$$(k_{-2})_{obsd} = \gamma_1 - b(\gamma_1 - \gamma_2) \quad (12)$$

which allows to find k_{-2} as the slope of a $(k_{-2})_{obsd}$ vs. $[Fe^{3+}]$ plot (Figure 4c). In this manner, we obtain a value of 206 $dm^3\ mol^{-1}\ s^{-1}$ for k_{-2}. Secondly, we note in Figure 4a that the apparent rate constant γ_1 varies linearly with ferric ion, $\gamma_1 = m[Fe^{3+}] + n$, showing a steady increase in the range 0.520–5.20 mM (m = 599 $dm^3\ mol^{-1}\ s^{-1}$) and a small, but definitely nonzero, extrapolated intercept at $[Fe^{3+}]$ = 0 (n = 0.17 s^{-1}). This linear behavior of γ_1, first order in ferric, can be deduced from eq 7 considering that when $[Fe^{3+}]$ is small, γ_1 approaches Y, which can thus be identified as the intercept of the γ_1 vs. $[Fe^{3+}]$ plot. The small value observed for Y, and thus for k_{-1}, allows to neglect the term $4(k_1)_{obsd}k_{-1}$ in eq 7 at intermediate ferric concentrations, and, therefore, under those conditions, the slope of the γ_1 plot can be approximated by $(k_{-2} + k_1)$. This allows to obtain approximate values for $Y = (k_{-3} + k_{-1}) = n$ and $X = (k_{-2} + k_1) = m$ and in turn for $k_1 = X - k_{-2}$ = 393 $dm^3\ mol^{-1}\ s^{-1}$. The small value found for the intercept n permits to set a maximum value for k_{-3} of the order of 0.17 s^{-1}.

Third, equating the two square root terms in eq 7 and 8, we find the sum of the observed rate constants as

$$(X + Y)_{obsd} = \gamma_1 + \gamma_2 \quad (13)$$

which gives an expression for $(k_1)_{obsd}$ as

$$(k_1)_{obsd} = (\gamma_1 + \gamma_2) - Y - (k_{-2})_{obsd} \quad (14)$$

and yields a second estimate for k_1 as the slope of a $(k_1)_{obsd}$ vs. $[Fe^{3+}]$ plot (Figure 4b). The value of 405 $dm^3\ mol^{-1}\ s^{-1}$ found in this fashion compares very well with the value of 393 obtained from k_{-2} and the slope of the γ_1 plot.

Lastly, we obtain an estimate of the relative value of the first-order rate constants $k_{-3} + k_{-1}$ contained in Y, considering that the values of γ_2 are much smaller than those of γ_1 and show, instead of a linear behavior, a Michaelis-type dependence with ferric (Figure 5), $\gamma_2 = p[Fe^{3+}]/(q + [Fe^{3+}])$. Nonlinear least-squares fitting of the γ_2 values as a function of ferric concentration gives $p = (\gamma_2)_{max}$ = 0.10 s^{-1} and $q = [Fe^{3+}]_{1/2}$ = 3.0 mM. Evaluation of eq 8 as a function of $[Fe^{3+}]$ is in agreement with this observation since, for small $[Fe^{3+}]$, γ_2 vanishes, and, although the dependence with ferric is complex, we can show that the observed Michaelis behavior for the slow phase of this system can be deduced from the analytical expression for γ_2. Rearranging eq 8 gives eq 15.

$$\gamma_2 = \tfrac{1}{2}\{(X + Y)_{obsd} - ((X + Y)_{obsd}^2 - 4(Y(k_{-2})_{obsd} + (k_1)_{obsd}k_{-3}))^{1/2}\} \quad (15)$$

This equation can be expressed by a binomial expansion of the form

$$\gamma_2 = \{(Y(k_{-2})_{obsd} + (k_1)_{obsd}k_{-3})/(X + Y)_{obsd}\} + \{(Y(k_{-2})_{obsd} + (k_1)_{obsd}k_{-3})^2/(X + Y)_{obsd}^3\} + \ldots$$

The condition for the first term to be a good approximation for the series is that

$$\{(4Y(k_{-2})_{obsd} + (k_1)_{obsd}k_{-3})/(X + Y)_{obsd}^2\} \ll 1$$

and this is fulfilled under any of the two following circumstances: (a) $(k_1)_{obsd} \gg k_{-3}$ or (b) $(k_1)_{obsd} \gg k_{-1}$. In this fashion, at high ferric concentrations, we obtain eq 16 as an approximate expression for γ_2 consistent with the observed Michaelis behavior.

$$\gamma_2 = (Y(k_{-2})_{obsd} + (k_1)_{obsd}k_{-3})/(X + Y)_{obsd} \quad (16)$$

When $[Fe^{3+}]$ is large, $\gamma_2 \rightarrow p$ in $\gamma_2 = p[Fe^{3+}]/(q + [Fe^{3+}])$, and thus we can write eq 17

$$p = (Yk_{-2} + k_1k_{-3})/(X + Y) \quad (17)$$

which gives a value of 0.06 s^{-1} for k_{-3} and 0.11 s^{-1} for k_{-1}.

Inert Carbon Free Radicals. 7. "The (Kinetic) Reverse Effect" and Relevant Synthesis of New Monofunctionalized Triphenylmethyl Radicals and Their Nonradical Counterparts

Manuel Ballester,* Jaime Veciana, Juan Riera, Juan Castañer, Concepción Rovira, and Olga Armet

Instituto de Química Orgánica Aplicada (C.S.I.C.), C. Jorge Girona Salgado 18-26, 08034 Barcelona, Spain

Received November 14, 1985

The high chemical passivity of the so-called "inert free radicals" (IFRs), particularly those derived from perchlorotriphenylmethyl (PTM), has allowed one to ascertain the kinetic influence of the free radical character on the reactivity of their nonradical substituents. In all cases here reported (including homolysis of the carbon–halogen bond, nucleophilic substitutions, and radical-chain bromination), a moderate to dramatic increase of the reaction rates is observed. These results are accounted for in terms of transition-state stabilization by the radical character. In that connection, the following IFRs have been synthesized for the first time from other monosubstituted IFRs as immediate reaction precursors: methanol **15**, propionic acid **16**, bromomethane **18**, acetate **19**, tosylate **20**, diradical **21**, malonate **25**, propionyl chloride **26**, propionylalanine **27**, and chloromethane **29**. The nonradical compounds here described for the first time are bromomethane **2**, acetate **3**, tosylate **4**, iodomethane **5**, acetonitrile **6**, malonate **7**, acetamidomalonate **8**, methanol **9**, aldehyde **10**, acetic acid **11**, propionic acid **12**, chloromethane **13**, and propionylalanine **14**. Spectral (ESR, ^1H NMR, IR, UV–vis) and magnetic susceptibility data are reported.

The so-called "inert free radicals" (IFR) are trivalent-carbon species which are by far the most passive free radicals known.[1] A paradigm of an IFR is perchlorotriphenylmethyl (PTM).[1a] A significant number of

0022-3263/86/1951-2472$01.50/0

Scheme I[a]

$$(C_6Cl_5)_2CHC_6Cl_4R \xrightarrow{base} (C_6Cl_5)_2\bar{C}C_6Cl_4R \xrightarrow{(-e)} (C_6Cl_5)_2\dot{C}C_6Cl_4R$$

[a] $-C_6Cl_4-$ stands for tetrachloro-*p*-phenylene.

Scheme II[a]

$$(C_6Cl_5)_2CHC_6Cl_4CH_3 \xrightarrow[h\nu \text{ or AIBN}]{Br_2} (C_6Cl_5)_2CHC_6Cl_4CH_2Br \longrightarrow (C_6Cl_5)_2CHC_6Cl_4CH_2X$$

1 2 3-8

[a] X = $OCOCH_3$ (3), OTs (4), I (5), CN (6), $CH(COOC_2H_5)_2$ (7), $C(NHCOCH_3)(COOC_2H_5)_2$ (8).

"functionalized" IFRs devised by substitution of one, two, or three para chlorines of PTM by substituents such as Br, OH, OCOR, NH_2, NHCOR, NO_2, CH_3, COOR, CONHR, C_6Cl_5, etc., are known.[1]

The IFRs are widening the theoretical, experimental, and even the applicational prospects for free radicals. They have been the substrates allowing the discovery of the "two-step mechanism" for the "hydride-ion transfer to carbenium ions",[1e,2] and the "*spin*-charge exchange" in radical ions.[3] In the majority of the molecular species where the free radical character and the functional groups coexist, the chemical reactivity of the former overrides completely that of the latter. The influence of the substituents on the free radical reactivity has been, and still is, an intensively studied, dispersed subject.[4] The IFRs are making possible a systematic, general study of the reciprocal effect: the influence of the free radical character on the reactivity of the substituents. In fact, we have published two short preliminary communications on the first examples of such an influence that we called the "reverse effect".[5] The results achieved so far are being described here in detail and supplemented with closely related research work.

For the purpose of studying the "reverse effect", the synthesis of a number of "functionalized" IFRs of the PTM series, as well as their αH compounds, has been carried out. Although the αH compounds are often the chosen synthetic precursors for the IFRs,[1a,d,h] as shown in Scheme I, most of the syntheses of the latter, reported next, start nevertheless from a monosubstituted PTM radical, its substituent being submitted to chemical conversion, without impairment of the radical character. Such a fact emphasizes dramatically the IFRs chemical passivity.

