

Syntheses and Properties of Hexa- and Heptachlorostyrenes with Fully Chlorinated Aromatic Nuclei

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All six possible hexa- and heptachlorostyrenes with fully chlorinated aromatic nuclei have been synthesized. Their ultraviolet and infrared spectra are discussed, fragmentation in the mass spectrometer described and from the ¹H and ¹³C NMR spectra all parameters have been determined, including ¹J_{CH}, ²J_{CH} and ³J_{CH} coupling constants. UV and NMR data indicate that the styrene system is nonplanar.

Chlorinated styrenes together with chlorinated benzenes and polychlorinated biphenyls (PCB) have been found in water, sediment and fish samples from the Norwegian fjord, Frierfjorden.¹ The source of these pollutants seems to be the production of magnesium, where a high temperature process is used involving chlorine gas and graphite electrodes. The pollutants have also been detected in the bloodstream of workers in this magnesium plant. Several isomers of hexa- and heptachlorostyrenes were identified without the precise knowledge of their stereochemical identity.

The uptake and bioaccumulation of the styrenes were as effective as for chlorinated benzenes and PCB. The biological effects of the latter are well known, while effects of the highly chlorinated styrenes are unknown. In order to gain some information of this nature and to help identify the different isomers analytically, a synthetic study of these styrenes was initiated.

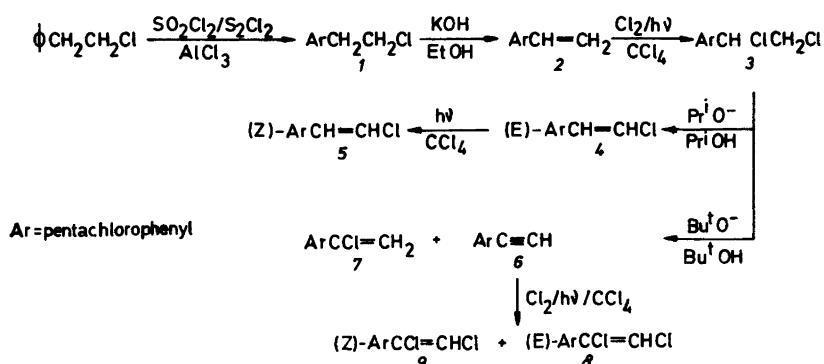
SYNTHESES

Most of the six possible title compounds have been synthesized before. Thus *α,2,3,4,5,6-hexachlorostyrene* (7) was obtained in 31 % yield by pyrolysis of a highly chlorinated bicycloheptadiene.² *β,2,3,4,5,6-Hexachlorostyrene* (4 or 5) was made by dehydrobromination of 1-bromo-2-chloro-1-pentachlorophenylethane.³

β,β,2,3,4,5,6-Heptachlorostyrene (13) was obtained as a minor component in the electrochemical reduction of octachlorostyrene,⁴ while the same author obtained both (*E*)- and (*Z*)-*α,β,2,3,4,5,6-heptachlorostyrene* (8) and (9) by chlorination of acetylene 6.

Since only one of the hexachlorostyrenes 4 and 5 was known, its stereochemistry was uncertain and since 7 was obtained in a rather complicated way, it was decided to see if a unifying synthetic strategy could be followed. Since much is known about the rather simple chemistry involved in preparing side chain halogenated styrenes,⁵ analogue routes were tried.

It was soon realized that the pentachlorophenyl group exerted a large influence on the chemistry of the two-carbon chain. For instance, the easy route from acetophenone through 1,1-dichloro-1-phenylethane to *α*-chlorostyrene must be abandoned due to complete unreactivity of the carbonyl group in 2,3,4,5,6-pentachloroacetophenone towards any chlorinating agent. Treatment of pentachlorobenzonitrile (commercially available) with Grignard reagents or methyl lithium to build up the side chain, unexpectedly led to rupture of the aryl-nitrile bond to give



Scheme 1.

