

Monofunctionalized Tridecachlorodiphenyl(2-pyridyl)methyl Radicals. Synthesis and Spectral Analysis

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Highly chlorinated diphenyl(2-pyridyl)methyl radicals and their α -H precursors with a carboxy, chlorocarbonyl, or allyloxycarbonyl substituent in the 4-position of one phenyl ring have been synthesized. All of them are stable red solids, completely dissociated (magnetic susceptibility), decomposing when melting (200–240 °C). Their ESR, UV-VIS and IR spectra are given.

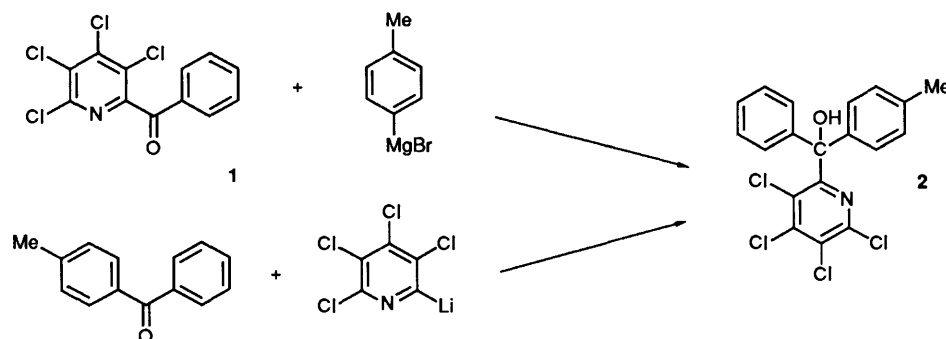
The most stable carbon free radicals described so far belong to the so-called PTM (perchlorotriphenylmethyl) series.¹ Their exceptionally high chemical passivity and thermal stability are mainly attributed to steric shielding of their molecular carbon backbone by the chlorine substituents.¹ Since perchloroaromatic triphenylmethyl radicals with an active functional group in the *para* position react at the functional group without impairment of their radical character, some of them have been used as spin labels.² However, they display only either a single line or unsatisfactory multiplets in their ESR spectra. In order to overcome this inconvenience, preliminary studies showed that the ESR spectrum of remarkably stable perchlorodiphenyl(2-pyridyl)methyl (PDPM) radical displays a fairly well resolved 1:1:1 triplet due to the coupling with ¹⁴N nuclear spin.³ Therefore, the synthesis of functionalized perchloroaromatic diphenyl(2-pyridyl)methyl radicals was undertaken.

An additional incentive to synthesize these radicals was that they might be useful in the preparation of polymeric materials with magnetic properties (polyradical polymers) by attaching the stable radical to a preformed polymer, through the appropriate functional group.⁴ In this paper, we report on the synthesis, thermal stability, and spectra of some perchloroaromatic diphenyl(2-pyridyl)methyl radicals with a functional group in the 4-position of a substituent phenyl group.

Synthesis of Precursors.—*p*-Methylphenylmagnesium bromide adds to 2-benzoyltetrachloropyridine **1** to give the adduct phenyl(tetrachloro-2-pyridyl)(*p*-tolyl)methanol **2** in moderate yield. Alternatively, this adduct was prepared by addition of tetrachloro-2-pyridyllithium to 4-methylbenzophenone but in poor yield † (Scheme 1).⁵

The pyridine **1**⁶ was prepared by a sequence of reactions

† This low yield can be explained, at least partially, in terms of the formation of 3-lithio and 4-lithio isomers in the preparation of tetrachloro-2-pyridyllithium.⁵



Scheme 1

Table 1 Recoveries (%)^a of the radicals after being heated in air for 1 h

Radical	Temp.	
	180 °C	210 °C
13	100	98
14	93	87
15	97	16

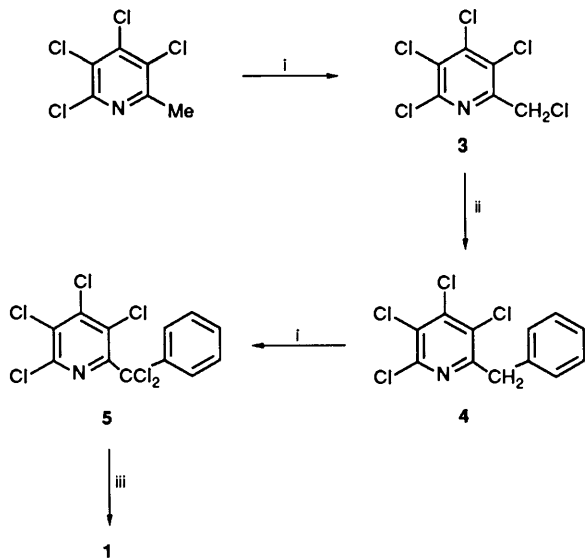
^a The recovered radicals were identified by IR spectroscopy. The recoveries were determined by combining weight and the absorptivity of the band at 575 nm.

starting from tetrachloro-2-methylpyridine, as indicated in Scheme 2.

