is an ORTEP drawing[35] of compound **16**.

Compound 21. A crystal of dimensions 0.42 × 0.17 × 0.17 mm was used to collect all data. The unit cell is orthorhombic, and the systematic absences are consistent with space group *Pbca*.

Crystal data: $C_{16}H_{18}O_5$, M_r = 290.32, a = 26.059 (3) Å, b = 11.132 (1) Å, c = 9.542 (1) Å, V = 2768.0 (6) Å^3, Z = 8, d_c = 1.39 g cm^{-3}, μ = 8.69 cm^{-1} (Cu Kα).

Of the 2015 independent reflections measured, 1160 had intensities greater than $3\sigma(I)$. Phases were calculated for the 200 $|E|$ values greater than 1.28, and the phase set with the highest combined figure of merit yielded all nonhydrogen atoms. All hydrogen atoms were located in a difference Fourier map, and full-matrix least-squares refinement with anisotropic thermal parameters for nonhydrogen atoms led to a final R of 0.029 and a weighted R of 0.032. The data were corrected for extinction through use of the equation[36] $|F_c^*| = k|F_c|(1 + 2r^*|F_c|^2\delta)^{-1/4}$, where δ is a dimensionless constant. During the final cycle of refinement r^* was refined to a value of 6.79 (8) × 10^{-3}. Figure 5 is an ORTEP drawing[35] of compound **21**.

Acknowledgment. We thank the Robert A. Welch Foundation and the National Science Foundation for support of this work.

Registry No. **4**, 6675-72-5; **5**, 75725-33-6; **7**, 872-36-6; **8**, 17994-23-9; **9**, 108-31-6; **10**, 930-60-9; **11**, 26154-22-3; **12**, 82918-59-0; **13**, 82918-60-3; **14**, 82918-61-4; **15**, 82918-62-5; **16**, 82950-40-1; **17**, 82918-63-6; **18**, 82918-64-7; **19**, 82918-65-8; **20**, 82918-66-9; **21**, 82918-67-0; **24**, 765-69-5; **25**, 3883-58-7; **26**, 26154-26-7; **27**, 3883-56-5; **28**, 762-42-5; succinic acid, 110-15-6; propionyl chloride, 79-03-8; cyclopentadiene, 542-92-7.

Supplementary Material Available: Tables 1–5, atomic positional parameters for compounds **12**, **13**, **15**, **16**, and **21**; Tables 6–10, anisotropic thermal parameters for compounds **12**, **13**, **15**, **16**, and **21**. Table 11, interatomic distances (in angstroms) for **12**, **13**, **15**, and **16**. Table 12, valence angles (degrees) for **12**, **13**, **15**, and **16**. Table 13, interatomic distances (in angstroms) for **21**. Table 14, valence angles (degrees) for **21**. Table 15, short intramolecular contacts. Table 16, interplanar angles. Table 17, selected torsion angles. Figure 18, ORTEP drawing of compound **12**. Figure 19, ORTEP drawing of compound **13** (19 pages). Ordering information is given on any current masthead page.

(36) Larson, A. C. "Crystallographic Computing"; Ahmed, F. R., Hall, S. R., Huber, C. P. Eds.; Munksgaard: Copenhagen, 1970; pp 291–294.
(37) Alder, K.; Flock, F. H.; Janssen, P. *Chem. Ber.* **1956**, *89*, 2689.
(38) A series of other weak dienophiles has been examined in high-temperature addition to isodicyclopentadiene and found also to add to isomer **5** in preference to **4**: Paquette, L. A.; Williams, R. V.; Carr, R. V. C.; Charumilind, P., forthcoming publication. We thank Dr. Paquette for a copy of this manuscript.

Inert Carbon Free Radicals. 3. Monofunctionalized Radicals from Perchlorotriphenylcarbenium Hexachloroantimonate

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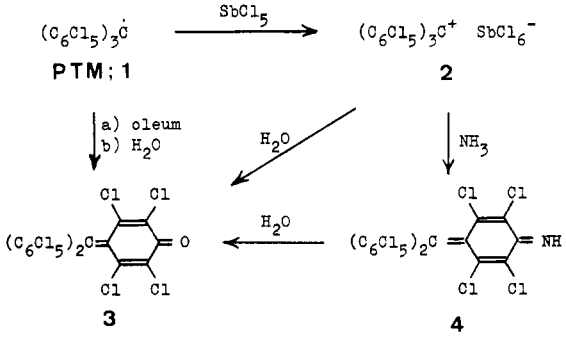
Perchlorotriphenylcarbenium hexachloroantimonate (**2**) is prepared from perchlorotriphenylmethyl radical (PTM; **1**) and $SbCl_5$. Salt **2** by hydrolysis or ammonolysis yields perchlorofuchsone (**3**) or *NH*-tetradecachlorofuchsonimine (**4**), respectively, two quinonoid compounds which are shown to be direct and indirect precursors for the synthesis of some new inert carbon free radicals, monofunctionalized at the 4-position with hydroxy (**13**), sodium oxido (**12**), methoxy (**14**), acetoxy (**15**), bromoacetoxy (**16**), (ethoxyformyl)oxy (**17**), amino (**19**), sodium amido (**20**), chloroacetamido (**21**), and bromoacetamido (**22**) groups. Most of them are isolated in pure (magnetic susceptibility), crystalline form, being insensitive to O_2 and displaying the characteristic chemical inertness of the radicals of the PTM series, caused by steric shielding. Spectral (IR, UV–vis, and ESR) data, including hyperfine couplings with ^{14}N, ^1H, and ^{13}C and some remarkable effects of solvents are reported and discussed. Other reactions either giving some of these radicals or starting from them are described, particularly one-electron transfers caused by $SbCl_5$, cycloheptatriene, 9,10-diphenylanthracene, KBr, KI, HI/I_2, ascorbic acid, and $NaOH/Me_2SO$. Supporting evidence for two-step hydride-shift mechanisms to carbenium ions is given. Evidence for steric shielding of cation **2** in some reactions leading to the formation of abnormal, novel products is described here.

The so-called "inert carbon free radicals", such as those of the perchlorotriphenylmethyl (PTM) radical series,[1,2] are passive in bond-formation processes on account of steric shielding of their central carbon atom by their six ortho chlorines and three benzene rings.[3] They do not dimerize, are quite insensitive to oxygen, even near 300 °C, and do not react with typical radical reagents or with aggressive chemical species such as concentrated mineral acids, halogens, etc.[1,2] However, they are active in electron-transfer processes, where shielding is ineffectual.[1,2,4,5] In fact, this paper concerns the synthesis and some prop-

Scheme I



(1) (a) Ballester, M.; Riera, J.; Castañer, J.; Badia, 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.
(2) Ballester, M.; Castañer, J.; Riera, J.; Ibáñez, A.; Pujadas, J. *J. Org. Chem.* **1982**, *47*, 259.
(3) See ref 1a, Figure 2.

