values.[9,10] While the spectra unambiguously indicated the presence of a barrier on the excited-state surface, they give no information about the height of that barrier.

The tremendous decrease in isomerization barrier height upon excitation is consistent with almost complete reversal of bond alternation in the lowest energy excited singlet state. Calculations of bond orders for the polyene 2^1A_g state[11,12] predict significant weakening of the ground-state double bonds in the 2^1A_g state. Bond order changes in going from the ground state to the 1^1B_u state are predicted to be much smaller as is born out by the observed spectra.[13,14]

These data unequivocably identify a thermally activated isomerization channel on the excited state surface that proceeds over a 1 kcal mol^{-1} barrier. They do not, of course, specify the trajectory for this isomerization. While it reasonable to associate this barrier with simple twisting about the isomerizing bond, a detailed microscopic interpretation will require more extensive experimental and theoretical work.

Registry No. *cis,trans*-1,3,5,7-Octatetraene, 1871-51-8; *trans,trans*-1,3,5,7-octatetraene, 3725-31-3.

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A New Method for the Synthesis of Organic Nitro Compounds

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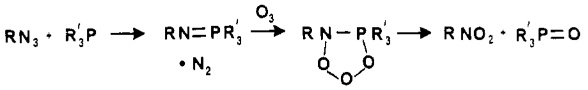
In connection with recent studies in this laboratory on the synthesis of tunicamycin, the nitro galactose derivative **1** was required as a key intermediate.[1,2] Numerous attempts at its synthesis by known methods[1] ended in complete failure. In particular, synthesis from the corresponding 6-iodogalactose derivative **2** using the Kornblum silver nitrite displacement method,[1c] which seemed most appropriate in this case, led to no detectable amount of **1** under a variety of conditions.[3] Motivated by these results, we have devised a new route from halides and sulfonates to nitro compounds.

The hypothesis leading to the method described herein is depicted by the overall equation:



$$RN_3 + R'_3P \longrightarrow \underset{+\,N_2}{RN{=}PR'_3} \xrightarrow{O_3} RN{-}PR'_3\ (\text{cyclic } O{-}O{-}O) \longrightarrow RNO_2 + R'_3P{=}O$$

The azides required for this process are generally readily available by S_N2 displacement and their conversion to phosphine imines occurs smoothly under mild conditions (Staudinger reaction[4]). Cycloaddition of ozone to the phosphine imine would provide an unstable adduct, which we speculated could decompose to phosphine oxide and the desired nitro compound, although the mechanism by which such decomposition would occur may not be simple.

The azide **3**, readily prepared by reaction of the corresponding iodide (**2**) with excess lithium azide in dimethylformamide (4 mL/g of LiN_3, 75 °C, 16 h), upon stirring with 1.1 equiv of triphenylphosphine in methylene chloride (CH_2Cl_2) at 35 °C for 16 h under nitrogen was converted to the phosphine imine **4** cleanly. Slow addition of this solution of **4** in CH_2Cl_2 to a saturated solution of ozone (3.3–4 equiv) in CH_2Cl_2 at −78 °C, nitrogen purging to remove excess ozone, and chromatography on silica gel afforded the desired nitro compound **1** as a colorless oil in 61% yield. Reaction of **3** with tri-*n*-butylphosphine (CH_2Cl_2, 23 °C, 4 h) produced the phosphine imine, which was ozonized in the same manner to form nitro sugar **1** in ca. 50% yield. 2,2,2-Trichloroethyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranoside (**5**) was similarly converted to a phosphine imine (tri-*n*-butylphosphine, 6 h at 23 °C and 0.5 h at 40 °C in CH_2Cl_2),[5] which was ozonized to form 2,2,2-trichloroethyl 3,4,6-tri-*O*-acetyl-2-nitro-2-deoxy-α-D-galactopyranoside (**6**) in 54% overall yield. In another example the azide **7** was transformed into nitro sugar **8** in 57% yield.

For each of the above cases the ozonolytic conversion of phosphine imine to nitro compound required at least *3 equiv* of ozone and proceeded in better yield if the solution of phosphine imine was added to the cold solution of ozone rather than inversely.

