The Kinetics and Mechanisms of Additions to Olefinic Substances. Part 16.[1] Addition of Halogens to 1,4-Benzoquinone and to 1,4-Naphthoquinone, and Dehydrohalogenation of the Resulting Adducts

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The products of acid-catalysed halogenation of 1,4-benzoquinone and 1,4-naphthoquinone in acetic acid have been investigated under conditions which could lead to the formation of dichloride, dibromide, and bromochloride. The variation in ratio of bromochloride to dibromide with relative availability of bromine and chlorine as electrophile and nucleophile suggests that the first entering halogen atom is attached nucleophilically as the result of ' 1,4 '- (rather than ' 1,2 '-) addition, and that the second halogen atom is then attached electrophilically. Acetate ion does not compete effectively with chloride ion in the nucleophilic stage of the reaction; and chlorine acetate does not add, even with sulphuric acid as catalyst, to 1,4-benzoquinone. The mechanistic significance of these results is discussed. The kinetics and products of solvolytic eliminations from the dihalides derived from 1,4-benzoquinone have been studied in 95% ethanol; the effects of structure on the rate make it probable that the reactions lie towards the *E*1cB end of the spectrum of elimination mechanisms.

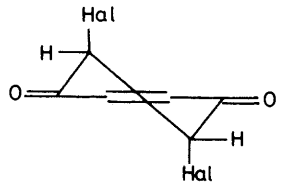
Much is now known about the many possible complexities in the pathways taken when electrophilic halogen reacts with unsaturated compounds. The expected structural effects so characteristic of these reactions are in marked contrast to those evident when the double bond is conjugated with certain electron-attracting substituents, of which the carbonyl group is the most important. Under these conditions, abnormally rapid additions occur under catalysis by hydrogen halides,[2] which often can be formed in trace amounts in the course of the more usual halogenations. Despite some later investigations,[3-5] the detailed pathways adopted in these additions are still to some extent uncertain. The fact that hydrogen halides are specific catalysts suggests that they are concerned first in addition to the carbonyl group, but whether the species then attacked electrophilically is the ' 1,2 '- or the ' 1,4 '-adduct is uncertain. Both possibilities have been considered.[4,5]

Of the groups of compounds for which these acid-catalysed additions are important, the quinones perhaps show the effects most spectacularly.[3] The derived dihalides, 5,6-dichloro- and 5,6-dibromo-cyclohex-2-ene-1,4-dione (1; Hal = Cl or Br) are known to be kinetically reasonably stable, despite the fact that they are tautomers of the corresponding dichlorohydroquinones. The dichloride has been degraded to DL-dichlorosuccinic acid, so it is established to be the *trans*-isomer,[6] and its ^{1}H n.m.r. spectrum is consistent with structure (1), with both chlorine atoms axially disposed.[7] A claim to have observed the formation of the corresponding *cis*-dichloride [8] has been refuted,[9] and there is every reason to believe that the known dibromide has the same stereochemistry.[7]

When mixed halogens (*e.g.* bromine chloride) add to olefinic compounds, the higher halogen (*e.g.* bromine) is unambiguously the electrophilic fragment, and the lower halogen is the nucleophile. For a reaction in which addition to a carbonyl group is concerned, however, both bromide and chloride ion could act as the nucleophile. It was hoped, therefore, that a study of the addition of bromine chloride to 1,4-benzoquinone and to 1,4-naphthoquinone in the presence and absence of added halide ions might give further information concerning the pathway taken.

Experimental

The general methods used in this investigation have been described in earlier papers in this series.[1] N.m.r. spectra were recorded in $CDCl_3$ as solvent except where otherwise stated. Assignments marked with asterisks may be interchanged.



(1)

1,4-Benzoquinone was purified by sublimation *in vacuo*. 1,4-Naphthoquinone was purified by chromatography on a column of activated alumina with chloroform as eluant, and was purified further by sublimation *in vacuo*.

Choroform for use as a solvent for preparative chlorinations was washed (H_2O, $NaHCO_3$), dried ($CaCl_2$), and distilled. Acetic acid had m.p. 16.5—16.6 °C. Light petroleum had b.p. 60—80 °C except where otherwise stated.

Derivatives of 1,4-*Benzoquinone*.—5,6-Dichlorocyclohex-2-ene-1,4-dione was prepared by reaction of equimolar quantities of 1,4-benzoquinone and chlorine in chloroform in the dark. After 10 min, excess of light petroleum was added and the precipitated dichloride was filtered off and recrystallised twice from light petroleum–chloroform (4 : 1) to give crystals, m.p. 145.5—146 °C (lit.,[9] 146.0—146.5 °C), $\lambda_{max.}$ ($CHCl_3$) 245 nm (Found: C, 40.2; H, 2.25; Cl, 39.5. Calc. for $C_6H_4Cl_2O_2$: C, 40.2; H, 2.25; Cl, 39.7%). Its ^{1}H n.m.r. spectrum accorded with Norris and Sternhell's description,[7] being deceptively simple with two apparent singlets which on expansion were triplets, δ 4.62 (H-5, -6) and 6.74 (H-2, -3), $J_{2,5} + J_{2,6}$ 1.4 Hz. Its proton- and noise-decoupled ^{13}C n.m.r. spectrum ($CDCl_3$) had signals at δ 186.96 (C-1, -4), 137.33 (C-2, -3), and 58.05 p.p.m. (C-5, -6).

2-Chloro-1,4-benzoquinone was prepared by heating 5,6-dichlorocyclohex-2-ene-1,4-dione (1.4 g) in a mixture of ethanol (65 cm^3) and water (10 cm^3) until the solution became yellow. The mixture was cooled to 0 °C; the chloroquinone crystallised overnight, and was filtered off and dried, m.p. 55—56 °C (lit.,[10] 55.3—56.3 °C). Its ^{1}H n.m.r. spectrum varied somewhat with solvent, and in $CDCl_3$ consisted of two multiplets centred at δ 7.02 (H-3) and 6.88 (H-5, -6) which could be analysed to be consistent with expectation for an ABC spectrum, $J_{3,5}$ 2.2, $J_{5,6}$ 10, $J_{3,6}$ −0.6 Hz.