Scheme III

(a) 3 $\xrightarrow[(OH^- \text{ or } H^+)]{H_2O}$ $(C_6Cl_5)_2CHC_6Cl_4CH_2OH$ (9)

9 $\xrightarrow{TsCl}$ 4 (tosylate)

9 $\xrightarrow{CrO_2Cl_2}$ $(C_6Cl_5)_2CHC_6Cl_4CHO$ (10)

(b) 6 $\xrightarrow[(H^+)]{H_2O}$ $(C_6Cl_5)_2CHC_6Cl_4CH_2COOH$ (11)

7 $\xrightarrow[H^+]{H_2O}$ $(C_6Cl_5)_2CHC_6Cl_4CH_2CH_2COOH$ (12)

(c) 4 $\xrightarrow{TiCl_4}$ $(C_6Cl_5)_2CHC_6Cl_4CH_2Cl$ (13)

9 $\xrightarrow[DMAP]{TsCl}$ 13

(d) 12 + $NH_2CH(CH_3)COOC_2H_5$ $\xrightarrow{C_6H_{13}N{=}C{=}NC_6H_{13}}$ $(C_6Cl_5)_2CHC_6Cl_4CH_2CH_2CONHCH(CH_3)COOC_2H_5$ (14)

Scheme IV

$$(C_6Cl_5)_2CHC_6Cl_4CH_2OH \xrightarrow[ether\text{-}Me_2SO]{NaOH} (C_6Cl_5)_2\bar{C}C_6Cl_4CH_2OH \xrightarrow{I_2} (C_6Cl_5)_2\dot{C}C_6Cl_4CH_2OH$$

9 15

$$(C_6Cl_5)_2CHC_6Cl_4CH_2CH_2COOH \xrightarrow[ether\text{-}Me_2SO]{NaOH} (C_6Cl_5)_2\bar{C}C_6Cl_4CH_2CH_2COOH \xrightarrow{I_2} (C_6Cl_5)_2\dot{C}C_6Cl_4CH_2CH_2COOH$$

12 16

Results and Discussion

Synthesis of the αH compounds. The synthesis of the monofunctionalized αH compounds here reported has been effected as shown in Scheme II, most of them starting from αH-4-(bromomethyl)tetradecachlorotriphenylmethane (**2**) which in turn has been obtained by bromination of αH-tetradecachloro-4-methyltriphenylmethane[1d] (**1**) with Br_2, either by illumination with white incandescent light or using AIBN as a radical-chain initiator. The conversions of bromomethane **2** include nucleophilic substitution by $OCOCH_3$ (in CH_3COOH; 82% yield), OTs (CH_3CN; 88), I (dioxane–acetone; 83), CN (dioxane–H_2O; 65), diethyl malonate carbanion (K_2CO_3, dioxane; 82) and diethyl acetamidomalonate carbanion (K_2CO_3, dioxane; 82), the products being αH compounds **3–8**. The substitutions with nucleophiles diethylmalonate carbanion, diethyl acetamidomalonate carbanion and CN^- have also been performed starting from tosylate **4**.

Acidic or basic hydrolysis of acetate **3** gives excellent yields of methanol **9**, which by oxydation with CrO_2Cl_2 and by acylation with tosyl chloride is readily converted into aldehyde **10** and tosylate **4**, respectively (Scheme IIIa). Acidic hydrolysis of acetonitrile **6** and malonate **7** affords very good yields of acetic acid **11** and propionic acid **12**, respectively (Scheme IIIb).

High-yield syntheses of chloromethane **13** have been carried out by the reaction of methanol **9** with tosyl

(1) (a) Ballester, M.; Riera, J.; Castañer, J.; Badía, C.; Monsó, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215. (b) Ballester, M.; Castañer, J.; Pujadas, J. *Tetrahedron Lett.* 1971, 1699. (c) Ballester, M.; Castañer, J.; Riera, J.; Ibáñez, A. *Tetrahedron Lett.* **1980**, 2435. (d) Ballester, M.; Castañer, J.; Riera, J.; Ibáñez, A.; Pujadas, J. *J. Org. Chem.* **1982**, *47*, 259. (e) Ballester, M.; Riera, J.; Castañer, J.; Rodríguez, A.; Rovira, C.; Veciana, J. *J. Org. Chem.* **1982**, *47*, 4498. (f) Ballester, M.; Riera, J.; Castañer, J.; Rovira, C.; Veciana, J.; Onrubia, C. *J. Org. Chem.* **1983**, *48*, 3716. (g) Ballester, M.; Castañer, J.; Riera, J.; Pujadas, J.; Armet, O.; Onrubia, C.; Rio, J. A. *J. Org. Chem.* **1984**, *49*, 770. (h) Ballester, M.; Castañer, J.; Riera, J.; Pujadas, J. *J. Org. Chem.* **1984**, *49*, 2884. (i) Ballester, M. *Acc. Chem. Res.* **1985**, *18*, 380.

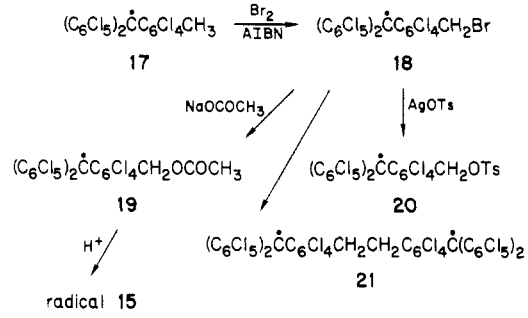
(2) Ballester, M.; Riera, J.; Castañer, J.; Rodríguez, A. *Tetrahedron Lett.* **1971**, 2079.

(3) (a) Ballester, M.; Castañer, J.; Riera, J.; Pascual, I. *J. Am. Chem. Soc.* **1984**, *106*, 3365. (b) Ballester, M.; Pascual, I. *Tetrahedron Lett.* **1985**, *26*, 5589.

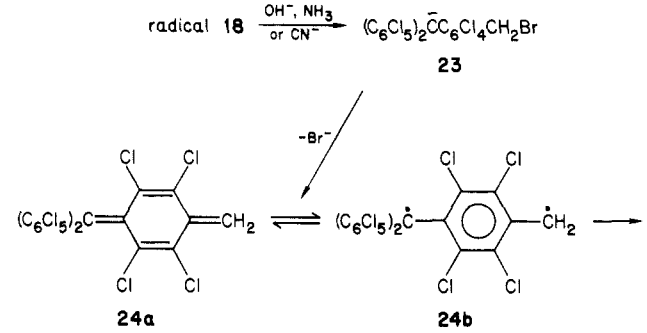
(4) Kochi, J. K. *Free Radicals*; Wiley: New York, 1973; Vol. I and II Nonhebel, D. C.; Walton, J. C. *Free Radical Chemistry*, Cambridge Univ. Press: Cambridge, 1974.

(5) Ballester, M.; Veciana, J.; Riera, J.; Castañer, J.; Rovira, C.; Armet, O. *Tetrahedron Lett.* **1982**, *23*, 5075. Ballester, M.; Veciana, J.; Riera, J.; Castañer, J.; Armet, O.; Rovira, C. *J. Chem. Soc., Chem. Commun.* **1983**, 982.

Scheme V

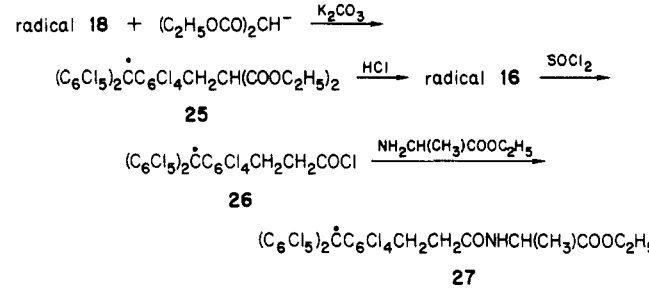


Scheme VI



diradical **21**

Scheme VII



chloride and DMAP and by reaction of tosylate **4** with $TiCl_4$ (Scheme IIIc).

Propionic acid **12** reacts with a mixture of L-alanine ethyl ester and dicyclohexylcarbodiimide to give *N*-acyl-L-alanine **14** (Scheme IIId).

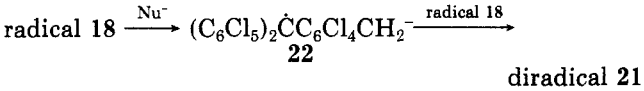
Synthesis of Functionalized Radicals. (a) From *αH* Compounds. It has already been mentioned that the usual precursors of IFRs are their *αH* analogues (Scheme I). In this way, tetradecachloro-4-(hydroxymethyl)triphenylmethyl (**15**) and 4-(2-carboxyethyl)tetradecachlorotriphenylmethyl (**16**) radicals are obtained from methanol **9** and propionic acid **12**, respectively (Scheme IV).

The method above is rather inadequate for benzyl halide precursors such as **2**, **5**, and **13** because of the strong nucleophilic conditions involved (hydroxide ion in Me_2SO-containing media), and accordingly, some tests with these halides resulted in very complex reaction mixtures containing some methanol radical **15**. This method does not work satisfactorily either with acetic acid **11**. In fact it is known that the carboxylate group may be oxidized to carboxyl radical with I_2, which undergoes immediate decarboxylation.[1d]

(b) From Other IFRs. (b1) 4-(Bromomethyl)-tetradecachlorotriphenylmethyl Radical (18). As in the case of its *αH* compound **2**, bromomethane radical **18** has been obtained in an almost quantitative yield by bromination of tetradecachloro-4-methyltriphenylmethyl radical[1d] (**17**) with Br_2 and AIBN (CCl_4) (Scheme V). Photobromination is not possible since it is known that PTM radicals are light-sensitive.[1b,g] The mechanistic aspects of that bromination are discussed later.

(b2) Nucleophilic Substitution Reactions. Bromomethane radical **18** reacts in a normal way with a variety of nucleophilic species as its *αH* analogue **2**: With sodium acetate (CH_3OH–dioxane) and with silver tosylate (CH_3CN–dioxane) it gives acetate **19** and tosylate **20** radicals, respectively, in excellent yields (Scheme V). The acidic hydrolysis of acetate **19** (HCl, dioxane–H_2O) gives a good yield of methanol radical **15**. In no case is impairment of the radical character observed. For substitution with ethyl malonate carbanion, see the Malonic Ester Synthesis section.