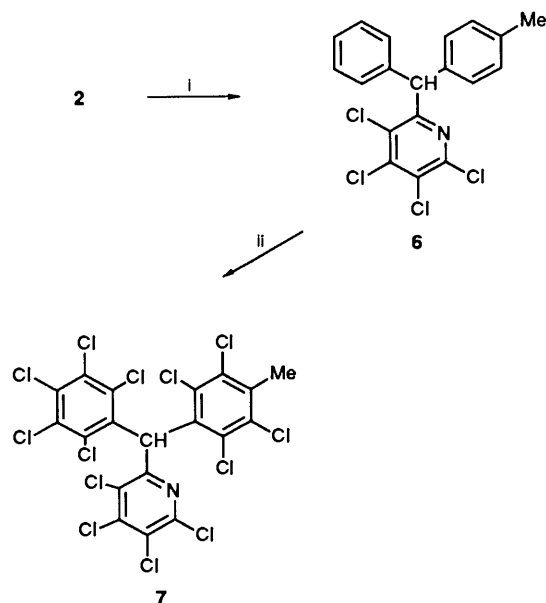
The methanol **2** was reduced with aq. HI/I₂ in refluxing hexane to afford phenyl(tetrachloro-2-pyridyl)(*p*-tolyl)methane **6**, which was chlorinated with reagent BMC (SO₂Cl₂, AlCl₃, S₂Cl₂)⁷ to compound **7** (Scheme 3). Long reaction times must be avoided in order to minimize the formation of fragmentation sub-products, which have been characterized as chloro(pentachlorophenyl)(tetrachloro-2-pyridyl)methane and 2,3,4,5,6-pentachlorotoluene.

Another sequence of reactions, as illustrated in Scheme 4, leads to triarylmethanes **10** and **12**, as immediate reaction precursors of the radicals **13** and **15**, respectively. Hence, photochlorination of compound **7** yielded compound **8**, which by treatment with oleum (30%) and water gave the aldehyde **9**. Oxidation with KMnO₄ afforded the acid **10**, which on reflux with SOCl₂ yielded the acid chloride **11**. Finally, compound **11** reacted readily with allylic alcohol to give the condensation product **12**.

Synthesis of Radicals.—Triarylmethanes **10** and **12** were converted into the corresponding radicals **13** and **15** by the conventional two-step process used for the radicals of the PTM



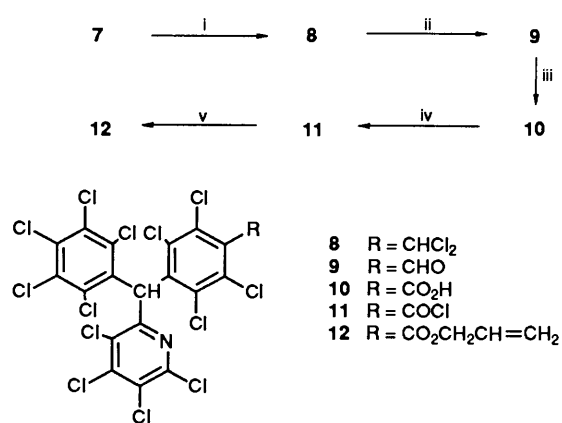
Scheme 2 Reagents and conditions: i, Cl_2 , $h\nu$, CCl_4 ; ii, AlCl_3 , C_6H_6 ; iii, aq. H_2SO_4



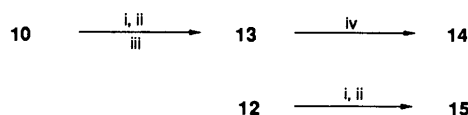
Scheme 3 Reagents: i, HI (57%), hexane; ii, AlCl_3 , S_2Cl_2 , SO_2Cl_2

series, *i.e.* treatment of the substrate with reagent BCR (NaOH , Me_2SO , diethyl ether)⁸ to give red solutions of the corresponding carbanions, and then oxidation of these anions to give the radicals with I_2 (Scheme 5). The preparation of radical **14** was not attempted directly from the triarylmethane **11** because the basic nature of the BCR reagent is strong enough to hydrolyse the COCl substituent. Hence, compound **14** was obtained by treatment of the carboxy radical **13** with SOCl_2 or PCl_5 in POCl_3 . All these new radicals, stable red solids which decompose when melting, were characterized by elemental analysis and spectroscopy. Thermal stabilities in air are shown in Table 1; as radical **15** melts at 202°C , the recovery is low at 210°C .

