^{13}C Nuclear Magnetic Resonance Spectra of Some Bromo- and Methyl-substituted Cyclohexa-2,5-dienones

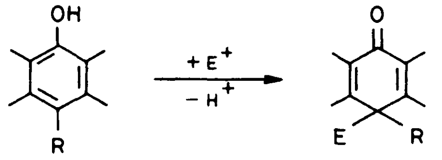
Judith M. Brittain, David J. Calvert, Peter B. D. de la Mare,* and Judith J. Rozsas
Chemistry Department, University of Auckland, Auckland, New Zealand

The ^{13}C n.m.r. spectra of cyclohexa-2,5-dienones produced by bromination or nitration of a variety of methyl-substituted phenols are reported. Most of the signals have been assigned with the assistance of selective decoupling. Correlations of chemical shifts resulting from replacement of hydrogen by methyl and by bromine in the positions originally *ortho* and *meta* to the hydroxy group have been attempted. The effects resulting from changing the substituents at the 4-position from Br,Br to Me,Br to Me,NO_2, and to Me,OH have also been analysed. Comparison is made with effects found in related systems. Single-resonance spectra have been used to determine coupling constants $\{J(^1H,^{13}C)\}$, and these also are compared with cognate results.

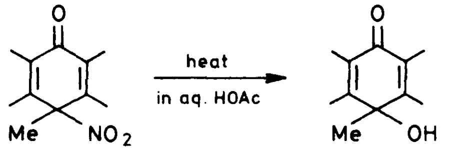
Phenols very commonly react with electrophiles to give cyclohexa-2,5-dien-1-ones [equation (1)], which if suitably substituted are often isolable as crystalline compounds. The literature relating to such reactions, to which Zincke[1] and Auwers[2] made extensive preparative contributions, has been reviewed.[3-5]

These cyclohexadienones tend to be unstable, undergoing rearrangements of several kinds to give ring-substituted products. Some of them, however, can undergo replacements in which the cross-conjugated structure is retained. Thus for compounds in which R is methyl and E is nitro, the conversion shown in equation (2) is easily accomplished. When both R and E can be detached as nucleophiles, such dienones are readily converted into quinones [equation (3)]. Little is known about the mechanism of these displacements.

In the course of investigating some electrophilic substitutions with rearrangement of the type illustrated in equation (1), and the rearrangements of the resulting dienones, we have had occasion to record the ^{13}C n.m.r. spectra of a number of these compounds. Details concerning some of them have been given, or outlined, in earlier papers.[6-8] Here the earlier results are amplified with information relating to a number of other compounds, and the chemical shifts accompanying replacements by bromo substituents in various positions are compared with those for other cyclohexa-2,5-dienones[9-11] and for related unsaturated systems. The single-resonance ('undecoupled') spectra have been analysed as far as possible to give coupling constants $\{^1J(^1H, ^{13}C), ^2J(^1H, ^{13}C), ^3J(^1H, ^{13}C), ^5J(^1H, ^{13}C)\}$, and these also have been compared with cognate values available in the literature.



(1)



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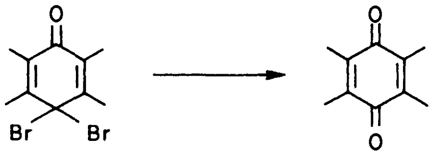

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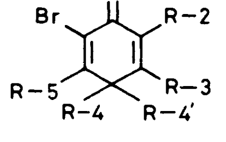

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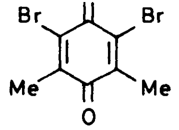

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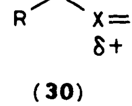


(30)

Experimental

Many of the materials and methods have been described elsewhere.[6-8] A JEOL FX60 spectrometer was used for determining the ^{13}C n.m.r. spectra. Samples were usually examined as solutions in $CDCl_3$ at *ca.* 34 °C; concentrations of *ca.* 0.5M were normally employed, except in the case of representative examples for which the effect of dilution was examined. For the hydroxy-dienones, however, CD_3CN or a mixture of $(CD_3)_2SO$ and $CDBr_3$ was used to improve the solubility of the compounds.

The dienones **(1)**—**(27)** which were examined are listed in Table 1. The carbon atoms and substituents are numbered as in **(28)**; all compounds have a 6-bromo-group.

Bromodienones.—The preparation and properties of **(18)** are given in ref. 6; of **(1)**—**(4)**, **(11)**, **(12)**, **(15)**—**(17)** are in ref. 7; and of **(5)** are in ref. 8. The general procedures used for bromination and isolation of other products were as in these papers. Thus 2,4,5-trimethylphenol (a commerical specimen; K and K Laboratories Inc.) gave 3,6-dibromo-2,4,5-trimethylphenol, m.p. 148 °C (lit.,[12] 149 °C); δ($CDCl_3$) 2.39 (9 H, s) and

Table 1. Chemical shifts of the ring-carbon atoms (p.p.m. downfield from Me_4Si) in the ^{13}C n.m.r. spectra of some 6-bromo-substituted cyclohexa-2,5-dienones in $CDCl_3$ or (for 4-hydroxydienones only) in CD_3CN at 34 °C

