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Experiments Directed Towards the Synthesis of Anthracyclinones. V‡ Double Claisen Rearrangement of 1,4-Bis(allyloxy)anthraquinones

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Abstract

The Claisen rearrangements of 1,4-bis(prop-2′-enyloxy)anthraquinone (4) and 1,4-bis(2′-chloroprop-2′-enyloxy)anthraquinone (3) in *o*-dichlorobenzene have been examined. The former gives a low yield of 1,4-dihydroxy-2,3-bis(prop-2′-enyl)anthraquinone (22), and 1,4-dihydroxy-2-(prop-2′-enyl)-anthraquinone (5) as the major product. Also formed is 1-hydroxy-4-propanoyl-2-(prop-2′-enyl)-anthraquinone (6) which arises from an unprecedented rearrangement of one allyloxy group. 1,4-Bis(2′-chloroprop-2′-enyloxy)anthraquinone (3) gives mainly 2-(2′-chloroprop-2′-enyl)-4-(2′-chloroprop-2′-enyloxy)-1-hydroxyanthraquinone (11) and a variety of minor products which are dependent on the time of reaction. Treatment of compound (11) with ethanolic potassium hydroxide, followed by a further Claisen rearrangement, gives a high yield of the synthetically useful 4-(2′-chloroprop-2′-enyl)-5-hydroxy-2-methyl-6,11-dihydroanthra[1,2-*b*]furan-6,11-dione (19).

Introduction

Recently there has been considerable interest in the synthesis of aglycones of the anthracyclines daunomycin, adriamycin and carminomycin,[1] as a result of the widespread use of these antibiotics for the treatment of some types of human cancer.[2] With the report that 4-demethoxydaunomycin is more active than daunomycin itself,[3] attention has turned to syntheses of the aglycone moiety, 4-demethoxydaunomycinone (1).[4–6] Although annulation of a suitable derivative of 1,4-dihydroxy-

‡ Part IV, *Heterocycles*, 1977, **7**, 201.

[1] Kelly, T. R., *Annu. Rep. Med. Chem.*, 1979, **14**, 288.

[2] Henry, D. W., in 'Cancer Chemotherapy' Am. Chem. Soc. Symp. Ser. No. 30, (Ed. A. C. Sartorelli) p. 15 (American Chemical Society: Washington D.C. 1976).

[3] Arcamone, F., Bernadi, L., Giardino, P., Patelli, B., di Marco, A., Casazza, A. M., Pratesi, G., and Reggiani, P., *Cancer Treatment Rep.*, 1976, **60**, 829; Arcamone, F., *Lloydia*, 1977, **40**, 45.

[4] Wiseman, J. R., French, N., Hallmark, R. K., and Chiong, K. G., *Tetrahedron Lett.*, 1978, 3765; Krohn, K., and Tolkiehn, K., *Tetrahedron Lett.*, 1978, 4023; Kelly, T. R., and Tsang, W., *Tetrahedron Lett.*, 1978, 4457; Jackson, D. K., Narasimhan, L., and Swenton, J. S., *J. Am. Chem. Soc.*, 1979, **101**, 3989; O'Connor, U., and Rosen, W., *Tetrahedron Lett.*, 1979, 601; Hauser, F. M., and Prasanna, S., *J. Org. Chem.*, 1979, **44**, 2596; Rao, A. V. R., Deshpande, V. H., and Reddy, N. L., *Tetrahedron Lett.*, 1980, **21**, 2661.

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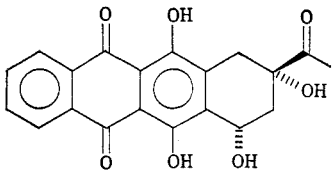
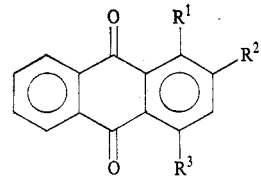
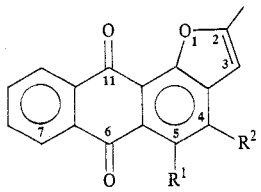
[6] Lee, N. W., Martinez, A. P., Smith, T. H., and Henry, D. W., *J. Org. Chem.*, 1976, **41**, 2296; Kende, A. S., Curran, D. P., Tsay, Y., and Mills, J. E., *Tetrahedron Lett.*, 1977, 3537; Kerdesky, F. A. J., and Cava, M. P., *J. Am. Chem. Soc.*, 1978, **100**, 2272; Garland, R. B., Palmer, J. R., Schulz, J. A., Sollman, P. B., and Pappo, R., *Tetrahedron Lett.*, 1978, 3669; Farina, F., and Prados, P., *Tetrahedron Lett.*, 1979, 477.



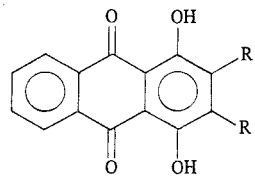
(1)



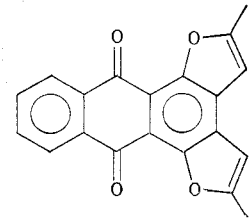
	R^1	R^2	R^3
(2)	OH	H	OH
(3)	$OCH_2C(Cl)=CH_2$	H	$OCH_2C(Cl)=CH_2$
(4)	$OCH_2CH=CH_2$	H	$OCH_2CH=CH_2$
(5)	OH	$CH_2CH=CH_2$	OH
(6)	OH	$CH_2CH=CH_2$	$COCH_2Me$
(7)	OH	H	$OCH_2CH=CH_2$
(8)	OH	$CH_2CH=CH_2$	$OCH_2CH=CH_2$
(9)	OH	CH=CHMe	OH
(10)	OH	CH=O	OH
(11)	OH	$CH_2C(Cl)=CH_2$	$OCH_2C(Cl)=CH_2$
(12)	OH	$CH_2C(Cl)=CH_2$	OH
(13)	$OCH_2C(Cl)=CH_2$	H	OH
(14)	$OCH_2C(Cl)=CH_2$	H	H
(15)	OH	$CH_2C(Cl)=CH_2$	H
(16)	OMe	$CH_2CH=CH_2$	OMe
(17)	OMe	CH=CHMe	OMe
(18)	OMe	CH=O	OMe



	R^1	R^2
(19)	OH	$CH_2C(Cl)=CH_2$
(20)	$OCH_2C(Cl)=CH_2$	H
(21)	H	H



(22) $R = CH_2CH=CH_2$
(23) $R = CH_2C(Cl)=CH_2$



(24)

anthraquinone (2) would appear to offer ready access to compound (1), such syntheses have had only limited success when they have involved intramolecular attack of a polar species on the relatively unreactive anthraquinone ring system.[5] This problem has been circumvented by modification of the anthraquinone to allow its participation either as the diene or as the dienophile in [4+2] cycloaddition reactions.[6] Claisen rearrangements[7] of allyl ethers of both phenolic hydroxyl groups in compound (2) would appear to offer an attractive and versatile alternative synthetic strategy. As pericyclic processes the rearrangements should be little affected by the strong electron-withdrawing propensity of the anthraquinone carbonyl groups while the allyl moieties

