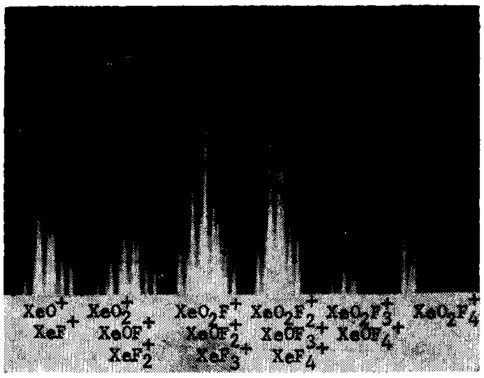

Figure 1. The mass spectrum of XeO_2F_4; source pressure, 2×10^{-6} Torr; ionizing electron energy, 70 eV.

made by the reaction $XeO_3F_2 + XeF_6 \rightarrow XeOF_4 + XeO_2F_4$ and identified by mass spectroscopy. It is the most volatile of the known xenon compounds and may therefore possess the symmetrical, nonpolar, D_{4h} symmetry predicted by Gillespie.[1] An attempt will be made to verify this supposition by obtaining the compound's vibrational spectra.

XeO_3Fe, which originally was made by the reaction of XeF_6 with Na_4XeO_6,[2] is made[3] in much better yield by the reaction of XeF_6 (in a Kel-F system) with XeO_4. It is destroyed by more than brief contact with the XeF_6, being converted to $XeOF_4$. While thus preparing XeO_3F_2 for a study of its vibrational spectra,[4] an extremely small xenon pattern corresponding to $XeO_2F_4^+$ was observed in its mass spectrum; apparently XeO_3F_2 is fluorinated by XeF_6 to XeO_2F_4 which then decomposes rapidly in the presence of XeF_6 to $XeOF_4$ and O_2. By conducting this reaction in solvent $XeOF_4$ it was possible to increase sufficiently the steady-state amount of XeO_2F_4 to allow a sufficient quantity to be separated and identified (Figure 1) by its qualitative mass spectrum.

In addition to the parent molecule ion all fragment ions to be expected from XeO_2F_4 are observed, and no other, permitting unambiguous identification of the compound. A notable feature of the spectrum is the relative abundance of the molecule ion which, unlike the molecule ions of all other xenon compounds, is more intense than the fragment ions formed by removal of one F or one O. The smallest ion in the spectrum is XeF_4^+ and the largest is $XeOF_3^+$.

The yield of XeO_2F_4 from this reaction is quite small but no other fluorinating agents have been found to make the compound. ClF_3 and ClF_5 react as reducing agents with XeO_3F_2, being oxidized to ClO_3F with formation of lower xenon compounds. SbF_5 and IF_7 apparently form solid adducts with XeO_3F_2, but no XeO_2F_4. FSO_2OH was not observed to react with XeO_4.

Solid samples of XeO_3F_2 and XeO_2F_4 give mass spectra of comparable intensity when the XeO_2F_4 is at a temperature about 20° lower than the temperature of the XeO_3F_2, showing the greater volatility of XeO_2F_4. This difference in volatility is sufficient to allow separation by fractional distillation. Residual XeO_3F_2 can then be combined with XeF_6 and XeO_4 to make more XeO_2F_4. A background of $XeOF_4$ was observed in the Kel-F line after distillation of XeO_2F_4, indicating some decomposition of XeO_2F_4 to $XeOF_4$, even in the absence of XeF_6.

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Oxidation of Organic Compounds with Cerium(IV). XIV. Formation of α-Azido-β-nitratoalkanes from Olefins, Sodium Azide, and Ceric Ammonium Nitrate[1]

Sir:

It has been known for some time that ceric salts oxidize metallic azides to nitrogen quantitatively.[2] The azido radical has been suggested as an intermediate[2c] and there seems to be little doubt that the azido radical exists since it has been observed spectroscopically during flash photolysis of aqueous sodium azide solutions.[3]

$$Ce^{IV} + N_3^- \longrightarrow Ce^{III} + N_3\cdot$$

$$2N_3\cdot \longrightarrow 3N_2$$

The possibility of the intermediacy of the azido radical during the reaction of cerium(IV) and azide ion led us to attempt to trap the azido radical by carrying out the reaction in the presence of olefins.

The oxidation of sodium azide by ceric ammonium nitrate (CAN) in acetonitrile has been shown to yield quantitatively stochiometric amounts of nitrogen.[4] The addition of an olefin causes an almost complete cessation of gas evolution and the products isolated have azide and nitrate functional groups as inferred from their ir spectra (2110 and 1645 cm^{-1}, respectively[5]). Cyclohexene, 1-methylcyclohexene, 1,3,5-cycloheptatriene, norbornene, α-pinene, α-methylstyrene, stilbene, 2,4-dimethylbutadiene, and 1,4-diphenylbutadiene are some of the olefins which suppress gas evolution. Gas evolution is not suppressed by diethyl fumarate, maleic anhydride, 4,4-dimethylcyclohexenone, phenylacetylene, 2-methyl-3-butyn-2-ol, *trans*-cinnamic acid, or cholesterol (perhaps due to low solubility in the reaction mixture). These unsaturated compounds can be recovered intact.