Electron Spin Resonance Spectra.—X-Band ESR spectra of radicals **13–15** were recorded in CH_2Cl_2 solution at room temperature. As an example, the spectrum of radical **13** is shown in Fig. 1 together with a computer simulation. All the data for the three radicals are collected in Table 2. The g -values are close to 2.0027, the normal value for a radical of the PTM series.



Scheme 4 Reagents and conditions: i, Cl_2 , $h\nu$, CCl_4 ; ii, 30% oleum, water; iii, KMnO_4 , acetone; iv, SOCl_2 ; v, $\text{CH}_2=\text{CHCH}_2\text{OH}$, CH_2Cl_2 and DMAP



Scheme 5 Reagents: i, NaOH , $\text{DMSO-Et}_2\text{O}$; ii, I_2 , Et_2O ; iii, H_3O^+ ; iv, SOCl_2 or PCl_5 , POCl_3

Table 2 ESR Spectral data of the radicals^a

Radical	g -Value	ΔH_{pp} ^b	Splitting (G) ^c		
			N	α - ^{13}C	atom- ^{13}C
13	2.0033	1.83	3.33	28.8	10.9, 10.5
14	2.0032	1.86	3.42	29.0	11.8, 10.5
15	2.0033	1.90	3.37	28.75	11.8, 10.5

^a All the spectra were recorded in CH_2Cl_2 solution ($\approx 10^{-3}$ mol dm^{-3}) at room temperature. ^b Peak-to-peak derivative width. ^c Found by computer simulation.

All the spectra consist of a fairly well resolved triplet due to electron-spin interaction with the ^{14}N nucleus. As in the case of radical PDPM it is assumed that the nitrogen-coupling constant is increased by a hyperconjugative mechanism because of the high angular tilting of the heteroaromatic ring with respect to the plane of the trivalent carbon sp^3 bonds.³

At higher gain, some additional lines of low intensity arising from ^{13}C appear in the spectrum. As usual, these satellite lines (shown by pairs of triplets) are assigned to spin coupling with the trivalent and aromatic (bridgehead and *ortho*) carbon atoms.³

Ultraviolet-Visible Spectra.—The data corresponding to the B, C and D bands of the radicals **13–15** are shown in Table 3. All these radicals display the typical radical band D with a negligible shift in correlation with radical PDPM.³ This is also in accord with the lack of appreciable differences in their ESR spectra.

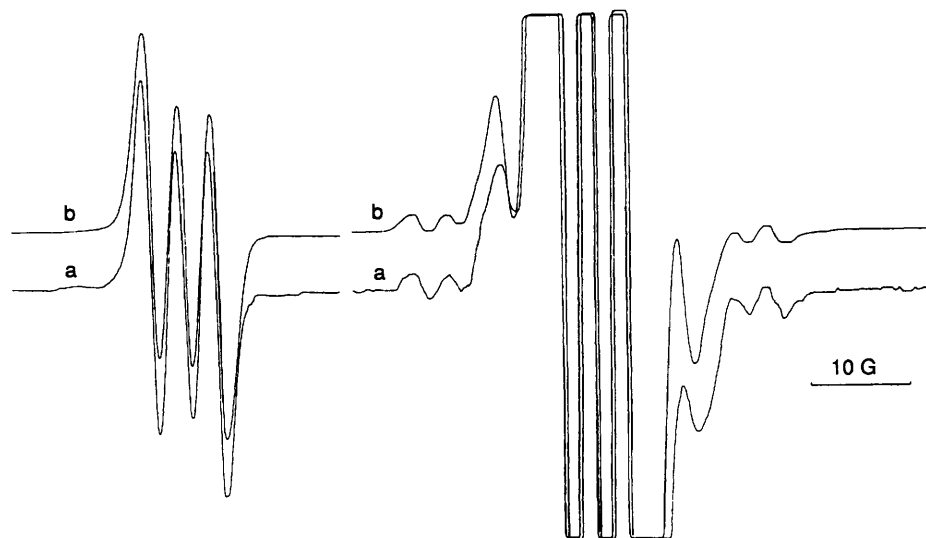


Fig. 1 (a) ESR spectrum of carboxy radical 13, and fifteen-fold amplification showing ^{13}C couplings. (b) Computer simulation.

