaction routes.

By this behaviour, as well as by their stability, 9-benzoylanthracene and 9-anthryl styryl ketone stand in marked contrast with other known 9-anthryl ketones. Unless steric factors preclude spatial accomodation of the ketonic complex, acylation of anthracene normally takes place first at the 9-position, but the reactions are reversible and rearrangement to the thermodynamically more stable 1- and 2-isomers is common.[6–8] In most Friedel-Crafts acylations of anthracene isolation of the 9-anthryl ketone is possible only under the mildest conditions, if at all.[1,7,9] Acetylation of anthracene, for example, gives first 9-acetylanthracene, which rearranges to give 1- and 2-acetylanthracenes, which in turn partially undergo further acetylation to give a complex mixture of monoacetyl- and diacetylanthracenes.[9] However, 9,10-diacetylanthracene was not detected among the products and, apart from the 9-benzoylanthracene and 9-anthryl styryl ketone under investigation, no example of disproportionation of any 9-anthryl ketone to anthracene and the corresponding 9,10-diacylanthracene has been recorded.

The greater steric requirements of the acetyl over the benzoyl group has been established by Brown *et al.*,[10] who obtained an approximately ten times greater *ortho-para* ratio on benzoylation than on acetylation of toluene. This was rationalised in terms of the greater Van der Waals radius for the tetrahedral methyl group than for the phenyl group,[11] and was first suggested by Gore and Hoskins[1] as an explanation for the greater stability of 9-benzoylanthracene than 9-acetylanthracene. A similar explanation in terms of the steric requirements of the cinnamoyl group can be given for the stability of 9-anthryl styryl ketone, and it may be that, provided the migrating group can be sufficiently stabilised, disproportionation of 9-anthryl ketones is preferred on thermodynamic grounds to simple rearrangement whenever steric interaction between the acyl group and the neighbouring *peri* hydrogens is small enough to permit.



SCHEME 2

The disporportionation of 9-anthryl styryl ketone contrasts with the cyclisation of 1-naphthyl styryl ketone (6) to phenalen-1-one (7) under similar conditions, which was first reported by Koelsch and Anthes[12] and which we confirm. No trace of an acid-soluble analogue of phenalen-1-one, e.g. 1H-Benz(de)anthracene-1-one (8), was found among the products of reaction of 9-anthryl styryl ketone. The cyclisation of 1-naphthyl styryl ketone is accompanied by loss of benzene, which enables the extensive conjugation of phenalen-1-one to be achieved. The cyclisation and loss of benzene are probably synchronous and may be regarded as a four-centred electron shift (Scheme 2). The analogous cyclisation of 9-anthryl styryl ketone does not take place presumably because of steric interaction between the second *peri* hydrogen and the carbonyl-aluminium chloride complex, which must attain co-planarity with the anthracene ring before cyclisation is possible.

EXPERIMENTAL

Chromatography was on alumina (Brockmann Activity No. 1). IR spectra were measured for Nujol mulls and were recorded on a Unicam SP 200 G spectrometer. NMR spectra were recorded on a Perkin Elmer R 10 instrument and were determined for solns in $CDCl_3$ with TMS as internal reference. Cinnamoyl chloride and benzoyl chloride were redistilled and $AlCl_3$ (anhydrous) was ground to a fine powder before use. Light petroleum had b.p. range 80–100°.

9-Benzoylanthracene was prepared according to method (c),[1] except that the reaction mixture was boiled under reflux for only 15 min. Anthracene (11·58 g, 0·065 mol) and benzoyl chloride (9·84 g, 0·07 mol) gave 9-benzoylanthracene (16·9 g, 92%), m.p. 147–148° (lit,[1,4] 148°), yellow needles (toluene), Prussian blue turning to deep olive-green with sulphuric acid, ν_{max} 1663s (C=O), 896s cm^{-1} (isolated Ar-H), τ 1·58 (s, Ar, 1H), 1·9–2·8 (m, Ar, 13H).

9-Anthryl styryl ketone. This was similar to the preparation of 9-benzoylanthracene, but cinnamoyl chloride (11·65 g, 0·07 mol) was used instead of benzoyl chloride. Recrystallisation of the crude product gave 9-anthryl styryl ketone (18·2 g, 91%), m.p. 202° (lit,[1] 201·5–202·5°), bright yellow rhombic crystals (toluene), deep blue-green with sulphuric acid, ν_{max} 1633s (C=O), 1619m (C=C), 884m cm^{-1} (isolated Ar-H), τ 1·55 (s, Ar, 1H), 1·9–2·3 (m, 4H), 2·45–2·85 (m, Ar, 13H).

9,10-Dibenzoylanthracene. Anthracene (4·45 g, 0·025 mol) and benzoyl chloride (3·51 g, 0·025 mol) were stirred into CS_2 (110 ml). $AlCl_3$ (15 g) was added over a period of 5 min and the mixture was then boiled under reflux for 30 min. The organic products were extracted as in the preparation of 9-benzoylanthracene and the solid residue was first washed well with cold acetone, then dried and carefully chromatographed on alumina. Elution with a 5:1 light petroleum benzene gave anthracene (1·07 g, 24%) and further elution with chloroform gave 9,10-dibenzoylanthracene (2·59 g, 28%), m.p. 329–330° (lit, 331–333°,[1] 320°[4]), small pale cream crystals (toluene), persistent deep violet with sulphuric acid, (Found: C, 87·34; H, 4·95. Calc. for $C_{28}H_{18}O_2$: C, 87·0; H, 4·7%), ν_{max} 1660 cm^{-1} (C=O), τ 2·05–2·8 (m, Ar).

