### The Chlorination of 4-Chloro-2,3,6trimethylphenol. Some Addition Reactions of 4,6-Dichlorocyclohexa-2,4-dienones

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#### Abstract

Reaction of a mixture of 6-chlorocyclohexa-2,4-dienones (4) and (5) with chlorine in acetic acid gives the tetrachloro ketones (2) and (3), the major products of chlorination of 2,3,6-trimethylphenol (1a) or 4-chloro-2,3,6-trimethylphenol (1b). Reactions of this mixture of 6-chlorocyclohexa-2,4-dienones (4) and (5) in acetic acid with chlorine acetate, chlorine, chlorine in the presence of sodium acetate, and in benzene with nitrogen dioxide are described. X-Ray crystal structure determinations are reported for compounds (3), (6)–(8) and (11)–(13).

#### Introduction

Reaction of 2,3,6-trimethylphenol (1a) with excess chlorine in acetic acid containing concentrated hydrochloric acid has been shown to give a mixture containing c. 50% (total) of the C2-epimeric tetrachloro ketones (2) and (3) in a ratio c.  $1:1.^{1,2}$  A mixture (c. 1:3) of the tetrachloro ketones (2) and (3) was isolated by crystallization; the components of this mixture were separated by chromatography, and identified by their spectroscopic data and an X-ray crystal analysis of isomer (2).<sup>2</sup> As part of our continuing study of *ipso* substitution reactions we became interested in the mode of formation of polychlorocyclohex-3-enones such as compounds (2) and (3), it appeared at the outset that these compounds might be formed by 2,3-addition of chlorine to the 4,6-dichlorocyclohexa-2,4-dienone (5). We therefore prepared what transpired



<sup>1</sup> Martyn, R. J., unpublished data.

<sup>2</sup> Hartshorn, M. P., Martyn, R. J., and Vaughan, J., Aust. J. Chem., 1984, **37**, 795.

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to be an inseparable mixture of the two dichlorocyclohexa-2,4-dienones (4) and (5), and studied the addition reactions of this mixture with chlorine under a variety of reaction conditions, with chlorine acetate, and with nitrogen dioxide in benzene. We now report the results of these studies.

#### Discussion

(a) Preparation of a Mixture (c. 6:1) of 4,6-Dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4) and 4,6-Dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5)

Reaction of 4-chloro-2,3,6-trimethylphenol (1b) with chlorine  $(1 \cdot 2 \text{ mole})^*$  in carbon tetrachloride containing pyridine gave an oil which was shown (<sup>1</sup>H n.m.r.) to be a mixture (*c*. 6:1) of the isomeric 6-chlorocyclohexa-2,4-dienones (4) and (5). The mixture was not separable on a Chromatotron silica gel plate, and the components of the mixture were identified by their <sup>1</sup>H n.m.r. spectra and results of nuclear Overhauser effect (n.O.e.) experiments (Experimental section). The composition of the mixture of the 6-chlorocyclohexa-2,4-dienones (4) and (5) in a variety of solvents (CDCl<sub>3</sub>, CCl<sub>4</sub>, CD<sub>3</sub>CN, C<sub>6</sub>D<sub>6</sub>, CD<sub>3</sub>OD, and CD<sub>3</sub>CO<sub>2</sub>D) was shown by <sup>1</sup>H n.m.r. spectra to be *c*. 6:1, but in (D<sub>6</sub>)dimethyl sulfoxide the composition of the mixture was *c*. 9:1.



**Fig. 1.** Perspective drawing of compound (3). Double bonds are shown in black in Figs 1–7.

Table	1.	Fractional	coordinates	for	atoms	in	r-2,4,c-5,t-6-tetrachloro-2,3,6-tri-
			methy	lcyclo	ohex-3-e	none	2 (3)

The equivalent isotropic temperature factor in Tables 1–7 is defined as one-third of orthogonalized U tensor  $(\dot{A}^2)$ 

Atom	104 <i>X/a</i>	10 <sup>4</sup> Y/b	10 <sup>4</sup> Z/c	10 <sup>3</sup> U	Atom	10 <sup>4</sup> X/a	10 <sup>4</sup> Y/b	10 <sup>4</sup> Z/c	10 <sup>3</sup> U
Cl(2)	8547(1)	5224(1)	6029(1)	26(1)	C(3)	8609(2)	2533(2)	6204(2)	15(1)
Cl(4)	7237(1)	357(1)	5257(1)	21(1)	C(4)	7313(3)	1765(2)	6036(2)	15(1)
Cl(5)	4522(1)	3058(1)	5563(1)	22(1)	C(5)	5798(3)	2012(2)	6449(2)	16(1)
Cl(6)	7210(1)	1577(1)	8346(1)	19(1)	C(6)	6063(3)	2730(2)	7471(2)	15(1)
O(1)	6922(2)	4989(2)	7827(1)	19(1)	C(7)	10107(3)	3884(2)	7651(2)	20(1)
C(1)	7151(2)	3940(2)	7418(2)	14(1)	C(8)	10104(3)	2272(2)	5757(2)	23(1)
C(2)	8603(3)	3770(2)	6865(2)	16(1)	C(9)	4546(3)	3087(2)	7883(2)	19(1)

\* Proportion of chlorine with respect to the substrate.

(b) Reactions of a Mixture (c. 6:1) of 4,6-Dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4) and 4,6-Dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5) with Chlorine in Acetic Acid

Reaction of the mixture of dichloro dienones (4) and (5) with chlorine  $(1 \cdot 1 \text{ mole})$  in acetic acid for 1 h gave a mixture (*c*. 4:5) of the tetrachloro ketones (2) and (3). The X-ray crystal analysis of tetrachloro ketone (2) was reported earlier,<sup>2</sup> but the structure of the second isomer (3) had been based only on a consideration of spectroscopic data.<sup>2</sup> The X-ray crystal analysis of this second compound (3) is now reported and is consistent with the structure assigned previously. A perspective drawing of *r*-2,4,*c*-5,*t*-6-tetrachloro-2,3,6-trimethylcyclohex-3-enone (3), C<sub>9</sub>H<sub>10</sub>Cl<sub>4</sub>O, m.p. 126–127° is presented in Fig. 1 with corresponding atomic coordinates in Table 1.

The reaction of the mixture of the dichloro dienones (4) and (5) with chlorine in acetic acid is rapid, with a short term reaction (2 min) resulting in almost complete conversion (c. 95%) into the tetrachloro ketones (2) and (3). The addition of concentrated hydrochloric acid to the reaction medium for the chlorination of the mixture of dichloro dienones (4) and (5) did not affect the ratio of tetrachloro ketones (2) and (3) formed.



