Only one accurate study of bridging isocyanide groups has been reported, *i.e.*, for $[(h^5\text{-}C_5H_5)Ni(CNCH_3)]_2$, and only a very slight asymmetry was observed.[12]

The structure affords a good basis for understanding the complex reactivity patterns[1] of the compound with phosphines and other donors. It also can account for the infrared spectrum of $(C_5H_5)_2V_2(CO)_5$ and *mutatis mutandis* of the $(C_5H_5)_2V_2(CO)_4L$ derivatives if C(11)–O(1) is assumed to be replaced by L.

Finally, this structure is significant with respect to carbonyl scrambling processes since these presumably occur and account for the appearance of only one cyclopentadienyl proton resonance at 25°. Of particular interest is the likelihood that the orientation and bonding of each of the grossly unsymmetrical CO bridges resembles the transition configuration for a CO group as it passes back and forth from bridge to terminal positions in molecules such as $(C_5H_5)_2Fe_2(CO)_4$.[13]

[12] R. D. Adams, F. A. Cotton, and G. A. Rusholme, *J. Coord. Chem.*, 1, 275 (1971).

[13] Generous support by The Robert A. Welch Foundation, including funds for purchase of the diffractometer, is gratefully acknowledged.

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Reaction between Azide and Nitronium Ions. Formation and Decomposition of Nitryl Azide

Sir:

Although a significant effort has been associated with studies of the preparation and decomposition of nitrosyl azide (N_4O),[1] there has been no report of any attempt to prepare or examine the decomposition of the analogous nitryl azide (N_4O_2). By analogy to nitrosyl azide, which decomposes at temperatures as low as −50° to nitrogen and nitrous oxide,[1h] nitryl azide might also be expected to be unstable and exhibit the loss of nitrogen. We wish to report that nitryl azide can be directly prepared from nitronium and azide salts in organic solvents, is significantly more stable than nitrosyl azide, and decomposes solely to nitrous oxide.

When an equimolar amount (2.2 mmol) of nitronium tetrafluoroborate[2] in anhydrous acetonitrile (10 ml) is added to a stirred solution of lithium azide in the same solvent (160 ml) at temperatures below −10°, no apparent change is observed. When the solution is warmed above 0°, however, 4.4 mmol (2.0 equiv based on the amount of $NO_2^+BF_4^-$ used) of a colorless gas is rapidly evolved. Similar results are observed with sodium and potassium azides[3] and when carbon tetrachloride or chloroform is used as the solvent.[4] Spectrometric analyses of the acetonitrile and carbon tetrachloride solutions immediately after the nitronium and azide salts are added and mixed gives good evidence for the existence of nitryl azide.

The ir spectra of solutions obtained from the reaction between $NO_2^+BF_4^-$ and LiN_3 in both carbon tetrachloride and acetonitrile exhibit absorptions, given in Table I, that are consistent with the nitryl azide formulation. The band at 1609 (1602) cm^{-1} is consistent with the asymmetric stretching vibration of the nitro group.[5] The asymmetric stretching vibration of the azido group is commonly found between 2080 and 2200 cm^{-1};[6] however, the multiplicity of bands observed in this region does not permit this assignment to any single absorption given in Table I. Ir samples were filtered solutions obtained after mixing LiN_3 and $NO_2^+BF_4^-$ in the appropriate solvent. No attempt was made to examine the spectra at frequencies less than 1400 cm^{-1}. Each absorption assigned to nitryl azide was observed to decrease in intensity with time as the solution was warmed. Other absorptions, also observed, were assignable to dinitrogen tetroxide,[7] dinitrogen pentoxide,[7] or nitrous oxide based on the spectra of authentic samples (Table I); with the exception of those due to N_2O, these absorptions did not change in intensity with time as the solution was warmed. No absorption assignable to hydrazoic acid or nitric acid was observed.

Table I. Ir Absorption Frequencies of the Nitronium–Azide Reaction Product and of Related Compounds[a]

Bands assigned to N_4O_2,[b] cm^{-1}		
in CCl_4	in CH_3CN	Related compounds, cm^{-1}
2330 (m)	*c*	$NO_2^+BF_4^-$; 2360 (Nujol)[d]
2185 (s)	2190 (s, b)	LiN_3; 2100 (KBr)
2165 (s)		HN_3; 2140 (CCl_4)
2070 (m)	2090 (m)	N_2O_5; 1680 (CCl_4), 1660 (CH_3CN)
1609 (s)	1602 (s)	N_2O_4; 1810 (CCl_4), 1850 (CH_3CN)

[a] Spectra were taken on a Perkin-Elmer Model 621 recording spectrophotometer using, except when noted otherwise, NaCl salt plates. Frequencies from 4000 to 1400 cm^{-1} were recorded. Nitryl chloride was not observed in any spectrum. [b] Bands exhibiting greater than 20% transmission are reported; s = strong, m = medium, b = broad. [c] Band obscured by solvent absorption. [d] AgCl plates were used; spectrum was identical with that previously obtained: D. Cook, S. J. Kuhn, and G. A. Olah, *J. Chem. Phys.*, 33, 1669 (1960).

