The reaction of heptachlor on alumina impregnated with sulfuric acid in the presence of various aromatic compounds[1]

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Solid phase-matrix catalysed (H_2SO_4 on alumina) substitution of heptachlor (**1**) by a variety of aromatic species has been studied and the structures of the compound obtained using benzene, toluene, phenol, *o*-dichlorobenzene, and nitrobenzene have been determined by extensive use of 250 MHz proton nmr spectroscopy and mass spectrometry.

Preliminary comments are made concerning the variety of orientation modes noted.

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On a étudié la substitution, catalysée par une matrice en phase solide (H_2SO_4 sur alumine), de l'heptachlore (**1**) par une série de produits aromatiques et on a déterminé les structures des composés obtenus, par réaction avec le benzène, le toluène, le phénol, l'*o*-dichlorobenzène et le nitrobenzène, en faisant appel à la spectroscopie de rmn du proton à 250 MHz et à la spectrométrie de masse.

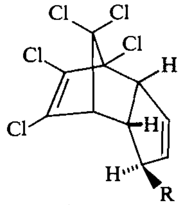
On fait des commentaires préliminaires au sujet de la diversité des modes d'orientation observés.

[Traduit par le journal]

We have recently reported in preliminary form (1) the formation of 1-aryl-chlordene **2** by the reaction of heptachlor **1** with aromatic species on an alumina/sulfuric acid solid matrix. In this article we present our evidence for the structures of compounds arising from the above reaction of heptachlor in the presence of benzene, toluene, phenol, *ortho*-dichlorobenzene, and nitrobenzene as being **2**, **3**, **4**, **5**, and **6** respectively.

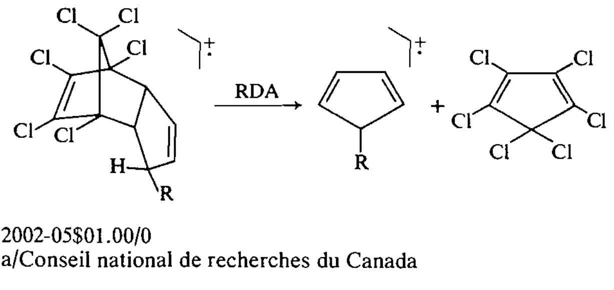
The impetus for this work arises from one of the procedures reported for the confirmation of heptachlor identity in trace amounts using the technique of solid matrix derivatization (2) and the need to isolate the derivatives formed as analytical standards together with the search for more sensitive analytical methods.

All of the products obtained have been examined thoroughly using spectral methods, in particular by the use of proton and carbon-13 nuclear magnetic resonance (nmr). Tables 1 and 2 present the data obtained and analysed with attribution of signals to particular nuclei and include data for chlordene **7** and heptachlor **1** for comparison purposes. Table 3 presents substituent effects on the ^{13}C chemical shifts of the compounds studied.



1 R = Cl
2 R = ϕ
3 R = *p*-tolyl
4 R = *o*-hydroxyphenyl
5 R = 2′,3′-dichlorophenyl
6 R = —O-3-*exo*-chlordene
7 R = H

The nmr spectra and the mass spectra of all compounds studied indicate that no skeletal rearrangements have occurred during the solid matrix reaction but rather that allylic substitution has taken place. Thus all of the mass spectra in this series show, as the base peak, a fragment resulting from the reverse Diels–Alder process as shown



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[1] Part XII in the CCIW series, Confirmation of Pesticide Residue Identities. For Part XI see ref. 1.

