%) CCH was isolated after column chromatography and recrystallization from ethanol; mp 51–52 °C (lit.[35] mp 53.5–54.5 °C).

Product Balances. In the experiments performed to obtain the product balances, THF was added (if necessary) before the workup in order to restore the original volume. Then a 10-mL sample was hydrolyzed by 10 mL of 2 N HCl and extracted with $CHCl_3$ (benzophenon case) or pentane and ether (cyclohexanone experiments). A 1-mL extract was mixed with 1 mL of an internal standard solution of dodecane by using calibrated micropipets and analyzed by gas chromatography. Concentrations of TPE were also measured by UV analysis starting from a 2-mL sample treated in the usual way and diluted to the desired dilution factor. Absorbances at λ_{max} = 309 nm ($CHCl_3$) were compared against absorbances of standard solutions of TPE. No interferences were observed.

ESR Measurements. The reduction of $TiCl_3$ with Mg at a 1:1.7 $TiCl_3$/Mg ratio was followed by ESR. At regular intervals (about every 30 min) an aliquot of the reaction mixture was transferred with the help of a syringe into the ESR tube, which was flushed before with Ar and carefully closed immediately after being filled. Spectra were recorded at room temperature. Step 1 (eq 1) was also followed as a function of the $TiCl_3$/Mg ratio ranging from 1:0.2 to 1:1.8. In each case [M] was prepared as stated (3 h reflux) by using the same ESR conditions as before. The results were completely analoguous; i.e., for example, a spectrum of [M] with a 1:0.8 $TiCl_3$/Mg ratio was equivalent to one recorded with a 1:1.7 $TiCl_3$/Mg ratio after half the reduction time.

The reduction of $TiCl_3$ by $LiAlH_4$ is fast and was only followed as a function of $TiCl_3/LiAlH_4$ ratios. For each ratio, the reaction mixture was prepared by addition of the appropriate amount of $LiAlH_4$ to an ice-cooled $TiCl_3$–THF mixture. After the addition, the mixture was allowed to warm to room temperature and stirred for 30 min under an argon atmosphere. As before, samples were transferred into an ESR tube under a vigorous Ar stream, and room-temperature spectra recorded.

The coupling (eq 2) was studied by starting from an [M], generated under optimal conditions (Table I), which showed no ESR activity. Then, again under a vigorous Ar stream, the ketone was added in one portion up to a $TiCl_3$/ketone ratio of 1:1. After hydrogen evolution, the tubes were closed, and ESR signals were followed with respect to time at room temperature.

The ESR tubes, solvents, and reagents were checked to be inactive in the ESR spectrometer.

Acknowledgment. Much of this investigation could not have been performed without the equipment kindly put at our disposal by other institutes. We express our sincerest gratitude to Professor Dr. J. Reedijk (State University Leiden, The Netherlands), Dr. P. Van der Put (Technical University Delft, The Netherlands), and Professor Dr. D. Schoemaker (Department of Physics, UIA) for their permission to use the X-band and Q-band ESR spectrometers and above all for their professional expertise. The help of Drs. P. Bloch with the electron microscope and of Professor Dr. M. Herman (University of Antwerp, RUCA) with the IR spectroscopy and thermogravimetry is gratefully acknowledged. Professor Dr. F. Alderweireldt, Dr. E. Esmans, Dr. R. Dommisse, and Mr. Y. Luyten (University of Antwerp, RUCA) are thanked for their assistance with the gas chromatographic analyses and for recording NMR and mass spectra. Dr. Jerzy Herlich and Dr. I. Wolochowicz (Technical University, Warsaw, Poland) are thanked for stimulating discussions and critical remarks. M. M. is grateful for receiving a postdoctoral grant within the framework of the Polish-Belgian Exchange Treaties. R. Dams thanks the Belgian organization IWONL for a predoctoral grant.

Registry No. Benzophenone, 119-61-9; cyclohexanone, 108-94-1; tetraphenylethene, 632-51-9; cyclohexylidenecyclohexane, 4233-18-5; benzil, 134-81-6; fluorenone, 486-25-9; anthrone, 90-44-8; anthraquinone, 84-65-1; benzophenone radical ion 1–, 16592-08-8; benzil radical ion 1–, 16827-94-4; fluorenone radical ion 1–, 3101-67-5; anthrone radical ion 1–, 34500-64-6; anthraquinone radical ion 1–, 3426-73-1; acetophenone, 98-86-2; 3-pentanone, 96-22-0; cyclohexanol, 108-93-0; 3-pentanol, 584-02-1; benzhydrol, 91-01-0; 2,3-dimethyl-2-butene, 563-79-1; $TiCl_3$, 7705-07-9.

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Inert Carbon Free Radicals. 2. Monofunctionalized Tetradecachlorotriphenylmethyl Radicals and Related Compounds

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Perchlorinated triphenylmethyl radicals, and their nonradical α-H precursors, with hydrogen (**2**), carboxy (**3**), carbomethoxy (**4**), ammonium carboxylate (**5**), bromo (**6**), iodo (**7**), and methyl (**8**) substituents in the 4-position have been synthesized and their reactivities studied. The radicals are completely disassociated even in the solid (magnetic susceptibility), and their radical character is not changed by O_2 or highly reactive chemical agents. Their decomposition points in air range from 270 °C to beyond 300 °C. Their remarkable spectra (ESR, UV–vis, and IR) are given and interpreted. A novel substitutive–oxidative decarboxylation with I_2 has been found in carboxy radical **3**.

