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The Chlorination of 4-Methylbenzene-1,2-diamine: the Formation of 2,3,4,5,5-Pentachloro-6,6-dihydroxy-4-methylcyclohex-2-enone Hydrate and Some Transformation Products

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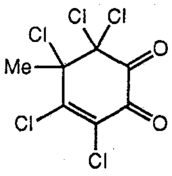
Abstract

Chlorination of 4-methylbenzene-1,2-diamine gives the pentachloro ketone (3) which, on treatment with base, is converted mainly into the hydroxy acid (4). Methylated derivatives (5) and (6), and an unexpected transformation product of the hydroxy acid (4) are described. The chlorination of tetrachlorocatechol (8) gives the hexachloro ketone (9). X-Ray crystal structure determinations are reported for compounds (3)–(7) and (9).

Introduction

In 1897 Zincke and coworkers reported the chlorination of 3,4-diaminotoluene (4-methylbenzene-1,2-diamine) with chlorine in acetic acid containing concentrated hydrochloric acid to give the dihydrate of the pentachloro α-diketone (1) or its isomer (2).[1] In view of this structural uncertainty for the chlorination product, (1) or (2), and our continuing interest in the chlorination of polysubstituted amines and phenols we reexamined the chlorination of 3,4-diaminotoluene. In the event, the product was the monohydrate of 2,3,4,5,5-pentachloro-6,6-dihydroxy-4-methylcyclohex-2-enone (3). We now report the X-ray crystal analysis of this compound and those of several of its transformation products.



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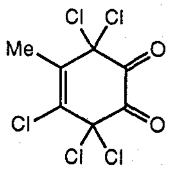

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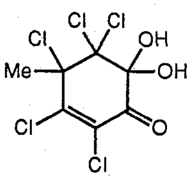

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Discussion

Chlorination of 3,4-diaminotoluene by the procedure of Zincke *et al.*[1] gave a red oil which on crystallization from wet benzene gave the expected product as pale yellow plates, m.p. 86–87° (lit.[1] 90°). The structure of this compound was determined by single-crystal X-ray analysis. The best model produced from the

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[1] Zincke, T., Bergmann, F., and Francke, B., *Justus Liebigs Ann. Chem.*, 1897, **296**, 159.

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data consists of a non-stoichiometric disordering of the substituent atoms C(7) and Cl(4) about carbon atom C(4) with a site occupancy of 0·64 for molecule 1, and a site occupancy factor of 0·36 for the disordered pair C(7′) and Cl(4′) in molecule 2. A perspective drawing of 2,3,4,5,5-pentachloro-6,6-dihydroxy-4-methylcyclohex-2-enone (3) monohydrate, $C_7H_5Cl_5O_3.H_2O$, m.p. 86–87°, is presented in Fig. 1 (for molecule 1) with corresponding atomic coordinates in Table 1. In the solid state the alicyclic ring exists in a flattened [C(1), sp^2] half chair conformation [torsional angles: C(2)–C(3)–C(4)–C(5) −18·7(9)°; C(3)–C(2)–C(1)–C(6) −7(1)°] with the C(4)–C(7) bond in the pesudo-axial orientation in molecule 1. The substituents on neighbouring carbon atoms at C(4), C(5) and C(6) are in close-to-staggered orientations, with the C(1)–O(1) and C(6)–O(62) bonds close to being eclipsed [torsinal angle: O(1)–C(1)–C(6)–O(62) −26·2(8)°]. The structure determined above is related to structure option (1) proposed by Zincke *et al.*[1] except that the non-conjugated carbonyl group exists as the covalent hydrate, presumably as a result of the dipolar repulsions between (i) the α-diketone functions, and (ii) the non-conjugated carbonyl group and the adjacent Cl–C–Cl function.

Zincke *et al.*[1] reported that the α-diketone, (1) or (2), rearranged on treatment with aqueous sodium carbonate, followed by aqueous acid, to give a pentachloro hydroxy acid monohydrate (m.p. 99·5°) with a cyclopentene ring structure. In the present study, a dichloromethane solution of compound (3) was shaken with cold saturated sodium bicarbonate solution for 1 min. The dichloromethane

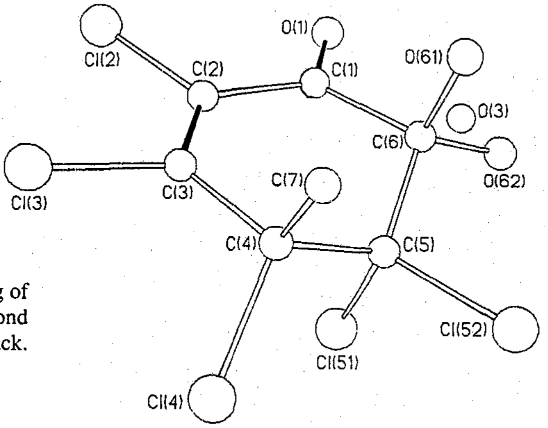
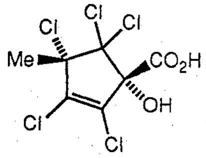


Fig. 1. Perspective drawing of compound (3). Double bond is shown in black.