Attempts were made to prepare 2,3,5,6-tetrachlorocyclohexane-1,4-dione (a) by treating 1,4-benzoquinone (1 mol. equiv.) with chlorine (2 mol. equiv.) in $CHCl_3$ or in CH_3CO_2H and (b) by treating 5,6-dichlorocyclohex-2-ene-1,4-dione (1 mol. equiv.) with chlorine (1 mol. equiv.) in $CHCl_3$. The product was precipitated by adding an excess of light petroleum to the reaction mixture, and was only sparingly soluble in solvents except in those like acetone in which it decomposed. Samples were obtained containing typically 54.3% of chlorine (calc. for $C_6H_4Cl_4O_2$, 56.8%) and having a signal in the ^1H n.m.r. spectrum at δ 5.02 (s). The product is probably a mixture of geometric isomers since other much weaker signals at δ 4.65 (s) and 5.34 (s), shown not to be spinning side bands, were observed also.

5,6-Dibromocyclohex-2-ene-1,4-dione was prepared by adding bromine (8.0 g) in CCl_4 (75 cm^3) and Et_2O (7.5 cm^3) to 1,4-benzoquinone (5.4 g) in CCl_4 (100 cm^3). The solvent was then evaporated to 20 cm^3 and the dibromide was precipitated with light petroleum, filtered off, and crystallised from light petroleum as pale green needles, m.p. 86 °C (lit.,[9] 86 °C), $\lambda_{max.}$ ($CHCl_3$) 247 nm (Found: C, 27.0; H, 1.55; Br, 59.9. Calc. for $C_6H_4Br_2O_2$: C, 26.9; H, 1.55; Br, 59.7%). Its ^1H n.m.r. spectrum resembled that of the dichloride, with signals at δ 4.85 (apparent s) and 6.75 (apparent s), $J_{2,5} + J_{2,6}$ 1.7 Hz on expansion. Its fully proton- and noise-decoupled ^{13}C n.m.r. spectrum had signals at δ 186.87 (C-1, -4), 136.49 (C-2, -3), and 42.32 p.p.m. (C-5, -6). This compound could also be prepared by reaction in acetic acid as solvent. It was normally stored at 0 °C, but it did not decompose, interchange halogen, or otherwise react under the conditions used in the experiments described later. Its m.p. was depressed by admixture with either 5,6-dichloro- or 5-bromo-6-chlorocyclohex-2-ene-1,4-dione.

2-Bromo-1,4-benzoquinone was prepared by heating 5,6-dibromocyclohex-2-ene-1,4-dione in 85% ethanol until it had dissolved. Most of the solvent was then removed *in vacuo*, and the remainder was set aside at 0 °C overnight, when yellow crystals, m.p. 56 °C (lit.,[11] 56 °C) were obtained. Its ^1H n.m.r. spectrum was in accord with the literature,[7] δ 7.25 (d, H-3), 6.92 (d, H-6), and 6.80 (dd, H-5), $J_{5,6}$ 10.5, $J_{3,5}$ 2.6 $J_{3,6}$ −0.6 Hz. 2,3,5,6-Tetrabromocyclohexane-1,4-dione was prepared by treating 1,4-benzoquinone with bromine (2 mol. equiv.) in carbon tetrachloride. A powder was obtained which could not be successfully recrystallised and decomposed on attempted sublimination *in vacuo*. Its ^1H n.m.r. spectrum had a major peak at δ 5.02 (s) and two minor peaks at δ 4.80 (s) and 5.22 (s) which were shown not to be spinning side bands. A similar product was obtained when 5,6-dibromocyclohex-2-ene-1,4-dione was treated with bromine (1 mol. equiv.) in carbon tetrachloride. We believe it to be, like the corresponding tetrachloride, an intractable mixture of diastereoisomers (geometric isomers).

2,5,6-Tribromocyclohex-2-ene-1,4-dione, prepared by reaction of equimolar quantities of bromine and 2-bromo-1,4-benzoquinone in carbon tetrachloride, had a ^1H n.m.r. spectrum which accorded with that reported in the literature,[7] δ 7.20 (d, H-3), 5.10 (d, H-6), and 4.90 (dd, H-5), $J_{3,5}$ 1.9, $J_{5,6}$ 3.0 Hz. The analogous 2,5,6-trichlorocyclohex-2-ene-1,4-dione, prepared similarly, had signals at δ 7.02 (d, H-3), 4.80 (d, H-6), and 4.62 (dd, H-5), $J_{3,5}$ 1.2, $J_{5,6}$ 3.5 Hz.

Bromochlorination of 1,4-*Benzoquinone*.—A solution of bromine chloride in acetic acid was prepared by mixing appropriate volumes of bromine and of chlorine in acetic acid, each previously standardized ($Na_2S_2O_3$). To this solution was added a filtered solution of 1,4-benzoquinone (1 mol. equiv.) in acetic acid. The mixture was added to light petroleum, and the resulting precipitate was recrystallised from light petroleum to give 5-*bromo*-6-*chlorocyclohex*-2-*ene*-1,4-*dione*, m.p. 104 °C, $\lambda_{max.}$ ($CHCl_3$) 244 nm (Found: C, 32.2; H, 1.7; Cl, 15.3; Br, 35.4. $C_6H_4BrClO_2$ requires C, 32.2; H, 1.8; Cl, 15.9; Br, 35.8%), δ 4.78 (apparent s), 6.79 (apparent s), giving on expansion $J_{2,5} + J_{2,6}$ 1.13 Hz. Because of the deceptively simple nature of this spectrum, it was run also in $(CD_3)_2CO$, $Cl_2C{:}CCl_2$, and C_6D_6; no additional splitting was found. In $(CD_3)_2SO$ and in C_5D_5N it decomposed. Its ^{13}C n.m.r. spectrum had signals at δ 186.87 (C-1, -4), 45.32 (C-5), 57.01 (C-6), and 136.48 and 136.88 p.p.m. (C-2, -3).

These deceptively simple spectra are similar to what would be expected for an equimolar mixture of 5,6-dichloro- and 5,6-dibromo-cyclohex-2-ene-1,4-dione, but it was shown conclusively that this does not represent the product isolated, which is instead the pure bromochloride. Mixtures of the dibromide and dichloride give ^1H and ^{13}C n.m.r. spectra in which the signals of both the components can be recognised clearly, and do not overlap with the signals of the bromochloride. The three compounds are clearly differentiated also through their i.r. spectra, which are given in Table 1.