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TABLE 1. Proton chemical shifts (ppm from internal TMS) and coupling constants (Hz) for compounds 1–7 in $CDCl_3$ solutions at 250 MHz

	Compound						
Parameter	7[b]	1	2	3[c]	4[c]	5[d]	6
δ_4	5.838	5.958	5.923	5.892	5.882	5.901	5.962
δ_5	5.638	5.919	5.879	5.848	5.846	5.757	5.942
δ_6	3.865	4.080	3.992	3.976	4.056	4.058	3.998
δ_2	3.464	3.650	3.283	3.252	3.344	3.277	3.188
δ_3	2.363	4.826	3.876	3.854	4.148	4.504	4.564
$J_{4,5}$	5.8	5.6	5.7	5.7	5.7	5.5	5.7
$J_{4,6}$	−2.1	−2.0	−1.9	−1.9	−1.9	−2.1	−1.5
$J_{4,2}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$J_{4,3}$	2.1	2.1	2.3	2.3	2.3	2.2	2.1
$J_{5,6}$	2.2	2.0	2.0	2.0	2.0	2.0	1.9
$J_{5,2}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$J_{5,3}$[a]	−2.4	−1.3	−2.2	−2.2	−2.2	−2.1	−2.0
$J_{6,2}$	8.2	7.5	8.0	8.0	8.0	7.9	7.3
$J_{6,3}$	3.1	2.8	3.1	3.1	3.1	3.3	2.8
$J_{2,3}$	3.5	2.1	3.2	3.2	3.2	3.3	1.6

[a] These signs have not been determined. Nevertheless they have been introduced in the calculations as allylic couplings are normally negative.

[b] δ_{3exo} = 2.507 ppm, $J_{4,3exo}$ = 2.1 Hz, $J_{5,3exo}$ = −2.2 Hz, $J_{6,3exo}$ = 2.1 Hz, $J_{2,3exo}$ = 9.9 Hz, $J_{3endo,3exo}$ = 18.4 Hz.

[c] $\delta_{3'}$ = 6.794 ppm, $\delta_{4'}$ = 7.145 ppm, $\delta_{5'}$ = 6.904 ppm, $\nu_{6'}$ = 6.988 ppm, $J_{3'4'}$ = 8.0 Hz, $J_{3'5'}$ = 1.0 Hz, $J_{3'6'}$ = 0.0, $J_{4'5'}$ = 7.5 Hz, $J_{4'6'}$ = 1.5 Hz, $J_{5'6'}$ = 7.6 Hz.

[d] $\nu_{4'}$ = 7.369 ppm, $\nu_{5'}$ = 7.144 ppm, $\delta_{6'}$ = 6.926 ppm, $J_{4'5'}$ = 7.7 Hz, $J_{4'6'}$ = 1.9 Hz, $J_{5'6'}$ = 7.7 Hz.

[e] $\delta_{2'} = \delta_{6'}$ = 7.04 ppm, $\delta_{3'} = \delta_{5'}$ = 7.14 ppm; this AA'BB' system has not been analysed because insufficient small transitions are observable, 5_{Me} = 2.334 ppm.

TABLE 2. Carbon-13 chemical shifts (ppm from internal TMS) measured in $CDCl_3$ solutions for the compounds studied

	Compound						
Carbon	1	2	3	4	5	6	7
1[a]	80.3	81.5	81.5	81.7	81.3	80.0	81.9
2	60.5	58.7	58.9	58.1	58.9	58.2	49.3
3	60.1	50.9	50.5	45.4	48.5	81.2	32.4
4	137.7	138.8	139.1	139.2	138.9	136.3	136.1
5	131.1	127.6	127.4	127.7	128.2	132.2	126.4
6	60.8[c]	61.2	61.2	61.7	61.8	60.6	61.2
7	82.1	82.2	82.3	82.4	82.2	81.7	82.5
8[b]	132.3	131.9	131.8	132.1	132.1	131.6	132.0
9[b]	128.9	129.2	129.2	129.2	129.8	128.8	129.3
10	103.7	103.4	103.5	103.8	103.7	103.9	103.8
1'	—	143.2	140.3	129.6	142.9	—	—
2'	—	127.2	127.1	153.2	132.0	—	—
3'	—	128.8	129.5	116.5	134.1	—	—
4'	—	127.1	136.7	136.7	129.5	—	—
5'	—	128.8	129.5	121.5	127.7	—	—
6'	—	127.2	127.1	128.6	127.3	—	—
CH_3	—	—	21.0	—	—	—	—

[a], [b], [c] Assignments can be reversed.

below. A rapid detection of the carbon skeleton present is therefore available.