[7] Tarbell, D. S., *Org. React.*, 1944, **2**, 1; Jefferson, A., and Scheinmann, F., *Q. Rev., Chem. Soc.*, 1968, **22**, 391; Hansen, H.-J., and Schmid, H., *Chem. Br.*, 1969, **5**, 111; Rhoads, S. J., and Raulins, N. R., *Org. React.*, 1975, **22**, 1.

may be chosen to allow concomitant introduction of side chains suitable for elaboration to the anthracyclinone A-ring. The recent synthesis by Wong *et al.*[8] of the unsymmetrically substituted anthraquinone (19) by a double Claisen rearrangement of compound (3) in *o*-xylene containing *N,N*-dimethylbenzylamine demonstrates the potential of the method and prompts us to report our work on double Claisen rearrangements, including an alternative synthesis of the anthrafuran (19) from 1,4-dihydroxyanthraquinone (2) by means of two Claisen rearrangements.

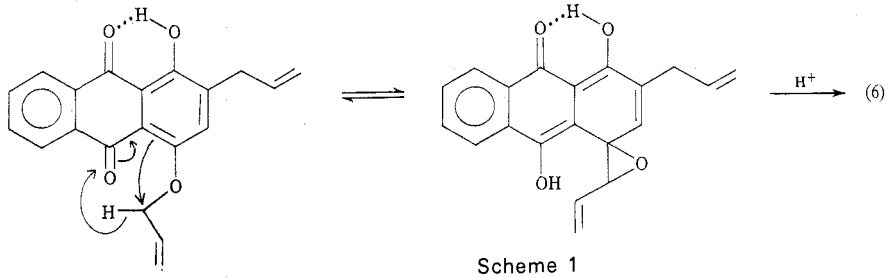
Discussion

Claisen rearrangement of the bis-allyl ether (4) in *o*-dichlorobenzene gave 1,4-dihydroxy-2,3-bis(prop-2′-enyl)anthraquinone (22) (14%), 1,4-dihydroxy-2-(prop-2′-enyl)anthraquinone (5) (33%), 1,4-dihydroxyanthraquinone (2) (5%), and 1-hydroxy-4-propanoyl-2-(prop-2′-enyl)anthraquinone (6) (18%). The structures of compounds (22) and (5) followed from an examination of their spectral parameters (see Experimental). However, the formation of compound (6) was unexpected and is unprecedented; its structure was deduced as follows. The molecular formula, $C_{20}H_{16}O_4$, was established from elemental analysis and a molecular ion at *m/z* 320·1072 in the high-resolution mass spectrum. The base peak in this spectrum at *m/z* 291·0681 together with a three-proton triplet at δ 1·25 (*J* 7 Hz) coupled to a two-proton quartet at 2·85 in the ^{1}H n.m.r. spectrum, and a strong carbonyl absorption at 1702 cm^{-1} in the i.r. spectrum suggested the presence of a propanoyl group. The i.r. spectrum also included peaks due to quinonoid carbonyl groups at 1675 cm^{-1} (C10) and 1619 cm^{-1} (C9, hydrogen-bonded),[9] while the u.v. spectrum displayed the normal benzenoid and quinonoid absorption bands of anthraquinones,[10] and bands characteristic of hydroxyanthraquinones at 226 and 406 nm.[11,12] The ^{1}H n.m.r. spectrum revealed that the molecule contained one hydrogen-bonded hydroxy group (δ 13·18), an allyl group bonded to an aromatic ring (5·05, 5·50, 6·0), an isolated aromatic proton (singlet at 7·21, H2), and an unsubstituted anthraquinone ring (7·68–7·82, H6,7; 8·12–8·40, H5,8). The presence of only two aromatic hydrogen atoms *peri* to the quinone carbonyl groups requires that a substituent be placed at C4, and logically this is the propanoyl chain since the allyl group would be expected to be *ortho* to the phenolic hydroxy group. The absence of conjugation between the side-chain carbonyl group and the aromatic ring, as indicated by carbonyl absorption in the i.r. spectrum at 1702 cm^{-1}, confirmed that the propanoyl group was at C4 since it has been shown[13] that steric interaction with the oxygen atom of a quinone carbonyl group can force such a side chain out of the plane of the aromatic ring. Similarly, the chemical shift (δ 206·9) of the signal of the aliphatic carbonyl carbon atom in the ^{13}C n.m.r. spectrum of compound (6) showed that the carbonyl group must be out of the plane of the aromatic ring.[14] The remainder of

[8] Wong, C. M., Singh, R., Singh, K., and Lam, H. Y. P., *Can. J. Chem.*, 1979, **57**, 3304.
[9] Bloom, H., Briggs, L. H., and Cleverley, B., *J. Chem. Soc.*, 1959, 178.
[10] Thomson, R. H., 'Naturally Occurring Quinones' 2nd Edn, pp. 40, 61 (Academic Press: London 1971).
[11] Ikeda, T., Yamamoto, Y., Tsukida, K., and Kanatomo, S., *J. Pharm. Soc. Jpn*, 1956, **76**, 217 (*Chem. Abstr.*, 1956, **50**, 7590).
[12] Briggs, L. H., Nicholls, G. A., and Paterson, R. M. L., *J. Chem. Soc.*, 1952, 1718.
[13] Sutherland, M. D., and Wells, J. W., *Aust. J. Chem.*, 1967, **20**, 515.
[14] Dhami, K. S., and Stothers, J. B., *Can. J. Chem.*, 1965, **43**, 498.

the ^{13}C n.m.r. spectrum was consistent with structure (6).[15] Moreover, a detailed analysis of the single resonance spectrum in conjunction with selective heteronuclear double irradiation experiments ruled out the possibility of an isomeric structure in which the allyl and propanoyl groups were interchanged. For example, low power irradiation at the resonance frequency of the methylene protons in the allyl group caused the six-line signal due to C 1 to collapse to a doublet of doublets ($^2J_{COH}$ and $^3J_{CCCH}$). The magnitude of the coupling loss (*c.* 4·5 Hz) was consistent with the destruction of three-bond coupling between benzylic methylene protons and a carbon atom *ortho* to the substituent;[16] this result requires that the carbon atom bearing the allyl group is also directly attached to C 1. Similarly, irradiation of the isolated aromatic proton at δ 7·21 in the ^1H n.m.r. spectrum reduced the pattern due to C 1 to a quartet ($^2J_{COH} \approx {}^3J_{CCC_1'H}$), this simplification being consistent with the loss of aromatic *meta* C–H coupling (*c.* 8 Hz).[15]

Pyrolysis of the bis-allyl ether (4) in the absence of solvent did not give compound (6) but afforded compounds (22), (7) and (2) in yields of 17, 14 and 7%, respectively. Thus, reactions involving the loss of allyl groups again competed effectively with the double rearrangement. We suggest that rearrangement of the first allyl group of the bis-allyl ether (4) proceeds normally to give compound (8), but that the [3,3] sigmatropic rearrangement of the second allyl group of the latter is inhibited, presumably because of strong hydrogen-bonding between the phenolic proton and the quinone carbonyl group. Consequently other reactions can compete. One of these, a reversible 1,5-homodienyl migration of hydrogen, gives an epoxide which may undergo rearrangement catalysed by acid present in the *o*-dichlorobenzene, to generate the propanoyl side chain of compound (6) (Scheme 1). Although the overall conversion of (4) into (6) can be formulated in terms of pericyclic processes only, such a sequence is unlikely since the propanoylanthraquinone should then have been isolated from the pyrolysis experiment.