Some years ago, the authors reported the discovery of the so-called "inert carbon free radicals".[1] These are trivalent carbon species which are completely disassociated even in crystalline form, do not react with oxygen in solution or with typical radical reagents (nitric oxide, quinone, hydroquinone, toluene, etc.), and are remarkably inert toward reactive chemical species (concentrated H_2SO_4, concentrated HNO_3, Cl_2, Br_2, etc.). Furthermore, in air they withstand temperatures as high as 300 °C. Their chemical inertness and thermal stability are traced to steric shielding rather than to electronic effects.[1a] The

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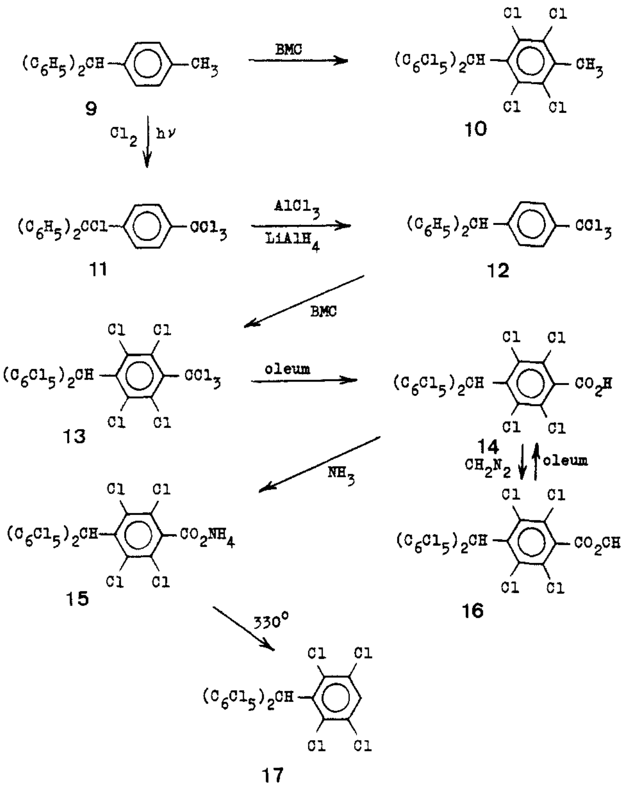
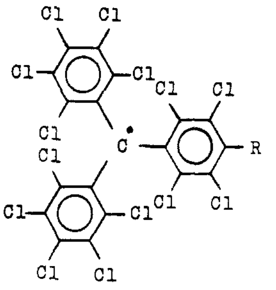
[1] (a) Ballester, M.; Riera, J.; Castañer, J.; Badía, C.; Monsó, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215. (b) Ballester, M.; Riera, J.; Castañer, J. Spanish Patent 311 621 (1965); U.S. Patent 3 347 941 (1967); Canadian Patent 805 963 (1969).

Scheme I



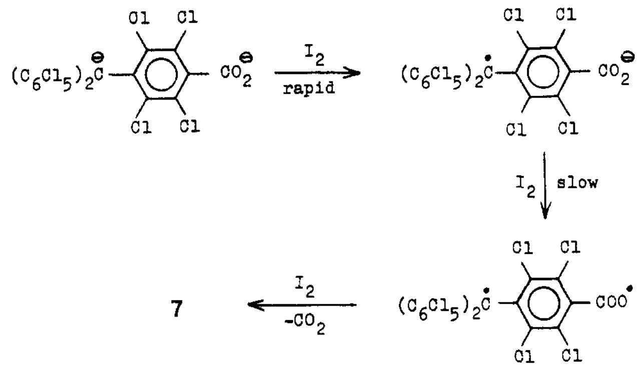
paradigm of these "inert free radicals" is perchlorotriphenylmethyl (PTM, 1).



1, R = Cl
2, R = H
3, R = CO_2H
4, R = CO_2CH_3
5, R = CO_2NH_4
6, R = Br
7, R = I
8, R = CH_3

Electron-transfer processes of PTM involving the formation of the corresponding exceptionally stable carbanion and carbonium ions have been reported.[2-6] The ESR, UV-vis, and IR spectra have also been studied,[1,7,8] as well as its photochemical and thermal behavior up to over 300 °C.[1,9,10]

Scheme II



Since the extreme stability of these radicals is due mainly to the shielding of the trivalent carbon by six ortho chlorines[1a] replacement of chlorine in para positions by other substituents would provide them with chemical reactivity at the substitution site without affecting significantly their radical inertness.

Accordingly, we report here the synthesis and study of a new series of PTM-type radicals with a substituent other than chlorine in one para position (R = H, CO_2H, CO_2CH_3, $CO_2^-NH_4^+$, Br, I, and CH_3; 2-8).

Results

Synthesis of Precursors. 4-Methyltriphenylmethane (9,[11] Scheme I) was photochlorinated with Cl_2 to **α-chloro-4-(trichloromethyl)triphenylmethane** (11), which was reduced selectively with the system $AlCl_3$–$LiAlH_4$ to **4-(trichloromethyl)triphenylmethane** (12). (Note: In the absence of $AlCl_3$, reduction of the CCl_3 group also takes place.) The latter, by aromatic perchlorination with reagent BMC[12] (initial components: $AlCl_3$, S_2Cl_2, and SO_2Cl_2) gave **α-*H*-heptadecachloro-4-methyltriphenylmethane** (13), which by treatment with hot oleum and then with water gave **α-*H*-tetradecachlorotriphenylmethane-4-carboxylic acid** (14). This acid with N_2CH_2 gave the methyl ester 16, which reverted to 14 with oleum.

Acid 14, with NH_3, gave the ammonium salt 15, which was decarboxylated by heating it at 330 °C with finely ground Pyrex glass to **α-*H*,4-*H*-tetradecachlorotriphenylmethane** (17).

Aromatic perchlorination of hydrocarbon 9 with reagent BMC[12] yielded **α-*H*-tetradecachloro-4-methyltriphenylmethane** (10).

α-H compound 13 is a sterically strained, distorted molecule on account of the repulsions between the Cl_3C group and the neighboring ortho chlorines, as it occurs with perchlorotoluene and perchloro-*p*-xylene[12a,13] (see UV discussion), which also has been synthesized by means of reagent BMC.[12]

Radicals. The α-H precursors 14, 16, 17, and 10 were converted into the inert free radicals **4-carboxytetradecachlorotriphenylmethyl (3)**, **4-(carbomethoxy)tetradecachlorotriphenylmethyl (4)**, **4-*H*-tetradecachlorotriphenylmethyl (2)**, and **tetradecachloro-4-methyltriphenylmethyl (8)**, respectively, in a

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[2] Ballester, M.; de la Fuente, G. *Tetrahedron Lett.* **1970**, 4509.

