membranes made from I–III imply that a difference of eight methylene groups between two phospholipids is sufficient to produce domains in the fluid phase. The striking dichotomy between I/III/II and I/V/IV further reveals that NNR can depend on *both* molecular structure and the physical state of the membrane.

Studies that are now in progress are aimed at examining the influence of (i) differences in chain length, (ii) unsaturation within the *sn*-1 and/or *sn*-2 chains, (iii) cholesterol, (iv) membrane proteins, (v) temperature, and (vi) head-group structure on nearest-neighbor recognition within phospholipid membranes. Detailed kinetic analyses are also being carried out in order to probe the supramolecular organization of the *initial* state of these bilayers.

Tetraphenyldistibine: A Most Useful Reagent for Discriminating Radical Reactions

Anthony G. M. Barrett* and Laura M. Melcher

Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

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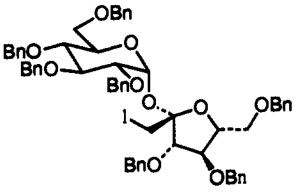
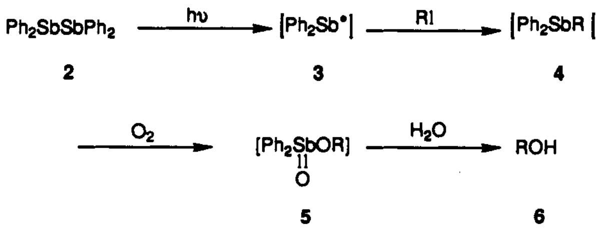
Recently, during our studies on the synthesis of sucrose,[1,2] we encountered a serious problem in effecting the S_N2 displacement of iodide **1** by oxygen-centered nucleophiles. Since all attempted bimolecular displacement reactions were unsuccessful, we sought solace in radical chemistry. Irradiation of **1** gave the corresponding alkyl radical, which was trapped with TEMPO, and the resultant adduct was subsequently converted into sucrose. These tribulations sensitized us to examine alternative, radical methods for the conversion of alkyl iodides into alcohols. Herein we report preliminary observations on the use of tetraphenyldistibine (**2**)[3,4] as a reagent for such substitution chemistry. Much to our surprise, **2** showed a remarkable chemoselectivity on photolysis in the presence of various alkyl iodides.



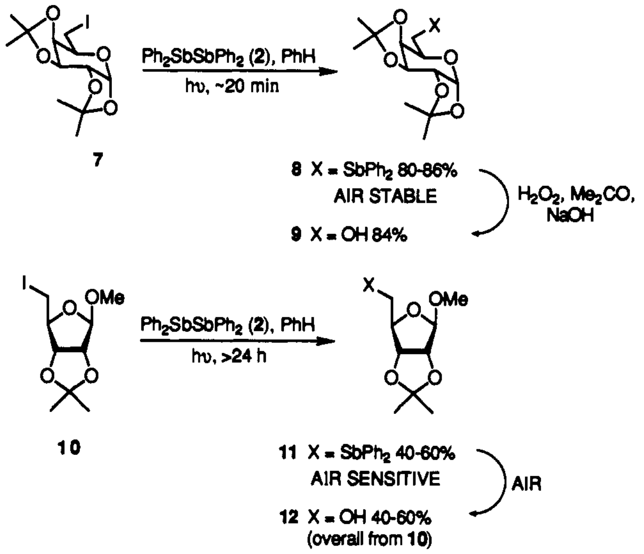
1

We considered that tetraphenyldistibine (**2**) should undergo homolysis, on irradiation, to produce the diphenylantimony(II) radical (**3**).[5] In turn, **3** should react with alkyl iodides, via a chain radical process,[6] to produce the air-sensitive[7] alkyl(diphenyl)stibine (**4**). In situ air oxidation and hydrolysis of the resultant compound **5** should provide the alcohol **6** (Scheme I). These expectations were reasonable since the conversion of **4** into **6** has precedent.[7]

Scheme I



Scheme II



Irradiation of **2** in the presence of iodide **7**[8] rapidly gave the stibine **8**[9] (80–88%) (Scheme II). Much to our surprise and in contrast to precedent,[4,5,7] this substance was not air sensitive although it was oxidized to produce **9** using basic H_2O_2. In contrast, the iodide **10**[8] reacted at a much slower rate with **2** on irradiation under identical conditions. Even after prolonged reaction, only 40–60% conversion into **11** was observed. The properties of **11** were also curious since aerial oxidation gave the alcohol **12** (40–60% overall).

