the mixture was cooled to room temperature, it was poured carefully into a large amount of ice–water and was extracted with benzene (100 mL × 2). The extract was washed with 10% aqueous HCl, water, and brine, dried ($MgSO_4$), and evaporated in vacuo. The residue was chromatographed (hexane) to give a colorless solid that was recrystallized from MeOH to afford 1.74 g (96%) of **3a** as colorless prisms: mp 232–235 °C; IR 3050, 2950, 1610, 1590 cm^{-1}; ^1H NMR δ 1.60 (18 H, s), 2.91 (6 H, s), 8.02 (2 H, s), 8.15 (2 H, d, J = 1.8 Hz), 8.38 (2 H, d, J = 1.8 Hz); MS m/z 342 (M^+). Anal. Calcd for $C_{26}H_{30}$: C, 91.17; H, 8.85. Found: C, 90.91; H, 9.07.

Compounds **5** and **7** were similarly prepared.

2,7-Di-*tert*-butyl-4,5,9-trimethylpyrene (5). This compound was obtained as colorless prisms (MeOH) from **4** (700 mg), $LiAlH_4$ (400 mg), and $AlCl_3$ (1.3 g) in 80% (538 mg) yield: mp 220–224 °C; IR 2980, 2880, 1600 cm^{-1}; ^1H NMR δ 1.58 (9 H, s), 1.61 (9 H, s), 2.90 (9 H, s), 7.87 (1 H, s), 8.08 (1 H, d, J = 1.5 Hz), 8.27 (1 H, d, J = 1.5 Hz), 8.33 (1 H, d, J = 1.5 Hz), 8.40 (1 H, d, J = 1.5 Hz); MS m/z 356 (M^+). Anal. Calcd for $C_{27}H_{32}$: C, 90.95; H, 9.05. Found: C, 91.12 H, 9.04.

This compound was also prepared from the mixture of **2a–c** according to the same procedure described previously (see Scheme II). In each step, the products were purified by column chromatography and obtained methyl or formylpyrenes were used into next step. The yields of each step were 71% (1.3 g), from the mixture of **2a–c** to dimethyl mixture, 83% (1.17 g), formylation of dimethyl mixture, and 61% (687 mg), reduction of formyldimethylpyrenes.

2,7-Di-*tert*-butyl-4,5,9,10-tetramethylpyrene (7). This compound was obtained as colorless prisms (EtOH) from **6** (860 mg), $LiAlH_4$ (400 mg), and $AlCl_3$ (1.4 g) in 90% (743 mg) yield: mp 251–257 °C; IR 3020, 2980, 2880, 1600 cm^{-1}; ^1H NMR δ 1.61 (18 H, s), 2.91 (12 H, s), 8.36 (4 H, s); MS m/z 370 (M^+). Anal. Calcd for $C_{28}H_{34}$: C, 90.75; H, 9.25. Found: C, 90.78; H, 9.22.

2,7-Di-*tert*-butyl-4-methyl-5-(hydroxymethyl)pyrene (3b). To a suspension of 500 mg (13.2 mmol) of $LiAlH_4$ in 20 mL of absolute ether was added 790 mg (2.2 mmol) of **2a** in 30 mL of absolute ether at room temperature during 30 min. After the addition was completed, the mixture was heated under reflux for 3 h and was cooled to room temperature. Then, the mixture was poured into a large amount of ice–water and was extracted with benzene. The extract was washed with 10% aqueous HCl and brine, dried ($MgSO_4$), and evaporated in vacuo. The residue was recrystallized from hexane to afford 718 mg (90%) of **3b** as colorless prisms; mp 206–208 °C; IR 3340, 3030, 2950, 1600 cm^{-1}; ^1H NMR δ 1.60 (18 H, s), 3.02 (3 H, s), 5.48 (2 H, s), 8.02 (2 H, s), 8.17 (1 H, d, J = 1.4 Hz), 8.22 (1 H, d, J = 2.2 Hz), 8.44 (1 H, d, J = 2.2 Hz), 8.57 (1 H, d, J = 1.4 Hz); MS m/z 358 (M^+). Anal. Calcd for $C_{28}H_{30}O$: C, 87.10; H, 8.44. Found: C, 87.04; H, 8.67.

