Cleavage of Anthraquinones to Benzoic Acids

By D. G. DAVIES and PHILIP HODGE*

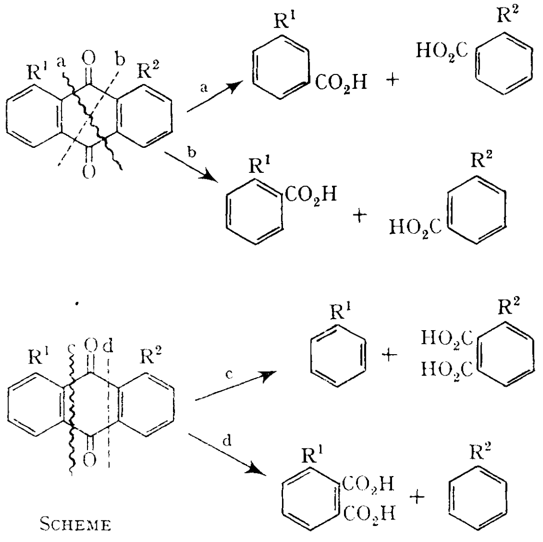
(*Chemistry Department, University of Lancaster, Lancaster*)

ANTHRAQUINONE is cleaved in high yield to a mixture of benzoic and phthalic acids when treated for 15 hr. with an excess of potassium t-butoxide and water (molar ratio 3 : 1) in refluxing toluene–ether (3 volumes to 1).[1] Treatment of anthraquinone with a suspension of sodamide in refluxing toluene[2] or xylene[3] does not effect cleavage, but Hodge and Rickards[3] have shown that 1,8-dimethoxyanthraquinone can be cleaved in 16% yield by use of sodamide in refluxing ethylbenzene. This suggests that α-methoxy-groups aid cleavage, and prompted us to investigate the action of the butoxide–water reagent on some substituted anthraquinones. We report now that several methoxyanthraquinones can be cleaved in high yield when treated for up to 4 hr. with an excess of the butoxide–water reagent in refluxing 1,2-dimethoxyethane (*ca.* 85°).

TABLE

Substrate	Reflux time (hr.)	Yield % of acids[a]	Major acid products	% Composition of the acid fraction[b]
Anthraquinone	4	98	Benzoic	97
			Phthalic	3
1-Methoxy-anthraquinone	2	91	Benzoic	44
			3-Methoxybenzoic	50
			Phthalic	6
1,2-Dimethoxy-anthraquinone	2	98	Benzoic	46
			3,4-Dimethoxybenzoic	44
			Phthalic	7
1,3-Dimethoxy-anthraquinone	2	94	Benzoic	47
			3,5-Dimethoxybenzoic	44
			Phthalic	6
1,5-Dimethoxy-anthraquinone	2	97	3-Methoxybenzoic	100
1,8-Dimethoxy-anthraquinone	4[c]	89	2-Methoxybenzoic	49
			3-Methoxybenzoic	49
			3-Methoxyphthalic	2
2,6-Dimethoxy-anthraquinone	6	33	3-Methoxybenzoic	22
			4-Methoxybenzoic	78
2-Methyl-anthraquinone	7	2	Not identified	—

[a] Calculated assuming the acid fraction was entirely benzoic acids.
[b] Major components only; determined by g.l.c. of the esterified (diazomethane) acid fraction.
[c] At 20°.

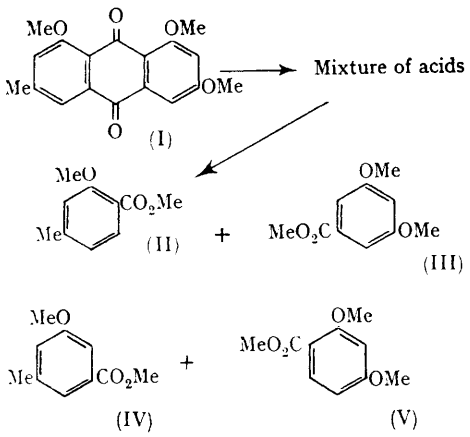


SCHEME

In general, cleavage could occur in two ways (a and b, Scheme), each of which affords a pair of benzoic acids in equal yields, and two ways (c and d) each of which affords a phthalic acid and a non-acid fragment. Thus a maximum of four benzoic acids and two phthalic acids could be obtained. These cleavages are shown in the Scheme for a 1,8-disubstituted anthraquinone as an example.

The results are summarised in the Table. In all cases the acid fraction was esterified and the resulting ester mixture was analysed by g.l.c. In most cases the major components of the acid fractions were also identified by isolating the acids, or by comparing n.m.r. spectra of the acid or ester mixtures with the spectra of authentic samples. It is clear that (i) cleavage takes place to afford mainly benzoic acids, (ii) an α-methoxy-group facilitates cleavage of the neighbouring bond, and (iii) introduction of a β-methyl group into anthraquinone makes cleavage much less favourable.

Cleavage of anthraquinones in this way promises to be a useful method for degrading naturally occurring anthraquinones, especially as a very large proportion have one or more α-hydroxy-groups.[4] However, many of these anthraquinones also contain a β-methyl group[4] and it is important to know whether the presence of this group will



result in cleavages only taking place in low yields. As a test emodin trimethyl ether (I) (80 mg.) was treated for 2 hr. with the butoxide–water reagent in refluxing 1,2-dimethoxyethane. The acid fraction (65% yield) was esterified and the ester mixture analysed by g.l.c. There were four products. Three of these were identified by comparison with authentic esters as (II) (22%), (III) (26%), and (V) (22%). The fourth was presumed to be (IV) (30%). The good yield in this cleavage indicates that, in this case at least, the effect of the methoxy-groups outweighs that of the β-methyl group.

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

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