Polychlorodimethylcyclohexenones, Polychlorotrimethylcyclohexenones, and Related Polychlorocyclohexadienones

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The structures of 29 polychloroalicyclic ketones prepared by the chlorination of polymethylated phenols and anilines and three related polychloro-2-cyclohexenones were determined by nuclear magnetic resonance, infrared, and ultraviolet spectroscopy. The effects of neighboring groups on the chlorination sequence and the stereochemistry of these cyclic ketones are discussed.

Polychloro-cyclohexadienones and -cyclohexenones were found to be active promoters for the cross-linking of polymers (*3*). It was desirable to study the structure of these compounds to determine the relation of promoter activity and structure. Denivelle and Fort (*1*) reported the ir and uv spectra of the polychlorohexenones formed by the chlorination of pentachlorophenol. The ir spectra of polychloroketones prepared from 3,5-dimethylphenol were reported by Kumamoto and Kato (*2*). Recently, Vollbracht and co-workers (*6*) determined the structure of similar products derived from 2,5-dimethyl-, 2,6-dimethyl-, and 3,5-dimethylphenols by ir, uv, and nmr spectroscopy. In our previous report (*4*), the structure of numerous novel alicyclic polychloroketones obtained from phenols, cresols, and toluidienes were determined by similar spectroscopic methods.

In this study the stereochemistry of the polychloroketones obtained mainly by the chlorination of dimethyl and trimethylphenols and the corresponding methylated anilines is investigated and discussed.

EXPERIMENTAL METHODS

The uv spectra were obtained as methanol solutions with a Cary model-11 spectrophotometer; the ir spectra of solids as nujol mulls and liquids as thin films with the Perkin-Elmer model 21 spectrophotometer; and the nmr spectra as chloroform-d solutions with the Varian Associates A-60 spectrometer.

The polychloroketones given in Table I were prepared by the procedures described previously (*4*). The majority of the starting materials were obtained from Aldrich Chemical Co. and used without further purification. The trichlorophenols were

Table I. Preparations of Polychloro-hexadienones and -hexenones

Polychloroketones	Mp, °C	Empirical formula	Starting materials
1	Liquid	$C_8H_6Cl_4O$	Trichloro-2,3-dimethylphenol[a]
2	53–54	$C_8H_6Cl_4O$	Trichloro-2,5-dimethylphenol[a]
3	Liquid	$C_8H_6Cl_4O$	Trichloro-2,6-dimethylphenol[a]
4	78–79	$C_8H_6Cl_4O$	Trichloro-3,5-dimethylphenol[a]
5	Liquid	$C_8H_7Cl_3O$	4,6-Dichloro-2,3-dimethylphenol[a]
6	57–58	$C_8H_7Cl_3O$	4,6-Dichloro-2,5-dimethylphenol[a]
7	Liquid	$C_8H_7Cl_3O$	3,4-Dichloro-2,6-dimethylphenol[a]
8	Liquid	$C_8H_8Cl_2O$	4-Chloro-2,6-dimethylphenol[a]
9	Liquid	$C_9H_9Cl_3O$	Dichloro-2,3,5-trimethylphenol[a]
10 (70%)	Liquid	$C_9H_9Cl_3O$	Dichloro-2,3,6-trimethylphenol[a]
11	Liquid	$C_9H_{10}Cl_2O$	4-Chloro-2,3,6-trimethylphenol[a]
12	105–106	$C_8H_6Cl_4O$	3,5-Dimethylphenol[b]
13, 2	Liquid	$C_8H_6Cl_4O$	Trichloro-2,5-dimethylphenol[b]
14, 1	Liquid	$C_8H_6Cl_4O$	Trichloro-2,3-dimethylphenol[c]
15	132–133	$C_8H_7Cl_5O$	2,5-Dimethylphenol[b]
15, 16	119–120	$C_8H_7Cl_5O$	2,5-Dimethylaniline[c]
17	131–132	$C_8H_7Cl_5O$	4,6-Dichloro-2,3-dimethylphenol[b]
17, 18	87–89	$C_8H_7Cl_5O$	2,3-Dimethylaniline[c]
19	120–121.5	$C_8H_7Cl_5O$	2,6-Dimethylphenol[b]
20	Liquid	$C_8H_8Cl_4O$	2,6-Dimethylaniline[c]
21	118–119	$C_9H_{10}Cl_4O$	2,3,6-Trimethylphenol[c]
22	94	$C_8H_6Cl_6O$	Trichloro-2,5-dimethylphenol[c]
23	82–83	$C_8H_6Cl_6O$	3,5-Dimethylphenol[b]
24	142–143	$C_8H_6Cl_6O$	2,3-Dimethylphenol[b]
25	88–89	$C_8H_6Cl_6O$	2,3-Dimethylphenol[b]
26, 27	Liquid	$C_9H_9Cl_5O$	Dichloro-2,3,5-trimethylphenol[c]
28, 3	Liquid		2,5-Dimethylphenol[b]
29, 25, 14	Liquid		2,3-Dimethylphenol[b]
30	Liquid	C_6HCl_7O	3-Chloroaniline[c]
31, A	Liquid	$C_7H_4Cl_6O$	3-Chloro-6-methylaniline[c]
32, B	Liquid	$C_7H_4Cl_6O$	3-Chloro-2-methylaniline[c]