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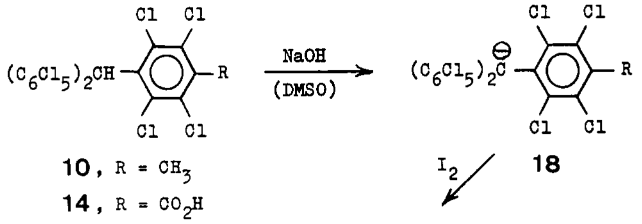
[13] Ballester, M.; Castañer, J. *J. Am. Chem. Soc.* **1960**, *82*, 4259.



10, R = CH_3
14, R = CO_2H
16, R = CO_2CH_3
17, R = H

18

2, R = H
3, R = CO_2H
4, R = CO_2CH_3
8, R = CH_3

two-step process, i.e., conversion into the corresponding tetradecachlorotriphenylcarbanions (**18**) with NaOH–Me_2SO–ether, followed by oxidation with I_2. The yields ranged from 70% to 85%.

In the synthesis of carboxy radical **3**, **4-iodotetradecachlorotriphenylmethyl radical (7)** was eventually isolated as a byproduct (Scheme II). The yield of the latter increased greatly (up to 43%) with both I_2 concentration and contact time. This product is regarded as resulting from a sort of Hunsdieker–Borodin decarboxylation which is known to be promoted by electron-attracting substituents such as chlorine.

It is noteworthy that under the very strong basic conditions employed in the preparation of 4-carbomethoxy radical **4**, no significant hydrolysis occurred.

Carboxy radical **3** was converted quantitatively into **ammonium tetradecachlorotriphenylmethane-4-carboxylate radical (5)**. Iodo radical **7** reacts with Br_2 or with Cl_2 in CCl_4, giving **4-bromotetradecachlorotriphenylmethyl (6)** or PTM (**1**), respectively, without loss of the radical character. Bromo radical **6** is similarly converted with Cl_2 into PTM (**1**).

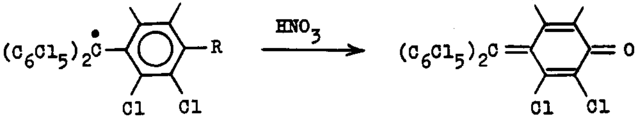
The synthesis of the perchloro-4-methyltriphenylmethyl radical was unsuccessfully attempted. It was found that α-H compound **13**, under the conditions leading usually to the formation of the carbanions (the precursors of the radicals), reacts at the trichloromethyl group to give the corresponding α-H acid **14** (hydrolysis) and α-H,p-H compound **17** (demethylation).

Electron Transfers. Radicals **2**–**4** were reduced with the mixture NaOH–Me_2SO–ether (see above), giving the corresponding carbanions, which by treatment with acid gave α-H compounds **17**, **14**, and **16**, respectively. Those radicals were also reduced with HI; in the case of carbomethoxy radical **4**, hydrolysis to acid **14** also took place. The latter reductions with HI had not been observed before and are also regarded essentially as electron-transfer processes, either eq 1 or 2.

$$R\cdot + HI \rightarrow R^- (HI)^{+\cdot} \rightarrow RH + {}^1/{}_2I_2 \qquad (1)$$

$$H^+ + R\cdot + I^- \rightarrow H^+ \cdots \dot{R} \cdots I^- \rightarrow RH + {}^1/{}_2I_2 \qquad (2)$$

While toward concentrated HNO_3 hydrogen and carbomethoxy radicals **2** and **4** are remarkably stable, carboxy and iodo radicals **3** and **7** are slowly oxidized, giving perchlorofuchsone (**19**).



3, R = CO_2H
7, R = I

19

Table I. Percent Recovery of **2**–**4** and **7** after 1 h

4-R	compd	temp, °C 230	260	270	300	330
H	2	100	97		0	
CO_2H	3			93	88.5	60
CO_2CH_3	4			97.5	0	
I	7	97		73	0	

Chemical Stabilities of the Radicals. The stabilities of most of the radicals here described toward some radical reagents and other chemical agents were tested. The recoveries were ascertained by comparing weight and absorptivity for bands C and D (see UV–vis section).[1a]

Radicals with hydrogen (**2**), carboxy (**3**), carbomethoxy (**4**), bromo (**6**), and iodo (**7**) substituents are stable toward refluxing toluene (2 days, recovery >95%), hydroquinone in ether (7 days, recovery >95%), *p*-quinone in ether (7 days, recovery >93%), powdered NaOH in ether (2 days, recovery >91%), concentrated H_2SO_4 (2 days, recovery >90%), nitric oxide in CCl_4 (40 min, recovery >94%), and O_2 in $CHCl_3$ (30 days, recovery 100%). Radicals **4**, **3**, and **2** are also stable to Br_2 in CCl_4 (dark, 3 days; recovery >91%) and Cl_2 in CCl_4 (dark, 3 days; recovery >95%). As mentioned, bromo radical **6** and iodo radical **7** are not stable to chlorine. While hydrogen radical **2** and carbomethoxy radical **4** are also stable toward concentrated HNO_3 (2 days, recovery 92%), carboxy radical **3** and iodo radical **7** do react (2 days, recovery ≤64%).

Thermal Stabilities of the Radicals. Some thermal stabilities were tested in the air (see Table I) and analyzed as above.[1a] Decomposition seems to be closely associated with melting. While in solid form the radicals are stable toward white light, in solution they are not, giving presumably fluorenyl radicals.[10]

Electron Spin Resonance. The ESR data are collected in Table II. The *g* values vary from 2.0024 to 2.0038, in good agreement with those found for the PTMs previously reported (PTM, PPTM, PDTM, PTTM, and PTBT).[1a] The values for bromo radical **6** and iodo radical **7** are somewhat higher than usual due possibly to slight *spin*–orbit coupling with Br or I.