Table 3 Electronic absorptions ($\lambda_{\text{max}}/\text{nm}$) and extinction coefficients ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) of radicals^a

Radical	Band B ($10^{-3} \epsilon$)	Band C ($10^{-3} \epsilon$)	Band D ($10^{-3} \epsilon$)
PDPM ⁷	277 (7.10) 290sh (6.70)	335sh (10.80) 368sh (23.50) 381 (25.60) 425sh (2.50)	505sh (1.39) 527 (1.40) 574 (1.70)
13	277 (6.40) 285 (6.40)	333sh (9.81) 373 (23.63) 418sh (2.62)	530 (1.28) 576 (1.51)
14	278 (6.61) 286 (6.55)	334sh (9.77) 376 (24.62) 418sh (2.71)	535 (1.33) 579 (1.68)
15	278 (6.40) 285 (6.44)	333sh (9.55) 373 (23.48) 417sh (2.59)	520 (1.23) 575 (1.52)

^a All the spectra were recorded in CHCl_3 solution.

Table 4 Magnetic properties of radicals

Radical	μ_{B}	Diamagnetic susceptibility $10^6 \chi_{\text{dia}} (\text{emu})$			10^{23} Spins mol^{-1}
		Curie-Weiss	Pascal	θ (K)	
13	1.72	-0.495	-0.482	-0.8	5.97
15	1.70	-0.523	-0.542	-0.8	5.85

Magnetic Susceptibilities.—The specific magnetic susceptibilities of radicals 13 and 15 have been measured from 77 K to room temperature. Least-squares correlation of the resulting Curie-Weiss plot gave the Bohr magnetons (μ_{B}), the specific diamagnetic susceptibilities (χ_{dia}), and the Weiss constants (θ), reported in Table 4. From μ_{B} -values the radical purity of radicals 13 and 15 has been calculated to be $\sim 100\%$.

Experimental

General Methods.—IR, UV-VIS and ESR spectra were recorded with Perkin-Elmer 682, 7300 and Varian E-109E spectrometers, respectively. Mass spectral data were obtained with a Magnetic Trisector, TS-250, VG TRITECH, Manchester UK (70 eV; 100 μA emission). The ESR simulations were

carried out by using a modified version of the software package of a Varian E-935 Data Acquisition System.

Handling of radicals in solution was performed in the dark. For the registration of the ESR spectra, the solution of the radicals in the ESR tubes was carefully degassed by a freeze-pump-thaw technique. Full IR spectra of perchlorinated radicals are included in this section; for other compounds only strong and medium peaks are recorded. Extracts were dried over Na_2SO_4 .

Tetrachloro-2-(chloromethyl)pyridine 3.—A slow stream of dry Cl_2 was passed (0.5 h) through a refluxing solution of 3,4,5,6-tetrachloro-2-methylpyridine (4.80 g) in CCl_4 (400 cm^3) illuminated with a 500 W incandescent lamp situated underneath the Pyrex container, thus providing a source of heat as well as light. Evaporation of the solvent afforded a residue, which was chromatographed on a column (silica gel; hexane and mixtures of hexane- CHCl_3 as eluent) to afford (i) tetrachloro-2-(trichloromethyl)pyridine³ (0.45 g, 6.5%), (ii) tetrachloro-2-(dichloromethyl)pyridine³ (2.1 g, 33.0%), (iii) tetrachloro-2-(chloromethyl)pyridine 3⁹ (3.34 g, 60.5%), m.p. 55.5–60 °C (Found: C, 27.3; H, 0.9; N, 5.2. Calc. for $\text{C}_6\text{H}_2\text{Cl}_5\text{N}$: C, 27.2; H, 0.8; N, 5.3%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1270, 1240, 1225, 1150, 956, 920, 840, 735 and 710; $\delta_{\text{H}}(\text{CCl}_4)$ 5.32 (s).

2-Benzyltetrachloropyridine 4.—A mixture of the pyridine 3 (1.00 g), anhydrous AlCl_3 (1.01 g), and benzene (100 cm^3) was refluxed and stirred (18 h) and then evaporated to dryness. The residue was treated with aq. 2 mol dm^{-3} HCl and diethyl ether. The ethereal layer was washed with water, dried, and evaporated, and the residue was purified by column (silica gel; CHCl_3) chromatography and recrystallized from hexane to give the title product 4 (0.467 g), m.p. 51–54 °C (Found: C, 47.1; H, 2.3; N, 4.5. $\text{C}_{12}\text{H}_7\text{Cl}_4\text{N}$ requires C, 46.9; H, 2.3; N, 4.5%); $\lambda_{\text{max}}(\text{C}_6\text{H}_{12})/\text{nm}$ 209, 236sh, 285 and 291 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 39 300, 8790, 4730, 4760); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1530, 1509, 1494, 1367, 1343, 1235, 830, 730, 712 and 691; $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$ 7.24 (5 H, m) and 4.26 (2 H, s).