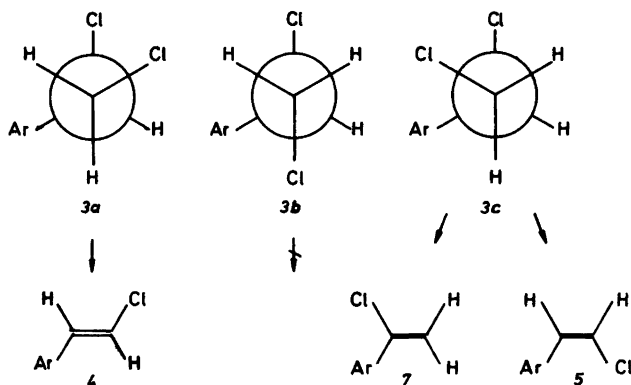
pentachlorobenzene.

The extreme ease whereby the aromatic nucleus was chlorinated without any attack on the side chain was then utilized,⁶ with slight modification. Thus 1-chloro-2-phenylethane was smoothly chlorinated to 1-chloro-2-pentachlorophenylethane in excellent yield.⁷ The reactions leading to the three isomeric hexachlorostyrenes (4, 5 and 7) and the (*E*)- and (*Z*)-heptachlorostyrenes 8 and 9 are summarized in Scheme 1 and detailed in Experimental.

It must be mentioned that in most of the synthetic steps mixtures of compounds were obtained. Since all compounds contain the dominating pentachlorophenyl group, this will make the different compounds physically almost indistinguishable. In column chromatography all compounds follow the solvent front due to their lipophilicity; likewise the solubility is almost the same for all compounds rendering recrystallisa-

tion a poor tool for achieving the high purity required for the aims intended, *viz.* biological testing and analytical standard-making. Preparative GLC proved to be the only method to get the high purity required. Even then large head and tail fractions had to be discarded.

The choice of base applied in the dehydrohalogenation of 1,2-dichloro-1-pentachlorophenylethane 3 was important. The less hindered methoxide or ethoxide ion led to formation of considerable amounts of β -alkoxy compounds. They could be formed either by nucleophilic substitution in the starting material and subsequent dehydrohalogenation of the intermediate 1-alkoxy-2-chloro compound, by an addition-elimination reaction of a first formed β -chlorostyrene derivative or by addition to the acetylene 6, as discussed elsewhere.^{3,8} As expected, no alkoxy derivative was found when isopropoxide or *tert*-butoxide was used. The outcome of the



Scheme 2.

Table 1. Dehydrohalogenation of 3 (1 mol) by base (q mol) at t °C. Yields corrected for unreacted 3. Traces of 5 formed in all experiments.

		Yield (%) of		
q	t	4	6	7
Base Me_2CHO^-				
1	108	41	40	19
1	60	82	7	10
Base Me_3CO^-				
1	83	35	53	12
1	60	38	51	10
2	83	5	84	9

elimination reaction (Table 1) could be rationalized on a conformational basis (Scheme 2).

Of the three staggered rotamers only 3a and 3c can give *trans* elimination products. 3a is probably the most stable rotamer. Elimination would lead to excess of 4 (*E*-isomer) with isopropoxide at the lower temperature. Increasing temperature leads to increasing double elimination to form acetylene 6 and also to increased population of conformer 3c which on elimination would give the α -isomer 7. 3c would also theoretically give the (*Z*)- β -isomer 5. But steric hindrance imposed by the pentachlorophenyl group would effectively shield the β -hydrogen to be removed in an E2-elimination, thus only traces of the *Z*-isomer 5 were observed. However, one cannot exclude the possibility that 5 most easily could undergo a *trans* elimination to the acetylene 6.