If the reaction of bromomethane radical **18** with acetate ion is performed in refluxing acetic acid instead of CH_3OH–dioxane, although acetate radical **19** is formed, the major product is nevertheless 1,2-ethylenebis(4-tetradecachlorotriphenylmethyl) (**21**). This remarkable,



diradical **21**

unexpected result can hardly be accounted for in terms of S_N2 displacement of Br in bromomethane radical **18** by radical carbanion **22**, formed in a "positive bromine" abstraction (nucleophilic substitution on bromine[6]), for when the reaction is performed in acetic acid, that radical carbanion would immediately pick up a proton to give methane radical **17** instead. Furthermore, the substitution on carbon should be sterically hindered due to the repulsions among the four ortho chlorines around the two carbons involved in the relevant transition state. The authors favor instead the existence of a competing thermolytic condensation of bromomethane radical **18** giving diradical **21**. In fact, while closely related *αH*-compound **2** does not decompose up to 180 °C in solution, radical **18** does at temperatures as low as 110 °C to give diradical **21**. In this connection it is emphasized that such a conversion can easily be effected also with a reducing agent. These homolytic processes are accounted for later.

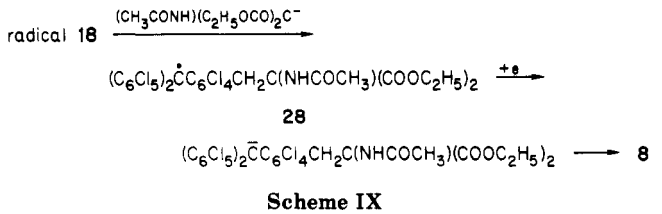
The reactions of bromomethane radical **18** with NaOH and with NH_3 in dioxane–water do not give the corresponding substitution products but diradical **21** instead in an almost quantitative yield. Since it has been found that under basic reaction conditions PTM radical is reduced to its carbanion,[1i,3b] the formation of **21** is explained by assuming a one-electron transfer from the base to radical **18** giving bromomethane carbanion **23**, followed by elimination of Br^- to yield *p*-xylylene (*p*-quinodimethane) **24** (see later), which would dimerize to diradical **21**. It is pointed out that the attempted substitution of Br by CN in radical **18** has also afforded diradical **21** (Scheme VI).

(b3) Malonic Ester Synthesis. Bromomethane radical **18** undergoes nucleophilic substitution with diethylmalonate carbanion to give an excellent yield of diethylmalonate radical **25** (C alkylation), which by decarboxylative hydrolysis affords a good yield of propionic acid radical **16** (Scheme VII), obtained independently (Scheme IV). This radical is converted in boiling $SOCl_2$ into its acid chloride radical **26**. The latter can be used as spin-label reagent, and it has been successfully tested with L-alanine ethyl ester, giving amino acid radical **27** (Scheme VII).

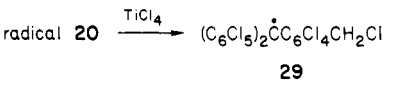
In the reaction of bromomethane radical **18** with diethyl acetamidomalonate carbanion as the nucleophile (K_2CO_3,

(6) Ballester, M.; Molinet, C.; Rosa, J. *Tetrahedron* **1959**, *6*, 109.

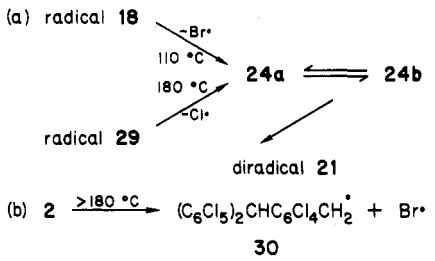
Scheme VIII



Scheme IX



Scheme X



dioxane), although substitution takes place, αH compound 8 is obtained. When the reaction is performed in the cavity of an EPR spectrometer, the disappearance of the broad signal due to bromomethane radical 18 and the transient appearance of a new sharp ESR line is observed. This fact suggests the formation of αH compound 8 through the sequence of Scheme VIII, involving the transient formation of acetamidomalonate radical 28.

In this connection it is mentioned that the IFRs, although passive in reaction involving bond-formation and/or bond-rupture, are active in certain electron-transfer processes giving the corresponding carbanions[7] or carbenium ions.[1e,8] Furthermore, there exists strong evidence indicating that diethylmalonate carbanion may be a one-electron donor to some neutral species.[9] Accordingly, the reaction of PTM radical with this carbanion, under those reaction conditions, yields αH-pentadecachlorotriphenylmethane.

(b4) Tetradecachloro-4-(chloromethyl)triphenylmethyl Radical (29). The photochlorination of methane radical 17 could hardly be effected since PTM radicals are light-sensitive, as already indicated. The synthesis of chloromethane radical 29 has been achieved in an excellent yield from tosylate radical 20 with $TiCl_4$ in ether (Scheme IX), as in the case of its αH compound 13.

The "Reverse Effect". Influence of the Free Radical Character on the Reactivity of Benzylic Systems. (a) Homolyses of the Carbon–Halogen Bond in Halomethane Radicals. While bromomethane 2, as well as chloromethane 13 and iodomethane 5, is still stable at 180 °C, bromomethane radical 18 decomposes at temperatures as low as 110 °C giving diradical 21. This process is assumed to be initiated by a singularly assisted homolysis of the C-Br bond giving transient *p*-xylylene 24, which would dimerize next to give the diradical 21, as shown (Scheme Xa). At sufficiently high temperatures, nonradical bromomethane 2 would give the corresponding benzyl radical 30 instead (Scheme Xb).

The homolysis of the chloromethane radical 29 C–Cl bond to give diradical 21 takes place at higher temperatures (~180 °C), as expected (Scheme Xa).

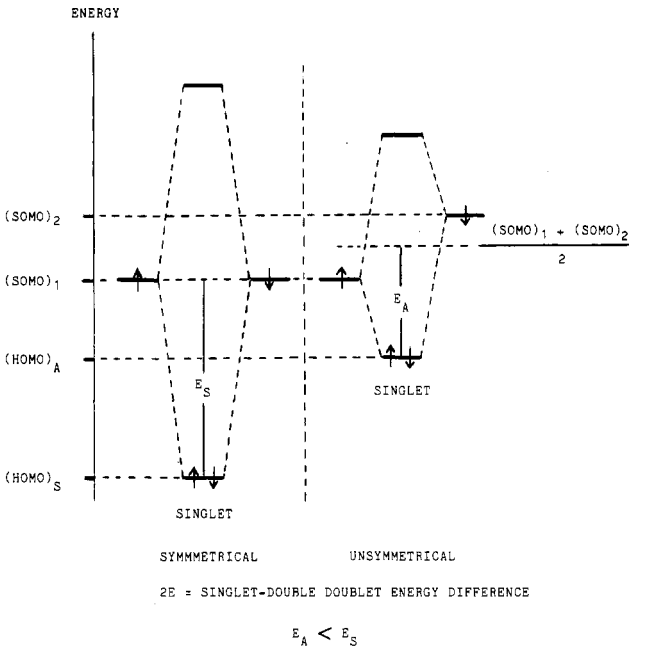


Figure 1. *p*-Xylylenes. SOMO–SOMO frontier-orbital interaction diagram.

The synthesis of tetradecachloro-4-(iodomethyl)triphenylmethyl radical (31) by I^- substitution on bromomethane radical 18 (as in its αH counterpart 2) has failed. Even at temperatures as low as −20 °C and in the presence of I_2 (to trap the intermediate *p*-xylylene 24) the reaction product is invariably diradical 21 in excellent conversions (Scheme XI). An extrapolation of the decomposition temperatures of chloromethyl radical 29 and bromomethyl radical 18 indicates, however, that hypothetical iodomethane radical 31 should start to decompose about 40 °C. In this connection it is mentioned that under the relevant reaction conditions iodide ion would likely release an electron to radical 31—as it presumably occurs with bromomethane radical 18—and therefore it would appear as if the homolytic decomposition temperature is lower than its extrapolated value. Nevertheless, whatever the interpretation is, the low C–I bond energy is regarded as a decisive factor as far as the author's failure to isolate the iodomethane radical 31. Consequently, the thermal reactivity of halomethane radicals and their αH compounds is in agreement with the bond-strength of the C–X bond.

In connection with the mechanism of these thermolyses, it is pointed out that in symmetrically substituted *p*-xylylenes stabilization of the singlet state over that of the double doublet (diradical) state—and probably the triplet—must be significant, as predicted by straightforward frontier-orbital considerations (Figure 1). This is the case of chemically inert, pure singlet (ESR and magnetic susceptibility) perchloro-*p*-xylylene[10] and perchloro-$\alpha,\alpha,\alpha',\alpha'$-tetraphenyl-*p*-xylylene.[11] The abnormal[12] chemical passivity of these two *p*-xylylenes is presumably conferred by the cumulative negative effect and steric shielding of their formal ethylene bonds, both provided by their numerous chlorines, some effects found in the IFRs as well.[1]

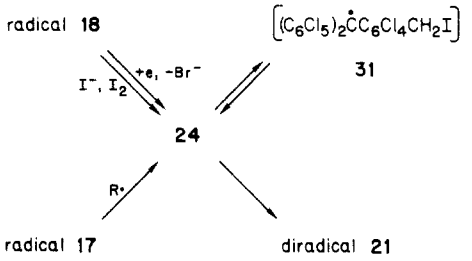
(7) Ballester, M.; de la Fuente, G. *Tetrahedron Lett.* **1970**, 4509.
(8) Ballester, M.; Riera, J.; Rodríguez, A. *Tetrahedron Lett.* **1970**, 3615.
(9) Kornblum, N. *Angew. Chem., Intl. Ed. Engl.* **1975**, *14*, 734.
(10) Ballester, M.; Castañer, J. *Anales Real Soc. Espań. Fis. Quim.* **1960**, 56B, 207.
(11) Ballester, M.; Castañer, J.; Riera, J. *U.S. Clearinghouse Fed. Sci. Tech. Inform.* **1968**, AD 672319. From *U.S. Govt. Res. Develop. Rep.* **1968**, *68*(18), 48; *Chem. Abstr.* **1969**, *70*, 46980t.
(12) Wagner, H.-V.; Gomper, R. In *The Chemistry of Quinonoid Compounds*, Patai, S., Ed.; Wiley: New York, **1974**; Part 2, Chapter 18; pp 1145–1175.