Table 1. I.r. spectra (1.9×10^{-2}M solutions in CS_2, KBr cells) of the 5,6-dihalogenocyclohex-2-ene-1,4-diones

	$\nu_{max.}/cm^{-1}$	
5,6-Dibromocyclohex-2-ene-1,4-dione	5,6-Dichlorocyclohex-2-ene-1,4-dione	5-Bromo-6-chlorocyclohex-2-ene-1,4-dione
485	540	520
580	580	580
635		630
		690m
	720m	
	755	750
		815
840	840	840
909	918	919
1 000	1 010m	1 005m
1 096	1 102	1 098
1 118	1 170	1 135
1 202		1 210sh
1 220	1 220	1 220
1 272m	1 280m	1 280m
	1 365	1 360
		1 378
	1 680sh	
1 702s	1 710s	1 740s
1 730	1 740	1 738

Derivatives of 1,4-*Naphthoquinone*.—1,4-Naphthoquinone (B.D.H.) was purified by column chromatography by using activated alumina, type H, 100—200 mesh, and chloroform as eluting solvent. The purest product was obtained from early fractions; later fractions were purified further by sublimation *in vacuo*. Chlorination of this in acetic acid gave 2,3-dichloro-1,2,3,4-tetrahydronaphthalene-1,4-dione, m.p. 165 °C (decomp.) (lit.,[12] 176 °C), δ_H 4.84 (2 H, s, H-2, -3) and 8.00 (4 H, m, ArH), δ_C 58.05 (C-2, -3), 128.17 (C-5, -8)*, 130.83 (C-4a, -8a), 135.38 (C-6, -7)*, and 186.22 p.p.m. (C-1, -4).

Similar bromination gave 2,3-dibromo-1,2,3,4-tetrahydronaphthalene-1,4-dione, m.p. >82 °C (decomp.) (lit.,[12] >92 °C), δ_H 5.00 (2 H, s, H-2, -3) and 7.94 (4 H, m, ArH), δ_C ($CDCl_3$) 45.94 (C-2, -3), 127.94 (C-5, -8)*, 130.18 (C-4a, -8a), 135.19 (C-6, -7)*, and 186.06 p.p.m. (C-1, -4).

2-Bromo-3-chloro-1,2,3,4-tetrahydronaphthalene-1,4-dione has not been reported previously. It was prepared from 1,4-naphthoquinone and bromine chloride in acetic acid and had m.p. >65 °C (decomp.), δ_H 4.93 (2 H, apparent s, H-2, -3)

Table 2. Product proportions in acid-catalysed reactions of bromine and of bromine chloride with 1,4-benzoquinone (0.1M) in acetic acid at 25 °C

No.	Halogen	Halogen acid	Other additives	Formal components of reaction mixture [a]				Product		
				Br^+	Cl^-	Br^-	H^+	Bromochloride (%)	Dibromide (%)	Other (%)
11	BrCl, 0.1M	HCl, 0.01M	LiCl, 0.1M	1	2.1		0.1	100		
5	BrCl, 0.1M	HCl 0.1M		1	2		1	70		30 [b]
9	Cl_2, 0.05M, Br_2,[c] 0.05M			1	1			76	16	8
12	BrCl, 0.1M	HBr, 0.02M		1	1	0.2	0.2	75	25	
6	Cl_2, 0.1M	HBr, 0.1M		1	2		1	70		30 [b]
13	BrCl, 0.1M	HBr, 0.05M		1	1	0.5	0.5	51	47	2
14	BrCl, 0.1M	HBr, 0.1M		1	1	1	1	21	72	7
3	Br_2, 0.1M	HCl, 0.1M		1	1	1	1	20	80	
4	BrCl, 0.1M	HBr, 0.1M		1	1	1	1	24	72	4
7	BrCl, 0.1M	HCl, 0.1M, HBr, 0.1M		1	2	1	2	20	80	
10	BrCl, 0.1M	HBr, 0.01M	LiBr, 0.1M	1	1	1.1	0.1		100	

[a] Relative to amount of quinone. [b] Mainly products of addition of hydrogen halide. [c] Not previously mixed.

and 7.94 (4 H, m, ArH), δ_C ($CDCl_3$) 46.20 (C-2), 57.66 (C-3), 130.51, 130.61 (C-4a, -8a), 128.08 (C-5, -8)*, 135.25 (C-6, -7)*, and 186.48 p.p.m. (C-1, -4). This compound was found to be unstable at room temperature.

These three adducts were easily distinguishable in mixtures through the positions of signals in their ^1H n.m.r. spectra. By heating the dichloride with 85% ethanol, we prepared for reference 2-chloro-1,4-naphthoquinone, m.p. 113—115.5 °C (lit.,[12] 117—118 °C), δ 7.17 (1 H, s, H-3) and 7.90 (4 H, m, ArH). Similarly, 2-bromo-1,4-naphthoquinone was prepared, m.p. 128—130 °C (lit.,[12] 130 °C), δ 7.50 (1 H, s, H-2) and 7.90 (4 H, m, ArH).

Proportions of Products of Halogenation.—The products of reaction of bromine, bromine chloride, and chlorine with 1,4-benzoquinone under a variety of conditions in acetic acid are recorded in Table 2. Reaction mixtures were made up from known weights of quinone in acetic acid to which were added appropriate volumes of standardized solutions of the necessary reagents. The reactions were allowed to proceed to completion in the dark at 25 °C. Work-up was then normally by removal of the solvent *in vacuo*, benzene being added to ensure removal of all the acetic acid. Product analysis was by ^1H n.m.r. spectroscopy, and is considered to be reliable to within 5 units %. The corresponding results obtained by using 1,4-naphthoquinone are included in Table 3.

Additional experiments were performed to check on particular points, as follows. The reactions of hydrogen chloride and of hydrogen bromide with 1,4-benzoquinone in acetic acid under conditions similar to those used for halogen additions were examined separately. In both cases, mixtures of products of 1,4-addition followed by prototropic rearrangement or further addition were obtained. Thus 1,4-benzoquinone (0.1M) and hydrobromic acid (0.1M) in acetic acid gave 2-bromohydroquinone, δ ($CDCl_3$) 7.02, 7.05 (dd), 6.85, and 6.40 (OH), together with other polyhalogenated products. Similar results were obtained by using hydrogen chloride

Table 3. Product proportions in acid-catalysed reactions of bromine and of bromine chloride with 1,4-naphthoquinone (0.1M) in acetic acid at 25 °C

Halogen	Halogen acid	Formal components of reaction mixture [a]				Product	
		Br^+	Cl^-	Br^-	H^+	Bromochloride	Dibromide
BrCl, 0.1M	HCl, 0.1M	1	2		1	81	19
Cl_2, 0.05M, Br_2,[b] 0.05M		1	1			56	44
Cl_2, 0.1M	HBr, 0.1M	1	2		1	55	45
Br_2, 0.1M	HCl, 0.1M	1	1	1	1	24	76
BrCl, 0.1M	HBr, 0.1M	1	1	1	1	14	86
BrCl, 0.1M	HCl, 0.1M, HBr, 0.1M	1	2	1	2	15	85

[a] Relative to amount of quinone. [b] Not previously mixed.