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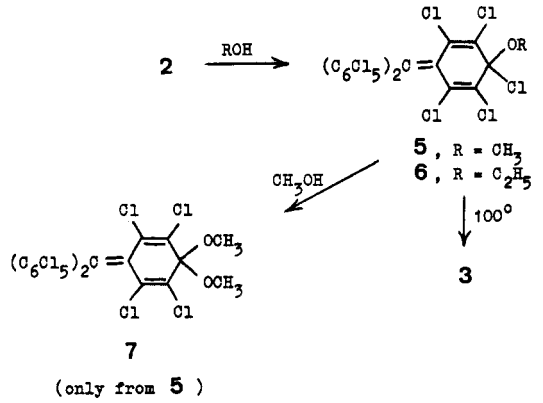
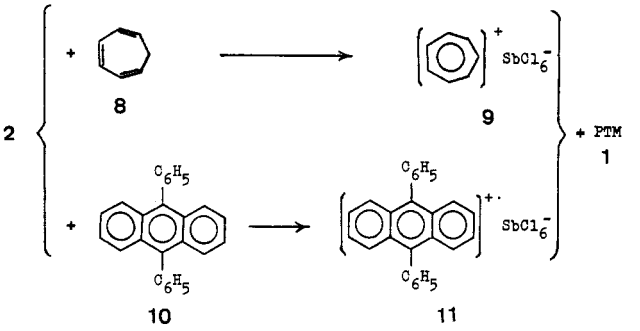
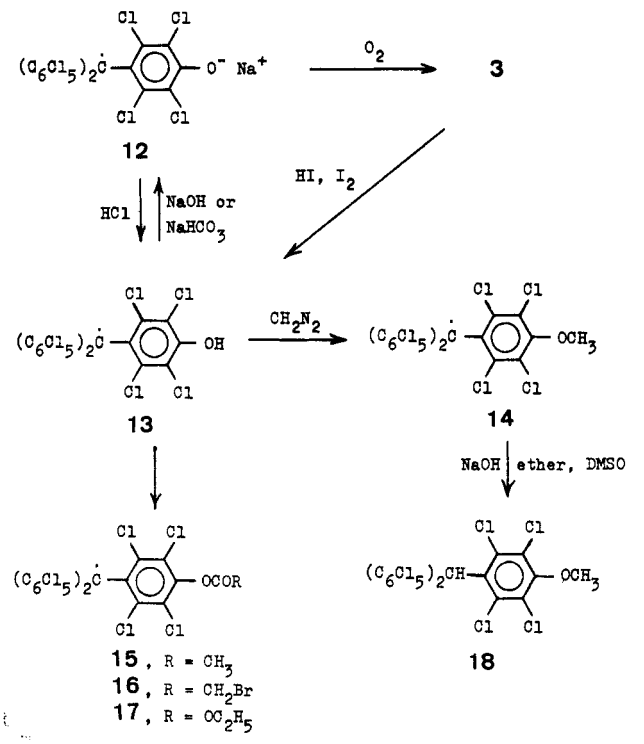
Scheme II



Scheme III



Scheme IV



erties and reactions of perchlorotriphenylcarbenium hexachloroantimonate (2)[6] and radicals therefrom.

Results and Discussion

Synthesis of Carbenium Salt 2. The detailed synthesis of carbenium salt 2 by oxidation of radical PTM (1) with $SbCl_5$ in SO_2Cl_2 is described in the Experimental Section. It has been found that the same reaction can be carried out, although less conveniently, in CCl_4 instead of SO_2Cl_2. Oxidation of radical PTM (1) to the green cation of salt 2 also occurs with SO_2Cl_2–$AlCl_3$.

Hydrolysis of Carbenium Salt 2. Although salt 2, in solid form, is remarkably stable toward water, its hydrolysis takes place readily in a solution of humid CH_2Cl_2, giving perchlorofuchsone (3),[6] no perchlorotriphenylcarbinol being detected (Scheme I). That abnormal hydrolysis is also interpreted in terms of steric shielding of the central α-carbon from the H_2O. Consequently, the attack takes place in the 4-position, followed by elimination of HCl.

Fuchsone 3 is also obtained directly from the PTM radical (1) by oxidation with lukewarm oleum, followed by treatment with water. This oxidation is an one-electron transfer to give carbenium ion 2 (green), which undergoes subsequent hydrolysis.

Ammonolysis of Carbenium Salt 2. Salt 2 in CH_2Cl_2 reacts with dry NH_3, giving *NH*-tetradecachlorofuchsonimine (4) which is difficult to purify and hydrolizes easily to fuchsone 3.

Alcoholyses of Carbenium Salt 2. Solid salt 2 reacts with methanol and with ethanol to give pentadecachloro-3-methoxy- (5) and pentadecachloro-3-ethoxy-6-(diphenylmethylene)cyclohexa-1,4-diene (6), respectively, both being insoluble in the alcohol (Scheme II). However, methoxy derivative 5, when dissolved in $CHCl_3$, reacts further with methanol to give tetradecachloro-3,3-dimethoxy-6-(diphenylmethylene)cyclohexa-1,4-diene (7). At 100 °C both 5 and 6 are converted into fuchsone 3. These eliminations take place also at room temperature, although very slowly.

Reduction of Carbenium Salt 2 with Solid Halides. Salt 2, when mixed with solid KBr or KI, gives radical 1 quantitatively, with evolution of the halogen. However, solid KCl does not react, and, consequently, it was used to prepare the pellet for recording the IR spectrum of 2.[6]

One-Electron-Transfer Reactions with Carbenium Salt 2. It is noteworthy that carbenium ion 2 does not cause a hydride shift to give αH-pentadecachlorotriphenylmethane with donors such as cycloheptatriene (8; Scheme III). With this reagent it undergoes instead a one-electron-transfer process, yielding quantitatively PTM radical (1) and tropylium hexachloroantimonate (9). This abnormal behavior is attributed to steric shielding of PTM (1) from hydrogen atom transfer.[4]

There exists evidence showing that a hydrogen shift to carbenium ions takes place, at least in some cases, through a two-step process: (1) a one-electron transfer and (2) a hydrogen atom shift. This has been observed in the reaction of perchlorodiphenylcarbenium ion with 8, where perchlorodiphenylmethyl radical is easily detected as a transient species.[4] Consequently, that abnormal reaction of carbenium ion 2 is traced specifically to steric hindrance of step 2 caused by the six *o*-chlorines.[3]

In fact, carbenium salt 2 reacts also with 9,10-diphenylanthracene (10), an exclusive one-electron donor, to give radical PTM (1) and 9,10-diphenylanthryliumyl hexachloroantimonate (11).[4]

Radicals from Perchlorofuchsone (3). By treatment of fuchsone 3 in benzene (or hexane) with aqueous HI/I_2 at room temperature, tetradecachloro-4-hydroxytriphenylmethyl radical (13; Scheme IV) is obtained quantitatively. If I_2 *is not* present, no reaction occurs. Therefore, that process is regarded tentatively as a reduction by HI_3 taking place in the nonaqueous layer. It

(4) Ballester, M.; Riera, J.; Castañer, J.; Rodriguez, A. *Tetrahedron Lett.* **1971**, 2079.
(5) Ballester, M.; Riera, J.; Castañer, J.; Casulleras, M. *Tetrahedron Lett.* **1978**, 643.
(6) Short notices have been advanced on carbenium salt 2,[7] fuchsone 3,[2,7,8] fuchsonimine 4,[9] hydroxy radical 13,[10] and amino radical 19.[9]

is noteworthy that under the reaction conditions this reduction stops at the radical stage (it does not give any αH-tetradecachloro-4-hydroxytriphenylmethane), and this is being attributed to the steric shielding already referred to.[3]

Solid hydroxy radical **13** oxidizes slowly to fuchsone **3** in the air. This conversion is effected also by passing radical **13** in ether, in the air, through silica gel. A transient green adsorbate is observed.