(c) Reaction of a Mixture (c. 6:1) of 4,6-Dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4) and 4,6-Dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5) with Chlorine Acetate in Acetic Acid

Reaction of the mixture of dichloro dienones (4) and (5) with chlorine acetate in acetic acid gave essentially (*c*. 80%) a mixture (3:7:4) of compounds (6), (7) and (8); six minor products were present in the mixture, including small amounts (<5%) of the tetrachloro ketones (2) and (3). The structures of the three major products were determined by X-ray crystal analysis, and in each case the spectroscopic data obtained were consistent with the structure determined. A perspective drawing of r-2,4,c-5,t-6-tetrachloro-2-chloromethyl-3,6-dimethylcyclohex-3-enone (6), C<sub>9</sub>H<sub>9</sub>Cl<sub>5</sub>O, m.p. 93–95°, is presented in Fig. 2 with corresponding atomic coordinates in Table 2. Corresponding information is presented for r-2-acetoxy-4,c-5,t-6-trichloro-2,5,6-trimethylcyclohex-3-enone (7), C<sub>11</sub>H<sub>13</sub>Cl<sub>3</sub>O<sub>3</sub>, m.p. 65–67° (Fig. 3, Table 3), and for r-2-acetoxy,4,c-5,t-6-trichloro-2,3,6-trimethylcyclohex-3-enone (8), C<sub>11</sub>H<sub>13</sub>Cl<sub>3</sub>O<sub>3</sub>, m.p. 100–101° (Fig. 4, Table 4).

The alicyclic ring of the chloromethyl ketone (6) exists in the solid state in a flattened boat conformation [torsional angles:  $C(1)-C(2)-C(3)-C(4) - 17(4)^{\circ}$ ;  $C(3)-C(4)-C(5)-C(6) 27(4)^{\circ}$ ] with the C(5)-Cl(5) bond in the flagpole orientation and *anti* to the C(6)-Cl(6) bond [torsional angle:  $Cl(5)-C(5)-C(6)-Cl(6) - 173(1)^{\circ}$ ].



These data were derived from measurements on a crystal of poor quality, but the chemical structure of compound (6) is adequately defined.

In contrast to the structure of the chloromethyl ketone (6), the two trichloro acetates (7) and (8) exist in the solid state in closely similar flattened [C(1),  $sp^2$ ] half-chair conformations with the C(5)–Cl(5) bond in the pseudo-axial orientation. Each compound contains the *r*-2-acetoxy-*c*-5,*t*-6-dichloro structural feature, and they differ only in the attachment of a methyl group either at C(5) as in compound (7), or at C(3) as in compound (8).

(d) Reaction of a Mixture (c. 6:1) of 4,6-Dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4) and 4,6-Dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5) with Chlorine in Acetic Acid Containing Sodium Acetate

Reaction of the mixture of dichloro dienones (4) and (5) with chlorine  $(1 \cdot 2 \text{ mole})$  in acetic acid containing sodium acetate (1 mole) gave a mixture

Table 2. Fractional coordinates for atoms in r-2,4,c-5,t-6-Tetrachloro-2-chloromethyl-3,6-dimethylcyclohex-3-enone (6)

Atom	$10^{4}X/a$	10 <sup>4</sup> Y/b	$10^{4}Z/c$	10 <sup>3</sup> U	Atom	$10^{4}X/a$	10 <sup>4</sup> Y/b	10 <sup>4</sup> Z/c	10 <sup>3</sup> U
Cl(2)	705(7)	-57(8)	-2295(11)	70(5)	C(3)	1102(18)	2508(25)	-2410(29)	19(6)
Cl(4)	263(5)	4691(7)	-1926(8)	32(3)	C(4)	991(17)	3257(26)	-1302(29)	19(6)
Cl(5)	571(5)	2057(7)	1042(8)	36(3)	C(5)	1486(19)	3002(25)	691(30)	26(6)
Cl(6)	3300(5)	3396(7)	1233(8)	32(3)	C(6)	2425(18)	2264(26)	1410(29)	20(6)
Cl(71)	3045(8)	1841(13)	-2479(14)	90(6)	C(7)	2247(25)	818(36)	-2646(43)	56(9)
O(1)	2804(13)	86(17)	837(20)	30(8)	C(8)	715(23)	2793(32)	-4295(34)	39(8)
C(1)	2349(16)	1079(23)	229(28)	11(5)	C(9)	2854(19)	1899(29)	3345(29)	28(7)
C(2)	1683(19)	1233(26)	-1748(31)	26(7)					

 Table 3. Fractional coordinates for atoms in r-2-acetoxy-4,c-5,t-6-trichloro-2,5,6-trimethylcyclohex-3-enone (7)

Atom	$10^{4}X/a$	10 <sup>4</sup> Y/b	10 <sup>4</sup> Z/c	10 <sup>3</sup> U	Atom	10 <sup>4</sup> X/a	10 <sup>4</sup> Y/b	10 <sup>4</sup> Z/c	$10^{3}U$
Cl(4)	-4577(2)	950(1)	1212(1)	26(1)	C(4)	-3907(6)	2404(5)	1993(3)	16(2)
Cl(5)	189(2)	1127(1)	2494(1)	24(1)	C(5)	-2643(7)	1653(5)	2955(3)	18(2)
Cl(6)	-5424(2)	3169(1)	4393(1)	22(1)	C(6)	-2703(6)	2976(5)	3751(3)	16(2)
O(1)	-1430(4)	5629(4)	3520(2)	22(1)	C(7)	-6141(6)	6455(5)	2634(3)	23(2)
O(2)	-2999(4)	6622(3)	1542(2)	19(1)	C(8)	-3375(7)	18(5)	3476(3)	25(2)
O(21)	79(4)	4806(3)	1344(2)	22(1)	C(9)	-1091(7)	2499(5)	4619(3)	24(2)
C(1)	-2558(7)	4749(5)	3190(3)	18(2)	C(21)	-945(7)	6160(5)	1149(3)	17(2)
C(2)	-4026(7)	5400(5)	2258(3)	17(2)	C(22)	-173(7)	7609(5)	463(3)	24(2)
C(3)	-4491(6)	4005(5)	1679(3)	19(2)					

Table 4. Fractional coordinates for atoms in *r*-2-acetoxy-4,*c*-5,*t*-6-trichloro-2,3,6trimethylcyclohex-3-enone (8)

Atom	10 <sup>4</sup> X/a	10 <sup>4</sup> Y/b	10 <sup>4</sup> Z/c	10 <sup>3</sup> U	Atom	10 <sup>4</sup> X/a	10 <sup>4</sup> Y/b	$10^{4}Z/c$	10 <sup>3</sup> U
Cl(4)	3127(3)	1402(2)	6132(2)	62(1)	C(4)	2876(5)	2462(7)	5051(5)	33(2)
Cl(5)	4634(3)	4429(2)	5527(2)	54(1)	C(5)	3019(7)	4019(8)	5279(5)	42(2)
Cl(6)	779(3)	4896(2)	4611(2)	53(1)	C(6)	2439(7)	4994(7)	4442(4)	43(2)
O(1)	2633(7)	5193(6)	2683(4)	60(2)	C(7)	1098(7)	2502(11)	2699(6)	64(3)
O(21)	3174(5)	2313(5)	2457(4)	44(1)	C(8)	4384(7)	2665(7)	2623(5)	38(2)
O(22)	4757(5)	3391(6)	3326(4)	51(2)	C(9)	5106(8)	1993(9)	1843(6)	56(3)
C(1)	2533(6)	4396(7)	3380(4)	35(2)	C(10)	2501(8)	256(7)	4001(7)	61(3)
C(2)	2359(5)	2789(7)	3218(4)	36(2)	C(11)	2777(10)	6572(7)	4545(6)	61(3)
C(3)	2594(5)	1857(7)	4148(5)	37(2)					

