

Two Functionalized Free Radicals of the Tris(2,4,6-trichlorophenyl)methyl Radical Series. Synthesis, Stability and EPR Analysis.

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Abstract: *Tris(2,4,6-trichlorophenyl)carbenium hexachloro-antimonate (2), (2,6-dichloro-4-hydroxyphenyl)bis(2,4,6-trichlorophenyl)methyl radical (4) and its methyl ether derivative 5 have been synthesized and isolated as crystalline solids. In contrast to 5, radical 4 is not very stable in air, and the disappearance of 4 by aerial oxidation has been monitored by UV-vis spectroscopy. The EPR spectra of 4 and 5 are reported and commented upon.*

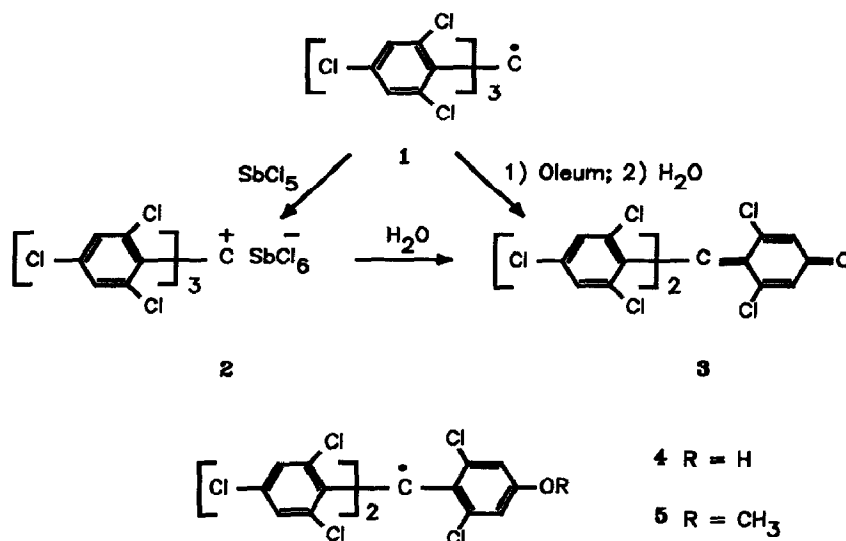
The most stable carbon free radicals described to date belong to the so-called perchlorotriphenylmethyl (PTM) series.^{1,2} Their stability is mainly ascribed to steric shielding of the trivalent carbon by the six *ortho*-chlorines and the three benzene rings attached to it. Replacement of *para*-chlorines in PTM by chemically active substituents affords radicals which usually react at these substituents without impairment of the radical character.¹ Some of these functionalized PTM Radicals have been used successfully as spin-labels and for study of the "Reverse Effect".¹

More recently, tris(2,4,6-trichlorophenyl)methyl radical (TTM) (1) has been synthesized and isolated in solid state.^{2a} Its stability and physical properties have been reported to be similar to those of PTM, indicating that the absence of the *meta*-chlorines does not exert an important effect on the stability of the molecule. In view of this result, it was decided to eliminate the steric shielding of the above-mentioned active substituents in order to increase their reactivity. In this context, now we report the synthesis of (2,6-dichloro-4-hydroxyphenyl)bis(2,4,6-trichlorophenyl)methyl radical (4) and its methyl ether derivative 5. The aim of this work was principally to seek information on the relevant synthetic aspects.

Our synthetic strategy to get radicals 4 and 5 was inspired by the activity of PTM in electron transfer reactions with inorganic oxidants.¹ Thus treatment of radical 1 with SbCl₅ in CCl₄ gives tris(2,4,6-trichlorophenyl)carbenium hexachloroantimonate (2) as a dark blue microcrystalline solid.³ Although salt 2 is remarkable stable in solid form, its hydrolysis takes place readily in humid CH₂Cl₂ to give 3,5-dichloro-4-[bis(2,4,6-trichlorophenyl)methylen]cyclohexa-2,5-dien-1-one (3).³ Fuchson 3 is also obtained directly by oxidation of radical 1 with oleum, followed by treatment with water. Salt 2 reverts to radical 1 when mixed

with solid KBr, but not with KCl.

By treatment of fuchstone **3** with aqueous HI/I₂ in benzene at room temperature, (2,6-dichloro-4-hydroxyphenyl)bis(2,4,6-trichlorophenyl)methyl radical (**4**) is obtained.³ Solid hydroxy radical **4** oxidizes slowly to fuchstone **3** in air. When cyclohexane solutions of radical **4** (~10⁻³ M) in air are monitored by electronic spectroscopy, characteristic radical bands at 372, 501, and 541 nm decrease while that corresponding to **3** at 397 nm increases. After 2 h, only ~35% of radical **4** was detected in the solution. Hydroxy radical **4** can be methylated (CH₂N₂ in diethyl ether) to give an excellent yield of (2,6-dichloro-4-methoxyphenyl)bis(2,4,6-trichlorophenyl)methyl radical (**5**)³ which is stable in air either in solution (electronic spectroscopy) or in solid form. Radicals **4** and **5** behave qualitatively in the same way in air as their perchloroaromatic analogues.¹



As the EPR spectrum of **1** in solution,^{2a} the spectra of radicals **4** and **5** consist of an overlapped septet of lines corresponding to the coupling with six equivalent protons (Figure 1). Spectral data of **1**, **4** and **5**, obtained by computer simulation, are shown in Table 1. These data suggest that: i) the geometries of **1**, **4** and **5** are similar, being governed by the steric effects of the six *ortho*-chlorines of the molecule as usual; and ii) the replacement of one *para*-chlorine of **1** by one hydroxy or methoxy group does not modify essentially the spin density distribution on the three rings.