		Substituents					Chemical shifts (p.p.m. downfield from Me_4Si)								
Compound	References	R-2	R-3	R-4	R-4′	R-5	C-1	C-2	C-3	C-4	C-5	C-6	C-2Me	C-3Me (5)	C-4Me
(1)	7	Me	H	Br	Br	H	176.0	129.8	144.1	45.4	147.6	122.3	15.4		
(2)	7	Me	Br	Br	Br	H	173.3	133.6	144.8	50.9	146.5	119.9	17.3		
(3)	7	Me	H	Br	Br	Br	174.5	127.7	143.4	50.6	147.3	128.8	15.2		
(4)	7	Me	Br	Br	Br	Br	172.1	132.3	144.0	57.0	146.1	127.6	17.7		
(5)	8	Me	H	Br	Me	H	178.0	131.8	146.0	55.0	150.1	123.4	16.3		30.4
(6)	This paper	Me	Br	Br	Me	Me	174.6	134.3	147.8	62.4	156.2	124.3	17.5	24.4	30.4
(7)	This paper	Me	Br	NO_2	Me	Me	174.6	138.4	138.6	94.2	149.8	127.1	17.1	20.8	24.3
(8)	This paper	Me	Br	OH	Me	Me	176.7	134.5	153.6	75.3	162.2	123.2	17.2	21.4	28.2
(9)	This paper	Me	Br	NO_2	Me	Br	173.2	138.5	137.6	95.2	139.9	132.3	17.3		26.6
(10)	This paper	Me	Br	OH	Me	Br	175.2	134.6	151.3	76.2	153.9	128.0	17.3		30.2
(11)	7	Br	Me	Br	Br	H	170.0	121.9	153.8	51.4	147.4	118.6		24.8	
(12)	7	Br	Me	Br	Br	Br	168.3	120.4	153.8	57.4	147.8	125.7		27.2	
(13)	This paper	Br	Me	Br	Br	Me	169.9	120.8	153.6	59.6	153.6	120.8		25.7	
(14)	This paper	Br	Me	Br	NO_2	Me	169.9	126.0	147.0	95.7	147.0	126.0		21.1	
(15)	7	Br	H	Br	Me	H	171.2	123.8	150.1	54.4	150.1	123.8			30.0
(16)	7	Br	Br	Br	Me	H	169.8	127.7	150.4	57.7	149.2	119.5			31.9
(17)	7	Br	Br	Br	Me	Br	168.2	127.1	149.1	61.4	149.1	127.1			34.3
(18)	6	Br	Me	Br	Me	H	171.0	123.1	156.4	58.4	150.0	120.0		22.6	29.0
(19)	This paper	Br	Me	Br	Me	Br	169.5	122.3	156.2	62.1	150.6	127.3		24.7	30.8
(20)	This paper	Br	Me	NO_2	Me	Br	169.2	125.3	150.5	95.4	141.7	130.6		21.0	24.7
(21)	This paper	Br	Me	OH	Me	Br	171.2	121.1	162.9	77.4	156.9	126.0		21.6	28.0
(22)	This paper	Br	Br	NO_2	Me	Br	168.1	130.6	140.7	96.2	140.7	130.6			27.0
(23)	This paper	Br	Br	OH	Me	Br	170.1	126.0	154.8	78.2	154.8	126.0			30.1
(24)	This paper	Br	Me	Br	Me	Me	170.8	122.8	156.2	63.0	156.2	122.8		23.4	27.7
(25)	This paper	Br	Me	NO_2	Me	Me	170.7	125.6	150.4	94.3	150.4	125.6		20.3	22.9
(26)	This paper	Br	Me	OH	Me	Me	172.4	121.4	163.5	76.6	163.5	121.4		20.6	26.6
(27)	This paper	Me	Br	Br	Me	Br	173.4	134.1	146.4	61.4	148.4	128.9	17.8		33.8

5.68 (1 H, s, OH). This on further bromination gave 3,4,6-*tribromo*-2,4,5-*trimethylcyclohexa*-2,5-*dienone* (**6**), m.p. 76.5 °C (Found: C, 29.7; H, 2.7; Br, 62.5. $C_9H_9Br_3O$ requires C, 29.1; H, 2.4; Br, 64.3%); δ($CDCl_3$) 2.05 (3 H, s), 2.13 (3 H, s), and 2.48 (3 H, s). Similarly, 3,4,5-trimethylphenol gave 2,6-dibromo-3,4,5-trimethylphenol, m.p. 146 °C (lit.,[13] 142.5—143 °C, 144 °C); δ($CDCl_3$) 2.22 (3 H, s), 2.38 (6 H, s), and 5.82 (1 H, s, OH). This on further bromination gave 2,4,6-*tribromo*-3,4,5-*trimethylcyclohexa*-2,5-*dienone* (**24**), yellow plates after recrystallization from MeOH, m.p. 109—110 °C (decomp.); δ($CDCl_3$) 1.95 (3 H, s) and 2.45 (6 H, s) (Found: C, 29.1; H, 2.6; Br, 63.5%).

The bromination of 3,5-dimethylphenol gave 2,4,6-tribromo-3,5-dimethylphenol, m.p. 161 °C (lit.,[14] 162.5 °C); δ($CDCl_3$) 2.60 (6 H, s) and 5.99 (1 H, br s, OH), and this on bromination gave 2,4,4,6-tetrabromo-3,5-dimethylcyclohexa-2,5-dienone (**13**), m.p. 114 °C (lit.,[15] 113 °C); δ($CDCl_3$) 2.68 (s).

The further bromination of 2,5,6-tribromo-3,4-dimethylphenol[6] gave 2,4,5,6-*tetrabromo*-3,4-*dimethylcyclohexa*-2,5-*dienone* (**19**), m.p. 104 °C (Found: C, 21.7; H, 1.5; Br, 73.4%).

The further bromination of 3,5,6-tribromo-2,4-dimethylphenol[8] gave 3,4,5,6-*tetrabromo*-2,4-*dimethylcyclohexa*-2,5-*dienone*, m.p. 101 °C (decomp.) (Found: C, 27.1; H, 1.3; Br, 72.1. $C_8H_6Br_4O$ requires C, 21.9; H, 1.4; Br, 73.0%).

Nitrodienones.—These were prepared readily in good yield by following procedures used by earlier workers. Thus 2,5,6-tribromo-3,4-dimethylphenol (5 g) was stirred with concentrated nitric acid (89.5 g) in a stoppered blackened flask overnight. The resulting suspension was poured onto crushed ice, and the product was filtered off and dried *in vacuo*. It was then heated under reflux with n-hexane for 5 min, and the remaining 2,5,6-tribromo-3,4-dimethyl-4-nitrocyclohexa-2,5-dienone (**20**) was filtered off and again dried *in vacuo*. It was spectroscopically pure; to obtain crystalline material, it was dissolved in the minimum quantity of warm chloroform, and precipitated by the gradual addition of n-hexane. The product had m.p. 94 °C (lit.,[16] 97—99 °C) (Found: C, 23.6; H, 1.5; N, 3.5; Br, 59.6. Calc. for $C_8H_6Br_3NO_3$: C, 23.8; H, 1.5; N, 3.5; Br, 59.4%), δ($CDCl_3$) 2.08 (3 H, s) and 2.21 (3 H, s).

