

1086. *Studies in the Acylation of Anthracene.*

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High yields of 9-benzoylanthracene are formed in the Friedel-Crafts benzylation of anthracene in several solvents, including nitrobenzene, with aluminium chloride as catalyst. Other metal chlorides likewise catalyse this reaction, and their reactivity follows the sequence $\text{AlCl}_3 \sim \text{TiCl}_4 \sim \text{ZrCl}_4 > \text{SbCl}_5 \sim \text{FeCl}_3 \sim \text{SnCl}_4 \gg \text{ZnCl}_2$. 1- and 2-Benzoylanthracene are not formed in these acylations. The enhancing influence of phosphoryl chloride on the catalytic activity of zinc chloride, and the weak catalytic activity of chlorosulphonic acid, are reported. 9-Acetylanthracene is converted into 9-benzoylanthracene under Friedel-Crafts conditions, even in the absence of free aluminium chloride. Some *meso*-benzylation occurs with 9-bromo- and 9,10-dibromoanthracene, at the expense of dehalogenation.

Solid 9-benzoylanthracene is autoxidised, in the presence of light, giving anthraquinone.

THE recorded Friedel-Crafts benzoylations of anthracene¹ show some unusual features, including orientation and stability of the products, and the present work describes a detailed study of this acylation reaction. Acylations of anthracene (I), with aluminium chloride as catalyst, as a rule give the "normal" *meso*-product only under specially mild reaction conditions, and by the use of a solvent which permits the precipitation of a ketone-catalyst addition complex.^{1,2} It is noteworthy, therefore, that Friedel-Crafts benzoylations have been reported to yield 9-benzoylanthracene exclusively, under a wide variety of experimental conditions.³⁻⁶ Moreover, reported substitutions of the outer ($\alpha\beta$) positions of anthracene cannot be regarded as proven. Thus, in carbon disulphide, benzoylations with benzoyl chloride and either anhydrous⁷ or partially hydrated aluminium chloride⁴ as catalyst have been reported to give mixtures of 1-, 2-, and 9-benzoylanthracene. From such a reaction Perrier⁷ claimed the isolation of two benzoylanthracenes, of m. p. 75° and 208°. More recently, without reference to the earlier claim, authentic 1- (m. p. 141°) and 2-benzoylanthracene (m. p. 187°) have been prepared⁸ from the appropriate anthronitrile, and these preparations have now been repeated. The 2-isomer exists in two modifications of m. p. 174—175° and 190—191°, respectively. An alternative claim exists in a vague patent⁹ for

¹ Gore, *Chem. Rev.*, 1955, **55**, 229.

² Gore, *J. Org. Chem.*, 1957, **22**, 135.

³ Krollpfeifer and Schütz, *Ber.*, 1923, **56**, 2360.

⁴ Lippmann and Fleissner, *Ber.*, 1899, **32**, 2249; Lippmann and Keppich, *Ber.*, 1900, **33**, 3086; Lippmann and Pollack, *Ber.*, 1901, **34**, 2766.

⁵ Cook, *J.*, 1926, 1282.

⁶ (a) Nenitzescu, Isacescu, and Ionescu, *Annalen*, 1931, **491**, 210. (b) Rona and Feldman, *J.*, 1958, 1737.

⁷ Perrier, *Ber.*, 1900, **33**, 815; *Bull. Soc. chim. France*, 1903, **31**, 859; "Thèse inaugurale de la Faculté des Sciences de Paris," 1896, through Rivkin, *Zhur. obshchei Khim.*, 1935, **5**, 277.

⁸ Waldmann and Oblath, *Ber.*, 1938, **71**, 366.

⁹ Lulek and Perkins, U.S.P. 1,991,687 (1935).

the preparation of the 1-isomer, but this was not further pursued. A detailed study was consequently undertaken to establish whether 1- or 2-benzoylanthracene could in fact be formed in the Friedel-Crafts benzoylation of anthracene. Methods of analysis (using infrared spectral analysis and thin-layer chromatography) were devised, which could detect about 0.1% of any isomer, and determine as little as 1% with some accuracy.

A benzoylation carried out according to Perrier's original method⁷ gave us a 98% yield of 9-benzoylanthracene. The choice of carbon disulphide as solvent seemed less promising for the formation of α - and β -isomers than did nitrobenzene. In fact in nitrobenzene only α - and β -isomers have been obtained from anthracene in acetylations,^{10,11} propionylations,^{8,10} or succinoylations.¹² The only reported benzoylation of anthracene in nitrobenzene claimed³ the formation of the 9-benzoyl derivative under mild conditions (-10° , duration 5 min.). This result has now been confirmed. Even at 0° , the *meso*-isomer is the only one formed; a quantitative yield can be obtained after 24 hr. Removal of hydrogen chloride in a current of dry nitrogen from a reaction at 0° led to a lowering of yield of the 9-benzoyl compound from 74% to 18%. This result is in contrast with the increased yield of ketone obtained similarly, in the acetylation of benzene¹³ and the phthaloylation of chlorobenzene.¹⁴ This result suggests a possible hydrogen chloride co-catalysis in some aluminium chloride-catalysed acylations, which might be connected with the occasional preferred use of a partially hydrated aluminium chloride as catalyst.^{4,15}

Under vigorous benzoylating conditions (room temperature, 45 hr.) an unidentified ketone, m. p. $145-148^\circ$, was the only isolable product; the isomeric benzoylanthracenes were not formed, neither was 9,10-dibenzoylanthracene, which had earlier been reported¹⁶ to be formed from the 9-benzoyl compound in nitrobenzene at 50° .