These products were investigated only to the point of establishing that the products of direct reaction between hydrogen halides and the quinones could be recognized in the reaction mixtures involving halogens.

When a 1,4-benzoquinone or 1,4-naphthoquinone (0.1M) and chlorine (0.1M) were mixed in acetic acid containing sodium acetate (0.5M), the starting material was recovered unchanged after 12 h.

A standardized solution of chlorine acetate in acetic acid was prepared by allowing chlorine to react with mercury(II) acetate, and then distilling off the product under reduced pressure.[13] This was mixed with an equimolar amount of 1,4-benzoquinone in acetic acid. After 48 h, iodometric titration showed that no loss of active halogen had occurred. Two drops of H_2SO_4 (98%) were added to the mixture; after a further 12 h, there was still no decrease in titre of active halogen. So chlorine acetate does not add to 1,4-benzoquinone under these conditions.

Bromine (0.66 cm^3) in CCl_4 (12 cm^3) was added dropwise to a suspension of AgOAc (2.66 g) in CCl_4 (108 cm^3) at 0 °C. The mixture was stirred for 2 h; the supernatant liquid containing bromine acetate was decanted off and the concentration of active halogen was determined iodometrically. 1,4-Benzoquinone (0.54 g) was dissolved in CCl_4 (10 cm^3) at 0 °C. To this was added an equivalent quantity of bromine acetate in CCl_4 (50 cm^3). After 12 h, the ^1H n.m.r. spectrum of the product established that no addition had occurred.

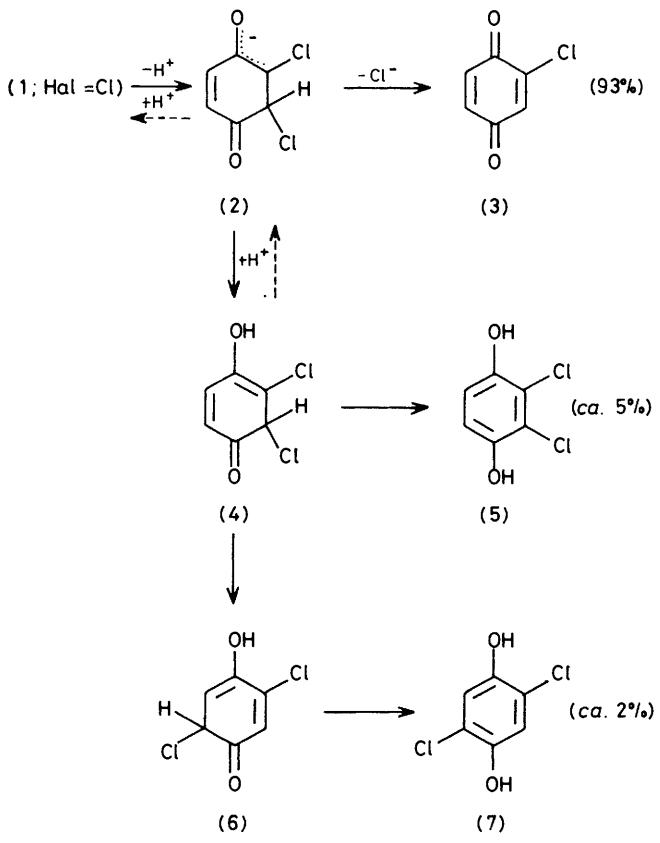
From the following attempted reactions of 1,4-benzoquinone, equimolar amounts of reagents being used, only undecomposed starting materials were recovered: with $PhICl_2$ in $CHCl_3$ or in HOAc; with *N*-bromosuccinimide and lithium chloride in HOAc; with *N*-bromoacetamide and lithium chloride in acetic acid.

Solvolytic Elimination from the Dihalides obtained from 1,4-Benzoquinone.—The adducts derived from 1,4-benzoquinone were characterized also by following their rates of solvolytic elimination. A solvent mixture containing ethanol, water, and acetone in the ratio 95 : 5 : 1 by volume was used. A known weight of the substrate was dissolved in acetone (1 cm^3) and to it was added 100 cm^3 of 95% ethanol at 25 °C. Aliquot parts (4.96 cm^3) were removed at intervals and added to chilled acetone for titration with standardized sodium ethoxide, lacmoid being used as indicator.[14] Experimental infinity values determined after *ca.* 10 half-lives were used. The following are the details of a typical kinetic run in which 5,6-dichlorocyclohex-2-ene-1,4-dione (0.055 60 g) was used.

Time (s)	180	360	720	1 200	1 515	1 800	2 100	2 410	2 705
Titre (cm^3)	0.25	0.60	1.25	2.20	2.68	2.85	3.20	3.52	3.80
$10^4 k_1/s^{-1}$		3.00	3.02	3.40	3.31	3.06	3.05	3.03	3.02
Time (s)	3 015	3 300	3 620	4 620	5 400	∞			
Titre (cm^3)	3.95	4.26	4.48	4.92	5.40	6.90			
$10^4 k_1/s^{-1}$	2.87	2.96	2.94	2.73	2.85				

Mean values of k_1 from concordant runs which showed no significant trend in the rate coefficients over 70—90% reaction were for 5,6-dichlorocyclohex-2-ene-1,4-dione, 3.0×10^{-4} s^{-1}; for 5-bromo-6-chlorocyclohex-2-ene-1,4-dione, 2.4×10^{-4} s^{-1}; for 5,6-dibromocyclohex-2-ene-1,4-dione, 1.1×10^{-4} s^{-1}. Eliminations at 25 °C in the same solvent with 0.005M-NaOEt were too fast to measure by the type of method used above.

The ^1H n.m.r. spectra of the recovered products showed that the dichloride and the bromochloride gave mainly 2-chloro-1,4-benzoquinone, and that the dibromide gave mainly 2-bromo-1,4-benzoquinone. Infinity titrations were stable, but were usually *ca.* 10—20% lower than was expected. Careful analysis was carried out by adding excess of silver nitrate to the aqueous products of hydrolysis, filtering off the precipitated silver chloride, and back-titrating the excess of silver nitrate with ammonium thiocyanate, itself standardized by a similar procedure with weighed, dried, AnalaR sodium chloride, iron(III) ammonium sulphate being the indicator. It was found that for each mole of 5,6-dichlorocyclohex-2-ene-1,4-dione hydrolysed, 0.93 moles of chloride ion were liberated. This result implies that 7% of the starting material is used up in a side-reaction, the most likely being prototropic rearrangement leading to a dichlorohydroquinone.