Table I. ESR Spectral Data on Radicals $(C_6Cl_5)_2\dot{C}C_6Cl_4CH_2X$

	X	solvent	g	no. of lines	line width (MHz)	spins/mol × 10^{23}	splittings (MHz)[b] halogen	H	^{13}C	Ar ^{13}C
15	OH	$CHCl_3$	2.0027	1	5.6	6.0			84.0	31.4
16	CH_2COOH	CCl_4	2.0024	1	4.8	6.3			84.0	33.0
18	Br	ether	2.0031	4	7.0	6.3	10.3, 14.4	3.7		
19	$OCOCH_3$	$CHCl_3$	2.0025	1	4.8	6.0			84.3	31.4
20	$OSO_2C_6H_4CH_3$	CCl_4	2.0023	1	4.9	6.0			84.0	30.5
21	dimer	ether	2.0026	1	9.8	12.6				
25	$CH(COOC_2H_5)_2$	CCl_4	2.0023	3	2.4	6.2		3.2	84.0	29.1, 36.4
27	CH_2CO-alanine	CCl_4	2.0024	3[a]	2.9	6.3		3.0	84.2	29.1, 36.4
29	Cl	CCl_4	2.0027	1[a]	10.5	6.2		1.96	83.0	

[a] Distorted line. [b] Computer simulated.

Scheme XI



In electronically unsymmetrical *p*-xylylenes stabilization of the singlet over the diradical form may be significantly lower, even insufficient to overcome the loss of aromaticity (Figure 1). It is reasonable to assume that in such a case the ground state might be the diradical (or triplet) form—perhaps in equilibrium with the singlet—and therefore that the reactivity would be higher, as it may occur in highly chlorinated *p*-xylylene **24**. Additional reactivity of the latter is due to the low steric shielding of its CH_2 carbon and the low frontal strain of its dimer **21**.

The dramatic acceleration observed in those homolyses due to the radical character is accounted for in terms of stabilization of the relevant transition state, as shown in Figure 2, where the right-hand moiety represents the transition state (HOMO) of a nonassisted homolysis, and the left-hand moiety, the radical character (SOMO). The two moieties of the αH compound, corresponding to a given radical, are almost noninteracting.

Diradical **21** is synthesized in an excellent yield by reduction of bromomethane radical **18** with $SnCl_2$ at room temperature. Under the same reaction conditions its αH counterpart **2** is recovered almost quantitatively. Diradical **21** can also be obtained by heating a solution of methane radical **17** containing a substantial proportion of benzoyl peroxide. The likely mechanisms are given in Scheme XI.

(b) Competitive Bromination of αH Compound 1 and Radical 17. The AIBN-induced bromination of an equimolecular mixture of **1** and **17** with Br_2 in refluxing CCl_4 gives a mixture of bromomethane **2**, bromomethane radical **18**, and starting materials. From the proportion of the products it is found that radical **17** reacts *8* times faster than its αH counterpart **1**. Reasonable propagation steps for this unique bromination of radical **17** are

$$\text{radical 17} + Br\cdot \rightarrow 24 + HBr$$

$$24 + Br_2 \rightarrow \text{radical 18} + Br\cdot$$

The hydrogen-abstraction step (which is likely to be the rate-determining) is assisted by the radical character of **17** much in the fashion as in the above mentioned thermolyses.

(c) Competitive Nucleophilic Substitution by Acetate Ion in αH Compound 2 and Radical 18. The reaction of acetate ion with an equimolecular mixture of bromomethane **2** and bromomethane radical **18** in CH_3OH–dioxane at 66 °C has given a mixture of acetate **3** and acetate radical **19**, along with starting materials. From the relative amounts of the products it is inferred that the rate of substitution in radical **18** is faster than in its nonradical analogue **2** by a factor of *4*, approximately.

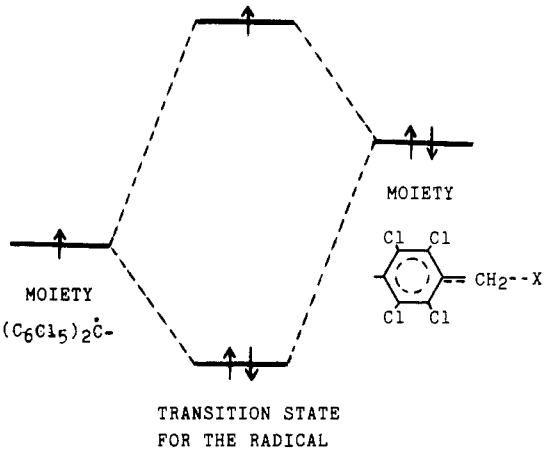


Figure 2. Simplified frontier-orbital interaction diagram concerning the homolysis of radicals **18** and **29**.

(d) Competitive Nucleophilic Substitution by Diethylmalonate Carbanion in αH Compound 2 and Radical 18. This reaction has been performed by treating a dioxane solution of equimolecular amounts of bromomethane **2** and bromomethane radical **18**, and an excess of diethyl malonate, with an excess of solid K_2CO_3,[13] at 90 °C. Malonic ester compound **7** and malonic ester radical **25** were obtained, starting materials being recovered. From the proportions of the products it is concluded that the reaction with radical **18** is about *9* times faster than that with its αH counterpart **2**.

A current quantum mechanical approach constructs the S_N2 transition state as a combination of a few main electronic configurations for the system formed by the reactants (the nucleophilic reagent D^- and the substrate A), the most significant one being the charge transfer, diradical configuration $D\cdot A^-$ resulting from an electron jump from D^- to an empty (σ^*) orbital of A.[15] Therefore, in the "reverse effect" studied here, it is expected that interactions of such a diradical configuration with the SOMO of the free radical would cause an additional stabilization of the transition state as shown in the energy diagram of Figure 2 for the homolyses, by replacing "the S_N2 transition-state MO" for moiety "$-C_6Cl_4\cdots CH_2\cdots X$". The ob-

(13) For the use of K_2CO_3 in alkylations with diethyl malonate carbanion, see ref 14.
(14) Fedorynski, M.; Wojeiechowski, K.; Mataez, Z.; Makosza, M. *J. Org. Chem.* **1978**, *43*, 4682.
(15) Pross, A. Sheik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3702.

Table II. Magnetic Susceptibility Data on Radicals $(C_6Cl_5)_2\dot{C}C_6Cl_4CH_2X$

radical	X	μ	10^6 dia (emu) Curie–Weiss	10^6 dia (emu) Pascal	(K)	spins/mol × 10^{23}
15	OH	1.73	−0.487	−0.515	−1.5	6.0
16	CH_2COOH	1.77	−0.447	−0.515	−1.3	6.3
18	Br	1.77	−0.468	−0.504	−1.5	6.3
19	$OCOCH_3$	1.72	−0.518	−0.520	5.5	6.0
20	$OSO_2C_6H_4CH_3$	1.73	−0.512	−0.522	−0.5	6.0
21	dimer	3.54	−0.520	−0.517	7.5	12.6
25	$CH(COOC_2H_5)_2$	1.75	−0.528	−0.527	0.5	6.2
27	CH_2CO-alanine	1.77	−0.517	−0.526	1.5	6.3
29	Cl	1.75	−0.490	−0.517	1.0	6.2

served increase in the rate of nucleophilic substitutions is therefore accounted for.

Electron Spin Resonance Spectra. The ESR spectral data on the radicals here reported for the first time are given in Table I. As expected, the g values and the hyperfine couplings with the ^{13}C do not differ significantly from those of other radicals of the PTM series.[1]

Magnetic Susceptibility Data. The magnetic susceptibility data for the radicals here described are shown in Table II. The least-squares correlation of their Curie–Weiss plot (from 77 K to room temperature) shows that they are magnetically pure (spins/mol), the values of their specific diamagnetic susceptibilities being in good agreement with those calculated with revised Pascal systematics.[1e,16]

Conclusions

The synthesis of substituted PTM radicals may be performed from other properly substituted PTM radicals, without impairment of the radical character. In all radicals here studied, the free radical character causes a rate increase of the reactions at the functional substituents. In the thermolysis of chloro- (**29**), and bromomethane radicals (**18**), where the carbon–halogen bond undergoes homolysis, the enhancement is dramatic since, under the same conditions, their nonradical structural analogues (**13** and **2**) do not react at all. In other radicals, the rate increase, although quite apparent, is moderate, as in the AIBN-induced bromination of methane radical **17** and the nucleophilic substitutions on bromomethane radical **18** with acetate ion and with diethyl malonate carbanion.

Experimental Section

General Methods. The IR, UV–vis, ^1H NMR, and ESR spectra were recorded with Perkin-Elmer 457, Beckman Acta M VI, Perkin-Elmer R 12B, and Varian E4 spectrometers, respectively. The magnetic susceptibilities were 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, they are included in this section.

Synthesis and Reactions of the αH Compounds. αH-4-(Bromomethyl)tetradecachlorotriphenylmethane (2). (a) Br_2 (0.2 mL) was added to a refluxing solution of αH-tetradecachloro-4-methyltriphenylmethane[1d] (**1**) (0.300 g) in CCl_4 (35 mL), while illuminating (5 h) with a 500-W incandescent lamp located 15 cm from the reaction flask. The resulting solution was evaporated, and the residue was purified through silica gel (CCl_4) and digested with pentane giving bromomethane **2** (0.314 g; 95%): mp 313–315 °C dec; IR (KBr) 2910 (w), 1525 (w), 1430 (w), 1360 (s), 1333 (s), 1298 (s), 1240 (m), 1214 (m), 1138 (m), 885 (m), 848 (m), 804 (s), 755 (s), 715 (m), 670 (s), 643 (m), 520 (s), 474 (m) cm^{-1}; UV (C_6H_{12}) 223 nm, 303 (ϵ 104 000, 1630); ^1H NMR (CCl_4) δ 4.77 (s, 2 H, CH_2Br), 7.01 (s, 1 H, αH). Anal. Calcd for $C_{20}H_3Cl_{14}Br$: C, 29.3; H, 0.4; Cl, 60.6; Br, 9.7. Found: C, 29.3; H, 0.3; Cl, 60.3; Br, 9.6.

(b) A mixture of αH compound **1** (0.100 g), Br_2 (0.2 mL), azobis(isobutyronitrile) (0.025 g), and CCl_4 (1.5 mL) was refluxed under argon (24 h). The resulting solution was evaporated, and the residue was purified by TLC ($CHCl_3$) yielding bromomethane **2** (0.090 g; 82%). Some starting material **1** was recovered (0.009 g; 9%).