The following compounds were prepared analogously. 3,5,6-Tribromo-2,4-dimethyl-4-nitrocyclohexa-2,5-dienone (**9**) had m.p. 95 °C (lit.,[16] 97 °C) (Found: C, 23.9; H, 1.6; N, 3.0; Br, 58.9%), δ($CDCl_3$) 2.17 (3 H, s) and 2.21 (3 H, s).

2,4,6-*Tribromo*-3,5-*dimethyl*-4-*nitrocyclohexa*-2,5-*dienone* (**14**) had m.p. 83 °C (the reaction mixture having been stirred only for 3 h, since decomposition occurred overnight). Analysis was unsatisfactory because of the instability of this compound, but its ^{13}C n.m.r. spectrum showed clearly the signals for five different carbon atoms, δ(CCl_4) 2.25 (s).

3,6-Dibromo-2,4,5-trimethyl-4-nitrocyclohexa-2,5-dienone (**7**) had m.p. 95.5 °C (lit.,[17] 102—103 °C) (Found: C, 31.7; H, 3.0; N, 3.7. Calc. for $C_9H_9Br_2NO$: C, 31.9; H, 2.7; N, 4.1%), δ($CDCl_3$) 2.03 (3 H, s), 2.13 (3 H, s), and 2.19 (3 H, s).

2,6-Dibromo-3,4,5-trimethyl-4-nitrocyclohexa-2,5-dienone (**25**) had m.p. 103 °C (lit.,[13] 108 °C) (Found: C, 31.8; H, 2.7; N, 3.6%), δ($CDCl_3$) 1.70 (3 H, s) and 2.07 (6 H, s).

2,3,5,6-Tetrabromo-4-methyl-4-nitrocyclohexa-2,5-dienone (**22**) had m.p. 96.5 °C (lit.,[18] 100 °C) (Found: C, 17.8, H, 0.6; N, 2.6; Br, 67.6. Calc. for $C_7H_3Br_4NO_3$: C, 17.9; H, 0.6; N, 3.0; Br, 68.2%), δ($CDCl_3$) 2.21 (s).

Hydroxydienones.—4-Alkyl-4-nitrocyclohexa-2,5-dienones are readily converted into 4-alkyl-4-hydroxycyclohexadienones by treatment with water, aqueous acetone, or aqueous acetic acid [*e.g.* (**2**)].[3] Since this reaction can be carried out when the 4-alkyl group is t-butyl, it has been regarded as having an ionic mechanism.[3] An elimination–addition sequence (loss of HNO_2 to give a methylene quinone, followed by addition of water) is

Table 2. Coupling constants involving ring-hydrogen atoms in the ^{13}C n.m.r. spectra of some substituted 6-bromocyclohexa-2,5-dienones

Compound	$^1J_{3\text{-H,C-3}}$	$^1J_{5\text{-H,C-5}}$	$^2J_{3\text{-H,C-2}}$	$^2J_{3\text{-H,C-4}}$	$^2J_{5\text{-H,C-6}}$	$^2J_{5\text{-H,C-4}}$	$^3J_{3\text{-H,C-5}}$	$^3J_{3\text{-H,C-1}}$	$^3J_{5\text{-H,C-3}}$	$^3J_{5\text{-H,C-1}}$	$^3J_{3\text{-H,C-2-Me}}$	$^3J_{3\text{-H,C-4-Me}}$	$^3J_{5\text{-H,C-4-Me}}$
(1)	172.8	180.7	N.r.	Small	4.9	Small	5.9	N.r.	*ca.* 6.1	N.r.	5.0		—
(2)	—	182.6	—	—	4.4	Small	—	N.r.	*ca.* 7.6	N.r.	—	—	—
(3)	175.3	—	Small	Small	—	—	9.8	—	—	—	5.0	Small	—
(5)	*ca.* 166	*ca.* 176	N.r.	N.r.	5.6	N.r.	6.4	N.r.	N.r.	N.r.	5.3	N.r.	N.r.
(11)	—	181.6	—	—	3.9	Small	—	—	*ca.* 4[a]	7.8	—	—	—
(15)	173.8	173.8	3.9	Small	3.9	Small	5.9	7.8	5.9	7.8	—	Small	Small
(16)	—	175.8	—	—	4.9	N.r.	—	—	N.r.	8.8	—	—	2.4
(18)	—	173.8	—	—	3.9	N.r.	—	—	N.r.	9.8	—	—	*ca.* 2

—, Not present in the molecule. N.r., Not resolved through complexity of signal, or not apparent in the single-resonance spectrum. Small, Coupling constant approximately zero; no splitting of signal when other couplings removed.

[a] May have been reduced by decoupling.

Table 3. Coupling constants involving the 2-methyl hydrogen atoms in the ^{13}C n.m.r. spectra of some substituted 6-bromo-2-methylcyclohexa-2,5-dienones.

Compound	$^1J_{H_3,C\text{-Me}}$	$^2J_{H_3,C\text{-2}}$	$^3J_{H_3,C\text{-1}}$	$^3J_{H_3,C\text{-3}}$
(1)	129.6	6.8	N.r.	*ca.* 6.1
(2)	131.0	6.5	N.r.	*ca.* 7.6
(3)	129.9	6.5	4.0	6.4
(4)	131.0	6.5	3.6	6.5
(5)	128.9	*ca.* 6	N.r.	N.r.
(6)	130.2	6.4	3.6	N.r.
(7)	130.5	6.8	3.2	N.r.
(8)	129.9	6.5	*ca.* 3	N.r.
(9)	130.9	6.8	3.6	N.r.
(10)	129.9	6.5	3.6	N.r.
(27)	130.5	6.5	3.6	N.r.

See notes to Table 2.