In view of the experimental confirmation of the stability of a *meso*-benzoyl group in anthracene, compared with an acetyl group (see below), it was considered of interest to examine the stabilities, under benzoylating conditions, of certain *meso*-substituent groups in anthracene. First, the observation¹⁶ that 9-acetylanthracene could be converted into 9-benzoylanthracene, with benzoic anhydride and aluminium chloride in carbon disulphide, has been confirmed, in improved yield. The same conversion was also achieved, in 92% yield, in ethylene chloride solution under Perrier conditions, *i.e.*, avoiding free aluminium chloride. The most likely reaction path is *via* anthracene and not *via* 9-acetyl-10-benzoylanthracene; synchronous replacement of acetyl by benzoyl is likewise considered improbable. Under similar conditions, an attempted reverse acyl displacement from 9-benzoylanthracene yielded only small traces of 9-acetylanthracene and free anthracene, the original ketone remaining largely unchanged. In keeping with this finding is the reported failure to effect an acyl exchange, in a reaction between the 9-benzoyl compound and *p*-nitrobenzoyl chloride.¹⁶ Next, two systems were examined with *meso*-halogen blocking groups, *viz.*, 9-bromoanthracene and 9,10-dibromoanthracene. In boiling ethylene chloride the former gave a 37% yield of the expected 9-bromo-10-benzoylanthracene, as well as about 5% yield of 9,10-dibenzoylanthracene. Two paths appear possible for the formation of the 9,10-dibenzoyl compound: the first is a direct replacement of the bromine, *via* a σ -complex transition state, which should not be precluded for steric reasons; the other would proceed *via* 9-benzoylanthracene, which is known to yield the 9,10-dibenzoyl compound under a variety of conditions.^{4,5,16} The debromination stage would require a proton source (here hydrogen

¹⁰ Lüttringhaus and Kacer, G.P. 492,247 (1926); cf. B.P. 289,587 (1927); F.P. 633,071 (1928).

¹¹ Bassilios and Salem, *Bull. Soc. chim. France*, 1952, [5] 19, 586.

¹² Mayer, G.P. 376,635 (1923); Fieser and Peters, *J. Amer. Chem. Soc.*, 1932, 54, 4354; Cook and Robinson, *J.*, 1938, 505; Bergmann and Weizmann, *J.*, 1938, 1243; Fieser and Heymann, *J. Amer. Chem. Soc.*, 1941, 63, 2333 (footnote).

¹³ Salmi and Väihkönen, *Suomen Kem.*, 1946, 19, B, 132; Smeets and Verhulst, *Bull. Soc. chim. belges*, 1952, 61, 694.

¹⁴ Dermer, Mori, and Suguitan, *Proc. Oklahoma Acad. Sci.*, 1948, 29, 74; Groggins, "Unit Processes in Organic Synthesis," McGraw-Hill Book Co. Inc., New York, 1952, p. 846.

¹⁵ Fröschl and Harlass, *Monatsh.*, 1932, 59, 275; Scholl, Dehnert, and Wanka, *Annalen*, 1932, 493, 57; Windaus and Raichle, *ibid.*, 1939, 537, 157; Fairbrother and Frith, *J.*, 1953, 2975.

¹⁶ Batten, Ph.D. Thesis, London University, 1933.

chloride), the concentration of which is unlikely to be high enough in this solvent. On the other hand, debrominations have been known to accompany certain acylations of bromobenzene.^{17,18} 9,10-Dibromoanthracene under similar benzoylating conditions gave a small amount (2%) of 9-bromo-10-benzoylanthracene, but no evidence for the formation of 9-bromo- or 9,10-dibenzoyl-anthracene was found.

In the light of the successful use of ethylene chloride as indicated above, and for related polycyclic systems,^{10,19} this solvent was here tried, and found to be most satisfactory, a quantitative yield of 9-benzoylanthracene being obtained very conveniently, in a 24 hr. reaction at 0°. This success prompted an investigation of the comparative reactivities, based on yields of 9-benzoylanthracene (the only product) obtainable in reactions carried out for 5 min., 1½ hr., and 24 hr. at 0°, of a number of catalysts, mainly metal chlorides of proven catalytic power: the results are collected in the Table.

Yields (%) of 9-benzoylanthracene obtained in Friedel-Crafts benzoylations of anthracene, in ethylene chloride, at 0°.

