Action of Base on Non-enolisable Carbonyl Compounds. Part II.[1] Cleavage of Some Anthraquinones

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Anthraquinone, several methoxyanthraquinones, and 1- and 2-chloroanthraquinone are cleaved in high yield to afford mixtures of benzoic and/or phthalic acids when treated for up to 4 h with an excess of the butoxide–water reagent in 1,2-dimethoxyethane at *ca.* 85°. In favourable cases cleavage can be conveniently effected at 20°. To determine how substituents affect the pattern of cleavage the mixtures of acids produced were esterified and the mixtures of esters analysed by g.l.c. Phenanthrene-9,10-quinone undergoes a benzilic acid rearrangement when treated with the butoxide–water reagent and in the presence of oxygen a high yield of biphenyl-2-carboxylic acid is obtained.

ANTHRAQUINONES are more resistant to cleavage by base than many other types of non-enolisable carbonyl compound. Thus, a suspension of sodamide in refluxing toluene or xylene cleaves many non-enolisable carbonyl compounds [2] but not anthraquinone.[3,4] Cleavage of anthraquinone has usually been achieved by treating it with alkali metal hydroxides under drastic conditions such as treatment with a suspension of potassium hydroxide in an inert solvent at 250°.[5] Few substituted anthraquinones have been cleaved.[4,6] It has been reported [7] that anthraquinone is cleaved in high yield when treated for 15 h with potassium t-butoxide–water (molar ratio, 10 : 3) in refluxing toluene–ether (3 : 1 v/v). Even though this reagent cleaves anthraquinone efficiently under relatively mild conditions its action on other quinones has not been studied. We have now investigated its action on some methoxyanthraquinones, 1- and 2-chloroanthraquinone, and phenanthrene-9,10-quinone and report the results. Most of the anthraquinones studied were cleaved in high yield when treated for up to 4 h with an excess of the reagent in refluxing monoglyme (1,2-dimethoxyethane) (*ca.* 85°).

[1] Part I, D. G. Davies, M. Derenberg, and P. Hodge, *J. Chem. Soc.* (*C*), 1971, 455. Table 1 of this paper contained a numerical error. The composition of the acid fraction from the cleavage of benzophenone-2-carboxylic acid was benzoic acid (97%), phthalic acid (3%).

[2] K. E. Hamlin and A. W. Weston, *Org. Reactions*, 1957, **9**, 1.

[3] A. Haller and E. Bauer, *Compt. rend.*, 1908, **147**, 824.

[4] P. Hodge and R. W. Rickards, unpublished results.

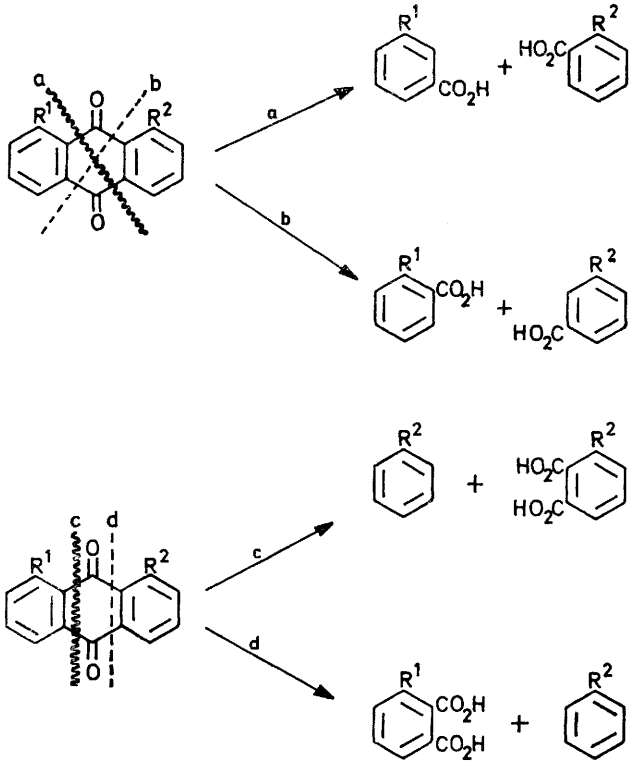
[5] J. Schneider, *Chem. průmsyl*, 1956, **6**, 188 (*Chem. Abs.*, 1957, **51**, 3541*f*).