Table 4. Coupling constants involving the 3- and/or 5-methyl hydrogen atoms in the ^{13}C n.m.r. spectra of some substituted 6-bromo-3- and/or 5-methylcyclohexa-2,5-dienones

Compound	$^1J_{H_3,C\text{-Me-3}}$	$^1J_{H_3,C\text{-Me-5}}$	$^2J_{H_3,C\text{-3}}$	$^2J_{H_3,C\text{-5}}$	$^3J_{H_3,C\text{-2}}$	$^3J_{H_3,C\text{-4}}$	$^3J_{H_3,C\text{-6}}$
(6)	—	130.2	—	N.r.	—	3.9	5.9
(7)	—	130.4	—	N.r.	—	*ca.* 3.8	6.5
(8)	—	129.9	—	N.r.	—	N.r.	6.5
(11)	130.9	—	*ca.* 7	—	5.9	5.2	—
(12)	131.5	—	6.7	—	6.1	4.7	—
(13)	131.2	131.2	6.5	6.5	6.2	4.9	6.2
(14)	131.5	131.5	6.8	6.8	6.5	4.4	6.5
(18)	130.2	—	5.9	—	6.2	3.9	—
(19)	130.5	—	N.r.	—	6.2	4.2	—
(20)	130.9	—	N.r.	—	5.9	*ca.* 4.6	—
(21)	130.2	—	N.r.	—	6.5	*ca.* 3.4	—
(24)	130.2	130.2	5.9	5.9	6.2	N.r.	6.2
(25)	130.5	130.5	N.r.	*ca.* 3	6.5	N.r.	6.5
(26)	129.7	129.7	—	N.r.	6.3	N.r.	6.3

See notes to Table 2.

also possible for cases in which the 4-alkyl group is primary or secondary.

We used this method to prepare 2,6-dibromo-4-hydroxy-3,4,5-trimethylcyclohexa-2,5-dienone (**26**), m.p. 218 °C (lit.,[13] 213 °C).

Somewhat to our surprise, we found that the reaction could be effected in quite good yield under conditions in which only traces of water appeared to be available. Thus 2,5,6-tribromo-3,4-dimethyl-4-nitrocyclohexa-2,5-dienone (5 g) was heated under reflux in distilled CCl_4 (25 ml) for 10 min. The resulting solution was cooled (ice); 2,5,6-tribromo-4-hydroxy-3,4-dimethylcyclohexa-2,5-dienone (**21**) was filtered off (yield, 70%) and recrystallized from diethyl ether, giving a product, m.p. 184 °C (lit.,[16] 178—180 °C) (Found: C, 25.5; H, 1.8; Br, 63.6. Calc. for $C_8H_7Br_3O_2$: C, 25.6; H, 1.9; Br, 64.0%); δ($CDCl_3$) 1.65 (3 H, s), 2.38 (3 H, s), and 2.1 (1 H, br s, OH).

Other hydroxy-dienones were prepared by heating the corresponding nitro-dienones under reflux in wet carbon tetrachloride for varying times up to 120 min. The following compounds were obtained.

3,5,6-Tribromo-4-hydroxy-2,4-dimethylcyclohexa-2,5-dienone (**10**), had m.p. 173.5 °C (lit.,[18] 179 °C) (Found: C, 25.4; H, 1.9; Br, 64.0%), δ($CDCl_3$) 1.77 (3 H, s), 2.13 (3 H, s), and 2.87 (s, OH).

3,6-Dibromo-4-hydroxy-2,4,5-trimethylcyclohexa-2,5-dienone (**8**) had m.p. 161 °C (lit.,[19] 158—159 °C) (Found: C, 35.0; H, 3.4; Br, 52.4. Calc. for $C_9H_{10}Br_2O_2$: C, 35.0; H, 3.2; Br, 51.8%), δ(CCl_4) 1.57 (3 H, s), 2.07 (3 H, s), 2.25 (3 H, s), and 2.73 (br s, OH).

2,3,5,6-Tetrabromo-4-hydroxy-4-methylcyclohexa-2,5-dienone (**23**) had m.p. 203 °C (lit.,[18] 205 °C) (Found: C, 19.3; H, 0.9; Br, 72.5. Calc. for $C_7H_4Br_4O_2$: C, 19.1; H, 0.9; Br, 72.7%), δ(CCl_4) 1.78 (s) and 3.0 (br s, OH).

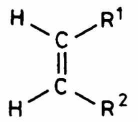
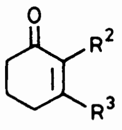
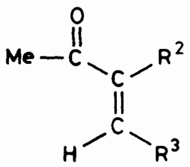
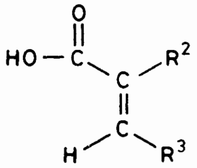
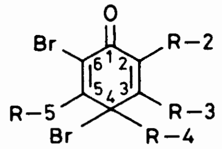
Quinones.—2,6-Dibromo-3,5-dimethyl-1,4-benzoquinone (**29**) was obtained in 64% yield by heating 2,4,6-tribromo-3,5-dimethyl-4-nitrocyclohexa-2,5-dienone (**14**) under reflux in wet CCl_4 until the evolution of nitrous fumes had ceased. It had

Table 5. Coupling constants involving the 4-methyl hydrogen atoms in the ${}^{13}C$ n.m.r. spectra of some substituted 6-bromo-4-methylcyclohexa-2,5-dienones

Compound	${}^1J_{H_3,C\text{-}Me}$	${}^2J_{H_3,C\text{-}4}$	${}^3J_{H_3,C\text{-}3}$	${}^3J_{H_3,C\text{-}5}$
(5)	131.8	N.r.	N.r.	3.9
(6)	132.4	3.91	N.r.	N.r.
(7)	133.5	3.8	N.r.	N.r.
(8)	130.9	N.r.	N.r.	N.r.
(9)	134.4	3.9	N.r.	4.2
(10)	131.8	N.r.	N.r.	4.4
(15)	132.8	3.9	4.9	4.9
(16)	133.5	N.r.	4.7	4.2
(17)	133.8	4.2	4.9	4.9
(18)	132.2	3.9	N.r.	4.6
(19)	133.1	4.2	N.r.	4.9
(20)	134.1	4.6	N.r.	4.6
(21)	131.2	*ca.* 3.4	N.r.	4.6
(22)	134.8	3.9	4.2	4.2
(23)	131.5	N.r.	4.2	4.2
(24)	132.2	N.r.	N.r.	N.r.
(25)	133.5	N.r.	N.r.	N.r.
(26)	130.2	N.r.	N.r.	N.r.
(27)	133.5	4.2	N.r.	4.6

See notes to Table 2.