2,7-Di-*tert*-butyl-4-methyl-5-(chloromethyl)pyrene (3c). To a solution of 2.88 g (8.0 mmol) of **3b** in 80 mL of benzene were added 5.0 mL of $SOCl_2$ and then 0.5 mL of pyridine. After the mixture was stirred for 1 h at room temperature and refluxed for 1 h, it was poured into ice–water and extracted with benzene. The extract was washed with 10% aqueous $NaHCO_3$ (100 mL × 3) and water, dried ($MgSO_4$), and evaporated in vacuo. The residue was recrystallized from hexane to afford 2.68 g (87 %) of **3c**: brown prisms; mp 165–166 °C; IR 3030, 2960, 2950, 1600 cm^{-1}; ^1H NMR δ 1.59 (9 H, s), 1.61 (9 H, s), 2.99 (3 H, s), 5.39 (2 H, s), 8.01 (2 H, s), 8.17 (1 H, d, J = 1.8 Hz), 8.21 (1 H, d, J = 1.8 Hz), 8.43 (1 H, d, J = 1.4 Hz), 8.46 (1 H, d, J = 1.4 Hz); MS m/z 376 (M^+), 378 (M + 2). Anal. Calcd for $C_{26}H_{29}Cl$: C, 82.84; H, 7.75. Found: C, 82.54; H, 7.99.

2,7-Di-*tert*-butyl-4,5-dimethylpyrene (3a) from 3c. To a suspension of 1.0 g (26 mmol) of $LiAlH_4$ in 30 mL of absolute ether was added dropwise 2.68 g (7.8 mmol) of **3c** at room temperature with stirring. After the addition was completed, the mixture was refluxed for 3 h and cooled. It was poured into a large amount of ice–water and was extracted with benzene. The extract was washed with water and brine and then evaporated. The residue in 10 mL of benzene was purified by column chromatography (hexane) to give 2.38 g (97%) of **3a**.

General Procedure for the Trans-*tert*-butylation of 2,7-Di-*tert*-butylmethyl-Substituted Pyrenes. A mixture of 2,7-di-*tert*-butylmethyl-substituted pyrenes (200 mg) and Nafion-H (200 mg) in toluene (5 mL) was refluxed for 12 h. The Nafion-H was then filtered from the cooled mixture, and the filtrate was concentrated in vacuo. The residue was chromatographed (hexane) to afford a colorless solid that was recrystallized from EtOH in all cases.

4,5-Dimethylpyrene (8a): (84%, 113 mg); colorless prisms; mp 206–208 °C (lit.[13] 210.5–211.5 °C).

4,5,9-Trimethylpyrene (8b): (84%, 115 mg); colorless prisms; mp 165–167 °C (lit.[14] 173 °C).

4,5,9,10-Tetramethylpyrene (8c): (80%, 112 mg); colorless prisms; mp 250–254 °C; IR 2950, 2900, 1590, 1450, 1360, 1340, 1250, 1080, 880, 790, 700 cm^{-1}; ^1H NMR δ 2.90 (12 H, s), 7.90 (2 H, t, J = 7.7 Hz), 8.06 (4 H, d, J = 7.7 Hz); MS m/z 258 (M^+). Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.82; H, 6.67.

Nucleophilic Substitution of Chlorine in Triphenylmethyl Radicals. "Reverse Effect" and a Related Single-Electron Transfer

Manuel Ballester* and Isabel Pascual

Institut de Ciència de Materials (CSIC), Martí i Franquès s/n, 08028 Barcelona, Spain

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The "inert carbon free radicals" (IFRs) are trivalent carbon species that not only are completely disassociated, but their half-life times in solution, in contact with air, are on the order of 100 years.[1] They are also provided with an astonishingly high thermal stability (up and beyond 300 °C in air) and chemical inertness vs hydrogen donors, NO, NO_2, Cl_2, Br_2, concd. H_2SO_4, etc. Perchlorotriphenylmethyl radical (PTM•) is the paradigm of the IFRs (Scheme I).[2]