[6] A. Eckert, *Ber.*, 1925, **58***B*, 321.

[7] G. A. Swan, *J. Chem. Soc.*, 1948, 1408.

In favourable cases cleavage could be effected conveniently at 20°. Since our preliminary communication,[8] Hausigk has successfully cleaved anthraquinone-2-carboxylic acid and several benzanthraquinones with butoxide–water in dioxan at 150°.[9]

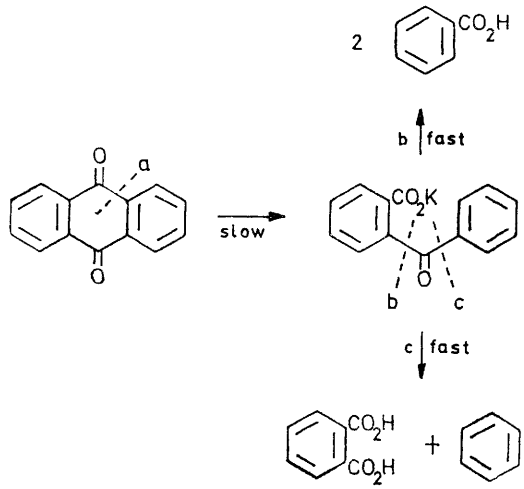
In general, anthraquinones could be cleaved in four ways; two ways (Scheme 1, a and b) afford a pair of benzoic acids in equal yield, and the other two (Scheme 1, c and d) a phthalic acid and a non-acidic fragment. Thus a maximum of four benzoic acids and two phthalic acids could be obtained (*e.g.* Scheme 1). One of the principal objects of our investigation has been to determine how methoxy- and chloro-substituents affect the ease and pattern of cleavage of anthraquinones.



SCHEME 1

The efficiency with which butoxide–water cleaves benzophenone [7] and nortricyclanone [10] varies considerably with the proportions of water and potassium t-butoxide used and a water : butoxide ratio of 3 : 10 is optimal.[7,10] In this work butoxide–water was prepared in monoglyme using these proportions. The mixtures of acids produced by the cleavages were esterified and the ester mixtures analysed by g.l.c. Results are in the Table.

Mechanism of the Cleavage Reaction. Cleavage of Anthraquinone.—Cleavages of anthraquinones almost certainly take place in two distinct stages (Scheme 2), the first stage being cleavage at one carbonyl group to afford the potassium salt of a benzophenone-2-carboxylic acid and the second, cleavage of this salt. Anthraquinones are generally cleaved much less readily than benzophenones [1] (especially benzophenone-2-carboxylic



SCHEME 2

acids [1,11]) and hence the first stage would in general be expected to be slower than the second and thus to be rate determining. In agreement with this, benzophenone-2-carboxylic acids were not found amongst the products, even in cases where substantial amounts of starting material were recovered. The intermediacy of the potassium salt of benzophenone-2-carboxylic acid in the cleavage of anthraquinone is supported by the fact that cleavages of benzophenone-2-carboxylic acid [1] and anthraquinone both afford benzoic and phthalic acids in the same proportions.

The mechanism of the initial cleavage is probably analogous to that for the cleavage of benzophenone.[1] Benzophenone-2-carboxylic acid is cleaved mainly at the bond nearer the carboxy-substituent (Scheme 2, b) [1] and hence cleavage of anthraquinone affords benzoic acid as the main product.

Cleavage of Methoxyanthraquinones.—The results obtained from these cleavages can be readily rationalised in terms of mechanisms similar to Scheme 2 if substituents affect the initial cleavages in the same way that they affect the cleavages of benzophenones. The relevant results from the benzophenone study [1] are as follows. (i) The rates of cleavage of the methoxy-substituted benzophenones decrease in the order *o*-MeO ≫ H ≫ *p*-MeO. The position of *m*-methoxybenzophenone in the series is not clear. It is certainly cleaved much more readily than *p*-methoxybenzophenone and probably more readily than benzophenone but less readily than *o*-methoxybenzophenone. (ii) Substituents favour cleavage of the bond to the ring bearing the substituent in the order *o*-MeO ≫ *o*-CO_2^- ≫ *m*-MeO > H > *p*-MeO.