Scheme 1

During its characterization, the mono *C*-allyl product (5) from rearrangement of compound (4) was isomerized to 1,4-dihydroxy-2-(prop-1′-enyl)anthraquinone (9). It was also converted in 65% overall yield into 1,4-dihydroxy-2-formylanthraquinone (10) by *O*-methylation, migration of the olefinic bond,[17] ozonolysis and demethylation.

In their work on the Claisen rearrangement of the bis(2′-chloroprop-2′-enyl) ether (3) in the presence of base, Wong and coworkers[8] isolated the compound (23), and the furans (19) and (24) formed by intramolecular displacement of the side-chain

[15] Arnone, A., Fronza, G., Mondelli, R., and Pyrek, J. St., *J. Magn. Reson.*, 1977, **28**, 69.
[16] Gotlieb, H. E., *Israel J. Chem.*, 1977, **16**, 57.
[17] Roberts, J. L., and Rutledge, P. S., *Aust. J. Chem.*, 1977, **30**, 1743.

halogen atoms (Table 1). Presumably the formation of furan rings prevents loss of the 2′-chloropropenyl groups from the initial *C*-allylated rearrangement products. Also, by removing the hydrogen-bonding phenolic group from the product of the first rearrangement such furan formation may facilitate the second rearrangement to form compound (19).

Table 1. Claisen rearrangements of compound (3)

Solvent	Time (h)	(3)	(2)	(11)	(12)	(23)	(13)	(19)	(24)
o-Dichlorobenzene	20	21	—	56	3	2	—	—	—
o-Dichlorobenzene	40	9	2	21	21	16	6	—	—
No solvent	20	5	10	[A]	14	3	3	—	—
Xylene/*N*,*N*-dimethylbenzylamine[8]	60	—	—	—	—	5	—	40	15

[A] Trace.

In independent work we have found that if the pyrolysis of compound (3) is carried out in *o*-dichlorobenzene for 20 h the major product (11) is that of a single Claisen rearrangement. The relative yields of this and other products were dependent on the time of reaction and on the presence or absence of solvent (Table 1). Although the furan (19) was not obtained in these reactions its formation in 48% overall yield from compound (3) was achieved by treatment of the allyl ether (11) with ethanolic potassium hydroxide followed by Claisen rearrangement of the resulting furan (20). Moreover, the starting material recovered from the original Claisen rearrangement of compound (3) could be re-treated under our Claisen conditions to give another 11% of furan (19) leading to an overall conversion of compound (3) into (19) of 58%.

We have also found that whereas the Claisen rearrangement of 1-(2′-chloroprop-2′-enyloxy)anthraquinone (14) in *o*-dichlorobenzene does not give the furan (21) directly, the latter compound was obtained in low yield when the reaction was carried out in a mixture of *N*,*N*-diethylaniline and acetic anhydride. Again the *o*-(2′-chloropropenyl) phenol (15), obtained by rearrangement of compound (14), was readily converted into the furan (21) by treatment with either potassium hydroxide in ethanol or concentrated sulfuric acid in methanol.

Experimental

Melting points were determined on a Reichert Kofler hot stage and are uncorrected. U.v. spectra were measured for 95% ethanol solutions with a Unicam SP 800A spectrophotometer. I.r. spectra were recorded for chloroform solutions or as KBr discs with Perkin–Elmer 337 or 397 spectrophotometers. ^{1}H n.m.r. spectra were measured for solutions in deuterochloroform on a Varian T60 spectrometer with tetramethylsilane as internal reference. ^{13}C n.m.r. spectra were recorded in deuterochloroform or deuterotetramethylurea on a Jeol JNM-FX60 Fourier transform instrument. Assignments marked with an asterisk or a dagger may be interchanged. Low-resolution mass spectra were determined with a Varian-MAT CH7 mass spectrometer at a nominal electron beam energy of 70 eV; high-resolution mass spectra were determined with an AEI MS-30 instrument.

Analytical t.l.c. was carried out on plates (0·3 mm thickness) of Kieselgel DG (Riedel de Haën) and preparative t.l.c. (p.l.c.) was carried out on Kieselgel $PF_{254+366}$ (Merck) with benzene as solvent. All solvents were purified by conventional methods[18] and, unless otherwise stated, all anthraquinones were crystallized from acetone.

[18] Perrin, D. D., Armarego, W. L. F., and Perrin, D. R., 'Purification of Laboratory Chemicals' (Pergamon Press: Oxford 1966).

1,4-Bis(prop-2′-enyloxy)anthraquinone (4)

A mixture of 1,4-dihydroxyanthraquinone (2) (10·0 g, 41·7 mmol), anhydrous potassium carbonate (27·0 g, 0·20 mol), and allyl bromide (67 g, 0·55 mol) in dry acetone (1 l.) was heated under reflux for 30·5 h, and then partitioned between 5% aqueous sodium hydroxide and ether. Workup of the aqueous solution followed by p.l.c. gave *1-hydroxy-4-(prop-2′-enyloxy)anthraquinone* (7) (80 mg, 0·7%), red needles, m.p. 127·5° (Found: C, 73·0; H, 4·5. $C_{17}H_{12}O_4$ requires C, 72·8; H, 4·3%). λ_{max} 222 (log ε 4·24), 247 (4·26), 272 (3·95), 323 (3·46), 412 nm (3·48). ν_{max} 1680 (CO), 1640 cm^{-1} (CO, hydrogen-bonded). ^1H n.m.r. δ 4·73, m, 2H, H1′; 5·25, m, H3′; 5·50, m, H3′; 6·05, m, H2′; 7·20, s, 2H, H2,3; 7·67, m, 2H, H6,7; 8·13, m, 2H, H5,8; 13·00, s, OH. *m/z* 280 (M), 239 (M − $CH_2CH{=}CH_2$); and 1,4-dihydroxyanthraquinone (17 mg).