(4:2:2:1:3) of compounds (3), (9), (10), (7) and (8). Pure samples of compounds (3), (10), (7) and (8) were isolated, but compound (9) was obtained only in admixture with the tetrachloro ketone (3), and identified tentatively on the basis of analytical data and the <sup>1</sup>H n.m.r. spectra for the mixture. The structure of compound (10) was assigned on the basis of its analytical and spectroscopic data, and the relative stereochemistry at C(5) and C(6) assigned on the basis of the observed *trans* stereochemistry of the other products of the reaction. Notable in the composition of the mixture of produces is the ratio (*c*. 1:3) of the isomeric trichloro acetates (7) and (8); in contrast, reaction of the dichloro dienone mixture with chlorine acetate, above, gave a ratio (*c*. 7:4) of these acetates.



(e) Reaction of a Mixture (c. 6:1) of 4,6-Dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4) and 4,6-Dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5) with Nitrogen Dioxide in Benzene Solution

Reaction of the mixture of dichloro dienones (4) and (5) with nitrogen dioxide in benzene solution gave essentially (c. 84%) a mixture (3:1:2:1) of the four isomeric dichloro dinitro ketones (11)-(14), and some five minor The four dichloro dinitro ketones unidentified products (total c. 16%). (11)-(14) were isolated and their structures determined: (i) by the general similarity of their spectroscopic data, including where experimentally possible the results of n.O.e. experiments (Experimental section); (ii) as a result of X-ray crystal analyses for isomers (11)-(13); and (iii) analytical data for the fourth isomer (14). A perspective drawing of 4,c-6-dichloro-2,5,6trimethyl-*r*-2,*t*-5-dinitrocyclohex-3-enone (11), C<sub>9</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>5</sub>, m.p. 112–113°, is presented in Fig. 5 with corresponding atomic coordinates in Table 5. Corresponding information is presented for 4,t-6-dichloro-2,5,6-trimethyl-r-2,t-5-dinitrocyclohex-3-enone (12), C9H10Cl2N2O5, m.p. 114-116° (Fig. 6, Table 6), and for 4,*t*-6-dichloro-2,5,6-trimethyl-*r*-2,*c*-5-dinitrocyclohex-3-enone (13),  $C_9H_{10}Cl_2N_2O_5$ , m.p. 112–114° (Fig. 7, Table 7). In the solid state the alicyclic ring of each of the dichloro dinitro ketones (11)-(13) exists in a flattened [C(1),  $sp^2$ ] boat conformation with the C(5)–N(5) bond in the flagpole orientation.



Fig. 5. Perspective drawing of compound (11).

 

 Table 5. Fractional coordinates for atoms in 4,c-6-dichloro-2,5,6-trimethyl-r-2,t-5dinitrocyclohex-3-enone (11)

Atom	10 <sup>4</sup> X/a	10 <sup>4</sup> Y/b	$10^{4}Z/c$	10 <sup>3</sup> U	Atom	10 <sup>4</sup> X/a	10 <sup>4</sup> Y/b	$10^{4}Z/c$	10 <sup>3</sup> U
Cl(4)	2583(1)	287(1)	4934(1)	39(1)	C(1)	1326(3)	3522(2)	2813(2)	21(1)
Ci(6)	2135(1)	4302(1)	4756(1)	29(1)	C(2)	-25(3)	2670(2)	2961(2)	23(1)
O(1)	1155(2)	4165(2)	2065(1)	37(1)	C(3)	524(3)	1704(2)	3719(2)	24(1)
O(21)	-1904(3)	4232(2)	2877(2)	66(1)	C(4)	2060(3)	1544(2)	4192(2)	23(1)
O(22)	-1634(2)	3115(2)	4241(1)	40(1)	C(5)	3474(3)	2339(2)	4106(2)	21(1)
O(51)	5604(2)	1511(2)	3339(1)	37(1)	C(6)	2862(2)	3569(2)	3690(2)	20(1)
O(52)	3269(2)	1798(2)	2308(1)	33(1)	C(7)	-898(3)	2206(3)	1881(2)	39(1)
N(2)	-1301(2)	3403(2)	3400(2)	33(1)	C(8)	4798(3)	2389(2)	5096(2)	31(1)
N(5)	4189(2)	1824(2)	3172(1)	24(1)	C(9)	4170(3)	4313(2)	3356(2)	30(1)



Fig. 6. Perspective drawing of compound (12).

For the two *trans*-2,5-dinitro compounds, (11) and (12), the planes of the nitro groups at C(2) and C(5) are close to eclipsed with the corresponding C(2)–C(7) or C(5)–C(8) bond. In contrast, the planes of the two nitro groups in the *cis*-2,5-dinitro compound (13) are significantly displaced from coplanarity with the corresponding C(2)–C(7) or C(5)–C(8) bonds, presumably as a result of the *syn* relationship of the two groups (Fig. 7).

 

 Table 6. Fractional coordinates for atoms in 4,t-6-dichloro-2,5,6-trimethyl-r-2,t-5dinitrocyclohex-3-enone (12)

Atom	10 <sup>4</sup> X/a	10 <sup>4</sup> Y/b	10 <sup>4</sup> Z/c	10 <sup>3</sup> U	Atom	10 <sup>4</sup> X/a	10 <sup>4</sup> Y/b	10 <sup>4</sup> Z/c	10 <sup>3</sup> U
Cl(4)	2643(1)	278(1)	5043(1)	31(1)	C(1)	1056(3)	3489(2)	2882(2)	17(1)
Cl(6)	4034(1)	4418(1)	3318(1)	25(1)	C(2)	-224(3)	2610(2)	3064(2)	17(1)
O(1)	783(2)	4122(2)	2107(2)	30(1)	C(3)	439(3)	1649(2)	3836(2)	18(1)
O(21)	-2116(3)	4132(2)	3012(2)	57(1)	C(4)	2000(3)	1517(2)	4280(2)	18(1)
O(22)	-1632(3)	3051(2)	4433(2)	30(1)	C(5)	3322(3)	2340(2)	4142(2)	17(1)
O(51)	5294(3)	1561(2)	3258(2)	33(1)	C(6)	2587(3)	3567(2)	3798(2)	15(1)
O(52)	2874(3)	1856(2)	2280(2)	29(1)	C(7)	-1180(4)	2137(3)	1980(2)	29(1)
N(2)	-1432(3)	3328(2)	3543(2)	24(1)	C(8)	4749(4)	2400(3)	5418(2)	24(1)
N(5)	3900(3)	1874(2)	3145(2)	22(1)	C(9)	2152(4)	4199(2)	4759(2)	21(1)



Fig. 7. Perspective drawing of compound (13).