αH-4-(Acetoxymethyl)tetradecachlorotriphenylmethane (3). (a) A mixture of bromomethane **2** (0.297 g), anhydrous sodium acetate (0.792 g), and glacial acetic acid (25 mL) was refluxed (3 days) and then evaporated to dryness. The residue was extracted with $CHCl_3$, and the resulting solution was washed with water, dried, and evaporated. The product was purified through silica gel ($CHCl_3$), giving acetate **3** (0.238 g; 82%): mp 227–229 °C; IR (KBr) 2920 (w), 1745 (s), 1535 (w), 1460 (w), 1368 (s), 1352 (s), 1332 (s), 1294 (s), 1216 (s), 1136 (m), 1028 (m), 847 (m), 805 (s), 712 (m), 682 (m), 662 (m), 643 (m), 526 (m), 490 (m) cm^{-1}; UV (C_6H_{12}) 221 nm, 294, 304 (ϵ 114 000, 1350, 1510); ^1H NMR ($CDCl_3$) δ 2.08 (s, 3 H, CH_3CO), 5.40 (s, 2 H, CH_2Br), 7.02 (s, 1 H, αH). Anal. Calcd for $C_{22}H_6Cl_{14}O_2$: C, 33.1; H, 0.7; Cl, 62.2. Found: C, 33.2; H, 0.9; Cl, 62.0.

(b) A solution of anhydrous sodium acetate (0.100 g) in methanol (4 mL) was added to a solution of bromomethane **2** (0.100 g) in dioxane (8 mL), and the resulting mixture was refluxed (70 min), evaporated to dryness, and extracted with $CHCl_3$. The organic extract was evaporated and the residue submitted to TLC (silica gel; $CHCl_3$), giving acetate **3** (0.021 g; 22%), most of the starting material **2** being recovered (0.066 g; 66%).

2,3,5,6-Tetrachloro-4-(bis(pentachlorophenyl)methyl)-α-hydroxytoluene (9). (a) Aqueous concentrated HCl (50 mL) was added to a solution of acetate **3** (2.007 g) in dioxane (200 mL), and the mixture was refluxed (21 h), diluted next with water (20 mL), and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water, dried, and evaporated, and the residue was purified through silica gel ($CHCl_3$), giving methanol **9** (1.630 g; 85%): mp over 350 °C; IR (KBr) 3590 (w), 3400 (w), 2950 (w), 2920 (w), 2900 (w), 1520 (w), 1365 (s), 1340 (s), 1298 (s), 1240 (m), 1135 (s), 1030 (s), 845 (m), 807 (s), 750 (s), 712 (m), 685 (m) cm^{-1}; UV ($CHCl_3$) 294 nm, 304 (ϵ 1600, 1790); ^1H NMR ($CDCl_3$) δ 2.20 (s, 1 H, OH), 5.08 (s, 2 H, CH_2), 7.02 (s, 1 H, CH). Anal. Calcd for $C_{20}H_4Cl_{14}O$: C, 31.8; H, 0.5; Cl, 65.6. Found: C, 32.0; H, 0.5; Cl, 65.8.

(b) Aqueous 1 N NaOH (0.24 mL) was added to a solution of acetate **3** (0.052 g) in dioxane (15 mL) and the solution was left at room temperature (20 h), acidified with aqueous HCl (20 mL), and extracted with $CHCl_3$. Working as described in the preceding hydrolysis, methanol **9** (0.040 g; 82%) was obtained, some starting material **3** (0.007 g; 13%) being recovered.

αH-Tetradecachloro-4-formyltriphenylmethane (10). A solution of methanol **9** (0.100 g) in CH_2Cl_2 (5 mL) was added to a mixture of CrO_2Cl_2, SiO_2, Al_2O_3 (0.500 g; prepared according to San Filippo[17]), and CH_2Cl_2 (5 mL) and stirred (5.5 h) at room temperature. Methanol (2 mL) was added, and the stirring was continued (5 min). The resulting mixture was filtered and the solid residue left behind was extracted with $CHCl_3$. The combined solutions were evaporated and the product was purified through silica gel (CCl_4–$CHCl_3$), giving aldehyde **10** (0.072 g; 72%): mp

(16) Foex, G.; Gorter, C.; Smith, J. L. *Constants Sélectionées. Diamagnétisme et Paramagnétisme. Rélaxation Paramagnétique*; Masson et Cie.: Paris, 1957; pp 222–225.

(17) San Filippo, J., Jr.; Chern, C. I. *J. Org. Chem.* 1977, *42*, 2182.

290–292 °C; IR (KBr) 2920 (w), 2850 (w), 1715 (s), 1535 (w), 1362 (s), 1338 (s), 1298 (s), 1240 (m), 1140 (s), 924 (m), 810 (s), 790 (m), 768 (m), 690 (m), 680 (m), 648 (m), 612 (m), 525 (m), 500 (m) cm^{-1}; UV ($CHCl_3$) 273 (sh) nm, 306, 332 (ϵ 70 000, 1970, 1630). Anal. Calcd for $C_{20}H_2Cl_{14}O$: C, 31.1; H, 0.3; Cl, 65.8. Found: C, 31.6; H, 0.3; Cl, 65.7.

2,3,5,6-Tetrachloro-4-(bis(pentachlorophenyl)methyl)-α-(tosyloxy)toluene (4). (a) From Bromomethane 2. A solution of silver tosylate (0.100 g) in acetonitrile (4 mL) was added to another solution of bromomethane **2** (0.100 g) in dioxane (8 mL) in the dark. The mixture was stirred at 70 °C for 24 h, evaporated to dryness, and extracted with $CHCl_3$. The $CHCl_3$ layer was evaporated, and the residue was submitted to chromatography (silica gel; CCl_4–$CHCl_3$), giving starting material **2** (0.007 g; 7%) and tosylate **4** (recrystallized from pentane–ethyl ether) (0.098 g; 88%): mp 135–140 °C; IR (KBr) 3020 (w), 2910 (w), 1592 (w), 1455 (w), 1365 (s), 1335 (m), 1292 (s), 1185 (s), 1173 (s), 1137 (m), 1090 (m), 1014 (m), 955 (s), 825 (m), 805 (s), 782 (m), 732 (m), 710 (m), 682 (m), 658 (s), 640 (m) cm^{-1}; UV (C_6H_{12}) 222 nm, 253 (sh), 296, 325 (ϵ 123 300, 30 800, 1900, 2130); ^1H NMR (CCl_4) δ 2.45 (s, 3 H, CH_3), 5.45 (s, 2 H, CH_2), 7.03 (s, 1 H, CH), 7.35 (d, J = 8.0 Hz, 2 H, Ar*CH*CCH_3), 7.85 (d, J = 8.0 Hz, 2 H, $ArCHCSO_3$). Anal. Calcd for $C_{27}H_{10}Cl_{14}O_3S$: C, 35.6; H, 1.1; Cl, 54.5. Found: C, 35.9; H, 1.1; Cl, 54.4.

(b) The preceding reaction was repeated, the reaction time being of 70 min. Tosylate **4** (61%) and starting material **2** (32%) were obtained.

(c) From Methanol 9. A solution of NaOH (0.114 g) in water (5 mL) was added to another of methanol **9** (0.123 g) and tosyl chloride (0.207 g) in dioxane (10 mL), stirred at room temperature for 35 h, and then, after addition of water (20 mL), extracted with $CHCl_3$. The organic layer was washed with water, dried, and evaporated, giving a solid which was recrystallized (ether–pentane), affording tosylate **4** (0.128 g; 87%).

***αH*-Tetradecachloro-4-(2,2-bis(ethoxycarbonyl)ethyl)-triphenylmethane (7). (a) From Bromomethyl Compound 2.** A mixture of bromomethane **2** (0.207 g), diethyl malonate (0.4 mL), K_2CO_3 (0.352 g), and dioxane (16 mL) was refluxed for 18 h while stirring under argon. The solids were filtered off, and the solution was evaporated in vacuo. The residue was purified by TLC (silica gel, $CHCl_3$) and recrystallized (pentane), giving malonate **7** (0.163 g; 72%): mp 203–205 °C; IR (KBr) 2985 (m), 2920 (w), 1730 (s), 1515 (w), 1440 (m), 1362 (s), 1335 (s), 1290 (s), 1230 (s), 1200 (m), 1145 (s), 1130 (s), 1018 (s), 842 (m), 802 (s), 710 (m), 682 (m), 660 (m), 642 (m) cm^{-1}; UV (C_6H_{12}) 222 nm, 292, 302 (ϵ 119 200, 1210, 1250); ^1H NMR (CCl_4) δ 1.21 and 1.26 (two triplets, 6 H, J = 6.0 Hz, CH_2CH_3), 3.65 (s, 3 H, CH_2CH), 4.16 (q, 4 H, J = 6.0 Hz, CH_2CH_3), 7.04 (s, 1 H, Ar_3CH). Anal. Calcd for $C_{27}H_{14}Cl_{14}O_4$: C, 36.1; H, 1.6; Cl, 55.2. Found: C, 36.3; H, 1.7; Cl, 55.2.

(b) The preceding reaction was repeated with a reaction time of 70 min. Malonate **7** (47%) and starting material **2** (48%) were obtained.

(c) From Tosylate 4. A mixture of tosylate **4** (0.183 g), diethyl malonate (0.31 mL), K_2CO_3 (0.291 g), and dioxane (5 mL) was refluxed (20 h) with stirring and under argon. Water was added (20 mL) and then the mass was extracted with $CHCl_3$. The organic layer was washed with water, dried, and evaporated to a solid residue which was purified by TLC (silica gel, $CHCl_3$) and recrystallized (pentane), yielding malonate **7** (0.150 g; 83%).