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(9) The preparation of **8** and **9** is representative. A solution of **7** (275 mg) and **2** (500 mg) in dry PhH (10 mL) under N_2 was irradiated with a sun lamp for 20 min, cooled to 25 °C, and centrifuged, the supernatant layer was evaporated in vacuo, and the residue was chromatographed (silica; Et_2O/hexanes, 1:9) to afford **8** (341 mg, 88%) as a colorless oil: $[\alpha]_D$ −51° (*c* 3, $CHCl_3$); IR ($CHCl_3$) 3430, 2916, 1637, 1430, 1382, 1256, 1212, 1171, 1068, 1019, 896, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.50 (m, 4 H), 7.29–7.25 (m, 6 H), 5.53 (d, 1 H, $J = 5.0$ Hz), 4.57 (dd, 1 H, $J = 1.9, 7.9$ Hz), 4.26 (dd, 1 H, $J = 2.4, 5.1$ Hz), 4.14 (dd, 1 H, $J = 1.9, 7.9$ Hz), 3.98 (m, 1 H), 2.34 (dd, 1 H, $J = 8.8, 12.3$ Hz), 2.09 (dd, 1 H, $J = 6.1, 12.3$ Hz), 1.48 (s, 3 H), 1.31 (s, 3 H), 1.27 (s, 3 H), 1.22 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.3, 136.1, 135.7, 128.5, 128.4, 128.3, 128.1, 109.1, 108.3, 96.7, 73.8, 71.2, 70.3, 65.9, 26.0, 25.6, 24.8, 24.3, 22.6; MS (EI) *m/e* 518 ($M^{\bullet+}$) 441, 325, 275, 243; HRMS calcd for $C_{24}H_{29}O_5Sb$ ($M^{\bullet+}$) 518.1053, found ($M^{\bullet+}$) 518.1038. Anal. Calcd for $C_{24}H_{29}O_5Sb$: C, 55.63; H, 5.64. Found: C, 55.66; H, 5.83. H_2O_2 (30%, 2 mL) and Me_2CO (5 mL) were added to **8** (100 mg), THF (3 mL), and NaOH (30 mg) at 0 °C, and the mixture was warmed up to 25 °C. After 2 h, saturated $Na_2S_2O_3$ (15 mL) was added at 0 °C and the solution neutralized (1 M HCl) and evaporated in vacuo. The residue was extracted with EtOAc (4 × 40 mL), and the extract was dried ($MgSO_4$) and evaporated. Chromatography (silica; Et_2O/hexanes, 2:3) gave **9** (42 mg, 84%).

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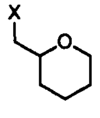
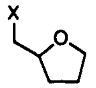
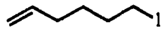
This remarkable selective reactivity and difference in product stability is not unique to **7** and **10**. Iodide **13a** reacted rapidly with **2** to produce the air-stable stibine **13b** (65%). In contrast, iodide **14a** only slowly gave an air-sensitive adduct, presumably **14b**, and this was readily oxidized in air to produce the alcohol **14c** (40–60% overall). This difference in reactivity is underscored by a competition experiment. *Brief reaction of a 1:1 mixture of iodides* ***13a*** *and* ***14a*** *with* ***2*** *gave only the stibine* ***13b*** *(60%) and unchanged iodide* ***14a*** *(98%).*


13

a X = I
b X = SbPh$_2$


14

a X = I
b X = SbPh$_2$
c X = OH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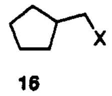
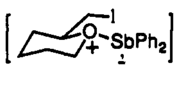
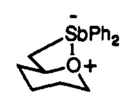

16

a X = I
b X = SbPh$_2$
c X = OH


17


18

These photolytic reactions are certainly radical in nature. The iodide **15**[10] reacted slowly with **2** on irradiation to produce an air-sensitive organoantimony compound, presumably **16b**, and this was easily air oxidized to produce **16c** (59% overall). In the blank experiment, photolysis of **2** and **16a** and air oxidation gave **16c** but at a slower rate. Irradiation of 3α-iodo-5α-cholestane[8,11] slowly gave, via an air-sensitive stibine, 5α-cholestan-3-ol (α:β = 3:4, 10–20%). Generation of 1-adamantyl radicals,[12] in the presence of **2**, gave an air-sensitive antimony derivative, probably (1-adamantyl)diphenylstibine. Again, air oxidation rapidly gave 1-adamantanol (58% overall). Finally, the fact that tetraphenyldistibine (**2**) is an excellent radical trap is underscored by two competition experiments. Generation of 1-adamantyl radicals in the presence of **2** and ethyl acrylate gave only 1-adamantanol (54%) on aerobic workup rather than acrylate-trapped adducts. In the same way, the addition of ethyl acrylate did not divert the conversion of **7** into **8**.

