band of **2** is selectively excited ($\lambda > 420$ nm, isolated by Corning glass filter CS-3.73) and not upon photosensitization (benzophenone, *p,p'*-dibromobiphenyl and fluorenone) demonstrates that these originate from the lowest n,π^* singlet state of **2**. In conformity with this, alloocimine, a triplet quencher, failed to quench the formation of **1** and **6**.

The above results are summarized below: (a) 1,3-Dithione **1** gives **3** and **4** in nonhydroxylic solvents and **3–5** in methanol from the *first excited triplet state.*[5] (b) Dithiolactone **2** gives 1,3-dithione **1** in nonhydroxylic solvents and a 1:1 adduct (**6**) in methanol from the *first excited singlet state.*

The results of our study can be rationalized by the occurrence of an unprecedented (in thiocarbonyls) α-cleavage in **1** and **2** as illustrated in Schemes I and II. The suggested mechanism for these reactions involve diradical and/or carbene intermediates. Photoproduct **3** must arise through sulfur incorporation of the intermediate carbene or diradical (**a** or **b**) by the ground-state thione. Though substantial evidence for this carbene pathway is not provided, such sulfur incorporation in other systems has been reported.[2,6]

Interestingly, the photochemical behavior of **1** and **2** is different from that of the corresponding carbonyl compounds.[7] The diradical derived from analogous oxygenated compounds either eliminates carbon monoxide or cleaves to give dimethylketene, whereas evidence for like products are not to be seen in **1** and **2**. In the case of 1,3-diketone **1** (S = O) and the corresponding β-lactone **2** (S = O), no evidence for the formation of a carbene intermediate is reported.[7]

In summary, we have established the occurrence of Norrish type I α-cleavage in thiocarbonyl compounds.[8,9] A detailed understanding of the mechanism of the above reactions and a study of related thiocarbonyl systems await our further investigation.

Acknowledgment. We are grateful to the Department of Science and Technology, Government of India, for financial support and to Professors R. S. H. Liu and N. J. Turro for mass spectra. K.M. thanks the University Grants Commission, New Delhi, for a Junior Research Fellowship.

Registry No. **1**, 10181-56-3; **2**, 10181-61-0; **3**, 74835-36-2; **4**, 74835-37-3; **5**, 74835-38-4; **6**, 74835-39-5; **7**, 74835-40-8.

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(5) The irradiation of 1 in an oxygen atmosphere was reported earlier to give the corresponding 1,3-diketones (1, S = O) only: Worman, J. J.; Shen, M.; Nichols, P. C. *Can. J. Chem.* **1972**, *50*, 3923.

(6) Hoffmeister, E. H.; Tarbell, D. S. *Tetrahedron* **1965**, *21*, 35, 2857, 2865.

(7) Turro, N. J.; Cole, T. *Tetrahedron Lett.* **1969**, 3451.

(8) The photochemical cleavage reactions of *S*-aryl and *S*-acyl xanthates, dithio- and trithiocarbonates, and thiocarboxylic *O*-esters have been reported: Barton, D. H. R.; George, M. V.; Tomeda, M. *J. Chem. Soc.* **1962**, 1967; Singh, S. N.; George, M. V. *J. Org. Chem.* **1972**, *37*, 1375; Schonberg, A.; Sodete, U. *Tetrahedron Lett.* **1967**, 4977; Heine, H.; Metzner, W. *Justus Liebigs Ann. Chem.* **1969**, *724*, 223; Lundersdorf, R.; Martens, J.; Pakzad, B.; Praefeke, K. *Ibid.* **1977**, 1992; Rungwerth, D.; Schwetlick, K. *Z. Chem.* **1974**, *14*, 17; Schmidt, V.; Kabitzke, K. H. *Angew. Chem.* **1964**, *76*, 687.

(9) The direct comparison of the behavior of diradical and carbene intermediates (**a–d**) derived from **1** and **2** is not possible due to the different spin states involved in the reaction.

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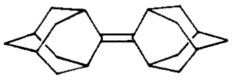
Unusual Reactions of Adamantylideneadamantane with Metal Oxidants. Isolation of Stable Chloronium Salts

Summary: Reaction of adamantylideneadamantane with OsO_4 has provided the first spectroscopic evidence for coordination of an olefin to a d° metal species, while its reactions with $SbCl_5$ or $MoOCl_4$ give remarkably stable chloronium salts $[AdAdCl^+][SbCl_6^-]$ and $[AdAdCl^+][Mo_2O_2Cl_7^-]$.