Table 6. Chemical shifts ($\delta_{R.R'}$ p.p.m. downfield) of signals for unsaturated carbon atoms resulting from replacement of R′ at *ipso-* or adjacent (*vic-*) unsaturated positions

System											
Position affected	C-1 or C-2	C-2	C-3	C-2	C-3	C-2	C-3	C-2	C-6	C-3	C-5
$\delta_{Me.H}(ipso)$	+10	+7	+12	+8	+14	+8	+12	—	—	+5	+5
$\delta_{Br.H}(ipso)$	−7	—	—	—	−3	−6	−4	—	—	+1	+5
$\delta_{Me.Br}(ipso)$	+17	—	—	—	+17	+14	+16	+7	—	+4	+5
$\delta_{Me.H}(vic)$	−7	−3	−5	−5	−5	−6	−5	−1	+3	—	—
$\delta_{Br.H}(vic)$	−1	—	—	0	—	+3	+1	+4	+7	—	—
$\delta_{Me.Br}(vic)$	−6	—	—	−6	—	−9	−6	−5	−4	−3	—
Ref.	23	23, 25		23, 26		23, 26		This work; R-2 = Me or Br; R-3, R-5 = H, Me, or Br, R-4 = Me or Br; compounds **(1)**, **(2)**, **(3)**, **(15)**, **(17)**, **(18)**, **(24)**, **(27)**			

—, Comparison not available.

m.p. 167 °C (lit.,[20] 176 °C) (Found: C, 33.0; H, 2.2; Br, 54.3. Calc. for $C_8H_6Br_2O_2$: C, 32.7; H, 2.0; Br, 54.4%), $\delta(CDCl_3)$ 2.3 (s).

${}^{13}C$ *N.m.r. Spectra.*—Chemical shifts (p.p.m. downfield from Me_4Si) in the ${}^{13}C$ n.m.r. spectra are included in Table 1; they are quoted only to ±0.05 p.p.m., since effects of concentration on the positions of the signals render greater precision meaningless.

Assignments of the signals could usually be made without difficulty. Chemical shifts of the signals for C-1 (*ca.* 170 p.p.m.), and of C-4 (below 100 p.p.m.) were well separated from those of C-2 and C-6 (118—135 p.p.m.) which themselves were separated from those for C-3 and C-5 (138—163 p.p.m.). Distinction between the last two pairs was usually made on the basis of the corresponding single-resonance (undecoupled) spectra, amplified where necessary by the use of appropriate partially decoupled spectra. Single-frequency off-resonance decoupling and low-power single-frequency decoupling were used where appropriate and necessary.

From these spectra, a number of coupling constants have been measured. They are catalogued in Tables 2—5. The fully coupled spectrum of 2,6-dibromo-3,5-dimethyl-1,4-benzoquinone had signals centred at 181.3 (C-4, septet, *J* 3.7 Hz), 171.9 (C-1), 146.0 (C-3, C-5, q, *J* 7.1 Hz), and 134.1 (C-2, C-6, q, *J* 6.8 Hz). Differentiation between the 2(6) and 3(5) positions has been made on the basis of the chemical shifts, with Berger and Rieker's[21] finding that the signal for the 2-position in 2-methylbenzoquinone is downfield of the signal for the 2-position in 2-chlorobenzoquinone being used for guidance.

Discussion

Chemical Shifts.—We have not examined in detail the effect of dilution or of solvent on the positions of the signals, which consequently are quoted only to the first decimal place in p.p.m. downfield from Me_4Si, though they were determined with much greater apparent precision. In the few cases for which the spectra of the hydroxy compounds were examined in more than one solvent, the signals were not significantly changed in position.

(a) *Signals for the carbonyl carbon atom.* The chemical shift for the carbonyl carbon atom in cyclohexanone lies at 209 p.p.m.,[22,23] and is moved upfield by α-halogen[24] and by αβ-unsaturation.[10] In 2,5-dienones, the signal is moved further upfield, as in a number of 4,4′-substituted compounds.[10] Alkyl substituents in the 2- and 6-positions have little influence on the position of absorption;[9,11] the same is true in substituted quinones.[21]

Our compounds fall broadly into two groups: those having the 2-methyl-6-bromo structure, with absorption in the range 173—178 p.p.m.; and those having the 2,6-dibromo structure, with absorption in the range 168—171 p.p.m. Clearly each additional 2- or 6-bromo-substituent has moved the signal upfield, and this effect of α-bromine is approximately additive. Additivity is shown to a good approximation also in the effect of αβ-unsaturation; the comment (ref. 23, p. 294) that cross-conjugated carbonyl groups may be abnormally shielded relative to those in conjugated systems does not seem to be justified by the results[9,10] in these cyclic systems.

Further small upfield shifts appear to follow the replacement of hydrogen or methyl by bromine in the 3-, 4-, or 5-positions

(Table 1). Replacement of bromo by nitro in the 4-position has little effect; replacement by OH apparently moved the signal a little downfield, but this may be the result of the use of CD_3CN as the solvent for the hydroxy-compounds.

(b) *Signals for the unsaturated carbon atoms.* (i) Additivity parameters. It is known from studies of substituted benzenes and mono-substituted alkenes that a bromo-substituent moves the signal of the carbon atom to which it is attached upfield by 5 or more p.p.m., but has little effect on the signal for an adjacent olefinic carbon atom. The effects of a methyl substituent, on the other hand, involve a downfield shift for the signal of an attached carbon atom and an upfield shift for that of an adjacent carbon atom (Table 6).