Two structural questions have to be answered for the isolated compounds: (a) the site and stereochemistry of substitution on the chlordane nucleus, and (b) the substitution site on the aromatic moiety, if this is not phenyl.

The first point is readily answered in part by the mass spectral information described above (i.e. at C-3 or C-5, both sites are identical after allylic substitution occurs) and the stereochemical fate of substitution is evident from the nmr studies where $J_{2,3}$ indicates that no change in geometry at C-3[3] takes place. Thus substitution occurs in all cases with retention of configuration at C-3, not a surprising observation when the geometry of heptachlor and access to any derived allylic carbonium ions at C-10 is considered.[4]

The site of substitution on the benzene ring in compounds 2–5 was solved by an analysis of the 250 MHz ^1H nmr spectra of these compounds using LAOCN 3 (3) and summarized in Table 1 in footnotes *b*–*e*. These assignments are unequivocal and

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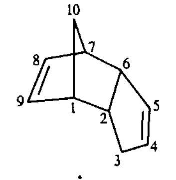
[3] The numbering system for the chlordene skeleton that we use here is based on the *endo*-tricyclo[5,2,1,$0^{2,6}$]deca-4,8-diene skeleton i following the IUPAC nomenclature system.



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Thus, heptachlor is named as 1-*exo*-3,7,8,9,10,10-heptachloro-*endo*-tricyclo[5,2,1,$0^{2,6}$]deca-4,8-diene.

[4] Of course S_N2' reactions with retention of configuration are also possible.