Red 4-(dimethylcarbamoyl)tetradecachlorotriphenylmethyl radical (Me_2NCO-PTM•) was synthesized by the reaction of acid chloride (ClCO-PTM•) in THF with dimethylamine, in the study of SETs between chlorinated triphenylmethyl radicals and triphenylmethyl anions (Scheme III).[3] A small proportion of a *green* radical was obtained suggesting that a simultaneous nucleophilic substitution of chlorine by the dimethylamino group had also taken place. In fact, the vast majority of highly chlorinated perchlorotriphenylmethyl radicals, except green 4-aminotetradecachlorotriphenylmethyl radical (NH_2-PTM•),[4] are red. Accordingly, it is well-known that, on account of the cumulative inductive effect of their numerous chlorines, perchlorinated aromatic substrates are susceptible to substitution by nucleophiles (S_NAr).[5-7,8b] In this connection it is mentioned that nucleophilic substitutions are believed to proceed via either polar or SET ($S_{RN}1$) pathways.[9]

Consequently, the reaction of radical PTM• with a saturated solution of dimethylamine in THF, at room temperature, has been investigated. The product consists in an inseparable mixture of PTM• and αH-tetradeca-

(1) Ballester, M. *Acc. Chem. Res.* **1985**, 380 and references thereof.
(2) Ballester, M.; Riera, J.; Castañer, J.; Badía, C.; Monsó, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215.
(3) Ballester, M.; Pascual, I.; Torres, J. *J. Org. Chem.* **1990**, *55*, 3035.
(4) Ballester, M.; Riera, J.; Castañer, J.; Rodríguez, A.; Rovira, C.; Veciana, J. *J. Org. Chem.* **1982**, *47*, 4498.
(5) Ballester, M.; Olivella, S. In *Polychloroaromatic Compounds*; Suschitzy, H., Ed.; Plenum Press: London, 1974, pp 26–30.
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(9) (a) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (b) Amatore, C.; Pinson, J.; Savéant, J.-M.; Thiébault, A. *J. Am. Chem. Soc.* **1981**, *103*, 6930. (c) *Ibid.* **1982**, *104*, 817. (d) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212.

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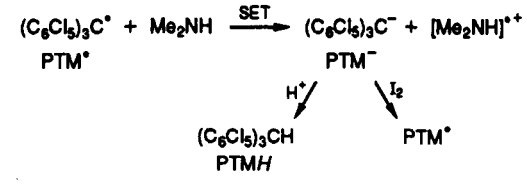
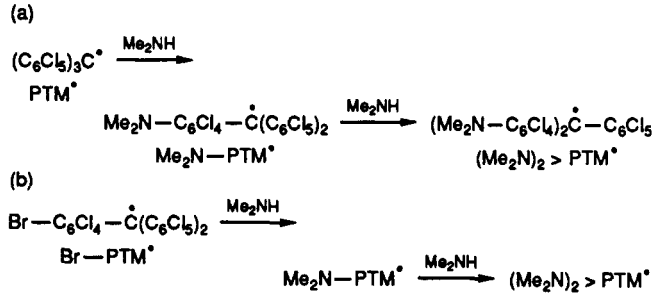
Scheme I



Scheme II



chlorotriphenylmethane (PTM*H*) (60 and 40%, respectively; IR and UV–vis spectra), the main products being two green species, as shown by flash chromatography.

That formation of PTM*H* shows that some *PTM• undergoes a single-electron transfer (SET),*[3,9d] *giving carbanion PTM⁻, where Me_2NH acts as a donor* (Scheme I), as it occurs in the one-electron reduction of the PTM radicals with HO^-.[10] That carbanion is protonated to PTM*H* in the subsequent treatment with aqueous HCl (to destroy the great excess of Me_2NH). It is pointed out that the PTM carbanions are stable in basic, even in neutral aqueous homogensous media,[3,8a] due to steric shielding of their carbanion trivalent carbon vs relatively bulky proton-donor species.