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[1] (a) Part XIII: W. S. Trahanovsky, M. D. Robbins, and D. Smick, *J. Amer. Chem. Soc.*, **93**, 2086 (1971). (b) This work was partially supported by Public Health Service Grant No. GM 13799 from the National Institute of General Medical Sciences and Grant No. GP-18031 from the National Science Foundation. We are grateful for this support. (c) Based on work by M. D. R. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

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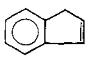
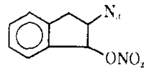
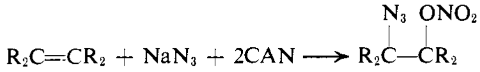
Table I. Absolute Yields of Products from the Oxidation of Sodium Azide by Ceric Ammonium Nitrate in the Presence of Olefins

Substrate (mmol)	NaN_3, mmol	CAN, mmol	Product	Yield, %[a,b]
 (4.4)	4.7	10.0		70 ± 1
trans-$PhCH{=}CHCH_3$[c] (4.3)	4.5	9.2	$PhCH(-O_2NO)CH(-N_3)CH_3$	76 ± 1
$PhCH{=}CH_2$ (4.9)	5.3	10.0	$PhCH(-ONO_2)CH_2N_3$	73 ± 1
n-$C_4H_9CH{=}CH_2$ (6.0)	6.1	12.8	*n*-$C_4H_9CH(-ONO_2)CH_2N_3$	56 ± 7[d]
n-$C_3H_7(CH_3)C{=}CH_2$ (6.0)	6.0	12.8	*n*-$C_3H_7(CH_3)C(-ONO_2)CH_2N_3$	49 ± 3

[a] Yield of unpurified products determined by nmr using dibenzyl ether as internal standard. [b] Standard deviations are based on at least two runs. [c] Both erythro and threo isomers were formed. [d] The large deviation is due to problems with emulsion formation in the work up.

The products derived from the reactions with several olefins were characterized as α-azido-β-nitratoalkanes.

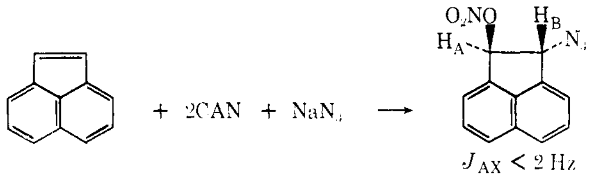


$$R_2C{=}CR_2 + NaN_3 + 2CAN \longrightarrow R_2\overset{\displaystyle N_3}{\overset{|}{C}}-\overset{\displaystyle ONO_2}{\overset{|}{C}}R_2$$

In Table I are listed several olefins for which the products have been characterized and absolute yields determined. Two equivalents of CAN (*ca.* 1 *M*) in acetonitrile was added to a solution of 1 equiv each of the olefin and sodium azide (each *ca.* 0.5 *M*) in acetonitrile[6] and the reaction was complete as soon as addition was over. Little or no gas was evolved. The products were isolated by flooding the reaction mixture with water and extracting with pentane. A known amount of standard, dibenzyl ether, was added and the yields were determined by nmr analysis. As no starting olefin remained the pentane extracts yielded only the azidonitrates. Further purification was accomplished by thin-layer chromatography or distillation and the products were identified by their nmr, ir, and mass spectra. Only the single isomers reported in Table I were observed. Also, no diazides were ever found.

The indane derivative was characterized in the following manner. The nmr spectrum of 2-azido-1-nitratoindane showed peaks at δ 7.32 (m, 4), 6.20 (d, 1, J = = 4 Hz), 4.27 (m, 1), and 3.6–2.6 (m, 2). The single proton signal at δ 6.20 is assigned to the proton on C-1 which bears the nitrate group. The chemical shift is that expected for a benzylic nitrate with a strong electron-withdrawing group on the β carbon atom.[7] The single proton signal at δ 4.27 is assigned to the proton on C-2 bearing the azide group, a shift very similar to that reported[8] for 2-azido-1-hydroxyindane of δ 3.92. The ir spectrum showed very strong bands at 2115, 1652, 1283, and 850 cm^{-1}. The bands at 2115 cm^{-1} and the last three bands are exactly those of azide and nitrate groups, respectively. An acceptabe elemental analysis was obtained for $C_9H_8N_4O_3$.[9] Finally, the mass spectrum further confirmed the assigned structure. With the ionization voltage at 16 eV, a small peak appears at *m/e* 220 ($M\cdot^+$ for $C_9H_8N_4O_3$). Among other fragmentations are noted peaks at *m/e* 178 (trace, loss of N_3), 145 (cobase, loss of HNO_2 and N_2), and 129 (cobase, loss of HNO_3 and N_2) which further confirm the presence of azide and nitrate functional groups.