Scheme 1. Probable pathways in the solvolysis of 5,6-dichlorocyclohex-2-ene-1,4-dione in 95% ethanol

Scheme 1 anticipates points to be brought out in later discussion.

Attempts to establish the presence of dichlorodihydroxybenzenes in the product of hydrolysis gave inconclusive results, so the following procedure was adopted. 5,6-Dichlorocyclohex-2-ene-1,4-dione (0.40 g) was dissolved in ethanol containing 5% water (250 cm^3) and was allowed to react at room temperature for 16 h. The solvent was then removed under reduced pressure, and the residue was dissolved in dry diethyl ether and dried ($MgSO_4$). Removal of the solvent gave a red oil (0.3 g) which was dissolved in dry diethyl ether (20 cm^3). The solution was stirred for 20 min with $MgSO_4$ (2 g) and freshly prepared Ag_2O (1 g); the solid was filtered

off, and solvent was removed from the filtrate to give a blackish red solid (0.3 g). The ^1H n.m.r. spectrum of this showed that it was mainly 2-chloro-1,4-benzoquinone, but that 2,3-dichlorobenzoquinone was present also, as was indicated by the presence of a signal at δ 6.97, identical in position with that found in an authentic sample prepared for reference by Norris and Sternhell's method [15] and having m.p. 98—100 °C (lit.,[15] 100—101 °C). A second singlet, at δ 7.03, was also evident in the spectrum, and suggests the presence of an isomeric dichlorobenzoquinone.

One mechanism of the dehydrochlorination of the dione involves the reversible formation of the carbanion (2). To test this possible reversibility, the solvolysis was run to completion with ethanol containing 5% deuterium oxide as solvent. The products were examined by mass spectrometry and compared with those obtained when H_2O rather than D_2O had been included in the mixed solvent. No difference was discernible; the main signals were at *m/e* 144 and 146, corresponding with the formation of 2-chloro-1,4-benzoquinone and its reduction by the product of prototropic rearrangement or in the inlet system of the mass spectrometer, as is frequently noted for quinones.[16] The molecular ion of 2-chloro-1,4-benzoquinone might also have been expected to be observed, but its signals relative to those of its dihydro-derivative have been shown, by study of mixtures, to be weak relative to those of its product of reduction. We estimate that the incorporation of 1 atom % of deuterium into the final product would have been detectable experimentally.

The mass spectrum included signals at *m/e* 178, 180, and 182, corresponding to the presence of a dichloro-1,4-dihydroxybenzene. A good deal more than ten half-lives had been allowed for the solvolysis, so the starting material (1) (which has the same molecular weight) cannot have been responsible for these signals. We consider that these results confirm the deduction that a small proportion of (1) rearranges in the course of solvolysis to give (4) and hence (5) and (7).

It was shown in separate experiments that homolytic elimination of hydrogen chloride from 5,6-dichlorocyclohex-2-ene-1,4-dione could be initiated in carbon tetrachloride by adding a catalytic amount of peracetic acid, but that after about two days and 60% reaction, an insoluble red oil precipitated from the reaction mixture and no more 2-chloro-1,4-benzoquinone was formed. Irradiation of the dione with u.v. light also resulted in the formation of insoluble and intractable coloured products.

Discussion

Additions.—The results obtained in the present work confirm the preparative work of earlier investigators [9-12] who established that the kinetically controlled product of addition of one molecular equivalent of bromine or of chlorine to 1,4-benzoquinone is the dihalogeno-enedione obtained by simple addition to a double bond, rather than an aromatized derivative produced by prototropic rearrangement. No evidence has been obtained for the production of more than one stereoisomer, and it seems clear from the evidence obtained by oxidation that this is the *trans*-, rather than the *cis*-isomer.[6,9] These results have now been extended by the use of the mixed halogen, bromine chloride. This gives a bromochloride having unexpectedly and deceptively simple ^1H and ^{13}C n.m.r. spectra, but nevertheless distinguishable in mixtures from both the dibromide and the dichloride.

Our results confirm also that addition in acetic acid is very slow in the absence of added or adventitiously developing hydrogen halide.[3] It is particularly significant that the very reactive electrophile chlorine acetate [13] reacts very slowly, if at all, with 1,4-benzoquinone, even in the presence of added sulphuric acid.

When a hydrogen halide is used as a catalyst for halogenation of 1,4-benzoquinone in acetic acid, the main competing reaction is the formation of the product of addition of hydrogen halide followed by its prototropic rearrangement. This reaction is a more important competitor when the nucleophile is provided as Cl^- than when it is provided as Br^-, and appears also to be more important at higher than at lower acidities. No evidence has been obtained for a competing reaction giving acetoxybromide adducts.

Bromine being much more electropositive than chlorine, it would be expected that, however the two halogens were provided (*e.g.* as BrCl + HCl or as Cl_2 + HBr), rapid equilibration would lead to there being as much bromine as possible in the form of bromine chloride and hence available for providing positive bromine. The fact that no dichloride was produced in any of the additions in which a bromine was present in amount equivalent to the quinone appears to imply that electrophilic bromine is provided to the quinone in one stage of the addition.

In the phase of the addition in which the halogen atom becomes attached nucleophilically, bromide and chloride are in competition, with bromide being the more effective. Dibromide is formed whenever enough bromine is present to supply some bromide, and is formed exclusively when sufficient excess of bromide ion is present. There is no certainty that the entity delivering nucleophilic halide must be a free halide ion; none of our experiments exclude the participation of the $(Cl{-}Br{-}Br)^-$ or $(Cl{-}Br{-}Cl)^-$ ion in this phase of the reaction.

