# Chemistry of Quinones. Part II.[1] Some Base-catalysed Reactions of Alkylanthraquinones

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When 1- and 2-methyl-, 2-ethyl-, and 2-isopropyl-anthraquinone are treated with the reagent formed by adding water (3 equiv.) to potassium t-butoxide (10 equiv.) in 1,2-dimethoxyethane, the main reaction is oxidation to give dehydro-dimers. 2-Methylanthraquinone, for example gives 1,2-di(anthraquinon-2-yl)ethylene. 2-t-Butyl-anthraquinone, however, is cleaved in high yield when treated with the same reagent giving a mixture of benzoic and 3- and 4-t-butylbenzoic acids.

ANTHRAQUINONE and some methoxy- and chloro-derivatives are cleaved in high yield to give mixtures of benzoic and/or phthalic acids when treated with the butoxide–water reagent.[1] We have investigated the action of this reagent on some alkylanthraquinones and now report the results. Very little cleavage occurs when 1- and 2-methyl-, 2-ethyl-, and 2-isopropyl-anthraquinone are treated with the reagent, the main reaction being oxidation to give dehydro-dimers. 2-t-Butylanthraquinone is, however, cleaved in high yield.

2-Methylanthraquinone is reported[2] to react with alcoholic potassium hydroxide at 150—170° to give 1,2-di(anthraquinon-2-yl)ethylene (I) (no yield given). We find that the quinone reacts with the butoxide–water reagent at 85° under nitrogen to give the same product in 84% yield. The structure of our product has been confirmed by spectroscopic measurements, in particular the mass spectrum (M^+ 440) and the ^{1}H n.m.r. spectrum (signals only in the vinyl and aromatic proton regions). In the absence of clear evidence it is assumed that this product, and the ethylene derivatives (II) and (III) described later, are the *trans*-isomers.

ACH=CHA
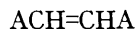
(I) A = anthraquinon-2-yl

(II) A = anthraquinon-1-yl

Scholl and Wallenstein have reported[3] that 1-methyl-anthraquinone reacts with potassium hydroxide and sodium acetate at 165° to give 1,2-di(anthraquinon-1-yl)-ethylene (II), and we have found that this quinone gives the same product (20%) when treated with the butoxide–water reagent. The reaction was more complex than that with the 2-methyl compound and several other dimeric products (each less than 12%) were found.

The action of base on 2-ethylanthraquinone has not been reported previously. This compound reacted with the butoxide–water reagent to give two main products: the butene derivative (III) (33%), M^+ 468, and only δ 2·52 (s) in addition to the aromatic proton signals; and the butane (IV) (38%), only δ 1·50 (d, methyl groups) and 3·26 (m, benzylic protons) in addition to the aromatic proton signals. The mass spectrum of compound (IV) had a small molecular ion peak at m/e 470 and base peaks at m/e 235 and 236. The former base peak is almost certainly due to benzylic cleavage

and the latter to a McLafferty rearrangement of the type shown in Scheme 1 both of which have ample analogies in the fragmentation of simple arylaromatic compounds.[4] Both (±)-and *meso*-forms of structure (IV) could have been produced but we only isolated one product. It may be that the other product was only formed in low yield or that it reacted much more rapidly than the one isolated to give the butene derivative (III).

(III)   (IV)

A = anthraquinon-2-yl

SCHEME 1
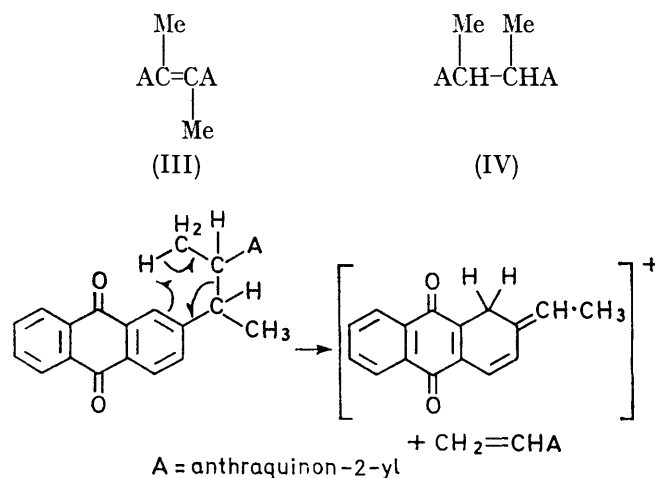
The reaction between 2-isopropylanthraquinone and the butoxide–water reagent clearly could not give a product analogous to compounds (I)—(III). Two main products were obtained: the ethane derivative (V) (56%), M^+ 498, and only δ 1·47 (s) in addition to the aromatic proton signals; and 2-isopropenylanthraquinone (VI) (35%) identified from its ^{1}H n.m.r. spectrum. The base peak in the mass spectrum of compound (V) at m/e 250 is probably due to fragmentation of the type shown in Scheme 1, and the smaller peak at m/e 249 to benzylic cleavage.