Marr and Stothers[25] have examined a number of methyl-substituted cyclohexenones. The effects of the introduction of a methyl substituent are qualitatively as expected from the simpler vinyl system. Whereas the influence of the carbonyl group on an adjacent carbon atom is that of only a small downfield shift, the effect on the more distant C-3 atom, at the terminus of the conjugated system, is that of a large downfield shift of more than 20 p.p.m. This influence is reflected in results for the cyclohexadienones studied in the present work (Tables 1 and 6); in general, signals for C-2 and C-6 were upfield from those for C-3 and C-5, as in the compounds studied by Gramlich.[10] It should be noted, however, that with the 2-methyl-3-bromo pattern of substitution, the signals for these two types of position are moved closer together, as the result of the downfield effect of an attached methyl group at the 2-position combined with the upfield effect of a vicinal methyl group and of an attached bromo-substituent at the 3-position. The effect of an attached alkyl group is augmented in the 2,6-di-t-butyl-substituted compounds examined by Rieker and Berger;[9] here the signals for the C-2 atom lie downfield from those for the C-3 atom.

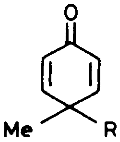
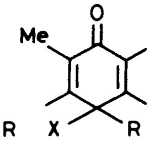
Attempts have been made to develop additivity factors which would allow prediction of the effects of substituents on chemical shifts in olefinic compounds, including those involving αβ-unsaturated carbonyl groups[26] (for a review, see ref. 23, pp. 183*ff*) and it is of interest to explore the extent to which such factors are applicable to the cross-conjugated dienones studied in this work. The results are summarised in Table 6, in which illustrative individual comparisons rather than average values have been used. Of the various parameters measured, the downfield shift caused by an *ipso*-methyl group is the most uniform, though its magnitude varies from system to system. The upfield shift attributable to an *ipso*-bromo-substituent is not observed in the cyclohexadienones, and as a consequence the difference caused by replacing bromine by methyl is much reduced in this series.

The influence of vicinal methyl, which in ethane and most of the examples from αβ-unsaturated carbonyl systems is that of an upfield shift, is small or absent in the cyclohexadienones; the influence of vicinal bromine, which in the other systems is generally small, has become a significant downfield shift. Both of these changes are in the direction expected if conjugative or hyperconjugative effects of Br or Me respectively, normally contributing to the shielding of the 2- and 6-positions, were substantially reduced by the presence of the conjugated carbonyl group. Only a small change in this direction is, however, seen in the corresponding example from the cyclohexenones.

It is evident that the parameters useful for description of other systems could not be used without modification to estimate effects of substituents on the chemical shifts of the carbon atoms in the 6-bromocyclohexa-2,5-dienones.

(ii) Substituents at the 4-position. Changes at the C-4 atom have a significant influence on the positions of the signals for C-3 and C-5. Replacing the bromo-substituent by a methyl group at the 4-position results in a small downfield shift [compounds (**1**) and (**5**); (**4**) and (**27**); (**12**) and (**19**); (**13**) and (**24**)]. Corresponding replacement of bromo by nitro results in a considerable upfield shift [compounds (**6**) and (**7**); (**27**) and (**9**); (**19**) and (**20**); (**17**) and (**22**)]. Replacement of bromo by hydroxy results in a downfield shift [compounds (**6**) and (**8**); (**27**) and (**10**); (**19**) and (**21**); (**17**) and (**23**); (**24**) and (**26**)]. Other related work shows that replacement of a 4-methyl group by a 4-ethoxycarbonyl group moves the signal for C-3 and -5 upfield,[10] and is in agreement with the present work in showing also that replacement of a 4-bromo by a 4-nitro group moves the signals for C-3 and -5 upfield.[9] We can, therefore, write the sequence HO < Me < Br < CO_2Et < NO_2 for the 'upfield' influence of the 4-substituent on the position of the signal for C-3 or -5. In general terms, these results can be interpreted on the basis that a dipolar 4-substituent polarizes the adjacent 2,3- and 5,6-double bonds in such a way as to increase the shielding of C-3 and -5 (structure (**30**), as is required by the concept of π-polarization (for a review, see ref. 27). The influence of the hydroxy-group is, however, abnormally small, perhaps because its effective partial positive charge is not borne exclusively on the atom attached to the ring.

Table 7. Chemical shifts ($\delta_{R,Me}$) of the signals for attached (*ipso*) saturated carbon atoms resulting from changing Me to R

			System[c]	
R	σ_I[a]	CH_3-R[b]		
Br	+0.47	+4.3		−4.4[d]
Me	−0.04	0	0	0
Bu^t	−0.07	+22.0		+6.5[g]
Ph	+0.09	+15.4	+7.7	+7.0[h]
CO_2Et	+0.34	+14.4	+11.0	+10.3[h]
$CHCl_2$	+0.31	+26.6		+10.3[h]
OH	+0.25	+43.4		+10.4[e]
CCl_3	+0.41	+40.4		+18.0[h]
NO_2	+0.72	+51.4		+29.4[f]

[a] Selected values; ref. 27. [b] Ref. 23. [c] Ref. 10. [d] X = Br; compounds (**27**) and (**4**). [e] X = Me; compounds (**27**) and (**10**). [f] X = Me; compounds (**27**) and (**9**). [g] Ref. 9; X = OH. [h] Ref. 10; X = Me.

(c) *The signals for* C-4. Changes in the *ipso*-substituents at C-4 cover the range Br,Br; Br,Me; NO_2,Me; and OH,Me. Changing a bromo to a methyl substituent [compounds (**5**) and (**1**); (**27**) and (**4**); (**19**) and (**12**); (**24**) and (**13**)] results in a downfield shift by a varying amount, usually *ca.* 5 p.p.m. Changing bromo to hydroxy produces a large downfield shift (*ca.* 15 p.p.m.), and changing bromo to nitro results in an even larger change (30—35 p.p.m.). These comparisons can be put together with those of other workers[9,10] to show the influence of changes at the 4-position on the position of the signal for C-4. They are compared with the results of similar replacements in methane[22,23] and in a limited number of cyclohexenones[10] in Table 7. Values[28] of the substituent parameter σ_I, which gives a measure of the inductive effect of the substituent, are included for comparison.