 

 Table 7. Fractional coordinates for atoms in 4,t-6-dichloro-2,5,6-trimethyl-r-2,c-5dinitrocyclohex-3-enone (13)

Atom	$10^{4}X/a$	10 <sup>4</sup> Y/b	10 <sup>4</sup> Z/c	$10^{3}U$	Atom	$10^{4}X/a$	10 <sup>4</sup> Y/b	10 <sup>4</sup> Z/c	10 <sup>3</sup> U
Cl(4)	11972(2)	10083(1)	2749(2)	25(1)	C(1)	7788(7)	9761(4)	483(3)	18(1)
Cl(6)	9363(2)	7688(1)	972(1)	24(1)	C(2)	9772(7)	10498(4)	435(3)	14(1)
O(1)	6556(5)	9779(3)	-53(2)	28(1)	C(3)	10977(7)	10529(4)	1211(2)	14(1)
O(21)	8664(6)	12074(3)	-444(2)	42(1)	C(4)	10385(6)	10034(4)	1903(2)	14(1)
O(22)	8973(6)	12501(3)	830(2)	33(1)	C(5)	8310(7)	9444(4)	2030(3)	15(1)
O(51)	6810(6)	10899(4)	2911(2)	39(1)	C(6)	7557(7)	8884(4)	1215(3)	13(1)
O(52)	6053(5)	11032(3)	1628(2)	27(1)	C(7)	11028(7)	10067(5)	-284(3)	23(1)
N(2)	9082(6)	11817(4)	254(2)	20(1)	C(8)	8182(8)	8590(4)	2754(3)	28(2)
N(5)	6909(6)	10550(4)	2208(2)	22(1)	C(9)	5447(7)	8341(4)	1252(3)	23(2)

(f) Overview of the Addition Reactions of the Mixture (c. 6:1) of 4,6-Dichloro-2,5,6trimethylcyclohexa-2,4-dienone (4) and 4,6-Dichloro-2,3,6-trimethylcyclohexa-2,4dienone (5)

The products (and yields) of reactions of the mixture of 6-chlorocyclohexa-2,4-dienones (4) and (5) with the variety of reagents reported above are given in Table 8.

Table 8. Products, and yields, for reactions of a mixture (c. 6:1) of 4,6-dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4) and 4,6-dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5)

Reagent system	Products from (4)	Products from (5)	Products of unknown origin
NO <sub>2</sub> /benzene	(11)–(14) total 84%		14%
Cl-OAc/AcOH	(7) 40%	(6) 17%; (8) 23%	20%
Cl <sub>2</sub> /NaOAc/AcOH	(7) 8%; (9) 17%	(3) 33%; (8) 17%; (10) 17%	
Cl <sub>2</sub> /AcOH		(2) 45%; (3) 55%	—



Reaction with nitrogen dioxide.—The reactions of nitrogen dioxide with polysubstituted cyclohexa-2,4-dienones (15) to give 2,5-dinitrocyclohex-3-enones (16) are known to occur by initial attack of nitrogen dioxide at C(5) to give a delocalized radical (17) which couples with a second nitrogen dioxide molecule (Scheme 1).<sup>3</sup> This addition process appears to be unaffected by the presence or absence of a methyl substituent at C(3) or C(5),<sup>4</sup> and accordingly the reaction seemed to be a suitable probe of the reactivity of the mixture of the 6-chlorocyclohexa-2,4-dienones (4) and (5). In the event, products (*c*. 84%) were isolated which are the result of 2,5-addition of nitrogen dioxide to the major (*c*. 86%) component of the 6-chlorocyclohexa-2,4-dienone (4). No products could be isolated which might have arisen by 2,5-addition of nitrogen dioxide to the minor 6-chlorocyclohexa-2,4-dienone (5), but some five minor products (total *c*. 16%) were detected.

*Reaction with chlorine acetate.*—In contrast to the additions of nitrogen dioxide, which are free-radical processes, the addition of chlorine acetate to the mixture of 6-chlorocyclohexa-2,4-dienones (4) and (5) will proceed by an ionic reaction pathway, probably involving nearly free positive chlorine as the

<sup>&</sup>lt;sup>3</sup> Blunt, J. W., Hartshorn, M. P., Jensen, R. G., Waller, A. G., and Wright, G. J., *Aust. J. Chem.*, 1989, **42**, 675, and references cited therein.

<sup>&</sup>lt;sup>4</sup> Hartshorn, M. P., Penfold, B. R., Sutton, K. H., and Vaughan, J., *Aust. J. Chem.*, 1984, **37**, 809; Hartshorn, M. P., Robinson, W. T., Vaughan, J., White, J. M., and Whyte, A. R., *Aust. J. Chem.*, 1984, **37**, 1489; Hartshorn, M. P., Readman, J. M., Robinson, W. T., and Vaughan, J., *Aust. J. Chem.*, 1985, **38**, 587.

effective reagent.<sup>5</sup> Of the products isolated, it is clear that the 4,5,6-trichloro-2,5,6-trimethyl acetate (7) (c. 40%) arises by addition of the elements of chlorine acetate to the diene system of 4,6-dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4). Similarly, the 4,5,6-trichloro-2,3,6-trimethyl acetate (8) (c. 23%) arises by addition of chlorine acetate to 4,6-dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5). It is interesting to note that the chlorine and acetate functions are introduced in a mutually *cis* relationship, and *trans* to the 6-chloro substituent in the substrate. The mode of formation of the chloromethyl ketone (6) (c. 17%) is uncertain, but is more likely to have been formed by initial attack of chlorine acetate at C(5) of the 2,3,6-trimethylcyclohexa-2,4-dienone (5). No information is available as to the mode of formation of the remaining minor products (c. 20%).

Reaction with chlorine in the presence of sodium acetate.—Reaction of the mixture of dichloro dienones (4) and (5) with chlorine in acetic acid containing sodium acetate gave lower yields of the trichloro acetates (7) (8%) and (8) (17%). If it is assumed that the 4,4,5,6-tetrachloro ketone (10) (17% yield) is a product of addition of chlorine to a 6-chlorocyclohexa-2,4-dienone, it would have been formed by 4,5-addition of chlorine to 4,6-dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5).

The remaining two products from the reaction with chlorine in the presence of sodium acetate are the tetrachloro ketones (3) (33%) and (9) (17%), both of which contain the *cis*-2,5-dichloro structural feature. The non-appearance of the trans-2,5-dichloro ketone (2) among the products of reaction is notable, but potentially explicable in terms of its transformation under the reaction conditions into the related (but C2-epimeric) trichloro acetate (8). However, the recovery of unreacted tetrachloro ketone (2) from treatment with sodium acetate in acetic acid eliminated this possibility. There is no direct evidence on the mode of formation of the two tetrachloro ketones (3) and (9) from the mixture of dichloro dienones (4) and (5), but by analogy with the 2,5-addition of the elements of chlorine acetate to the dichloro dienones, either in the direct reaction with chlorine acetate or in the present reaction with chlorine in the presence of sodium acetate, it appears likely that these compounds also arise by 2,5-addition to a 6-chlorocyclohexa-2,4-dienone (4) or (5). If this assumption is made, the implication is that compounds (7) and (9) (total 25%) arise by addition to 4,6-dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4), and that compounds (3), (8) and (10) (total 67%) arise by addition to 4,6-dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5). This outcome should be contrasted with that for the addition of the more reactive chlorine acetate where products arose by addition to the 2,5,6-trimethyl dienone (4) (40%) and to the 2,3,6-trimethyl dienone (5) (40%). These results can be accommodated only if interconversion of the 2,5,6-trimethyl dienone (4) and 2,3,6-trimethyl dienone (5) occurs during the reactions.

