In summary, the data presented above indicate the great propensity that exists for heterolytic cleavage of the N–O bond of suitably derivatized *N*-arylhydroxamic acids. It provides a solid basis for the proposal that sulfate esters of *N*-arylhydroxamic acids can ionize to produce acylarylnitrenium ions as the ultimate carcinogens derived from certain aromatic amines.

Acknowledgment. We are indebted to the National Cancer Institute and to the Institute of General Medical Sciences of the National Institutes of Health for grants that supported this investigation.

Registry No. **4a**, 121-73-3; **4b**, 619-50-1; **4c**, 98-46-4; **4d**, 619-24-9; **4e**, 402-54-0; **4f**, 619-72-7; **4g**, 100-25-4; **6a**, 88730-41-0; **6b**, 62641-35-4; **6c**, 88730-42-1; **6d**, 80584-66-3; **6e**, 88730-43-2; **6f**, 80584-65-2; **6g**, 67274-52-6; **7a**, 88730-34-1; **7b**, 88730-35-2; **7c**, 88730-36-3; **7d**, 88730-37-4; **7e**, 88730-38-5; **7f**, 88730-39-6; **7g**, 88730-40-9.

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(12) Product yields[8] were determined by HPLC analysis vs. an internal standard. The yields were as follows: **8a**, 100% (29:71 ratio of 1,2,3- to 1,2,5-substitution); **8b**, 86%; **8c**, 100% (45:55 ratio of 1,2,3- to 1,2,5-substitution); **8d**, 100% (46:54 ratio of 1,2,3- to 1,2,5-substitution); **8e**, 87%; **8f**, 96%; **8g**, 96%. All products were stable to the reaction conditions.

Transfer of Hydrogen from Carbon–Hydrogen Bonds. Synthesis, Structure, and Reactions of 1,3,5-Triphenyl-2,4,6-trithia-1,3,5-tristannaadamantane

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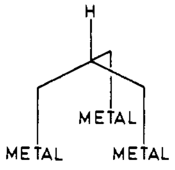
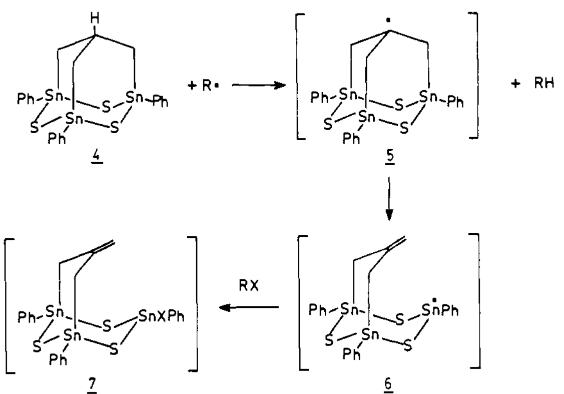
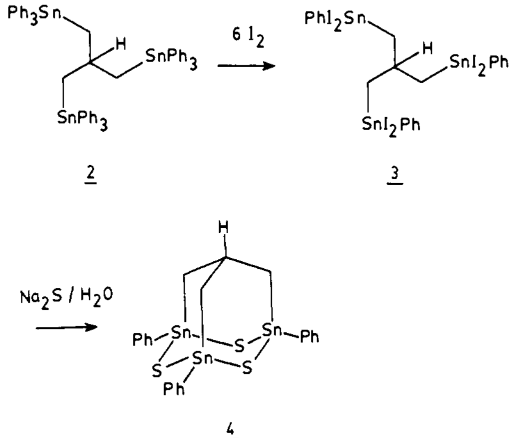
Many important redox reactions involve the formal transfer of hydride from a carbon–hydrogen bond.[2,3] Compounds in which a carbon–hydrogen bond is adjacent to several carbon–metal bonds should be especially reactive,[3b] since loss of hydride or hydrogen may yield a cation or radical stabilized by hyperconjugation.[4,5] Loss of hydrogen is fastest when the carbon–hydrogen and carbon–metal bonds are antiperiplanar,[6] so the best donors should resemble structure **1**. The first synthesis of a compound of this kind and the unusual reactivity of its central carbon–hydrogen bond are described below.