Elemental analyses (Cl) for isolated compounds or mixtures of isomers in agreement with theoreitcal values have been obtained and submitted for review.

[a] Chlorinated in carbon tetrachloride in the presence of pyridine. [b] Chlorinated in 95% acetic acid. [c] Chlorinated in mixture of concentrated hydrochloric acid and acetic acid.

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Table II. Spectroscopic Data of Cyclohexadienones

	Nmr					Ir		Uv	
Cyclohexadienones	2 C, ppm	3 C, ppm	5 C, ppm	6 C, ppm	Coupling constant, Hz	$\nu_{C=O}$, cm^{-1}	$\nu_{C=C}$, cm^{-1}	λ_{max}, mμ	ϵ_{max}, D
2,4-Cyclohexadien-1-ones									
1 2,3,4,6-Tetrachloro-5,6-dimethyl-	...	...	2.28 (s)	1.87 (s)	...	1692	1602 1540	352	3020
2 2,4,5,6-Tetrachloro-3,6-dimethyl-	...	2.49 (s)	...	1.98 (s)	...	1685	1600 1538	353	3430
3 3,4,5,6-Tetrachloro-2,6-dimethyl-	2.13 (s)	...	...	1.91 (s)	...	1690	1602 1560	342	...
4 2,4,6,6-Tetrachloro-3,5-dimethyl-	...	2.47 (s)	2.38 (s)	...	...	1678	1615 1552	363	2910
5 2,4,6-Trichloro-5,6-dimethyl-	...	7.26 (m)[a]	2.18 (s)	1.84 (s)	$J_{H-CH_3} = 0.4$	1690	1620 1572	350	2230
6 2,4,6-Trichloro-3,6-dimethyl-	...	2.37 (d)	6.48 (m)[a]	1.78 (s)	$J_{H-CH_3} = 0.4$	1685	1630 1558	342	2525
7a 3,4,6-Trichloro-2,6-dimethyl	2.14 (d)	...	6.54 (m)[a]	1.77 (s)	$J_{H-CH_3} = 0.8$	1687	1650 1618 1575	337	2773
7b 4,5,6-Trichloro-2,6-dimethyl-	2.00 (d)	6.85 (m)[a]	...	1.88 (s)	$J_{H-CH_3} = 1.5$				
8 4,6-Dichloro-2,6-dimethyl-	2.00 (m)	6.72 (m)[a]	6.35 (m)	1.73 (s)	Broad	1678	1636 1586	326	1643
9 2,4,6-Trichloro-3,5,6-trimethyl-	...	2.42 (m)	2.20 (m)	1.82 (s)	Broad	1685	1616 1563	353	...
10 3,4,6-Trichloro-2,5,6-trimethyl-	2.13 (m)	...	2.24 (m)	1.77 (s)	$J_{CH_3-CH_3} = 0.6$	1677	1612 1573	340	2491
11 4,6-Dichloro-2,5,6-trimethyl-	1.96 (m)	6.80 (m)[a]	2.10 (m)	1.74 (s)	$J_{H-CH_3(2)} = 1.4$	1677	1639 1599	337	2563
2,5-Cyclohexadien-1-ones									
12 2,4,4,6-Tetrachloro-3,5-dimethyl-	...	2.51 (s)	2.51 (s)	...	...	1681	1607	255	14690
13 2,4,4,5-Tetrachloro-3,6-dimethyl-	...	2.53 (s)	...	2.15 (s)	...	1675	1600	250	...
14 2,3,4,4-Tetrachloro-5,6-dimethyl-	...	...	2.39 (m)	2.02 (m)	$J_{CH_3-CH_3} = 1.1$	1678	1600	253	...