Catalyst	Reaction time			Catalyst	Reaction time 24 hr.
	5 min.	1½ hr.	24 hr.		
AlCl ₃	79	86	99	ZnCl ₂	4.7
TiCl ₄	76	90	93	ZnCl ₂ -POCl ₃	9.6
ZrCl ₄	67	97	89	CISO ₃ H	7.2
FeCl ₃	22	73	84	POCl ₃	0
SbCl ₅	15	77	—	CdCl ₂	0
SnCl ₄	7.3	76	90	HgCl ₂	0
				VCl ₃	0
				AlF ₃	0

The sequence of catalytic efficiency of the chlorides here appears to be AlCl₃ ~ TiCl₄ ~ ZrCl₄ > SbCl₅ ~ FeCl₃ ~ SnCl₄ ≫ ZnCl₂. This was also the precise sequence of the ease with which the benzoyl chloride-catalyst addition compounds were formed, and this may therefore be regarded as a precondition for successful acylation. In a related study, of the acetylation of toluene,²⁰ a similar sequence was found: AlCl₃ > SbCl₅ > FeCl₃ > SnCl₄ > TiCl₄ > ZnCl₂. From general evidence Calloway²¹ concluded that the order is generally AlCl₃ > FeCl₃ > SnCl₄ > TiCl₄. More recently Jensen and Brown²² established a kinetic comparison of the reactivities in the benzoylation of toluene in benzoyl chloride as solvent; relative rates were SbCl₅ 1300, FeCl₃ 570, AlCl₃ 1, SnCl₄ 1/350. From the data in the Table it is apparent that in the present acylation system the variation of catalyst reactivities is much smaller. If one can accept the earlier conclusion²³ that acylation at the *meso*-anthryl position must involve attack by a free acyl cation (*i.e.*, here by PhCO⁺), then the relative reactivities found represent the ease of dissociation of the preformed addition compounds, *viz.*, PhCOCl_xMCl_x → PhCO⁺ + MCl_(x+1)⁻, which will be a direct measure of their strengths as Lewis acids. Previous direct comparisons of the strengths of these catalysts as Lewis acids were AlCl₃ > FeCl₃ > TiCl₄ > SnCl₄ for the decomposition of benzoyle azide,²⁴ and SnCl₄ > FeCl₃ > AlCl₃ > TiCl₄ for the depolymerisation of paraldehyde.²⁵

¹⁷ Bardone, *Compt. rend.*, 1953, **236**, 828.

¹⁸ Sulzbacher and Bergmann, *J. Org. Chem.*, 1948, **13**, 303.

¹⁹ Baddeley, *J.*, 1949, S 99; Siemons and Vignau, *Bull. Soc. chim. France*, 1951, [5] **18**, 91; Baddeley, Holt, Makar, and Ivinson, *J.*, 1952, 3605; Bassilios, Makar, and Salem, *Bull. Soc. chim. France*, 1954, [5] **21**, 72; Reinheimer and Taylor, *J. Org. Chem.*, 1954, **19**, 802; Bassilios, Shawky, and Salem, *Rec. Trav. Chim.*, 1963, **82**, 298.

²⁰ Dermer and Billmeier, *J. Amer. Chem. Soc.*, 1942, **64**, 464; Wilson, Johnson, and Dermer, *ibid.*, 1941, **63**, 2881.

²¹ Calloway, *Chem. Rev.*, 1935, **17**, 327.

²² Jensen and Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 3039.

²³ Gore, *Chem. and Ind.*, 1954, 1385.

²⁴ Coleman, Newman, and Garrett, *J. Amer. Chem. Soc.*, 1954, **76**, 4534.

²⁵ Bell, *J.*, 1952, 2955.

Zirconium tetrachloride has not been much used as an acylation catalyst,²⁶ but is here strongly recommended for its high yields, and the very pure product it gives (comparable only with that obtainable with titanium tetrachloride). It is the only catalyst here investigated with which the yield of ketone reaches a maximum before 24 hr. Such "optimum time" conditions have been reported elsewhere for acylations using AlCl₃,²⁷ SbCl₅,²⁰ FeCl₃,²⁰ and TiCl₄.^{20, 28} Antimony pentachloride has been shown to be of very high reactivity (see above), but has apparently been used preparatively only rarely.²⁹ This is not surprising since this catalyst is difficult to handle, and in the present work gave appreciable amounts of resinous by-products, necessitating repeated chromatography for purification. The catalysts SbCl₅ and FeCl₃, but only in the 1½ hr. experiments, afforded a modification of 9-benzoylanthracene, of m. p. 161—162°. Mercuric chloride has previously been claimed³⁰ to effect benzoylation of anthracene in the absence of solvent, but it has been found to be ineffective in ethylene chloride. Similarly CdCl₂, VCl₃, and AlF₃* have been shown to be inert.

The combination ZnCl₂-POCl₃ has been employed with success in acylations using the free carboxylic acid.³² It was here found to give, under standard conditions, a 10% yield of 9-benzoylanthracene, whilst ZnCl₂ alone gives only a 5% yield. Phosphorus oxychloride by itself is here inactive, although several instances of its use in acylations with acyl chlorides have been reported.³³

Chlorosulphonic acid has also been shown to be of slight activity as a catalyst in the benzoylation of anthracene, a 7% yield being formed. In this reaction hydrogen chloride evolution was unusually rapid at first, and is due probably not to an acylation but to extraneous decomposition by means of water produced during an accompanying (and predominating) chlorosulphonation reaction. Fluorosulphonic acid has been reported to be catalytically active in acylations using acid anhydrides,³⁴ but chlorosulphonic acid has not been used before.