The conversion of a number of other primary and secondary azides to the corresponding nitro compounds was studied to ascertain the scope of the phosphine imine → nitro transformation. The following nitro compounds were obtained in the overall percent yields indicated from the corresponding azides via the tri-*n*-butylphosphine imines (from secondary azides) or triphenylphosphine imines (from primary azides): 3-phenylpropyl (60%), *n*-octyl (70%), 2-octyl (71%), *trans*-4-*tert*-butylcyclohexyl (50%), cyclooctyl (41%).

Benzyl azide proved to be an exceptional case since it afforded under standard conditions no α-nitrotoluene but instead benzaldehyde as major product (53%).[6]

The following procedure for the preparation of 1-nitrooctane is illustrative:

To a stirred solution of 1-azidooctane (200 mg, 1.29 mmol) in dry CH_2Cl_2 (0.5 mL) under nitrogen in a flame-dried flask was added a solution of triphenylphosphine (372 mg, 1.42 mmol) in 0.5 mL CH_2Cl_2 with stirring. Evolution of nitrogen was visible within 5 min after the addition of phosphine. Stirring was continued at room temperature for 5.0 h. The reaction mixture was then diluted with dry CH_2Cl_2 (4.0 mL) and added dropwise by cannula into 106 mL of a saturated solution of ozone (4.23 mmol) in CH_2Cl_2. After the addition of the phosphine imine was complete, the reaction mixture was stirred at −78 °C for 10 min and purged of ozone at −78 °C with argon or nitrogen until the blue color was completely discharged. Concentration of the reaction mixture under reduced pressure at room temperature and flash chromatography (30:70, petroleum ether:diethyl ether) of the residual oil yielded 143 mg (70%) of 1-nitrooctane,[7] bp 66–68 °C (2 mm). 1-Octanal was eluted as a minor component (22 mg, 13%).

The synthesis of nitro compounds from azides via the ozonolysis of phosphine imines is obviously limited to those substrates that are tolerant of ozone at −78 °C. Apart from this restriction, the process seems to be both predictable and reliable. It is obviously

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(1) For reviews, see: (a) Schickh, O. v.; Apel, G.; Padeken, H. G.; Schwarz, H. H.; Segnitz, A.; Houben-Weyl-Müller. "Methoden der Organischen Chemie;" Georg Thieme Verlag: Stuttgart, **1971**; Vol. X/1. (b) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734. (c) Kornblum, N. *Org. React.* **1962**, *12*, 101. (d) Gilbert, K. E.; Borden, W. T. *J. Org. Chem.* **1979**, *44*, 659.

(2) Ito, T.; Takatsuki, A.; Kawamura, K.; Sato, K.; Tamura, G. *Agric. Biol. Chem.* **1980**, *44*, 695.

(3) Various 6-nitro-D-glucopyranoside derivatives have been prepared successfully by silver nitrite displacement in this laboratory and previously. See: (a) Sugihara, J. M.; Teerlink, W. T.; MacLeod, R.; Dorrence, S. M.; Springer, C. H. *J. Org. Chem.* **1963**, *28*, 2079. (b) Richardson, A. C. *MTP Int. Rev. Sci.: Org. Chem., Ser. One* **1973**, *7*, 105. The failure of the silver nitrite displacement process to generate the 6-nitrogalactopyranoside **1** (nitrite ester is the main byproduct) seems to correlate with the slowness of backside displacement in the galacto series relative to the gluco series.

(4) Gololobov, Yu. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437.

(5) In general phosphine imine formation from an azide occurs at a faster rate with tri-*n*-butylphosphine than with the less nucleophilic triphenylphosphine.

(6) The formation of aldehyde or ketone as byproduct (0–13%) was observed in the ozonolysis of phosphine imines derived from 1° or 2° azides, respectively.

(7) Kornblum, N.; Powers, J. W. *J. Org. Chem.* **1957**, *22*, 455.