[8] D. G. Davies and P. Hodge, *Chem. Comm.*, 1968, 953.
[9] D. Hausigk, *Tetrahedron Letters*, 1970, 2447.
[10] P. G. Gassman, J. T. Lumb, and F. V. Zalar, *J. Amer. Chem. Soc.*, 1967, **89**, 946.
[11] M. Derenberg and P. Hodge, unpublished results.

Cleavage of anthraquinones by water–butoxide

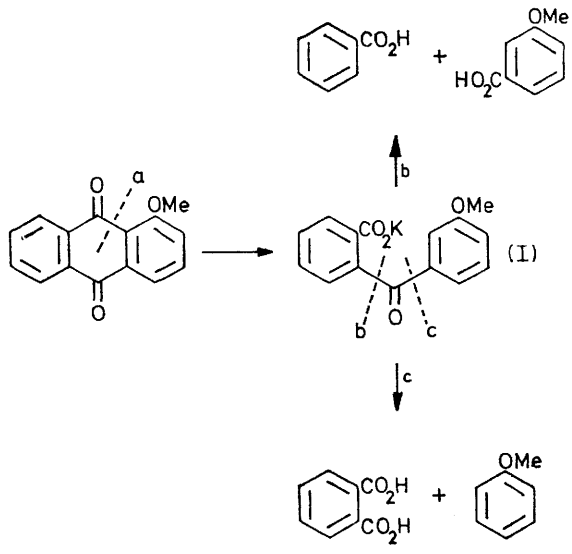
Substituent(s)	Reaction time (t/h) [a]	Yield (%) of acids [b]	Acid(s) produced [c]	Composition (%) of the acid fraction [d]
None	2	60 [e]	Benzoic	97
	4	98	Phthalic	3
1-Methoxy	2 [f]	85	Benzoic	44
	2	91	3-Methoxybenzoic	50
			Phthalic	6
1,2-Dimethoxy	2	98	Benzoic	46
			3-Methoxybenzoic	1·5
			4-Methoxybenzoic	1·5
			Phthalic	7
			3,4-Dimethoxybenzoic	44
1,3-Dimethoxy	2	94	Benzoic	47
			Phthalic	6
			Unidentified	3
			3,5-Dimethoxybenzoic	44
1,4-Dimethoxy	2	98	Phthalic	93
			Unidentified	7
1,5-Dimethoxy	2	97	3-Methoxybenzoic	100
1,8-Dimethoxy	4 [f]	89	2-Methoxybenzoic	49
			3-Methoxybenzoic	49
			3-Methoxyphthalic	2
2,6-Dimethoxy	6	33 [g]	3-Methoxybenzoic	22
			4-Methoxybenzoic	78
1-Chloro	2 [f]	90	Benzoic	23
	2	96	3-Chlorobenzoic	32
			Phthalic	45
2-Chloro	2	97	Benzoic	39
			3-Chlorobenzoic + 4-Chlorobenzoic	39 [h]
			Phthalic	22

[a] Reactions carried out at reflux temperature (*ca.* 85°) unless indicated otherwise. [b] Calculated assuming the acid fraction had the composition given in the last column. [c] Acids are listed in order of increasing retention times of the corresponding esters (Apiezon L; 195°). [d] Determined by g.l.c. of the methylated acid fraction. Results are probably accurate to within 3%. The esters of unidentified acids were assumed to have the same molecular weight and response ratio as methyl benzoate. [e] 31% Starting material recovered. [f] Reaction carried out at 20°. [g] 64% Starting material recovered. [h] Methyl 3- and 4-chlorobenzoates were not resolved under the g.l.c. conditions used. I.r. spectral analysis indicated that both isomers were present and that the 4-chloro-isomer was the more abundant.