Sir: The initial step in the reaction of olefins with metal oxidants has been proposed[1] to be coordination of the reactants to form a complex. Virtually nothing is known about these key intermediates, possibly because they rapidly collapse to organometallic species[1] and ultimately to products. Because of its unusual structure, adamantylideneadamantane,[2] I, fails to undergo[3] many addition reactions typical of olefins and yet forms complexes with a variety of Lewis acids.[4] Therefore, it was expected that complexes between I and metal oxidants might be directly observable. This expectation was borne out for reactions involving I and OsO_4. However, I readily reacted with metal chloride oxidants such as $MoOCl_4$ in an unexpected way as described below.


I

In general, the rate of reaction of olefins with OsO_4 increases with increasing alkyl substitution of the olefinic double bond along the series mono- < di- < tri- < tetrasubstituted.[5] In contrast, tetrasubstituted I reacted with 0.1 M OsO_4 in hexane 370 times more slowly than even monosubstituted 1-octene.[6,7] A solution containing 0.05 M OsO_4 and 0.05 M I in heptane was pale red-orange in color. The electronic spectrum of such a solution immediately on mixing showed a new absorbance in the visible region not present in solutions containing only OsO_4 or I (see Figure 1). Subtraction of the contribution due to unreacted OsO_4 indicated an absorbance maximum at 415 nm. We assign this absorbance to ligand to metal charge transfer in a weak complex involving OsO_4 and I. Consistent with this assignment, the intensity of this band did not increase with time but gradually diminished as the reactants were consumed.

Antimony pentachloride and molybdenum oxytetrachloride are members[8,9] of a class[10] of oxidants which in-

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(1) Sharpless, K. B.; Teranishi, A. Y.; Backvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120–3128.

(2) I utilized in this study was prepared by the procedure of McMurry and was additionally purified by chromatography (alumina) and repeated recrystallization from 1:1 $EtOH/CHCl_3$: McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708–4709.

(3) (a) Strating, J.; Wieringa, J. H.; Wynberg, H. *J. Chem. Soc. D* **1969**, 907–908. (b) Wieringa, J. H.; Strating, J.; Wynberg, H. *Tetrahedron Lett.* **1970**, 4579–4582. (c) See also: Garratt, D. G. *Tetrahedron Lett.* **1978**, 1915–1918.

(4) Olah, G. A.; Schilling, P.; Westerman, P. W.; Lin, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 3581–3589.

(5) Sharpless, K. B.; Williams, D. R. *Tetrahedron Lett.* **1975**, 3045–3046.

(6) Pseudo-first-order rate constants were determined for the reaction of I and of 1-octene with a large excess of 0.1 M OsO_4 in hexane at 22.5 °C. These rates were, respectively, 8.3×10^{-6} and $3.1 \times 10^{-3}\ s^{-1}$. Reactions were followed by monitoring the disappearance of starting olefin.

(7) The product of this interaction is the osmate ester derived from I. This was converted upon reductive workup ($LiAlH_4$) to the corresponding glycol, with properties identical with those produced by reductive coupling of adamantanone: Wynberg, H.; Boelman, E.; Wieringa, J. H.; Strating, J. *Tetrahedron Lett.* **1970**, 3613–3614.

(8) Uemura, S.; Onoe, A.; Okano, J. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 692–697.