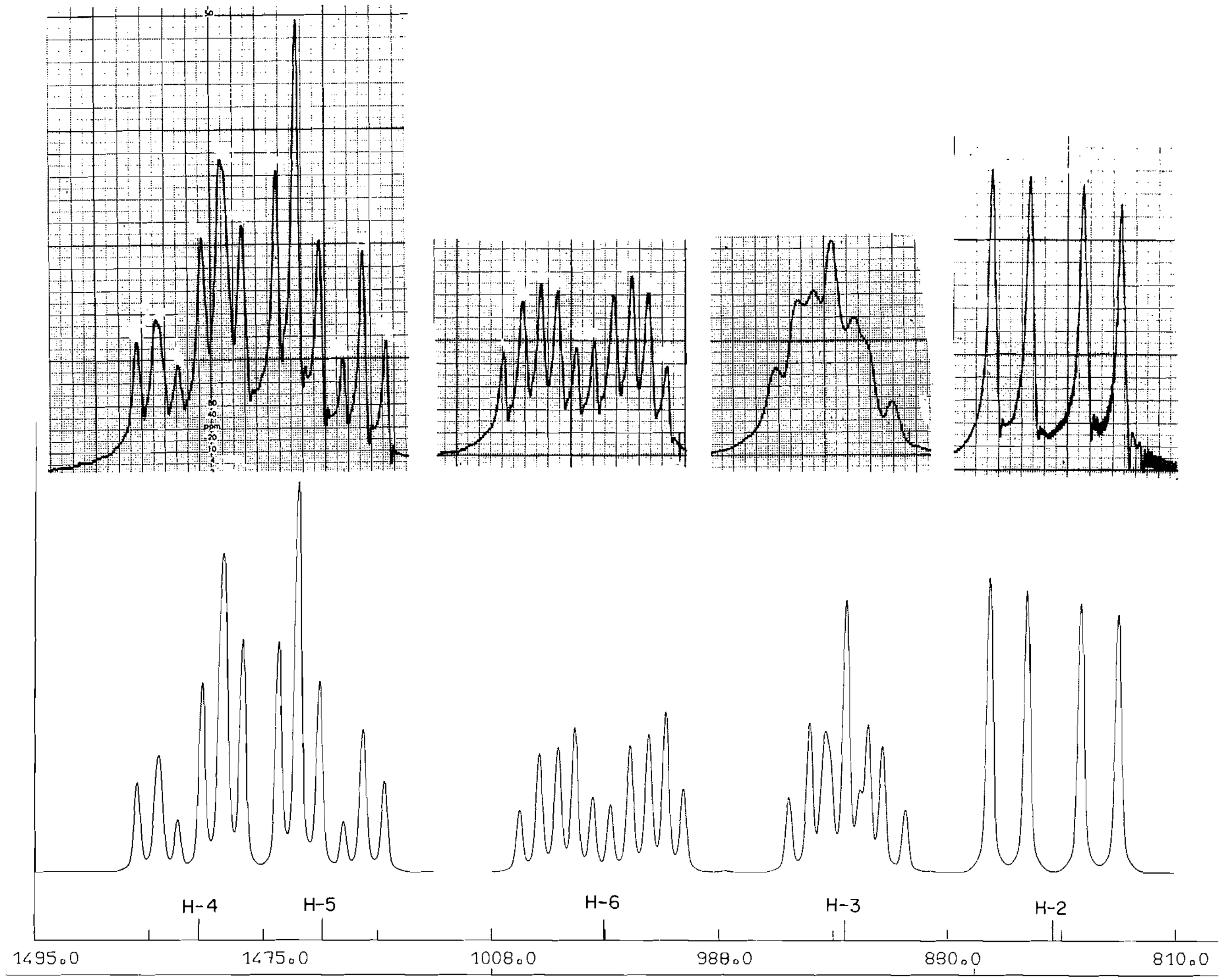


FIG. 1. Comparison of the 250 MHz experimental proton nmr spectrum of 3-*exo*-γ-phenylchlordene (**2**) (phenyl signals excluded) compared to the simulated spectrum (lower trace).

TABLE 3. Influence of the substituent R on the carbon-13 chemical shifts of the chlordene skeleton

	Compound					
Carbon	**1**	**2**	**3**	**4**	**5**	**6**
1[a]	−1.6	−0.4	−0.4	−0.2	−0.6	−1.9
2	11.2	9.4	9.6	8.8	9.6	8.9
3	27.7	18.5	18.1	13.0	16.1	48.8
4	1.6	2.7	3.0	3.1	2.8	0.2
5	4.7	1.2	1.0	1.3	1.8	5.8
6	−0.4	0.0	0.0	0.5	0.6	−0.6
7[a]	−0.4	−0.3	−0.2	−0.1	−0.3	−0.8
8[b]	0.3	−0.1	−0.2	0.1	0.1	−0.4
9[b]	0.6	−0.1	−0.1	−0.1	0.5	−0.5
10	−0.2	−0.4	−0.3	0.0	−0.1	0.1

[a, b] Assignments can be reversed.

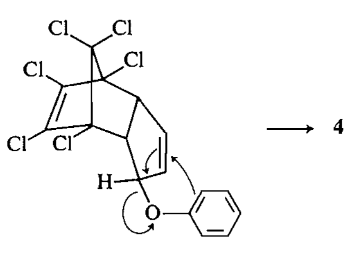
lead to the derivation of the structures depicted herein.

The power of this method is exemplified by Fig. 1 where portions of the experimental and calculated spectra for 1-*exo*-phenylchlordene (**2**) are compared. In the experimental spectrum the signal for H-5 centred at 3.926 ppm is broadened compared to the simulated spectrum because of small long-range benzylic couplings that we did not include in the simulation but are present as indicated by double irradiation.