In the benzophenone series an *ortho*-methoxy-substituent not only enhances the rate of reaction more than any other substituent listed, but also promotes cleavage of the bond to the ring bearing the substituent more than any other. It is so effective in the latter respect that *o*-methoxybenzophenone cleaves to give an acid fraction that is >99% benzoic acid. By analogy it would be expected that in the anthraquinone series α-methoxy-substituents would play the major role in determining the ease and site(s) of initial cleavage. As an α-methoxy-substituent is *ortho* with respect to the carbonyl group nearer to it, it would be expected that the rate of reaction at this carbonyl group would be considerably enhanced and as a consequence the rate of overall cleavage of an α-methoxyanthraquinone would be greater than that of anthraquinone. Also cleavage at such a carbonyl group would be expected to occur almost entirely at the bond to the ring bearing the α-methoxy-substituent.

The results are fully in accord with this. All the anthraquinones containing α-methoxy-substituents were cleaved more readily than anthraquinone and in each case the composition of the acid fraction obtained can be explained by cleavage initially of a bond *ortho* to an α-methoxy-substituent.

1-Methoxyanthraquinone was conveniently cleaved at 20°. The major acid products were benzoic acid and 3-methoxybenzoic acid; phthalic acid was a minor

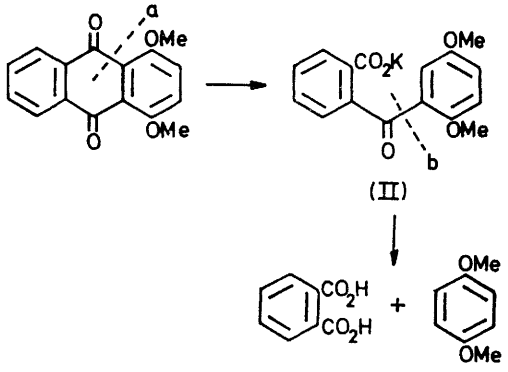


SCHEME 3

product. The formation of these acids can be explained by initial cleavage at position a (Scheme 3) and cleavage of the product mainly at position b. The benzophenone

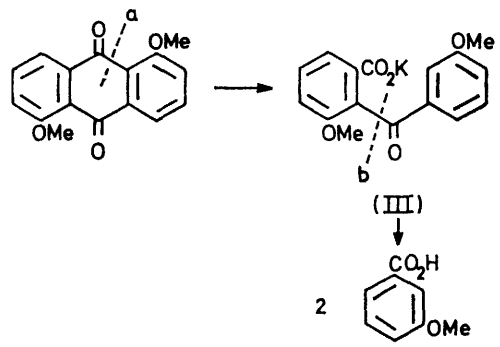
(I) would be expected to cleave mainly at position b because an *o*-carboxylato-substituent favours cleavage of the bond nearer to it more than a *m*-methoxy-substituent. The latter does, however, favour cleavage, and it was not surprising that the cleavage of 1-methoxy-anthraquinone afforded a greater yield of phthalic acid than the cleavage of anthraquinone.

The cleavages of 1,2- and 1,3-dimethoxyanthraquinone followed a similar pattern to that of 1-methoxyanthraquinone. Apart from the expected acids the reaction of 1,2-dimethoxyanthraquinone afforded small amounts of acids which, on the basis of the g.l.c. retention times of their esters, were probably 3- and 4-methoxybenzoic acids, and the reaction of 1,3-dimethoxyanthraquinone afforded a small amount of an unidentified acid. It is not known how these minor products arise.



SCHEME 4

The principal acid product from the cleavage of 1,4-dimethoxyanthraquinone was phthalic acid; a small amount of an unidentified acid was also obtained. The formation of phthalic acid can be explained by cleavage at position a (Scheme 4) to give the benzophenone (II) and cleavage of this at position b in accord with (ii).