Table 1. Fractional coordinates for atoms in 2,3,4,5,5-pentachloro-6,6-dihydroxy-4-methylcyclohex-2-enone hydrate (3)

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U$ (Å^2)	Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U$ (Å^2)
Cl(2)	8323(3)	6744(3)	3524(2)	40(1)	O(62)	2193(7)	3329(6)	591(3)	18(1)
Cl(3)	6763(4)	3317(3)	4759(1)	42(1)	C(1)	5276(9)	4749(8)	1958(4)	15(2)
Cl(4)	1780(3)	1103(3)	4058(1)	32(1)	C(2)	6184(10)	4745(9)	3013(4)	18(2)
Cl(51)	793(2)	3914(2)	2484(1)	21(1)	C(3)	5412(10)	3281(9)	3555(4)	18(2)
Cl(52)	−4(2)	−156(2)	1589(1)	21(1)	C(4)	3484(10)	1516(9)	3148(4)	19(2)
O(1)	5897(7)	6124(6)	1481(3)	23(1)	C(5)	2080(9)	1986(8)	2176(4)	14(2)
O(3)	2527(7)	7317(6)	46(3)	18(1)	C(6)	3499(9)	2851(8)	1423(4)	14(2)
O(61)	4582(7)	1418(6)	1152(3)	17(1)	C(7)	4294(7)	−550(6)	2973(3)	42(2)

layer gave some unreacted compound (3), but acidification and extraction of the aqueous layer gave a residue shown (^{1}H n.m.r.) to be a mixture (*c.* 9:1:1) of three compounds. The major component of this mixture was isolated by fractional crystallization and its structure determined by single-crystal X-ray analysis. A perspective drawing of 2,3,*t*-4,5,5-pentachloro-1-hydroxy-4-methylcyclopent-2-ene-*r*-1-carboxylic acid (4) monohydrate, $C_7H_5Cl_5O_3.H_2O$, m.p. 91–93°, is presented in Fig. 2 with corresponding atomic coordinates in Table 2. In the solid state the cyclopentene ring exists in an envelope conformation [torsional angles: C(3)–C(2)–C(1)–C(5) −19·4(9)°; C(2)–C(3)–C(4)–C(5) 16·2(9)°; Cl(2)–C(2)–C(1)–C(6) 47(1)°; Cl(3)–C(3)–C(4)–C(7) −40(1)°], the deviation of the cyclopentene ring from planarity allowing significant staggering of the substituents on neighbouring carbon atoms, C(1) and C(5), and C(4) and C(5) [torsional angles: e.g. Cl(4)–C(4)–C(5)–Cl(52) −43·4(7)°; C(7)–C(4)–C(5)–Cl(52) 78·7(8)°]. The plane of the carboxylic acid group is close to perpendicular to the C(1)–C(5) bond [torsional angle: C(5)–C(1)–C(6)–O(61) −106(1)°]. The stereochemistry of the



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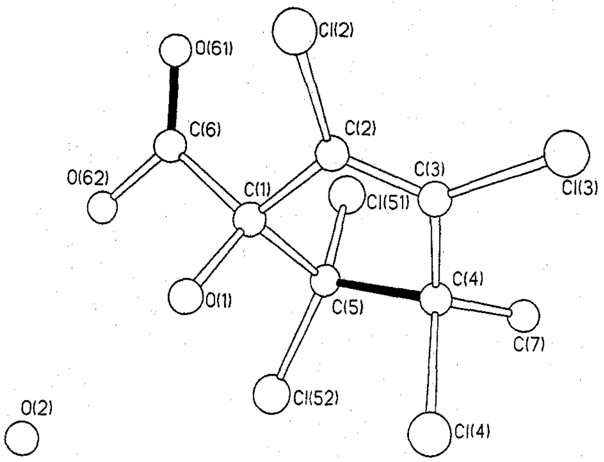


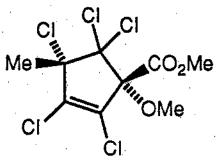
Fig. 2. Perspective drawing of compound (4).

Table 2. Fractional coordinates for atoms in 2,3,*t*-4,5,5-pentachloro-1-hydroxy-4-methylcyclopent-2-ene-*r*-1-carboxylic acid hydrate (4)

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U$ (Å^2)	Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U$ (Å^2)
Cl(2)	1264(2)	−848(3)	5586(2)	33(1)	O(62)	1055(7)	3566(8)	3344(5)	27(3)
Cl(3)	3486(2)	−3255(3)	5185(2)	29(1)	C(1)	1801(8)	725(11)	3801(7)	14(3)
Cl(4)	2939(2)	−2800(3)	2660(2)	30(1)	C(2)	2099(7)	−551(10)	4627(6)	11(3)
Cl(51)	3750(2)	2516(3)	3876(2)	22(1)	C(3)	2972(8)	−1530(10)	4486(6)	13(3)
Cl(52)	2777(2)	1315(3)	2037(2)	20(1)	C(4)	3517(6)	−1103(10)	3523(6)	18(3)
O(1)	968(5)	−67(7)	3213(5)	17(2)	C(5)	2931(8)	802(11)	3294(6)	14(3)
O(2)	18(5)	1551(7)	1515(4)	15(2)	C(6)	1407(8)	2654(11)	4115(7)	13(3)
O(61)	1438(6)	3160(8)	4948(5)	29(3)	C(7)	4702(6)	−1154(12)	3476(7)	25

hydroxy acid (4), with the *syn* arrangement of the methyl and carbonyl groups, is consistent with the rearrangement in solution of the dihydroxy ketone (3) in the half chair conformation given in Fig. 1.