From Table 1 it can be seen that increasing base-substrate ratio expectedly led to increasing yield of acetylene 6 at the expense of 4. The α -isomer 7 seems to be unaffected by base, a result that is understandable both from steric and electronic considerations. Molecular model considerations reveal that the vinyl hydrogen *cis* to

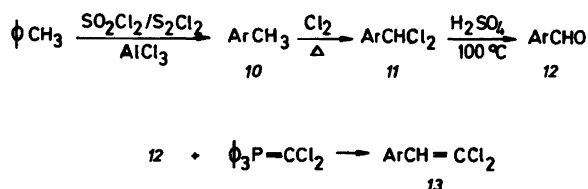
the aromatic group in 7 (*i.e.* the hydrogen lost in a *trans* elimination) is sterically more hindered than the α -hydrogen in 4. In addition the latter hydrogen must be more acidic as the substituent effect of five chlorine atoms on the aromatic ring has been estimated to $\sigma=3.49$,⁹ stabilizing a negative charge on the α -carbon of 4 much better than on the β -carbon of 7.

$\beta,\beta,2,3,4,5,6$ -Heptachlorostyrene 13 was prepared by a Wittig reaction of pentachlorobenzaldehyde with dichloromethylene triphenylphosphorane (Scheme 3).¹⁰

ULTRAVIOLET SPECTRA

Data from the absorption spectra in the region from 200 nm and upwards for the chlorostyrenes and some other compounds pertinent to the discussion are given in Table 2.

First of all it should be mentioned that the auxochromic effect of chlorine atoms on the benzene chromophore is not at all additive, as demonstrated by a survey of the absorption maxima of polychlorinated benzenes in the *K*-region.¹¹ Thus the highest λ_{max} , 224 nm, is observed for 1,4-dichloro- and 1,2,3-trichlorobenzene; $\log \epsilon$ 4.11 and 3.91, respectively. It is not surprising, since electron diffraction data show that already in 1,2-dichlorobenzene the chlorine atoms are twisted out of the plane of the aromatic ring, one to each side, torsion angle 15°. ¹² And in hexachlorobenzene a chair-like conformation is observed where the chlorine atoms are displaced alternatively over and below the mean plane of the benzene ring.¹² This lack of coplanarity reduces the overlapping of the non-bonded electrons of chlorine atoms with the aromatic π -system and may also be responsible for the large positive σ -value of the pentachlorophenyl group (see above); the +M-effect of the chlorine atoms being reduced.



Scheme 3.

Table 2. Absorption maxima (λ_{\max} , nm) and molar absorptivity ($\log \epsilon$) of chlorostyrenes 2, 4–5, 7–9, 13 and some related compounds.

Compound	E-band	K-band	B-band	Solv.	Ref.
C ₆ H ₆	184(4.83)	204(3.94)	254(2.31)	MeOH	13
C ₆ HCl ₅		219(4.33)	289(2.87);298(2.59)	Cyclohexane	14
C ₆ Cl ₆		222(4.41)	291(2.40);298(2.36)	Cyclohexane	14
C ₆ H ₅ CH=CH ₂		248(4.24)	282(2.87);291(2.70)	MeOH	13
C ₆ H ₅ CH=CHCl		254(4.22)		N.i. ^a	11
2	221(4.64)	240(4.24)	297(2.50)	EtOH	^b
4	227(4.55)	244(4.30)	310(2.60);325(2.13)	EtOH	^b
5	213(4.65)	240(4.06)	290(2.47);298(2.46)	EtOH	^b
7	216(4.80)	239(3.99)	292(2.70);297(2.73)	EtOH	^b
8	216(4.81)	240(4.08)	293(2.77);300(2.81)	EtOH	^b
9	216(4.81)	242(4.11)	295(2.82);304(2.80)	EtOH	^b
13	217(4.70)	240(4.15)	290(2.62);300(2.58)	EtOH	^b
C ₆ H ₅ CH=CCl ₂		260(4.20)		N.i. ^a	11

^a No information. ^b This work.Table 3. IR absorption (ν_{\max} , cm⁻¹) of chlorostyrenes.