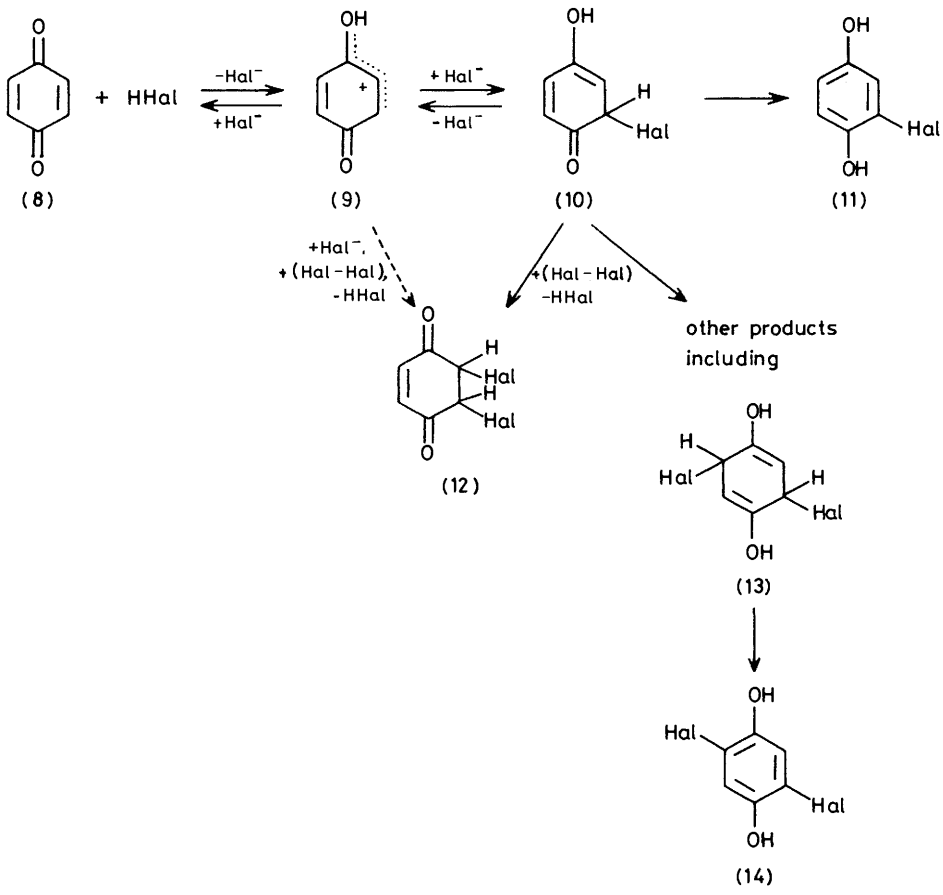
It is not essential for preparative use of the reaction to supply hydrogen chloride or hydrogen bromide separately; their catalytic power is sufficient that traces formed by other reactions can ensure very rapid, presumably autocatalytic, additions even when no extra hydrogen halide is supplied.

The most natural way of depicting the course of the reaction is shown in Scheme 2.

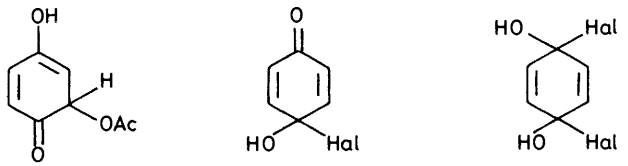
We have not investigated in detail the competing reactions which we show as leading to the hydroquinones (11) and (14), but our observations are consistent with earlier work,[17] and with Cason *et al.*'s [18] conclusion that the reaction of HCl or HBr with 1,4-benzoquinone in organic solvents always gives mixtures of organic products including dihalogenated hydroquinones. The ' 1,4 '-adduct (10), which is an expected precursor of these products, has a hydroxy-group conjugated with a double bond, and hence would be very reactive with electrophilic halogen, and therefore would be expected to be diverted by a halogen or mixed halogen molecule to the adduct (12), kinetically stable under the conditions of reaction.

The sequence (8) ⟶ (9) ⟶ (10) ⟶ (11) provides no ready interpretation of the degree of *anti*-stereoselectivity in these halogenations other than its attribution to the steric influence of the already attached halogen in (10). A possible alternative explanation is that the reaction of the cation (9) with nucleophile and electrophile is concerted, and hence is subject to stereoelectronic control involving greater geometrical restrictions than would be required by the stepwise process. Other instances of highly stereoselective third-order additions involving halogens and halide ions have been noted.[1,19,20]

At first sight the lack of competition between acetate ions and halide ions in the nucleophilic stage of the reaction is surprising. This seems, however, to be a general rule in the more stereoselective additions in acetic acid, and would be consistent with attributing the formation of (12) to a concerted process. Otherwise it has to be concluded that the



Scheme 2. Proposed pathway in the addition of bromine, chlorine, or bromine chloride to 1,4-benzoquinone in acetic acid under catalysis by hydrogen halides (HHal)



formation of the hypothetical adduct (15) is so greatly disfavoured, either thermodynamically or kinetically, that no reaction through this is possible. Acetic acid has been established [21] to be a very poor nucleophilic solvent.

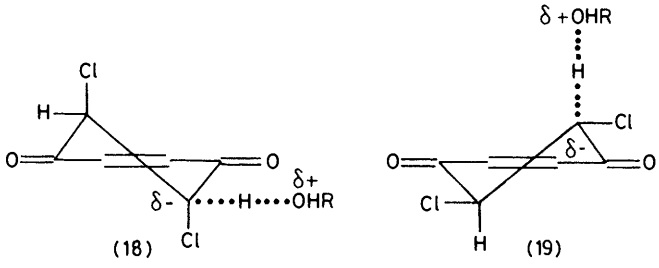
Other adducts which hypothetically could take part in the reaction are the ' 1,2 '-adducts (16) and (17). A pathway like that shown in Scheme 2 but starting with (16) rather than with (8) could equally be used to explain the observed results, but does not seem to be required or to help the interpretation. For the normal reaction with electrophiles, both (16) and (17) are expected to be deactivated. The influence of one and of two CH_2Cl groups on the rate of bromination of an olefinic double bond was established by Swedlund and Robertson,[22] who showed that $CH_2{:}C(CH_2Cl)_2$ has reactivity similar to that of $PhCH{:}CH{\cdot}CO_2Et$, and much less than that of 1,4-benzoquinone under conditions of catalysis by hydrogen bromide. The cumulative deactivating influence of the inductively electron-withdrawing halogen, hydroxy, and vinyl substituents in (17) would, we think, make a compound of this type too unreactive to play a significant role in the additions under study.

The results obtained for addition to 1,4-naphthoquinone (Table 3) can be interpreted similarly; here competition with reactions leading to addition of hydrogen bromide seems to be less important. Although the dichloride and dibromide were prepared first by Zincke and Schmidt,[12] who showed them to undergo the expected dehydrohalogenation, they and their analogues have not been much studied since that time. The rapidity of these halogenations under catalysis by hydrogen halides is, however, shown by the fact that Thomson [23] was able to prepare the dichloride and dibromide of 5-hydroxy-1,4-naphthoquinone despite the expected competing activation of the 6- and 8-position by the hydroxy-group.