In an attempt to isolate the minor components of the mixture of products from the base-catalysed rearrangement of the dihydroxy ketone (3), a sample of the mixture was reacted with diazomethane in the expectation that the hydroxy esters might be more amenable to chromatography on a silica gel Chromatotron plate. In the event, the Chromatotron separation of the products gave two crystalline fractions and small amounts of intractable mixtures. The two crystalline products (5) and (6) were identified by single-crystal X-ray



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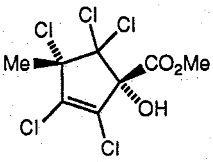

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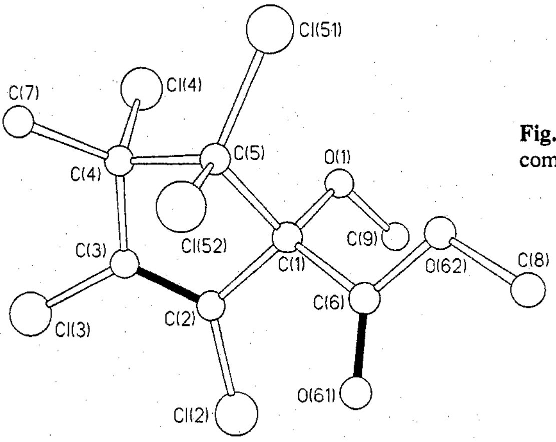
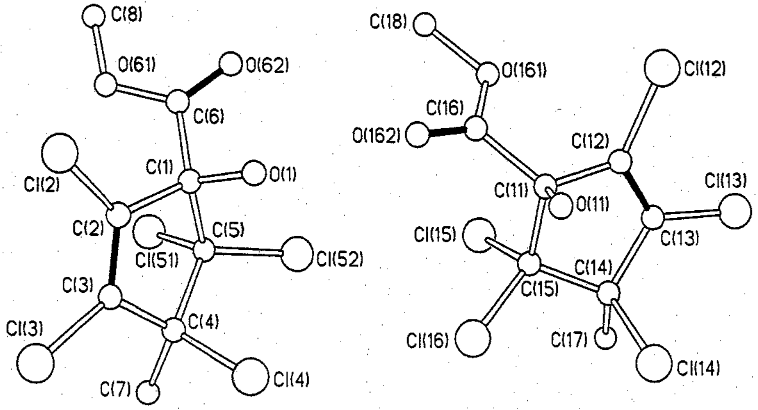


Fig. 3. Perspective drawing of compound (5).

Fig. 4. Perspective drawing of compound (6).



analysis. A perspective drawing of methyl, 2,3,*t*-4,5,5-pentachloro-1-methoxy-4-methylcyclopent-2-ene-*r*-1-carboxylate (5), $C_9H_9Cl_5O_3$, m.p. 91–92°, is presented in Fig. 3, with corresponding atomic coordinates in Table 3. Corresponding data are presented for methyl 2,3,*t*-4,5,5-pentachloro-1-hydroxy-4-methylcyclopent-2-ene-*r*-1-carboxylate (6), $C_8H_7Cl_5O_3$, m.p. 71–72° (Fig. 4 and Table 4). In the solid state, compounds (5) and (6) exist with the cyclopentene ring in closely similar envelope conformations. The significant difference between the conformations of the two compounds lies in the orientation of the CO_2Me group [torsional angles: for (5), O(61)–C(6)–C(1)–C(2) −4·9(8)°; for (6), O(62)–C(6)–C(1)–C(2) 160·9(5)°].

An early, and unrepeatable, reaction of the hydroxy acid mixture (*c*. 9 : 1 : 1) with diazomethane, apparently as above, gave a mixture from which a pure compound (7) could be isolated by chromatography on a silica gel Chromatotron plate followed by crystallization of a major fraction. The structure of this compound was determined by single-crystal X-ray analysis. A perspective drawing of methyl 4,5-dichloro-3-methyl-2-oxo-2*H*-pyran-6-carboxylate (7), $C_8H_6Cl_2O_4$, m.p. 92–95°, is presented in Fig. 5 with corresponding atomic coordinates in Table 5. In the solid state, the heterocyclic ring is essentially planar, and the orientation of the methoxycarbonyl group is indicated by the torsional angle. C(5)–C(6)–C(8)–O(81)