Cinnamoyl chloride has been used frequently to acylate aromatic compounds; the acylation may proceed normally (*e.g.*, with aromatic ethers³⁵) or abnormally (*e.g.*, with benzene³⁶). It is strange, therefore, that the only polycyclic system which has been directly cinnamoylated is pyrene.³⁷ Consequently, anthracene was submitted to the action of cinnamoyl chloride, using the Elbs procedure³⁸ (*i.e.*, final addition of aluminium chloride), which avoids interaction between the unsaturated halide and the catalyst. Below 15°, in carbon disulphide, a 90% yield of 9-anthryl styryl ketone and a trace of 9,10-dicinnamoylanthracene were obtained. In boiling carbon disulphide the latter was the major product (yield 56%). The former could also be obtained (in 52% yield) from a reaction carried out in nitrobenzene solution below 10°. At 30°, the yield of the monocinnamoyl compound fell to 18%, whilst a 5% yield of a compound, m. p. 275—276°, could be isolated, but its structure was not established.

The differences between the benzoylation and acetylation of anthracene are remarkable

* Cf. ref. 31.

²⁶ Krishnamurti, *J. Madras Agr. Students Union*, 1928, 40; Heine, Cottle, and van Mater, *J. Amer. Chem. Soc.*, 1946, **68**, 524.

²⁷ Calloway and Green, *J. Amer. Chem. Soc.*, 1937, **59**, 809.

²⁸ Cullinane, Chard, and Leyshon, *J.*, 1952, 376.

²⁹ Petrova, *Zhur. obshchei Khim.*, 1954, **24**, 491.

³⁰ Ogata and Ishiguro, *Science (Japan)*, 1949, **19**, 134.

³¹ Calloway, *J. Amer. Chem. Soc.*, 1937, **59**, 1474.

³² Bose and Shah, *Indian P.*, 57,888 (1958); Stanley, U.S.P. 2,854,485 (1958); Kane, Kulkarni, and Shah, *J. Sci. Ind. Res., India*, 1959, B **18**, 28.

³³ Newton, U.S.P. 2,645,663 (1953); Fellman, *Nature*, 1957, **179**, 265; Treibs and Hintermeier, *Annalen*, **605**, 35; Remizov, *Zhur. obshchei Khim.*, 1958, **28**, 2530.

³⁴ Hartough and Kosak, *J. Amer. Chem. Soc.*, 1947, **69**, 3093.

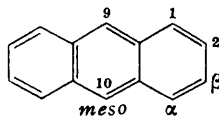
³⁵ Stockhausen and Gattermann, *Ber.*, 1892, **25**, 3521; Kohler, Heritage, and Burnley, *Amer. Chem. J.*, 1910, **44**, 60; Simonis and Lear, *Ber.*, 1926, **59**, 2908; Simonis and Danischewski, *Ber.*, 1926, **59**, 2914; Bergmann and Eschinazi, *J. Amer. Chem. Soc.*, 1943, **65**, 1413.

³⁶ Auwers and Risse, *Annalen*, 1933, **502**, 282.

³⁷ Scholl, Meyer, and Donat, *Ber.*, 1937, **70**, 2181; U.S.P. 2,069,683 (1937).

³⁸ Elbs, *J. prakt. Chem.*, 1887, [2], **35**, 503; Friedel and Crafts, *Ann. Chim. Phys.*, 1884, [6], **1**, 507.

enough to invite interpretation. A benzoyl group in the *meso*-anthryl position is remarkably stable under Friedel–Crafts acylating conditions, and this would be in keeping with the general pattern of irreversibility of acylation reactions.³⁹ The extreme lability of a *meso*-acetyl group,⁹ involving migration to the outer positions under Friedel–Crafts conditions,^{2, 9} or replacement by another acyl group (see above), is in sharp contrast. This migration probably involves deacylation, and substitution in the outer positions. In benzene the intermediate product 9-acetylanthracene could actually be isolated,² but from acetylations in nitrobenzene only α - and β -isomers can be isolated; it is uncertain whether these latter are formed directly, or indirectly *via* the *meso*-isomer. For such reversible substitution to occur, with migration away from the nuclear position (*meso*-), several factors must operate.⁴⁰ Analogous to the removal of a nitro-⁴⁰ or a sulphonic acid substituent² from the *meso*-anthryl position, the removal of an acyl group will depend on its geometry relative to the anthracene moiety. The *peri*-hydrogen atoms, by steric interference with the atoms of the acyl group, can effect a twisting of the latter relative to the aromatic ring, with resultant relief of strain, but a lowering of resonance stabilisation. Although *meso*-anthryl ketones can be deacylated^{2, 3, 5} by a solution of sulphuric acid in glacial acetic acid, the likelihood of a deacylation under Friedel–Crafts conditions can be much enhanced, because of complex formation between the carbonyl oxygen and aluminium chloride, *viz.*, $\text{ArCR}=\text{O} \cdot \text{AlCl}_3$. This will promote deacylation by increasing the effective size of the grouping. The role of a solvent such as nitrobenzene is not quite clear; it may, to some extent, solvate such a complex to give an even bulkier entity, at the same time as removing the co-ordinated aluminium chloride in the equilibrium $\text{ArCR}=\text{O} \cdot \text{AlCl}_3 + \text{PhNO}_2 \rightarrow \text{ArCR}=\text{O} + \text{PhNO}_2 \cdot \text{AlCl}_3$, by means of the basic solvent molecules. To account for the observed difference between an acetyl and a benzoyl group in the *meso*-anthryl position, it must be recalled that the acetyl group has greater steric requirements than has the benzoyl group.^{22, 41} In consequence the ketone–catalyst complex is bulkier in the former case, less coplanar and less stabilised than with the latter, and readier to undergo the deacylation stage.