(V)   (VI)

A = anthraquinon-2-yl
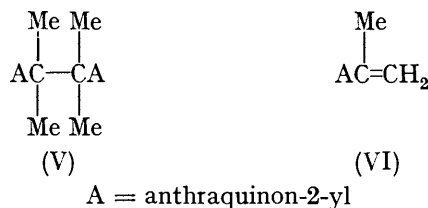
[1] D. G. Davies and P. Hodge, *J. Chem. Soc.* (*C*), 1971, 3158 is considered to be Part I of this series.

[2] Ger.P. 199,756/1908; *Chem. Zentr.*, 1908, II, 460.

[3] R. Scholl and H. Wallenstein, *Chem. Ber.*, 1936, **69**B, 503.

[4] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 81.

The yields of acidic products from the foregoing reactions were very small, equivalent to only 1—2% cleavage. In each case benzoic acid was a major component of the acidic fraction. The reaction of 1-methylanthraquinone produced a comparable amount of phthalic acid. No alkylbenzoic acids were detected in two of the acidic fractions and only relatively small amounts were found in the other two. Presumably the other acidic products were stilbene and bibenzyl derivative and in two cases mass spectrometric evidence was obtained for the presence of such acids.

2-t-Butylanthraquinone clearly cannot undergo oxidation reactions of the foregoing type. When this compound was treated with the butoxide–water reagent cleavage was the only reaction. As expected [1] from the work on the cleavage of the methylbenzophenones,[5] the alkyl quinone reacted more slowly than anthraquinone itself, 8 h at reflux temperature being required to obtain a high yield. The acidic fraction contained benzoic acid and 3- and 4-t-butylbenzoic acids in the molar ratio 49 : 24 : 27.

The results are summarised in the Table.

Products formed by action of butoxide–water reagent on alkylanthraquinones

| | Yield (%) of major products | | | | |
Substituent	Ethylene-type dimer	Ethane-type dimer	Alkenyl-quinone	Acids	Starting material
2-Me	84			2	10
1-Me	20			1	27
2-Et	33	38		2	
2-Pr^i	*	56	35	1	
2-Bu^t	*	*	*	89	8

* Formation of this type of product not possible.

Several oxidative dimerisations of a similar type are known. For example, 4-nitrotoluene reacts with potassium t-butoxide in t-butyl alcohol to give 4,4'-dinitrobibenzyl,[6] 3-benzyl-2-methyl-1,4-naphthoquinone reacts with aqueous ethanolic sodium hydroxide to give the dimer (VII),[7] and methyl 4-methylbenzoate reacts with potassium t-butoxide in t-butyl alcohol–dimethyl sulphoxide in the presence of air to give 4,4'-bismethoxycarbonylstilbene.[8]


(VII)
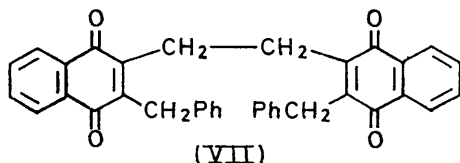
It is not clear how the quinonoid products described in this paper are formed. Scheme 2 is the simplest reasonable scheme but others are possible.[9] The reactions were carried out under nitrogen; consequently

in those in which oxidative dimerisation occurred a substantial proportion of the quinone molecules was reduced, the quinones being regenerated during work-up. In agreement with this it was observed that addition of the final reaction mixtures to water gave deep red solutions (anthraquinol is this colour in alkali) and that when these were exposed to air the colour faded and some of the final products precipitated.