When a solution of radical **13** in ether is shaken with aqueous $NaHCO_3$ in the absence of air, the red color of the ethereal layer is discharged, and, in turn, in the aqueous layer a green color appears. This process is reversed upon acidification. However, in the presence of air, the green color disappears, fuchsone **3** being formed. This is a compelling evidence for the formation of sodium tetradecachloro-4-oxidotriphenylmethyl radical (**12**), which oxidizes in the air with extreme easiness. This salt has recently been isolated, and it is being studied.[11]

Hydroxy radical **13** methylates (N_2CH_2, ether) to give a very high yield of tetradecachloro-4-methoxytriphenylmethyl radical (**14**). This radical, by reduction with NaOH–Me_2SO–ether and then treatment with aqueous HCl, is converted into αH-tetradecachloro-4-methoxytriphenylmethane (**18**), as in PTM.[1a]

When hydroxy radical **13** is refluxed in acetic anhydride, 4-acetoxytetradecachlorotriphenylmethyl radical (**15**) is obtained. The latter, by the treatment with NaOH–Me_2SO–ether, as before, gives hydroxy radical **13**, no αH-tetradecachloro-4-hydroxytriphenylmethane being formed. This is traced to radical oxide **12** being incapable of undergoing reduction to the corresponding highly unfavorable methide–oxide dianion, the would be precursor of that αH compound under the reaction conditions.

Hydroxy radical **13** with refluxing bromoacetyl chloride or ethoxyformyl chloride gives high yields of radicals 4-(bromoacetoxy)tetradecachlorotriphenylmethyl (**16**) or tetradecachloro-4-[(ethoxyformyl)oxy]triphenylmethyl (**17**), respectively.

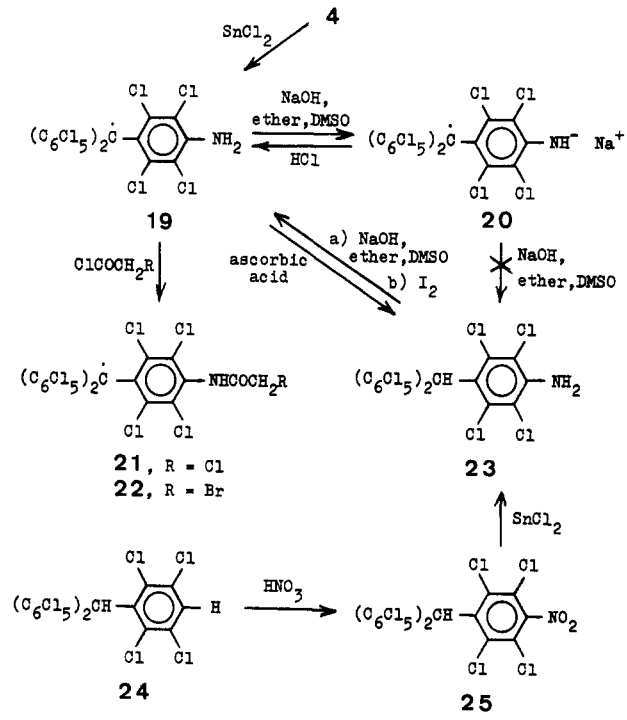
The fact that the radical character in all these radicals is not destroyed by N_2CH_2 or by acetic anhydride, ethoxyformyl chloride, or bromoacetyl chloride, at refluxing temperatures, emphasizes its chemical inertness.

Radicals from *NH*-Tetradecachlorofuchsonimine (4). Fuchsonimine **4** reacts with $SnCl_2$ in ether to give 4-aminotetradecachlorotriphenylmethyl radical (**19**, 62%). The reduction of fuchsonimine **4** can also be performed with diethyl phosphite in the same solvent with similar maximum yields. However, it has been found that high, reproducible yields are difficult to attain by the latter method.

The synthesis of amino radical **19** (Scheme V) was also effected by the conventional method,[1] i.e., from αH-4-aminotetradecachlorotriphenylmethane (**23**). However, the yield in amino radical **19** was low, some **23** being recovered. The preparation of αH compound **23** was performed from $\alpha H,4H$-tetradecachlorotriphenylmethane (**24**)[2] through αH-tetradecachloro-4-nitrotriphenylmethane (**25**).

We attempted to obtain αH-amino compound **23** by the reductive treatment with NaOH–Me_2SO–ether of amino

Scheme V



radical **19**, referred to in the preceding section. However, it has been found that under this treatment sodium 4-amidotetradecachlorotriphenylmethyl radical (**20**) is formed almost quantitatively (see ESR section). This radical reverts to amino radical **19** upon addition of acid. Therefore, under that treatment no significant reduction to αH compound **23** takes place, in contrast with the methoxy radical **14** or PTM (**1**) itself.[1a,2] Consequently, sodium amido radical **20** is incapable of reduction since the formation of the corresponding dianion is hindered, as in hydroxy radical **13**. Nevertheless, reduction of amino radical **19** to αH compound **23** can easily, although slowly, be effected with ascorbic acid in aqueous THF, as in PTM (**1**).[5]

The abnormally low yield in the synthesis of amino radical **19** from its αH compound **23** is accounted for partly by assuming the formation of a salt, a sodium 4-amidotetradecachlorotriphenylmethane, which would hinder the formation of the corresponding dianion intermediate, and partly by reaction of that salt with the iodine to give by-products.

Amino radical **19** reacts with chloroacetyl and with bromoacetyl chlorides, giving radicals 4-[(chloroacetyl)-amino]tetradecachlorotriphenylmethyl (**21**) and 4-[(bromoacetyl)amino]tetradecachlorotriphenylmethyl (**22**), respectively.

Ultraviolet–Visible Spectra. As in the "inert free radicals" reported previously,[1a,2] almost all radicals here described display in nonpolar solvents two radical bands around 385 and 500–560 nm, with the usual absorptivity values, as well as a very intense band around 220 nm and a much weaker absorption around 280 nm, both assigned to the benzenoid character.[1a,2,12] The radical-character absorptions involve two one-electron transitions: from SOMO to LUMO and from HOMO to SOMO, which correspond to the two first excited configurations.

The spectrum of amino radical **19** in nonpolar solvents is abnormal. In fact, while monoradicals of the PTM series

(7) Ballester, M.; Riera, J.; Rodriguez, A. *Tetrahedron Lett.* **1970**, 3615.
(8) Ballester, M.; Riera, J.; Rovira, C. *An. Quim.* **1976**, *72*, 489.
(9) Ballester, M.; Riera, J.; Rodriguez, A.; Rovira, C. *Tetrahedron Lett.* **1977**, 2355.
(10) Ballester, M.; Castañer, J.; Riera, J.; Veciana, J. *Tetrahedron Lett.* **1978**, 479.
(11) Ballester, M.; Veciana, J.; Castañer, J.; Riera, J., forthcoming publication.
(12) Ballester, M.; Riera, J.; Spialter, L. *J. Am. Chem. Soc.* **1964**, *86*, 4276.

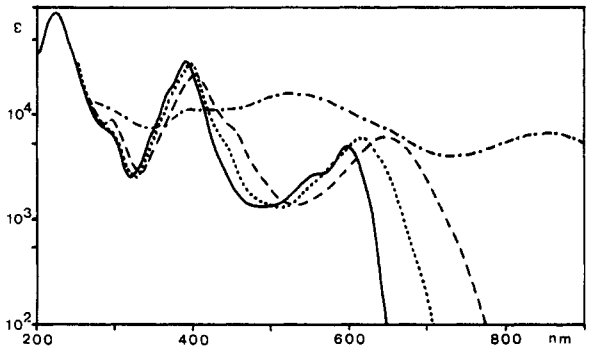


Figure 1. UV–vis spectra of: (1) amino radical **19** in cyclohexane (—), dioxane (···), and Me_2SO (– – –). (2) sodium amido radical **20** in Me_2SO (–·–).