Consequently, the reaction of radical PTM• with Me_2NH has been repeated, but after its completion, iodine has been added to oxidize the PTM^- formed back to PTM• (Scheme I),[8a] and accordingly no PTM*H* was detected. It is pointed out that although protonation of carbanion PTM^- takes place with H_3O^+ in aqueous media, it does not occur with the alkylammonium ions present in the Me_2NH saturated THF. Otherwise, in the following treatment with I_2, PTM*H* would remain inalterated. It is well-known that the PTM*H*s do not oxidize with I_2. In fact, they even withstand vigorous oxidizing agents (HNO_3/60% oleum, chromic acid, etc.).

The two above-mentioned green species have been isolated from the resulting reaction mixture, along with radical PTM• (11% recovery), being 4-(dimethylamino)-tetradecachlorotriphenylmethyl radical (Me_2N-PTM•; 67%) and 4,4′-bis(dimethylamino)tridecachlorotriphenylmethyl radical ($(Me_2N)_2$>PTM•; 15%) (Scheme IIa). These two dimethylamino radicals have been characterized by elemental analyses, and IR, UV–vis and ESR spectra.[8] In order to ascertain the position of the dimethylamino substituent, the reaction of dimethylamine with 4-bromotetradecachlorotriphenylmethyl (Br-PTM•), a radical of known structure,[3] has been performed under the same conditions, a mixture of those two green radicals being obtained (Scheme IIb), thus showing that it takes place in para. Since such a substitution takes place because of the already-mentioned cumulative electron-withdrawing effect of the chlorines, the introduction of strong electron-releasing Me_2N group causes complete

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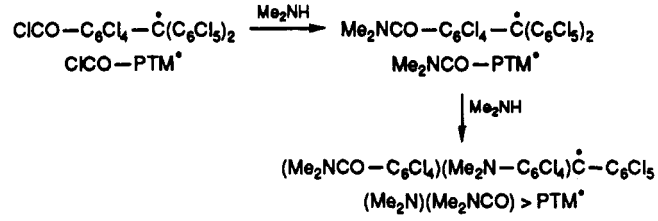
Scheme III



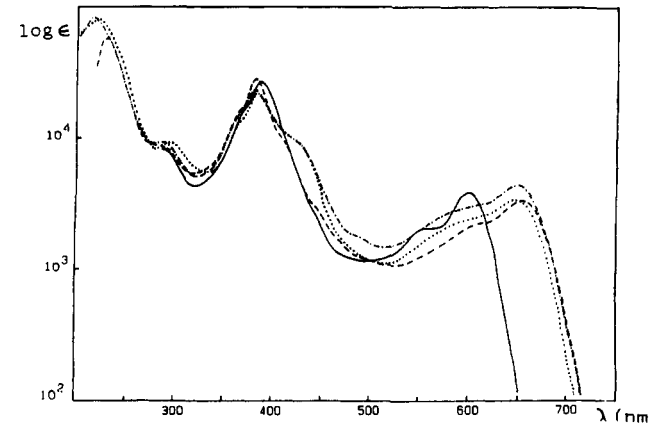


Figure 1. UV–vis of radicals: NH_2-PTM• (—); Me_2N-PTM• (- - -); $(Me_2N)_2$>PTM• (· · ·); $(Me_2N)(Me_2NCO)$>PTM• (···).

deactivation of the benzene ring which is attached to, and consequently the second Me_2N group goes to the para position of a second benzene ring. In this connection it is mentioned that substitution of a chlorine in an ortho position is unknown in the perchloro alkaromatic field, this being attributed to steric shielding by the two vicinal substituents; in the present case, one bulky chlorine and a huge $C(C_6Cl_5)_2$ group.