A = anthraquinon-1- or 2-yl
R and R' = H or Me
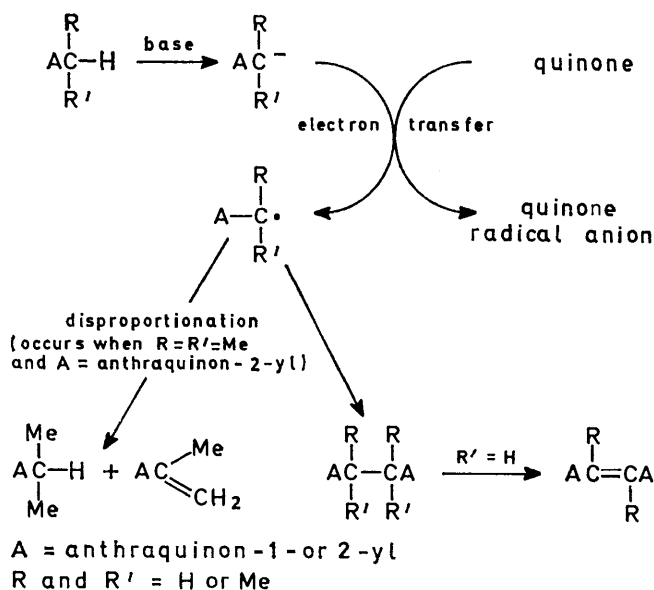
SCHEME 2

EXPERIMENTAL

General experimental procedures are the same as previously [1,5] with the following additions. Ethyl acetate was used for extractions unless indicated otherwise. Many of the products described were virtually insoluble in common organic solvents and consequently some spectra were not measured using the usual solvents. ^{1}H N.m.r. spectra recorded at 60 MHz were for ca. 10% solutions in the solvents indicated. Those recorded at 100 MHz were for ca. 1% solutions in CDCl$_3$ and a CAT attachment was used.

Action of the Butoxide–Water Reagent on 2-Methylanthraquinone.—Water (0·16 ml) was added to a vigorously stirred mixture of potassium t-butoxide (4·25 g) and 1,2-dimethoxyethane (40 ml) under nitrogen. The quinone (500 mg) was then added and the mixture heated under reflux for 4 h. Treatment of the cold mixture with saturated aqueous sodium chloride (150 ml) afforded a deep red solution. When this was vigorously stirred in the presence of air the colour faded and a yellow solid precipitated. The solid was filtered off and dried and the aqueous filtrate worked up in the usual way [5] to give base-insoluble and acidic fractions.

Repeated washing of the precipitated solid with hot chloroform gave 1,2-*di*(*anthraquinon-2-yl*)*ethylene* (I) (427 mg, 84%) shown to be >97% pure by comparison of i.r., u.v.,

[5] D. G. Davies, M. Derenberg, and P. Hodge, *J. Chem. Soc.* (C), 1971, 455.

[6] G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, 1967, **89**, 300.

[7] K. Chandrasenan and R. H. Thomson, *Tetrahedron*, 1971, **27**, 2529.

[8] G. A. Russell, E. G. Janzen, H. Becker, and F. J. Smentowski, *J. Amer. Chem. Soc.*, 1962, **84**, 2652.

[9] See discussions on the mechanisms of the related reactions in refs. 6 and 7.

and ^{1}H n.m.r. spectra with those of a pure sample obtained by subliming (340° and 0·5 mmHg) a portion of the product and recrystallising the sublimate from nitrobenzene. The pure sample, yellow needles, m.p. >350° (lit.,[10] 434°), had $\nu_{max.}$ (Nujol) 1675 cm^{-1}; δ (60 MHz; conc. H$_2$SO$_4$) ca. 7·5 p.p.m. (complex m, ArH and vinyl H); m/e 440 (M^+) (Found: C, 82·0; H, 3·9. C$_{30}$H$_{16}$O$_4$ requires C, 81·8; H, 3·6%). The solution in concentrated sulphuric acid was purple [10] and had $\lambda_{max.}$ 256, 328, 430, and 572 nm (log ε 4·51, 4·51, 4·13, and 4·47). A portion of the product was treated with zinc dust.[11] The product condensing on the cool parts of the tube was analysed by g.l.c. (SE30 column at 195°) and i.r. and u.v. spectra (in comparison with authentic samples of anthracene and 1- and 2-methylanthracene). The product contained anthracene (35%) and 2-methyl-anthracene (65%).

The residue obtained by evaporation of the chloroform washings (30 mg) and the base-insoluble fraction (20 mg) were both shown to be starting material (10% recovery).

The acidic fraction (11 mg; equivalent to 2% cleavage) was treated with diazomethane in ether and the ester mixture analysed by g.l.c.[5] The major volatile components were methyl benzoate and dimethyl phthalate (molar ratio 87 : 13); no methyl 3- or 4-methylbenzoate was detected.