Eliminations.—The kinetics of dehydrohalogenation of the dihalides derived from 1,4-benzoquinone reveal some interesting features. These compounds, being not very rapidly soluble in ethanol, underwent significant decomposition before kinetic measurements could be started in this solvent or in aqueous ethanol, so the compound under study was first dissolved in a little acetone. The final solvent therefore contained ethanol (95 parts v/v), water (5 parts), and acetone (1 part). The progress of the solvolytic reaction was in each case uniform within experimental error over at least 70% reaction, and the simple product of 1,2-elimination of hydrogen halide was the main product. The kinetic behaviour differentiated clearly between the dichloride, the dibromide, and the bromochloride. No kinetic evidence was found for the presence of any isomeric dihalide in any of the starting materials. The reactions were not significantly catalysed by the acid which develops in the course of the solvolysis, so the

Table 4. Positions (δ, p.p.m. downfield from Me_4Si) of the signals in the ^{13}C n.m.r. spectra of dihalides derived from 1,4-benzoquinone and 1,4-naphthoquinone

Compound				
Benzoquinone	C-1, C-4	C-2, C-3	C-5, C-6	
dichloride	186.96	137.33	58.05	
dibromide	186.87	136.49	42.32	
bromochloride	186.87	136.48, 136.88	45.32, 57.01	
Naphthoquinone	C-1, C-4	C-4a, C-8a	C-2, C-3	C-5, C-8; C-6, C-7
dichloride	186.22	130.83	58.05	128.17, 135.38
dibromide	186.06	130.18	45.94	127.94, 135.19
bromochloride	186.48	130.51, 130.61	46.20, 57.66	128.08, 135.25



entity undergoing first-order reaction is the dihalogeno-enedione itself, and not its protonated form.

Light on the mechanism of these eliminations is provided by the fact that the dichloride is more reactive than the dibromide or the bromochloride. When the statistical factor is allowed for (since the dibromide and dichloride have two equivalent sites for elimination), it is apparent that in this series the loss of HBr from the system ClC–CBr is actually a little faster than the loss of HCl from ClC–CCl. The loss of HBr from CCl–CBr is about four times greater than the corresponding loss from BrC–CBr, corresponding with a slightly larger inductive influence of chlorine, as is paralleled in some other comparisons.[24] These results are consistent with the dominant but not exclusive loss of HBr rather than of HCl from the bromochloride, as was found experimentally.

For unimolecular (*E*1) eliminations, organic bromides are more reactive than organic chlorides by quite a large factor.[25] The same is true [25] of concerted bimolecular (*E*2) eliminations towards the central region of the spectrum [26] of bimolecular transition states. The solvolyses recorded in the present paper appear, therefore, to be well towards the *E*1cB end of the spectrum, so that the dominant structural feature determining the rate becomes the loss of a proton to the solvent. The transition state is thus as shown in structure (18) or (19). The dominance of reaction by this pathway must be helped by the fact that the geometrical requirements for rapid concerted (*E*2) elimination are not present in either of the conformationally isomeric transition states.

Other examples of reactions in which proton loss has become so dominant that the overall rate of loss of hydrogen chloride is similar to that of loss of hydrogen bromide have been recorded by Stirling *et al.*[27]

The solvolytic loss of a proton [structure (12) or (19)] may lead to the carbanion (2) (Scheme 1) as a discrete intermediate. Return to starting material from this carbanion must be slow relative to loss of chloride ion, since no deuterium had become incorporated in the final product of solvolysis in a solvent in which the DO : HO ratio was *ca.* 1 : 2. Reversible incorporation of deuterium would have been followed by preferential loss of HCl, and so would have allowed a build-up of deuteriated product; our experiment was not a very sensitive test for reversibility, but can probably be assessed as indicating that the reversible (as distinct from the irreversible) *E*1cB mechanism did not contribute more than at the most 10% to the reaction path. If the loss of hydrogen halide proceeds exclusively through the carbanion, then a more conclusive assessment of the speed of loss of chloride ion comes from the fact that it competes by a rate ratio of more than 10 : 1 with the rate of proton capture at oxygen and subsequent aromatization to give the dichlorohydroquinone [(5), Scheme (1)]. We think that this means that the conversion of (2) into (3) is a very rapid process.

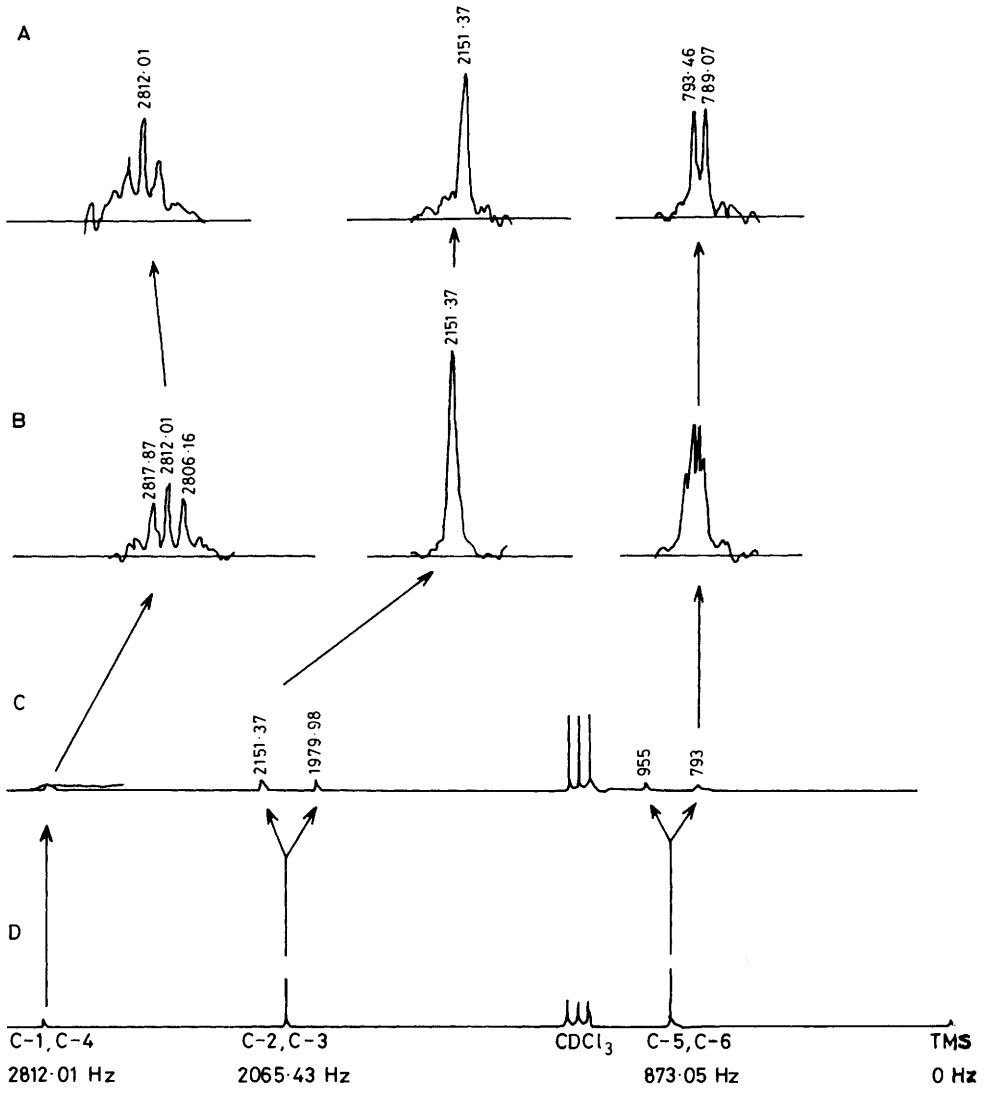
The overall reaction path for our solvolytic eliminations can be represented as in Scheme 1, in which a hypothetical path for the conversion of (4) into (7) is included to account for our finding that the quinones obtained by oxidation of the product of solvolysis included a small proportion of an additional component.