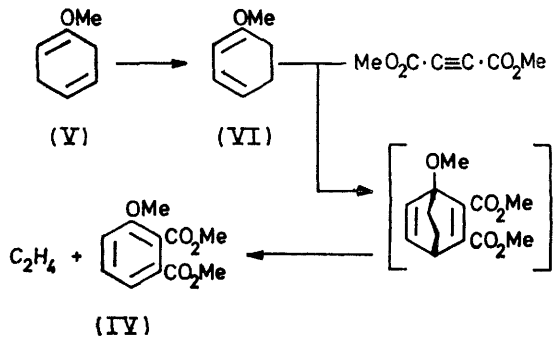


SCHEME 5

Cleavage of 1,5-dimethoxyanthraquinone at position a (Scheme 5) would give the benzophenone (III). This would be expected to be cleaved entirely at position b because both the *o*-methoxy- and *o*-carboxylato-substituents strongly favour cleavage at this site. In agreement with this, 3-methoxybenzoic acid was the only product obtained. As this substrate afforded only one acid product an attempt was made to prepare the ring-deuteriated acid by using the deuterium oxide–butoxide reagent. Under the usual work-up conditions the acid rapidly lost deuterium by exchange. To minimise this the aqueous solution was carefully acidified with acetic acid in the presence of ether, so that the product was immediately extracted from the aqueous layer. The product was shown by ^{1}H n.m.r. spectroscopy to be [2-^{2}H]-3-methoxybenzoic acid (98% pure). The position of the deuterium atom was established by determining the coupling constants between the aromatic protons. The aromatic proton signals were analysed as an ABC system with the aid of a computer. The magnitudes of two of the coupling constants (8·55 and 7·76 Hz) were typical of those between *ortho*-protons [12] and the magnitude of the third (1·06 Hz) was typical of those between *meta*-protons.[12]

1,8-Dimethoxyanthraquinone was cleaved more readily than anthraquinone and the reaction could be conveniently carried out at 20°. The main products were 2- and 3-methoxybenzoic acid, in equal amounts. Similar results were obtained by Hodge and Rickards [4] using a different base reagent. They found that whilst anthraquinone was unaffected by treatment with a suspension of sodamide in xylene heated under reflux, 1,8-dimethoxyanthraquinone was cleaved in 16% yield to a mixture of 2- and 3-methoxybenzamide when treated with sodamide in ethylbenzene heated under reflux. These results can be rationalised in a similar way to those for the cleavage of 1-methoxyanthraquinone.

The preparation of dimethyl 3-methoxyphthalate (IV), required as a g.l.c. standard in the analysis of the cleavage products from 1,8-dimethoxyanthraquinone, deserves a brief mention. This compound has previously been prepared by the reaction sequence in Scheme 6.[13] In the present work the same sequence was used but instead of isomerising the non-conjugated diene (V) to the conjugated diene (VI) by using a base



SCHEME 6

reagent such as potassium amide in liquid ammonia [14] and then treating the product with the acetylene, we

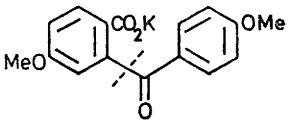
[12] F. A. Bovey, 'Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York and London, 1969, p. 368.

[13] A. J. Birch and P. Hextall, *Austral. J. Chem.*, 1955, **8**, 96.

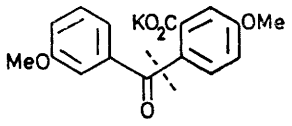
[14] A. J. Birch, *J. Chem. Soc.*, 1947, 1642.

carried out the isomerisation and the subsequent reactions in a single step by heating together the unconjugated diene (V) and dimethyl acetylenedicarboxylate in a Carius tube at 170—180° for 36 h. The yield of the desired phthalate was 91%. Some similar *in situ* conjugations have recently been described.[15,16]

2,6-Dimethoxyanthraquinone, in which there are no α-methoxy-groups, was cleaved less readily than anthraquinone. It would be expected that the initial cleavage would be chiefly of one of the bonds *meta* to a methoxy-substituent, to give the benzophenone (VII), which would



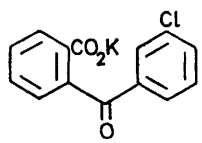
(VII)



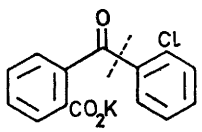
(VIII)

then suffer cleavage at the bond indicated to give 4-methoxybenzoic acid. Initial cleavage would be expected to occur to a lesser extent at one of the bonds *para* to a methoxy-substituent to give the benzophenone (VIII), which would then be cleaved mainly at the bond indicated to give 3-methoxybenzoic acid. In agreement with this the acid products were 3- and 4-methoxybenzoic acids, with the latter present in greater amount.