The stereochemistry of addition was determined by adding across the double bond of acenaphthylene. The



reaction proceeded as for the olefins in Table I and the product was characterized by its nmr and ir spectrum. The observed coupling constant between H_A (δ 6.5) and H_X (δ 5.3) was less than 2 Hz. Dewar[10] has shown that in trans 1,2-disubstituted acenaphthenes, J_{AX} is of the order of 2 Hz while in cis isomers J_{AX} is greater than 6 Hz. Thus, a trans stereochemistry is assigned to the reaction.

The thermal stability of the azidonitrates seem to be reasonably high. 1-Azido-2-nitratohexane was refluxed in benzene, toluene, or glacial acetic acid for 16 hr and only starting material recovered. Furthermore 2′-azido-1′-nitratoethylbenzene and 1-azido-2-nitratohexane may both be molecularly distilled at *ca.* 100° at 0.1 mm pressure without significant decomposition.[11]

The details of the mechanism of this reaction are still not clear, but the regioselectivity of the reaction is consistent with the initial addition of the azide group.[12] This initial addition step could involve the azido radical or a cerium–azide species. The direction of addition is consistent with the addition of a radical but the lack of reaction of α,β-unsaturated carbonyl compounds suggests that some positive character develops on the α or β carbon atoms. If a radical intermediate is formed, it could be converted to the nitrate by one of the pathways suggested for other radical–nitrate conversions in CAN reactions.[13]

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(9) The elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz. In general, the azidonitrates did not give acceptable elemental analyses which may be a result of the close proximity of the two nitrogen-containing functional groups. Usually the carbon and nitrogen percentages were a few per cent too high; *e.g.* (for the product from 1-hexene): *Anal.* Calcd for $C_6H_{12}N_4O_3$: C, 38.29; H, 6.42; N, 29.77. Found: C, 41.19; H, 6.63; N, 33.16.

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(11) Although these azidonitrates seem to be thermally stable, one should exercise reasonable care in handling these compounds since some of them may decompose violently under certain conditions or may be physiologically active as are some alkyl nitrates and some alkyl azides. Dr. Spang of the Spang Microanalytical Laboratory, Ann Arbor, Mich., reported to us that the azidonitrate derived from acenaphthylene exploded violently upon heating.

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Other workers have reported the preparation of variously β-substituted alkyl azides from olefins, and in several cases the initial step is thought to be the addition of the azido radical to the olefin.[12,14]

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Lanthanide Shift Reagents. The X-Ray Structure of the Eight-Coordinate Bis(4-picoline) Adduct of 2,2,6,6-Tetramethylheptane-3,5-dionatoholmium, $Ho(dpm)_3(4\text{-}pic)_2$[1]

Sir:

Following the 1969 report by Hinckley,[2] there has been considerable interest shown[3–45] in paramagnetic lanthanide shift reagents. The mechanism of action of shift reagents is generally attributed to dipolar interactions[46] between the electronic magnetic moment and the nuclear spin moments which do not vanish for magnetically anisotropic complexes. Several authors have attempted to obtain information about the geometry of the substrate molecule with the assumption that the shifts should follow a $(3 \cos^2 \theta - 1)r^{-3}$ dependence.[47] This assumption is justified only for axially symmetric systems.[46e]

The dpm chelate of praeseodymium is known to be dimeric in the solid state with seven-coordination for each metal atom achieved by bridging oxygen atoms.[48] The **X**-ray structure of the seven-coordinate monohydrate, $Dy(dpm)_3H_2O$, has recently been reported.[49] In this structure the coordination polyhedron resembles a monocapped trigonal prism with the water molecule occupying a prism corner, a site of no real or approximate symmetry. While solid state and solution structures need by no means be identical, particularly in stereochemically nonrigid lanthanide complexes, it is of some interest to determine the **X**-ray structure of a shift reagent adduct as a focus for our thinking about its solution stereochemistry. Furthermore, in order to assess directly the dipolar shifts[46a] from single-crystal magnetic anisotropy[50] data,[51] the crystal structure of a shift reagent adduct is necessary. We report here the structure of the bis(4-picoline) adduct of $Ho(dpm)_3$.

The crystals, obtained by slow evaporation of a 4-picoline solution of $Ho(dpm)_3$,[52] are orthorhombic, space group *Pbcn* (D_{2h}^{14}, no. 60). The cell dimensions are $a = 10.260$ (8), $b = 23.08$ (3), $c = 20.23$ (2) Å, $V = 4789$ (4) Å^3, $Z = 4$. Computer-controlled diffractometer data were obtained using Mo K$\bar{\alpha}$ radiation (λ 0.71069 Å) and a θ–2θ scan technique. The structure was solved by direct methods[53] using the program MAGIC[54] employing 1121 reflections with $I \geq 3\sigma(I)$. Least-squares refinement yielded an R of 0.077 with isotropic temperature factors for all but the holmium and seven peripheral carbon atoms which were refined anisotropically.

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