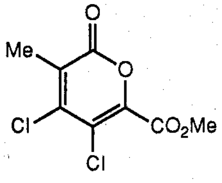
Table 3. Fractional coordinates for atoms in methyl 2,3,*t*-4,5,5-pentachloro-1-methoxy-4-methylcyclopent-2-ene-*r*-1-carboxylate (5)

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U (Å^2)	Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U (Å^2)
Cl(2)	7858(2)	9669(1)	2918(1)	31(1)	C(2)	5736(9)	9624(4)	2570(4)	27(2)
Cl(3)	5382(3)	11391(1)	2992(1)	39(1)	C(3)	4717(10)	10322(4)	2618(4)	28(2)
Cl(4)	2267(2)	9934(1)	3896(1)	31(1)	C(4)	2916(9)	10099(4)	2375(4)	26(2)
Cl(51)	1313(2)	8479(1)	1870(1)	33(1)	C(5)	3031(9)	9181(4)	1719(4)	25(2)
Cl(52)	3041(2)	9386(1)	111(1)	30(1)	C(6)	5554(10)	8191(4)	1306(4)	28(2)
O(1)	4472(7)	8254(3)	3286(3)	30(2)	C(7)	1738(10)	10793(4)	1709(5)	32(2)
O(61)	6723(7)	8417(3)	831(3)	38(2)	C(8)	5394(11)	6871(4)	173(5)	36(2)
O(62)	4708(6)	7439(3)	1088(3)	31(2)	C(9)	5900(11)	7864(4)	3966(5)	39(2)
C(1)	4747(9)	8772(4)	2253(4)	27(2)					

Table 4. Fractional coordinates for atoms in methyl 2,3,*t*-4,5,5-pentachloro-1-hydroxy-4-methylcyclopent-2-ene-*r*-1-carboxylate (6)

	Molecule 1					Molecule 2			
Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U (Å^2)	Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U (Å^2)
Cl(2)	1675(2)	5589(1)	874(1)	32(1)	Cl(12)	6666(2)	−2565(1)	722(1)	33(1)
Cl(3)	3342(2)	7481(1)	2875(1)	32(1)	Cl(13)	8274(2)	−2860(2)	2743(1)	47(1)
Cl(4)	5325(2)	5023(1)	3430(1)	27(1)	Cl(14)	10190(2)	47(1)	3308(1)	30(1)
Cl(51)	−333(2)	4705(1)	3558(1)	23(1)	Cl(15)	4546(2)	436(1)	3380(1)	22(1)
Cl(52)	2513(2)	3072(1)	3443(1)	29(1)	Cl(16)	7415(2)	1962(1)	3238(1)	26(1)
O(1)	3090(4)	3333(3)	1556(3)	20(1)	O(11)	7998(4)	217(3)	1385(2)	18(1)
O(61)	−1268(5)	4158(3)	1437(3)	24(1)	O(161)	3640(4)	−733(3)	1259(3)	22(1)
O(62)	−225(5)	2346(3)	1358(3)	28(1)	O(162)	4650(5)	1051(3)	1201(3)	28(1)
C(1)	1684(7)	4047(4)	1996(4)	17(2)	C(11)	6593(6)	−159(4)	1821(3)	15(2)
C(2)	1986(7)	5287(4)	1925(4)	16(2)	C(12)	6928(7)	−1438(4)	1772(4)	19(2)
C(3)	2709(7)	6035(4)	2713(4)	17(2)	C(13)	7618(7)	−1561(5)	2569(4)	19(2)
C(4)	3044(7)	5466(4)	3482(4)	16(2)	C(14)	7897(7)	−389(5)	3334(4)	20(2)
C(5)	1810(6)	4315(4)	3102(4)	17(2)	C(15)	6693(7)	452(5)	2926(4)	17(2)
C(6)	−57(7)	3416(4)	1552(3)	17(2)	C(16)	4853(7)	134(4)	1386(4)	19(2)
C(7)	2763(7)	6255(5)	4513(3)	18(2)	C(17)	7555(6)	−339(4)	4411(3)	7(1)
C(8)	−3007(8)	3615(6)	1086(5)	32(2)	C(18)	1886(8)	−468(6)	936(5)	32(2)

−19·1(6)°. The spectroscopic data for compound (7) are in accord with the established structure. The precise mode of formation of compound (7) is uncertain, but it is believed that its genesis from the hydroxy acid (4) was due to the accidental introduction of base during the distillation of diazomethane into the reaction vessel. If this thesis is accepted, the formation of compound (7) could be accounted for in terms of the reaction sequence given in Scheme 1.