A sample of pure 9-benzoylanthracene underwent a darkening where direct light could reach it; the coloured compound could be concentrated, but not identified, but some anthraquinone was formed at the same time. This autoxidation presumably takes place by attack of oxygen on the *meso*-position to give an intermediate hydroperoxide, to be followed by elimination of the benzoyl group.

EXPERIMENTAL

Infrared spectra were measured on a Grubb-Parsons model GS3 spectrometer, and u.v. spectra on a Unicam SP500 spectrophotometer, or a Unicam 137 recording spectrometer.

Thin-layer Chromatography.—Separations by thin-layer chromatography were effected on 20-cm. glass plates, coated to 0.25 mm. with silica gel G, activated for 20 min. at 110°, and developed by using 1 : 1 chloroform–carbon tetrachloride or 5% ether in benzene. The chromatograms were revealed by u.v., and spraying with *ca.* 20N-sulphuric acid followed by charring at 220° for 30 min. Occasionally charring was permitted for only 5 min., and the colour and fluorescence of the spots noted (2-benzoylanthracene: puce spot with red-brown fluorescence; 9-benzoylanthracene: grey

³⁹ Baddeley, through Ansell and Dewar, *Nature*, 1955, **175**, 982.

⁴⁰ Gore, *J.*, 1957, 1437.

⁴¹ Brown, Marino, and Stock, *J. Amer. Chem. Soc.*, 1959, **81**, 3310.

spot); this was of value to distinguish these substances from impurities with similar R_F values. A typical separation gave the following R_F values, relative to anthraquinone, in 1:1 chloroform-carbon tetrafluoride (with behaviour in u.v. light in parentheses): 9,10-dibenzoylanthracene 0.71 (absorbs, olive green), anthraquinone 1.00 (absorbs, black), 2-benzoylanthracene 1.11 (fluoresces, yellow), 9-acetylanthracene 1.30 (fluoresces, chalky yellow), 1-benzoylanthracene 1.36 (fluoresces, pale yellow), 9-benzoylanthracene 1.44 (absorbs, olive-green), and anthracene 2.08 (fluoresces, blue).

A two-dimensional double development method, as described by Stahl,⁴² was also used.

9-Benzoylanthracene.—(a) *General method, with ethylene chloride.* A mixture of the catalyst (0.055 mole), benzoyl chloride (11.5 g.), and ethylene chloride (100 ml.) was stirred for 20 min. at room temperature, then cooled to 0°. Anthracene (8.9 g.) was then added, and the reaction allowed to proceed for the appropriate time at 0°. Cold 6*N*-hydrochloric acid (100 ml.) was then added, and stirring continued until clean separation of the layers resulted. Any undissolved solid (*i.e.*, anthracene, obtained only in the low yield experiments, and occasionally free benzoic acid) was filtered off, the organic layer separated, with the aid of added chloroform (50 ml.), washed with *n*-sodium hydroxide, then with water, and evaporated on the steam-bath, finally *in vacuo*. If the odour of benzoyl chloride persisted, some ethanol was then added and the evaporation repeated. The residue of 9-benzoylanthracene was generally purified by chromatography on alumina (Spence, Type H; 50–100 g.) from benzene, and/or direct crystallisation (from glacial acetic acid, or ethanol). The ketone formed yellow crystals, m. p. 148° (reported values: 148°, ^{5,6a} or 148–149°^{6b}); λ_{\max} (MeOH): 2535, 3450, 3640, and 3830 Å, inflection at 3300–3340 Å, $\epsilon = 137,000, 5600, 7700, 6900$, and 3100, respectively (quoted maxima at 2560, 3150, 3460, 3640, and 3830 Å⁴³); ν_{\max} (CCl₄) at 1670 cm.⁻¹ (C=O), $\epsilon = 584$ [quoted^{6b} ν_{\max} (CHCl₃) at 1667 cm.⁻¹]. In certain cases, especially in the low yield experiments, the yield of ketone was determined (generally in duplicate) using the infrared band. Occasionally a C=O band was observed at 1721 cm.⁻¹, due to ethyl benzoate.

The catalysts were commercial grades, not especially purified. The ZrCl₄ used had Hf:Zr = 1.8%. The solid catalysts were coarsely ground. The experiment with VCl₃ was conducted under dry, oxygen-free nitrogen. Another modification of 9-benzoylanthracene was isolated in the 1½ hr. experiments with FeCl₃ or SbCl₅. The m. p. 154–156° (crude) or 161–162° pure, (benzene-petrol), was depressed to 148° by admixture with the modification, m. p. 148° (Found: C, 90.0; H, 5.4. C₂₁H₁₄O requires C, 89.4; H, 5.0%). Its infrared spectrum (KBr) was very similar to that of the modification, m. p. 148°.