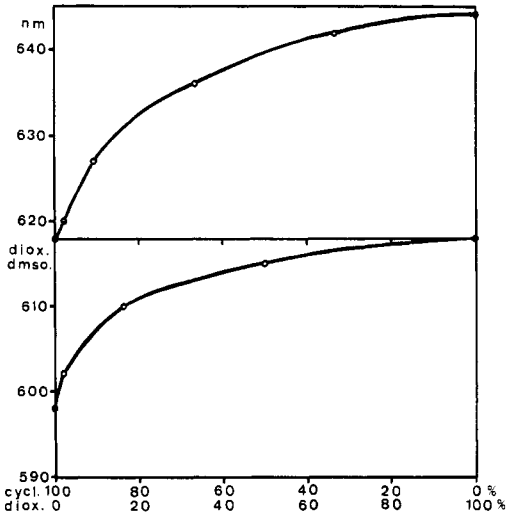


Figure 2. Plot of the wavelength maximum vs. the composition of the solvent in the UV–vis spectrum of amino radical **19**.

are red,[1a,2] radical **19** is green. Also, its color depends upon the solvent; i.e., it shows solvatochromy. In cyclohexane its solutions are reddish, while in ethers they are bright green.

The spectrum of amino radical **19** has been recorded in cyclohexane, dioxane, and Me_2SO, the radical-band maxima being found at 390 and 598, 394 and 618, and 400 and 644 nm, respectively (Figure 1). The bathochromic shifts with solvent polarity are therefore very significant, the highest wavelength band being the more sensitive one. Figure 2 shows the curves of the wavelength maximum for the latter band vs. the composition of the solvent. Notice the great influence of small amounts of a second solvent when added to a solvent of lower polarity, indicating a solvation rather than a dielectric constant effect.

While in cyclohexane the spectrum of hydroxy radical **13** is normal, in Me_2SO it is abnormal, showing, in addition, evidence for extensive ionization, as discussed later. When in order to minimize ionization some trifluoroacetic acid is added, bathochromic shifts of the radical-character bands are observed, although smaller than those of amino radical **19**, the maxima being located at 391 and 584 nm (Figure 3).

Those red shifts indicate that solvation stabilizes the relevant excited states more than the ground state, a result which is consistent with simple MO calculations. Actually assignments of the two radical bands to their excited states in such complex, highly chlorinated molecules as those delt with here is at present an extremely difficult task.

When the spectrum of hydroxy radical **13** is recorded in pure (neutral) Me_2SO, a new band around 741 nm ap-

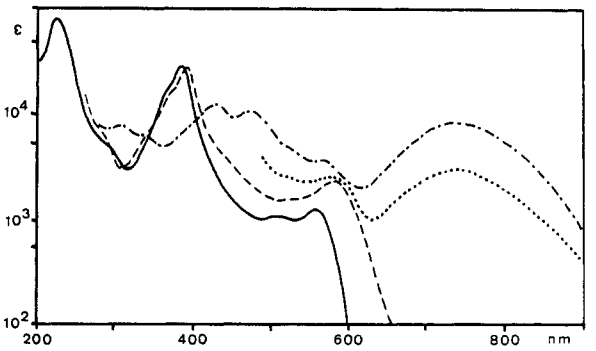


Figure 3. UV–vis spectra of: (1) hydroxy radical **13** in cyclohexane (—), neutral Me_2SO (···), and acidic Me_2SO (– – –); (2) sodium oxido radical **12** in Me_2SO (–·–).

pears (Figure 3), which is due to the oxide radical ion. In fact, that spectrum is the overlap of those of **13** (acidic Me_2SO) and pure sodium tetradecachloro-4-oxidotriphenylmethyl radical (**12**) which is also reported here (Figure 3). From the absorptivities at the concentration tested (7.36×10^{-4} mol L^{-1}) it is found that the ionization is about 36%, which corresponds to a dissociation constant of about 1.5×10^{-2} mol L^{-1}.

The spectrum of sodium 4-amidotetradecachlorotriphenylmethyl radical (**20**) in Me_2SO has high absorptivities all over the recorded range (275–900 nm) and even beyond, the flattened maxima being located at 400, 520, and 852 nm (Figure 1). This allows us to conclude that no significant ionization of amino radical **19** takes place in Me_2SO, as might have been expected.

The spectra of radical salts **12** and **20** suggest that the typical radical-character bands around 385 and 500–560 nm are shifted in the anions to around 450 and 741 and around 520 and 850 nm, respectively. These collossal shifts are traced to an increased delocalization of the lone electron due to the negative charge (see ESR section). As expected, the red shifts increase with the resonance effect of the atom bonded to the 4-carbon, i.e., Cl < O < N.

The radical bands of acetylamino radicals **21** and **22** are so shifted hypsochromically with respect to those of amino radical **19** that their spectra are regarded as "normal". This is attributed partly to inhibition to the resonance between the amino group and the aromatic system caused by the steric repulsions among the acetyl and the two ortho neighboring chlorines and partly to the electron-withdrawing effect of the carbonyl group. With respect to this electronic effect, it has just been shown that negative charge migration from the nitrogen to the benzene ring causes bathochromic shifts. Since the carbonyl group opposes that charge migration, it must also contribute to those hypsochromic shifts.

Electron Spin Resonance Spectra. The ESR spectra of the radicals here synthesized are collected in Table I. The g values are close to 2.0027, a normal value for a radical of the PTM series.[1a,2] The spectra of radicals **13–17** consist of a single main line and three pairs of ^{13}C satellites.[1a,2]

In C_2Cl_4, acetylamino radicals **21** and **22** also display a single symmetrical main line, although somewhat deformed near its center on account of coupling with N and H nuclear *spins*, as ascertained by (computer) simulation. However, in dioxane hyperfine coupling becomes quite evident (two lines) because of the combination of two effects: an increase in the coupling constants, mainly with the N proton, and a decrease in line width.

The ESR spectrum of amino radical **19** shows some remarkable features: although when taken in C_2Cl_4 or dioxane it appears "normal", with a symmetrical, somewhat

Table I. ESR Spectral Data of Radicals

compd	substituent	solvent	g	lines	line width, MHz	splittings, MHz			
						N[b]	H[b]	^{13}C α	^{13}C aromatic[b]
1	Cl	C_2Cl_4	2.0026	1	4.0			82.0	30.2, 34.2
13	OH	C_2Cl_4	2.0026	1	3.4			82.5	30.0, 35.5
		Me_2SO	2.0027	1	3.4			81.4	29.7, 34.9
14	OCH_3	C_2Cl_4	2.0027	1	3.8			82.5	30.0, 35.0
15	$OCOCH_3$	C_2Cl_4	2.0027	1	4.5			82.9	29.4, 35.0
16	$OCOCH_2Br$	C_2Cl_4	2.0027	1	3.6			82.3	30.2, 36.1
17	$OCO_2C_2H_5$	C_2Cl_4	2.0028	1	2.9			81.5	29.1, 34.7
19	NH_2	C_2Cl_4	2.0027	1[a]	2.6	2.80	1.76	78.1	27.4, 31.1
		dioxane	2.0027	1[a]	3.1	3.35	2.10	78.4	27.5, 31.2
		Me_2SO	2.0027	5[a]	3.3	3.35	3.35		
		HMPT	2.0027	5[a]	3.2	3.50	3.50		
20	NH^-Na^+	Me_2SO	2.0032	6[a]	3.9	8.68	14.00		
21	$NHCOCH_2Cl$	C_2Cl_4	2.0028	1[a]	2.4	1.23	3.78	82.9	29.1, 35.4
		dioxane	2.0028	2[a]	2.2	1.29	4.59	82.9	28.8, 35.3
22	$NHCOCH_2Br$	C_2Cl_4	2.0027	1[a]	2.4	1.23	3.78	82.9	29.1, 35.4
		dioxane	2.0027	2[a]	2.2	1.29	4.59	82.9	28.8, 35.3

[a] Deformed lines. [b] Found by spectrum simulation.