***αH*-4-(2-Carboxyethyl)tetradecachlorotriphenylmethane (12).** A mixture of malonate **7** (0.163 g), aqueous concentrated HCl (5 mL), and dioxane (20 mL) was refluxed (48 h). The resulting mass was diluted with water and then extracted with ether. The ethereal layer was washed with water and shaken with aqueous $NaHCO_3$. The aqueous layer, containing a white precipitate, was acidified with HCl, and the resulting suspension was extracted with ether. The ethereal extract was washed with water, dried, and evaporated, yielding a solid, which by recrystallization (pentane–$CHCl_3$) gave propionic acid **12** (0.120 g; 83%): mp 162–173 °C dec; IR (KBr) 3300–2500 (w), 1710 (s), 1520 (w), 1450 (w), 1410 (w), 1365 (s), 1335 (s), 1295 (s), 1210 (m), 1132 (m), 1015 (m), 850 (m), 807 (s), 712 (m), 685 (m), 670 (m), 643 (m), 528 (m) cm^{-1}; UV ($CHCl_3$) 294 nm, 303 (ϵ 1240, 1220). Anal. Calcd for $C_{22}H_6Cl_{14}O_2$: C, 33.1; H, 0.8; Cl, 62.1. Found: C, 33.4; H, 1.0; Cl, 62.1.

***αH*-4-(2-Acetamido-2,2-bis(ethoxycarbonyl)ethyl)-tetradecachlorotriphenylmethane (8). (a) From Bromomethane 2.** The reaction of bromomethane **2** (0.140 g) with diethyl acetamidomalonate (0.188 g) and K_2CO_3 (0.296 g) in dioxane (11 mL) was carried out as in the synthesis of malonate **7** (48 h reaction time). After TLC ($CHCl_3$–methanol), pure acetamidomalonate **8** (0.134 g; 82%), mp 134–139 °C, was obtained: IR (KBr) 3410 (m), 2970 (m), 2920 (m), 2845 (w), 1734 (s), 1688 (s), 1485 (s), 1440 (m), 1365 (s), 1338 (s), 1292 (s), 1196 (s), 1130 (m), 1052 (m), 1013 (m), 855 (m), 805 (s), 712 (m), 685 (m), 663 (m), 644 (m), 515 (m), 503 (m), 485 (m) cm^{-1}; UV (C_6H_{12}) 222 nm, 293, 304 (ϵ 113 000, 1420, 1530); ^1H NMR ($CDCl_3$) δ 1.26 (t, 6 H, J = 7.5 Hz, CH_2CH_3), 1.95 (s, 3 H, $COCH_3$), 4.20–4.22 (overlapped s, 2 H, Ar CH_2, and q, 4 H, J = 7.5 Hz, CH_2CH_3), 6.5 (s, 1 H, NH), 7.0 (s, 1 H, CH). Anal. Calcd for $C_{29}H_{17}Cl_{14}NO_5$: C, 36.4; H, 1.8; Cl, 51.9; N, 1.5. Found: C, 36.6; H, 1.8; Cl, 52.1; N, 1.4.

(b) From Tosylate 4. Acetamidomalonate **8** (0.161 g; 76%) was also prepared from tosylate **4** (0.204 g), diethyl acetamidomalonate (0.253 g), and K_2CO_3 (0.338 g) in dioxane (5 mL), in the preceding reaction conditions.

***αH*-Tetradecachloro-4-(cyanomethyl)triphenylmethane (6). (a) From Tosylate 4.** A mixture of tosylate **4** (0.112 g), KCN (0.160 g), dioxane (4.8 mL), and water (0.35 mL) was stirred (48 h) at room temperature. Water (20 mL) was added to the resulting mixture, which was then extracted with $CHCl_3$. The residue from the $CHCl_3$ layer was purified by TLC (silica gel; CCl_4-$CHCl_3$) and recrystallized (ether-CH_2Cl_2) giving nitrile **6** (0.076 g; 81%), mp 325–329 °C dec; IR (KBr) 2920 (w), 2230 (w), 1520 (w), 1410 (w), 1370 (s), 1338 (s), 1297 (s), 1237 (m), 1190 (m), 1132 (s), 920 (m), 848 (m), 808 (s), 712 (m), 685 (m), 670 (m), 655 (m) cm^{-1}: UV ($CHCl_3$) 293 nm, 303 (ϵ 1600, 1760); ^1H NMR ($CDCl_3$) δ 4.11 (s, 2 H, CH_2), 7.10 (s, 1 H, CH). Anal. Calcd for $C_{21}H_3Cl_{14}N$: C, 33.0; H, 0.4; Cl, 64.8; N, 1.8. Found: C, 33.0; H, 0.2; Cl, 64.6; N, 1.8.

(b) From Bromomethane 2. Nitrile **6** (0.239 g; 65%) was also obtained from bromomethane **2** (0.400 g), KCN (0.638 g), dioxane (60 mL), and water (1.4 mL) under the conditions described in the preceding reaction (60 h).

***αH*-4-(Carboxymethyl)tetradecachlorotriphenylmethane (11).** A mixture of nitrile **6** (0.076 g), aqueous 6 N H_2SO_4 (1 mL), and dioxane (5 mL) was refluxed (22 h). After dilution with water, the mass was extracted with ether, and the ethereal layer was washed with water and extracted with aqueous $NaHCO_3$. The aqueous suspension was acidified with HCl and extracted with ether. After washing with water, drying, and evaporation, a solid was obtained, which by crystallization (pentane) afforded acetic acid **11** (0.064 g; 82%): mp 285 °C dec; IR (KBr) 3500–2500 (w), 1720 (s), 1530 (w), 1415 (w), 1370 (s), 1342 (s), 1300 (s), 1225 (m), 1138 (m), 950 (m), 810 (s), 760 (m), 685 (m), 668 (m), 646 (m), 523 (m) cm^{-1}; UV ($CHCl_3$) 296 nm, 305 (ϵ 1250, 1260). Anal. Calcd for $C_{21}H_4Cl_{14}O_2$: C, 32.2; H, 0.5; Cl, 63.3. Found: C, 32.3; H, 0.7; Cl, 63.2.

***αH*-Tetradecachloro-4-(chloromethyl)triphenylmethane (13). (a) With $TiCl_4$.** A mixture of $TiCl_4$ (0.114 g), tosylate **4** (0.100 g), and ether (12 mL) was refluxed under argon (1 h), poured onto ice–water, and extracted with $CHCl_3$. The organic layer was washed with water, dried, and evaporated to a residue which after filtration through silica gel (CCl_4) yielded chloromethane **13** (0.078 g; 91%): mp 339–341 °C; IR (KBr) 2935 (w), 2860 (w), 1530 (w), 1445 (w), 1370 (s), 1340 (s), 1302 (s), 1273 (m), 1242 (m), 1144 (s), 925 (m), 815 (s), 768 (s), 715 (s), 695 (s), 670 (m), 650 (m), 635 (m) 530 (m) cm^{-1}; UV (C_6H_{12}) 221 nm, 250 (sh), 297, 305 (ϵ 113 000, 32 900, 1660, 1780); ^1H NMR ($CDCl_3$) δ 4.94 (s, 2 H, CH_2), 7.01 (s, 1 H, CH). Anal. Calcd for $C_{20}H_3Cl_{15}$: C, 31.0; H, 0.4. Found: C, 31.0; H, 0.4.

(b) With Tosyl Chloride and 4-(Dimethylamino)pyridine. A mixture of tosyl chloride (0.168 g), methanol **9** (0.120 g), DMAP (0.111 g), and $CHCl_3$ (1 mL) was refluxed (1 h) under argon. The mass was diluted with more $CHCl_3$ (25 mL; to dissolve the precipitate formed), washed with water, dried, and evaporated. The resulting solid was purified as before to give chloromethane **13** (0.088 g; 72%).

***αH*-Tetradecachloro-4-(iodomethyl)triphenylmethane (5).** A mixture of bromomethane **2** (0.300 g), NaI (0.549 g), dioxane (36 mL), and acetone (20 mL) was stirred (3 h) under argon at

room temperature, poured into water, and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water, dried, and evaporated to a residue which was recrystallized ($CHCl_3$–pentane), yielding iodomethane **5** (0.262 g; 83%): mp 285–289 °C dec; IR (KBr) 2940 (w), 2920 (w), 2840 (w), 1520 (w), 1420 (w), 1370 (s), 1333 (s), 1298 (s), 1240 (m), 1160 (m), 1133 (m), 850 (m), 835 (m), 805 (s), 715 (m), 685 (m), 668 (m) cm^{-1}; UV (C_6H_{12}) 222 nm, 291 (sh), 302 (sh) (ϵ 94 000, 3700, 3400); ^1H NMR ($CDCl_3$) δ 4.74 (s, 2 H, CH_2), 7.01 (s, 1 H, CH). Anal. Calcd for $C_{20}H_3Cl_{14}I$: C, 27.7; H, 0.3. Found: C, 28.0; H, 0.6.

αH-4-(2-(Alaninocarbonyl)ethyl)tetradecachlorotriphenylmethane Ethyl Ester (14). A mixture of propionic acid **12** (0.100 g), dicyclohexylcarbodiimide (0.038 g), L-alanine ethyl ester hydrochloride (0.029 g), triethylamine (0.026 g), and CH_2Cl_2 (5 mL) was stirred (4 h) at room temperature, poured into aqueous $NaHCO_3$, and extracted with $CHCl_3$. The organic layer was washed with aqueous HCl and with water, dried, and evaporated. The residue was purified by TLC (silica gel, $CHCl_3$), giving propionylalanine **14** (0.057 g; 51%): mp 132–134 °C; IR (KBr) 3300 (m), 2975 (m), 2910 (m), 1735 (s), 1660 (s), 1525 (s), 1445 (m), 1365 (s), 1335 (s), 1295 (s), 1200 (s), 1158 (m), 1130 (s), 1050 (m), 1010 (m), 850 (m), 803 (s), 710 (m), 680 (m), 660 (m), 640 (m), 522 (m), 480 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (t, 3 H, J = 7.3 Hz), 1.26 (t, 3 H, J = 7.3 Hz), 3.55 (s, 3 H), 4.16 (q, 4 H, J = 7.3 Hz), 7.03 (s, 1 H). Anal. Calcd for $C_{27}H_{15}Cl_{14}NO_3$: C, 36.2; H, 1.6; N, 1.6. Found: C, 36.4; H, 1.8; N, 1.4.