Cleavage of Chloroanthraquinones.—The results for the cleavages of 1- and 2-chloroanthraquinone can be rationalised in a similar manner. The relevant results from the benzophenone study [1] are (i) all three chlorobenzophenones cleave more readily than benzophenone, *o*- and *m*-chlorobenzophenone being the most rapid; (ii) substituents favour cleavage of the bond to the ring bearing the substituent in the order *o*-Cl ≫ *m*-Cl and *o*-CO_2^- > *p*-Cl > H. Rationalisation of the results is more complicated than in the case of the α-methoxyanthraquinones, because initial cleavage is likely to occur to a substantial extent at each carbonyl group.

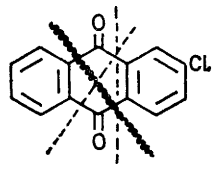


(IX)



(X)

As anticipated 1-chloroanthraquinone was cleaved more readily than anthraquinone itself, and the reaction could be conveniently effected at 20°. Initial cleavage at the carbonyl group nearer the substituent would probably be exclusively of the bond to the substituted ring to give the benzophenone (IX), cleavage of which would be likely to occur in each direction, the products being either benzoic and 3-chlorobenzoic acids or phthalic acid and chlorobenzene. Initial cleavage at the other carbonyl group would probably give mainly the benzophenone (X), and this would almost certainly be cleaved to afford phthalic acid and chlorobenzene. Although the observed products are those predicted by the former pathway, cleavage probably also occurs by the latter. The cause of the substantial difference between the yield of benzoic acid and the yield of 3-chlorobenzoic acid is not known. The result was reproducible and the most likely explanation appeared to be that the starting material was contaminated with a dichloroanthraquinone, possibly the 1,5-isomer. This was not, however, supported by the mass spectrum of the starting material, which showed no peaks at the positions required for a dichloroanthraquinone molecular ion.



(XI)

It would be anticipated that 2-chloroanthraquinone (XI) would cleave in the directions shown. The results can be explained by postulating that cleavage occurred to some extent in each direction.

Action of Butoxide–Water on Phenanthrene-9,10-quinone.—It is known that the phenanthrene-9,10-quinone undergoes a benzil–benzilic acid-type rearrangement when treated with aqueous sodium hydroxide,[17] and it was found that with the present reagent the same rearrangement occurred. The acid (XII) produced was, however, largely transformed into other products.

Treatment of the quinone with butoxide–water at *ca.* 85° for 4 h under nitrogen gave the acid (XII) (11%), fluorenol (XIII) (30%), fluorenone (XIV) (36%), biphenyl-2-carboxylic acid (XV) (3%), and unchanged quinone (7%). Fluorenol (XIII) was probably formed by decarboxylation of the acid (XII).[18] Fluorenone (XIV) is rapidly cleaved to biphenyl-2-carboxylic acid (XV) by butoxide–water [1,10] and thus probably arose by oxidation of fluorenol (XIII) during work-up. Biphenyl-2-carboxylic acid (XV) almost certainly arose by cleavage of a small amount of fluorenone which may have been formed directly from the acid (XII) [19] or by oxidation of some of the fluorenol before the cleavage mixture was quenched.

It was anticipated that treatment of the quinone with butoxide–water under oxygen would afford biphenyl-2-carboxylic acid (XV) in high yield. This was the case.

Since this work was completed Hausigk has reported [9] that treatment of phenanthrene-9,10-quinone with butoxide–water in dioxan affords the rearrangement product (XII).

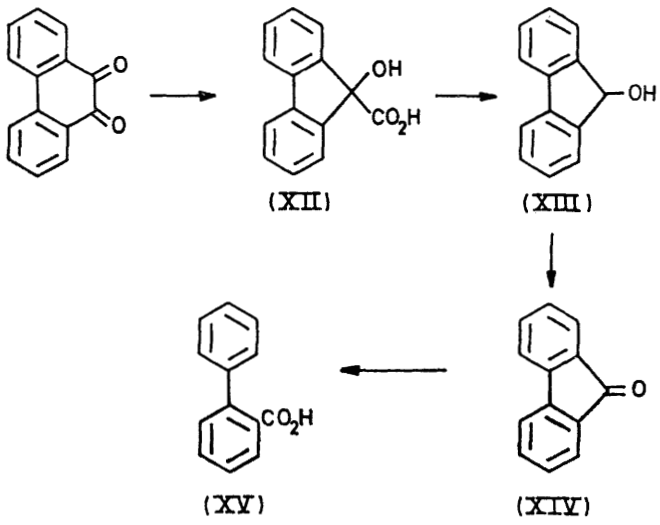
[15] I. Alfaro, W. Ashton, L. D. McManus, R. C. Newstead, K. L. Rabone, N. A. J. Rogers, and W. Kernick, *Tetrahedron*, 1970, **26**, 201.