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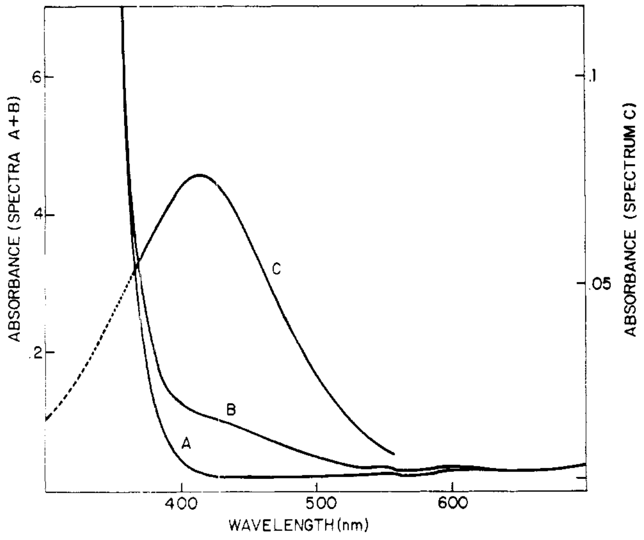
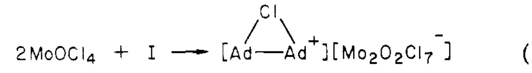
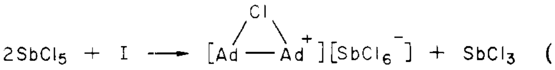


Figure 1. UV-visible spectra in heptane (25 °C) of (A) 0.05 M OsO_4, (B) 0.05 M OsO_4 with 0.05 M I, and (C) difference spectrum (6×).

troduce two chlorine atoms across simple olefins with cis stereochemistry. In contrast to the reactions involving OsO_4, I reacts with these cis-chlorination reagents rapidly, even at −78 °C. Competition studies indicate that $SbCl_5$ reacts ca. 10 times faster with I than with 1-octene. It is noteworthy in this regard that these reagents are ostensibly more sterically congested than OsO_4.[11] The products from this reaction were found to be salts of adamantylideneadamantanechloronium ion (eq 1 and 2) which exhibited remarkable thermal stability.[12] Both salts gave satisfactory analyses (C, H, Cl).



$$2\mathrm{MoOCl_4} + \mathrm{I} \longrightarrow [\overset{\mathrm{Cl}}{\mathrm{Ad}{-}\mathrm{Ad}^{+}}][\mathrm{Mo_2O_2Cl_7}^{-}] \quad (1)$$



$$2\mathrm{SbCl_5} + \mathrm{I} \longrightarrow [\overset{\mathrm{Cl}}{\mathrm{Ad}{-}\mathrm{Ad}^{+}}][\mathrm{SbCl_6}^{-}] + \mathrm{SbCl_3} \quad (2)$$

The gold, paramagnetic[13] molybdate from eq 1 (mp 110–111 °C dec) exhibited infrared absorbances due to the terminal oxo ligand at 993 cm^{-1} and due to terminal and bridging chlorides, respectively, at 360 and 308 cm^{-1}. Thus, the $Mo_2O_2Cl_7^-$ anion in this species appears to have the usual[14] triply bridged structure of M_2X_9 dimers, with chloride ligands constituting all three of the bridges. The white, diamagnetic hexachloroantimonate salt exhibited the expected[15] very strong $SbCl_6^-$ absorbance at 340 cm^{-1}. The remaining infrared bands[16] in each case were common to both salts and are assigned to the adamantylideneadamantanechloronium ion. The ^{13}C NMR spectrum[17] of this $SbCl_6^-$ derivative (24 °C, CD_2Cl_2) was virtually identical with that of (thermally unstable) adamantylideneadamantanechloronium chloride (−70 °C, liquid SO_2) reported by Olah.[4] It is also noted that, although discreet compounds[18] containing the $Mo_2O_2Cl_7^-$ anion have not previously been reported, we have been able to prepare several tetraalkylammonium derivatives[19] corresponding to this formulation via eq 3.

$$2\mathrm{MoOCl_4} + \mathrm{NR_4I} \rightarrow [\mathrm{NR_4}^+][\mathrm{Mo_2O_2Cl_7}^-] + \mathrm{ICl} \quad (3)$$

Taken as a whole, the observed chemistry of I suggests that its coordination to all of the oxidants in this study occurs readily[20] but that collapse of the resultant complex to organometallic intermediates is considerably more sterically demanding than the initial complexation. For OsO_4, the result is a slow reaction. In the case of $SbCl_5$ and $MoOCl_4$, a less sterically demanding alternative pathway, collapse to an ion pair is available and it is this pathway which predominates. The stability of these salts suggests the possibility of their structural characterization by X-ray crystallography.

Registry No. I, 30541-56-1; 1-octene, 111-66-0; OsO_4, 20816-12-0; $SbCl_5$, 7647-18-9; $MoOCl_4$, 13814-75-0.