It is most significant that, under the same conditions PTM*H*, the PTM• nonradical counterpart, *does not react* at all (over 95% recovery), showing that *the radical character enhances dramatically the rate of aromatic nucleophilic substitution by Me_2N.* Such effect has been found in other reactions with substrates provided with the free-radical character, namely substitution of aromatic iodine by Cl or Br with Cl_2 or Br_2, respectively, and aromatic bromine by Cl with Cl_2;[11] aromatic side-chain bromination with Br_2 and AIBN or benzoyl peroxide;[12,13] substitution of benzylic bromine by a variety of nucleophilic reagents;[13,14] thermolysis of benzylic carbon–halogen bond;[12,13] reductive dimerization of benzylic halides.[13,14] It is noted that this is the first known case of "reverse (kinetic) effect"[15] *in aromatic nucleophilic substitution.*

In view of the preceding results, the reaction between ClCO-PTM• and Me_2NH[3] has been repeated but in Me_2HN-saturated THF, at room temperature (52 h). This has allowed to characterize (analyses, IR, UV–vis, and ESR) its deep-green byproduct as 4-(dimethylamino)-4′-(dimethylcarbamoyl)tridecachlorotriphenylmethyl radical ($(Me_2N)(Me_2NCO)$>PTM•) (80% yield). Therefore, the reaction occurs as in Scheme III.

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(15) The effect of the radical character on the reactivity of a substituent, as opposed to the conventional effect of the latter on the reactivity of the former.[11-14] Its mechanism had already been discussed.[1,8d]

Table I. ESR Data

radical	solvent	g value	linewidth (G)	hcc[a] (G) α-^{13}C	aromatics-^{13}C	
PTM•[b]	C_2Cl_4	2.0026	1.43	29.3	12.7[c]	10.7[c]
NH_2-PTM•[d]	C_2Cl_4	2.0027	0.93	27.9	11.1[c]	9.8[c]
	HMPT	2.0027	1.1	-	-	-
Me_2N-PTM•	C_2Cl_4	2.0030	1.3	29.8	11.0	
	HMPT	2.0034	2.6	29.5	11.4	
$(Me_2N)_2$>PTM•	C_2Cl_4	2.0032	1.7	29.8	11.2	
	HMPT	2.0034	2.5	29.0	11.5	
(Me_2N)-(Me_2NCO)>PTM•	C_2Cl_4	2.0031	1.7	30.0	11.4	
	HMPT	2.0036	2.3	30.0	11.4	

[a] hcc = hyperfine coupling constants. [b] Reference 2. [c] By computer simulation (bridgehead and ortho, respectively). [d] Reference 4.

Ultraviolet-Visible Spectra. The spectra of red PTM radicals includes bands C and D, found about 385 and 560 nm, respectively,[8e] due to the radical character. In terms of a rough frontier-orbital approach, the two "radical bands" have been attributed to one-electron transitions HOMO → SOMO and SOMO → LUMO, which correspond to the two first excited configurations.[8e]

In green radicals NH_2-PTM•, Me_2N-PTM•, $(Me_2N)_2$>-PTM•, and (Me_2N)(Me_2NCO)>PTM• the positions of band C are almost coincident with that of PTM• (383–390 nm), while band D is shifted to 598, 655, 648, and 645, respectively (Figure 1), the corresponding bathochromic shifts being 38, 95, 88, and 85 nm with respect to PTM•. Those shifts are due to conjugation involving the nitrogen nonbonding electron pair. As expected, the effect of the Me_2N is greater than that of the NH_2 group. Since, in general, π-n conjugation raises the π-orbital energy levels,[16] the lesser the latter the greater the effect (bathochromic shifting), it is reasonable to assume that band D corresponds to HOMO → SOMO transition. This also explains the insensitivity of band C to substituents.