Alkali-catalysed eliminations in the same solvent were very rapid ($k_2 > 20$ l mol^{-1} s^{-1}). A lower limit for the ratio $k_2(OR^-)/k_2(HOR)$ can be estimated to be 10^5—10^6, depending on whether H_2O (*ca.* 3M) or EtOH (*ca.* 18M) is considered to be the effective nucleophile under the chosen conditions.

^{13}C *N.m.r. Spectra.*—The positions of the signals in the ^{13}C n.m.r. spectra of the dihalides of 1,4-benzoquinone and 1,4-naphthoquinone are recorded in the Experimental section, and are collected for comparison in Table 4. The signals for the carbonyl carbon atoms, C-1 and -4, all lie close to the position of this signal in the spectrum of 1,4-benzoquinone (δ 188).[28] In the single-resonance spectrum of 5,6-dichlorocyclohex-2-ene-1,4-dione, the essential features of which are shown in the Figure, this signal appears as a multiplet, spacing 5.8 Hz, which is sharpened to a triplet of similar spacing by low-power single-resonance decoupling at the frequency of the olefinic protons. We interpret this as indicating that each of the two couplings $^2J_{H\text{-}6,C\text{-}1}$ (≡ $^2J_{H\text{-}5,C\text{-}4}$) and $^3J_{H\text{-}5,C\text{-}1}$ (≡ $^3J_{H\text{-}6,C\text{-}4}$) must be about the same, and *ca.* 5.8 Hz.

The signals for the olefinic carbon atoms in the adducts from 1,4-benzoquinone all lie at δ *ca.* 137 p.p.m., and those for the quaternary carbon atoms in the adducts from 1,4-naphthoquinone at δ *ca.* 130 p.p.m. In the single-resonance spectrum of 5,6-dichlorocyclohex-2-ene-1,4-dione, this signal is a doublet, ^1J 171.4 Hz. This value is rather higher than in ethylene (156 Hz),[29] presumably reflecting the electron-withdrawing properties of the attached carbonyl groups.

Neither branch of the doublet representing these carbon atoms in the single-resonance spectrum is fully resolved.



Features of the ^{13}C n.m.r. spectrum of 5,6-dichlorocyclohex-2-ene-1,4-dione in $CDCl_3$: A, low-power single-frequency decoupling at the frequency of H-2, H-3; selected signals expanded; B, single-resonance spectrum; selected signals expanded; C, single-resonance spectrum; D, proton- and noise-decoupled spectrum

Geminal couplings to olefinic carbon atoms are variable over a wide range,[30] so it is perhaps not surprising that $^2J_{H\text{-}2,C\text{-}3}$ ($\equiv {}^2J_{H\text{-}3,C\text{-}2}$) in 5,6-dichlorocyclohex-2-ene-1,4-dione is small. The coupling $^3J_{H\text{-}6,C\text{-}2}$ ($\equiv {}^3J_{H\text{-}5,C\text{-}3}$) must also be small. This probably would be expected, because the coupling path involves a carbonyl carbon atom,[31] and the value would be further reduced because of the electronegative substituent.

The signals for the sp^3-hybridized carbon atoms fall into two groups, those with Br attached are at δ *ca.* 45 p.p.m., and those with Cl attached are at δ *ca.* 57 p.p.m., thus allowing assignment of the signals in the bromochlorides to correspond. These values are in qualititative accord with differences found between chlorine and bromine in their effects on the positions of signals of attached carbon atoms in a number of acyclic systems.[30] In the single-resonance spectrum of 5,6-dichlorocyclohex-2-ene-1,4-dione, the doublet centred at δ 58.05 p.p.m. (C-5, -6) had a spacing of 163.6 Hz; similar, generally slightly lower values of ^1J have been recorded for some naphthalene tetrachlorides.[32] Each of these doublets was itself a slightly asymmetrical pentet, mean spacing 2.1 Hz, reduced to a doublet ($^2J_{H\text{-}5,C\text{-}6} \equiv {}^2J_{H\text{-}6,C\text{-}5} = 4.4$ Hz) by low-power single-frequency decoupling at the frequency of the olefinic protons. We deduce that the coupling $^3J_{H\text{-}2,C\text{-}6}$ ($\equiv {}^3J_{H\text{-}3,C\text{-}5}$) must be *ca.* 4 Hz, similar but not identical with the value of ^2J, and that there is a further small coupling, $^4J_{H\text{-}2,C\text{-}5} \equiv {}^4J_{H\text{-}3,C\text{-}6} = ca.$ 2 Hz, combining with the other two couplings to give the observed multiplet.

The chlorides derived from 1,4-naphthoquinone can be regarded as symmetrically or nearly symmetrically *ortho*-disubstituted benzenes. The signals for the aromatic hydrogen-bearing carbons (C-5, -8; C-6, -7) lie in the expected general region of the spectrum; but they are much more separated (by *ca.* 7 p.p.m.) than would be expected from the empirical parameters recommended as appropriate for substituents containing carbonyl groups attached to a benzene ring.[30] From the tabulated analogies, little difference between the effects of COR groups on *ortho*-(5, 8) and *meta*-(6, 7) positions would have been anticipated. For this reason, we cannot distinguish with any certainty which signals represent which pair of carbon atoms.

Acknowledgements

We thank Mr. D. J. Calvert for ^{13}C n.m.r. spectra, Mr. B. Dobson for mass spectra, Dr. D. J. McLennan for helpful discussions, and the New Zealand University Grants Committee for grants for equipment.

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Received 14*th June* 1982; *Paper* 2/1002