Synthesis and Reactions of the Radicals. 4-(Bromomethyl)tetradecachlorotriphenylmethyl Radical (18). (a) A mixture of tetradecachloro-4-methyltriphenylmethyl radical[1d] (**17**) (1.000 g), Br_2 (1.750 g), azobis(isobutyronitrile) (0.090 g, and CCl_4 (20 mL) was refluxed under argon (24 h). The resulting solution was evaporated, and the residue was purified through silica gel (hexane–CCl_4) giving bromomethane radical **18** (1.070 g; 97%), red crystals: mp 311–312 °C dec; IR (KBr) 2910 (w), 1500 (w), 1430 (w), 1350 (m), 1330 (s), 1318 (s), 1257 (m), 1210 (m), 1152 (m), 1042 (m), 810 (m), 730 (m), 710 (m), 695 (m), 668 (m), 648 (m), 518 (m) cm^{-1}; UV–vis (C_6H_{12}) 223 nm, 290, 340 (sh), 370 (sh), 388, 482 (sh), 508, 566 (ϵ 80 200, 6400, 5700, 18 600, 36 300, 1045, 1100, 1015); ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{20}H_2Cl_{14}Br$: C, 29.6; H, 0.2; Cl, 60.6; Br, 9.8. Found: C, 29.4; H, 0.2; Cl, 60.8; Br, 9.9.

(b) The preceding reaction was also performed by using benzoyl peroxide (0.034 g) as a catalyst. Bromomethane radical **18** (1.050 g; 95%) was also obtained.

Reaction of Bromomethane Radical 18 with Sodium Acetate. 4-(Acetoxymethyl)tetradecachlorotriphenylmethyl Radical (19) and 1,2-Ethylenebis(4-tetradecachlorotriphenylmethyl) Diradical (21). (a) In Acetic Acid. A mixture of bromomethane radical **18** (0.100 g), anhydrous sodium acetate (0.241 g), and glacial acetic acid (7.5 mL) was refluxed for 4.25 h and evaporated to dryness, and the residue was extracted with $CHCl_3$. The organic solution was washed with water, dried, and evaporated, and the residue was chromatographed through silica gel (CCl_4), giving (a) diradical **21** (0.065 g; 72%) [red crystals, mp 313–316 °C dec; IR (KBr) 2905 (w), 2850 (w), 1500 (w), 1435 (w), 1320 (s), 1250 (s), 1142 (m), 1030 (m), 995 (m), 808 (m), 722 (m), 705 (m), 682 (m), 660 (m), 640 (m), 523 (m) cm^{-1}; UV–vis ($CHCl_3$) 283 nm, 370, 385, 510, 562 (ϵ 12 100, 38 900, 73 800, 2470, 2430); ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{40}H_4Cl_{28}$: C, 32.5; H, 0.3; Cl, 67.2. Found: C, 32.5; H, 0.5; Cl, 67.4.] and (b) acetate radical **19** (0.028 g; 25%) [red crystals, mp 225–228 °C; IR (KBr) 2920 (w), 2840 (w), 1740 (s), 1510 (w), 1460 (w), 1332 (s), 1320 (s), 1255 (m), 1220 (s), 1152 (m), 1045 (m), 1020 (m) 850 (m), 812 (m), 750 (m), 730 (m), 710 (m), 660 (m), 650 (m) cm^{-1}; UV–vis (C_6H_{12}) 223 nm, 287, 366 (sh), 384, 506, 562 (ϵ 96 900, 7000, 19 000, 38 900, 1140, 1060); ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{22}H_5Cl_{14}O_2$: C, 33.1; H, 0.6; Cl, 62.2. Found: C, 33.1; H, 0.7; Cl, 62.0.].

(b) In Dioxane. A solution of sodium acetate (0.050 g) in methanol (2 mL) was added to a solution of bromomethane radical **18** (0.050 g) in dioxane (4 mL) and the mixture was refluxed for 5 h. Working up the product as usual afforded acetate radical **19** (0.043 g; 88%), along with some starting material **18** (0.002 g; 4%).

(c) The preceding reaction was repeated with a 70-min. reaction time. The products were acetate radical **19** (0.025 g; 51%) and starting material **18** (0.023 g; 46%).

Tetradecachloro-4-(hydroxymethyl)triphenylmethyl Radical (15). (a) From Methanol 9. A mixture of methanol **9** (0.101 g), powdered NaOH (0.500 g), ethyl ether (5 mL), and Me_2SO (10 mL) was stirred (24 h). The resulting mixture was filtered through sintered glass, and the filtrate was treated with I_2 (4.4 g; 20 h) and then with aqueous $NaHSO_3$ (to eliminate the excess of I_2), washed with water (to eliminate Me_2SO), dried, and evaporated. The residue was purified by TLC (silica gel, $CHCl_3$), giving methanol radical **15** (0.037 g; 37%), red crystals: mp 290–293 °C dec; IR (KBr) 3610 (w), 3430 (w), 2940 (w), 2870 (w), 1505 (w), 1340 (s), 1330 (s), 1268 (s), 1160 (m), 1055 (m), 1022 (m), 820 (m), 762 (m), 740 (m), 722 (m), 708 (m), 672 (m), 658 (m), 533 (m), 502 (m) cm^{-1}; UV–vis (C_6H_{12}) 220 nm, 289, 369 (sh), 386, 509, 565 (ϵ 82 000, 6700, 17 400, 36 000, 1100, 1020); ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{20}H_3Cl_{14}O$: C, 31.8; H, 0.4; Cl, 65.7. Found: C, 31.7; H, 0.6; Cl, 65.4.

(b) From Acetate Radical 19. The hydrolysis of acetate radical **19** (0.063 g) with aqueous concentrated HCl (1.6 mL) in dioxane (6.4 mL) was carried out as in the preparation of methanol **9**, giving methanol radical **15** (0.045 g; 75%).

Tetradecachloro-4-[(tosyloxy)methyl]triphenylmethyl Radical (20). The reaction of bromomethane radical **18** (0.100 g) with silver tosylate (0.100 g) was carried out as in the tosylation of bromomethane **2** (70-min. reaction time). The product was tosylate radical **20** (0.086 g; 77%), red powder: mp 145–149 °C dec; IR (KBr) 3040 (w), 1600 (w), 1500 (w), 1450 (w), 1370 (m), 1325 (s), 1258 (m), 1190 (m), 1177 (s), 1158 (m), 1095 (m), 1048 (m), 960 (s), 832 (m), 820 (s), 758 (m), 740 (m), 715 (m), 670 (m), 652 (m) cm^{-1}; UV–vis (C_6H_{12}) 222 nm, 291, 336 (sh), 366 (sh), 386, 512, 563 (ϵ 96 900, 7480, 7200, 18 500, 35 300, 1050, 990): ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd. for $C_{27}H_9Cl_{14}O_3S$: C, 35.6; H, 1.0; Cl, 54.7. Found: C, 35.5; H, 1.0; Cl, 54.7. Some starting material **18** (0.008 g; 8%) was recovered.

Tetradecachloro-4-(2,2-bis(ethoxycarbonyl)ethyl)triphenylmethyl Radical (25). A mixture of brominated radical **18** (0.100 g), diethyl malonate (0.20 mL), K_2CO_3 (0.170 g), and dioxane (8 mL) was refluxed (70 min.) under argon. The resulting mixture was worked up as in the corresponding αH compound, yielding the malonate radical **25** (0.103 g; 94%), red crystals: mp 215–217 °C; IR (KBr) 2975 (m), 2930 (w), 1732 (s), 1440 (m), 1365 (m), 1320 (s), 1285 (m), 1255 (m), 1212 (m), 1150 (s), 1055 (m), 1030 (s), 852 (m), 813 (m), 732 (m), 708 (m), 658 (m) cm^{-1}; UV–vis (C_6H_{12}) 223 nm, 287, 366 (sh), 383, 510, 563 (ϵ 93 700, 6800, 17 000, 35 100, 1065, 1040); ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{27}H_{13}Cl_{14}O_4$: C, 36.1; H, 1.5; Cl, 55.3. Found: C, 36.4; H, 1.7; Cl, 55.2. Some starting material **18** (0.005 g; 5%) was recovered.

4-(2-Carboxyethyl)tetradecachlorotriphenylmethyl Radical (16). (a) Under Acidic Conditions. The decarboxylative hydrolysis of malonate radical **25** (0.099 g) with aqueous concentrated HCl (5 mL) in dioxane (20 mL) was carried out as in the corresponding αH compound **7** (22 h), yielding propionic acid radical **16** (0.073 g; 83%), red crystals: mp 95 °C dec; IR (KBr) 3650–2500 (m), 1708 (s), 1615 (m), 1500 (w), 1400 (m), 1333 (s), 1300 (m), 1258 (m), 1152 (m), 1030 (m), 855 (m), 815 (m), 785 (m), 758 (m), 732 (m), 713 (m), 663 (m), 650 (m), 528 (m) cm^{-1}; UV–vis ($CHCl_3$) 288 nm, 367 (sh), 384, 510, 563 (ϵ 6900, 16 900, 35 200, 1050, 1020); ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{22}H_5Cl_{14}O_2$: C, 33.1; H, 0.6; Cl, 62.2. Found: C, 33.4; H, 0.8; Cl, 62.0.

(b) Under Alkaline Conditions. A mixture of propionic acid **12** (0.140 g), powdered NaOH (0.400 g), ethyl ether (80 mL), and Me_2SO (16 mL) was treated as in the synthesis of methanol radical **15**, yielding propionic acid radical **16** (0.093 g; 66%).

Attempted Synthesis of 4-(2-Acetamido-2,2-bis(ethoxycarbonyl)ethyl)tetradecachlorotriphenylmethyl Radical (28). The reaction of bromomethane radical **18** (0.224 g) with diethyl acetamidomalonate (0.301 g) and K_2CO_3 (0.377 g) in dioxane (16 mL) was carried out as in the corresponding αH compound **8** (24-h reaction time). The product was acetamidomalonate **8** (0.137 g; 52%) instead.