*Reaction with chlorine in acetic acid.*—In the light of the foregoing, it appears most likely that the tetrachloro ketones (2) and (3) arise by 2,5-addition of chlorine to the *minor* 4,6-dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5). The implications of this observation for the reaction with chlorine in acetic acid

<sup>&</sup>lt;sup>5</sup> de la Mare, P. B. D., O'Connor, C. J., and Wilson, M. A., *J. Chem. Soc., Perkin Trans. 2,* 1975, 1150.

are: (i) that the initial attack of chlorine on a 6-chlorocyclohexa-2,4-dienone occurs at C(5); (ii) that given two possible 6-chlorocyclohexa-2,4-dienones such as compounds (4) and (5), attack will occur preferentially at C(5) on that isomer (5) which is unsubstituted at this position; and (iii) that the isomeric 6-chlorocyclohexa-2,4-dienones (4) and (5) interconvert during the reaction presumably by a [1,5]-sigmatropic shift of the 6-chloro substituent. Such an apparent [1,5]-sigmatropic shift has been noted earlier.<sup>6</sup>

From a comparison of the results from reactions of the 6-chlorocyclohexa-2,4-dienone mixture (4) and (5), it is clear that the selectivity of the three chlorinating reagent systems for reaction at the unsubstituted C(5)-position in chloro dienone (5), relative to the methyl-occupied C(5) position in chloro dienone (4), is  $Cl_2/AcOH > Cl_2/NaOAc/AcOH > Cl-OAc$ . Chlorine acetate is known to have a greater reactivity than molecular chlorine towards unsaturated systems, because chlorine acetate more readily transfers positive chlorine to the olefinic substrate.<sup>7</sup> Presumably the effect of added sodium acetate is to assist the ionization of molecular chlorine in those reactions.

PM3 calculations<sup>8</sup> were carried out on the two chloro dienones (4) and (5) with PM3 parameters as implemented in the MOPAC program.<sup>9</sup> Calculated heats of formation for 4,6-dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4) and 4,6-dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5) were -170.4 and -166.1 kJ mol<sup>-1</sup> respectively. Application of the Boltzmann distribution gave an equilibrium ratio of the dichloro dienones (4) to (5) of 85:15, which is close to the experimentally observed value.

Further PM3 calculations were conducted to characterize the transition state in the proposed [1,5]-signatropic shift of the chlorine atom. An appropriate transition state structure was determined and refined by using the gradient minimization procedure in the MOPAC program. Vibrational analysis showed a single negative eigenvalue demonstrating that the structure represents a saddle point on the PM3 potential surface. The heat of formation for the transition state was -31.6 kJ mol<sup>-1</sup>. This leads to a calculated barrier for the [1,5]-sigmatropic shift of approximately 139 kJ mol<sup>-1</sup> in the conversion of dichloro dienone (4) into dichloro dienone (5). Although this value appears to be relatively large, previous calculations for similar [1,5]-sigmatropic shifts by using analogous semiempirical calculations tended to overestimate the barrier to the transformation.<sup>10</sup> It is likely, therefore, that the PM3 value calculated here is also an overestimate of the barrier to the transformation. AM1 calculations<sup>11</sup> gave similar values to those obtained above.

#### Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Pye–Unicam SP3-300 spectrometer; <sup>1</sup>H n.m.r., <sup>13</sup>C n.m.r., and nuclear Overhauser enhancement (n.O.e.) experiments,

<sup>6</sup> Hartshorn, M. P., Judd, M. C., and Robinson, W. T., Aust. J. Chem., 1986, **39**, 2121.

<sup>7</sup> de la Mare, P. B. D., 'Electrophilic Halogenation' pp. 101–4 (Cambridge University Press, 1976).

<sup>8</sup> Stewart, J. J. P., J. Comput. Chem., 1989, **10** (2), 209.

<sup>9</sup> MOPAC 5.00 is available from the Quantum Chemistry Program Exchange (QCPE).

<sup>10</sup> Dewar, M. J. S., Merz, K. M., and Stewart, J. J. P., *J. Chem. Soc., Chem. Commun.*, 1985, 166.
 <sup>11</sup> Dewar, M. J. S., Zoebisch, E. G., Healy, E. A., and Stewart, J. J. P., *J. Am. Chem. Soc.*, 1985, 107, 3902.

were recorded on a Varian XL-300 spectrometer with SiMe<sub>4</sub> as an internal standard; ultraviolet spectra were recorded on a Varian DMS-100 spectrometer. Silica gel used on Chromatotron (Harrison & Harrison) plates was Merck type 60 P.F. 254.

## Preparation of a Mixture of 4,6-Dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4) and 4,6-Dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5)

A solution of chlorine (0.49 g) in carbon tetrachloride (3 ml) was added to a stirred solution of 4-chloro-2,3,6-trimethylphenol (1b)  $(1 \cdot 0 \text{ g})$  in carbon tetrachloride (10 ml) and pyridine (0.48 ml) in a darkened flask. The mixture was stirred at 0–5° for 15 min, poured into ice-water, and the product isolated by means of ether. The product, an oil, was shown (<sup>1</sup>H n.m.r.). to be a mixture of the two isomeric 6-chlorocyclohexa-2,4-dienones (4) and (5), which could not be separated by chromatography. The products were identified from their <sup>1</sup>H n.m.r. spectra.

4,6-Dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4) (c. 86%).—<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$  1.76, s, 6-Me; 1.97, dq,  $J_{Me,H3}$  1.8,  $J_{Me,Me}$  0.6 Hz, 2-Me; 2.13, q,  $J_{Me,Me}$  0.6 Hz, 5-Me; 6.79, q,  $J_{H3,Me}$  1.8 Hz, H3. N.O.e. experiments gave the following results: irradiation at  $\delta$  1.76 gave enhancements of signals at  $\delta$  2.13 (11%) and 6.79 (2%); irradiation at  $\delta$  1.97 gave an enhancement at  $\delta$  6.79 (6%); irradiation at  $\delta$  2.13 gave enhancements at  $\delta$  1.79 (2%) and 6.79 (1%).

4,6-Dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5) (c. 14%).—<sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$  1.74, s, 6-Me; 2.00, m, 2-Me; 2.18, m, 3-Me; 6.43, s, H5.