The results obtained for the cyclohexadienones correlate only moderately well with those found for substituted methanes. Downfield shifts resulting from deshielding appear to be associated with electron-withdrawing influences, but there are superimposed factors. The t-butyl group moves the signal downfield, rather than upfield as would be expected from its inductive effect, presumably for steric reasons. In the monosubstituted methanes, a bromine substituent moves the signal downfield, but to a much lesser extent than would be expected from its inductive effect; in the dienones, where the comparisons are of $>\mathrm{C}<^{\mathrm{Br}}_{\mathrm{Me}}$ with $>\mathrm{C}<^{\mathrm{Br}}_{\mathrm{Br}}$, the signals are now moved upfield when methyl is changed to bromine, thus providing further illustrations of the effect of diamagnetic shielding by the electrons of heavy atoms.[29]

Our comparisons show also that adjacent vinylic methyl moves the signal for C-4 downfield [compounds **(15)**, **(18)**, and **(24)**] by 4—5 p.p.m. per methyl group; and that adjacent vinylic bromine has a similar effect [compounds **(1)**, **(2)**, and **(4)**; **(1)**, **(3)**, and **(4)**; **(15)**—**(17)**].

(d) *Signals for the carbon atoms of the methyl groups.* The signals for the 2-methyl group all lie upfield of those for the 3-, 5-, or 4-methyl group; the mean value for the compounds having a 3-hydrogen atom is 15.6, and for those with a 3-bromine substituent is 17.4.

The signals for the 3- and 5-methyl substituent fall into three groups: those compounds with NO_2 or OH at the 4-position, where the signal lies at 21.0 ± 0.6 p.p.m.; those with Me and Br at the 4-position, which lie over the range 22.6—24.7 p.p.m.; and those with Br and Br at the 4-position, lying over the range 24.8—27.2 p.p.m.

The signals for the 4-methyl group cover a wider range, from 22.9 to 34.3 p.p.m., and are generally downfield of those for a 3- or 5-methyl group on the same molecule. It is noteworthy that the compounds **(17)** and **(27)**, having three bromines adjacent (3, 5, 4′) to the 4-methyl group, have the signal lying farthest downfield (34.3 and 33.8 p.p.m.), whereas compound **(25)**, having no bromo-substituents in these positions, has the signal lying farthest upfield (22.9 p.p.m.). Direct comparison of the effect of changing the *gem*-substituent from bromo [compound **(17)**; 34.3 p.p.m.] to hydroxy [compound **(23)**; 30.1 p.p.m.] and nitro [compound **(22)**; 27.0 p.p.m.] shows that the last two groups both move the signal of the 4-methyl group upfield. This change differs from that produced at the unsaturated 3-carbon atom by the same change in the 4-substituent, where the hydroxy-group moves the signal downfield, whereas the nitro-group moves it upfield.

Coupling Constants.—Many of the coupling constants recorded in the Tables have been derived from clearly spaced doublets, quartets, or septets. Most of the compounds were evidently stable under the conditions used for accumulation of the spectra; an exception was the 4,4′-dibromide **(13)**, which underwent some decomposition, but this did not interfere with identification of the signals.

The centre points of the ^1J couplings to the methyl carbon atoms could always be located satisfactorily, so we regard the derived coupling constants as being established quite reliably. The same is true of the ^1J couplings to the ring carbon atoms, except for compound **(5)**, for which the two signals were each split by two methyl groups and gave slightly asymmetrical signals. There is no doubt, however, that the entered value of ^1J is the lowest encountered for this type of signal.

Low-power single-frequency decoupling, carried out in a few instances to confirm assignment of the signals [*e.g.* for compounds **(11)**, **(15)**, **(18)**, **(21)**, **(25)**, **(26)**], was not very useful for eliminating couplings involving pairs of methyl groups because their individual decoupling frequencies were too close together.

Some signals [*e.g.* of C-4 in compound **(21)**; C-3 in compounds **(1)** and **(2)**; C-4 in compounds **(6)**—**(8)**] where two couplings were expected (from H and from CH_3, or from CH_3 and from CH_3) appeared as well resolved and nearly equally spaced quintets or septets. In these cases we assumed that two couplings of similar magnitude were present, and values were assigned from the mean spacing of the signals. In a number of other cases, the observed multiplets could not be dissected to yield two couplings constants reliably, and the results have been entered as 'non-resolved.'

(i) *Values of* ^{1}J *involving the vinylic hydrogen atoms* (*Table* 2). These values are generally larger than those for aromatic carbon atoms in benzene or the naphthalene tetrachlorides (*ca.* 163—165 Hz).[30] They cover the range 166—183 Hz, and are increased by an adjacent bromo as compared with a methyl substituent, whether on a saturated or an unsaturated position. Thus the lowest couplings are observed for the 3-H in the 2-methyl-substituted compounds **(1)** and **(5)**; and the highest for the 5-H in compounds **(1)**, **(2)**, and **(11)**, all with three adjacent bromine atoms.

(ii) *Values of* ^{1}J *involving the methyl groups* (*Tables* 3—5). The values for the couplings within the 2-methyl group (Table 3) cover the range 128.9—131.0 Hz, and are slightly lower for those compounds **(1)**, **(3)**, and **(5)** having adjacent hydrogen than for the remainder with adjacent bromine.

The values for the couplings within the 3- and 5-methyl groups (Table 4) cover a similar range (129.7—131.5 Hz), and are slightly affected by the nature of the adjacent substituents at the 4-position, the sequence of increasing coupling with changing 4-substituent being OH ~ Me < Br < NO_2.

The values for the couplings within the 4-methyl groups (Table 5) tend to lie at rather higher values, and cover a slightly greater range (130.2—134.8 Hz).

The values are more affected by change at the 4-position than at the 3- and 5-position, and the changes are consistent with those found within the 2- and 3-methyl groups, the sequence of 4-substituents giving higher couplings being OH ~ Me < Br < NO_2 [compare compounds **(8)**, **(6)**, and **(7)**, which are otherwise similarly substituted].