Vibration	2	4	5	7	8	9	13
=C–H	3093 (w)	3079 (w)	3080 (vw)	2921 (w)	3083 (w)	3067 (w)	3015 (vw)
Olef. C=C	N.o. ^a	1614 (m)	1623 (w)	1634 (s)	1652 (vw)	1616 (w)	1616 (w)
Arom. C=C	1362 (s)	1371 (m)	1371 (m)	1400 (m)	1373 (m)	1369 (m)	1377 (m)
	1345 (m)	1344 (s)	1346 (s)	1346 (s)	1350 (s)	1346 (s)	1340 (s)
	1330 (s)	1308 (m)	1319 (m)	1324 (s)	1326 (s)	1319 (m)	1319 (m)
Others	1417 (m)	1241 (m)	1240 (m)	1418 (w)	1270 (m)	1242 (m)	1239 (w)
	1232 (m)	1125 (w)	1168 (m)	1231 (s)	1126 (m)	875 (s)	918 (s)
	1122 (m)	924 (m)	1120 (m)	1147 (s)	653 (m)	647 (m)	663 (w)
	936 (m)	855 (s)	667 (m)	1080 (m)			
	660 (w)	684 (m)		920 (m)			
				897 (s)			
				674 (s)			
				657 (s)			

^a N.o.: Not observed.

This great steric demand of the chlorine atoms also makes it difficult to obtain coplanarity in the styrene system. The bathochromic effect observed for styrene as compared to benzene (44 nm) is greatly reduced when the benzene ring is perchlorinated (C₆HCl₅ → 2: $\Delta\lambda_{\max}$ =21 nm). Similar blue shifts upon perchlorination of the aromatic ring is observed for the pair *trans* β -chlorostyrene *vs.* 4 (10 nm) and β,β -dichlorostyrene *vs.* 13 (20 nm).

INFRARED SPECTRA

The infrared spectra of the chlorostyrenes are summarized in Table 3.

The C–H stretching vibration is very weak in all styrenes; likewise the C=C stretch in all compounds apart from α -hexachlorostyrene 7 where this vibration gives rise to a rather strong absorption at 1634 cm⁻¹; in fact, the absorption band in this region for 2 is completely absent.

The terminal methylene group in 2 and 7 is represented by the characteristic scissoring vibration band at 1417 and 1418 cm^{-1} , respectively. The unifying structure element, the pentachlorophenyl group, is represented with three medium to strong bands which have been assigned to the C=C stretching in the aromatic ring.^{2,15} The *trans* position of the hydrogens in 4 is confirmed¹⁶ by the absorption at 924 cm^{-1} , absent in the *cis* compound 5. The strong absorption at 918 cm^{-1} in 13 is characteristic for the =CCl₂ group.¹⁷ The out-of-plane hydrogen vibration for 1,1-disubstituted terminal olefin 7 gives rise to the strong absorption at 897 cm^{-1} .

MASS SPECTRA

Some of the features from the mass spectra of the chlorostyrenes are given in Table 4.

All the chlorine-containing fragments show the correct intensities (within a few percent) for the isotope peaks. The base peak in all compounds is either M^+ or M^+-Cl . The three most abundant fragments in all spectra are M^+ , M^+-Cl and M^+-2Cl and account for 46–60 % of the total ion current. Since also pentachlorostyrene 2 follows this fragmentation pattern, one may conclude that these fragments have lost their chlorine atoms from the ring. There are no differences in the fragmentation of the (*E*)- and (*Z*)-heptachlorostyrenes as judged from the relative abundance of consecutive chlorine expulsions, and apart from a switch in intensities of the M^+ and M^+-Cl peaks, the (*E*)- and (*Z*)-hexachlorostyrenes follow a similar pattern.

Table 4. Relative abundance of ions M^+-nCl produced by chlorostyrenes on electron impact.

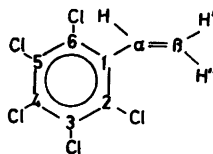
<i>n</i>	2	4	5	7	8	9	13
0	100	100	96	50	70	71	100
1	87	79	100	100	100	100	65
2	59	34	55	47	75	73	68
0–2 ^a	52	60	46	48	51	53	50
3	6	3	9	7	15	14	12
4	9	4	5	4	12	11	10
5		4	5	3	8	8	7
6					11	11	7
0–6 ^a	55	65	50	51	61	63	58

^a Per cent of total ion current.