Workup of the ether extract gave *1,4-bis(prop-2′-enyloxy)anthraquinone* (11·5 g, 86%) which crystallized from methanol as orange needles, m.p. 107–107·5° (Found: C, 74·6; H, 5·1. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%). λ_{max} 225 (log ε 4·90), 250 (4·98), 273 (4·70), 318 (3·95), 410 nm (4·35). ν_{max} 1670 cm^{-1} (CO). ^1H n.m.r. δ 4·73, m, 4H, H1′,1″; 5·25, m, 2H, H3′,3″; 5·45, m, 2H, H3′,3″; 6·10, m, 2H, H2′,2″; 7·30, s, 2H, H2,3; 7·74, m, 2H, H6,7; 8·21, m, 2H, H5,8. ^{13}C n.m.r. δ 70·5, t, C1′,1″; 117·8, t, C3′,3″; 122·1, s, C4a,9a; 123·2, d, C2,3; 126·2, d, C5,8; 133·1, s, C8a,10a; 133·5, d, C2′,2″*; 134·0, d, C6,7*; 153·1, s, C1,4; 182·6, s, C9,10. *m/z* 320 (M), 279 (M − $CH_2CH{=}CH_2$), 238 [M − 2($CH_2CH{=}CH_2$)], 41 ($CH_2CH{=}CH_2$).

Claisen Rearrangements of 1,4-Bis(prop-2′-enyloxy)anthraquinone (4)

(A) *In o-dichlorobenzene.*—A solution of the compound (4) (0·50 g, 1·56 mmol) in *o*-dichlorobenzene (75 ml) was heated under reflux for 25 h. Solvent was removed from the mixture under reduced pressure and the resulting dark red solid (0·48 g) was separated by p.l.c. into (i) *1,4-dihydroxy-2,3-bis(prop-2′-enyl)anthraquinone* (22) (70 mg, 14%), red needles, m.p. 109·5–111° (Found: C, 74·7; H, 5·3. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%). λ_{max} 232 (log ε 3·55), 253 (3·85), 258 (3·84), 286 (3·32), 330 nm (2·66). ν_{max} 1623 cm^{-1} (CO, hydrogen-bonded). ^1H n.m.r. δ 3·48, d, $J_{1',2'} = J_{1'',2''}$ 6·0 Hz, 4H, H1′,1″; 4·82, 5·12, 2m, 4H, H3′,3″; 5·85, m, 2H, H2′,2″; 7·56, m, 2H, H6,7; 8·12, m, 2H, H5,8; 13·4, s, 2H, OH. *m/z* 320 (M), 279 (M − $CH_2CH{=}CH_2$), 238 [M − 2($CH_2CH{=}CH_2$)], 41 ($CH_2CH{=}CH_2$); (ii) *1,4-dihydroxy-2-(prop-2′-enyl)anthraquinone* (5) (0·14 g, 32%), red needles, m.p. 158–159° (Found: C, 72·9; H, 4·5. $C_{17}H_{12}O_4$ requires C, 72·8; H, 4·3%). λ_{max} 232 (log ε 3·62), 251 (3·88), 257 (3·80), 288 nm (3·30). ν_{max} 1630 cm^{-1} (CO, hydrogen-bonded). ^1H n.m.r. δ 3·49, d, *J* 7·0 Hz, 2H, H1′; 5·08, 2m, 2H, H3′; 6·05, m, H2′; 7·15, s, H3; 7·72, m, 2H, H6,7; 8·23, m, 2H, H5,8; 12·62, s, 4-OH; 13·06, s, 1-OH. *m/z* 280 (M), 239 (M − $CH_2CH{=}CH_2$); (iii) 1,4-dihydroxyanthraquinone (2) (20 mg, 5%); and (iv) *1-hydroxy-4-propanoyl-2-(prop-2′-enyl)anthraquinone* (6) (90 mg, 18%), yellow needles, m.p. 166–167° (Found: C, 74·7; H, 5·0. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%). λ_{max} 226 (log ε 4·40), 248 (4·48), 256 (4·92), 277 (4·21), 287 (4·05), 324 (3·81), 406 (4·04); (EtOH/NaOH) 225sh (4·32), 252 (4·52), 285 (4·11), 325 (3·95), 513 nm (3·98). ν_{max} 1702 (CO), 1675 (CO), 1619 cm^{-1} (CO, hydrogen-bonded). ^1H n.m.r. δ 1·25, t, *J* 7·0 Hz, 3H, CH_3CH_2; 2·85, q, *J* 7·0 Hz, 2H, CH_2CH_3; 3·50, d, *J* 7·0 Hz, 2H, H1′; 5·05, 5·50, 2m, 2H, H3′; 6·00, m, H2′; 7·21, s, H3; 7·75, m, 2H, H6,7; 8·26, m, 2H, H5,8; 13·18, s, OH. ^{13}C n.m.r. δ 8·6, q, CH_3; 33·8, t, C1′; 36·7, t, CH_2CH_3; 115·0, s, C9a; 117·7, t, C3′; 126·9, d, C8; 127·4, d, C5; 128·4, s, C4a; 132·9, s, C10a; 133·4, s, C8a; 133·6, d, C3; 134·2, d, C7,12; 134·8, d, C6; 136·6, d, C2 or C4; 137·2, d, C4 or C2; 161·1, s, C1; 182·1, s, C10; 188·7, s, C9; 206·9, $COCH_2$. *m/z* 320·1072 ($M^{+\cdot}$, calc. 320·1044), 291·0681 ($M^{+\cdot}$ − $\cdot CH_2CH_3$).

(B) *In the absence of solvent.*—Compound (4) (0·20 g, 0·63 mmol) was heated in a Kugelrohr distillation apparatus at 200° for 3 h and then at 200°/0·1 mm for a further 3·5 h. An orange-red solid (0·17 g) distilled out, leaving a black residue (25 mg). P.l.c. of the sublimate gave (i) 1,4-dihydroxy-2,3-bis(prop-2′-enyl)anthraquinone (22) (34 mg, 17%); (ii) 1,4-dihydroxyanthraquinone (2) (10 mg, 7%); (iii) 1-hydroxy-4-(prop-2′-enyloxy)anthraquinone (7) (25 mg, 14%); (iv) 1,4-bis(prop-2′-enyloxy)anthraquinone (4) (88 mg, 44%).

1,4-Dihydroxy-2-(prop-1′-enyl)anthraquinone (9)

Hot 2% methanolic sodium hydroxide solution (40 ml) was added to a solution of compound (5) (0·20 g, 0·71 mmol) in methanol (40 ml) and the resulting solution refluxed for exactly 20 min. Workup gave *1,4-dihydroxy-2-(prop-1′-enyl)anthraquinone* (0·196 g, 98%), red needles, m.p. 205–206°

(Found: C, 72·8; H, 4·2. $C_{17}H_{12}O_4$ requires C, 72·8; H, 4·3%). λ_{max} 219 (log ε 4·34), 229 (4·21), 262 (4·48), 304 (3·88), 407 nm (3·59). ν_{max} 3060–2850 (OH), 1640 cm^{-1} (CO). ^1H n.m.r. δ 2·00, d, J 5·0 Hz, 3H, H3′; 5·82, m, H2′; 6·80, perturbed d, H1′; 7·78, m, 3H, H3,6,7; 8·32, m, 2H, H5,8; 12·99, s, 4-OH; 13·67, s, 1-OH. m/z 280 (M).