Table III. $RC_6Cl_4CH_2X$

no.	R	X	solvent	temp, °C	time, h	recovery, %	yield, %
29	$(C_6Cl_5)_2\dot{C}$	Cl	o-$C_6H_4Cl_2$	165	34	74	9
18	$(C_6Cl_5)_2\dot{C}$	Br	o-$C_6H_4Cl_2$	165	74	7	75
18	$(C_6Cl_5)_2\dot{C}$	Br	C_6HCl_5	110	72	10	72
13	$(C_6Cl_5)_2CH$	Cl	o-$C_6H_4Cl_2$	180	40	98	0
2	$(C_6Cl_5)_2CH$	Br	o-$C_6H_4Cl_2$	180	40	95	0
5	$(C_6Cl_5)_2CH$	I	o-$C_6H_4Cl_2$	180	40	85	0

Attempted Synthesis of Tetradecachloro-4-(cyanomethyl)triphenylmethyl Radical. A mixture of bromomethane radical **18** (0.100 g), KCN (0.159 g), dioxane (10 mL), and water (0.35 mL) was stirred (1 h) at room temperature and under argon. The resulting mixture was treated as in the corresponding αH-compound **6**, giving diradical **21** (0.045 g; 50%).

Reaction of Bromomethane Radical 18 with Ammonia. A mixture of bromomethane radical **18** (0.100 g; 0.122 mmol), aqueous ammonia (1 mL; 2.44 mmol), and dioxane (20 mL) was stirred (1 h) at room temperature and under argon. The resulting mixture was treated as usual, the product being diradical **21** (0.083 g; 92%).

Reaction of Bromomethane Radical 18 with NaOH. A mixture of bromomethane radical **18** (0.030 g), aqueous 3 N NaOH (0.35 mL) and dioxane (15 mL) was treated as in the preceding reaction. The product was diradical **21** (0.026 g; 96%).

Attempted Synthesis of 4-(Carboxymethyl)tetradecachlorotriphenylmethyl Radical. The reaction of acetic acid **11** (0.082 g), powdered NaOH (0.250 g), ethyl ether (50 mL), Me_2SO (10 mL), and I_2 (0.019 g) was carried out as in the synthesis of methanol radical **15**. The isolated products were ethylene diradical **21** (0.025 g; 32%) and methanol radical **15** (0.014 g; 18%).

Tetradecachloro-4-(chloromethyl)triphenylmethyl Radical (29). A mixture of $TiCl_4$ (0.228 g), tosylate radical **20** (0.200 g), and ethyl ether (16 mL) was treated as in the synthesis of chloromethane **13** (method a), yielding chloromethane radical **29** (0.154 g; 91%), red crystals: mp 307–308 °C dec: IR (KBr) 2910 (w), 2840 (w), 1500 (w), 1438 (w), 1335 (s), 1320 (s), 1258 (s), 1155 (m), 1045 (m), 922 (m), 815 (m), 780 (m), 730 (m), 700 (m) cm^{-1}; UV–vis (C_6H_{12}) 222 nm, 290, 338 (sh), 370 (sh), 385, 482 (sh), 515, 565 (ϵ 100 000, 6600, 5900, 19 100, 37 800, 1050, 1070, 998); ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{20}H_2Cl_{15}$: C, 31.0; H, 0.3. Found: C, 31.1; H, 0.4.

Attempted Synthesis of Tetradecachloro-4-(iodomethyl)triphenylmethyl Radical. (a) From Bromomethane Radical 18. The reaction of bromomethane radical **18** (0.300 g) with NaI (0.549 g) in dioxane (35 mL)-acetone (20 mL) was performed as in the reaction of bromomethane **2** with NaI. The product was diradical **21** (0.243 g; 90%).

(b) From Methane Radical 17. A mixture of radical **17** (0.100 g), an excess of I_2, and benzoyl peroxide in o-dichlorobenzene (20 mL) was heated (125 °C; 19 h) under argon. The resulting mixture was evaporated and the residue submitted to TLC (silica gel; hexane), yielding diradical **21** (74%).

Tetradecachloro-4-(2-(chlorocarbonyl)ethyl)triphenylmethyl Radical 26. A solution of propionic acid radical **16** (0.198 g) in $SOCl_2$ was refluxed (17 h) and next evaporated to dryness. The residue was recrystallized (hexane) in a dry atmosphere affording propionyl chloride radical **26** (0.175 g; 85%) as red needles: IR (KBr) 2920 (w), 1795 (s), 1500 (w), 1448 (w), 1400 (w), 1325 (s), 1258 (m), 1140 (m), 950 (m), 860 (m), 810 (m), 710 (m), 690 (m), 662 (m), 520 (m) cm^{-1}; UV–vis ($CHCl_3$) 283 nm, 340 (sh), 368 (sh), 383, 480 (sh) 507, 560 (ϵ 6180, 6950, 19 900, 37 700, 1070, 1150, 1120). Anal. Calcd for $C_{22}H_4Cl_{15}O$: C, 32.4; H, 0.5. Found: C, 32.0; H, 0.7.

4-(2-(Alaninocarbonyl)ethyl)tetradecachlorotriphenylmethyl Radical Ethyl Ester (27). A mixture of propionyl chloride radical **26** (0.090 g), L-alanine ethyl ester hydrochloride (0.026 g), triethylamine (0.035 g), and CH_2Cl_2 (5 mL) was stirred (1 h) at room temperature in a dry atmosphere, poured into aqueous HCl, and extracted with ether. The organic layer was washed with water, dried, and evaporated to a residue which was purified by TLC (silica gel, $CHCl_3$), giving alaninocarbonyl radical **27** (0.063 g; 64%), red powder: mp 115–117 °C; IR (KBr) 3280 (w), 2910 (w), 1730 (s), 1650 (s), 1500 (m), 1448 (m), 1325 (s), 1255 (m), 1195 (m), 1155 (m) 1010 (m), 808 (m), 725 (m), 702 (m), 645 (m) cm^{-1}; UV–vis ($CHCl_3$) 285 nm, 335 (sh), 365 (sh), 383, 475 (sh), 507, 560 (ϵ 6710, 7230, 20 800, 40 200, 1150, 1210, 1190); ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{27}H_{14}Cl_{14}NO_3$: C, 36.2; H, 1.5; N, 1.6. Found: C, 36.4; H, 1.7; N, 1.4.

Thermal Treatments of Radical and Nonradical Benzyl Halides: starting halide, 0.100 g; solvent, 40 mL, under argon; isolation of final components, by TLC (silica gel, hexane). The yield refers to diradical **21**; the recovery, to starting halide (Table III).

Reductions with $SnCl_2$. (a) Bromomethane Radical 18. A solution of radical **18** (0.050 g) and $SnCl_2 \cdot 2H_2O$ (0.274 g) in ethyl ether (60 mL) was stirred (24 h) at room temperature and under argon. The resulting solution was washed with aqueous 2 N HCl and with water, dried, and evaporated, and the residue obtained was purified as usual, giving diradical **21** (0.047 g; 92%).

(b) Bromomethane 2. The preceding reaction was repeated with bromomethane **2** (0.050 g), 96% of it being recovered.

Competitive Reactions. Bromination of αH Compound 1 and Radical 17. An equimolecular mixture of αH compound **1** (0.110 g), radical **17** (0.102 g), Br_2 (0.5 mL), azobis(isobutyronitrile) (0.0045 g), and CCl_4 (30 mL) was refluxed (3 h) under argon. The resulting solution was evaporated and the residue submitted to TLC (silica gel; hexane), yielding (a) a fraction (0.102 g) formed by starting components **1** and **17**; (b) a fraction (0.110 g) constituted of brominated products **2** and **18**. Quantitative analysis[18] gave the following proportions: αH compound **1**, 74% recovery; bromomethane **2**, 25%; radical **17**, 9% recovery; bromomethane radical **18**, 70%.

Acetolysis of Bromomethane 2 and Bromomethane Radical 18. Operating at 66 °C, in a thermostat, a solution of anhydrous sodium acetate (0.100 g) in methanol (4 mL) was added to another of an equimolecular mixture of bromomethane **2** (0.050 g) and bromomethane radical **18** (0.050 g) in dioxane (9 mL). After 75 min, the resulting solution was worked up as usual, giving (a) a fraction (0.070 g) formed by starting components **2** and **18** and (b) a fraction constituted of acetates **3** and **19**. Quantitative analysis[18] gave the following figures: bromomethane **2**, 86% recovery; acetate **3**, 13%; bromomethane radical **18**, 53% recovery; acetate radical **19**, 36%.

Reaction of Bromomethane 2 and Bromomethane Radical 18 with Diethylmalonate. Operating at 90 °C, in a thermostat, a mixture of bromomethane **2** (0.050 g; 0.061 mmol), bromomethane radical **18** (0.050 g; 0.061 mmol), diethylmalonate (0.21 mL; 0.61 mmol), K_2CO_3 (0.170 g; 0.73 mmol), and dioxane (10 mL) was stirred under argon. After 20 min, the resulting solution was treated as in the synthesis of the malonate **7**, giving (a) a fraction constituted of the starting components **2** and **18** and (b) a fraction the components of which were the malonates **7** and **25**. Quantitative analysis[18] gave the following proportions: bromomethane **2**, 56% recovery; malonate **7**, 16%; bromomethane radical **18**, 6% recovery; malonate radical **25**, 88%.

Registry No. **1**, 79839-38-6; **2**, 101998-20-3; **3**, 101980-92-1; **4**, 101980-93-2; **5**, 101980-94-3; **6**, 101980-95-4; **7**, 101980-96-5; **8**, 101980-97-6; **9**, 101980-98-7; **10**, 101980-99-8; **11**, 101981-00-4; **12**, 101981-01-5; **13**, 101981-02-6; **14**, 101981-03-7; **15**, 101981-04-8; **16**, 101981-05-9; **17**, 79855-18-8; **18**, 81221-80-9; **19**, 101981-06-0; **20**, 101981-07-1; **21**, 85632-68-4; **25**, 101981-08-2; **26**, 101981-09-3; **27**, 101981-10-6; **29**, 85615-95-8; diethyl malonate, 105-53-3; diethyl acetamidomalonate, 1068-90-2; L-alanine ethyl ester hydrochloride, 1115-59-9.

(18) The proportions of the components were ascertained by IR and UV–vis spectroscopies.