The ESR spectra of radicals **3**–**7** consist, as for PTM itself, of a single main line and three pairs of ^{13}C satellites, two of which are close to the slope of the main line (around 27 and 35 MHz), which are assigned by spectrum simulation to the C_2, C_6, and C_1 aromatic ^{13}C, respectively. (The assignment for those ^{13}C's reported in ref 1 is incorrect; it should be reversed.) The third satellite pair (~82 MHz) is attributed the α-^{13}C.[1a]

On account of their low nuclear magnetic moment, couplings with Cl, Br, and I only contribute to some line broadening (~4 MHz). Radicals **2** and **8**, containing hydrogen, do show splitting of the main line, the coupling constant being higher in the methyl radical **8** (6.0 MHz) than in the H radical **2** (5.3 MHz), as expected (Table II). The ^{13}C splittings have the usual values.

Magnetic Susceptibility. The specific magnetic susceptibilities of the radicals have been measured from 77 K (liquid N_2) to room temperature. Least-squares correlation of the resulting Curie–Weiss plot gave the Bohr magnetons (μ), the specific diamagnetic susceptibility (χ_{dia}), and the Weiss constant (θ) (Table III). χ_{dia} values were independently calculated from Pascal's systematics,[14]

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(15) Ballester, M.; Castañer, J.; Riera, J.; Villanueva, J. unpublished results.

Table II

R	compd	g	lines	line width, MHz	splittings, MHz H	splittings, MHz α-^{13}C	splittings, MHz aromatic ^{13}C
Cl	1	2.0026	1	4.0		82.5	30.0, 35.5
H	2	2.0027	2	3.5	5.3	83.2	28.7, 35.3
CO_2H	3	2.0027	1	4.4		82.3	28.6, 34.5
CO_2CH_3	4	2.0024	1	4.4		82.5	29.1, 34.8
CO_2NH_4	5	2.0027	1	3.7		83.2	28.6, 34.3
Br	6	2.0033	1	4.8		81.8	25.2, ~35
I	7	2.0038	1	4.1		80.9	25.0, 34.0
CH_3	8	2.0027	4	3.5	6.0	82.9	29

Table III

R	compd	μ	$10^6\chi_{dia}$, emu Curie-Weiss	$10^6\chi_{dia}$, emu Pascal[15,17]	θ, K	spins/mol ($\times 10^{-23}$)
Cl	1	1.74	−0.505	−0.514	2.1	6.1
H	2	1.76	−0.549	−0.517	−4.8	6.2
CO_2H	3	1.74	−0.502	−0.506	0.9	5.9
CO_2CH_3	4	1.76	−0.511	−0.519	−3.8	6.2
CO_2NH_4	5	1.77		−0.512	0	6.3
Br	6	1.73	−0.498	−0.501	−3.4	6.0
I	7	1.74	−0.530	−0.490	−4.4	6.1
CH_3	8	1.72	−0.542	−0.523	−2.9	5.9

being in good agreement (Table III).[17] From μ the purities (spins per mole) were calculated.

The purity for radical salt **5** could not be found by that correlation since at low temperature (77 K) it apparently absorbs a trace of oxygen from the atmosphere of helium employed. Consequently, it was calculated from χ at room temperature by employing Pascal's systematics[14,17] for χ_{dia} and assuming $\theta = 0$ K (an average), and was close to the value for the PTMs.

Ultraviolet–Visible Spectra. (a) α-H Compounds. α-H compounds **10** and **14–17** show the so-called "primary band" group (maximum at ~220 nm) and a dentate "secondary band" (^1L_b) around 295 nm, characteristic of substituted benzenes.[1a,16] The ^1L_b band of trichloromethyl compound **13** presents, however, an additional peak at longer wavelengths (321 nm) which is due to steric strain and distorsion at the benzene ring bearing the trichloromethyl group[12a,13] (see Synthesis of Precursors).

(b) Radicals. The radicals display the four bands of the PTMs previously reported[1a] with the following approximate locations: A, 220 nm; B, 285 nm; C, 380 nm; D, 500–560 nm. Bands C (ϵ ~36 000) and D (~1100) are associated with the radical character; A and B are primary and secondary bands (see part a).

It is mentioned that the purity of radicals of the PTM series can be roughly estimated by absorptivity measurements of bands C and D.

Infrared Spectrum. With respect to the carbonyl peak, perchlorination of the benzene ring causes an upward shift (acid, ~50 cm^{-1}; ester, ~20 cm^{-1}; NH_4 salt, ~5 cm^{-1}) beyond the upper limit of the accepted normal intervals in both the radicals and α-H compounds. For the aromatic peaks, the benzenoid peaks found around 1600 and 1500 cm^{-1} in nonchlorinated compounds look as if they are[8] downshifted to about 1525–1500 and 1390–1300 cm^{-1}, respectively, in the highly chlorinated compounds here and in those previously[1a] reported. It has also been found that all the radicals show a medium-to-strong peak near 730 cm^{-1}, while in the α-H compounds it is close to 805 cm^{-1}.

Experimental Section

General Methods. The IR, UV–vis, and ESR have been recorded with Perkin-Elmer 457, Perkin-Elmer 350, and Varian E4 spectrometers, respectively. The magnetic susceptibilities have been measured in helium with a Varian 4-in. magnet with constant-force caps and a Cahn RG electrobalance.

The handling of radicals in solution was performed in the dark.

Since the locations of the IR peaks of perchloroorganic compounds differ markedly from those of their nonchlorinated counterparts, it is regarded as useful to include them in this section.