The <sup>1</sup>H n.m.r. spectra of the above mixture were determined for CCl<sub>4</sub>, CD<sub>3</sub>CN, C<sub>6</sub>D<sub>6</sub>, CD<sub>3</sub>OD, CD<sub>3</sub>CO<sub>2</sub>D, and CD<sub>3</sub>SOCD<sub>3</sub> solutions. The composition of the mixture was essentially as for the CDCl<sub>3</sub> solution, except for the CD<sub>3</sub>SOCD<sub>3</sub> solution where the ratio of (4) to (5) was 90:10.

#### Chlorination Reactions of the Mixture (c. 6:1) of 4,6-Dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4) and 4,6-Dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5)

#### (a) Longer Term (1 h) Reaction with Chlorine in Acetic Acid

To a solution of the mixture of dichloro dienones (4) and (5) (0.5 g) in acetic acid (5 ml) was added chlorine (0.18 g; 1.1 mole) as a solution in acetic acid. The mixture was stirred in a darkened flask for 1 h at 20°, and the excess chlorine and the solvent were then removed under reduced pressure. The residue (0.51 g) was shown (<sup>1</sup>H n.m.r.) to be a mixture (4:5) of the tetrachloro ketones (2) and (3), which were separated by chromatography on a Chromatotron silica gel plate to give in order of elution:

r-2,4,t-5,c-6-Tetrachloro-2,3,6-trimethylcyclohex-3-enone (2), m.p. 106–106 · 5°, identical with authentic material.<sup>2</sup>

r-2,4,c-5,t-6-Tetrachloro-2,3,6-trimethylcyclohex-3-enone (3), m.p. 126–127° (X-ray crystal structure determined, below), identical with authentic material; this compound was characterized earlier, but without an X-ray structure determination.<sup>2</sup>

#### (b) Shorter Term (2 min) Reaction with Chlorine in Acetic Acid

To a stirred solution of the dichloro dienones (4) and (5) (0.62 g) in acetic acid at 20° was added chlorine (0.26 g; 1.2 mole) as a solution in acetic acid. The mixture was stirred in a darkened flask for 2 min, and the excess chlorine and the solvent were then removed under reduced pressure. The residue (0.67 g) was shown  $(^{1}\text{H} \text{ n.m.r.})$  to be a mixture (c. 1:7:9) of unreacted dichloro dienone (4) and the tetrachloro ketones (2) and (3).

#### (c) Reaction with Chlorine in Acetic Acid Containing Concentrated Hydrochloric Acid

To a stirred solution of the dichloro dienones (4) and (5) (0.6 g) in acetic acid (6 ml) containing concentrated hydrochloric acid (0.11 ml) at 20° was added chlorine (0.25 g, 1.2 mole) as a solution in acetic acid. The mixture was stirred in a darkened flask for 1 h, and the excess chlorine and the solvents were then removed under reduced pressure. The residue (0.69 g) was shown  $(^{1}\text{H} \text{ n.m.r.})$  to be a mixture (c. 4:5) of the tetrachloro ketones (2) and (3).

#### (d) Reaction with Chlorine Acetate in Acetic Acid

To a stirred solution of the dichloro dienones (4) and (5) (0.4 g) in acetic acid (5 ml) was added chlorine acetate (16.4 ml; 0.132 mol l<sup>-1</sup>; 1.2 mole) as a solution in acetic acid. The mixture was stirred at 20° for 1 h, and the excess reagent and the solvent were removed under reduced pressure. The residue was shown (<sup>1</sup>H n.m.r.) to be essentially (*c.* 80%) a mixture (3:7:4) of three compounds which were separated on a Chromatotron silica gel plate and gave in order of elution:

*r-2,4,*c-5,t-6-*Tetrachloro-2-chloromethyl-3,6-dimethylcyclohex-3-enone* (6), m.p. 93–95° (X-ray crystal structure determined, below).  $\nu_{max}$  (KBr disc) 1740, C=O; 1640 cm<sup>-1</sup>, C=C. <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$  1.99, s, 6-Me; 2.15, s, 3-Me; 3.93, 4.35, AB q,  $J_{\rm H,H}$  11.3 Hz, CH<sub>2</sub>Cl.

*r*-2-Acetoxy-4,c-5,t-6-trichloro-2,5,6-trimethylcyclohex-3-enone (7), m.p. 65–67° (X-ray crystal structure determined, below).  $\nu_{max}$  (KBr disc) 1765, C=O; 1754, C=O; 1660, C=C; 1240 cm<sup>-1</sup>, OAc. <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$  1.89, s, 6-Me; 1.99, s, 2-Me; 2.03, s, 5-Me; 2.06, s, OCOCH<sub>3</sub>; 6.30, s, H3.

*r*-2-Acetoxy-4,c-5,t-6-trichloro-2,3,6-trimethylcyclohex-3-enone (8), m.p. 100–101° (X-ray crystal structure determined, below).  $\nu_{max}$  (Nujol) 1752, C=O; 1742, C=O; 1657, C=C; 1232 cm<sup>-1</sup>, OAc. <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$  1.81, 6-Me; 1.92, 6H, 2-Me and 3-Me; 2.07, s, OCOCH<sub>3</sub>; 4.97, H 5.

Six minor products (total *c*. 20%) were present in the original mixture including small amounts (<5%) of the tetrachloro ketones (2) and (3) which were presumably formed by reaction of traces of chlorine in the chlorine acetate solution used for the reaction.

#### (e) Reaction with Chlorine in Acetic Acid Containing Sodium Acetate (1.0 mole)

To a stirred solution of the dichloro dienone mixture (0.5 g) in acetic acid (5 ml) containing sodium acetate (0.24 g; 1.0 mole) at 20° was added chlorine (0.24 g; 1.2 mole) as a solution in acetic acid. The mixture was stirred in a darkened flask for 1 h at 20°, and then the excess chlorine and solvent were removed under reduced pressure. The organic material was isolated from the residue by means of ether to give an oil (0.7 g) which was shown  $(^1\text{H}$ n.m.r.) to be a mixture (4:2:2:1:3) of compounds (3), (9), (10), (7) and (8). Chromatography of this oil on a Chromatotron silica gel plate gave in order of elution.

r-2,4,c-5,t-6-Tetrachloro-2,3,6-trimethylcyclohex-3-enone (3), m.p. 126–127°, identical with authentic material.<sup>2</sup>

A mixture (c. 1:1) of r-2,4,c-5,t-6-tetrachloro-2,3,6-trimethylcyclohex-3-enone (3) and r-2,4,c-5,t-6-tetrachloro-2,5,6-trimethylcyclohex-3-enone (9), m.p. 90–95° (Found: C, 39·2; H, 3·7; Cl, 51·8. C<sub>9</sub>H<sub>10</sub>Cl<sub>4</sub>O requires C, 39·2; H, 3·65; Cl, 51·4%).  $\nu_{max}$  (KBr disc) 1740br, C=O; 1645 cm<sup>-1</sup>, C=C. The <sup>1</sup>H n.m.r. spectrum of r-2,4,c-5,t-6-tetrachloro-2,5,6-trimethylcyclohex-3-enone (9) was obtained by subtraction as: (CDCl<sub>3</sub>)  $\delta$  1·979, 1·983, 2·01, methyls; 6·20, s, H3.

trans-4,4,5,6-Tetrachloro-2,3,6-trimethylcyclohex-2-enone (10), an oil (Found: C, 39·3; H, 3·7; Cl, 51·2. C<sub>9</sub>H<sub>10</sub>Cl<sub>4</sub>O requires C, 39·2; H, 3·7; Cl, 51·5%).  $\nu_{max}$  (liquid film) 1697, conjugated C=O; 1627 cm<sup>-1</sup>, C=C. <sup>1</sup>H n.m.r.  $\delta$  1·82, 6-Me; 1·98, 2-Me; 2·35, 3-Me; 5·07, H 5.  $\lambda_{max}$  (CHCl<sub>3</sub>) 252 nm ( $\epsilon$ 10900).