1,4-Dimethoxy-2-formylanthraquinone (18)

Methylation of compound (5) with dimethyl sulfate/potassium carbonate in dry acetone gave *1,4-dimethoxy-2-(prop-2′-enyl)anthraquinone* (16) (97%), orange needles, m.p. 129·5–131° (Found: C, 73·6; H, 5·2. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). λ_{max} 227 (log ε 4·38), 250 (4·45), 275 (4·19), 319 (3·06), 400 nm (3·70). ν_{max} 1670 cm^{-1} (CO). ^1H n.m.r. δ 3·52, dt, J 7·0 Hz, 2H, H1′; 3·85, s, 3H, 1-OCH_3; 4·02, s, 3H, 4-OCH_3; 5·00, 5·20, 2m, 2H, H3′; 5·95, qt, H2′; 7·02, s, H3; 7·46, m, 2H, H6,7; 8·05, m, 2H, H5,8; m/z 308 (M), 277 (M−OCH_3).

Hot 2% methanolic sodium hydroxide solution (15 ml) was added to compound (16) (0·10 g, 0·22 mmol) in methanol (15 ml) and the resulting solution was refluxed for exactly 12 min. Workup gave *1,4-dimethoxy-2-(prop-1′-enyl)anthraquinone* (17) (0·80 g, 80%), orange plates, m.p. 160–162° (Found: C, 74·1; H, 5·4. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). λ_{max} 217 (log ε 4·33), 225 (4·33), 253 (3·47), 282 (4·12), 402 nm (3·76). ν_{max} 1680 cm^{-1} (CO). ^1H n.m.r. δ 1·93, d, J 5·0 Hz, 3H, H3′; 3·81, s, 3H, 1-OCH_3; 4·00, s, 3H, 4-OCH_3; 6·41, m, 2H, H1′,2′; 7·22, s, H3; 7·56, m, 2H, H6,7; 7·97, m, 2H, H5,8. m/z 308 (M), 277 (M−OCH_3).

The dimethyl ether (17) (0·10 g, 0·32 mmol) in anhydrous dichloromethane (30 ml) and anhydrous pyridine (30 ml) was ozonized at −78°. Workup gave 1,4-dimethoxy-2-formylanthraquinone (18) (95 mg), orange needles, m.p. 184° (lit.[19] 189–190°, with sublimation) (correct i.r. and ^1H n.m.r. spectra).

1,4-Dihydroxy-2-formylanthraquinone (10)

The dimethyl ether (18) (80 mg, 0·27 mmol) and concentrated sulfuric acid (1 ml) were heated in an oil bath at 200° for 2 h. The mixture was cooled, poured onto crushed ice, and the red precipitate was filtered off, washed, and dried to give 1,4-dihydroxy-2-formylanthraquinone (61 mg, 84%), red needles, m.p. 208°, with sublimation from 184°. λ_{max} 230 (log ε 4·33), 250 (4·48), 257 (4·40), 282 (3·92), 306 (3·74), 334 nm (3·57). ν_{max} 2850 (CHO), 1700 (CHO), 1625 cm^{-1} (CO, hydrogen-bonded). ^1H n.m.r. δ 7·86, m, 3H, H3,6,7; 8·32, m, 2H, H5,8; 10·72, s, CHO; 12·45, s, 4-OH; 13·35, s, 1-OH. m/z 268 (M), 240 (M−CO).

1,4-Bis(2′-chloroprop-2′-enyloxy)anthraquinone (3)

A mixture of 1,4-dihydroxyanthraquinone (2) (12·0 g, 50 mmol), anhydrous potassium carbonate (25·0 g, 0·18 mol), 2,3-dichloroprop-1-ene (18·4 ml, 0·20 mol), and potassium iodide (2·5 g) in dry acetone (500 ml) was heated under reflux for 176 h. After 56 h and 112 h further portions of 2,3-dichloroprop-1-ene (18·4 ml) and potassium iodide (2·5 g) were added. The disappearance of the starting material was monitored by t.l.c. The mixture was concentrated to dryness under reduced pressure and the residue was washed with hot chloroform until the washings were colourless. Concentration of the combined chloroform solutions under reduced pressure gave *1,4-bis(2′-chloroprop-2′-enyloxy)anthraquinone* (19·0 g, 98%) which crystallized from chloroform/ether as yellow needles, m.p. 156–157° (lit.[8] 145–147°) (Found: C, 61·8; H, 3·7; Cl, 18·3. $C_{20}H_{14}Cl_2O_4$ requires C, 61·7; H, 3·6; Cl, 18·2%). λ_{max} 244 (log ε 4·64), 248 (4·66), 388 nm (3·99). ν_{max} 1670 cm^{-1} (CO). ^1H n.m.r. δ 4·73, m, 4H, H1′,1″; 5·53, m, 2H, H3′,3″ *trans* to Cl; 5·93, m, 2H, H3′,3″ *cis* to Cl; 7·33, s, 2H, H2,3; 7·81, m, 2H, H6,7; 8·18, m, 2H, H5,8. ^{13}C n.m.r. δ 72·5, t, C1′,1″; 114·4, s, C4a,9a; 114·5, t, C3′,3″; 124·3, d, C2,3; 126·5, d, C5,8; 133·8, d, C6,7; 134·5, s, C8a,10a; 136·6, s, C2′,2″; 153·4, s, C1,4; 182·0, s, C9,10. m/z 388 (M), 353 (M−Cl), 317 (M−HCl−Cl).

Claisen Rearrangement of 1,4-Bis(2′-chloroprop-2′-enyloxy)anthraquinone (3)

(A) *In o-dichlorobenzene.*—A solution of the anthraquinone (3) (0·39 g, 1·0 mmol) in *o*-dichlorobenzene (60 ml) was refluxed at 180° under oxygen-free dry nitrogen for 20 h. Solvent was removed from the cooled solution under reduced pressure to yield a dark red solid which was separated

[19] Roberts, J. L., Rutledge, P. S., and Trebilcock, M. J., *Aust. J. Chem.*, 1977, **30**, 1553.