α-Chloro-4-(trichloromethyl)triphenylmethane (11). A slow stream of dry Cl_2 was passed (3 h) through a refluxing solution of 4-methyltriphenylmethane (**9**, 5.00 g) in purified CCl_4 (500 mL) while it was illuminated with an incandescent lamp (500 W) situated underneath the Pyrex container, thus providing the heat. Elimination of the solvent afforded a yellow resin (8.11 g) which by crystallization in hexane gave pure **11**: 4.99 g (65.1%); mp 122–124 °C; UV (C_6H_{12}) λ_{max} 236 nm (ϵ 15 700); IR (KBr) 3086, 3072, 3055, 1610, 1498, 1461, 1456, 1418, 1212, 1192, 878, 800, 765, 750, 718, 702 cm^{-1}; ^{1}H NMR (CCl_4) τ 2.05 (d, 2, H-3, H-5, J = 8 Hz), 2.60 (m, 12, aromatic H). Anal. Calcd for $C_{20}H_{14}Cl_4$: C, 60.6; H, 3.6; Cl, 35.8. Found: C, 60.8; H, 3.6; Cl, 35.6.

4-Trichloromethyltriphenylmethane (12). αChloro compound **11** (6.00 g) was added to a solution of $LiAlH_4$ (0.492 g) and anhydrous $AlCl_3$ (2.98 g) in anhydrous ether (500 mL), and the mixture was refluxed (5 h) under N_2. After cooling, ice–water (300 mL) was added slowly. Evaporation of the ethereal solution gave a yellow resin (5.58 g) which was passed through activated acid alumina in hexane and recrystallized from the same solvent to give **12**: 3.77g (68.8%); mp 115–116 °C; UV (C_6H_{12}) λ_{max} 238 nm (ϵ 13 800); IR (KBr) 3080, 3048, 3018, 2868, 1598, 1492, 1449, 1441, 1410, 1180, 1029, 878, 856, 822, 801, 755, 727, 704 cm^{-1}; ^{1}H NMR (CCl_4) τ 2.06 (d, 2, 3-H, 5 H, J = 8 Hz), 2.80 (m, 12, aromatic H). Anal. Calcd for $C_{20}H_{15}Cl_3$: C, 66.4; H, 4.2; Cl, 29.4. Found: C, 66.5; H, 4.2; Cl, 29.4.

α-*H*-Heptadecachloro-4-methyltriphenylmethane (13). A solution of trichloromethyl compound **12** (5.00 g) and S_2Cl_2 (2.6 g) in SO_2Cl_2 (160 mL) was added slowly to a refluxing solution of anhydrous $AlCl_3$ (1.3 g) in SO_2Cl_2 (340 mL). The resulting solution was concentrated by distillation to about 80 mL (1 h) and then refluxed (3 h), keeping the volume constant by gradual addition of SO_2Cl_2. The resulting reaction mixture was treated with water (600 mL) and most of the SO_2Cl_2 evaporated in vacuo. Solid $NaHCO_3$ was added gradually until no more gas evolution took place. The mixture was heated on a steam bath (1 h), acidified with concentrated aqueous HCl, and cooled. The col-

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[16] Ballester, M.; Riera, J.; Spialter, L. *J. Am. Chem. Soc.* **1964**, *86*, 4276.

[17] The atomic susceptibility contribution for Cl here applied is -18.15×10^{-6} emu. It has been calculated from a great number of poly- and perchlorinated compounds.[15] It differs significantly from the value generally accepted (-20.1×10^{-6}).[14]

lected solid was washed with water, dried (11.7 g), passed (CCl_4) through activated alumina, and recrystallized from the same solvent to give **13**: 6.69 g (57.4%); mp 272–274 °C; UV (C_6H_{12}) λ_{max} 222, nm (ϵ 99 400), 294 (1320), 306 (1660), 321 (1760); IR (KBr) 2905, 1529, 1366, 1357, 1328, 1306, 1289, 1129, 811, 805, 770, 709, 701, 662, 631, 530, 518 cm^{-1}. ^{1}H NMR (CCl_4) τ 2.88 (s, 1, α-H). Anal. Calcd for $C_{20}HCl_{17}$: C, 28.5; H, 0.1; Cl, 71.4. Found: C, 28.5; H, 0.3; Cl, 71.5.

α-*H*-Tetradecachlorotriphenylmethane-4-carboxylic Acid (14). A mixture of α-H compound **13** (0.500 g) and 20% oleum (250 mL) was heated (110–120 °C) with stirring (90 h). The final deep blue solution was cooled and poured slowly into cracked ice (1000 mL), and the collected solid was washed with water, dissolved in ether, and extracted with aqueous $NaHCO_3$. The aqueous layer (a suspension of the Na salt) was acidified with aqueous HCl and extracted with ether. The solid extracted (0.423 g) was recrystallized from CCl_4 to give acid **14**: 0.342 g (74.9%); mp 320–322 °C; UV (C_6H_{12}) λ_{max} 222, 237 (sh), 254 (sh), 284 (sh), 293, 302 nm (ϵ 110 900, 68 300, 24 200, 1230, 1640, 1770); IR (KBr) 3560–2700, 2905, 1757, 1730, 1371, 1328, 1314, 1298, 807, 520 cm^{-1}. Anal. Calcd for $C_{20}H_2Cl_{14}O_2$: C, 31.2; H, 0.3; Cl, 64.4. Found: C, 31.2; H, 0.5; Cl, 64.4.

Methyl α-*H*-Tetradecachlorotriphenylmethane-4-carboxylate (16). Acid **14** (1.515 g) was treated with an excess of CH_2N_2 in ether and evaporated, and the residue was passed (CCl_4) through activated silica gel and recrystallized from the same solvent to give ester **16**: 1.310 g (84.9%); mp 286–289 °C; UV (C_6H_{12}) λ_{max} 222, 236 (sh), 252 (sh), 282 (sh), 294, 303 nm (ϵ 112 500, 75 700, 30 100, 869, 1530, 1690); IR (KBr) 2948, 2920, 1750, 1740, 1554, 1528, 1433, 1370, 1355, 1331, 1311, 1296, 1263, 1228, 808, 669, 520 cm^{-1}; ^{1}H NMR (CCl_4) τ 2.95 (s, 1, α-H), 5.99 (s, 3, CH_3). Anal. Calcd for $C_{21}H_4Cl_{14}O_2$: C, 32.1; H, 0.5; Cl, 63.3. Found: C, 31.9; H, 0.7; Cl, 63.2.