*r*-2-Acetoxy-4,*c*-5,*t*-6-trichloro-2,5,6-trimethylcyclohex-3-enone (7), m.p. 65–67°, identical with authentic material.

*r*-2-Acetoxy-4,*c*-5,*t*-6-trichloro-2,3,6-trimethylcyclohex-3-enone (8), m.p. 100–101°, identical with authentic material.

## Treatment of r-2,4,t-5,c-6-Tetrachloro-2,3,6-trimethylcyclohex-3-enone (2) with Sodium Acetate in Acetic Acid

To a solution of the tetrachloro ketone (2) (6 mg) in acetic acid (5 ml) was added a solution of sodium acetate (0.24 g) in acetic acid (4.8 ml), and the resulting mixture stirred at 20° for 1 h. The solvent was then removed under reduced pressure, water added to the residue, and mixture extracted with ether. The ether phase yielded material (5 mg) shown (<sup>1</sup>H n.m.r.) to be unreacted tetrachloro ketone (2).

# Reaction of the Mixture (c. 6:1) of 4,6-Dichloro-2,5,6-trimethylcyclohexa-2,4-dienone (4) and 4,6-Dichloro-2,3,6-trimethylcyclohexa-2,4-dienone (5) with Nitrogen Dioxide in Benzene Solution

A solution of the dichloro dienones (4) and (5) (0 · 43 g) in benzene (5 ml) was deoxygenated with a stream of nitrogen. Nitrogen dioxide was then bubbled through the stirred solution at 5° for 30 s, and the mixture stirred at 20° under an atmosphere of nitrogen dioxide for 2 h. The excess nitrogen dioxide was removed in a stream of nitrogen, and the solvent removed under reduced pressure. The residue (0 · 48 g), an oil, was shown (<sup>1</sup>H n.m.r.) to be essentially (*c.* 84%) a mixture (*c.* 3:1:2:1) of the isomeric dichloro dinitro ketones (11), (12), (13) and (14). The components of this mixture were separated by chromatography on a Chromatotron silica gel plate at 0°, and gave in order of elution.

4,c-6-Dichloro-2,5,6-trimethyl-r-2,t-5-dinitrocyclohex-3-enone (11), m.p. 112–113° (X-ray crystal structure determined, below).  $\nu_{max}$  (KBr disc) 1757, C=O; 1565 cm<sup>-1</sup>, NO<sub>2</sub>. <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$  1.71, s, 6-Me; 2.06, s, 2-Me; 2.11, s, 5-Me; 6.84, s, H3. N.O.e. experiments gave the following results: irradiation at  $\delta$  1.71 gave enhancement of the signal at  $\delta$  2.11 (2%); irradiation at  $\delta$  6.84 gave enhancement at  $\delta$  2.06 (1%).

4,t-6-Dichloro-2,5,6-trimethyl-r-2,t-5-dinitrocyclohex-3-enone (12), m.p. 114-116° (X-ray crystal structure determined, below).  $\nu_{max}$  (KBr disc) 1770, C=O; 1565-1560 br cm<sup>-1</sup>, NO<sub>2</sub>. <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$  1.79, s, 6-Me; 2.08, s, 5-Me; 2.12, s, 2-Me; 6.74, s, H3.

4,t-6-Dichloro-2,5,6-trimethyl-r-2,c-5-dinitrocyclohex-3-enone (13), m.p. 112–114° (X-ray crystal structure determined, below).  $\nu_{max}$  (KBr disc) 1757, C=O; 1560 cm<sup>-1</sup>, NO<sub>2</sub>, <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$  1.79, s, 6-Me; 2.13, s, 5-Me; 2.20, s, 2-Me; 6.59, s, H3. N.O.e. experiments gave the following results: irradiation at  $\delta$  1.79 gave an enhancement at  $\delta$  2.13 (1%).

4,c-6-Dichloro-2,5,6-trimethyl-r-2,c-5-dinitrocyclohex-3-enone (14), m.p. 116–117° (Found: C, 36·5; H, 3·5; Cl, 23·8; N, 8·8. C9H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>5</sub> requires C, 36·4; H, 3·4; Cl, 23·9; N, 9·4%).  $v_{max}$  (KBr disc) 1757, C=O; 1565 cm<sup>-1</sup>, NO<sub>2</sub>. <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>)  $\delta$  1·82, s, 6-Me; 2·01, s, 5-Me; 2·06, s, 2-Me; 6·62, s, H3. N.O.e. experiments gave the following results: irradiation at  $\delta$  1·82 gave enhancements at  $\delta$  2·01 (1%), 2·06 (1%) and 6·62 (2%); irradiation at  $\delta$  2·06 gave enhancements at  $\delta$  1·82 (1%) and 6·62 (2%); irradiation at  $\delta$  6·62 gave enhancements at  $\delta$  1·82 (1%), 2·01 (1%), 2·01 (1%) and 2·06 (1%).

#### Crystallography

Crystal data, established from precession photographs and measured accurately, by means of a Nicolet XRD P3 four-circle diffractometer [molybdenum X-radiation,  $\lambda$ (Mo K $\alpha$ ) 0.71069 Å, from a crystal monochromator], are given below. The space group was determined unambiguously as a result of the structure analyses reported below, but initially indicated by the conditions limiting possible reflections. The  $\theta/2\theta$  or the  $\omega$ -scan technique was used to collect reflection intensities out to a maximum Bragg angle,  $\theta$ . The cell parameters were determined by least-squares refinements for which the setting angles of 25 high-angle reflections were used.