Table II. Magnetic Properties of Radicals

comp	substituent	μ_B	$10^6\chi_{dia}$, emu		θ, K	spins/mol $\times 10^{-23}$
			Curie-Weiss	Pascal		
13	OH	1.73	−0.565	−0.512	−4.8	6.1
14	OCH_3	1.71	−0.482	−0.518	−1.5	5.9
15	$OCOCH_3$	1.62	−0.505	−0.512	−1.5	5.3
16	$OCOCH_2Br$	1.69	−0.528	−0.497	−0.4	5.8
17	$OCO_2C_2H_5$	1.75	−0.561	−0.513	−6.6	6.2
19	NH_2	1.73	−0.483	−0.513	−1.5	6.0
21	$NHCOCH_2Cl$	1.75	−0.486	−0.512	−2.2	6.2
22	$NHCOCH_2Br$	1.75	−0.475	−0.500	−0.6	6.2

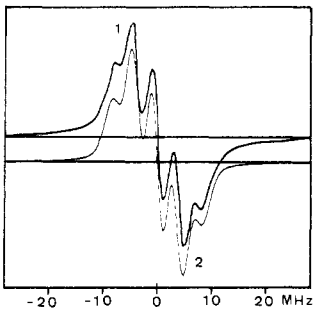


Figure 4. ESR spectrum of amino radical **19** (1) and its computer simulation (2).

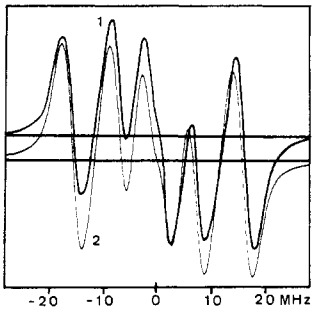


Figure 5. ESR spectrum of sodium amido radical **20** (1) and its computer simulation (2).

distorted single line, in Me_2SO of HMPT it clearly shows five (overlapping) lines out of the expected nine. Computer simulation (Figure 4) has allowed calculation of the H and N coupling constants.

The spectrum of sodium amido radical **20** in Me_2SO shows five (overlapping) lines (Figure 5), the coupling constants with H and N being greatly enhanced. Notice that while in radicals **20–22** the coupling constant for H is greater than that for N, in amino radical **19** it is not.

The surplisingly high coupling constants for sodium amido radical **20** are regarded as due to a great increase in both resonance involving the nitrogen p orbitals and N–H hyperconjugation caused by the negative charge.

The diminished coupling with N and the increased coupling with the proton in acetylamino radicals **21** and **22**, with respect to the amino radical **19**, are accounted for by assuming that the introduction of the acetyl group causes steric inhibition to *spin* delocalization on the N (see UV–vis section) and also places the proton further apart from the nodal plane of the lone-electron π orbital; i.e., it increases hyperconjugation. The electron-withdrawing character of the carbonyl group should diminish further the availability of the nitrogen p electron pair, and therefore it is reasonable to assume that it indirectly diminishes still further the *spin* coupling with the nitrogen.

The effect of polar solvation is assumed to be analogous to that of the negative charge in sodium amido radical **20**; i.e., it favors both nitrogen resonance and N–H hyperconjugation by spreading out the positive polarization charge on the amino group.

Magnetic Susceptibilities. The specific magnetic susceptibilities of the radicals have been measured form 77 K to room temperature. Least-squares correlation of the resulting Curie–Weiss plot gave the Bohr magnetons (μ_B), the specific diamagnetic susceptibility (χ_{dia}), and the Weiss constant (θ) (Table II). χ_{dia} values were calculated independently from Pascal's data, being in good agreement (Table II).[13,14] From μ_B the purities (spins/mol) were

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calculated, with the experimental values varying from 5.3 × 10^{23} to 6.2 × 10^{23}.

Experimental Section

General Methods. The IR, UV–vis, and ESR spectra 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 location of the IR peaks of perchloro organic compounds differs markedly from that of their nonchlorinated counterparts, it is useful to include them in this section.

Perchlorotriphenylcarbenium Hexachloroantimonate (2). $SbCl_5$ (30 mL) was added slowly, at room temperature, to a solution of PTM radical (**1**, 6.50 g) in SO_2Cl_2 (850 mL), and the resulting solution was left undisturbed (96 h). The small dark green cubes which formed were separated, washed with anhydrous CCl_4, and dried to give carbenium salt **2**:[6] 3.00 g; dec 190 °C. Precipitation from the mother liquors by addition of CCl_4 afforded more pure salt **2** (5.10 g). The total yield was 86.5% of theory.

Hydrolysis of Carbenium Salt 2. A solution of salt **2** (0.260 g) in CH_2Cl_2 (60 mL) was stirred with water (20 mL, 4 h). The organic layer was extracted with ether, and ethereal solution was washed with dilute aqueous HCl and with water, dried, and evaporated to give orange-yellow crystals of perchlorofuchsone (perchloro-α,α-diphenylquinomethane, perchloro(diphenylmethylene)cyclohexa-2,5-dienone; **3**): 0.169 g (96.1%); mp 312–315 °C (lit.[6] mp 309–311 °C); UV–vis (C_6H_{12}) 219 nm 284, 330 (sh), 407 nm (ε 75 000, 7900, 8000, 20 600); IR (KBr) 1660, 1565, 1510, 1470, 1350, 1340, 1310, 1130, 1120, 1020, 820, 755, 730, 720, 685, 650 cm^{-1}.

Ammonolysis of Carbenium Salt 2. Dry NH_3 was passed slowly (45 min) through a suspension of salt **2** (9.5 g) in CH_2Cl_2 (900 mL) saturated with dry NH_3. The anhydrization of the CH_2Cl_2 and the reaction were performed under extremely dry conditions. The resulting mixture was filtered, and the filtrate was evaporated to dryness, giving *NH*-tetradecachlorofuchsonimine[6] (*NH*-tetradecachloro(diphenylmethylene)cyclohexa-2,5-dien-1-imine; **4**, 7.25 g), which was purified by TLC (silica gel, hexane) and recrystallization from hexane–ether. Anal. Calcd for $C_{19}HCl_{14}N{\cdot}0.5C_6H_{14}$: C, 33.8; H, 1.0; Cl, 63.4; N, 1.8. Found: C, 33.1; H, 0.9; Cl, 65.0; N, 1.8; IR (KBr) 3275, 1510, 1365, 1350, 1330, 1310, 1270, 1125, 1018, 865, 817, 755, 697, 675, 663, 645, 538, 530 cm^{-1}.

