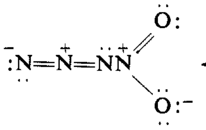
species is formed in acetonitrile as well as in carbon tetrachloride.

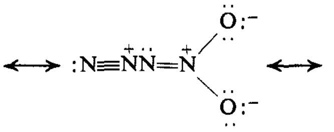
Acetonitrile and carbon tetrachloride solutions of the colorless nitronium–azide reaction product, prepared under the same conditions as those for ir spectroscopy, exhibited no uv absorption above 250 nm. Under our conditions dinitrogen tetroxide exhibits a λ_{max} at 343 nm (in CCl_4), and dinitrogen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

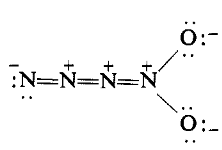
Although we have not isolated nitryl azide, the combined data support the existence of this species, which may be formulated by at least three Lewis structures (Ia, b, and c).



Ia



Ib

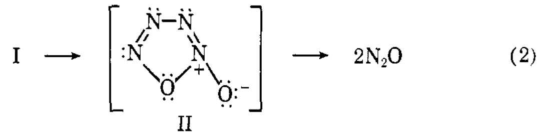


Ic

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.

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

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.

Acknowledgment. Support for this work from the National Science Foundation (GP-27587) is gratefully acknowledged. We wish to thank Mr. D. A. Kooistra for his preliminary work in this area and Dr. W. S. Mungall for his assistance in the mass spectral study.

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

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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).

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).

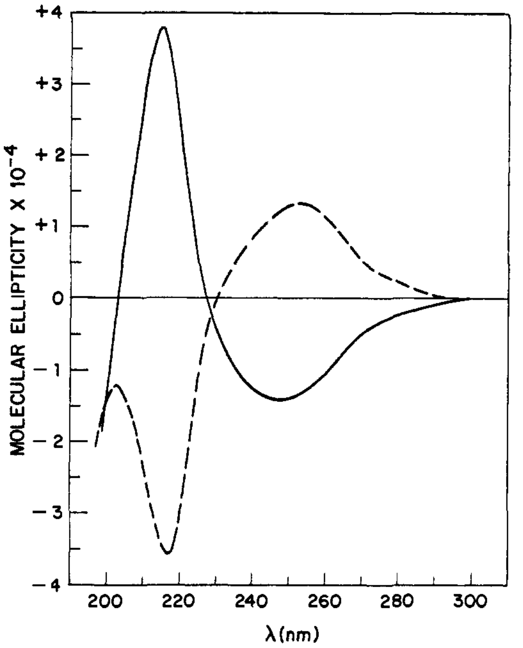
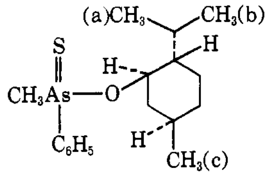


Figure 1. CD spectra (isooctane solution) of menthyl methylphenylthioarsinates: (— — —) for a diastereomerically pure sample of **1a**; (———) for a 95/5 mixture of **1b**/**1a**.

115–117°, and **1b**, mp 100–102°. The CD curves of



1

the two diastereomers are enantiomeric in type (Figure 1), as previously found for the analogous menthyl methylphenylphosphinates.[12] The ^{1}H nmr spectra (Table I) feature a characteristic pattern of signals in the isopropyl methyl region which closely resembles that of menthyl phosphinates,[12–14] menthyl methylphenylthiophosphinates,[15] and menthyl phenylphosphonates.[16] This pattern has proven useful as a reliable basis for correlating configurations in these systems.[12,14–17] Accordingly, based on the large upfield shift of one isopropyl methyl doublet for **1a**, the configurations at arsenic in **1a** and **1b** can be assigned as *R* and *S*, respectively.[18]

Table I. ^{1}H Nmr Chemical Shifts and Coupling Constants of Diastereomeric Thioarsinate Esters **1**^{a}

Compd	As-CH$_3$	C-CH$_3$ H$_a$	C-CH$_3$ H$_b$	C-CH$_3$ H$_c$
1a	7.84	9.60 (7.0)	9.26 (7.0)	9.08 (5.0)
1b	7.93	9.12 (7.0)	9.05 (7.0)	9.28 (5.0)

^{a} Chemical shifts are given in τ units, and coupling constants (in parentheses) are given in Hz.

Reaction of **1a** or **1b** with *2* molar equiv of alkyl- or aryllithium (RLi) in ether at −78°[20] leads *directly* to the target product, the optically active arsine. For example, reaction of **1a** (76% de[21] by nmr) with 2 molar equiv of *n*-propyllithium gave methylphenyl-*n*-propylarsine (**2**), $[\alpha]$D +10.7° (CH$_3$OH), in 51% yield, and reaction of **1b** (59% de) with 2 molar equiv of 2-naphthyllithium gave methylphenyl-2-naphthylarsine (**3**), $[\alpha]$D +1.7°, $[\alpha]_{350}$ +18.8° (CHCl$_3$) in 81% yield.