Compound **6**, prepared by the use of nitrobenzene in this reaction, does not fall into the category of substituted chlordenes. Inspection of its nmr spectra indicates no aromatic substitution has occurred, rather only chlordene type protons (see Table 1) and carbon atoms (see Table 2) appear to be present. For some time this compound presented a problem, until we were able to obtain a satisfactory mass spectrum under conditions of low electron impact energy, showing a molecular ion at 686 together with chlorine isotope peaks, indicating a molecular formula of $C_{20}H_{10}OCl_{12}$. In addition, a major fragment of *m/e* 335 corresponding to $C_{10}H_5Cl_6^+$ was observed. The mass spectral and nmr data are best reconciled by dimeric structure **6**; in particular, the C-3—O—C′-3 moiety accounts for the chemical shift of 81.2 ppm for the two C-3 positions in this compound, a substituent shift of 48.8 ppm. At this stage we have not pursued the mode of formation of this material.

The formation of compounds **2**–**5** appears to be a Friedel–Crafts type process with the alumina supported acid acting as a catalyst (4), the precedent for this process appearing once in the patent literature (5) using the standard Friedel–Crafts conditions. In our hands this latter process proved less convenient for the preparation of substituted chlordenes, from the point of view of yield, product homogeneity, and isolation, although it must be stressed that we have only pursued a limited number of examples.[5]

There remain some intriguing questions to be answered concerning the mode of formation of compounds **3**, **4**, and **5**. Thus formation of **3** results from exclusive *para* attack of toluene, whereas **4** arises from exclusive *ortho* attack of phenol.[6] If a steric argument is involved it is difficult to reconcile formation of **4**. It therefore appears reasonable to us to suggest that **3** arises via a normal electrophilic substitution of toluene in the *para*-position, the bulk of the chlordene allylic cationic species precluding *ortho* attack, whereas **4** arises via prior O-alkylation to **8** followed by a rapid thermal oxy-Cope rearrangement to **4** as shown. This possibility is being presently explored using *ortho*-substituted phenols.



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The formation of **5** is a direct alkylation, *ortho* to one of the chlorine atoms of *o*-dichlorobenzene. Here the previously used steric argument for the formation of **3** falls down.

Our continuing work includes an investigation of the questions raised by the formation of the above compounds and attempts to include, in the aromatic substituents, groups that are photochemically active that could lead to ready degradation of the chlordene skeleton. The agricultural implications of such a course are tantalizing.

Experimental

Proton nmr spectra were determined in the C.W. mode at 250 MHz on a Camera spectrometer at la Faculté de Pharmacie, Marseille, and analysed with the help of the LAOCN 3 program (3) or with a Varian XL-100 spectrometer at C.C.I.W. Carbon-13 spectra were determined in the FT mode on JEOL PS-100-FT and Bruker WP-80-DS spectrometers working at 25.03 and 20.11 MHz respectively in the Laboratoire de Mesures Physiques at U.S.T.L. The nmr data for the compounds described are presented in Tables 1 and 2. The ir spectra were recorded on a Unicon SP 110 spectrophotometer. Mass spectra were obtained

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[5] Benzene, toluene, and phenol have been reacted with heptachlor under the usual Friedel–Crafts conditions ($AlCl_3$) yielding **2**, **3**, and **4** in low yield (< 20%) in each case.

[6] We have been unable to detect minor amounts of materials resulting from alternate modes of attack.

on a JEOL JMS-D100 at U.S.T.L. or at C.C.I.W. The chlorine isotope patterns confirm the molecular formula for all fragments. Mass spectral molecular weights are calculated using the ^{35}Cl isotope.

Heptachlor was kindly provided by the Velsicol Chemical Corporation. Microanalyses were carried out by the Guelph Chemical Laboratories.