Hydrolysis of Methyl Ester 16. A mixture of methyl ester **16** (0.154 g) and 20% oleum (130 mL) was heated (70–80 °C, 26 h) with stirring. The reaction mixture was treated as in the synthesis of acid **14**, affording also the acid **14** (0.107 g, 70.7%) and some starting material (0.032 g, 20.7%). The conversion was 89.9% of theory.

Ammonium α-*H*-Tetradecachlorotriphenylmethane-4-carboxylate (15). A stream of dry NH_3 was passed (30 min) through a solution of acid **14** (1.98 g) in ether (1000 mL), and the mixture was then left overnight. The resulting precepitate was ammonium salt **15**: 1.956 g (96.7%); mp 312–315° dec; UV (C_2H_5OH), λ_{max} 221, 254 (sh), 282 (sh), 294, 302 nm (ϵ 110 400, 27 500, 842, 1320, 1410); IR (KBr) 3660–2400, 1600, 1400, 1369, 1350, 1332, 1311, 1296, 802, 520 cm^{-1}. Anal. Calcd for $C_{20}H_5Cl_{14}NO_2$: C, 30.5; H, 0.6; Cl, 63.0; N, 1.8. Found: C, 30.7; H, 0.6; Cl, 63.2; N, 1.8.

α-*H*,4-*H*-Tetradecachlorotriphenylmethane (17). A mixture of ammonium salt **15** (1.87 g) and finely ground Pyrex glass (10.0 g) was heated (330–335 °C, 30 min) in an inert atmosphere. The resulting reaction mass was treated with ether. The organic extract in CCl_4 was passed through activated alumina and crystallized from hexane to give the 4-H compound **17**: 0.994 g (57.6%); mp 238–240 °C; UV (C_6H_{12}) λ_{max} 221, 252 (sh), 282 (sh), 292, 302 nm (ϵ 112 800, 21 600, 900, 1520, 1660); IR (KBr) 3060, 2920, 1535, 1402, 1370, 1355, 1341, 1296, 1239, 802 cm^{-1}; ^{1}H NMR (CCl_4) τ 2.21 (s, 1 H); 2.90 (s, 1 H). Anal. Calcd for $C_{19}H_2Cl_{14}$: C, 31.4; H, 0.3; Cl, 68.3. Found: C, 31.4; H, 0.4; Cl, 68.5.

4-(Carbomethoxy)tetradecachlorotriphenylmethyl Radical (4). A mixture of methyl ester **16** (1.057 g) and powdered NaOH (4.0 g) was shaken (24 h) in the dark with a 15% solution of Me_2SO in ether (575 mL), a deep red color being formed. The mixture was filtered through a sintered-glass funnel into a solution of I_2 (1.5 g) in ether. The solution was left undisturbed in the dark (24 h), and it was then washed with an aqueous solution of $NaHSO_3$ (to destroy I_2), an aqueous solution of NaCl, and finally with water (to eliminate Me_2SO), dried, and evaporated. The residue (0.952 g) in CCl_4 was passed through activated silica gel and recrystallized from CCl_4–heptane to give bright red crystals of carbomethoxy radical **4**: 0.902 g (85.4%); mp 304–306 °C dec; UV-vis (C_6H_{12}) 222, 284, 330 (sh), 364 (sh), 382, 504, 558 nm (ϵ 85 700, 7052, 6170, 18 600, 34 500, 1150, 1050); IR (KBr) 2950, 2840, 1752, 1537, 1500, 1436, 1334, 1321, 1305, 1279, 1260, 1232, 815, 730, 710, 520 cm^{-1}; ESR (CCl_4), Table II; magnetic susceptibility, Table III. Anal. Calcd for $C_{21}H_3Cl_{14}O_2$: C, 32.2; H, 0.4; Cl, 63.3. Found: C, 32.1; H, 0.4; Cl, 63.2.

Reduction of Carbomethoxy Radical 4. (a) With NaOH in Ether–Me_2SO. A mixture of carbomethoxy radical **4** (0.035 g), powdered NaOH (0.4 g), ether (20 mL), and Me_2SO (3 mL) was shaken (22 h) in the dark under argon and at room temperature. The resulting red solution was poured into diluted aqueous HCl, and the ethereal layer was decanted, washed with water, and evaporated. The residue (0.036 g) was passed in CCl_4 through activated alumina to give methyl ester **16**, 0.030 g (85.6%).

(b) With HI in Acetic Acid. A mixture of carbomethoxy radical **4** (0.043 g), concentrated HI (2.5 mL), and acetic acid (15 mL) was refluxed (16 h) in the dark and under argon. The reaction mixture was poured over aqueous dilute $NaHSO_3$ and extracted with ether. The resulting ethereal solution was treated with aqueous $NaHCO_3$, giving a precipitate in the aqueous layer. Without filtration this layer was decanted, acidified with concentrated aqueous HCl, and extracted with ether. By evaporation of this solvent, carboxylic acid **14** (0.035 g, 82.8%) was obtained.

4-*H*-Tetradecachlorotriphenylmethyl Radical (2). The reaction was performed as in the synthesis of the carbomethoxy radical **4** (α-H,4-H compound **17**, 0.878 g; NaOH, 4.0 g; ether, 500 mL; Me_2SO, 75 mL; 24 h). Deep red crystals of the 4-H radical were obtained: 0.643 g (73.3%); mp 262–264 °C; UV-vis (C_6H_{12}) 220, 237 (sh), 280, 325 (sh), 364 (sh), 381, 503, 556 nm (ϵ 83 500, 54 200, 6230, 5380, 17 800, 31 400, 1070, 975); IR (KBr) 3095, 1538, 1504, 1382, 1336, 1329, 1255, 731, 700, 649, 508 cm^{-1}; ESR (CCl_4), Table II; magnetic susceptibility, Table III. Anal. Calcd for $C_{19}HCl_{14}$: C, 31.5; H, 0.1; Cl, 68.4. Found: C, 31.3; H, 0.1; Cl 68.5.