(7)

Table 5. Fractional coordinates for atoms in methyl 4,5-dichloro-3-methyl-2-oxo-2*H*-pyran-6-carboxylate (7)

Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U (Å^2)	Atom	$10^4X/a$	$10^4Y/b$	$10^4Z/c$	10^3U (Å^2)
Cl(4)	7294(1)	3739(1)	298(1)	28(1)	C(3)	7048(2)	3744(2)	3670(6)	19(1)
Cl(5)	8968(1)	3678(1)	1130(2)	32(1)	C(4)	7558(2)	3737(2)	2417(6)	19(1)
O(1)	8056(1)	3741(2)	5730(4)	19(1)	C(5)	8348(2)	3711(3)	2785(6)	23(1)
O(2)	6900(2)	3813(2)	6666(4)	24(1)	C(6)	8561(2)	3703(2)	4425(6)	21(1)
O(81)	9868(2)	3400(3)	4210(5)	45(1)	C(7)	6220(2)	3729(3)	3421(6)	29(1)
O(82)	9394(1)	3969(2)	6678(4)	28(1)	C(8)	9345(2)	3673(3)	5067(6)	25(1)
C(2)	7295(2)	3776(2)	5436(5)	16(1)	C(9)	10138(2)	3919(3)	7404(7)	33(1)

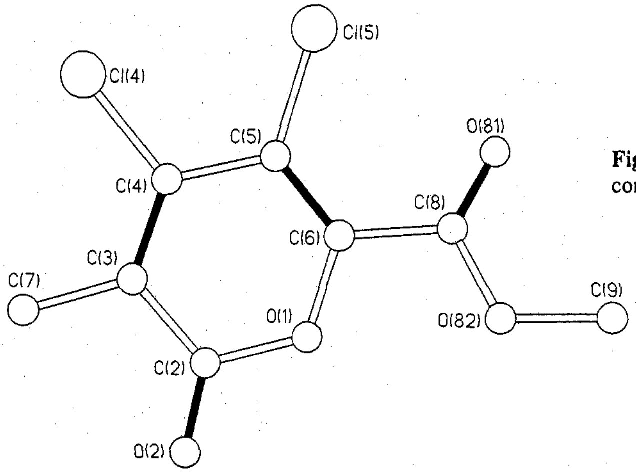


Fig. 5. Perspective drawing of compound (7).

Finally, chlorination[2] of tetrachlorocatechol (8) gave the hexachloro analogue of compound (3) reported above, and its structure was determined by single-crystal X-ray analysis. A perspective drawing of 2,3,4,4,5,5-hexachloro-6,6-dihydroxycyclohex-2-enone (9) hydrate, $C_6H_2Cl_6O_3.H_2O$, m.p. 85–87°, is presented in Fig. 6 with corresponding atomic coordinates in Table 6. In the solid state, the alicyclic ring of compound (9) exists in a half chair conformation closely similar to that reported for the monomethyl derivative (3).

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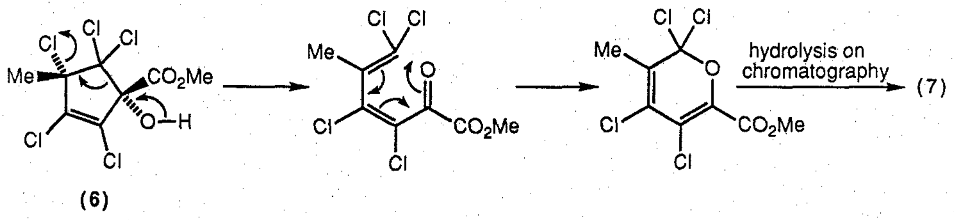
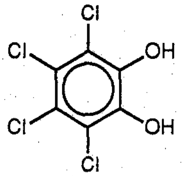
[2] Zincke, T., *Justus Liebigs Ann. Chem.*, 1897, **296**, 135.



Scheme 1



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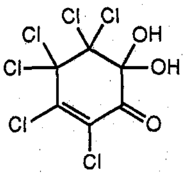

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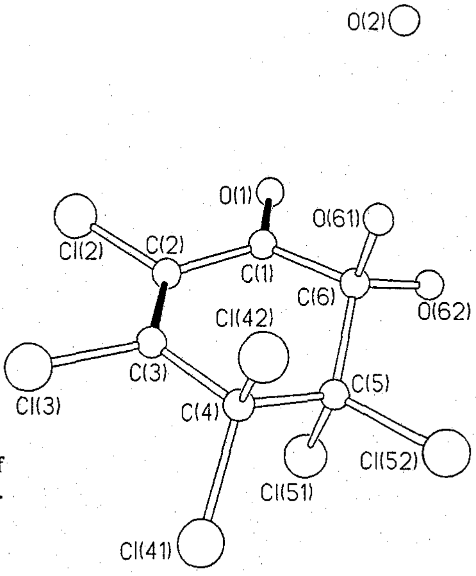

Fig. 6. Perspective drawing of compound (9).