The hexane mother liquors were dried and chromatographed on a column (silica gel). Pentane as eluent gave recovered reactant 3 (0.105 g, 10.5%), and CCl_4 gave more product 4 (0.427 g). The overall yield of compound was 78%.

Tetrachloro-2-(α,α -dichlorobenzyl)pyridine 5.—This compound was prepared as described for 3. Starting materials: pyridine 4 (0.518 g), CCl_4 (40 cm^3), reaction time, 1 h. The

crude reaction product was purified by column chromatography (silica gel; hexane) to give the *title compound 5* (0.296 g), m.p. 129–132 °C (from hexane) (Found: C, 38.4; H, 1.3; N, 3.7%. $C_{12}H_5Cl_6N$ requires C, 38.3; H, 1.3; N, 3.7%); $\lambda_{max}(C_6H_{12})/nm$ 216, 237sh, 276sh, 285 and 293 ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 41 970, 12 280, 2510, 3900, 3890); $\nu_{max}(KBr)/cm^{-1}$ 1500, 1352, 1323, 1303, 1219, 732, 688 and 623; $\delta_H(CCl_4)$ 7.24–7.55 (m).

The mother liquors, chromatographed on TLC plates (silica gel; hexane), gave more product **5** (0.237 g). The overall yield of compound **5** was 84%.

Phenyl Tetrachloro-2-pyridyl Ketone 1.—A mixture of the pyridine **5** (0.201 g) in conc. H_2SO_4 (20 cm^3) was stirred (30 min) at room temperature, then poured into ice-water, and extracted with diethyl ether. The extract was dried and evaporated to give ketone **1** (0.080 g), m.p. 89.5–90 °C (from hexane) (lit.,⁶ 88–89 °C) (Found: C, 45.0; H, 1.5; N, 4.3. Calc. for $C_{12}H_5Cl_4NO$: C, 44.9; H, 1.6; N, 4.4%); $\lambda_{max}(C_6H_{12})/nm$ 205, 251, 255sh, 286 and 291sh ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 37 900, 15 700, 15 300, 6280, 6120; $\nu_{max}(KBr)/cm^{-1}$ 1681, 1370, 1269, 1210, 984, 817, 711, 679 and 614; $\delta_H(CCl_4)$ 7.32–7.86 (m).

The mother liquors were dried, and washed with pentane, to give more *title product 1* (0.083 g). The overall yield of ketone **1** was 84%.

Phenyl(tetrachloro-2-pyridyl)(p-tolyl)methanol 2.—(a) From *phenyl tetrachloro-2-pyridyl ketone 1*. To a solution of 4-methylmagnesium bromide in diethyl ether [from 4-bromotoluene (0.512 g), Mg (0.115 g), diethyl ether (10 cm^3)] was added a solution of ketone **1** (1.0 g) in the same solvent (20 cm^3). The mixture was stirred at reflux (2 h), and then poured into aq. 2 mol dm^{-3} HCl. The ethereal solution was washed with water, dried and evaporated to dryness, and the residue was chromatographed on TLC plates (silica gel; hexane) to give recovered material (0.365 g, 36.5% recovery) and the *alcohol 2* (0.571 g, 44.0%), m.p. 117–119 °C (from hexane) (Found: C, 55.4; H, 3.1; N, 3.4; Cl, 34.8. $C_{19}H_{13}Cl_4NO$ requires C, 55.2; H, 3.2; N, 3.4; Cl, 34.3%); $\lambda_{max}(C_6H_{12})/nm$ 209, 233sh, 287 and 292 ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 52 900, 12 700, 5430, 5580); $\nu_{max}(KBr)/cm^{-1}$ 3473, 1506, 1335, 1316, 1042, 808, 761 and 694; $\delta_H(CCl_4)$ 7.21 (5 H, m), 7.05 (4 H, m), 5.19 (1 H, s) and 2.35 (3 H, s).

(b) From *4-methylbenzophenone*. To a solution of tetrachloro-2-pyridyllithium [from pentachloropyridine (30.0 g) in methylcyclohexane (250 cm^3); 1.6 mol dm^{-3} hexane solution of butyllithium (100 cm^3)] at room temperature was added a solution of 4-methylbenzophenone (16.8 g) in methylcyclohexane (200 cm^3). The mixture was stirred at room temperature (18 h) and then hydrolysed with water. The organic solution was dried and evaporated to dryness, and the residue was chromatographed on a column [silica gel; $CHCl_3$ – CCl_4 (1:1)] and recrystallized from hexane to give the *alcohol 2* (10.46 g, 29.0%).