[16] A. J. Birch, P. L. Macdonald, and V. H. Powell, *J. Chem. Soc.* (*C*), 1970, 1469.

[17] H. Staudinger, *Ber.*, 1906, **39**, 3062.

[18] P. Friedlander, *Ber.*, 1877, **10**, 534.

[19] R. Anschütz and F. R. Japp, *Ber.*, 1878, **11**, 211.



(XII) (XIII) (XIV) (XV)

EXPERIMENTAL

Experimental details are the same as for Part 1 [1] with the following addition. P.l.c. was carried out using plates coated with silica gel (Merck Kieselgel HF_{254}) and chloroform–hexane as eluant.

Substrates.—The following methoxyanthraquinones were prepared by methylating commercial samples of the corresponding hydroxyanthraquinones by (*a*) treating the substrate in chloroform with excess of methyl iodide and silver oxide and heating the mixture under reflux for 24 h or (*b*) treating the substrate in monoglyme with excess of methyl iodide and sodium hydride and heating the mixture under reflux for 20 h: 1-methoxy (method *a*, 95%); 1,2-dimethoxy (*a*, 20%); 1,4-dimethoxy (*b*, 40%); 1,5-dimethoxy (*a*, 92%); 1,8-dimethoxy (*a*, 97%); and 2,6-dimethoxy (*a*, 52%). 1,3-Dimethoxyanthraquinone was prepared by the method of Birch *et al.*[20] All other quinones were commercial samples purified by several crystallisations. All the substrates had physical data in good agreement with those in the literature.

Cleavage Reactions.—The cleavages were carried out on 0·5—2 mmol of substrate using a procedure similar to that in Part 1,[1] except that ethyl acetate was used for all extractions. The reactions were run for the times and at the temperatures given in the Table and were then worked up to afford base-insoluble and acid fractions. No attempts were made to isolate benzene, anisole, or chlorobenzene and in general, apart from any recovered starting material, the amount of base-insoluble product was <4% (w/w) of that of the starting material.

The acid fractions were methylated with diazomethane in ether and the mixtures of esters produced were analysed by g.l.c.[1] The mixture of esters derived from the cleavage of 2-chloroanthraquinone was expected to contain methyl 3-chlorobenzoate and the 4-chloro-isomer. These esters were not resolved under the g.l.c. conditions used but comparison of the i.r. spectrum of the ester mixture with those of authentic samples indicated that both esters were present and that the 4-chloro-isomer was present in greater amount. In favourable cases the acid or ester mixtures derived from the cleavages of methoxyanthraquinones were also analysed by ^{1}H n.m.r. spectroscopy, by comparing the areas of the signals due to the aromatic protons with those due to the *O*-methyl protons, or by comparing the relative intensities of *O*-methyl signals where these were characteristic and sufficiently well resolved.

Fractional recrystallisation from hexane of a portion of the acid fraction from the cleavage of anthraquinone afforded pure samples of benzoic acid and phthalic acid. A portion of the acid fraction from the cleavage of 1,4-dimethoxyanthraquinone was recrystallised from chloroform to afford phthalic acid, and a portion from the cleavage of 1,5-dimethoxyanthraquinone was recrystallised from hexane to give 3-methoxybenzoic acid. The acids were identified by comparison with authentic samples.

Dimethyl 3-Methoxyphthalate.—Dimethyl acetylenedicarboxylate (1·9 g), 2,5-dihydroanisole (1·4 g of crude; 79% pure, prepared by reduction of anisole [21]), and quinol (20 mg) were heated together in a Carius tube at 170—180° for 36 h. Chromatography of the product on alumina in hexane gave dimethyl 3-methoxyphthalate (2·1 g, 91%), m.p. 72—72·5° (from ethanol) (lit.,[22] 73—74°).