NMR SPECTRA

A comparison of the vinyl protons in pentachlorostyrene 2 with those of styrene itself shows that only for the proton *trans* to the aromatic group a rather large deshielding ($\Delta\delta \sim 0.6$ ppm) is observed (Table 5). This deshielding is probably caused by the large electron withdrawing effect from the pentachlorophenyl group (see above).

If one uses the observed chemical shifts for the olefinic protons in 2 one can calculate the



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empirical substituent constant $S(\delta)^{18}$ for the pentachlorophenyl group in ethylenes to be: $S(\delta)$: +1.37 (*gem.*), +0.44 (*cis*) and +0.54 (*trans*) ppm. These values together with the values for chlorine¹⁸ are then used to calculate the shifts for the vinyl protons in the hexa- and heptachlorostyrenes given in Table 5. The deviations from the experimental values are negligible (<0.1 ppm) for the *E*-isomer 4, but $\delta_{\text{calc}} - \delta_{\text{exp}}$ increases as the deviation from coplanarity increases (see discussion of UV-data). Changes in geometry of the system may effect both the diamagnetic term

Table 5. Calculated (see text) and experimental ¹H NMR chemical shifts (δ) for chlorostyrenes (14) in CDCl₃.

Compound	H	H'	H''
Styrene	6.63	5.18	5.72
2, exp	6.62	5.79	5.69
4, calc	6.80		6.77
4, exp	6.80		6.71
5, calc	6.75	6.87	
5, exp	6.57	6.63	
7, calc		5.97	5.82
7, exp		5.88	5.48
8, calc		7.05	
8, exp		6.53	
9, calc			6.90
9, exp			6.33
13, calc	6.93		
13, exp	6.64		

Table 6. Coupling constants ($J_{\text{H,H}}$, Hz) for chlorostyrenes and -ethylenes in CDCl_3 .

Compound	J_{gem}	J_{trans}	J_{cis}
Styrene ¹⁹	1.3	17.5	10.7
2	0.9	17.8	11.6
4, 5 and 7	2.1	13.9	7.7
$\text{CH}_2=\text{CHCl}$ ²⁰	1.4	14.6	7.3
$\text{ClCH}=\text{CHCl}$ ²¹	—	12.1	5.3

(σ^{dia}) and the neighbour anisotropic term (σ^{N}). If the pentachlorophenyl group reduces the electron density of the vinyl system by resonance (and not by inductive effect alone), this effect will decrease with gradual loss of coplanarity, thereby reducing the size of σ^{dia} . The large value of the Hammett substituent constant (+3.49) points to a substantial $-\text{M}$ effect, as inductive effect alone can hardly be responsible for this value.

Without precise knowledge of the geometry of this system, it is difficult to assess the change in σ^{N} .

The fully chlorinated aromatic ring does not seem to have any great influence on the proton-proton coupling constants in our styrenes (Table 6). Thus in 2 the values are about the same as in styrene,¹⁹ while the coupling constant for the hexachlorostyrenes 4, 5 and 7 are

close to those of vinyl chloride²⁰ and further away from those of 1,2-dichloroethylene.²¹ As conjugation is claimed to have little effect on the vicinal coupling constants,²¹ this again points to the operation of resonance effects as the main electronic effects from the pentachlorophenyl group.

The ^{13}C chemical shifts and the observed $^1J_{\text{CH}}$, $^2J_{\text{CH}}$ and $^3J_{\text{CH}}$ coupling constants are given in Table 7 and 8 respectively. The former parameters were obtained from the broad-band decoupled spectra, while the coupling constants were obtained from the undecoupled spectra combined with selective ^1H decoupling.