ESR Spectra. In radical NH_2-PTM•, the spin couplings should result in a 1:1:1 triplet (^{14}N) of (1:2:1) proton triplets. Nevertheless, the coupling constant values are low and consequently all lines merge in to a single broad line. In C_2Cl_4, they merely contribute to linewidth (0.93 G; PTM• 1.4; Table I).[8f]

The spectra of the amino radicals here described consist also in a single line. The linewidth of Me_2N-PTM• is considerably higher (1.3 G, Table I) than that of NH_2-PTM•. This is attributed to hindered rotation about the N–C(aromatic) bond caused by steric repulsions among the two methyl groups and the two ortho (to Me_2N) chlorines. Such repulsions lock the Me_2N substituent in a conformation where both methyls are on the same side of the mean plane of the benzene ring, which represents a maximum overlap between the nitrogen p-orbital and the triphenylmethyl π-orbitals, i.e., maximum coupling with the ^{14}N *spin* nucleus. This is even more apparent in radical $(Me_2N)_2$>PTM• where the ^{14}N cause an unresolved (1:2:3:2:1; two equivalent ^{14}C) quintuplet and, consequently, an even broader line is observed (1.7 G; Table I). That conjugation may be depicted as follows:

$$Me_2\dot{N}–C_6Cl_4–\dot{C}(C_6Cl_5)_2 \rightleftharpoons Me_2\dot{N}^{+}–C_6Cl_4–\bar{C}(C_6Cl_5)_2$$

Significant line broadening occurs in the ESR spectrum of all the amino radicals in HMPT. This solvent causes partial resolution of the NH_2-PTM• ESR line.[4] However, no appreciable effect is observed in the dimethylamino radicals here described (Table I). This might be attributed to the already-mentioned conformational locking of the NH_2 group, in this case by polar association with the HMPT molecules.

Experimental Section

Equipment. The IR, UV–vis, and ESR spectra have been recorded with Perkin-Elmer Model 682, Perkin-Elmer Model Lambda Array 3840, and Varian Model E109 spectrometers, respectively. Since the IR spectra of perchloro organic compounds differ markedly from their nonchlorinated counterparts, those of the species dealt with here are included in this section.

Precursors. The synthesis of the following compounds have been effected as previously described: α*H*-pentadecachlorotriphenylmethane (PTM*H*),[2] perchlorotriphenylmethyl radical (PTM•),[2] 4-(chlorocarbonyl)tetradecachlorotriphenylmethyl radical (ClCO-PTM•).[17]

Reaction of Perchlorotriphenylmethyl Radical (PTM•) with Me_2NH. (a) Preliminary Experiment. A solution of radical PTM• (0.072 g) in the THF (10 mL) was saturated with Me_2NH at room temperature and left undisturbed for 10 days. The resulting mass was poured into diluted aqueous HCl, it was shaken with $CHCl_3$, and the organic layer was washed with water, dried with Na_2SO_4, and evaporated to dryness. The resulting solid residue (0.070 g) was dissolved in a small amount of CCl_4, and flash chromatographed through silica gel using hexane as the eluent. The first fraction (0.017 g) was, according to IR, a mixture of radical PTM• (60%) and PTM*H* (40%) as ascertained by UV–vis measurements. **(b) Quenching with I_2.** The reaction was performed as in (a). A solution of radical PTM• (0.26 g) in THF (40 mL) was saturated with Me_2NH at room temperature and left undisturbed for 14 days. Next I_2 (0.06 g) was added, and the mixture was let stand for 45 min more. The resulting mass was poured into an aqueous solution of $NaHSO_3$, $CHCl_3$ was added, and the organic layer was washed with diluted aqueous HCl and with water, dried with Na_2SO_4, and evaporated to dryness. The solid obtained (0.27 g) was flash chromatographed through silica gel using hexane/CCl_4 (1:1) as the eluent, giving the following. (1) Radical PTM• (0.03; 11% recovery). (2) 4-(Dimethylamino)tetrachlorotriphenylmethyl radical (Me_2N-PTM•; 0.18 g, 67% yield), deep green solid, dec 310 °C; UV–vis (C_6H_{12}) (Figure 1) 220, 285 (sh), 365 (sh), 383, 410 (sh), 605 (sh), 655 nm (ε 85 500, 7000, 15 500, 28 000, 9200, 2150, 3400); IR (KBr) 2990, 2960, 2930, 2855, 2795, 1522, 1457, 1440, 1400, 1347, 1330, 1315, 1255, 1240, 1090, 975, 880, 810, 725, 695, 675, 660, 640, 530 cm^{-1}; ESR data, Table I. Anal. Calcd for $C_{21}H_6Cl_{14}N$: C, 32.8; H, 0.8; Cl, 64.5; N, 1.8. Found: C, 33.0; H, 0.9; Cl, 64.1; N, 1.8. (3) 4,4′-Bis(dimethylamino)tridecachlorotriphenylmethyl radical ($(Me_2N)_2$>PTM• (0.04; 15%), deep green solid, dec 290 °C; UV–vis (C_6H_{12}) (Figure 1) 220, 287 (sh) 383, 430 (sh), 593 (sh), 648 nm (ε 83 500, 9000, 23 000, 9000, 2950, 4200); IR (KBr) 2990, 2960, 2930, 2855, 2798, 1522, 1508, 1458, 1443, 1403, 1348, 1336, 1323, 1248, 1232, 1190, 1097, 1060, 988, 970, 880, 813, 728, 716, 690, 678, 660, 628, 593, 543 cm^{-1}; ESR data, Table I. Anal. Calcd for $C_{23}H_{12}N_2Cl_{13}$: C, 35,5; H, 1.5; Cl, 59.4; N, 3.6. Found: C, 34,7; H, 1,4; Cl, 60,1; N, 3.0.