Cleavage of 1,5-Dimethoxyanthraquinone to Afford [2-^{2}H]-3-Methoxybenzoic Acid.—The substrate (500 mg) was treated with potassium t-butoxide (4·55 g) and deuterium oxide (0·21 ml, 99·8% pure) in monoglyme (40 ml). The mixture was heated under reflux for 2 h, cooled, and added to brine (150 ml), and the solution was then washed with ether (4 × 60 ml). The basic aqueous layer was then divided into three equal portions, which were worked up separately. (i) Acidification with hydrochloric acid, extraction with ether, and recovery afforded an acid fraction (equivalent to 95% yield) which was shown by ^{1}H n.m.r. spectroscopy to be essentially 3-methoxybenzoic acid. (ii) Acidification with excess of acetic acid, extraction with ether, and recovery afforded an acid fraction (88% yield) which was shown by ^{1}H n.m.r. spectroscopy to consist of 3-methoxybenzoic acid (8%) and the deuteriated acid (92%). (iii) Acidification to pH 6 with acetic acid in the presence of ether, separation of the ether, and recovery afforded an acid fraction (35% yield) which was shown by ^{1}H n.m.r. spectroscopy to consist of 3-methoxybenzoic acid (2%) and [2-^{2}H]-3-methoxybenzoic acid (98%), δ 3·87 (3·00 H, s, Me) and 7·05—7·90 p.p.m. (3·02 H, m, ArH). The signals due to the aromatic protons were analysed as an ABC system using the computer programme LAME, a revised version of LAOCN3,[23] and a close fit was obtained between the calculated and observed line positions and intensities. The r.m.s. error of the frequencies was 0·057 Hz. The calculated chemical shifts were δ 7·11 (4-H), 7·42 (5-H), and 7·77 (6-H) p.p.m. The calculated coupling constants were $J_{4,5}$ 8·55 ± 0·07, $J_{4,6}$ 1·06 ± 0·08, and $J_{5,6}$ 7·76 ± 0·08 Hz. The first and third coupling constants are typical of those between *ortho*-protons and the second is typical of those between *meta*-protons.[12]

Action of Butoxide–Water on Phenanthrene-9,10-quinone.—(a) *Under nitrogen.* The quinone (500 mg) was treated with potassium t-butoxide (2·54 g) and water (0·12 ml) in monoglyme (40 ml) under nitrogen and the mixture was heated under reflux for 4 h.

[20] A. J. Birch, D. N. Butler, and J. B. Siddall, *J. Chem. Soc.*, 1964, 2941.

[21] A. L. Wilds and N. A. Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5360.

[22] 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

[23] C. W. Haigh, personal communication to Dr. T. N. Huckerby; A. A. Bothner-By and S. Castellano, *J. Chem. Phys.*, 1964, **41**, 3863.

The major components of the base-insoluble fraction (407 mg), separated by p.l.c. and identified by comparison with authentic samples, were fluorenone (156 mg, 36%), phenanthrenequinone (37 mg, 7% recovery), and fluorenol (136 mg, 30%). The acid fraction (108 mg) was treated with diazomethane in ether and the resultant ester mixture was analysed by g.l.c. (Apiezon L; 195°) by comparison with authentic samples. The major components were biphenyl-2-carboxylic acid (13 mg, 3%), 9-hydroxyfluorene-9-carboxylic acid (58 mg, 11%), and an unidentified compound (*ca.* 32 mg).

Authentic samples required for comparison with the products were prepared as follows: biphenyl-2-carboxylic acid (97%) by cleavage of fluorenone,[1] fluorenol (90%) by the reduction with potassium borohydride of fluorenone,[24] and 9-hydroxyfluorene-9-carboxylic acid (25%) by rearrangement of phenanthrenequinone with aqueous sodium hydroxide.[17]

(b) *Under oxygen.* The quinone (500 mg) was treated with water (0·58 ml) and potassium t-butoxide (11·95 g) in monoglyme (80 ml) at 20° and the mixture was heated under reflux for 4 h in an atmosphere of dry oxygen. The reaction was worked-up in the usual way. The acid fraction (387 mg) was shown to be biphenyl-2-carboxylic acid (90%) by comparison with an authentic sample.

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[24] A. I. Vogel, 'Textbook of Practical Organic Chemistry,' Longmans, London, 1956, p. 881.