1

Scheme I





Treatment of tris[(triphenylstannyl)methyl]methane (**2**)[3b] with 6 equiv of iodine cleanly produced hexaiodostannane **3**. Aqueous sodium sulfide converted this intermediate into 1,3,5-triphenyl-2,4,6-trithia-1,3,5-tristannaadamantane (**4**)[7,8] in 79% overall yield. The large coupling between the bridgehead hydrogen and tin ($^3J(^{119}\mathrm{Sn,H})$ = 206.5 Hz)[9] confirmed that all three carbon–tin bonds were antiperiplanar to the central carbon–hydrogen bond. The long tin–sulfur bonds (2.41 Å)[10] were expected to introduce a significant element of strain, and X-ray crystallographic study of compound **4** has shown that the bridgehead carbon is severely flattened as a result.[11]

In chloroform at 25 °C, stannaadamantane **4** reduced triphenylcarbenium hexafluorophosphate to triphenylmethane in 83% yield. Unlike the very slow reduction of triphenylcarbenium by tris[(triphenylstannyl)methyl]methane (**2**),[3b] reduction by stannaadamantane **4** is almost instantaneous. More impressive is the observation that stannaadamantane **4** reduces alkyl halides to the corresponding hydrocarbons. For example, when α-bromo-*p*-phenylacetophenone (27 μmol) was warmed with compound **4** (30 μmol) and AIBN (16 μmol) in benzene (1.5 mL, 75 °C, 3 h), *p*-phenylacetophenone was formed in 48% yield.[12] In general, iodides are reduced fastest, followed by bromides and then

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[1] Fellow of the Natural Sciences and Engineering Research Council of Canada.

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[8] The structure assigned to this new compound is consistent with its elemental analysis and its IR, NMR, and mass spectra. These data are included in the supplementary material.

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[12] Yields measured by NMR were nearly quantitative. We attribute the moderate isolated yields to the extremely small scale of our preparative reactions.

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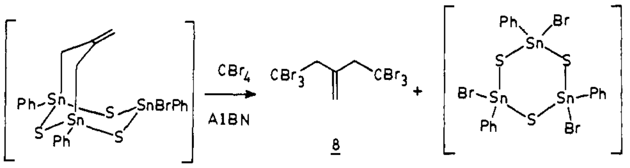
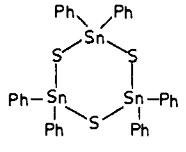
chlorides.[13] Trimethyltin chloride was not reduced, suggesting that the central carbon–hydrogen bond of stannaadamantane **4** is stronger than a representative tin–hydrogen bond.

Since these reductions are accelerated by AIBN, we believe that the central carbon–hydrogen bond of compound **4** is cleaved homolytically, producing radicals **5** or **6** (Scheme I). Allylstannanes **7** are then formed by abstraction of halogen.[14] These reactive compounds could not be isolated, but evidence for their formation comes from the following experiment. When allylstannane **7** (X = Br) was warmed with excess carbon tetrabromide (benzene, AIBN, 95 °C), 1,1,1,5,5,5-hexabromo-3-methylenepentane (**8**)[8,15] was formed in 60% overall yield by a reaction characteristic of allylstannanes.



7 8 9

The reductions of alkyl halides by stannaadamantane **4** are similar to dehalogenations effected by tin hydrides.[16] However, we doubt that compound **4** is actually converted into a tin hydride, since it is stable in the absence of reducible substrates, and no additions to carbon–carbon or carbon–oxygen double bonds have been observed. We therefore attribute the reactivity of stannaadamantane **4** to its unusual central carbon–hydrogen bond. Related compounds that lack this feature are in fact inert.[17] For example, trithiatristannacyclohexane **10** did not reduce 1,2-dibromoethane, nor did bis[(triphenylstannyl)methyl]methane (**11**)[3b] reduce α-bromoacetophenones in the presence of AIBN.