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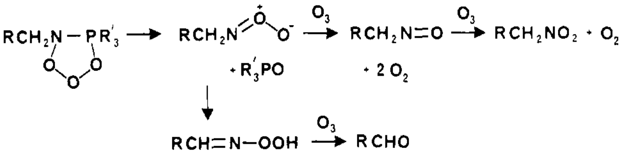
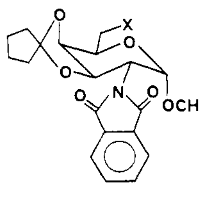
of interest to discover other oxidants that can replace ozone and modifications of the reaction that may produce higher yields.

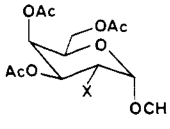
The mechanism by which a 1:1 adduct of ozone and a phosphine imine decomposes to form a nitro compound can only be surmised with the information now available. One attractive possibility is the following:



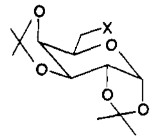
This mechanism requires that 3 equiv of ozone should be consumed relative to phosphine imine and also that the nitroso intermediate be converted by ozone to the corresponding nitro compound. Both of these are in accord with our expermental observations. 2-Nitroso-2,4,4-trimethylpentane[8] was oxidized instantaneously by ozone in CH_2Cl_2 at -78 °C to form the corresponding nitro compound.[9] Finally, this scheme is consistent with the observation that carbonyl compounds are formed as byproducts and are favored by an α-phenyl substituent in the azide precursor.[10]



1 X = NO_2
2 X = I
3 X = N_3
4 X = $N{=}P(C_6H_5)_3$



5 X = N_3
6 X = NO_2



7 X = N_3
8 X = NO_2

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(8) Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1984**, *25*, 491.

(9) The oxidation of α-chloro nitroso compounds to the corresponding nitro compounds by ozone at -60 °C has been reported: Barnes, M. W.; Patterson, J. M. *J. Org. Chem.* **1976**, *41*, 733.

(10) This research was assisted financially by grants from the National Institutes of Health and the Sweden-America Foundation.

A Sulfur-Ligated Molybdenum Complex That Reduces Dinitrogen to Ammonia. The Crystal and Molecular Structure of *trans*-$Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2SMe)$

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A primary objective of research into chemical systems that mimic the action of nitrogenase is the synthesis of dinitrogen complexes of molybdenum which contain sulfur-donor ligands.[1,2] Several iron-molybdenum-sulfur clusters have been prepared that have spectroscopic properties similar to the nitrogenase cofactor but they do not react with dinitrogen.[3] Dinitrogen complexes of transition metals containing sulfur ligands have proven difficult to make and to date only two complexes have been well characterized, one of osmium[4] and one of rhenium.[5] The complexes $[M(N_2)(SCN)(PPh_2CH_2CH_2PPh_2)_2]^-$, M = Mo, W, may contain an S-bonded SCN^- ligand.[6] An unstable complex, $Mo(N_2)_2(PMe_2Ph)_2(PhSCH_2CH_2SPh)$, was identified by elemental analysis as being the product of a substitution reaction of the sulfur chelate for phosphine ligands in *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ at -78 °C.[7] We have discovered that the complex *trans*-$Mo(N_2)_2(PMePh_2)_4$[8] undergoes a similar reaction with the ligand $PPh_2CH_2CH_2SMe$[9] to give the first stable molybdenum complex of this type, *trans*-$Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2SMe)$ (I). This complex reacts with sulfuric acid at 23 °C in methanol to give ammonia.

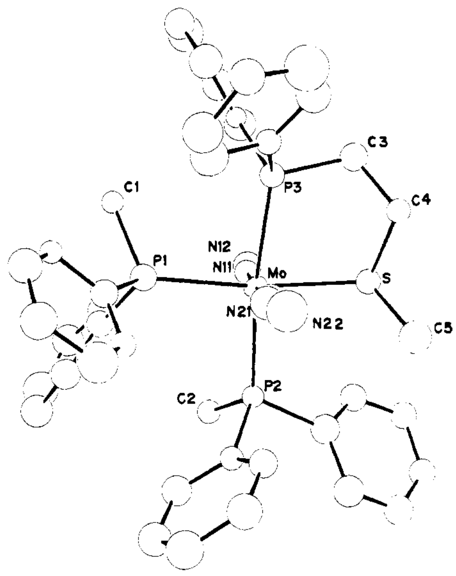

Figure 1. Molecular structure of I.