1-Methylanthraquinone.—A solution of 1,4-naphtho-quinone (30 g) and penta-1,3-diene (40 g; mixture of geometrical isomers) in ethanol (400 ml) was heated under reflux for 20 h. After excess of diene had been distilled off, potassium hydroxide (40 g) was added and oxygen was bubbled through the mixture while it was heated under reflux for 9 h. The cold mixture was acidified and extracted with chloroform. The dried extracts were evaporated and the residue sublimed (190° and 0·5 mmHg). Recrystallisation of the sublimate from ethanol gave 1-methylanthraquinone (23·3 g, 55%), m.p. 176—177° (lit.,[12] 171—172°).

Action of the Butoxide–Water Reagent on 1-Methylanthra-quinone.—The quinone (656 mg) was treated with the reagent and the reaction was worked up as in the previous case. Repeated washing of the precipitated solid with hot chloroform and sublimation (360° and 0·5 mmHg) of the residue gave 1,2-di(anthraquinon-1-yl)ethylene (II) (130 mg, 20%), yellow needles, m.p. >350° (lit.,[3] >360°); $\nu_{max.}$ (Nujol) 1672 cm^{-1}; δ (60 MHz; conc. H$_2$SO$_4$) ca. 8 p.p.m. (complex m, ArH and vinyl H); m/e 440 (M^+). The solution in concentrated sulphuric acid was yellow [3] and had $\lambda_{max.}$ 267, 308, 410, and 486 nm (log ε 4·86, 4·42, 4·29, and 3·76).

The chloroform washings (442 mg) and the base-insoluble fraction (80 mg) were of similar composition (t.l.c.) and they were, therefore, combined. P.l.c. of a portion (433 mg) of this material afforded starting material (equivalent to 27% recovery), and several minor (each less than 12%) products. Three of these had i.r. and u.v. spectra very similar to those of 1-methylanthraquinone and molecular ions at m/e 442. Another product also had similar i.r. and u.v. spectra but a molecular ion at m/e 440. These four products were not further investigated.

The acidic fraction (6·5 mg, equivalent to 1% cleavage), analysed similarly, contained benzoic and phthalic acids (molar ratio, 49 : 51) and traces (less than 1% of the amount

of benzoic acid) of 2- and 3-methylbenzoic acids. The mass spectrum of the esterified acid fraction had a strong peak at m/e 298 suggesting the presence of dimethyl bibenzyl-dicarboxylates.

Action of the Butoxide–Water Reagent on 2-Ethylanthra-quinone.—The quinone (678 mg) was treated with the reagent and the reaction was worked up as before except that the precipitate was washed successively with ethanol and ether. The precipitated solid, the ethanol and ether washings, and the base-insoluble fraction were of similar composition (t.l.c.) and they were, therefore, combined (665 mg). P.l.c. of a portion (358 mg) of this mixture gave two main products. The one with the greater R_F value was 2,3-di(anthraquinon-2-yl)butane (IV) (138 mg, equivalent to 38%), m.p. 213—214° (from chloroform), $\nu_{max.}$ (Nujol) 1675 cm^{-1}; $\lambda_{max.}$ (CHCl$_3$) 260 and 332 nm (log ε 5·13 and 4·26), $\lambda_{infl.}$ 280 nm (log ε 4·71); δ (100 MHz) 1·50 (6H, d, J 6 Hz, Me), 3·26br (2H, m, CH$_3$·CH), and 7·4—8·4 p.p.m. (14H, complex m, ArH); m/e 470 (M^+, <1%), 236 (100%), and 235 (100%) (Found: C, 81·4; H, 5·0. C$_{32}$H$_{22}$O$_4$ requires C, 81·7; H, 4·7%). The product with the lower R_F value was 2,3-dianthraquinon-2-ylbut-2-ene (III) (122 mg, equivalent to 33%), m.p. >350° (from chloroform), $\nu_{max.}$ (Nujol) 1672 cm^{-1}; $\lambda_{max.}$ (CHCl$_3$) 260 and 332 nm (log ε 5·11 and 4·23), $\lambda_{infl.}$ 280 (4·68); δ (100 MHz) 2·52 (6H, s, Me) and 7·6—8·4 p.p.m. (14H, complex m, ArH); m/e 468 (M^+, <1%) and 236 (100%) (Found: C, 81·8; H, 4·4. C$_{32}$H$_{20}$O$_4$ requires C, 82·1; H, 4·3%).