(b) *With aluminium chloride, in nitrobenzene.* (i) Method of Krollpfeifer and Schütz:³ A mixture of aluminium chloride (13.3 g.), anthracene (8.9 g.), and nitrobenzene (150 ml.) was stirred, and cooled to -10°. Benzoyl chloride (51.9 g.) (*i.e.*, molar proportions 2:1:7.4, as compared with 2:1:5 in the literature³) was added quickly, and the mixture decomposed after 5 min. The working up was similar to that described in (a), with the addition of steam-distillation of the nitrobenzene. The yield of 9-benzoylanthracene was 7.3 g. (53%) (reported³ yield 79%).

(ii) Similar to (i), at 0° for 2 hr., with a continuous stream of dry nitrogen (yield: 2.5 g., 18%).

(iii) As for (ii), but without the stream of nitrogen [yield; isolated, 74%; estimated (*i.r.*), 95%].

(iv) Similar to (i), at 0° for 24 hr., with molar proportions: anthracene 1.0, aluminium chloride 1.1, benzoyl chloride 1.65 (yield, 99%).

(v) As for (iii), at room temperature for 45 hr. After steam-distillation of the reaction extract, the dark residue was extracted with benzene, the extract concentrated, and then chromatographed on alumina. Eleven fractions were collected and evaporated separately. No benzoylanthracene could be detected by *i.r.* spectrum or thin-layer chromatography. A middle fraction gave substantial amounts, and other fractions further amounts on fractional crystallisation, of an unidentified pale-brown ketone, m. p. 136–138°, or 145–148° (benzene-petrol) (1.0 g.) (Found: C, 76.6; H, 5.1%); λ_{\max} (MeOH) 2110, and 2640 Å, $E_{1\text{cm}}^{1\%} = ca. 600$ and 710, respectively; ν_{\max} (KBr) at 1660 cm.⁻¹ (C=O).

(c) *With aluminium chloride, in carbon disulphide.*⁷ A mixture of aluminium chloride (8.9 g.), benzoyl chloride (9.4 g.), and carbon disulphide (70 ml.) was warmed and stirred for 15 min. Anthracene (11.9 g.) was added, and the mixture boiled for 2.5 hr. The working up proceeded as described under (a). The crude yield of product was 18.5 g. (98%), m. p. 143–155°, or 146–147° (methanol). Thin-layer chromatography showed the absence of 1- or 2-benzoylanthracene.

Autoxidation of 9-Benzoylanthracene.—Pure 9-benzoylanthracene kept in a stoppered glass

⁴² Stahl, *Parfümerie u. Kosmetik*, 1958, **39**, 564; *Chem.-Ztg.*, 1958, **82**, 323.

⁴³ Barnett, Cook, and Ellison, *J.*, 1928, 885.

bottle became gradually orange-brown, where exposed to direct light. A sample (1 g.) containing the dark product was chromatographed on alumina from benzene; the unchanged ketone was eluted first as a yellow band, and was followed by an orange band (with yellow fluorescence), which on concentration and storage gave bright yellow needles of anthraquinone (30 mg.), m. p. and mixed m. p. 283—285°. The identity was confirmed by its i.r. spectrum, and behaviour on thin-layer plates. The mother liquor contained an unknown reddish compound, which was not further purified; however, it had λ_{max} at 3620 and 3800 Å.

*1-Benzoylanthracene.*⁸—1-Anthronitrile⁴⁴ (1.5 g.) was added as a slurry in dioxan (20 ml., freshly distilled from sodium) to a solution of phenylmagnesium bromide (from bromobenzene, 11.6 g., and magnesium, 1.8 g.) in ether (100 ml.), and the mixture boiled under reflux for 6 hr. 3*N*-Sulphuric acid (75 ml.) was added, the mixture stirred for 1 hr., the organic layer separated, washed with aqueous sodium hydrogen carbonate, then with water, and the extract dried and evaporated. The residue was dissolved in a minimum of benzene and chromatographed on alumina, giving pale yellow crystals of 1-benzoylanthracene, m. p. 139—140° (benzene) (reported m. p. 141°⁸). (The total yield was 0.8 g., 40%; no yield was reported⁸); λ_{max} (MeOH) 2200, 2530, 3120, 3280, 3440, 3610, and 3790 Å, $\epsilon = 28,200, 89,700, 3000, 3100, 4000, 5000, \text{ and } 5100$, respectively; ν_{max} (KBr) at 1662 cm.^{-1} (C=O).

*2-Benzoylanthracene.*⁸—Method as for the 1-isomer. The product was yellow 2-benzoylanthracene, m. p. 174—175° (benzene, acetone-ethanol, or acetic acid-ethanol) (lit.,⁸ m. p. 175°) (Found: C, 89.0; H, 5.1. Calc. for C₂₁H₁₄O: C, 89.4; H, 5.0%). A second, stable form was obtained by crystallisation from chloroform, with m. p. 190—191° (lit.,⁸ 187°). The melt of the lower melting modification may resolidify, and will then remelt at about 188—190°. The X-ray powder patterns of the two modifications are closely similar, pointing to minor differences only in the arrangement of the lattice. Light absorption (MeOH) max. 1970, 2140, 2560, 3400, 3550, 3740, and 3950 Å, $\epsilon = 12,000, 19,500, 60,000, 3900, 2800, 2000, \text{ and } 1400$, respectively; ν_{max} (KBr) at 1659 cm.^{-1} .