[a] δCH.

prepared by the chlorination of appropriate phenols in acetic acid or by the dehydrochlorination of the appropriate 3-cyclohexenones.

RESULTS AND DISCUSSIONS

2,4-Cyclohexadien-1-ones. The 2,4-cyclohexadienones show a characteristic uv absorption peak at 335–65 mμ, while ir absorption for a conjugated double bond occurs as double peaks between 1650 and 1530 cm^{-1} (*1*, *4*). The spectral data of the 2,4-cyclohexadienones identified are given in Table II.

From phenols with an *o*-methyl group, 2,4-hexadienones with a 6-methyl group are predominantly obtained owing to the ease of chlorine addition of the methylated α-carbon. The structures of **1**, **2**, **3**, **5**, and **6** given in Table II are based on the significantly high field chemical shift of the 6-methyl protons characteristic of these 2,4-hexadienones (*4*).

The assignments determined for **9** are justified since the chemical shift of the 5-methyl group should be slightly upfield in relation to the $\delta CH_3 = 2.28$ ppm for the 5-methyl protons of **1** due to the presence of a third methyl group in **9**.

Conversely, since a third methyl group is absent in **4**, the proton chemical shifts of the 5-methyl group, and to a lesser degree the 3-methyl group, of **4** should be downfield relative to $\delta CH_3 = 2.20$ and 2.42 ppm of **9**, respectively. This is observed: the downfield $\delta CH_3 = 2.47$ ppm of **4** corresponding to the methyl at the 3-position. By analogy, the δCH_3 at 5C of **10** would be slightly downfield relative to $\delta CH_3 = 2.20$ ppm of **9**.

The liquid ketone **7** derived from 3,4-dichloro-2,6-dimethylphenol contained two isomers **7a** (60%) and **7b** (40%). The assignments of the proton chemical shifts of **7a** and **7b** were made by reference to the $\delta CH_3 = 2.13$ ppm at the 2-position of **3**. The difference in the magnitude of the coupling constants, $J_{H-CH_3} = 0.8$ Hz for **7a** and 1.5 Hz for **7b** also supports these assignments.

The assignments of the chemical shifts of **8** and **11** were made in relation to **7a** and **7b**, giving consideration to the additional olefinic proton in **8** and methyl group in **11**, respectively.

2,5-Cyclohexadien-1-ones. The 2,5-cyclohexadienones are less readily formed from *o*-methylated phenols (*4*). Those identified in this study are given in Table II. The ir absorption frequency of the carbonyl group of these ketones is lower and the uv absorption frequency higher than that of the 2,4-cyclohexadienones.

The spectral data of **12** were reported previously (*2*, *6*).

Ketone **13** was identified together with **2** in the liquid chlorination product of trichloro-2,5-dimethylphenol. It is clear from **12** that in **13** the δCH_3 = 2.53 ppm corresponds to the 3-methyl group and the upfield δCH_3 = 2.15 ppm to the 6-methyl group.