Table 6. Fractional coordinates for atoms in 2,3,4,4,5,5-hexachloro-6,6-dihydroxycyclohex-2-enone hydrate (9)

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U$ (Å^2)	Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U$ (Å^2)
Cl(2)	−1730(1)	−8353(1)	−6468(1)	18(1)	O(61)	−7804(3)	−11694(3)	−9446(1)	17(1)
Cl(3)	−3424(1)	−11858(1)	−5228(1)	27(1)	O(62)	−5458(3)	−13603(3)	−8861(1)	16(1)
Cl(41)	−8447(1)	−13901(1)	−5961(1)	24(1)	C(1)	−4783(4)	−10310(3)	−8062(2)	13(1)
Cl(42)	−5750(1)	−15660(1)	−7040(1)	25(1)	C(2)	−3890(4)	−10338(3)	−6980(2)	14(1)
Cl(51)	−9265(1)	−11091(1)	−7553(1)	18(1)	C(3)	−4682(4)	−11791(3)	−6439(2)	16(1)
Cl(52)	−10099(1)	−15138(1)	−8438(1)	18(1)	C(4)	−6689(4)	−13490(3)	−6864(2)	15(1)
O(1)	−4112(3)	−8952(3)	−8527(1)	20(1)	C(5)	−8027(4)	−13026(3)	−7863(2)	13(1)
O(2)	−2546(3)	−12281(3)	−10078(1)	18(1)	C(6)	−6522(4)	−12180(3)	−8607(2)	13(1)

Experimental

Melting points are uncorrected. Infrared spectra were recorded on Shimadzu IR-27G or Pye-Unicam SP-3 spectrometers; ^1H and ^{13}C n.m.r. spectra were recorded on a Varian XL-300 spectrometer with $SiMe_4$ as an internal standard. Ultraviolet spectra were recorded on a Varian Superscan spectrometer. Silica gel used on Chromatotron (Harrison & Harrison) plates was Merck type P.F. 254.

Reaction of 3,4-Diaminotoluene with Chlorine

Chlorine was bubbled for 12 h at 20° through a stirred solution of 3,4-diaminotoluene (20 g) in acetic acid (200 ml) and concentrated hydrochloric acid (40 ml) in a darkened flask. During the course of the reaction the colour of the solution changed from dark red-brown to golden yellow. The excess chlorine was removed in a stream of nitrogen and the precipitated ammonium chloride was removed by filtration to give an orange solution. The solvents were removed under reduced pressure, the residue was dissolved in dichloromethane and further ammonium chloride was removed by filtration. The solvent was removed under reduced pressure to give a red oil as a residue (42·3 g) which was dissolved in a mixture of benzene (45 ml) and water (4 ml). Pale yellow plates (14·3 g) separated which were identified as 2,3,4,5,5-pentachloro-6,6-dihydroxy-4-methylcyclohex-2-enone hydrate (3), m.p. 86–87° (lit.[1] 90°) (X-ray crystal structure determined below). ^1H n.m.r. ($CDCl_3$) δ 2·56, Me; 6·48, H_2O; 7·36, OH. ν_{max} (KBr) 3550 (OH), 3130 (H_2O), 1718 (C=O), 1650 (C=C), 1120 cm^{-1} (OH).

Base-Catalysed Rearrangement of 2,3,4,5,5-Pentachloro-6,6-dihydroxy-4-methylcyclohex-2-enone Hydrate (3)

A solution of the pentachloro ketone (3) (2 g) in dichloromethane (150 ml) and cold (0°) saturated aqueous sodium bicarbonate (75 ml) were mixed and shaken for 1 min. The dichloromethane solution was separated, washed with water, and dried with magnesium sulfate, and the solvent was removed under reduced pressure to give a residue (445 mg) identified as unreacted pentachloro ketone (3). The aqueous bicarbonate layer was acidified with dilute hydrochloric acid, and the resulting mixture was extracted with dichloromethane. The solvent was removed from the dichloromethane solution to give a pale yellow residue (1·823 g) which was shown (^1H n.m.r.) to be essentially a mixture (*c.* 9 : 1 : 1) of three components. This mixture was treated in three ways.

(i) Fractional crystallization of this mixture, initially from benzene and a trace of water, but finally from ether/light petroleum mixtures gave 2,3,*t*-4,5,5-pentachloro-1-hydroxy-4-methylcyclopent-2-ene-*r*-1-carboxylic acid hydrate (4), m.p. 91–93° (lit.[1] 99·5°) (X-ray crystal structure determined below). ^1H n.m.r. ($CDCl_3$) δ 2·03, Me; 4·35, H_2O, OH. ^{13}C n.m.r. ($CDCl_3$) δ 25·30, Me; 79·26, C 4; 87·54, C 5; 93·40, C 1; 129·45, C 3; 138·06, C 2; 168·70, CO_2H. ν_{max} (KBr) 2400–3600 (CO_2H, OH), 1728 (C=O), 1623 (C=C), 1100 cm^{-1} (OH).

(ii) Diazomethane, prepared by addition of potassium hydroxide (400 mg) in ethanol (10 ml) to a solution of *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide (2·14 g) in ether (30 ml) at 0°, was distilled into a solution of the hydroxy acid mixture (200 mg) in ether (10 ml) at −78° and the temperature of the mixture was then allowed to rise to 0°. The residue (203 mg), after removal of the solvent under reduced pressure, was absorbed onto a silica gel Chromatotron plate at 4°. Elution with pentane/ether mixtures gave two crystalline fractions and four fractions which were shown to be mixtures.