Benzoylation of 9-Acetylanthracene.—(i) The conditions were those used by Batten.¹⁶ 9-Acetylanthracene (5.5 g.) was dissolved by stirring in carbon disulphide (40 ml.), kept at 20°. Aluminium chloride (7.5 g.) was then added, followed by benzoic anhydride (8.6 g.). After 10 min., the mixture was boiled for 4 hr., and then worked up in the usual way. The product was 9-benzoylanthracene, m. p. and mixed m. p. 147—148° (yield 5.6 g., 79%; reported¹⁶ 52%).

(ii) A mixture of benzoyl chloride (7.7 g.), aluminium chloride (3.7 g.), and ethylene chloride was warmed and stirred until homogeneous, then placed in a bath at 18°. 9-Acetylanthracene (5.5 g.) dissolved in ethylene chloride (75 ml.) was then added, and the mixture then stirred at 18° for 6 hr., after which it was worked up in the usual way. The product (5.7 g.) had m. p. 138—140°, and the mother liquor afforded more solid (1.1 g.). The estimated yield of 9-benzoylanthracene was 6.5 g. (92%). Thin-layer chromatography showed the absence of other ketonic compounds.

Acetylation of 9-Benzoylanthracene.—A mixture of aluminium chloride (3.7 g.) and acetyl chloride (4.3 g.) was warmed in ethylene chloride (50 ml.) until a clear solution resulted. 9-Benzoylanthracene (7.1 g.) dissolved in ethylene chloride (50 ml.) was then slowly added, and the mixture boiled under reflux for 4 hr., followed by working up in the usual way (some accidental loss of material). The solid product, obtained after chromatography on alumina, was largely unchanged 9-benzoylanthracene, with small traces of anthracene and of two unidentified compounds; 9-acetylanthracene was, however, absent.

From a parallel experiment carried out for 48 hr., trace amounts of 9-acetylanthracene could be detected.

Benzoylation of 9-Bromoanthracene (with J. A. HOOPER).—A mixture of aluminium chloride (5.7 g.), benzoyl chloride (6.0 g.), and ethylene chloride (100 ml.) was stirred until homogeneous. 9-Bromoanthracene⁴⁵ (10 g.) was then added, and the mixture stirred at 15° for 3.5 hr. and at 50° for 30 min., and then boiled for 2.5 hr. After the mixture had been cooled, ice and 10*N*-hydrochloric acid were added, the organic layer separated, washed with *N*-sodium hydroxide, then with water, and evaporated to 20 ml. Benzene (20 ml.) was then added, and the mixture set aside. A buff solid (0.8 g., 5%), separated, m. p. 312—316°, giving white microcrystals of 9,10-dibenzoylanthracene, m. p. 331—333° [undepressed by admixture with an authentic⁵ sample, m. p. 329—335°, and having an identical i.r. spectrum; ν_{max} (KBr) at 1660 cm.^{-1} (C=O)]. The mother liquor was further evaporated, to yield a brown solid (1.4 g.), m. p. 210—250°, which could not be purified further. A second crop from these mother liquors finally afforded brownish crystals

⁴⁴ Gore, J., 1959, 311.

⁴⁵ Barnett, J., 1924, 124, 1084.

of 9-bromo-10-benzoylanthracene (5.3 g., 37%), 172—173° (glacial acetic acid), undepressed by admixture with an authentic sample, prepared by bromination⁵ of 9-benzoylanthracene, ν_{\max} (KBr) at 1667 cm^{-1} (C=O).

Benzoylation of 9,10-Dibromoanthracene (with J. A. HOOPER).—A mixture of aluminium chloride (3.9 g.) and benzoyl chloride (3.7 g.) in ethylene chloride (120 ml.) was stirred until homogeneous. 9,10-Dibromoanthracene (9 g.) was then added, and stirring continued at room temperature for 3 hr., and then at reflux temperature for 2 hr. The product, isolated in the usual way, separating slowly from the concentrated solution of the extract, was 9-bromo-10-benzoylanthracene (0.2 g., 2%), m. p. 170—173°, identical with an authentic specimen (mixed m. p., i.r. spectrum). The combined residues were chromatographed on alumina (from benzene), the eluate affording various fractions containing impure starting material, m. p. 195—200°.