The ir spectra obtained exhibit absorptions at 2330 and 2070 (2090) cm^{-1} which are approximately those frequencies that would be expected for NO_2^+ and N_3^-, respectively. For spectra in acetonitrile the assignment of these bands to solvated nitronium and azide ions must be considered, since both $NO_2^+BF_4^-$ and LiN_3 are soluble in this solvent. However, similar spectra are observed in carbon tetrachloride in which neither $NO_2^+BF_4^-$ nor LiN_3 is soluble to any extent.[8] We must reasonably conclude that the absorptions given in Table I are due to covalently bound nitryl azide, and that this

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[1] (a) H. Thiele, *Ber.*, **41**, 2681 (1908); (b) F. Sommer, *ibid.*, **48**, 1884 (1915); (c) T. Werner, *Proc. Roy. Soc., London*, **28**, 257 (1911); (d) E. Oliveri-Mandala, *Gazz. Chim. Ital.*, **51**, 101 (1922); (e) F. Seel, R. Wölfe, and G. Zwarg, *Z. Naturforsch. B*, **13**, 136 (1958), and preceding papers; (f) C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 1702 (1960), and preceding papers; (g) K. Clusius and H. Knopf, *Chem. Ber.*, **89**, 681 (1956); (h) H. W. Lucien, *J. Amer. Chem. Soc.*, **80**, 4458 (1958).

[2] Obtained from Ozark-Mahoning Co. and purified prior to use.

[3] These salts are much less soluble in acetonitrile; although the same number of equivalents of gas is produced, gas evolution is slower than with lithium azide under similar conditions.

[4] The nitronium and azide salts are insoluble in these solvents. However, nitryl azide is readily detectable in the filtered solutions.

[5] R. N. Haszeldine, *J. Chem. Soc.*, 2525 (1953); B. G. Gowenlock and W. Lüttke, *Quart. Rev., Chem. Soc.*, **12**, 321 (1958).

[6] E. Lieber, C. N. R. Rao, A. E. Thomas, E. Oftedahl, R. Minnis, and C. V. N. Nambury, *Spectrochim. Acta*, **19**, 1135 (1963); D. A. Dows and G. C. Pimentel, *J. Chem. Phys.*, **23**, 1258 (1955).

[7] The amounts of these compounds were variable in different solutions and, when present, were due to the reaction of $NO_2^+BF_4^-$ with traces of water.

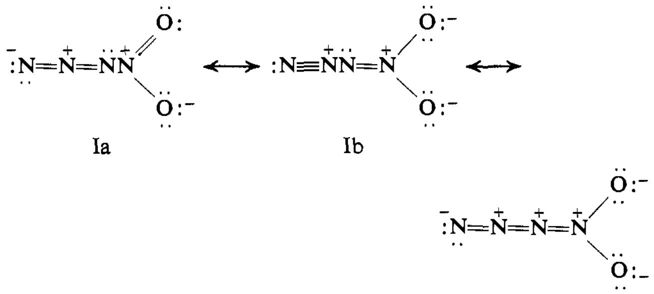
[8] Evaporation of carbon tetrachloride solutions that were used to obtain the ir spectra summarized in Table I left no residue.

species is formed in acetonitrile as well as in carbon tetrachloride.

Acetonitrile and carbon tetrachloride solutions of the colorless nitronium–azide reaction product, prepared under the same conditions as those for ir spectroscopy, exhibited no uv absorption above 250 nm. Under our conditions dinitrogen tetroxide exhibits a λ_{max} at 343 nm (in CCl_4), and dinitrogen pentoxide is observed with a λ_{max} at 265 nm (in CCl_4).

Mass spectral analysis[9] of a carbon tetrachloride solution of nitryl azide, filtered from unreacted nitronium and azide salts, shows peaks at *m/e* 42 (N_2) and 46 (NO_2), consistent with the known fragmentation of azides;[10] no molecular ion is observed. Individual solutions of carbon tetrachloride filtered from $NO_2^+BF_4^-$ and from LiN_3 showed no peak at *m/e* 46 or 42.

Although we have not isolated nitryl azide, the combined data support the existence of this species, which may be formulated by at least three Lewis structures (Ia, b, and c).