by p.l.c. (benzene) into (i) *2,3-bis(2′-chloroprop-2′-enyl)-1,4-dihydroxyanthraquinone* (23) (9 mg, 2%), red needles, m.p. 186–187°‡ (Found: C, 61·4; H, 3·7; Cl, 18·4. $C_{20}H_{14}Cl_2O_4$ requires C, 61·7; H, 3·6; Cl, 18·2%). λ_{max} 234 (log ε 4·20), 249 (4·43), 256 (4·40), 288 (3·90), 456sh (3·90), 473 (3·92), 498sh (3·85), 520 nm (3·72). ν_{max} (KBr) 3450br (OH, intramolecularly bonded), 3100 (OH), 1630 cm^{-1} (CO, hydrogen-bonded). ^1H n.m.r. δ 3·96, m, 4H, H1′,1″; 5·10, m, 2H, H3′,3″ *trans* to Cl; 5·30, m, 2H, H3′,3″ *cis* to Cl; 7·83, m, 2H, H6,7; 8·30, m, 2H, H5,8; 13·51, s, 2H, OH. ^{13}C n.m.r. δ 35·6, t, C1′,1″; 111·7, s, C4a,9a; 113·6, t, C3′,3″; 127·0, d, C5,8; 133·6, s, C8a,10a; 134·4, d, C6,7; 137·5, s, C2,3; 138·3, s, C2′,2″; 156·6, C1,4; 186·7, s, C9,10. *m/z* 388 (M), 353 (M−Cl), 317 (M−HCl−Cl); (ii) *2-(2′-chloroprop-2′-enyl)-1,4-dihydroxyanthraquinone* (12) (10 mg, 3·3%), red needles, m.p. 162–163° (Found: C, 64·9; H, 3·5; Cl, 11·3. $C_{17}H_{11}ClO_4$ requires C, 64·9; H, 3·5; Cl, 11·3%). λ_{max} 229 (log ε 4·46), 248 (4·61), 254 (4·57), 282 (4·15), 322 (3·70), 445sh (4·02), 468 (4·11), 511sh (3·90), 516 nm (3·90). ν_{max} (KBr) 3430 (OH, intramolecularly bonded), 1630 cm^{-1} (CO, hydrogen-bonded). ^1H n.m.r. δ 3·78, s, 2H, H1′; 5·38, m, 2H, H3′; 7·21, s, H3; 7·77, m, 2H, H6,7; 8·23, m, 2H, H5,8; 12·81, s, 4-OH; 13·28, s, 1-OH. ^{13}C n.m.r. δ 39·0, t, C1′; 111·8, s, C9a; 112·2, s, C4a; 115·5, t, C3′; 126·9, d, C5,8; 128·9, d, C3; 133·2, s, C10a†; 133·3, s, C8a†; 134·3, d, C6,7; 138·0, s, C2; 138·4, s, C2′; 156·4, s, C4; 157·2, s, C1; 186·2, s, C9; 186·9, s, C10. *m/z* 314 (M), 279 (M−Cl), 237 (M−CO−Cl); (iii) *2-(2′-chloroprop-2′-enyl)-4-(2′-chloroprop-2′-enyloxy)-1-hydroxyanthraquinone* (11) (0·22 g, 56%) which crystallized from chloroform/acetone as red needles, m.p. 166–167° (Found: C, 61·5; H, 3·8; Cl, 18·45. $C_{20}H_{14}Cl_2O_4$ requires C, 61·7; H, 3·6; Cl, 18·2%). λ_{max} 223sh (log ε 4·67), 251 (4·94), 227sh (4·67), 245sh (4·74), 251 (4·75), 272 (4·38), 276sh (4·36), 433 (4·19), 466sh (4·13), 486sh nm (3·98). ν_{max} (KBr) 3450–3400 (OH, intramolecularly bonded), 1660 (CO), 1638 cm^{-1} (CO, hydrogen-bonded). ^1H n.m.r. δ 3·80, br s, 2H, H1′; 4·70, m, 2H, H1″; 5·35, m, 2H, H3′; 5·53, m, H3″ *trans* to Cl; 5·91, m, H3″ *cis* to Cl; 7·33, s, H3; 7·75, m, 2H, H6,7; 8·27, m, 2H, H5,8; 13·46, s, OH. ^{13}C n.m.r. δ 39·0, t, C1′; 73·0, t, C2″; 114·9, s, C4a; 115·0, t, C3′; 116·1, s, C9a; 126·6, d, C8†; 127·3, d, C5†; 129·1, d, C3; 132·7, s, C8a; 133·8, d, C6; 135·2, s, C10a; 135·4, d, C7; 135·4, s, C2″; 136·8, s, C2′; 139·4, s, C2; 152·1, s, C4; 157·2, s, C1; 180·3, s, C10; 189·4, s, C9. *m/z* 388 (M), 353 (M−Cl), 313 (M−C_3H_4ClCl), and 1,4-bis(2′-chloroprop-2′-enyloxy)anthraquinone (3) (82 mg, 21%).

A similar reaction with compound (3) (5 mmol) for 40 h gave (i) 2,3-bis(2′-chloroprop-2′-enyl)-1,4-dihydroxyanthraquinone (23) (0·32 g, 16%); (ii) 2-(2′-chloroprop-2′-enyl)-1,4-dihydroxyanthraquinone (12) (0·33 g, 21%); (iii) 2-(2′-chloroprop-2′-enyl)-4-(2′-chloroprop-2′-enyloxy)-1-hydroxyanthraquinone (11) (0·40 g, 21%); (iv) 1,4-bis(2′-chloroprop-2′-enyloxy)anthraquinone (3) (0·175 g, 9%); (v) 1-(2′-chloroprop-2′-enyloxy)-4-hydroxyanthraquinone (13) (see below) (91 mg, 6%); (vi) 1,4-dihydroxyanthraquinone (2) (27 mg, 2%); (vii) unidentified material (54 mg, 3%).

(B) *In the absence of solvent.*—The compound (3) (4·0 g, 10·2 mmol) was heated in a Kugelrohr distillation apparatus at 180° for 20 h. A blood-red solid distilled out leaving a black residue. The distillate was extracted with chloroform and the extract was separated by p.l.c. to give (i) 2,3-bis-(2′-chloroprop-2′-enyl)-1,4-dihydroxyanthraquinone (23) (0·11 g, 3%); (ii) 2-(2′-chloroprop-2′-enyl)-1,4-dihydroxyanthraquinone (12) (0·46 g, 14%); (iii) 2-(2′-chloroprop-2′-enyl)-4-(2′-chloroprop-2′-enyloxy)-1-hydroxyanthraquinone (11) (3 mg); (iv) 1,4-bis(2′-chloroprop-2′-enyloxy)-anthraquinone (3) (0·21 g, 5%); (v) 1-(2′-chloroprop-2′-enyloxy)-4-hydroxyanthraquinone (13) (98 mg, 3%); (vi) 1,4-dihydroxyanthraquinone (2) (0·24 g, 10%); (vii) unidentified material (0·31 g, 8%).