Phenyl(tetrachloro-2-pyridyl)(p-tolyl)methane 6.—A mixture of compound **2** (5.87 g), aq. 57% HI (17.5 cm^3), and hexane (230 cm^3) was refluxed (4 h) and then treated with water. The organic layer was washed successively with aq. $NaHSO_3$, aq. $NaHCO_3$, and water, dried and evaporated to give *compound 6* (5.12 g, 90%), m.p. 118–120 °C (from hexane) (Found: C, 57.5; H, 3.3; N, 3.5; Cl, 35.7. $C_{19}H_{13}Cl_4N$ requires C, 57.5; H, 3.3; N, 3.5; Cl, 35.7%); $\lambda_{max}(C_6H_{12})/nm$ 207, 234sh, 268sh, 275sh, 288 and 293 ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 54 900, 13 400, 2820, 3020, 4830, 4870); $\nu_{max}(KBr)/cm^{-1}$ 1513, 1503, 1491, 1362, 1343, 1309, 728 and 691; $\delta_H(CCl_4)$ 7.18 (5 H, m), 7.03 (4 H, m), 5.92 (1 H, s) and 2.32 (3 H, s).

(*Pentachlorophenyl*)(*tetrachloro-4-methylphenyl*)(*tetra-*

chloro-2-pyridyl)methane **7.**—(a) A solution of compound **6** (2.05 g) and S_2Cl_2 (13.5 cm^3) in SO_2Cl_2 (200 cm^3) was added slowly to a refluxing solution of $AlCl_3$ (10.5 g) in SO_2Cl_2 (200 cm^3). The resulting solution was refluxed (2 h) while a solution of S_2Cl_2 (9.3 cm^3) in SO_2Cl_2 (30 cm^3) was gradually added. After the solution had cooled, the SO_2Cl_2 was eliminated under reduced pressure and the residue was treated with water. Solid $NaHCO_3$ was added gradually until no more gas evolution took place. The resulting mixture was heated (50 °C) on a steam-bath for 3 h, cooled, and strongly acidified with aq. 12 mol dm^{-3} HCl. The resulting solid was filtered off, dried, purified by column chromatography (silica gel; CCl_4) and then washed with pentane to give the *title compound 7* (2.188 g, 60%), m.p. 292–294 °C (Found: C, 32.2; H, 0.3; N, 2.1; Cl, 65.1. $C_{19}H_4Cl_{13}N$ requires C, 32.3; H, 0.6; N, 2.0; Cl, 65.2%); $\lambda_{max}(C_6H_{12})/nm$ 216, 230sh, 288 and 295 ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 101 200, 60 400, 5830, 5930); $\nu_{max}(KBr)/cm^{-1}$ 1357, 1330, 1312, 1279, 1245, 1128, 1081, 832, 814, 655 and 632; $\delta_H(CDCl_3)$ 6.94 (1 H, s) and 2.62 (3 H, s).

(b) When the reaction mixture was refluxed for 4 h, and then the crude product was chromatographed (silica gel; hexane), the following compounds were obtained: (i) 2,3,4,5,6-pentachlorotoluene (0.278 g, 21%); (ii) compound **7** (0.906 g, 25%), and (iii) *chloro(pentachlorophenyl)(tetrachloro-2-pyridyl)methane* (0.773 g, 30%), m.p. 227–228 °C (Found: C, 28.2; H, 0.05; N, 2.7; Cl, 69.0. $C_{12}HCl_{10}N$ requires C, 28.1; H, 0.2; N, 2.7; Cl, 69.0%).

(*Pentachlorophenyl*)[2,3,5,6-tetrachloro-4-(*dichloromethyl*)-*phenyl*](*tetrachloro-2-pyridyl*)methane **8.**—This compound was prepared in a similar method to that described for **3**. Starting materials: compound **7** (2.44 g); CCl_4 (170 cm^3); reaction time, 35 h. The crude reaction product was purified on a column (silica gel; $CHCl_3$) to give *title compound 8* (2.436 g, 91%), m.p. 282–284 °C (from hexane) (Found: 29.4; H, 0.3; N, 1.8; Cl, 68.8. $C_{19}H_2Cl_{15}N$ requires C, 29.4; H, 0.3; N, 1.8; Cl, 68.5%); $\lambda_{max}(C_6H_{12})/nm$ 217, 288, 296 and 308sh ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 101 600, 6220, 6840, 2170); $\nu_{max}(KBr)/cm^{-1}$ 1358, 1334, 1315, 1280, 1134, 1081, 816 and 711; $\delta_H(CCl_4)$ 7.62 (1 H, s) and 6.97 (1 H, s).