The calculated chemical shifts of the aromatic carbons of 2 were obtained by applying the empirical substituent constants²² of chlorine atoms on the reported shift values of styrene.²³ The agreement with the observed values for 2 is rather good with the largest deviation at C4 ($\Delta\delta=3.9$ ppm). The introduction of one or two chlorine atoms in the side chain hardly affects the chemical shifts of the *ortho*- and *meta*-carbon atoms ($\Delta\delta_{\text{max}}=1.3$ ppm).^{*} On the other hand, the effect on C1 and C4 is larger, which is not at all surprising. These two carbon atoms will experience changes in resonance effect more than the

* Compared with the observed values for 2.

Table 7. ^{13}C NMR chemical shifts (δ) for chlorostyrenes (14) in CDCl_3 . Calculated (see text) shifts in italics.

C	2	4	5	7	8	9	13
α	131.3	127.1 <i>125.3</i>	125.8 <i>123.3</i>	137.3 <i>134.3</i>	127.3 <i>128.5</i>	128.6 <i>128.5</i>	123.9 <i>119.3</i>
β	124.2	128.2 <i>127.2</i>	125.2 <i>127.2</i>	120.5 <i>118.2</i>	120.7 <i>121.2</i>	122.9 <i>121.2</i>	128.5 <i>130.5</i>
1	136.6 <i>138.0</i>	133.1	133.2	133.2	133.5	134.5	132.6
2+6	131.8 <i>132.7</i>	132.1	132.3	132.3	132.6	132.4	132.5
3+5	132.1 <i>134.1</i>	132.4	132.0	132.4	132.4	133.4	132.1
4	132.5 <i>136.4</i>	133.3	133.5	134.7	135.5	135.5	134.1

Table 8. Coupling constants ($J_{C,H}$, Hz) for chlorostyrenes (14) and some reference compounds.²⁵

Com- pound	1J α,H	$\beta,H'/H''$	2J		3J				
			1,H	α,H'	α,H''	β,H	2-6,H	1,H'	1,H''
2	163.7	160.8	2.2	3.8	2.1	3.2	4.0	6.0	12.6
4	168.7	197.2			2.7	9.7	3.6		2.8
5	167.5	199.2		7.5		6.0	3.4	8.8	
7		164.2		2.6	8.6			6.7	5.6
8		201.4		1.7				7.1	
9		196.9			13.5				2.5
13	171.5					0.9	2.8		
CH ₂ =CHCl	162	198							
CHCl ₂ =CHCl		198			16.5				
CHCl ₂ =CHCl		199		1.8					
CHCl=CCl ₂		201				1.3			

other ring carbons; a change caused by the reduced coplanarity of the hexa- and heptachlorostyrenes.

The calculated values for the side chain carbons were obtained by applying the empirical increments of chlorine in ethylenic compounds²⁴ on the observed values for 2,3,4,5,6-pentachlorostyrene 2. The agreement with the observed values is rather good ($\Delta\delta_{\max}=4.6$ ppm).

The $^1J_{CH}$ values for the side chain chlorinated styrenes are consistent with those for chloroethylenes (Table 8).²⁵ The lack of effect from the pentachlorophenyl group on the vicinal proton coupling constants is thus repeated for $^1J_{CH}$, and also to a large extent for $^2J_{CH}$. Thus the observed $^2J_{CH}$ for the heptachlorostyrenes 8, 9 and 13 are close to those of chloroethylenes. For the hexachlorostyrenes the situation is not that clear. For 7 similar patterns as for the heptachlorostyrenes are observed; $^2J_{\alpha H'}$ being smaller than $^2J_{\alpha H''}$, while for 4 and 5 it is opposite. Also for 2 the same situation prevails ($^2J_{\alpha H'} > ^2J_{\alpha H''}$). The $^3J_{CH}$ coupling constants also follow a somewhat inconsistent pattern. It is stated that the *cis* coupling constant across a double bond is smaller than the *trans* constant.²⁶ From Table 8 it can be seen that for the coupling between C1 and the β -protons this is true for the pair 4 and 5, in compound 7 and for the pair 8 and 9; for 2 it is the other way around. The constants for coupling between C2+C6 and the α -proton are between 2.4 and 4.0 Hz for all compounds (2, 4, 5 and 13).