Similarly, the upfield δCH_3 = 2.02 ppm of **14** corresponds to the 6-methyl group. The coupling of the methyl protons $J_{CH_3-CH_3}$ = 1.5 Hz indicates the methyl groups in **14** are both bound to the double bond. Ketone **1,** formed together with **14** by the chlorination of trichloro-2,3-dimethylphenol, was observed to transform slowly into **14** on standing at ambient temperature. Ketone **4** also transforms into **12** upon heating in acetic acid. These results indicate the greater stability of the 2,5-hexadienones relative to the 2,4-hexadienones.

3-Cyclohexen-1-ones. Usually, 3-cyclohexenones are the principal products of the exhaustive chlorination of phenols and anilines in acetic acid. The structure of these ketones is most interesting because of the occurrence of numerous stereoisomers as shown in Table III. The 3-cyclohexenones show a characteristic ir absorption peak for a nonconjugated carbonyl group with chlorinated α-carbons $\nu_{C=O}$ = 1730–1780 cm^{-1} and an uv absorption peak at the shorter wave length of 216–32 mμ.

A pentachlorocyclohexenone (**15**), mp 132–3°C, is obtained by the chlorination of 2,5-dimethylphenol (*5*). It was correctly identified as 2,2,4,5,6-pentachloro-3,6-dimethyl-3-cyclohexen-1-one and its 6-methyl group was reported to be equatorial from its ir spectrum (*6*). The fact that **15** may be readily

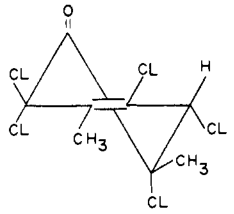
Table III. Spectroscopic Data of Cyclohexenones

		Nmr					Ir		Uv	
	Cyclohexenones	2 C, ppm	3 C, ppm	5 C, ppm	6 C, ppm	Coupling constant, Hz	$\nu_{C=O}$, cm^{-1}	$\nu_{C=C}$, cm^{-1}	λ_{max}, mμ	ϵ_{max}, D
	3-Cyclohexen-1-ones									
15	2,2,4,5,6-Pentachloro-3,6-dimethyl-	. . .	2.30 (d)	4.71 (m)[a]	1.93 (s), (e)[b]	J_{H-CH_3} = 0.6	1747	1640	220	8060
16	2,2,4,5,6-Pentachloro-3,6-dimethyl-	. . .	2.29 (d)	4.75 (m)[a]	2.10 (s), (a)[b]	J_{H-CH_3} = 0.6	. . .	. . .	. . .	. . .
17	2,4,5,6,6-Pentachloro-2,3-dimethyl-	2.06 (s), (a)	2.11 (d)	5.06 (m)[a]	. . .	J_{H-CH_3} = 0.4	1770	1640	222	7300
18	2,4,5,6,6-Pentachloro-2,3-dimethyl-	1.89 (s), (e)	2.14 (d)	5.04 (m)[a]	. . .	J_{H-CH_3} = 0.6	1752	1640	220	7100
19	2,3,4,5,6-Pentachloro-2,6-dimethyl-	2.11 (s), (e)	. . .	4.83 (s)[a]	1.93 (s), (a)	. . .	1746	1635	227	8300
20a	2,4,5,6-Tetrachloro-2,6-dimethyl-	1.99 (s), (a)	6.17 (d)[a]	4.66 (d)[a]	1.91 (s), (a)	J_{H-H} = 1.5	1730	1642	216	5930
20b	2,4,5,6-Tetrachloro-2,6-dimethyl-	1.87 (s), (e)	6.18 (d)[a]	4.65 (d)[a]	1.80 (s), (e)	J_{H-H} = 1.5				
21a	2,4,5,6-Tetrachloro-2,3,6-trimethyl-	2.02 (s), (a)	2.11 (d)	4.76 (m)[a]	1.92 (s), (a)	J_{H-CH_3} = 0.5	1755	1665	220	7673
21b	2,4,5,6-Tetrachloro-2,3,6-trimethyl-	1.89 (s), (e)	2.14 (d)	4.73 (m)[a]	1.82 (s), (e)	J_{H-CH_3} = 0.5				
22	2,3,4,5,6,6-Hexachloro-2,5-dimethyl-	2.19 (s), (e)	. . .	2.25 (s)	. . .	. . .	1755	1610	232	7400
23	2,2,4,5,6,6-Hexachloro-3,5-dimethyl-	. . .	2.31 (s)	2.21 (s)	. . .	. . .	1780	1620	224	6850
24	2,2,3,4,5,6-Hexachloro-5,6-dimethyl-	. . .	. . .	1.98 (s) (a)	1.98 (s). (a)	. . .	1768	1594	228	6450
25	2,2,3,4,5,6-Hexachloro-5,6-dimethyl-	. . .	. . .	2.06 (s) (e)	2.02 (s), (e)	. . .	1752	1599	231	6900
26	2,2,4,5,6-Pentachloro-3,5,6-trimethyl-	. . .	2.29 (s)	2.03 (s), (e)	2.01 (s), (e)	. . .	1760	1635	227	. . .
	2-Cyclohexen-1-ones									
27	2,4,4,5,6-Pentachloro-3,5,6-trimethyl-	. . .	2.47 (s)	2.21 (s)	2.07 (s)	. . .	1725	1610	252	. . .
28	2,4,4,5,6-Pentachloro-3,6-dimethyl-	. . .	2.53 (s)	5.08 (s)[a]	1.87 (s)	. . .	1715	1600	247	. . .
29	2,3,4,4,5,6-Hexachloro-5,6-dimethyl-	. . .	. . .	2.27 (s)	2.19 (s)	. . .	1717	1575	252	. . .
30	2,3,4,4,5,6,6-Hepta-chloro-	. . .	. . .	5.21 (s)[a]	. . .	. . .	1720	1568	263	. . .
31	2,3,4,4,5,6-Hexachloro-6-methyl-	. . .	. . .	5.17 (s)[a]	1.93 (s)	. . .	1720	1575	255	. . .
32	3,4,4,5,6,6-Hexachloro-2-methyl-	2.23 (s)	. . .	5.24 (s)[a]	. . .	. . .	1709	1610	253	. . .