(*Pentachlorophenyl*)(*tetrachloro-4-formylphenyl*)(*tetrachloro-2-pyridyl*)methane **9.**—A mixture of compound **8** (2.047 g) and 30% oleum (90 cm^3) was stirred (24 h) at room temperature, and the final solution was poured into ice-water and extracted with $CHCl_3$. The extract was purified by column chromatography (silica gel; $CHCl_3$), dried and evaporated to dryness, to give *aldehyde 9* (1.822 g, 96%), m.p. 271–272 °C (from hexane) (Found: C, 31.7; H, 0.3; N, 2.0; Cl, 63.7. $C_{19}H_2Cl_{13}NO$ requires C, 31.6; H, 0.2; N, 1.9; Cl, 63.9%); $\lambda_{max}(C_6H_{12})/nm$ 216, 268sh, 288, 295sh and 318sh ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 87 800, 8240, 6420, 6790, 1630); $\nu_{max}(KBr)/cm^{-1}$ 1718, 1356, 1331, 1281 and 1134; $\delta_H(CDCl_3)$ 10.34 (1 H, s) and 6.98 (1 H, s).

4-Carboxytetrachlorophenyl(*pentachlorophenyl*)(*tetrachloro-2-pyridyl*)methane **10.**—A solution of *aldehyde 9* (2.00 g) and $KMnO_4$ (2.052 g) in acetone (190 cm^3) was refluxed (2 h), and then an excess of ethanol was added. The mixture was poured into dil. aq. HCl and extracted with $CHCl_3$. The extract was washed with water, dried, and evaporated to dryness, and the residue was purified on a column (silica gel; CH_2Cl_2 –formic acid 2%) to give *acid 10* (1.756 g, 86%), m.p. 260–265 °C (from diethyl ether–hexane) (Found: C, 31.1; H, 0.3; N, 1.8; Cl, 62.5. $C_{19}H_2Cl_{13}NO_2$ requires C, 30.9; H, 0.3; N, 1.9; Cl, 62.5%); $\lambda_{max}(C_6H_{12})/nm$ 216, 288 and 296 ($\epsilon/dm^3 mol^{-1} cm^{-1}$ 93 200, 6300, 6650); $\nu_{max}(KBr)/cm^{-1}$ 1773, 1358, 1330, 1101, 1081, 651 and 606; $\delta_H(CDCl_3)$ 6.95 (s).

(Pentachlorophenyl)[tetrachloro-4-(chloroformyl)phenyl]-(tetrachloro-2-pyridyl)methane **11**.—A solution of acid **10** (0.90 g) in SOCl_2 (90 cm^3) was refluxed (24 h). Elimination of the solvent gave a residue, which was passed through silica gel in CHCl_3 , to give the acid chloride **11** (0.902 g, 97%), m.p. 258–261 °C (from hexane) (Found: C, 30.1; H, 0.2; N, 2.0; Cl, 65.7. $\text{C}_{19}\text{HCl}_{14}\text{NO}$ requires C, 30.2; H, 0.1; N, 1.8; Cl, 65.7%); $\lambda_{\text{max}}(\text{C}_6\text{H}_{12})/\text{nm}$ 215, 242sh, 289 and 295 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 98 400, 39 440, 6850, 7340); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1792, 1352, 1329 and 1142.

[4-(Allyloxy carbonyl)tetrachlorophenyl](pentachlorophenyl)(tetrachloro-2-pyridyl)methane **12**.—A solution of the acid chloride **11** (1.152 g), allyl alcohol (0.362 g), and 4-dimethylaminopyridine (DMAP) (0.350 g) in CH_2Cl_2 (40 cm^3) was stirred at room temperature under argon (24 h), and then was poured into aq. 2 mol dm^{-3} HCl and extracted with diethyl ether. The extract was washed with water, dried and evaporated to dryness, and the residue was purified by column chromatography (silica gel; CHCl_3) to give the ester **12** (1.058 g, 89%), m.p. 195–197 °C (from hexane) (Found: C, 34.2; H, 0.8; N, 1.8; Cl, 59.2. $\text{C}_{22}\text{H}_6\text{Cl}_{13}\text{NO}_2$ requires C, 34.0; H, 0.8; N, 1.8; Cl, 59.3%); $\lambda_{\text{max}}(\text{C}_6\text{H}_{12})/\text{nm}$ 216, 279sh, 289 and 295 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 105 400, 4140, 6680, 7020); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ (1749, 1359, 1330, 1255, 1231, 1221, 1202 and 816; $\delta_{\text{H}}(\text{CDCl}_3)$ 6.94 (1 H, s), 6.21–5.81 (1 H, m), 5.56–5.28 (2 H, m) and 4.92–4.86 (2 H, d).