EXPERIMENTAL

General. Melting points (uncorrected) were determined on a micro hotstage. IR spectra (KBr) were recorded on a Perkin-Elmer 281 B Infrared spectrophotometer, UV spectra on a Cary model 14 Recording spectrophotometer, NMR spectra on a Bruker WM 400 spectrometer and mass spectra on a VG-Micromass 7070 F instrument. Analytical GLC were performed on a Hewlett packard 5710A instrument and preparative GLC on Varian Aerograph model 711, both used with FID-detectors.

1-Chloro-2-pentachlorophenylethane (1). In a slightly modified and improved procedure⁷ a mixture of 1-chloro-2-phenylethane (70.2 g, 0.5 mol) and disulfur dichloride (4.1 g, 30.4 mmol) was added dropwise to a mixture of sulfur chloride (405 g, 3.0 mol) and dry aluminium chloride (2.5 g, 18.7 mmol) kept at 80 °C. After 3 h at this temperature gas evolution (HCl, SO₂) had subsided and benzene (400 ml) was added. After washing with dilute hydrochloric acid, sodium bicarbonate solution and finally water, the benzene layer was dried (MgSO₄) and solvent evaporated to give white crystals (150 g, 96 %). M.p. 92–93 °C (EtOH) (lit.⁷ 89–90 °C). ¹H NMR (CCl₄): δ 3.65 (4H,s).

2,3,4,5,6-Pentachlorostyrene (2) was made from 1 according to literature procedure⁷ in 95 % yield. M.p. 112–114 °C (EtOH) (lit.⁷ 113–114.5 °C).

1,2-Dichloro-1-pentachlorophenylethane (3). To a solution of chlorine (10.6 g, 0.15 mol) in tetrachloromethane (500 ml) was added 2 (30 g, 0.11 mol). After UV-irradiation for 2 h at room temperature, the solution was washed with sodium thiosulfate solution and water. After drying (MgSO₄) the organic solvent was evap-

orated to give 28.8 g (75 %) yellowish material. M.p. 94–96 °C (EtOH) (lit.³ 97–99 °C). ¹H NMR (CCl₄): AMX-spectrum: δ_A 4.03, δ_M 4.57, δ_X 6.04, J_{AM} =11.1 Hz, J_{AX} =6.3 Hz, J_{MX} =10.1 Hz.

(E)- β ,2,3,4,5,6-Hexachlorostyrene (4). To a solution of 3 (10.0 g, 28.8 mmol) in 2-propanol (400 ml) kept at 60 °C, was added dropwise a solution of sodium (0.7 g, 30.4 mmol) in 2-propanol (100 ml). The dropping funnel must be kept warm to avoid precipitation of sodium isopropoxide. The addition lasted for 3.5 h and the solution was stirred overnight at 60 °C, after which it was diluted with tetrachloromethane and washed with water to remove inorganic salts. After drying (MgSO₄) and evaporation of solvents, 8.7 g white residue was obtained. GLC (10 % SP 2100 at 250 °C) showed the presence of starting material (<1 %), 4 (72 %), 5 (10 %) and 6 (12 %). Two recrystallizations (EtOH) gave 4.6 g of 4 (95 % purity, GLC). The impurity (alkyne 6) was removed by preparative GLC (10 % Apiezon L at 260 °C). Purity of 4: 99.8 %. M.p. 120–120.5 °C (lit.³ 115–116 °C).

(Z)- β ,2,3,4,5,6-Hexachlorostyrene (5). (E)-isomer 4 (1.0 g, 3.2 mmol) was dissolved in tetrachloromethane (100 ml) and irradiated with UV-light. GLC-monitoring showed a very slow isomerization (~1.4 %/h). After 65 h the reaction was stopped and GLC showed a composition of (Z):(E)=89:11. Crystallization from mesitylene gave 5 of purity 99.9 % (GLC, SP 2100 at 250 °C). M.p. 126–129 °C.