The configuration at arsenic is *R* in **1a** and *S* in (+)-**2**.[22,23] It follows that the overall reaction sequence proceeds with inversion of configuration at arsenic. The stereochemistry of the two steps in the sequence, nucleophilic displacement of menthoxide and reduction of the intermediate arsine sulfide, was established by the following experiments. Sulfurization (sulfur in ethanol, reflux) of (+)-**2** gave methyl phenyl-*n*-propylarsine sulfide (**4**), $[\alpha]$D +13.5° (CH$_3$OH), 62% ee.[24] Reaction of **1a** (76% de) with *1* molar equiv of *n*-propyllithium gave (+)-**4** of identical enantiomeric purity.[24] Since the sulfurization undoubtedly proceeds with retention at arsenic, (+)-**4** has the *R* configuration. The first step of the two-step sequence, **1a** → (+)-**4**, therefore proceeds with inversion and the second step, (+)-**4** → (+)-**2**, with retention. Similar results were obtained in the reaction of **1b** with 2-naphthyllithium. Reaction of **1b** (59% de) with *1* molar equiv of reagent gave methylphenyl-2-naphthylarsine sulfide (**5**), $[\alpha]$D +7.8° (CH$_3$OH). Sulfurization of (+)-**3** also gave **5**, $[\alpha]$D +9.1° (CH$_3$OH). Assuming overall inversion in the two-step sequence (**1b** → (+)-(*S*)-**3**) and retention in the sulfurization of (+)-**3**, the first step in the two-step sequence, **1b** → (+)-(*R*)-**5**, therefore proceeds with inversion and the second step, (+)-(*R*)-**5** → (+)-(*S*)-**3**, with retention. The reduction of (+)-**5** with *n*-butyl-

[12] R. A. Lewis, O. Korpiun, and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 4786 (1967); W. B. Farnham, R. K. Murray, Jr., and K. Mislow, *ibid.*, **92**, 5809 (1970).

[13] The relative sense of shift of the As-C*H*$_3$ signals also resembles that of the P-C*H*$_3$ signals in the analogous menthyl methylphenylphosphinates, and these signals may additionally be used to estimate the ratio of diastereomers in mixtures of the thioarsinate esters.

[14] R. A. Lewis, O. Korpiun, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4847 (1968); T. L. Emmick and R. L. Letsinger, *ibid.*, **90**, 3459 (1968); W. B. Farnham, R. K. Murray, Jr., and K. Mislow, *Chem. Commun.*, 146 (1971).

[15] A. W. Herriott, *J. Amer. Chem. Soc.*, **93**, 3304 (1971); N. J. De'ath, K. Ellis, D. J. H. Smith, and S. Trippett, *Chem. Commun.*, 714 (1971).

[16] W. B. Farnham, K. Mislow, N. Mandel, and J. Donohue, *J. Chem. Soc., Chem. Commun.*, 120 (1972).

[17] Most recently, this method has been extended to the assignment of configuration at silicon in menthoxysilanes: A. Holt, A. W. P. Jarvie, and G. J. Jervis, Third International Symposium on Organosilicon Chemistry, Madison, Wis., Aug. 1972.

[18] Note that the sequence rule[19] reverses the sense of *R* and *S* compared to the analogous phosphinate esters; see also ref 15.

[19] R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).

[20] The menthyl ester (**1**) undergoes thermal epimerization; equilibration is essentially complete in 1 hr at 95°.

[21] de = diastereomeric excess = $D_1 - D_2$, and ee = enantiomeric excess = $E_1 - E_2$, where *D* and *E* represent mole fractions of diastereomers and enantiomers, respectively; see J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, p 10.

[22] L. Horner, H. Winkler, and E. Meyer, *Tetrahedron Lett.*, 789 (1965).

[23] A negative Cotton effect centered near 243 nm ($[\theta]_{\max}$ −4300°) is observed for (+)-**2** in CH$_3$OH; see L. Horner and W.-D. Balzer, *Chem. Ber.*, **102**, 3542 (1969).

[24] The enantiomeric purity of **4** was established through the use of tris(3-heptafluoropropylhydroxymethylene-(+)-camphorato)europium.[25a] A doubling of the As-C*H*$_3$ nmr signal is observed upon addition of the chiral shift reagent (*ca.* 0.4 mol equiv), $\Delta\nu$ 1.5 Hz at 60 MHz. No such resonance doubling was observed for the analogous arsine.