Reaction of 4-Bromotetradecachlorotriphenylmethyl Radical (Br-PTM•) with Me_2NH. A solution of Br-PTM• (0.04 g) in Me_2NH-saturated THF (10 mL) was left undisturbed at room temperature during 3 days. After distilling off the solvent, a residue was obtained which was redissolved in CCl_4 and passed through silica gel. By elimination of the solvent a mixture of radicals Me_2N-PTM• and $(Me_2N)_2$>PTM• was obtained as ascertained by TLC and IR spectra.

Attempted Reaction of α*H*-Pentadecachlorotriphenylmethane (PTM*H*) with Me_2NH. It has been performed as in the preceding reaction (14 days; room temperature). PTM*H*, 0.20 g; Me_2NH-saturated THF, 35 mL. Recovery of pure PTM*H*: 0.19 g; 95%.

Reaction of 4-(Chlorocarbonyl)tetradecachlorotriphenylmethyl Radical (ClCO-PTM•) with Me_2NH. (a) This

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reaction has been performed in THF, exactly as previously described.[3] Along with 4-((dimethylamino)carbonyl)tetradecachlorotriphenylmethyl radical (Me_2NCO-PTM•), green solid (10.5% yield) has been obtained which has been characterized as in (b).

(b) A solution of radical ClCO-PTM• (0.28 g) in THF (75 mL) was saturated with Me_2N at room temperature and let stand for 52 h. I_2 (0.065 g) was added, and it was left undisturbed for 45 min. The resulting mass was worked up as in the reaction with radical PTM•. However, $CHCl_3$ was used as the eluent, giving a solid (0.26 g), which was recrystallized from hexane/$CHCl_3$ yielding 4-(dimethylamino)-4′-(dimethylcarbamoyl)tridecachlorotriphenylmethyl radical ($(Me_2N)(Me_2NCO)$>PTM•; 0.23 g, 80.5%), deep green solid, mp 253–255 °C; UV–vis (C_6H_{12}) (Figure 1) 220, 293 (sh), 383, 427 (sh), 590 (sh), 645 nm (ε 80 000, 8300, 21 000, 7700, 2350, 3400); IR (KBr) 2960, 2930, 2910–2850, 2795, 1666, 1523, 1460, 1443, 1403, 1348, 1323, 1266, 1236, 1203, 1196–1168, 1098, 1058, 968, 940, 803, 778, 738, 718, 693, 650, 623, 608, 585, 533, 458 cm^{-1}; ESR data, Table I. Anal. Calcd for $C_{24}H_{12}N_2OCl_{13}$: C, 35.8; H, 1.5; N, 3.5. Found: C, 36.9; H, 1.8; N, 4.2.