5-(2′-Chloroprop-2′-enyloxy)-2-methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione (*20*)

A solution of the allyl ether (11) (2·98 g, 7·67 mmol) in absolute ethanol (1·3 l.) was treated with a solution of 2·6% ethanolic potassium hydroxide (20 ml, 20% molar excess) and the mixture was heated under reflux for 25 min. Solvent was removed from the cooled solution under reduced pressure to yield a solid which was washed with water and dissolved in chloroform. The solution was dried and the solvent was removed in a vacuum to yield *5-(2′-chloroprop-2′-enyloxy)-2-methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione* (2·68 g, 99%) which crystallized from chloroform/ether

‡ This compound is probably identical with that, m.p. 176–178°, isolated by Wong *et al.*[8] and given this name but assigned a different structure in their discussion.

(7 : 3) as yellow needles, m.p. 195–196° (Found: C, 68·0; H, 3·7; Cl, 10·3. $C_{20}H_{13}ClO_4$ requires C, 68·1; H, 3·7; Cl, 10·0%). λ_{max} 248 (log ε 4·42), 279 (4·34), 370sh (3·84), 390 nm (3·97). ν_{max} (KBr) 3125 (OH), 1670 (CO), 1660 cm^{-1} (CO). ^1H n.m.r. δ 2·60, br s, 3H, CH_3; 4·73, m, 2H, H1′; 5·56, m, H3′ *trans* to Cl; 6·06, m, H3′ *cis* to Cl; 6·40, m, H3; 7·30, s, H4; 7·75, m, 2H, H8,9; 8·27, m, 2H, H7,10; ^{13}C n.m.r. δ 14·5, q, CH_3; 72·3, t, C1′; 102·8, d, C3; 112·4, d, C4; 114·2, t, C3′; 118·4, s, C11a; 119·0, s, C5a; 127·0, d, C7,10; 133·0, d, C9†; 133·8, d, C8†; 134·9, s, C10a†; 135·6, s, C6a†; 137·2, s, C3a,2′; 147·7, s, C2; 154·6, s, C5; 163·2, s, C11b; 181·8, s, CO; 182·6, s, CO. *m/z* 352 (M), 317 (M−Cl), 289 (M−COCl), 278 (M−C_3H_3Cl).

4-(2′-Chloroprop-2′-enyl)-5-hydroxy-2-methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione (19)

A solution of the fura(a)anthraquinone (20) (0·20 g, 0·51 mmol) in *o*-dichlorobenzene (10 ml) was refluxed under oxygen-free dry nitrogen at 180° for 6·5 h. Solvent was removed from the cooled solution under reduced pressure to yield a solid which was purified by p.l.c. (benzene). This afforded *4-(2′-chloroprop-2′-enyl)-5-hydroxy-2-methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione* (0·17 g, 85%) which crystallized from chloroform/ether as orange-yellow needles, m.p. 199–200° (lit.[8] 194·5–196°) (Found: C, 68·3; H, 4·0; Cl, 9·3. $C_{20}H_{13}ClO_4$ requires C, 68·1; H, 3·7; Cl, 10·0%). λ_{max} 254 (log ε 3·86), 285 (3·73), 360sh (3·16), 425 (3·44), 450sh nm (3·37). ν_{max} (KBr) 3300–3500 (OH, intramolecularly bonded), 1674 (CO), 1638 cm^{-1} (CO, hydrogen-bonded). ^1H n.m.r. δ 2·63, s, 3H, CH_3; 3·93, br s, 2H, H1′; 5·20, m, H3′ *trans* to Cl; 5·33, m, H3′ *cis* to Cl; 6·50, m, H3; 7·75, m, 2H, H8,9; 8·26, m, 2H, H7,10. ^{13}C n.m.r. δ 14·7, q, CH_3; 36·3, t, C1′; 102·0, d, C3; 111·6, s, C5a; 113·6, t, C3′; 114·8, s, C11a; 122·9, s, C3a; 126·8, d, C7; 126·9, d, C10; 133·3, s, C6a; 133·7, d, C9; 133·9, s, C10a; 134·2, d, C8; 139·0, s, C2′; 140·2, s, C4; 146·7, s, C2; 157·0, s, C5; 164·1, s, C11b; 181·3, s, CO; 188·5, s, CO. *m/z* 354·0430 and 352·0488 ($M^{+\cdot}$), 317 (M−Cl), 299 (M−Cl−H_2O).

1-(2′-Chloroprop-2′-enyloxy)-4-hydroxyanthraquinone (13)

A mixture of 1,4-dihydroxyanthraquinone (2) (2·4 g, 10 mmol), anhydrous potassium carbonate (1·38 g, 10 mmol), 2,3-dichloroprop-1-ene (4·6 ml, 50 mmol), and potassium iodide (0·62 g, 3·8 mmol) in dry acetone (120 ml) was heated under reflux for 30 h. The cooled mixture was filtered and the residue was washed with hot acetone to leave a dark red solid. Solvent was removed from the combined filtrate and washings to give a dark blue solid which was dissolved in ethyl acetate (150 ml) and washed alternately with 5% aqueous sodium hydroxide solution and water until the alkaline washings were only a faint pink in colour. The combined sodium hydroxide and water washings were neutralized with dilute aqueous hydrochloric acid and the precipitate was collected and separated by p.l.c. (benzene) to give (i) *1-(2′-chloroprop-2′-enyloxy)-4-hydroxyanthraquinone* (0·28 g, 9%) which crystallized from chloroform/ether (1 : 1) as orange-red needles, m.p. 141–142° (Found: C, 64·6; H, 3·6; Cl, 11·8. $C_{17}H_{11}ClO_4$ requires C, 64·9; H, 3·5; Cl, 12·3%). λ_{max} 220 (log ε 4·51), 248 (4·53), 266 (4·24), 432 nm (3·91). ν_{max} 1670 (CO), 1640 cm^{-1} (CO, hydrogen-bonded). ^1H n.m.r. δ 4·70, m, 2H, H1′; 5·55, m, H3′ *trans* to Cl; 5·96, m, H3′ *cis* to Cl; 7·30, s, 2H, H2,3; 7·75, m, 2H, H6,7; 8·26, m, 2H, H5,8; 12·95, s, OH. ^{13}C n.m.r. δ 72·0, t, C1′; 114·3, t, C3′; 114·4, s, C10a; 115·8, s, C4a; 126·1, d, C3; 126·3, d, C5; 126·4, d, C8; 127·2, d, C2; 132·1, s, C8a; 133·3, d, C6; 143·3, s, C10a; 134·6, s, C2′; 134·7, d, C7; 151·9, s, C1; 158·1, s, C4; 181·0, s, CO; 188·5, s, CO. *m/z* 314 (M), 279 (M−Cl), 239 [M−$CH_2C(Cl)=CH_2$]; (ii) 1,4-dihydroxyanthraquinone (0·48 g).

The ethyl acetate solution was washed with water and brine, dried, and concentrated to give 1,4-bis(2′-chloroprop-2′-enyloxy)anthraquinone (0·30 g, 8%).