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Received August 12, 1980

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(9) Nugent, W. A. *Tetrahedron Lett.* **1978**, 3427–3430.

(10) (a) Uemura, S.; Onoe, A.; Okano, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 3121–3124. (b) San Filippo, J., Jr.; Sowinski, A. F.; Romano, L. J. *J. Am. Chem. Soc.* **1975**, *97*, 1599–1600.

(11) Molybdenum oxytetrachloride is monomeric in solution with square pyramidal coordination. Barraclough, C. G.; Key, D. J. *Aust. J. Chem.* **1970**, *23*, 2387–2396. Antimony pentachloride in nonpolar solvents is monomeric with trigonal bipyramidal coordination: Carlson, G. L. *Spectrochim. Acta* **1963**, *19*, 1291–1307; Beattie, I. R.; Gilson, T.; Livingston, K.; Fawcett, V.; Ozin, G. A. *J. Chem. Soc. A* **1967**, 712–718.

(12) Adamantylideneadamantanechloronium chloride has been prepared in solution in low temperature studies but such solutions rapidly decompose on warming. See ref 2b and 4.

(13) The magnetic susceptibility of this complex (per Mo atom) was determined by using the Evans technique in CH_2Cl_2 solution, $\mu_{\mathrm{eff}} = 1.51\ \mu_B$. This is close to the spin only value and suggests the absence of a significant Mo–Mo bonding interaction.

(14) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3821–3831 and references therein.

(15) Driessen, W. L.; den Heijer, M. *Inorg. Chim. Acta* **1979**, *33*, 261–264 and references therein.

(16) Remaining absorbances for the $SbCl_6^-$ salt (KBr pellet) follow: 2930 (vs), 2920 (vs), 2860 (s), 1451 (vs), 1430 (w), 1371 (w), 1353 (m), 1327 (m), 1305 (w), 1289 (w), 1230 (m), 1208 (w), 1089 (m), 1059 (w), 1027 (w), 1012 (w), 950 (m), 939 (w), 878 (m), 851 (w), 792 (w), 714 (w), 698 (m), 639 (w), 610 (w), 587 (m), 550 (w), 509 (w), 410 (w).

(17) ^{13}C NMR chemical shifts (parts per million vs. internal standard Me_4Si) are as follows, with literature values from ref 4 in parentheses: 27.0 (27.3), 36.4 (36.6), 37.9 (37.6), 39.9 (39.6), 43.6 (43.6), 158.6? (157.7).

(18) See, however: Eliseev, S. S.; Malysheva, L. E.; Vozhdaeva, E. E. *Russ. J. Inorg. Chem.* **1977**, *22*, 728–731.

(19) For instance, the gold tetrabutylammonium derivative, mp 163–164 °C, $\mu_{\mathrm{eff}} = 1.59\ \mu_B$. Anal. ($C_{16}H_{36}NMo_2O_2Cl_7$) C, H, N, Cl. However, this and all $Mo_2O_2Cl_7$ salts prepared in this way had an unaccounted for absorbance in the IR spectrum at 735 cm^{-1}, suggesting that at least some of the anions in this material contained bridging oxo ligands.

(20) In fact, a related complex between SbF_5 and I has been observed at low temperatures (ref 4). The absence of ^{19}F coupling in the ^{13}C NMR spectrum of this adduct suggests coordination to the antimony atom. It is interesting to note that a theoretical study of coordination of SbF_5 to polyunsaturated hydrocarbons favors coordination through the fluorine atom: Kasowski, R. V.; Caruthers, E.; Hsu, W. Y. *Phys. Rev. Lett.* **1980**, *44*, 676–679.

Directed Diastereotopic Lithiation of β-Heterosubstituted Alkyl Sulfones[1]

Summary: The directed, highly diastereoselective lithiation of β-aminoalkyl sulfones by organolithium reagents has been shown capable of producing *either* diastereomeric lithio derivative with greater than 90% selectivity, depending upon the type of amino group.

Sir: The recently reported α-lithiation of phenyl vinylic sulfones represents a highly convenient route to α-(phenylsulfonyl) vinyllithium reagents, which are potentially

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(1) Part 3 of the series Sulfone Reagents in Organic Synthesis; for previous parts, cf. *J. Org. Chem.*, 44, 3277, 3279 (1979).

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