Reduction of 4-H Radical 2. (a) With NaOH in Ether–Me_2SO. This reduction was performed as in that of the carbomethoxy radical **4** (4-H radical **4**, 0.047 g; NaOH, 0.2 g; ether, 25 mL; Me_2SO, 4 mL; 23 h). α-H,4-H compound **17** (0.032 g, 68.0%) was obtained.

(b) With HI in Acetic Acid. This reduction was performed as for that of the carbomethoxy radical **4** (4-H radical **2**, 0.059 g; concentrated HI, 2.5 mL; acetic acid, 15 mL; 6 days). α-H,4-H compound **17** (0.053 g, 89.7%) was obtained.

4-Carboxytetradecachlorotriphenylmethyl Radical (3) and 4-Iodotetradecachlorotriphenylmethyl Radical (7). Method a. The reaction was carried out as in the synthesis of the carbomethoxy radical **4** (carboxylic acid **14**, 2.00 g; NaOH, 10.0 g; ether, 1200 mL; Me_2SO, 200 mL; 24 h; I_2, 2.4 g; 24 h). The red residue (1.981 g) was dissolved in ether and treated with aqueous $NaHCO_3$, whereupon a red precipitate was formed. The clear ethereal layer was evaporated, and the residue (0.545 g[in CCl_4 was passed through activated alumina and recrystallized form CCl_4–hexane to give bright garnet-red crystals of 4-iodo radical **7**: 0.415 g (18.8%); mp 317–318 °C dec; UV-vis (C_6H_{12}) 223, 280 (sh), 320 (sh), 368 (sh), 389, 515, 567 nm (ϵ 82 300, 7350, 4610, 18 200, 33 700, 1360, 1420); IR (KBr) 1505, 1337, 1328, 1311, 1300, 811, 731, 701, 655, 631, 522, 520 cm^{-1}; ESR (CCl_4), Table II; magnetic susceptibility, Table III. Anal. Calcd for $C_{19}Cl_{14}I$: C, 26.8; Cl, 58.3; I, 14.9. Found: C, 26.9; Cl, 58.1; I, 14.8.

The aqueous layer (with the precipitate) was acidified with aqueous HCl and extracted with ether. Evaporation of the solvent gave a residue (1.294 g) which was recrystallized from CCl_4 to give bright red crystals of carboxy radical **3**: 1.018 g (51.0%); mp 331–332 °C dec; UV-vis (C_6H_{12}) 222, 284, 330 (sh), 364 (sh), 384, 480, 563 nm (ϵ 81 200, 6310, 5140, 17 900, 34 400, 1250, 1130); IR (KBr) 3660–2400, 1760, 1740, 1540, 1506, 1340, 1325, 1262, 730, 521 cm^{-1}; ESR (CCl_4), Table II; magnetic susceptibility, Table III. Anal. Calcd for $C_{20}HCl_{14}O_2$: C, 31.2; H, 0.1; Cl, 64.5. Found: C, 31.0; H, 0.1; Cl, 64.4.

Method b. The preceding reaction was repeated with a greater amount of I_2 (4.8 g). The yields were as follows: 4-iodo radical **7**, 43.6%; carboxy radical **3**, 32.4%.

Method c. The reaction described in method a was repeated with a shorter I_2 reaction time (carboxylic acid **14**, 0.999 g; NaOH, 5.0 g; ether, 600 mL, Me_2SO, 100 mL; 24 h; I_2, 0.205 g; contact with I_2, 50 min). Carboxy radical **3** (69.0%) was obtained.

Reduction of Carboxy Radical 3. (a) With NaOH in Ether–Me_2SO. This reduction was performed as in that of carbomethoxy radical **4** (carboxy radical **3**, 0.090 g; NaOH, 0.6 g; ether, 50 mL; Me_2SO, 8 mL; 24 h). Carboxylic acid **14** (0.072 g, 79.9%) was obtained.

(b) With HI in Acetic Acid. The reaction was performed as in the reduction of carbomethoxy radical 4 (carboxy radical 3, 0.042 g; HI, 2.5 mL; acetic acid, 15 mL; 6 days). Carboxylic acid 14 (0.032 g, 76.1%) was obtained.

Oxidation of Carboxy Radical 3. A mixture of carboxy radical 3 (0.059 g) and concentrated HNO_3 (10 mL) was stirred (6 days) at room temperature and in the dark. The reaction mixture was poured into water and extracted with ether, and the ethereal solution was treated with aqueous $NaHCO_3$. The aqueous layer (containing a red precipitate) was acidified with aqueous HCl and extracted with ether. By evaporation some starting material was recovered (0.024 g, 38.6%). The ethereal layer was evaporated, and the residue (0.034 g) was purified by TLC (silica gel, hexane–CCl_4), giving yellow crystals of perchloro(diphenylmethylene)cyclohexa-2,5-dienone (perchlorofuchsone, perchloro-α,α-diphenylquinomethane, 19), 0.028 g (49.3%).[3]

Oxidation of Iodo Radical 7. This reaction was performed as in the oxidation of carboxy radical 3. The yield in perchlorofuchsone (19) was 60.9%, along with a 38.4% recovery of radical 7.

Derivatives of Carboxy Radical 3. (a) Methyl Ester 4. The methylation of carboxy radical 3 (0.058 g) with CH_2N_2 in ether afforded, after recrystallization (CCl_4–hexane), carbomethoxy radical 4, 0.057 g (96.5%).