Complex I was prepared by stirring a suspension of $Mo(N_2)_2(PMePh_2)_4$ with 1.2 equiv of $PPh_2CH_2CH_2SMe$ in ether/benzene (5/1, v/v) for 2 h under dinitrogen. The product was isolated as slightly oxygen-sensitive, red-purple crystals by adding ether to the concentrated reaction solution and cooling to 5 °C (yield 40%). The complex was fully characterized[10] and a preliminary single-crystal X-ray structure determination has verified its molecular structure (Figure 1).[11] The coordination geometry

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(3) See references in: Averill, B. A. *Struct. Bonding (Berlin)* **1983**, *53*, 59.

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(7) Aresta, M.; Sacco, A. *Chim. Ital.* **1972**, *102*, 755.

(8) (a) George, T. A.; Kovar, R. A. *Inorg. Chem.* **1981**, *20*, 285. (b) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2139. (c) Azizian, H.; Luck, R.; Morris, R. H.; Wong, H. *J. Organomet. Chem.* **1982**, *238*, C24. (d) Morris, R. H.; Ressner, J. M. *J. Chem. Soc., Chem. Commun.* **1983**, 909.

(9) (a) Ross, E. P.; Dobson, G. R. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2363. (b) Adams, R. D.; Blankenship, C.; Segmuller, B. E.; Shiralian, M. *J. Am. Chem. Soc.* **1983**, *105*, 4319. (c) Bressan, M.; Morandini, F.; Rigo, P. *Inorg. Chim. Acta* **1983**, *77*, L139.

(10) Anal. Calcd for $C_{41}H_{43}N_4P_3SMo$: C, 60.59; H, 5.33; N, 6.89. Found: C, 60.90; H, 5.43; N, 6.33. IR (toluene) 2014 w, 1942 s cm^{-1}; ^{31}P NMR (THF, 85% H_3PO_4, atom numbers refer to Figure 1) 64.1 (dd, P(3)), 32.4 (dd, P(1)), 23.4 ppm (dd, P(2)), $^2J_{12} = 12.4$, $^2J_{13} = 13.3$, $^2J_{23} = 117.5$ Hz; ^1H NMR (C_6D_6, Me_4Si, refer to Figures 1 and 2, supplementary material) δ 1.44 (d, $^4J_{PH} = 1.0$ Hz, H_3CS), 1.63 (d, $^2J_{PH} = 5.0$ Hz, $H_3C(1)$), 1.77 (d, $^2J_{PH} = 5.0$ Hz, $H_3C(2)$), 1.86 (dd, $^3J_{PH} = 6.0$, $^2J_{HH} = 2.0$, $^3J_{HH} \leq 1$ Hz, HC(4)), 1.89 (s, br, $^2J_{PH}$, $^2J_{HH}$, $^3J_{HH} \leq 2$ Hz, $H_2C(3)$), 2.02 (dd, $^3J_{PH} = 4.0$, $^2J_{HH} = 2.0$, $^3J_{HH} < 2$ Hz, HC (4)).

(11) Crystal data for I: small red plates were obtained from benzene/ether solutions after several attempts. The small crystals scattered X-rays poorly so that only a partial data set was collected and this has limited the precision of the data. Space group: *Pbca*; $a = 18.48$ (2) Å, $b = 20.49$ (2) Å, $c = 20.67$ (2) Å, $U = 7825$ Å^3, and $D_{calcd} = 1.33$ g cm^{-3} for $Z = 8$; λ(Mo K$\bar{\alpha}$) = 0.71069 Å, μ(Mo K$\bar{\alpha}$) = 5.3 cm^{-1}. The structure was solved by the use of the Patterson Function and refined by least squares to $R = 0.095$, $R_W = 0.107$ for 1209 observed reflections ($I > 2.5\sigma(I)$). Selected bond distances (Å): Mo-S, 2.483 (8); Mo-P1, 2.443 (9); Mo-P2, 2.500 (8); Mo-P3, 2.457 (9); Mo-N11, 1.98 (2); Mo-N21, 2.00 (3).

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