Ethanolysis of Carbenium Salt 2. A mixture of salt **2** (0.382 g) and anhydrous ethanol (10 mL) was shaken (30 min) in an ultrasonic bath. The yellow solid formed was filtered, washed with ethanol, and dried to give pentadecachloro-3-ethoxy(diphemylmethylene)cyclohexa-1,4-diene (**6**): 0.269 g (95.7%); mp 273–277 °C dec; UV (C_6H_{12}) 233 nm, 292, 367 (ε 28 800, 11 400, 18 000); IR (KBr) 2980, 2940–2880, 1585, 1545, 1480, 1440, 1350, 1335, 1312, 1180, 1112, 1080, 815, 755, 750, 722, 710, 640, 520 cm^{-1}; ^1H NMR ($CDCl_3$) τ 6.64 (q, 2, J = 8 Hz, CH_2), 8.72 (t, 3, J = 8 Hz, CH_3). Anal. Calcd. for $C_{21}H_5Cl_{15}O$: C, 31.3; H, 0.6; Cl, 66.1. Found: C, 31.2; H, 0.8; Cl, 66.1.

Methanolysis of Carbenium Salt 2. A mixture of salt **2** (0.119 g) and anhydrous methanol (20 mL) was treated (10 min) as in the preceding ethanolysis to give pentadecachloro-3-methoxy-(diphenylmethylene)cyclohexa-1,4-diene (**5**): 0.083 g (96.5%); dec over 100°; IR (KBr) 2980, 2840, 1550, 1460, 1355, 1340, 1318, 1222, 1130, 1115, 1090, 813, 750, 722, 710, 640, 523 cm^{-1}; ^1H NMR ($CDCl_3$) τ 6.65 (s, CH_3). Anal. Calcd for $C_{20}H_3Cl_{15}O$: C, 30.4; H, 0.4; Cl, 67.2. Found: C, 30.4; H, 0.6; Cl, 67.0.

Methanolysis of Cyclohexadiene 5. A mixture of cyclohexadiene **5** (0.048 g), methanol (5 mL), and $CHCl_3$ (12 mL) was stirred (48 h) in the dark. Evaporation of the solvent and purification by TLC (silica gel, CCl_4) gave 3,3-dimethoxytetradecachloro(diphenylmethylene)cyclohexa-1,4-diene (**7**): 0.027 g (56.6%); mp 267–270 °C; UV (C_6H_{12}) 223 nm, 245 (sh), 289, 358 (ε 67 600, 31 000, 14 200, 22 000); IR (KBr) 2920, 2820, 1545, 1450, 1348, 1332, 1312, 1270, 1222, 1125, 1090, 845, 814, 755, 722, 712, 660, 645, 525 cm^{-1}; ^1H NMR τ 6.62 (s, CH_3). Anal. Calcd for $C_{21}H_6Cl_{14}O_2$: C, 32.1; H, 0.8; Cl, 63.1. Found: C, 32.0; H, 0.9; Cl 62.9.

Reduction of Carbenium Salt 2 with Potassium Iodide. The reaction was performed by mixing thoroughly salt **2** (0.086 g) with solid KI (0.200 g) in a mortar. A brown color developed immediately. The resulting solid was extracted with CCl_4, and the organic solution was evaporated to give PTM radical (**1**; 0.060 g, 100%).

Reduction of Carbenium Salt 2 with Potassium Bromide. The reaction was performed as in the preceding reduction, with KI also giving a high yield of PTM radical (**1**).

Reduction of Carbenium Salt 2 with Cycloheptatriene (8). Cycloheptatriene (**8**, 1.91 g) was added slowly to a cooled (0 °C) mixture of salt **2** (0.222 g) and CCl_4 (12 mL). The resulting mixture was stirred (3 h) in the dark. The precipitate formed was separated by filtration, washed with CCl_4, and dried, giving impure tropylium hexachloroantimonate (**9**, 0.084 g), identical (IR and UV) with a sample prepared by reaction of cycloheptatriene and $SbCl_5$.[16] The supernatant CCl_4 solution was evaporated to dryness to give PTM radical (**1**; 0.141 g, 91.5%).

Reduction of Carbenium Salt 2 with 9,10-Diphenylanthracene (10). Carbenium salt **2** reacts with anthracene **10** in CCl_4 at room temperature and under ultrasonic shaking, resulting in a precipitate of 9,10-diphenylanthryliumyl hexachloroantimonate (**11**), identified by its ESR spectrum (see next preparation). The filtered solution gave an almost quantitative yield of PTM radical (**1**), as ascertained also by ESR.

9,10-Diphenylanthryliumyl Hexachloroantimonate (11). This salt was prepared as in the literature,[17] but with CCl_4 instead of CH_2Cl_2 as the solvent. The analyses for C and H were correct; the ESR data coincide with those reported for the 9,10-diphenylanthrylium sulfate.[18] The yield of pure salt **11** was 79% as ascertained by weight and magnetic susceptibility measurements. Salt **11** reverts to hydrocarbon **10** (IR) when shaken with KI in CH_2Cl_2.

Perchloro-α,α-diphenylquinomethane (Perchlorofuchsone, 3). A mixture of PTM radical (**1**,[1] 9.00 g) and 20% oleum (200 mL) was stirred (35 °C, 24 h) in the dark. The resulting green solution was then poured into cracked ice and extracted with CCl_4. The resulting solution was washed with aqueous $NaHCO_3$ and with water, dried, and evaporated. The residue (8.30 g) was submitted (silica gel, CCl_4) to column chromatography, affording (**1**) PTM radical (**1**; 0.626 g, 5.4% recovery) and (2) orange crystals (8.45 g) which by recrystallization from $CHCl_3$–hexane gave fuchsone **3**,[6] 6.36 g 72.5%).

Thermolysis of Cyclohexadiene 5. Cyclohexadiene **5** (0.014 g) was heated at 100 °C (18 h) under argon in a sealed tube. The resulting solid was fuchsone **3**,[6] 0.013 g (99.2%).

Thermolysis of Cyclohexadiene 6. Cyclohexadiene **6** (0.025 g) was heated as in the preceding thermolysis (2 h), giving also fuchsone **3**,[6] 0.022 g (95.7%).

***αH*-Tetradecachloro-4-nitrotriphenylmethane (25).** A mixture of *αH*,4*H*-tetradecachlorotriphenylmethane (**24**, 0.391 g)[2] and fuming nitric acid (40 mL) was refluxed (18 h) in the dark. The resulting mass was poured onto cracked ice, and the precipitate formed was filtered, washed with water, and dried. The solid obtained was dissolved in CCl_4, passed through silica gel, and recrystallized from CCl_4–hexane to give nitro compound **25**: 0.238 g (57.4%); mp 334–336 °C dec; UV (C_6H_{12}) 222 nm, 254 (sh), 282 (sh), 293, 302 (ε 101 800, 24 300, 1080, 1640, 1810); IR (KBr) 2920, 1554, 1370, 1359, 1340, 1312, 1300, 1240, 1130, 809, 782, 760, 712, 671, 522 cm^{-1}; ^1H NMR (C_2Cl_4) τ 2.73 (s). Anal. Calcd for $C_{19}HCl_{14}NO_2$: C, 29.6; H, 0.1; Cl, 64.3; N, 1.8. Found: C, 29.4; H, 0.2; Cl, 64.3; N, 1.8.