These results are consistent with the operation of a coordinated radical mechanism. The Lewis amphoteric[4] diphenylantimony(II) (**3**) may be coordinated by oxygen as **17** prior to an intramolecular iodine atom transfer via a *trans*-hydrindan-like transition state. Subsequent alkyl radical trapping by **2** should produce **3**, **13b**, and Ph$_2$SbI. In addition, we propose that **13b** may indeed be chelated as **18** and this may account for its air stability. In contrast, the tetrahydrofuranyl analogues of the transition state derived from **17**[13] and **18** would be more strained and therefore of less consequence. Thus, the iodides **10**, **14a**, **16a**, and 3α-iodo-5α-cholestane probably undergo reaction via a slow intermolecular process to give nonchelated, air-sensitive stibines. It is possible that metal centered radical chelation may be involved in the controversial oxygen–carbon bond effects in radical reactions.[14,15] Whatever the mechanistic origin of these unusual effects, highly selective radical transformations of tetraphenyldistibine (**2**) and other Lewis acidic dimetallic systems should find considerable use in synthesis.

Acknowledgment. We thank the National Science Foundation for generous support of our research (CHE-9096322), GD Searle and Company for microanalyses, and the Department of Chemistry at Northwestern University for HRMS data.

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[13] The efficiency of intramolecular atom transfer reactions depends on the distance between the radical center and the atom undergoing transfer. Barton, D. H. R.; Hesse, R. H.; Pechet, M. M.; Smith, L. C. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1159. Breslow, R.; Heyer, D. *J. Am. Chem. Soc.* **1982**, *104*, 2045. The Breslow functionalization of steroids is similar to our observations since the process involves the precoordination of a chlorine atom by an aryl iodide group prior to hydrogen atom transfer.

[14] For examples of the acceleration of radical reactions by β-oxygen substituents, see: Barton, D. H. R.; Hartwig, W.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1982**, 447.

[15] Beckwith has disputed the accelerating effects of β-oxygen functionality at least in the reaction of 1,2-dimethoxyethane with the *tert*-butoxy radical; see: Beckwith, A. J.; Brimby, S. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1801.

Crystal Structure of an η^2-Acetonitrile Complex of Tungsten(II): Acetonitrile as a Four-Electron Donor

Joseph Barrera, Michal Sabat, and W. Dean Harman*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

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Although coordination of a nitrile to a transition metal through the nitrogen lone pair has been well established,[1] the ability of these ligands to donate through one of their π-orbitals has been demonstrated only recently.[2a–c] Of the few η^2-nitrile complexes which have been structurally characterized, most can be regarded as electronically saturated complexes by considering the nitrile as a two-electron donor. Presently, we report the preparation and characterization of the 16e$^-$ complex [W(bpy)(PMe$_3$)$_2$Cl(η^2-NCCH$_3$)]$^+$, along with structural and spectroscopic evidence for the nitrile ligand acting as a four-electron donor.

The addition of TlPF$_6$ to an acetonitrile solution of W(bpy)(PMe$_3$)$_2$Cl$_2$ produces a deep green material, [**1**]PF$_6$, in 67% yield.[3] In contrast to typical W(II) monomeric complexes, [**1**]$^+$ resists reaction with water or oxygen. Crystals of [**1**]PF$_6$ suitable for X-ray analysis[4] were obtained by allowing the acetone to diffuse from an acetone/water mixture. An ORTEP drawing for [**1**]$^+$ appears in Figure 1 featuring an acetonitrile ligand with C(1)–W (1.998 (5) Å) and N(1)–W (2.008 (4) Å) bonds which are virtually equal. The M–C bond is over 0.25 Å *shorter* than that found in typical W(II)–olefin complexes, yet is quite similar to what is reported for alkynes known to act as four-electron donors.[5] The C(1)–N(1) bond (1.267 (7) Å) has been lengthened by 0.12 Å compared to that of the free ligand,[6] the largest distortion reported to date for a nitrile with such coordination (Table I). Notably, this value is roughly equal to that observed for a *doubly*

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[3] TlPF$_6$ (0.0645 g, 0.185 mmol) was added to W(PMe$_3$)$_2$(bpy)Cl$_2$ (0.104 g, 0.185 mmol) in 5 mL of acetonitrile and stirred at room temperature for 5 h. The solution was filtered through Celite and the acetonitrile removed in vacuo. The resulting solid was dissolved in acetone (3 mL), and upon the slow addition of H$_2$O a precipitate formed, which was filtered and dried in vacuo (0.088 g, 67%).

[4] Crystal data: C$_{18}$H$_{23}$ClF$_6$N$_3$P$_3$W; monoclinic, $P2_1/c$ (No. 14), a = 14.932 (3) Å, b = 10.138 (4) Å, c = 17.271 (4) Å, β = 107.26 (2)°, V = 2497 (2) Å^3, Z = 4. The structure was solved by Patterson and Fourier techniques (TEXSAN 5.0) and refined to R(F) and R_w(F) of 0.026 and 0.039, respectively, by using 3687 absorption-corrected reflections with $I > 3\sigma(I)$ measured on a Rigaku AFC6S diffractometer at −120 °C (Mo Kα radiation, λ = 0.71069 Å).

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