[a] δCH. [b] (a) and (e) signify axial and equatorial, respectively.

prepared from, and dehalogenated back to, 4,6-dichloro-2,5-dimethylphenol supports the structure of **15** with the methine proton at the 5-position.

Rapid chlorination of 2,5-dimethylaniline gives a pentachloro-3-cyclohexenone, which melts at 119–20°C upon recrystallization from pet-ether. Its ir spectrum shows additional medium absorption bands at 873 and 944 cm^{-1} not present in **15**. Nmr spectra indicate that it contains 75% **15** and 25% of another ketone (**16**). Ketones **15** and **16** are stereoisomers with two nonequivalent methyl groups and the downfield methyl protons are coupled with the methine proton. The only significant difference in the nmr spectra of the two is the chemical shifts of the upfield 6-methyl protons. The chemical shifts of the equatorial and axial 6-methyl protons of the stereoisomers of 2,2,3,4,5,6-hexachloro-6-methyl-3-cyclohexen-1-one (A) have been previously determined to be $\delta\mathrm{CH_3}$ = 1.99 and 2.12 ppm, respectively (*4*). By reference to A, the 6-methyl group of **15**, which shows the higher field-proton chemical shift $\delta\mathrm{CH_3}$ = 1.93 ppm, is equatorial and the downfield 6-methyl group of **16** $\delta\mathrm{CH_3}$ = 2.10 ppm axial. This is in agreement with the aforementioned configuration proposed for **15**.