#### Crystal Data

r-2,4,c-5,t-6-*Tetrachloro-2-chloromethyl-3*,6-*dimethylcyclohex-3-enone* (6).---C<sub>9</sub>H<sub>9</sub>Cl<sub>5</sub>O, M 310·4, monoclinic, space group  $P2_1/n$ , a 15·26(2), b 10·05(1), c 8·68(1), Å  $\beta$  118·34(9)°, U 1172·0(2) Å<sup>3</sup>,  $D_c$  1·75 g cm<sup>-3</sup>, Z 4,  $\mu$ (Mo K $\alpha$ ) 12·0 cm<sup>-1</sup>. The crystal was colourless and of approximate dimensions 0·65 by 0·35 by 0·25 mm. The  $\omega$  scan technique (3° wide) was used to collect data at 163 K. Number of independent reflections measured 1480, number with  $I > 3\sigma(I)$  664; maximum Bragg angle  $\theta$  22.5°; g 0.00982; absorption corrections, maximum 0.954, mimimum 0.625; R factor 0.124, wR 0.128. The crystal was of a poor quality, giving correspondingly poor data and an R factor outside normal limits for publication; however, the structural information is sufficient to define the chemical nature of compound (6).

r-2-Acetoxy-4,c-5,t-6-trichloro-2,5,6-trimethylcyclohex-3-enone (7).—C<sub>11</sub>H<sub>13</sub>Cl<sub>3</sub>O<sub>3</sub>, M 299•6, triclinic, space group  $P\overline{1}$ , a 6-215(7), b 8-117(6), c 12-671(7) Å, a 82-85(5),  $\beta$  86-14(7),  $\gamma$  81-20(8)°, U 626-0(9) Å<sup>3</sup>, D<sub>c</sub> 1-58 g cm<sup>-3</sup>, Z 2,  $\mu$ (Mo Ka) 7-23 cm<sup>-1</sup>. The crystal was colourless and of appropriate dimensions 0-26 by 0-17 by 0-10 mm. The  $\theta/2\theta$  scan technique was used to collect data at 153 K. Number of independent reflections measured 1649, number with  $I > 3\sigma(I)$  1236; maximum Bragg angle  $\theta$  22-5°; g 0-00001; absorption corrections, maximum 0-78, minimum 0-73; R factor 0-039, wR 0-030.

r-2-Acetoxy-4,c-5,t-6-trichloro-2,3,6-trimethylcyclohex-3-enone (8).—C<sub>11</sub>H<sub>13</sub>Cl<sub>3</sub>O<sub>3</sub>, M 299•5, monoclinic, space group *Cc*, *a* 10•920(5), *b* 9•312(4), *c* 13•315(4), *β* 94•70(3)°, *U* 1349•4(9) Å<sup>3</sup>, *D*<sub>c</sub> 1•47 g cm<sup>-3</sup>, *Z* 4,  $\mu$ (Mo K $\alpha$ ) 6•74 cm<sup>-1</sup>. The crystal was colourless and of approximate dimensions 0•68 by 0•8 by 0•76 mm. The  $\omega$  scan technique was used to collect data at 193 K. Number of independent reflections measured 1388, number with *I* > 3 $\sigma$ (*I*) 1388; maximum Bragg angle  $\theta$  26•0°; *g* 0•00090; absorption corrections, maximum 0•606, minimum 0•570; *R* factor 0•060, *wR* 0•075.

4, c-6-Dichloro-2, 5, 6-trimethyl-r-2, t-5-dinitrocyclohex-3-enone (11).—C9H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>5</sub>, M 297·1, monoclinic, space group  $P_{2_1}/c$ , a 8.389(2), b 11.465(2), c 12.820(3) Å,  $\beta 101.37(2)^\circ$ , U 1208.9 Å<sup>3</sup>,  $D_c 1.63$  g cm<sup>-3</sup>, Z 4,  $\mu$ (Mo K $\alpha$ ) 5.50 cm<sup>-1</sup>. The crystal was colourless and of approximate dimensions 0.26 by 0.8 by 0.32 mm. The  $\theta/2\theta$  scan technique was used to collect data at 153 K. Number of independent reflections measured 1820, number with  $I > 3\sigma(I)$  1733; maximum Bragg angle  $\theta 26^\circ$ ; g 0.00045; absorption corrections, maximum 0.79, minimum 0.71; R factor 0.032, wR 0.035.

4, t-6-Dichloro-2, 5, 6-trimethyl-r-2, t-5-dinitrocyclohex-3-enone (12).—C9H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>5</sub>, M 297·1, monoclinic, space group  $P2_1/c$ ,  $a \approx 507(3)$ ,  $b \times 11.471(3)$ ,  $c \times 12.623(3)$  Å,  $\beta \times 103.57^{\circ}$ , U 1197.4(7) Å<sup>3</sup>,  $D_c \times 1.65$  g cm<sup>-3</sup>, Z 4,  $\mu$ (Mo K $\alpha$ ) 5.55 cm<sup>-1</sup>. The crystal was colourless and of approximate dimensions 0.38 by 0.32 by 0.50 mm. The  $\theta/2\theta$  scan technique was used to collect data at 153 K. Number of independent reflections measured 2356, number with  $I > 3\sigma(I) \times 1538$ ; maximum Bragg angle  $\theta \times 26^{\circ}$ ;  $g \times 0.00035$ ; absorption corrections, maximum 0.78, minimum 0.76; R factor 0.035,  $wR \times 0.034$ .

4, t-6-Dichloro-2, 5, 6-trimethyl-r-2, c-5-dinitrocyclohex-3-enone (13).—C9H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>5</sub>, M 297·1, orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, a 6·564(2), b 11·067(3), c 16·375(5) Å, U1189·5 Å<sup>3</sup>,  $D_c$  1·66 g cm<sup>-3</sup>, Z 4,  $\mu$ (Mo K $\alpha$ ) 5·59 cm<sup>-1</sup>. The crystal was colourless and of approximate dimensions 0·24 by 0·20 by 0·40 mm. The  $\theta/2\theta$  scan technique was used to collect data at 153 K. Number of independent reflections measured 1256, number with  $I > 3\sigma(I)$  919; maximum Bragg angle  $\theta$  26°; g 0·00023; absorption corrections, maximum 0·77, minimum 0·73; R factor 0·033, wR 0·030.

#### Structure Determination

The structures were solved by direct methods and difference-Fourier syntheses. Blocked cascade least-squares refinements (SHELXTL)<sup>12</sup> were employed, reflection weights  $1/[\sigma^2(F)+q(F^2)]$  being used. The function minimized was  $\Sigma w(|F_0| - |F_c|)^2$ . Anomalous dispersion corrections were from Cromer and Liberman.<sup>13</sup> All non-hydrogen atoms were assigned anisotropic thermal parameters, except for compound (6) where only the chlorine atoms and oxygen atom were assigned anisotropic thermal parameters. Methyl hydrogen atoms were included as rigid groups pivoting about their carbon atoms. Final Fourier syntheses show no significant residual electron density, and there were no abnormal discrepancies between observed and calculated structure factors. Material deposited with the Australian Journal of Chemistry, 314 Albert Street, East Melbourne, Vic. 3002: temperature factors, structure factor amplitudes, comprehensive interatomic distances, bond angles and torsional angles.

<sup>12</sup> Sheldrick, G. M., SHELX86; A Program for Crystal Structure Solution, Göttingen University, 1986; Sheldrick, G. M., SHELXTL User Manual, Revision 4, Nicolet XRD Corporation, Madison, Wisconsin.

<sup>13</sup> Cromer, D. T., and Liberman, D., J. Chem. Phys., 1970, **53**, 1891.

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