(b) Ammonium Tetradecachlorotriphenylmethane-4-carboxylate Radical (5). A slow stream of dry NH_3 was passed (30 min) through a solution of carboxy radical 3 (0.200 g) in ether (100 mL), and the mixture was left undisturbed (48 h) in the dark. The red precipitate was filtered and washed with ether to give ammonium salt 5: 0.202 g (98.8%); mp 330–331 °C dec; UV–vis (C_2H_5OH) 222, 282, 330 (sh), 364 (sh), 384, 515, 568 nm (ϵ 83 000, 5410, 1350, 17 300, 34 900, 1400, 1540); IR (KBr) 3680–2300, 1701, 1605, 1505, 1404, 1339, 1325, 1309, 1260, 730 cm^{-1}; ESR (CCl_4), Table II; magnetic susceptibility, Table III. Anal. Calcd for $C_{20}H_4Cl_{14}NO_2$: C, 30.5; H, 0.5; Cl, 63.1; N, 1.8. Found: C, 30.7; H, 0.5; Cl 63.0; N, 1.7.

Hydrolysis of Amonium Salt 5. A mixture of ammonium salt 5 (0.072 g) and aqueous HCl (10 mL) was stirred (2 h) in the dark. The ethereal layer was washed with water, dried, and evaporated. The residue was digested with hot hexane to give carboxy radical 3, 0.067 g (95.1%).

4-Bromotetradecachlorotriphenylmethyl Radical (6). 4-Iodo radical 7 (0.044 g) was treated with Br_2 (1 mL) in CCl_4 (25 mL) (dark, 3 days). Evaporation of the reaction solution gave a residue which, in CCl_4, was passed through activated silica gel and recrystallized from the same solvent to give 4-bromo radical 6: 0.041 g (98.5%); mp 314–316 °C dec; UV-vis (C_6H_{12}) 223, 278, 330 (sh), 364 (sh), 385, 510, 562 nm (ϵ 93 800, 7210, 7700, 19 000, 39 900, 1250, 1280); IR (KBr) 1506, 1339, 1318, 1311, 1260, 812, 732, 529 cm^{-1}; ESR (CCl_4), Table II; magnetic susceptibility, Table III. Anal. Calcd for $C_{19}Cl_{14}Br$: C, 28.4; Cl, 61.7; Br, 9.9. Found: C, 28.6; Cl, 61.6; Br, 9.9.

Reaction of 4-Iodo Radical 7 with Cl_2. A slow stream of dry Cl_2 was passed (dark, 72 h) through a solution of 4-iodo radical 7 (0.038 g) in CCl_4 (20 mL). Next, a stream of N_2 was passed through to eliminate the excess of Cl_2, and the solution was evaporated. The residue in CCl_4 was filtered through silica gel and recrystallized from the same solvent to give PTM radical 1, 0.030 g (88.5%).

Reaction of 4-Bromo Radical 6 with Cl_2. It was performed as in the preceding reaction (4-bromo radical 6, 0.046 g; CCl_4, 20 mL; 71 h). PTM radical 1 (0.040 g, 92.0%) was obtained.

***α-H*-Tetradecachloro-4-methyltriphenylmethane (10).** A solution of hydrocarbon 9 (1.60 g) in SO_2Cl_2 (50 mL) was added slowly to a refluxing solution of anhydrous $AlCl_3$ (0.32 g) and S_2Cl_2 (0.64 g) in SO_2Cl_2 (120 mL). The resulting solution was refluxed (dark, 10 h), keeping the volume constant by periodic small additions of SO_2Cl_2. The resulting black reaction solution was concentrated at to half its volume and then evaporated in vacuo. The residue was treated as in the synthesis of α-H compound 13 to afford the 4-methyl derivative 10: 2.325 g (50.7%); mp 336–339 °C; UV (C_6H_{12}) 219, 293, 302 nm (ϵ 115 000, 1000, 1000); IR (KBr) 2920, 1530, 1520, 1440, 1370, 1341, 1298, 805, 526 cm^{-1}; ^1H NMR (CCl_4) τ 2.75 (s, 1 H), 7.27 (s, 3 H). Anal. Calcd for $C_{20}H_4Cl_{14}$: C, 32.4; H, 0.5; Cl, 67.0. Found: C, 32.5; H, 0.5; Cl, 67.0.

Tetradecachloro-4-methyltriphenylmethyl Radical (8). 4-Methyl derivative 10 (0.500 g) was dissolved in a refluxing mixture of ether (300 mL) and Me_2SO (60 mL). Next, powdered NaOH (1.5 g) was added, and the mixture refluxed (dark, 2 h). The cool mixture was shaken (dark, 24 h), and a deep red color appeared. O_2 was then passed (45 min) through the solution, and the latter was filtered through a sintered-glass funnel over I_2 (1.5 g), and then it was left undisturbed (dark, 24 h). The resulting reaction mixture was treated as in the synthesis of carbomethoxy radical 4 to yield 4-methyl radical 8: 0.400 g (80.1%); red crystals; mp 303–320 °C dec; UV–vis (C_6H_{12}) 222, 280, 366 (sh), 383, 510, 560 nm (ϵ 84 800, 7700, 14 900, 33 900, 1100, 1000); IR (KBr) 2920, 1505, 1338, 1326, 1320, 1262, 811, 730, 702, 655, 647, 632, 527 cm^{-1}; ESR (CCl_4), Table II; magnetic susceptibility, Table III. Anal. Calcd for $C_{20}H_3Cl_{14}$: C, 32.5; H, 0.4; Cl, 67.1. Found: C, 32.7; H, 0.7; Cl, 67.3.

Attempted Preparation of Sodium Perchloro-4-methyltriphenylmethide. A mixture of α-H compound 13 (0.250 g), and powdered NaOH (0.30 g) was shaken (24 h) in the dark with a 15% solution of Me_2SO in ether (125 mL), a deep red color being formed. The mixture was filtered through sintered glass onto dilute aqueous HCl (500 mL). The resulting mixture was decanted, and the aqueous layer was extracted with ether. The combined organic layers were extracted with aqueous $NaHCO_3$. The aqueous layer (a suspension) was treated as in the synthesis of α-H acid 14, yielding acid 14, 0.043 g (19.9%).

The ethereal layer was washed with water, dried, and evaporated. The residue was passed in CCl_4 through activated alumina, and crystallized from hexane to give α-H,p-H compound 17 (0.115 g, 53.5%).

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