Alumina/sulfuric acid matrix

Precooled concentrated sulfuric acid (10 mL) and alumina (50 g) (Woelm neutral grade 1) were mixed rapidly in a mortar and pestle at 0°C in a dry nitrogen atmosphere. The mixture was then transferred to a tightly capped bottle and stored in a desiccator until used.

exo-*3-Phenylchlordene (2)*

Pure heptachlor (2 g) in benzene (200 mL) was shaken with alumina/sulfuric acid solid matrix (50 g) (2) to ensure uniform mixing. Enough benzene was removed under vacuum on a rotary evaporator to ensure that the alumina remained moist. The mixture was heated under reflux on a steam bath overnight when, after cooling to room temperature, the moist mass was extracted with warm acetone (3 × 80 mL). The combined acetone extracts were evaporated to dryness and the solid residue was recrystallized from hexane/benzene (5:1) to yield colorless prisms (1.9 g), mp 76–77°C (lit. (5) mp 77–78°C); ir ($CHCl_3$): 3080, 2020 (C—H), 1610 (Cl—C=C—Cl), 1495, and 1415 (C_6H_5) cm^{-1}. Mass spectra: M^+ 412 (5%) ($C_{16}H_{10}Cl_6$), 270 (10%) (M – C_5Cl_6, retro Diels–Alder), 142 (100%) ($C_{11}H_{10}$ retro Diels–Alder). *Anal.* calcd. for $C_{16}H_{10}Cl_6$: C 46.60, H 2.43, Cl 50.97; found: C 46.79, H 2.1, Cl 50.5.

3-Aryl-chlordenes

The above procedure was followed using, in separate experiments, toluene (200 mL), *o*-dichlorbenzene (200 mL), nitrobenzene (200 mL), or phenol (4 g) dissolved in isooctane/ether (8:2) (300 mL).

The following materials were obtained. (1) 3-(*p*-Tolyl)-chlordene (**3**), 70% yield, mp 127–128°C; ir (KBr): 1610 (Cl—C=C—Cl), 1512 (aromatic) cm^{-1}. Mass spectra: M^+ 426 (3%) ($C_{17}H_{12}Cl_6$); *m/e* 156 (100%) (M – C_5Cl_6, retro Diels–Alder). *Anal.* calcd. for $C_{17}H_{12}C_6$: C 47.89, H 2.81, Cl 49.30; found: C 47.65, H 2.62, Cl 48.88. (2) 3-(*o*-Hydroxyphenyl)-chlordene (**4**), 50% yield, mp 105°C; ir (KBr): 3300 (O—H), 1605 (Cl—C=C—Cl), 1500 (aromatic) cm^{-1}. Mass spectra: M^+ 428 (4%) ($C_{16}H_{10}Cl_6O$); *m/e* 158 (100%) (M – C_5Cl_6, retro Diels–Alder). *Anal.* calcd. for $C_{16}H_{10}Cl_6O$: C 44.85, H 2.33, Cl 49.07; found: C 44.73, H 2.08, Cl 48.76. (3) 3-(2′,3′-Dichlorophenyl)-chlordene (**5**), 25% yield, mp 153°C; ir (KBr): 1600 (Cl—C=C—Cl) cm^{-1}. Mass spectra: M^+ 480 (2%) ($C_{16}H_8Cl_8$); *m/e* 210 (100%) (M – C_5Cl_6, retro Diels–Alder). *Anal.* calcd. for $C_{16}H_8Cl_8$: C 40.00; H 1.66, Cl 58.33; found: C 39.82, H 1.30, Cl 57.97. (4) Dichlordene ether **6**, 8% yield, mp 258°C; ir (KBr): 1605 (Cl—C=C—Cl) cm^{-1}. Mass spectrum: M^+ 686 (5%) ($C_{20}H_{10}OCl_{12}$), 335 (100%) ($C_{10}H_5Cl_6$), 65 (95%) ($C_{10}H_5Cl_6$-C_5Cl_6, reverse Diels–Alder). *Anal.* calcd. for $C_{20}H_{10}Cl_{12}O$: C 34.98, H 1.46, Cl 61.22; found: C 34.62, H 1.13, Cl 61.54.

Acknowledgements

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