(14) The atomic susceptibility contribution for Cl here adopted 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} emu).[13]

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αH-4-Aminotetradecachlorotriphenylmethane (23). A mixture of nitro compound **25** (0.943 g), $SnCl_2 \cdot 2H_2O$ (4.07 g), concentrated aqueous HCl (25 mL), and ethanol (400 mL) was refluxed (120 h) with stirring. The resulting mass was poured into water and then extracted with $CHCl_3$. The $CHCl_3$ solution was washed with water, dried, and evaporated, giving a residue (0.861 g) which was passed in CCl_4 through silica gel, yielding amino compound **23**; 0.845 g (93.3%); mp 326–328 °C; UV (C_6H_{12}) 222 nm 270 (sh), 304, 314 (ε 105 000, 10 600, 3300, 3100); IR (KBr) 3500, 3395, 1600, 1440, 1355, 1340, 1298, 1142, 850, 800, 704, 680, 660, 640, 520 cm^{-1}; ^1H NMR ($CDCl_3$, 60 °C) τ 3.05 (s, 1, CH), 5.20 (s, 2, NH_2). Anal. Calcd for $C_{19}H_3Cl_{14}N$: C, 30.8; H, 0.4; Cl, 66.9; N, 1.9. Found: C, 31.0; H, 0.4; Cl, 66.6; N, 1.7.

Tetradecachloro-4-hydroxytriphenylmethyl Radical (13). Aqueous (57%) HI (12 mL, containing some I_2) was added to a solution of fuchsone **3** (1.727 g) in benzene (250 mL). The mixture was stirred (24 h) in the dark. The organic layer was decanted, washed with dilute aqueous H_3PO_2, with dilute aqueous HCl, and with water, dried, and evaporated. The residue was washed with CCl_4 and dried, giving pure hydroxy radical **13**: 1.723 g (99.6%);[6] red crystals; mp 318 °C dec; UV–vis (C_6H_{12}) 220 nm, 272 (sh), 368 (sh), 384, 509, 558 (ε 80 900, 5900, 16 900, 29 000, 1160, 1350); UV–vis (Me_2SO) 574 nm, 738 (ε 2650, 3120); UV–vis (Me_2SO–CF_3CO_2H) 275 nm (sh), 375 (sh), 391, 584 (ε 8000, 18 100, 28 800, 2420); IR (KBr) 3500, 1530, 1425, 1370, 1330, 1320, 1270, 1260, 1195, 950, 860, 810, 725, 700, 650, 640, 530 cm^{-1}; ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{19}HCl_{14}O$: C, 30.8; H, 0.1; Cl, 66.8. Found: C, 30.7; H, 0.2; Cl, 66.9.

UV–vis spectrum of sodium tetradecachloro-4-oxidotriphenylmethyl radical (12): UV-vis (Me_2SO) 305 nm 335, 426, 471, 564, 741 (ε 8100, 7050, 13 100, 11 200, 3750, 8600).

Tetradecachloro-4-methoxytriphenylmethyl Radical (14). An ethereal solution of CH_2N_2 (excess) was added to crude hydroxy radical **13** (0.167 g), and the mixture was stirred (1 h) in the dark. The resulting solution was evaporated and the residue purified by column chromatography (silica gel, hexane CCl_4) to give methoxy radical **14**: 0.154 g (90%); red crystals; mp 305–308 °C dec; IR (KBr) 2940, 2860, 1530, 1452, 1386, 1340, 1323, 1287, 1263, 1007, 852, 813, 730, 707, 668, 647, 540, 534 cm^{-1}; 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, 31.6; H, 0.6; Cl, 65.8.

4-Acetoxytetradecachlorotriphenylmethyl Radical (15). A solution of hydroxy radical **13** (0.105 g) in acetic anhydride (50 mL) was heated (160 °C, 4 h) in the dark. Evaporation of the solvent gave a residue (0.108 g) which by TLC (silica gel, CCl_4–hexane) afforded acetoxy radical **15**: 0.070 g (63%); red crystals; mp 259–263 °C; IR (KBr) 2910, 1795, 1500, 1392, 1365, 1332, 1255, 1172, 1150, 1005, 950, 870, 810, 730, 705, 663, 642, 520 cm^{-1}; ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{21}H_3Cl_{14}O_2$: C, 32.2; H, 0.4; Cl, 63.3. Found: C, 32.4; H, 0.7; Cl, 63.4.

4-(Bromoacetoxy)tetradecachlorotriphenylmethyl Radical (16). A mixture of hydroxy radical **13** (0.165 g), bromoacetyl chloride (2.5 g), and triethylamine (0.1 mL) was refluxed (1 h) in the dark. The resulting red solution was evaporated to dryness. The residue was dissolved in $CHCl_3$, washed with aqueous $NaHCO_3$ and with water, dried, evaporated, and recrystallized from hexane to give bromoacetoxy radical **16**: 0.177 g (92.2%); red crystals; mp 151–153 °C; UV–vis (C_6H_{12}) 220 nm, 274 (sh), 336 (sh), 366 (sh), 381, 500, 556 (ε 81 700, 5700, 6500, 20 600, 33 000, 1300, 1150); IR (KBr) 2920, 2845, 1800, 1780, 1510, 1390, 1340, 1325, 1310, 1280, 1260, 1220, 1200, 1090, 960, 815, 730, 710, 650, 530 cm^{-1}; ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{21}H_2Cl_{14}BrO_2$: C, 29.2; H, 0.2; Cl, 57.5; Br, 9.3. Found: C, 29.2; H, 0.4; Cl, 57.4; Br, 9.2.

Tetradecachloro-4-[(ethoxyformyl)oxy]triphenylmethyl Radical (17). Ethoxyformyl chloride (0.13 mL) and triethylamine (0.02 mL) were added successively to a solution of hydroxy radical **13** (0.101 g) in $CHCl_3$ (3 mL), and the resulting solution was refluxed (4 h) in the dark. Evaporation of the solvent gave a red solid which was purified (silica gel, CCl_4) by column chromatography, yielding (ethoxyformyl)oxy radical **17**: 0.099 g (89.3%); red crystals; mp 156–158 °C; UV–vis (C_6H_{12}) 219 nm, 275 (sh), 333 (sh), 364 (sh), 379, 484 (sh), 500, 554 (ε 82 900, 16 900, 5820, 5080, 33 100, 994, 1020, 990); IR (KBr) 2980, 2920, 2850, 1795, 1780, 1505, 1460, 1440, 1400, 1390, 1365, 1340, 1330, 1320, 1300, 1250, 1230, 1165, 990, 850, 810, 730, 710, 650 cm^{-1}; ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{22}H_5Cl_{14}O_3$: C, 32.5; H, 0.6; Cl, 61.0. Found: C, 32.6; H, 0.7; Cl, 61.1.

4-Aminotetradecachlorotriphenylmethyl Radical (19). (a) Anhydrous $SnCl_2$ (4.0 g) was added to a solution of crude fuchsonimine **4** (7.25 g) in ether (1800 mL), and the mixture was stirred in the dark. The resulting solution was filtered, washed with aqueous HCl and with water, dried, and evaporated. The residue was purified by column chromatography (silica gel, hexane–CCl_4), giving amino radical **19**: 4.50 g (62%),[6] dark green needles; mp 285 °C dec; UV–vis (C_6H_{12}) 222 nm, 290 (sh), 376 (sh), 390, 553, 598 (ε 93 400, 7700, 19 200, 32 100, 2680, 5030); UV–vis (dioxane) 290 nm (sh), 394, 437 (sh), 575 (sh), 618 (ε 7750, 29 900, 5000, 3100, 6140); UV–vis (Me_2SO) 295 nm, 400, 445 (sh), 644 (ε 8880, 23 700, 8000, 6160); IR (KBr) 3500, 3395, 1600, 1540, 1440, 1375, 1360, 1342, 1332, 1325, 1295, 1270, 820, 745, 710, 650 cm^{-1}; ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{19}H_2Cl_{14}N$: C, 30.8; H, 0.3; Cl, 67.0; N, 1.9. Found: C, 30.8; H, 0.3; Cl, 67.0; N, 1.8.