The dark red solid from above was dissolved in water and acidified with dilute hydrochloric acid. The precipitate was filtered off, washed with water and dried to give 1,4-dihydroxyanthraquinone (1·26 g).

Reaction of 1,4-dihydroxyanthraquinone with 2,3-dichloroprop-1-ene, potassium carbonate and potassium iodide (molar ratio 1 : 5 : 3 : 0·0038) and a reaction time of 56 h gave 1,4-bis(2′-chloroprop-2′-enyloxy)anthraquinone (2%), 1-(2′-chloroprop-2′-enyloxy)-4-hydroxyanthraquinone (2%) and 1,4-dihydroxyanthraquinone (94%).

Repetition of the reaction under the reported experimental conditions[8] gave 1,4-bis(2′-chloroprop-2′-enyloxy)anthraquinone (22%), 1-(2′-chloroprop-2′-enyloxy)-4-hydroxyanthraquinone (1%), and 1,4-dihydroxyanthraquinone (77%).

1-(2′-Chloroprop-2′-enyloxy)anthraquinone (14)

A mixture of 1-hydroxyanthraquinone (0·40 g, 1·78 mmol), anhydrous potassium carbonate (1·25 g, 9·1 mmol), and 2,3-dichloroprop-1-ene (8 ml, 87 mmol) in dry acetone (80 ml) was heated under reflux for 19 days. Further 2,3-dichloroprop-1-ene (20 ml, 0·22 mol) was added after 3 days. The mixture was concentrated and the resulting precipitate was filtered off, washed, and dried to give *1-(2′-chloroprop-2′-enyl)anthraquinone* (0·53 g, 100%), yellow needles, m.p. 181–182° (Found: C, 68·5; H, 3·7; Cl, 11·9. $C_{17}H_{11}ClO_3$ requires C, 68·3; H, 3·7; Cl, 11·9%). λ_{max} 254 (logε 4·86), 274 (4·46), 331 (3·82), 361 nm (4·03). ν_{max} 1680 cm^{-1} (CO). ^{1}H n.m.r. δ 4·61, m, 2H, H1′; 5·45, m, H3′ *trans* to Cl; 5·93, m, H3′ *cis* to Cl; 7·14, m, H2; 7·67, m, 3H, H3,6,7; 8·15, m, 3H, H4,5,8. *m/z* 298 (M), 223 [M−$CH_2C(Cl)=CH_2$].

Compound (14) was isolated in 33% yield after a mixture of 1-hydroxyanthraquinone (0·86 g, 3·9 mmol), anhydrous potassium carbonate (2·2 g, 16 mmol), potassium iodide (0·22 g, 1·3 mmol) and 2,3-dichloroprop-1-ene (1·65 ml, 18 mmol) had been heated under reflux for 6 days.

Claisen Rearrangement of 1-(2′-Chloroprop-2′-enyloxy)anthraquinone

(A) *In* o-*dichlorobenzene.*—A solution of the compound (14) (76 mg, 0·25 mmol) in *o*-dichlorobenzene (10 ml) was refluxed under oxygen-free dry nitrogen at 180° for 48 h until starting material was no longer present (t.l.c. monitoring). Solvent was removed from the cooled solution under reduced pressure to yield a yellow-green solid which was separated by p.l.c. (benzene) into (i) *2-(2′-chloroprop-2′-enyl)-1-hydroxyanthraquinone* (15) (42 mg, 55%), yellow needles, m.p. 128–131° (Found: C, 68·6; H, 3·8; Cl, 11·3. $C_{17}H_{11}ClO_3$ requires C, 68·3; H, 3·7; Cl, 11·9%). λ_{max} 224 (logε 4·13), 246 (4·24), 254 (4·29), 274 (3·89), 282 (3·83), 332 (3·17), 403 nm (3·55). ν_{max} 1670 (CO), 1635 cm^{-1} (CO, hydrogen-bonded). ^{1}H n.m.r. δ 3·83, s, 2H, H1′; 5·36, m, 2H, H3′; 7·75, m, 3H, H3,6,7; 8·30, m, 3H, H4,5,8; 13·01, s, OH. *m/z* 300, 298 (M), 263 (M−Cl), 224 (M−C_3H_3Cl); (ii) 1-hydroxyanthraquinone (7 mg, 13%); (iii) 1-(2′-chloroprop-2′-enyl)anthraquinone (11 mg, 15%).

(B) *In* N,N-*diethylaniline and acetic anhydride.*—A solution of the compound (14) (70 mg, 0·23 mmol) in *N,N*-diethylaniline (2 ml) and acetic anhydride (2 ml) was stirred under oxygen-free dry nitrogen at 200° for 6 h. The cooled mixture was diluted with an equal volume of ether and washed successively with 10% aqueous hydrochloric acid, water, saturated sodium hydrogencarbonate, water and brine, and dried. Removal of solvent under reduced pressure and p.l.c. of the resulting yellow solid (53 mg) gave 2-methylfura(a)anthraquinone (21) (see below), m.p. 185–186°. ^{1}H n.m.r. analysis of the crude product showed the presence of compounds (15) (42%), 1-hydroxyanthraquinone (7%), (14) (44%) and (21) (7%).

*2-Methyl-6,11-dihydroanthra[1,2-*b*]furan-6,11-dione (21)*

(A) A solution of the *o*-(2′-chloroprop-2′-enyl) phenol (15) (42 mg, 0·14 mmol) in absolute ethanol (18 ml) was heated under reflux with a solution of 0·9% ethanolic potassium hydroxide (1 ml, 20% excess) for 2·5 h. Solvent was removed from the cooled solution under reduced pressure to yield a solid which was washed with water and then dissolved in chloroform. Removal of solvent from the dried solution in a vacuum gave a solid which was purified by p.l.c. (benzene) to give *2-methyl-6,11-dihydroanthra[1,2-*b*]furan-6,11-dione* (27 mg, 74%), yellow needles, m.p. 192–193° [Found: M$^{+\bullet}$, 262·0630. $C_{17}H_{10}O_3$ requires M$^{+\bullet}$, 262·0630]. λ_{max} 234 (logε 4·34), 240 (4·36), 247 (4·31), 278 (4·78), 256 nm (3·84). ν_{max} (KBr) 1678 cm^{-1} (CO). ^{1}H n.m.r. δ 2·66, br s, 3H, CH_3; 6·55, m, H3; 7·82, m, 3H, H4,8,9; 8·27, m, 3H, H5,7,10. *m/z* 262 (M), 233 (M−CHO), 206 (M−C_3H_4O).

(B) A solution of the *o*-(2′-chloroprop-2′-enyl) phenol (15) (0·10 g, 0·33 mmol) in concentrated sulfuric acid (30 ml) and methanol (50 ml) was stirred at 20° for 24 h and then poured onto ice. P.l.c. of the resulting yellow solid (97 mg) gave 2-methyl-6,11-dihydroanthra[1,2-*b*]furan-6,11-dione (52 mg, 59%).

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