10

$Ph_3SnCH_2CH_2CH_2SnPh_3$

11

The central carbon–hydrogen bond in stannaadamantane **4** is an unusually reactive source of hydrogen, comparable in some respects to a tin–hydrogen bond. The efficient and selective reductions of alkyl halides by stannaadamantane **4** suggest that related, more accessible compounds may prove to be synthetically useful.

Acknowledgment. This work was financially supported by Research Corp., the Natural Sciences and Engineering Research Council of Canada, and le Ministère de l'Education du Québec. We are grateful to Michael J. Evans and Dr. M. T. Phan Viet, who recorded our mass and high-field NMR spectra.

Registry No. 2, 87549-81-3; **3**, 88563-24-0; **4**, 87922-35-8; **7**, 88563-23-9; **8**, 88563-25-1; α-bromo-*p*-phenylacetophenone, 135-73-9; triphenylmethane, 519-73-3; *p*-phenylacetophenone, 92-91-1; triphenylcarbenium hexafluorophosphate, 437-17-2.

Supplementary Material Available: Spectroscopic and analytical data for all new compounds (1 page). Ordering information is given on any current masthead page.

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Excited-State Distortions from Resonance Raman Overtone Intensities in $K_3[Cr(CN)_5NO]$

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Displacements of potential surfaces of excited electronic states relative to the ground-state surface are of fundamental importance in spectroscopy, photophysics, and photochemistry. The magnitudes of such displacements along specific normal modes are usually calculated from Franck–Condon factors.[1] Recently the multimode displacements in transition-metal complexes were calculated using the intensities of fundamentals in Raman spectra.[2-6] In principle, resonance Raman *overtone* intensities can provide complementary information, but in practice they rarely exhibit significant intensity in polyatomic molecules with many displaced normal modes.[3]

During the course of our studies of the excited-state properties of metal nitrosyl compounds, we discovered that the $Cr(CN)_5NO^{3-}$ ion possesses almost ideal spectroscopic characteristics for determining excited-state distortions from Raman overtone intensities. There are a relatively small number of significantly displaced normal modes, thus giving both a relative large overtone intensity (18% of that of the fundamental) and concomitantly enough fundamentals to provide a cross-check of the calculation. In addition, the electronic absorption spectrum exhibits enough vibronic structure at low temperature[7] to enable the E_{00} band to be observed and thus allow accurate tuning of the laser to exact resonance with the electronic origin. The successful calculation of the absorption spectrum from the Raman-determined displacements provides a second cross-check. We report here the first calculation of the displacement of a potential surface along a given normal mode in a multimode, polyatomic transition-metal complex from the intensity of its overtone.

The displacement of Δ_k of the excited-state potential surface along the kth normal model of frequency ω_k is given by[3]

$$\Delta_k^2 = \frac{I_{20}^k}{I_{10}^k}\frac{4\sigma^2}{\omega_k^2}\frac{\epsilon_1((W_I - E)/\sigma)}{\epsilon_2((W_I - E)/\sigma)} \qquad (1)$$

I_{20}^k/I_{10}^k is the intensity ratio of the overtone to the fundamental, σ^2 is related to the absorption bandwidth, and ϵ_n is a function based on the energy difference between the absorption band maximum and the laser Raman excitation.[3]

The resonance Raman and electronic absorption spectra are shown in Figure 1. By use of the first overtone intensity (Table I), the absorption spectral line width, and an ϵ_1/ϵ_2 ratio of 0.752, the displacement along the Cr–N stretching normal mode calculated by eq 1 is 2.20. (On the assumption that this coordinate is puely the uncoupled M–N stretch, this displacement is 0.09 Å.) As a check, the displacement along this normal coordinate is calculated from the intensities of the fundamentals by using methods previously described.[2-6] The displacement calculated by these complementary methods is 2.60 (~0.10 Å). The two calculated displacements agree within experimental error.

The value of the Raman methods for determining the displacement is especially apparent because the usual Franck–Condon calculation is not feasible. The electronic absorption band (as-

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