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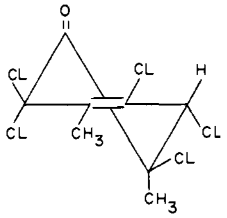

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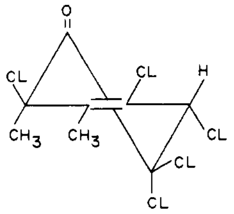
Rapid chlorination of 4,6-dichloro-2,3-dimethylphenol gives 2,4,5,6,6-pentachloro-2,3-dimethyl-3-cyclohexen-1-one (**17**), mp 131–2°C. However, a rapid chlorination of 2,3-dimethylaniline gives a mixture of 25% **17** and 75% of its stereoisomer (**18**). The high ir absorption frequency $\nu_{\mathrm{C-O}}$ = 1770 cm^{-1} of **17** clearly indicates that the chlorine at the 2-position is equatorial, therefore, the 2-methyl group ($\delta\mathrm{CH_3}$ = 2.06 ppm) is axial. The 2-methyl group ($\delta\mathrm{CH_3}$ = 1.89 ppm) of **18** is then equatorial. This is in agreement with the lower absorption frequency $\nu_{\mathrm{C-O}}$ = 1752 cm^{-1} of the above mixture in which **18** is the major component. This relationship between the steric configuration and the chemical shift of the 2-methyl proton is the reverse of that previously found for the stereoisomers of 2,3,4,5,6,6-hexachloro-2-methyl-3-cyclohexen-1-one (B) (*4*). In B, $\delta\mathrm{CH_3}$ = 2.01 and 2.17 ppm, correspond, respectively, to the axial and equatorial 2-methyl protons. The reversal may be due to the presence of an adjacent methyl group.



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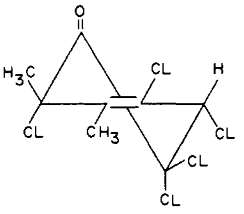

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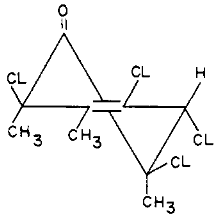
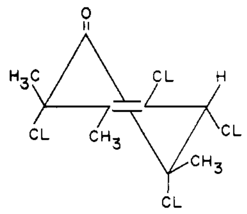
The 3-cyclohexenone **21**, mp 118–19°C, derived from 2,3,6-trimethylphenol contains two stereoisomers of 2,4,5,6-tetrachloro-2,3,6-trimethyl-3-cyclohexen-1-one, **21a** 82% and **21b** 18%. In both isomers, the downfield methyl protons are coupled with the methine proton. The coupling constant is equivalent and the chemical shifts of the methine protons are close to those of **15** and **16**, indicating the coupled methyl group is at 3 C and the methine proton at 5 C. The assignments and the configurations of the 2-methyl and 3-methyl groups were determined by reference to **17** and **18** and those of the 6-methyl groups by reference to **15** and **16**. This means that the α-methyl groups in **21a** should be both axial and in **21b** both equatorial. The ir absorption band $\nu_{\mathrm{C-O}}$ = 1755 cm^{-1} of the mixture, which contains a larger proportion of the isomer **21a**, is in agreement to the assigned configuration.



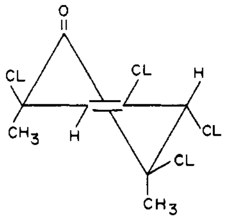
21a



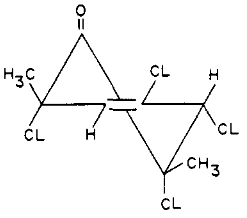
21b

Only a single 2,3,4,5,6-pentachloro-2,6-dimethyl-3-cyclohexen-1-one (**19**) is obtained from 2,6-dimethylphenol. Based on the ir absorption frequency of the carbonyl group, it was previously proposed that in **19**, one of the α-methyl groups is axial (a) and the other equatorial (ε) (*6*). The present study enables the specific assignment of the proton chemical shifts of the α-methyl groups as given in Table III. Due to the presence of the additional 2-methyl group, the $\delta\mathrm{CH_3}$ at 6 C in **19** should be upfield relative to the $\delta\mathrm{CH_3}$ at the 6 C of **15** or **16**. This is satisfied only when $\delta\mathrm{CH_3}$ = 1.93 ppm is assigned to an axial 6-methyl group. Similarly, due to the presence of a 6-methyl group in **19**, the 2-methyl group should be upfield relative to the corresponding methyl protons of B, $\delta\mathrm{CH_3}$ = 2.17 (e) or 2.01 (a) ppm. The 2-methyl of **19** should, therefore, be equatorial since $\delta\mathrm{CH_3}$ = 2.11 ppm. Comparison of **19** (or **21a**) to **16** and **21b** to **15** indicates that the presence of a 2-methyl group causes a relatively large upfield chemical shift of the 6-methyl protons.