All the values are somewhat higher than in substituted toluenes.[22,23] Presumably this reflects the greater electronegativity of the cyclohexadienone than of the benzenoid system, since this is thought to be an important factor in determining the magnitude of these couplings.[31] Generally speaking, the effects of substituents on ^1J coupling constants in our cyclohexadienones support this view, though the hydroxy-group appears again to be anomalous. It may be noted that in the substituted methanes, CH_3X, the order of increasing coupling is CH_3 < OH < NO_2 < Br, with the hydroxy-group falling approximately as expected in view of its electronegativity, but the nitro-group falling out of sequence.[32] The latter finding is not repeated in the comparisons made in the present work.

(iii) *Values of* ^{2}J *involving the vinylic hydrogen atoms* (*Table* 2). All of the values of the coupling constant between a 3- or 5-hydrogen atom and an unsaturated carbon atom carrying a bromine substituent were in the range 3.9—5.6 Hz, whereas those to an unsaturated carbon atom carrying a methyl group or to a saturated carbon atom, where they could be determined, were small (probably $\ngtr$ 1 Hz). Such coupling constants (*e.g.* in vinyl and in aromatic systems) are well known to be quite variable, so differences involving differently substituted positions are in no way abnormal.

(iv) *Values of* ^{2}J *involving the hydrogen atoms of methyl groups.* These values, where they involve coupling to an unsaturated carbon atom, were usually in the range 6—7 Hz, irrespective of whether the 2-, 3-, or 5-carbon atom was concerned (Tables 3 and 4). Where the methyl group was attached to C-4 (Table 5), lower values in the neighbourhood of 4 Hz were recorded, and within experimental error these were insensitive to change in the substitution pattern at the saturated centre, over the range (Br, Me), (NO_2, Me), (OH, Me).

(v) *Values of* ^{3}J *involving the protons of a methyl group.* Average couplings (^3J) from the hydrogen atoms of a methyl group through a saturated or unsaturated carbon atom to an unsaturated carbon atom are generally in the range 3—5.5 Hz, as in 2,5-dimethyl-1,4-benzoquinone,[33] methyl ethyl ketone,[34] and the 2-methylnaphthalene tetrachlorides.[30] In the present work, a number of further examples have been recorded. Thus for a number of the 6-bromocyclohexa-2,5-dienones the couplings from 4-methyl hydrogen atoms to C-3 or -5 are in the range 3.9—4.9 Hz; those from 2-methyl hydrogen atoms to C-1 are in the range 3—4 Hz (Table 3), and those from 3-methyl hydrogen atoms to C-4 are in the range 3.4—5.2 Hz (Table 4). Likewise the coupling from the 3- and 5-methyl groups to C-4 in 3,5-dimethyl-1,4-benzoquinone is 3.7 Hz. When these values are corrected to that expected for a single hydrogen atom in its best orientation (vicinal dihedral angle 180°), the resulting couplings (*ca.* 10 Hz) are larger than those from the hydrogen atoms of CHCl groups in naphthalene tetrachlorides (*ca.* 6.7 Hz),[30] no doubt because the latter values are reduced as the result of the electronegativity of the attached chlorine substituents.[35]

Average vicinal couplings from the hydrogen atom of a methyl group through a double bond are significantly larger than those through a single bond, and are fairly consistent within the examples we have studied. Thus the values of the coupling constants from the 2-methyl hydrogen atoms to C-3 are in the range 6.1—7.6 Hz (Table 3); those from the 3-methyl hydrogen atoms to C-2 are in the range 5.9—6.5 Hz (Table 4); and that from the methyl groups to C-2 and C-6 in 3,5-dimethyl-1,4-benzoquinone is 7.1 Hz (this work; *cf.* 6 Hz for the corresponding coupling in 2-chloro-5-methyl-1,4-benzoquinone[33]).

(vi) *Values of* ^3J *involving couplings from a vinylic hydrogen atom.* Our results provide examples of several different types of coupling pathway involving a vinylic proton. The first type to be considered involves a cisoid planar pathway to a saturated carbon atom. Those from the 3-hydrogen atom to the carbon atom of the 2-methyl group in the 6-bromocyclohexa-2,5-dienones (Table 2) are in the range 5.0—5.3 Hz. Other similar couplings[30,33,36,37] lie in the range 4.3—5.4 Hz.

The related planar couplings to a carbonyl carbon atom studied in this work were all transoid, and were high (${}^3J_{3\text{-H,C-1}}$ and ${}^3J_{5\text{-H,C-1}}$ 7.8—9.8 Hz; Table 2). Analogous systems having a geometrically similar coupling pathway also have relatively high values of this coupling.[33,36,37]

The remaining vicinal couplings of a vinylic hydrogen atom involved single bonds in the coupling pathway. It was not surprising that the couplings from 3- and 5-H to C-4 in the 6-bromocyclohexa-2,5-dienones were small <2.4 Hz; Table 2), since the dihedral angles between the relevant bonds were *ca.* 60°. These values are consistent with the relatively small value[38] for the ^{1}H–C–C–^{1}H coupling in 4-bromo-2,6-di-t-butylcyclohexa-2,5-dienone, since it is expected that long-range H ··· H couplings should be larger than the corresponding H ··· C couplings.[39] The results for the vicinal couplings between 3-H and C-5 or 5-H and C-3 (Table 2) are, however, somewhat more unusual. They vary over the range *ca.* 4—9.8 Hz, despite the fact that in all the compounds studied the unsaturated system within the ring should ensure that the dihedral angle between the relevant bonds is near 180°. The variation is in the direction that the introduction of an electronegative substituent at the coupled carbon atom in compounds (**2**) and (**3**) appears to be associated with an increased coupling constant.

The corresponding couplings in the quinones studied by Höfle[33] are reported to be in the range 4.5—7 Hz.

(vii) *Couplings through oxygen.* Couplings through oxygen were not in general apparent in the spectra of the hydroxydienones; but in compound (**10**), the ^{1}H–O–C–^{13}CH$_3$ coupling was observed as a splitting of the signals for the methyl group, ^3J 5.9 Hz. In this compound also, the expected quartet for C-1 appeared to be split further, perhaps indicating the presence of a ^5J coupling to the OH group. The coupling ^{1}H–O–C(4) appeared as a broadening of the signal for C-4 in compounds (**8**) and (**10**), and as an extra splitting in compound (**23**).

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