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Palladium-Catalyzed Synthesis of Some New Olefinic Stannanes

Vittorio Farina* and Sheila I. Hauck

Bristol-Myers Squibb Research Institute, 5 Research Pkwy., P.O. Box 5100 Wallingford, Connecticut 06492-7660

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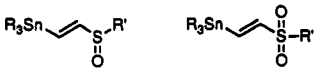
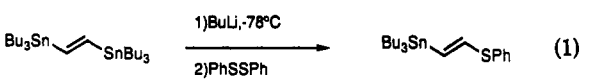
In connection with a medicinal chemistry project, we required a practical and general approach to a series of β-(trialkylstannyl)vinyl sulfoxides and sulfones exemplified by structures **1** and **2**. Olefinic stannanes have become very important synthetic intermediates, in the light of their versatile chemistry,[1] which has been recently expanded to include a variety of palladium-catalyzed coupling reactions.[2]



1 **2**

We initially examined a literature procedure,[3] describing the preparation of sulfones of the type represented by **2** from *trans*-1,2-bis(tributylstannyl)ethylene, **3**. It is reported that selective monolithiation of **3**, followed by quenching with phenyl disulfide, produced sulfide **4** in excellent yield. Oxidation then yielded the corresponding sulfone (eq 1).



(1)

3 **4**

In our hands, however, only poor yields of **4** could be obtained under a variety of experimental protocols (direct or inverse addition of the disulfide, temperatures as low as −100 °C). Control experiments established that monolithiation was a clean process (quenching with aldehydes produced allylic alcohols in almost quantitative yield), suggesting that the problematic step is the sulfenylation. Under our best conditions, 28–32% yields of **4** were obtained. We also found that aryl disulfides bearing electron-withdrawing groups on the ring failed completely to deliver the desired products. Both **5a** and **5b**, which are key compounds for our studies, could not be obtained at all by this protocol.

(2)

3

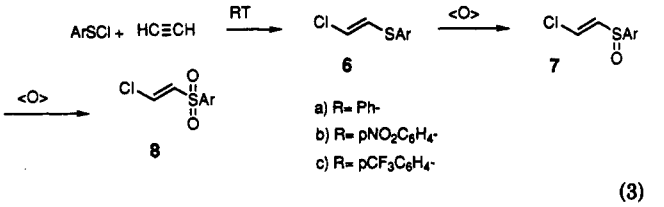
4 R=Ph, 28-32%

5a R=pNO$_2$-C$_6$H$_4$, 0%

5b R=pCF$_3$-C$_6$H$_4$, 0%

Due to the unsatisfactory results obtained, it was decided to investigate alternative approaches.

A potential route to **1** and **2** is suggested by the insertion reaction of acetylene with sulfenyl halides.[4] The procedure proved high-yielding and easy to scale up. Stepwise oxidation with *m*-chloroperbenzoic acid then provided sulfoxides **7** and sulfones **8** (eq 3).



(3)

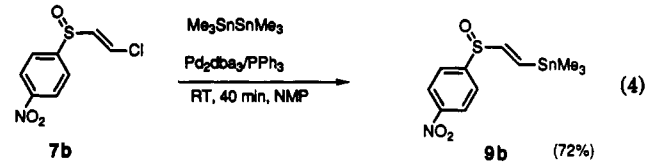
6 **7** **8**

a) R= Ph-

b) R= pNO$_2$C$_6$H$_4$-

c) R= pCF$_3$C$_6$H$_4$-

The only step left was now the introduction of the trialkylstannyl moiety. Unfortunately our preliminary attempts with Bu_3SnLi[5] and Bu_3SnCu,[6] using **7b** as a substrate, gave no reaction. We discovered, however, that when **7b** in *N*-methylpyrrolidinone (NMP) was treated with hexamethylditin and a catalytic amount of a homogeneous palladium catalyst at room temperature, the corresponding trimethylstannane was obtained in good yield (eq 4). The reaction was extended without problems to other sulfoxides and sulfones (see Table I).



(4)

7b **9b** (72%)

Several observations need to be made. The palladium catalyst employed was tris(dibenzylideneacetone)bispalladium with added triphenylphosphine, but other

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