9-Anthryl Styryl Ketone and 9,10-Dicinnamoylanthracene.—(i) To a mixture of anthracene (3.7 g.) and cinnamoyl chloride (3.4 g.) in carbon disulphide (80 ml.), powdered aluminium chloride (11 g.) was added in portions, with stirring, heat being evolved. The mixture was then boiled under reflux for 45 min. After removal of the solvent, the residue was treated with excess 10N-hydrochloric acid, and the brown product (5.4 g.) collected after dilution with water. This gave pale brown microcrystals (2.6 g., 56%) of 9,10-dicinnamoylanthracene (acetone-methanol), m. p. 231—232° (decomp.) (Found: C, 87.2; H, 5.1. $\text{C}_{32}\text{H}_{22}\text{O}_2$ requires C, 87.6; H, 5.1%); λ_{\max} (CHCl_3) 2510, 2570, 2920, 3490, 3700, and 3900 Å, $\epsilon = 76,400, 95,000, 46,000, 7400, 9400, \text{ and } 7400$, respectively. Dilute solutions exhibited a brown fluorescence; the ketone does not react with Brady's 2,4-dinitrophenylhydrazine reagent. A mixture of the ketone (0.84 g.), chromium trioxide (5.0 g.), 2N-sulphuric acid (10 ml.), and glacial acetic acid (100 ml.) was boiled under reflux for 2.5 hr.; a further quantity of chromium trioxide (5.0 g.) was then added and boiling continued for a further 1 hr. Dilution with much water gave a precipitate of crude anthraquinone (0.26 g., 65%), m. p. 267—270°; this formed pale yellow needles, m. p. 278—280° (glacial acetic acid), undepressed by admixture with an authentic specimen.

(ii) To a mixture of anthracene (10 g.) and cinnamoyl chloride (9.1 g.) in carbon disulphide (170 ml.), kept at 15°, a slurry of aluminium chloride (30 g.) in carbon disulphide (30 ml.) was added during 30 min. After the mixture had been stirred for 2 hr., chloroform (200 ml.) and excess of 10N-hydrochloric acid were added, and the organic layer was separated, washed with water, dried, and evaporated. The residue (19 g., m. p. 168—180°) was purified by chromatography on alumina from benzene, which gave, from the main band, bright yellow crystals of 9-anthryl styryl ketone (16.3 g., 90%), m. p. 201.5—202.5° (glacial acetic acid) (reported⁴⁶ m. p. 198—200°), undepressed by admixture with a specimen prepared⁴⁶ by the condensation of 9-acetylanthracene and benzaldehyde (Found: C, 89.9; H, 5.5. Calc. for $\text{C}_{25}\text{H}_{16}\text{O}$: C, 89.6; H, 5.2%); λ_{\max} (ethanol) 2510, 2670, 2910, 2990, 3040, 3450, 3630, and 3800 Å, $\epsilon = 139,000, 19,100, 23,400, 23,400, 23,400, 6000, 6800, \text{ and } 5700$, respectively; ν_{\max} (KBr) at 1631 cm^{-1} (C=O). The ketone had a strong purple fluorescence in methanol, did not react with Brady's reagent, and was oxidised to anthraquinone (yield 90%), as above. A more strongly adsorbed dark-yellow band, eluted with chloroform, yielded brown crystals (0.15 g., 0.6%), m. p. 225—228°, or 230—231° (glacial acetic acid), of 9,10-dicinnamoylanthracene, characterised by mixed m. p. and i.r. spectrum.

(iii) To a stirred mixture of aluminium chloride (4.1 g.) and cinnamoyl chloride (5.1 g.) in nitrobenzene (60 ml.), kept at 5—10°, anthracene (5.4 g.) was added during 5 min. After 2 hr. at 10°, benzene (200 ml.) was added, followed by careful addition of ice and 10N-hydrochloric acid. The organic layer was separated, washed with water, and left overnight over pellets of potassium hydroxide. The filtered extract was then evaporated *in vacuo* until all the benzene had been removed; the solution slowly deposited 9-anthryl styryl ketone (4.8 g., 52%), m. p. 197.5—200°. The mother liquor, on concentration, deposited more crystals (1.8 g.; m. p. *ca.* 165°), which proved to be a complex mixture.

(iv) To a stirred mixture of aluminium chloride (14.4 g.) and cinnamoyl chloride (11.9 g.) in nitrobenzene (220 ml.), kept at 28—30°, anthracene (6.4 g.) was added during 5 min., and stirring continued at 30° for 5.5 hr. Chloroform (250 ml.) and 6N-hydrochloric acid (200 ml.) were then added, the organic layer was separated, washed with water, then with N-sodium hydroxide, again with water, and dried, and the solvent removed *in vacuo*. The residual syrup (5.5 g.) set solid, m. p. 182—186°, and was separated into two components by fractional crystallisation from acetic acid and benzene. The more soluble fraction was 9-anthryl styryl ketone (1.8 g., 18%); the less soluble solid (0.5 g., 5%), m. p. 269—270° (decomp.), formed bright yellow clumps of a *compound*,

⁴⁶ Gagnon, D.I.C. Thesis, Imperial College of Science and Technology, London, 1931.

m. p. 275—276° (glacial acetic acid) [Found: C, 84.4; H, 5.1%; *M* (Rast), 434. $C_{32}H_{22}O_8$ requires C, 84.6; H, 4.9%; *M*, 454]; λ_{\max} . (dioxan) at 2280, 2360, 2510, 2670, 2800, 2900, 3020, 3140, and ca. 3360 Å, $E_{1\%}^{1\text{cm}}$ = 1200, 1200, 1000, 1200, 1200, 1200, 1200, 1000, and 750, respectively.

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