The less polar of the two crystalline fractions was identified as *methyl 2,3,*t*-4,5,5-pentachloro-1-methoxy-4-methylcyclopent-2-ene-*r*-1-carboxylate* (5) (18 mg), m.p. 91–92° (X-ray crystal structure determined below). ^1H n.m.r. ($CDCl_3$) δ 1·98, Me; 3·56, OMe; 3·92, CO_2Me. ν_{max} (KBr) 1749 (C=O), 1614 (C=C), 1455 cm^{-1} (C–O–Me).

The more polar of the crystalline fractions was identified as *methyl 2,3,*t*-4,5,5-pentachloro-1-hydroxy-4-methylcyclopent-2-ene-*r*-1-carboxylate* (6) (100 mg), m.p. 71–72° (X-ray crystal structure determined below). ^{1}H n.m.r. ($CDCl_3$) δ 1·99, Me; 3·93, CO_2Me. ν_{max} (KBr) 3450 (OH), 1724 (C=O), 1626 cm^{-1} (C=C).

(iii) One (unrepeatable) reaction of the hydroxy acid mixture (100 mg) with diazomethane, apparently as above, gave after the methylation procedure a residue (108 mg). Chromatography of this material on a silica gel Chromatotron plate at 4° gave a series of fractions which were complex mixtures and a single crystalline fraction (57 mg) shown (^{1}H n.m.r.) to be a mixture (*c.* 3:2) of two compounds. Crystallization of this material from pentane gave the major component identified as *methyl 4,5-dichloro-3-methyl-2-oxo-2*H*-pyran-6-caboxylate* (7), m.p. 92–95° (X-ray crystal structure determined below). ^{1}H n.m.r. ($CDCl_3$) δ 1·98, Me; 3·924, CO_2Me ν_{max} (KBr) 1729 cm^{-1} (C=O). λ_{max} (cyclohexane) 312 nm (ϵ 10170). The minor component of the mixture could not be isolated in a pure state but gave ^{1}H n.m.r ($CDCl_3$) δ 2·33, 3H; 3·96, 3H; 4·21, 1H.

Chlorination of Tetrachlorocatechol (8)

Chlorine was bubbled slowly through a stirred solution of tetrachlorocatechol (8) (5 g) in acetic acid (43 ml) for 1·5 h. The reaction flask was then stoppered and the mixture stored at 20° for 2 days. The mixture was then poured into excess water at 0° and the colourless solid (5·8 g) which separated was isolated by filtration. Crystallization from ether/light petroleum gave 2,3,4,4,5,5-hexachloro-6,6-dihydroxycyclohex-2-enone hydrate (9), m.p. 85–87° (lit.^{2} 90–95°) (X-ray crystal structure determined below). ν_{max} (KBr) 3600–3200 (OH, H_2O), 1730 (C=O), 1630 cm^{-1} (C=C).

Crystallography

Crystal data, established from precession photographs and measured accurately, by means of a Nicolet XRD P3 four-circle diffractometer [molybdenum X-radiation, λ(Mo Kα) 0·71069 Å, from a crystal monochromator], are given below. The space group was, in each case, determined unambiguously as a result of the structure analyses reported below, but initially indicated by conditions limiting possible reflections. $\theta/2\theta$, Wyckoff or ω-scans were used to collect reflection intensities out to a maximum Bragg angle, θ, given below. The cell parameters were determined, in each case, by least-squares refinements for which the setting angles of 25 accurately centred high-angle reflections were used.

Crystal Data

2,3,4,5,5-Pentachloro-6,6-dihydroxy-4-methylcyclohex-2-enone hydrate (3).—$C_7H_5Cl_5O_3.H_2O$, *M* 332·4, triclinic, $P\bar{1}$, *a* 6·381(2), *b* 6·923 (2), *c* 13·731(3) Å, α 93·86(2)°, β 100·28(2)°, γ 104·01(2)°, *V* 575·2(3) Å^3, D_c 1·92 g cm^{-3}, *Z* 2, μ (Mo Kα) 12·5 cm^{-1}. The crystal was pale yellow and of approximate dimensions 0·10 by 0·68 by 0·4 mm. $\theta/2\theta$-Scans were used to collect data at 153 K out to a maximum Bragg angle θ 25°. The number of independent reflections measured 2029, 1807 with $I > 3\sigma(I)$; *g* 0·00072; absorption corrections were not applied; *R*-factor 0·063, *wR* 0·073.

The model first refined (molecule 1), *R* 0·081, showed significant residual electron density around methyl carbon atom C(7) in the difference-Fourier map. This discrepancy could not be explained satisfactorily by a translational disordering of the methyl group or by total interchange of the substituents C(7) and Cl(4) attached to carbon atom C(4) (namely molecule 2). The best model produced from the data consists of a non-stoichiometric disordering of the substituent atoms C(7) and Cl(4) about C(4). The result was a site occupancy of 0·64 for the atoms C(7) and Cl(4) in the positions represented by molecule 1, and a site occupancy factor of 0·36 for the disordered pair C(7′) and Cl(4′) in the positions represented by molecule 2, *R*-factor 0·063.