The acid fraction (14 mg, equivalent to 2% cleavage), analysed as before, contained benzoic acid; no 3- or 4-ethyl benzoic acid or phthalic acid was detected. The mass spectrum of the esterified acid fraction had a strong peak at m/e 326 suggesting the presence of dimethyl esters of 2,3-bis-(3- or 4-carboxyphenyl)butanes.

2-Isopropylanthraquinone.—This substrate, prepared by the method of Scholl and his co-workers,[13] had m.p. 46—47° (lit.,[14] 45—46°), $\nu_{max.}$ (Nujol) 1675 cm^{-1}; δ (60 MHz; CDCl$_3$) 1·35 (6H, d, J 7 Hz, Me), 3·06 (1H, septet, J 7 Hz, CH), and 7·4—8·4 p.p.m. (7H, complex m, ArH).

Action of the Butoxide–Water Reagent on 2-Isopropyl-anthraquinone.—The quinone (607 mg) was treated with the reagent and the reaction was worked up as for the reaction of 2-ethylanthraquinone. The precipitated solid, the ethanol and ether washings, and the base-insoluble fraction were again combined (577 mg) after t.l.c. analysis. P.l.c. of a portion (400 mg) gave two compounds. The one of greater R_F was 2-isopropenylanthraquinone (VI) (146 mg, equivalent to 35%), m.p. 128—129° (from carbon tetra-chloride–petroleum), $\nu_{max.}$ (Nujol) 1678 cm^{-1}; $\lambda_{max.}$ (CHCl$_3$) 259 and 332 nm (log ε 4·50 and 3·65); δ (60 MHz; CDCl$_3$), 2·24 (3H, q, J 1·4 and 0·7 Hz, Me), 5·32 (1H, octet, J 1·4 and 1·2 Hz, vinyl H cis to Me), 5·62 (1H, octet, J 1·2 and 0·7 Hz, vinyl H trans to Me), and 7·5—8·5 p.p.m. (7H, complex m, ArH); m/e 248 (M^+, 100%) (Found: C, 82·0; H, 4·9. C$_{17}$H$_{12}$O$_2$ requires C, 82·2; H, 4·8%). The product with the lower R_F was 2,3-di(anthraquinon-2-yl)-2,3-dimethyl-butane (V) (237 mg, equivalent to 56%), m.p. 280—282° (from chloroform–carbon tetrachloride), $\nu_{max.}$ (Nujol) 1678 cm^{-1}; $\lambda_{max.}$ (CHCl$_3$) 260 and 334 nm (log ε 4·81 and 3·08), $\lambda_{infl.}$ 280 (log ε 4·40); δ (100 MHz) 1·47 (12H, s, Me), and

[10] V. Ramanthan, B. D. Tilak, and K. Venkataraman, *Proc. Indian Acad. Sci.*, 1953, 161 (*Chem. Abs.*, 1955, **49**, 265).

[11] Z. Valenta, 'Techniques of Organic Chemistry,' Inter-science, New York and London, 1963, vol. II, part 2, p. 643.

[12] Heilbron's 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

[13] R. Scholl, J. Potschiwauscheg, and J. Lenko, *Monatsh.*, 1911, **32**, 687.

[14] A. T. Peters and R. M. Rowe, *J. Chem. Soc.*, 1945, 181.

7·4—8·5 p.p.m. (14H, complex m, ArH); m/e 498 (M^+, <1%), 250 (100%), and 249 (10%) (Found: C, 81·7; H, 5·2. $C_{34}H_{26}O_4$ requires C, 81·9; H, 5·2%).

The acidic fraction (7·5 mg, equivalent to 1% cleavage), analysed as before, contained benzoic and 3- and 4-isopropylbenzoic acids (molar ratio 82 : 10 : 8).

Action of the Butoxidε-Water Reagent on 2-t-Butylanthraquinone.—(a) The quinone (204 mg) was treated with the reagent at reflux temperature for 4 h and the reaction was worked up as described in Part I.[1] The base-insoluble product (89 mg) was identified as starting material (44% recovered). The acidic fraction (128 mg, 55%), analysed as before, contained benzoic acid (49%), 3-t-butylbenzoic acid (24%), and 4-t-butylbenzoic acid (27%).

(b) A similar reaction was carried out but the mixture was heated under reflux for 8 h. Starting material was recovered (8%). The acidic fraction (89%) had a similar composition to that from (a).