Axial-type spectra of radicals **4** and **5** were obtained from microcrystalline samples of them, being $g_{\parallel} = 2.0052$ and $g_{\perp} = 2.0032$ for **4**, and $g_{\parallel} = 2.0054$ and $g_{\perp} = 2.0034$ for **5**.

It is emphasized that it has been obtained for first time TTM-type radicals containing functional groups not shielded by neighbouring substituents.



Figure 1. a) EPR spectrum of a solution of radical 4 in CCl_4 at room temperature.

Table 1. EPR parameters for radicals 1, 4, and 5

Radical	g	ΔH_{pp} , G	hfc constants, G		
			^1H	$\alpha\text{-}^{13}\text{C}$	arom- ^{13}C
1 ^a	2.0038	1.21	1.18	31.49	12.99; 9.99
4 ^b	2.0034	1.21	1.18	31.28	13.18; 10.58
5 ^a	2.0037	1.21	1.14	29.00	13.45; 10.80

All spectra were obtained at room temperature. a) In $\text{Cl}_2\text{C}=\text{CCl}_2$, b) In CCl_4 .

The authors are presently engaged in the study of this interesting and promising class of radicals, particularly (4-amino-2,6-dichlorophenyl)bis-(2,4,6-trichlorophenyl)methyl.

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3. The handling of the radicals **1**, **4** and **5** in solution was performed in the dark.

2: 97%; mp 180-2 °C (dec); IR (KCl) ν 3080 (w), 3060 (w), 1625 (w), 1550 (s), 1485 (m), 1395 (s), 1315 (s), 1185 (m), 1120 (s), 920 (w), 890 (w), 870 (m), 860 (m), 825 (m), 820 (m), 800 (m), 710 (m), 340 (s) cm^{-1} ; UV-vis (H_2SO_4) λ_{max} (e) 217 (76 900), 230 (46 900 sh), 261 (11 500 sh), 310 (8440 sh), 338 (9900), 564 (16 500 sh), 640 (26 900). Anal.: Calcd. for $\text{C}_{19}\text{H}_6\text{Cl}_4\text{Sb}$: C, 25.7; H, 0.7; Cl, 60.0. Found: C, 25.7; H, 0.7; Cl, 60.0.

3: 83%; mp 212-4 °C; IR (KBr) ν 3070 (w), 1620 (s), 1560 (s), 1535 (s), 1480 (m), 1430 (w), 1415 (w), 1375 (s), 1355 (s), 1260 (m), 1245 (w), 1190 (m), 1135 (s), 1125 (m), 1085 (w), 1025 (w), 920 (w), 910 (w), 900 (m), 885 (s), 855 (s), 815 (s), 805 (s), 790 (s), 765 (m), 660 (w) cm^{-1} ; ^1H NMR (CDCl_3) δ 7.36 (s, 4H), 6.66 (s, 2H); UV-vis (cyclohexane) λ_{max} (e) 210 (53 200), 229 (29 800 sh), 272 (11 200 sh), 279 (11 600), 395 (21 100). Anal.: Calcd. for $\text{C}_{19}\text{H}_6\text{Cl}_8\text{O}$: C, 42.7; H, 1.1; Cl, 53.1. Found: C, 42.8; H, 1.1; Cl, 53.1.

4: 90%; mp 212-4 °C (dec); IR (KBr) ν 3530 (m), 3410 (m), 3080 (w), 1590 (s), 1555 (s), 1525 (s), 1410 (m), 1370 (s), 1290 (m), 1260 (w), 1240 (w), 1180 (s), 1135 (m), 1080 (w), 1060 (w), 955 (m), 920 (w), 905 (w), 855 (s), 825 (s), 805 (s), 790 (s), 720 (w), 680 (w), 600 (w) cm^{-1} ; UV-vis (cyclohexane) λ_{max} (e) 213 (66 000), 228 (35 500 sh), 257 (6800 sh), 276 (4500 sh), 359 (19 900 sh), 372 (28 000), 403 (5590 sh), 501 (1140), 541 (1350). Anal.: Calcd. for $\text{C}_{19}\text{H}_7\text{Cl}_8\text{O}$: C, 42.6; H, 1.3; Cl, 53.1. Found: C, 42.7; H, 1.3; Cl, 52.9.

5: 84%; mp 218-20 °C; IR (KBr) ν 3080 (w), 2970 (w), 2940 (w), 2830 (w), 1580 (s), 1550 (s), 1525 (s), 1460 (s), 1420 (s), 1395 (s), 1380 (s), 1370 (s), 1295 (s), 1265 (s), 1235 (s), 1180 (s), 1135 (s), 1075 (s), 1060 (s), 1035 (s), 935 (w), 920 (m), 885 (m), 855 (s), 830 (m), 820 (s), 805 (s), 790 (s), 720 (m), 705 (w), 630 (w), 605 (w) cm^{-1} ; UV-vis (cyclohexane) λ_{max} (e) 213 (73 300), 229 (37 800 sh), 264 (6530 sh), 353 (17 200 sh), 372 (33 000), 501 (1310), 538 (1570). Anal.: Calcd. for $\text{C}_{20}\text{H}_6\text{Cl}_8\text{O}$: C, 43.7; H, 1.6; Cl, 51.7. Found: C, 43.9; H, 1.6; Cl, 51.5.

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