*2,3,*t*-4,5,5-Pentachloro-1-hydroxy-4-methylcyclopent-2-ene-*r*-1-carboxylic acid hydrate (4).*—$C_7H_5Cl_5O_3.H_2O$, *M* 332·4, monoclinic, space group $P2_1/c$, *a* 12·211(4), *b* 7·332(2), *c* 13·724(4) Å, β 92·66(3)°, *V* 1227·5(4) Å^3, D_c 1·804 g cm^{-3}, *Z* 4, μ(Mo Kα) 11·7 cm^{-1}. The crystal was colourless and of approximate dimensions 0·31 by 0·40 by 0·05 mm. ω-Scans were used to collect data at 173 K out to a maximum Bragg angle θ 22·5°. The number of independent reflections measured 1545, 1015 with $I > 3\sigma(I)$; g 0·0001; absorption corrections were not applied; R-factor 0·051, wR 0·053.

*Methyl 2,3,*t*-4,5,5-pentachloro-1-methoxy-4-methylcyclopent-2-ene-*r*-1-carboxylate (5).*—$C_9H_9Cl_5O_3$, M 342·5, monoclinic, space group, $P2_1/n$, a 8·092(4), b 14·97(1), c 10·914(7) Å, β 97·54(5)°, V 1311·0(1) Å^3, D_c 1·725 g cm^{-3}, Z 4, μ(Mo Kα) 11·04 cm^{-1}. The crystal was colourless and of approximate dimensions 0·14 by 0·60 by 0·64 mm. ω-Scans were used to collect data at 163 K out to a maximum Bragg angle θ 24·5°. The number of independent reflections measured 1752, 1016 with $I > 3\sigma(I)$; g 0·00031; absorption corrections were not applied; R-factor 0·048, wR 0·049.

*Methyl 2,3,*t*-4,5,5-pentachloro-1-hydroxy-4-methylcyclopent-2-ene-*r*-1-carboxylate (6).*—$C_8H_7Cl_5O_3$, M 328·5, triclinic, $P\bar{1}$, a 7·582(5), b 11·693(7), c 14·83(1) Å, α 72·26(5)°, β 87·56(5)°, γ 90·28(5)°, V 1251·5 Å^3, D_c 1·743 g cm^{-3}, Z 4, μ(Mo Kα) 11·53 cm^{-1}. The crystal was colourless and of approximate dimensions 0·79 by 0·44 by 0·04 mm. Wyckoff scans were used to collect data at 163 K out to a maximum Bragg angle θ 25·5°. The number of independent reflections measured 4258, 3140 with $I > 3\sigma(I)$; g 0·00111; absorption corrections, maximum 0·878, minimum 0·768; R-factor 0·052, wR 0·054. The structure consists of two crystallographically independent molecules in the asymmetric unit which are approximately related by a pseudo glide plane perpendicular to the a axis. This pseudosymmetry gives rise to some systematically weak reflections.

*Methyl 4,5-dichloro-3-methyl-2-oxo-2*H*-pyran-6-carboxylate (7).*—$C_8H_6Cl_2O_4$, M 237·04, orthorhombic, *Pbca*, a 7·844(6), b 13·10(1), c 17·98(2) Å, V 1846 Å^3, D_c 1·71 g cm^{-3}, Z 8, μ(Mo Kα) 6·85 cm^{-1}. The crystal was colourless and of approximate dimensions 0·84 by 0·46 by 0·24 mm. ω-Scans were used to collect data at 153 K out to a maximum Bragg angle θ 25°. The number of independent reflections measured 1624, 1267 with $I > 3\sigma(I)$; g 0·00719; absorption corrections, maximum 0·932, minimum 0·469; R-factor 0·085, wR 0·092.

2,3,4,4,5,5-Hexachloro-6,6-dihydroxycyclohex-2-enone hydrate (9).—$C_6H_2Cl_6O_3.H_2O$, M 352·82, triclinic, $P\bar{1}$, a 6·376(2), b 7·015(2), c 13·618(5) Å, α 93·49(3)°, β 99·90(3)°, γ 103·94(2)°, V 579·02 Å^3, D_c 2·03 g cm^{-3}, Z 2, μ(Mo Kα) 14·85 cm^{-1}. The crystal was colourless and of approximate dimensions 0·48 by 0·08 by 0·28 mm. ω-Scans were used to collect data at 153 K out to a maximum Bragg angle θ 25°. The number of independent reflections measured 3368, 2640 with $I > 3\sigma(I)$; g 0·00060; absorption corrections, maximum 0·840, minimum 0·730; R-factor 0·034, wR 0·035.

Structure Determination

The structures were solved by direct methods and difference-Fourier syntheses. Blocked cascade least-squares refinements[3] were employed, reflection weights $1/[\sigma^2(F)+g(F^2)]$ being used. The function minimized was $\sum w(|F_o|-|F_c|)^2$. Anomalous dispersion corrections were from Cromer and Liberman.[4] All non-hydrogen atoms 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, P.O. Box 89, East Melbourne, Vic. 3002: temperature factors, structure factor amplitudes, comprehensive interatomic distances, bond angles, torsional angles, and hydrogen atom coordinates.

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