Ia

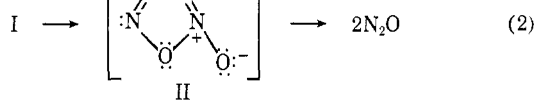
Ib

Ic

At temperatures above −10° nitryl azide decomposes to nitrous oxide, observed as the only gaseous product by both mass spectral and ir identification methods. In carbon tetrachloride solutions the ir absorptions for nitrous oxide are observed to increase in intensity as those of nitryl azide decrease in intensity. Two equivalents of N_2O are produced (based on the use of equimolar amounts of nitronium and azide salts), and eq 1 may be written to represent the stoichiometric relationship between reactants and products. Quantitative evolution of nitrous oxide is observed within 2 min at 25° and within 90 min at 0° in acetonitrile.

$$\mathrm{NO_2^+ + N_3^- \longrightarrow \underset{I}{N_4O_2} \longrightarrow 2N_2O} \qquad (1)$$

The decomposition of nitryl azide to nitrous oxide requires an oxygen transfer from the nitrogen of the nitro group to a nitrogen of the azido group and is quite unlike the decomposition of nitrosyl azide, which does not involve such a transfer.[1g] This novel transfer process may be represented as involving oxatetrazole 2-oxide (II, eq 2) and has analogy with the proposed decomposition of N_3CO_2.[11]



II

We are currently examining this reaction and its counterpart with organic azides in detail and studying related reactions with cyanates and thiocyanates.

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[9] Analyses were performed with a Finnigan Model 1015 quadrupole mass spectrometer using a variable leak inlet system.

[10] J. E. Gurst in "The Chemistry of the Azido Group," S. Patai Ed., Interscience, New York, N. Y., 1971, Chapter 3, and unreported results from our laboratory.

[11] D. W. Cornell, R. S. Berry, and W. Lwowski, *J. Amer. Chem. Soc.*, **87**, 3626 (1965).

[12] National Science Foundation Undergraduate Research Participant, summer 1972.

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A New Route to the Preparation and Configurational Correlation of Optically Active Arsines[1]

Sir:

In conjunction with current work on the pyramidal stability of arsines,[2] we have had occasion to develop a synthetic scheme which represents a significant improvement over existing methods for generating optically active arsines. Present synthetic routes require resolution of individual arsines,[3,4] or the resolution of quaternary arsonium salts with subsequent cleavage by cathodic reduction,[5] reduction with lithium aluminum hydride,[6] or cyanolysis.[7] In view of the potential usefulness of optically active arsines as ligands in coordination chemistry, a more versatile method is clearly desirable.

Our synthetic scheme is based, with some modifications, on an approach previously developed for the synthesis of optically active phosphine oxides[8] by way of nucleophilic displacement of menthoxide from diastereomerically enriched menthyl phosphinates. However, owing to the facile racemization of most arsine oxides by traces of water,[9] menthyl methylphenylthioarsinate (**1**) was chosen as a precursor. This compound was prepared in 76% overall yield by condensation of methylphenyliodoarsine[10] and sodium menthoxide (from *l*-menthol) to yield menthyl methylphenylarsinite (distilled at 116° (0.1 mm), hydrolyzes readily), followed by sulfurization (148°, neat). Separation of **1** into diastereomeric forms by fractional crystallization (hexane–isooctane)[11] afforded **1a**, mp

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[1] This work was supported by the National Science Foundation (GP-30257).

[2] G. H. Senkler, Jr., and K. Mislow, *J. Amer. Chem. Soc.*, **94**, 291 (1972); R. D. Baechler, J. P. Casey, R. J. Cook, G. H. Senkler, Jr., and K. Mislow, *ibid.*, **94**, 2859 (1972); R. H. Bowman and K. Mislow, *ibid.*, **94**, 2861 (1972).

[3] See, for example, I. G. M. Campbell and R. C. Poller, *J. Chem. Soc.*, 1195 (1956); K. Mislow, A. Zimmerman, and J. T. Melillo, *J. Amer. Chem. Soc.*, **85**, 594 (1963).

[4] B. Bosnich and S. B. Wild, *ibid.*, **92**, 459 (1970).

[5] L. Horner and H. Fuchs, *Tetrahedron Lett.*, 203 (1962).

[6] L. Horner and M. Ernst, *Chem. Ber.*, 103, 318 (1970).

[7] L. Horner and W. Hofer, *Tetrahedron Lett.*, 3321 (1966); L. Horner, W. Hofer, I. Ertel, and H. Kunz, *Chem. Ber.*, 103, 2718 (1970).

[8] (a) O. Korpiun and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 4784 (1967); (b) O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *ibid.*, **90**, 4842 (1968); (c) R. A. Lewis and K. Mislow, *ibid.*, **91**, 7009 (1969).

[9] See, for example, L. Horner and H. Winkler, *Tetrahedron Lett.*, 3271 (1964); Yu. F. Gatilov, L. B. Ionov, and S. S. Molodtsov, *Zh. Obshch. Khim.*, **42**, 1535 (1972).

[10] G. J. Burrows and E. E. Turner, *J. Chem. Soc.*, 1373 (1920).

[11] Diastereomers may also be separated by column chromatography (C_6H_6–C_6H_{12}, Florisil, all materials scrupulously dried).