(Pentachlorophenyl)acetylene (6) and α ,2,3,4,5,6-hexachlorostyrene (7). Compound 3 (8.0 g, 23 mmol) was dissolved in *tert*-butylalcohol (160 ml) and a solution of potassium *tert*-butoxide (5.26 g, 47 mmol) in *tert*-butylalcohol (160 ml) was added. After refluxing for 15 min tetrachloromethane was added and the mixture washed with water. Evaporation of the solvents (after drying) gave 5.7 g of a crude product which by GLC was found to contain 82 % of 6 and 10 % of 7. Two recrystallizations from ethanol gave 6 (3.5 g) of 98 % purity (GLC). M.p. 182–184 °C (lit.⁸ 185–186 °C). ¹H NMR (CCl₄): 3.67 (s) ppm.

The mother liquors were evaporated. After two recrystallizations from methanol, the residue gave a product containing 67 % of 7. Preparative GLC (10 % Apiezon L at 260 °C) gave 7 in 97.7 % purity. M.p. 88–94 °C (lit.² 83 °C).

(E)- and (Z)- α , β ,2,3,4,5,6-Heptachlorostyrenes (8) and (9). (Pentachlorophenyl)-acetylene (6) (3.5 g, 12.8 mmol) was dissolved in tetrachloromethane (100 ml), *cf.* Ref. 4. Chlorine (1.36 g, 19.2 mmol) dissolved in tetrachloromethane (30 ml) was added and the mix-

ture was irradiated (UV) for 90 min. Longer irradiation time increases the amount of impurities. After evaporation of solvent, a product (3.8 g) was obtained which contained 58 % of 8 and 39 % of 9. After two recrystallizations from acetone 8 (0.96 g) of 96 % purity (GLC) was obtained. Column chromatography (SiO₂ with hexane as eluent) increased the purity to 98.8 %. M.p. 114.5–115 °C (lit.⁴ 109–110 °C). Attempts to further increase the purity using preparative GLC led to partial isomerization to 9.

From the mother liquors was obtained a product (2.3 g) which contained 72 % of 9. Preparative GLC (10 % Apiezon L, 220–260 °C, 2 °/min) gave 9 of 98.7 % purity. M.p. 49–51 °C (lit.⁴ oil).

2,3,4,5,6-Pentachlorotoluene (10) was made in 58 % yield according to literature procedure.⁶ M.p. 217–218 °C (lit. 217.5 °C) ¹H NMR (CCl₄): δ 2.57 (s).

α , α ,2,3,4,5,6-Heptachlorotoluene (11).²⁷ 10 (10.0 g, 37.8 mmol) was heated to 240 °C. Chlorine gas was slowly passed through the melt for 5 h. The obtained crude product (10.1 g) was shown to contain 90 % of 11 and traces of α ,2,3,4,5,6-hexachlorotoluene (¹H NMR (CCl₄): δ 4.87 (s, 2H) ppm). It was, however, considered pure enough to use in the next synthetic step. ¹H NMR (CCl₄): δ 7.50 ppm (s).

2,3,4,5,6-Pentachlorobenzaldehyde (12) was made through reaction of 11 with conc. sulfuric acid at 100 °C for 18 h.²⁷ The conversion was quantitative. ¹H NMR (CCl₄): δ 10.23 (s).

β , β ,2,3,4,5,6-Heptachlorostyrene (13). Triphenylphosphine (11.35 g, 43.3 mmol) was dissolved in benzene (15 ml) and bromotrichloromethane (5.12 g, 25.8 mmol) was added. After stirring in nitrogen atmosphere for 1 h at 0 °C, pentachlorobenzaldehyde (12) (2.0 g, 7.2 mmol) dissolved in benzene (20 ml) was added in one portion. After stirring overnight, the solvent was evaporated and the residue exhaustively extracted with hexane. Purification using column chromatography (SiO₂, hexane) gave 1.9 g product which contained 90 % 13. Recrystallization did not improve the purity. Preparative GLC (SP 2100 at 220 °C) gave a product of 99.7 % purity. M.p. 112–113 °C (lit.⁴ 108–109 °C).

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