The chlorination product of 2,6-dimethylaniline is a mixture of stereoisomers of 2,4,5,6-tetrachloro-2,6-dimethyl-3-cyclohexen-1-one, **20a** 40% and **20b** 60%. Nmr spectra indicate the presence of two nonequivalent methyl groups and two methine protons for each isomer. The methine protons are coupled, $J_{\mathrm{H-H}}$ = 1.5 Hz. The assignments of the various protons were determined by comparison to **21a** and **21b**. Both methyl groups of **20a** are probably axial and both of **20b** equatorial. The ir absorption peak $\nu_{\mathrm{C-O}}$ = 1730 cm^{-1} reflects the higher proportion of **20b** than **20a**.



20a



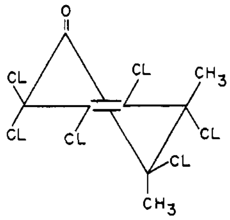
20b

Exhaustive chlorination of trichloro-2,5-dimethylphenol furnished a hexachloro-3-cyclohexenone (**22**). The $\delta\mathrm{CH_3}$ = 2.25 ppm is assigned to the 5-methyl protons, analogous to that of heptachloro-5-methyl-3-cyclohexen-1-one (*4*). The ir absorption band, $\nu_{\mathrm{C-O}}$ = 1755 cm^{-1}, suggests that the 2-methyl is equatorial. The $\delta\mathrm{CH_3}$ = 2.19 ppm for the 2-methyl protons is in agreement with the chemical shift of $\delta\mathrm{CH_3}$ = 2.17 ppm of the equatorial 2-methyl group of B.

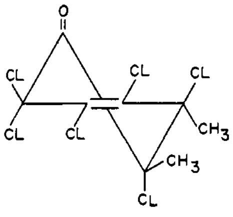
The ir spectra of the hexachloroketone, **23**, derived from trichloro-3,5-dimethylphenol was previously reported, but its structure was unidentified (*2*). Its spectral data with two nonequivalent methyl groups indicate that it is a 3-cyclohexen-1-one. The chemical shift of $\delta\mathrm{CH_3}$ = 2.31 ppm is assigned to the 3-methyl group by reference to **15** and **16**. Since the presence of a 3-methyl group causes an upfield shift, the assignment of $\delta\mathrm{CH_3}$ = 2.21 ppm to the 5-methyl group is consistent with the $\delta\mathrm{CH_3}$ of the 5-methyl of **22**.

A gradual exhaustive chlorination of 2,3-dimethylphenol produces a solid fraction consisting of two hexachloro-3-cyclohexenones. Fractional recrystallization from pet-ether gives **24**, mp 142–3°C, as the less soluble fraction and **25**, mp 88–

89°C, as the more soluble fraction. Although only a single $\delta CH_3 = 1.98$ ppm was observed for **24** in deuterochloroform, two separate peaks were observed in deuterobenzene. Two nonequivalent methyl groups were observed for **25** in deuterochloroform. The high-field chemical shifts of these methyl protons of **24** and **25** indicate that they are stereoisomers of 2,2,3,4,5,6-hexachloro-5,6-dimethyl-3-cyclohexen-1-one. The ir absorption frequencies of $\nu_{C-O} = 1768$ and $1752\ cm^{-1}$ for **24** and **25**, respectively, indicate that the methyl group at 6 C is axial in **24** and equatorial in **25**. The 5-methyl groups of **24** and **25** may probably be axial and equatorial, respectively.