9,10-Anthryl bis-(styryl ketone). This was similar to the preparation of 9,10-dibenzoylanthracene but cinnamoyl chloride (4·15 g, 0·025 mol) was used instead of benzoyl chloride. Chromatography gave anthracene (0·89 g, 20%) and 9,10-anthryl bis-(styryl ketone) (2·44 g, 22%), m.p. 238–239° without decomposition (lit,[1] 231–232° with decomposition), dull mustard-yellow needles (toluene), indigo with sulphuric acid, (Found: C, 87·66; H, 5·31%; M, 431. Calc. for $C_{32}H_{22}O_2$: C, 87·65; H, 5·06%; M, 438·5), ν_{max} 1644s (C=O), 1620vs cm^{-1} (C=C), τ 2·05–2·3 (m, 4H), 2·6–2·9 (m, Ar, 18H).

1-Naphthyl styryl ketone. This was prepared from 1-acetylnaphthalene (Baddeley[13]) by a Claisen-Schmidt condensation with benzaldehyde (Johnston and Shotter[14]).

Disproportionation of 9-benzoylanthracene and 9-anthryl styryl ketone

(a) *In carbon disulphide.* (i) A mixture of 9-benzoylanthracene (2·82 g, 0·01 mol) or 9-anthryl styryl ketone (3·08 g, 0·01 mol) with $AlCl_3$ (5 g) and CS_2 (30 ml) was boiled under reflux for 5 hr and then poured into ice-dil HCl. The products were worked up in the usual way and then carefully chromatographed on alumina. Elution with a 5:1 light petroleum benzene gave anthracene and further elution with benzene or chloroform gave the 9,10-diacyl derivative. No unchanged starting material was recovered.

9-Benzoylanthracene gave anthracene (0·32 g, 18%) and 9,10-dibenzoylanthracene (0·50 g, 13%). 9-Anthryl styryl ketone gave anthracene (0·35 g, 19·5%) and 9,10-anthryl bis-(styryl ketone) (0·51 g, 11·5%).

(ii) In similar experiments a stream of dry HCl was passed through the reaction mixtures, which were boiled for 30 min instead of for 5 hr. 9-Benzoylanthracene gave anthracene (0·58 g, 32·5%) and 9,10-dibenzoylanthracene (0·85 g, 22%); and 9-anthryl styryl ketone gave anthracene (0·50 g, 28%) and 9,10-anthryl bis-(styryl ketone) (0·89 g, 20·5%).

(b) *In nitrobenzene.* (i) This was similar to reaction in CS_2. The mixtures were stirred at 45° for 5 hr and the products then poured into ice-dil HCl. The organic extracts were washed well with water, and nitrobenzene was removed by steam distillation. Recrystallisation of the residue from toluene gave the 9,10-diacyl derivative, but anthracene, which was positively identified (m.p. and mixed m.p. 214°) from the steam distillate, was not estimated quantitatively.

9-Benzoylanthracene (2·82 g) gave 9,10-dibenzoylanthracene (0·33 g, 7%), and 9-anthryl styryl ketone (3·08 g) gave 9,10-anthryl bis-(styryl ketone) (0·40 g, 9%).

(ii) In similar experiments a stream of HCl was passed through the mixtures and the reactions were terminated after 30 min. 9-Benzoylanthracene (2·82 g) gave 9,10-dibenzoylanthracene (0·47 g, 10%) and 9-anthryl styryl ketone (3·08 g) gave 9,10-anthryl bis-(styryl ketone) (0·44 g, 11%).

Cyclisation of 1-naphthyl styryl ketone. A mixture of 1-naphthyl styryl ketone (5·16 g, 0·02 mol), $AlCl_3$ (10 g) and CS_2 (60 ml) was boiled under reflux for 4 hr. After extracting the organic products in the usual way a yellow-brown oil was obtained which partially solidified on standing. Recrystallisation of the solid material (1·15 g, 20%) gave phenalen-1-one, m.p. 153–154° (lit,[12] 153–154°), yellow scales (EtOH), soluble in conc HCl, orange in H_2SO_4 turning yellow with a green fluorescence, mixed m.p. with 3-phenylphenalen-1-one (m.p. 141–142·5°, Johnston and Shotter[14]) depressed to 120°.

Reactions of anthryl ketones at 20°

The following general procedure was followed. A mixture of the ketone (0·01 mol), aluminium chloride (5 g) and CS_2 (40 ml) was shaken at 20° for 72 hr. The mixture was then treated with ice-dil HCl and worked up in the usual way.

(a) 9-*Benzoylanthracene* gave a small yield of anthracene (0·1 g) and an unidentified orange-brown solid (2·66 g) which did not react with dil HCl and gave a white residue on strong ignition. No 9,10-dibenzoylanthracene or unchanged 9-benzoylanthracene was recovered.

(b) 9-*Anthryl styryl ketone* similarly gave a small yield of anthracene (0·14 g) and an acid-resistant brick-red *solid (3·30 g) which gave a white residue on strong* ignition as the only products.

(c) 9,10-*Dibenzoylanthracene and* 9,10-*anthryl bis-(styryl ketone*). Both substrates were recovered unchanged (~ 90%).

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