(4-Carboxytetrachlorophenyl)(pentachlorophenyl)(tetrachloro-2-pyridyl)methyl Radical **13**.—A mixture of acid **10** (0.460 g), powdered NaOH (2.5 g), diethyl ether (100 cm^3), and dimethyl sulphoxide (DMSO) (17 cm^3) was shaken (24 h) in the dark. The mixture was filtered through a sintered-glass funnel onto I_2 (0.110 g), the mixture was left in the dark (45 min) and then poured into dil. aq. NaHSO_3 whereupon a red precipitate was formed. Dil. aq. HCl was added to the stirred mixture, which was then extracted with diethyl ether. The extract was washed with water, dried, and evaporated to dryness, and the residue was passed through silica gel with CH_2Cl_2 -formic acid 2% to give acid radical **13** (0.326 g, 71%), m.p. 238–240 °C (from hexane) (Found: C, 31.3; H, 0.1; N, 2.0; Cl, 62.4. $\text{C}_{19}\text{HCl}_{13}\text{NO}_2$ requires C, 31.0; H, 0.1; N, 1.9; Cl, 62.6%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3452br, 3207br, 2924w, 1755s, 1729m, 1544w, 1515w, 1469w, 1404w, 1324s, 1280m, 1202m, 1135w, 1119w, 1082w, 1043w, 906w, 846w, 831w, 790m, 743m, 710w, 695w, 671w, 652w, 612m, 567w, 509w and 415w; m/z 735 (M^+ , 7%) and 700 (100, $\text{M} - \text{Cl}$).

(Pentachlorophenyl)[tetrachloro-4-(chloroformyl)phenyl]-(tetrachloro-2-pyridyl)methyl Radical **14**.—(a) With SOCl_2 . A solution of acid radical **13** (0.050 g) in SOCl_2 (5 cm^3) was refluxed (5 h), and the solvent was evaporated off. The residue was chromatographed on a column (silica gel; hexane- CHCl_3) to yield radical **14** (0.026 g, 51%), m.p. 236–237 °C (from hexane) (Found: C, 30.5; N, 1.9; Cl, 65.6. $\text{C}_{19}\text{Cl}_{14}\text{NO}$ requires C, 30.2; N, 1.8; Cl, 65.8%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1789s, 1514w, 1471w, 1334s, 1320s, 1309s, 1279m, 1218w, 1200m, 1156m, 1084w, 1058w, 984w, 944m, 868w, 830w, 797w, 765m, 738w, 708m, 684w, 670w, 652w, 640w, 630w, 619w, 606w, 594w, 564w, 534w, 503w and 480w; m/z 753 (M^+ , 2%), 718 (37, $\text{M} - \text{Cl}$) and 683 (100, $\text{M} - 2\text{Cl}$).

(b) With PCl_5 . A mixture of acid radical **13** (0.300 g), PCl_5 (0.855 g), and POCl_3 (14 cm^3) was stirred at 90 °C (4 h). Distillation of the solvent gave a residue, which was treated with cold water and extracted with CHCl_3 . Elimination of the solvent from the extract afforded a residue, which was passed through a column (silica gel; hexane- CHCl_3) to give free radical **14** (0.194 g, 63%).

[4-(Allyloxy carbonyl)tetrachlorophenyl](pentachlorophenyl)(tetrachloro-2-pyridyl)methyl Radical **15**.—The reaction was carried out in a similar manner to the synthesis of carboxy radical **13** [compound **12** (0.540 g), NaOH (2.1 g), diethyl ether (180 cm^3), DMSO (35 cm^3); 24 h; I_2 (0.80 g); 10 h]. The ethereal solution was treated with dil. aq. NaHSO_3 and water, dried, and evaporated to dryness to afford a residue, which was chromatographed on TLC plates (silica gel; hexane) to give recovered material **12** (0.100 g, 18.5% recovery) and radical **15** (0.282 g, 52%), m.p. 202–203 °C (from hexane) (Found: C, 34.2; H, 0.7; N, 1.9; Cl, 59.3. $\text{C}_{22}\text{H}_5\text{Cl}_{13}\text{NO}_2$ requires C, 34.0; H, 0.7; N, 1.8; Cl, 59.4%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2923w, 1748s, 1514w, 1461w, 1396w, 1326s, 1282m, 1239s, 1209m, 1136w, 1124w, 1080w, 1033w, 949w, 932w, 829w, 797w, 756w, 736w, 703w, 688w, 673w, 656w, 636w, 620w, 581w, 565w and 505w.

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