24



25

Chlorination of **9** or dichloro-2,3,5-trimethylphenol gives liquids containing a 3-cyclohexenone (**26**) and a 2-cyclohexenone (**27**) as the major components. No coupling of the methyl protons is observed for either compound. Therefore, the two adjacent methyl groups are not bound to a common double bond as in **14**. The proton chemical shifts of **26** are assigned by reference to the chemical shifts of the 5-methyl and 6-methyl groups of **25** and the 3-methyl groups of **23**, **15**, or **16**. The alternate structure of pentachloro-2,3,5-trimethyl-3-cyclohexen-1-one for **26** may be ruled out because the proton chemical shift of the 3-methyl group should then be in the region of 2.11 ~ 2.14 ppm as in **21a** or **21b**.

2-Cyclohexen-1-ones. The ir carbonyl absorption of a 2-cyclohexenone is intermediate of the corresponding 3-cyclohexenone and 2,4-cyclohexadienone. The 2-cyclohexenone is normally found in the liquid fraction of the chlorination products. Table III contains the 2-cyclohexenones identified. The absence of methyl coupling in **27** limits its structure to pentachloro-3,5,6-trimethyl-2-cyclohexen-1-one. The δCH_3 = 2.47 ppm is assigned to the 3-methyl group on the double bond conjugated to the carbonyl in agreement with those of **4**, **9**, **12**, and **13**.

The structures given for **28** and **29** are based on the relative proton chemical shifts and absence of proton coupling. Ketone **30** was obtained by repeated recrystallization of the solid fraction formed by chlorination of 3-chloroaniline. Ketones **31** and **32** were identified in the liquid fractions obtained by the chlorination of 3-chloro-6-methylaniline and 3-chloro-2-methylaniline, respectively (*4*). The elucidation of the steric configurations of these 2-cyclohexenones requires further investigation.

The identification of the numerous chlorination products indicates that the chlorination of the polymethyl phenols and anilines in acetic acid proceeds essentially in an analogous manner as in the chlorination of cresols and toluidines (*4*). However, the positions of the methyl groups and the conditions of the chlorination determine the composition of the products. In the case of 2,6-dimethyl phenols with different groups at the *m*-positions, the *o*-position adjacent to an unsubstituted or a methylated *m*-position is chlorinated preferentially than the *o*-position adjacent to a chlorinated *m*-position. Stereoisomers of 3-cyclohexenones are readily obtained by the chlorination of anilines rather than phenols. The relative chemical shifts of axial and equatorial α-methyl protons are influenced by the neighboring atomic groups.

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Synthesis of Bis-α-tetralones

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The synthesis of two bis-α-tetralones, 7,7′-oxydi-1-tetralone and 7,7′-ethylene-1-tetralone, are described.

In the course of studies aimed at producing photocondensation polymers (*2*) by the photolytic coupling of aromatic diketones, it was desirable to prepare some bis-α-tetralones as possible monomers. Although α-tetralone couples quite readily on exposure to uv light (*1*) to give the corresponding pinacol, we were unsuccessful in coupling the bis-α-tetralones under the same reaction conditions. However, since the bis-α-tetralones are important potential intermediates in the formation of binaphthalenes and fuse-ringed aromatic derivatives (*4*), we would like to report the synthesis of 7,7′-oxydi-1-tetralone (**3a**) and 7,7′-ethylenedi-1-tetralone (**3b**).

The formation of cyclic ketones by intermolecular acylation is a well-known method in organic chemistry (*3*). Such ring closures have been effected by a variety of methods generally involving either the direct cyclodehydration of the acids or the cyclodehydrohalogenation of the acid chlorides by intramolecular Friedel-Crafts reactions. The cyclization of γ-phenylbutyric acid in such a way gives α-tetralone in 70–80% yield. Using a similar procedure, we have been successful in the preparation of two bis-α-tetralones by the cyclization of the corresponding diacids (Figure 1).

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