(b) A mixture of αH compound **23** (0.079 g), finely powdered NaOH (0.840 g), ether (24 mL), and Me_2SO (6 mL) was shaken (48 h) in the dark. The reaction mixture was filtered through a sintered-glass filter, and I_2 (0.010 g) was added. The resulting solution was left (1 h) in the dark, washed with aqueous $NaHSO_3$ (to destroy I_2) and with water, dried, and evaporated, giving a residue (0.074 g), which by TLC (silica gel, pentane) gave starting material **23** (0.008 g, 10%) and amino radical **19** (0.019 g, 24%).

UV–vis spectrum of sodium 4-amidotetradecachlorotriphenylmethyl radical (20): UV-vis (Me_2SO) 400 nm, 520, 852 (ε 11 900, 15 800, 6020).

4-[(Chloroacetyl)amino]tetradecachlorotriphenylmethyl Radical (20). A solution of amino radical **19** (0.075 g) in chloroacetyl chloride (5 mL) was left (48 h) in the dark. On elimination of the solvent a residue was obtained, which by TLC (silica gel, CCl_4) afforded acylamino radical **20**: 0.047 g (56.8%); red needles; mp 192–194 °C dec; UV–vis (C_6H_{12}) 225 nm, 290, 365 (sh), 385, 496, 561 (ε 99 100, 7330, 21 700, 43 200, 1350, 1350); IR (KBr) 3380, 3170, 3000, 2950, 1675, 1530, 1490, 1402, 1325, 1320, 1260, 815, 760, 735, 710, 650 cm^{-1}; ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{21}H_3Cl_{15}NO$: C, 30.9; H, 0.4; Cl, 65.1; N, 1.7. Found: C, 31.1; H, 0.3; Cl, 65.1; N, 1.6.

4-[(Bromoacetyl)amino]tetradecachlorotriphenylmethyl Radical (21). A solution of amino radical **19** (0.500 g) in bromoacetyl chloride (5 mL) was left (3 days) in the dark. By use of the same procedure as in the preceding reaction there was obtained acylamino radical **21**: 0.439 g (75.5%); red needles; mp 249–252 °C dec; UV–vis (C_6H_{12}) 223 nm, 290 (sh), 364 (sh), 382, 512, 563 (ε 79 000, 6500, 19 000, 36 200, 1280, 1310); IR (KBr) 3160, 2980, 1660, 1530, 1480, 1430, 1400, 1330, 1255, 810, 730, 705, 665, 645 cm^{-1}; ESR data, Table I; magnetic susceptibility data, Table II. Anal. Calcd for $C_{21}H_3Cl_{14}NOBr$: C, 29.3; H, 0.4; Cl, 57.6; N, 1.6; Br, 9.3. Found: C, 29.4; H, 0.5; Cl, 57.7; N, 1.6; Br, 9.5.

Reduction of Methoxy Radical 14. A mixture of methoxy radical **14** (0.150 g), powdered NaOH (8 g), ether (50 mL), and Me_2SO (10 mL) was stirred (48 h) in the dark. The resulting mixture was filtered, and the solution was treated with diluted aqueous HCl. The ethereal layer was washed with water, dried, and evaporated to give a residue (0.147 g), which was purified by TLC (silica, CCl_4–hexane) and recrystallized form CH_2Cl_2 to give **αH-tetradecachloro-4-methoxytriphenylmethane** (**18**): 0.061 g (41.6%); mp 335–338 °C; IR (KBr) 2920, 2880, 1530, 1448, 1390, 1370, 1330, 1295, 1035, 983, 843, 802, 700, 670, 662, 640, 535, 525, 515 cm^{-1}. Anal. Calcd for $C_{20}H_4Cl_{14}O$: C, 31.7; H, 0.5; Cl, 65.6. Found: C, 32.0; H, 0.5; Cl, 65.5.

Attempted Reduction of Acetoxy Radical 15. This reaction was attempted as in the reduction of methoxy radical **14** [acetoxy radical **15** (0.100 g)]. Hydroxy radical **13** was formed (IR). When its purification by chromatography on silica gel was attempted, a green absorbate was formed, which in the process of elution with ether became oxidized to fuchsone **3** (0.078 g, 82%). No αH-tetradecachloro-4-hydroxytriphenylmethane was detected.

Reduction of Amino Radical 19. (a) A solution of ascorbic acid (0.055 g) in water (5 mL) was added to another of amino

radical 19 (0.233 g) in THF (90 mL), and the resulting mixture was left (4 days) under argon and in the dark. Evaporation of the solvent gave a solid, which by TLC (silica gel, pentane) afforded starting radical 19 (0.104 g, 45%) and the corresponding αH compound 23 (0.092 g, 39%).

(b) This reaction was also attempted as in the reduction of methoxy radical 14. Starting material was recovered (93%).

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Thermolysis of Highly Congested *tert*-Butyldialkylcarbinols with Bridgehead Substituents: Molecular Mechanics Treatment of Radical-Forming Processes

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The thermolysis rate constants of eight tertiary alcohols, $R^1R^2R^3COH$, bearing a *tert*-butyl group (R^3) with various combinations of *tert*-butyl, *tert*-amyl, 1-adamantyl, 1-bicyclo[2.2.2]octyl, and 1-norbornyl substituents at the tertiary carbon have been measured in dodecane. The effects of these groups on the rate of *tert*-butyl cleavage are roughly additive and in quantitative agreement with their known steric requirements, except for *tert*-amyl which appears to be smaller than E_s' would suggest. Activation energies can be interpreted in terms of strain energy changes, calculated by molecular mechanics; several different models are used to describe the reaction and, where possible, three different force fields. The most satisfactory description of the reaction is based upon Allinger's MM2 force field, with the assumption that the radical intermediate, $R^1R^2C{\cdot}OH$, can be represented by the corresponding dialkylcarbinol. Product analysis shows that the *tert*-butyl radical is formed in preference to any other, except *tert*-amyl, but small amounts of products arising from C–Ad fission are detected in certain cases. This result, in accordance with previous molecular mechanics calculations on thermolysis rates, indicates that the radical strain energies in bridgehead systems must be slightly greater than those of the corresponding alkanes but substantially less than those of the related carbocations.

Before ESR spectroscopy was able to provide detailed structural information about alkyl radicals,[1] attempts were made to investigate the geometric requirements of the radical center by measuring the rate of formation of bridgehead radicals by the thermolysis of peresters[2,3] and azoalkanes[3] or by determining the selectivity of radicals in certain reactions, such as decarbonylation,[4] or by other means.[5,6] While there was fairly good agreement on the order of radical stability, i.e., 1-adamantyl > 1-bicyclo-[2.2.2]octyl > 1-norbornyl, there was some doubt about the position of the *tert*-butyl radical, B·, on this scale. According to different criteria, it was reckoned to be less stable, as stable, or much more stable than 1-Ad·.[7,8]

In recent years there have been important developments in this area of free-radical chemistry. The idea that radical formation rates express their stability has given way to the understanding that rates refer only to transition states.[9] There has also been considerable reinvestigation of the azoalkane and perester thermolysis reactions upon which stabilities were based. Perester decomposition for a long time known has to be subject to polar effects[10] and is believed to have an early transition state, rather remote from the intermediate radical.[11] Recent studies have, moreover, shown that the mechanism of decomposition is not necessarily the same for all structures, the extent of R–C and O–O bond breaking varying considerably.[12]

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