[25] (a) R. R. Fraser, M. A. Petit, and J. K. Saunders, *Chem. Commun.*, 1450 (1971). (b) Dimethylphenylphosphine sulfide undergoes no observable reduction to the phosphine under comparable conditions (*n*-butyllithium in ether, −78°) or even at room temperature.

lithium to give **3**, $[\alpha]_D$ +1.4°, $[\alpha]_{350}$ +15.4° ($CHCl_3$), confirms this conclusion.[25b]

The stereochemical course of the organolithium displacement reaction parallels that of the analogous sulfoxide[26] and phosphine oxide[8] syntheses. Retention of configuration in the reduction of arsine sulfides by organolithium reagents is easily rationalized by assuming attack of the carbanionic species on sulfur, followed by extrusion of the arsine and formation of mercaptide ion. Perhaps, by analogy between this reaction and the reduction of phosphine sulfides by hexachlorodisilane, which proceeds with retention of configuration at phosphorus,[27] the reaction takes place by way of an intermediate of type $[R_3As{=}SR]^-$. Indeed, reduction of (+)-**5** with hexachlorodisilane under the conditions previously described for the reduction of the phosphorus analogs[27] gives **3**, $[\alpha]_D$ +1.4°, $[\alpha]_{350}$ +15.6° ($CHCl_3$), *i.e.*, the reaction proceeds with retention at arsenic.

Displacements of menthoxide from thioarsinate esters with lithium reagents proceeds with some degree of racemization, as was previously observed for reactions of organolithium reagents with analogous phosphinate esters.[8c] Since the enantiomeric purities of (+)-**4** obtained directly from reaction of **1a** (76% de) with *n*-propyllithium and of (+)-**4** obtained by sulfurization of (+)-**2** (from 76% de **1a**) are identical, the loss of stereospecificity does not occur in the desulfurization step.

Although the sequences described above have been restricted to only one precursor, thioarsinate **1**, it is anticipated that, by analogy with comparable phosphinates,[8] the method here described is a general one.

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[26] M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, *J. Amer. Chem. Soc.*, 90, 4835 (1968).

[27] G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *ibid.*, 91, 7203 (1969).

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A New Convenient Method of Producing Radical Anions Involving One-Electron Transfer from Trimethylsilylsodium[1-3]

Sir:

In the course of a survey of the reactions of trialkylsilyl anions,[2,4] we found that trimethylsilylsodium was excellent as an electron-transfer reagent to produce radical anions from a variety of compounds.

In typical examples 0.5–1.0 ml of a 0.5 *M* solution of trimethylsilylsodium in hexamethylphosphoramide (HMPA)[4a] was added from a hypodermic syringe under argon to 10–100 μg of naphthalene in a glass tube constructed with a 6 × 60 mm upper portion and a 0.5 × 80 mm thin-walled lower portion. The tube was then sealed off after three freeze–thaw cycles on a vacuum line.

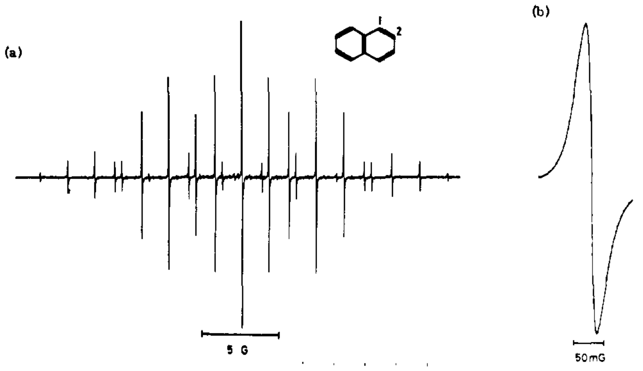

Figure 1. Esr spectra of the naphthalene radical anion in HMPA at room temperature, scan time 2 hr, modulation frequency 10 kHz, modulation amplitude 10 mG: (a) full spectrum, range 40 G, a_1 = 4.92 G, a_2 = 1.79 G; (b) an expanded spectrum of the center part, range 1 G.

An exceptionally well-resolved esr spectrum with the line width of 27 mG was recorded at room temperature as shown in Figure 1.[5] The spectrum was unchanged after storing this solution for 1 month at about −5°. Similar successful results were obtained from a wide variety of compounds including aromatic compounds, substituted benzenes, aromatic ketones, and olefins.

The reaction apparently involved one-electron transfer from trimethylsilylsodium to substrates. The trimethylsilyl radical thus formed can attack either HMPA or methoxytrimethylsilane[4a] to give finally hexamethyldisiloxane.

$$Me_3Si^- + ArH \longrightarrow Me_3Si\cdot + [ArH]^-$$

$$Me_3Si\cdot \xrightarrow[\text{or } Me_3SiOMe]{\text{solvent}} (Me_3Si)_2O$$

Although organic radical anions have been prepared successfully by reduction with alkali metals,[6,7] electrolytic reduction,[8-10] and photolytic reduction,[11] the following points can be made about the usefulness of the present new method.

(a) Preparation of the sample for esr measurement requires only simple injection of a small amount of the reagent from a stock solution to a substrate, no special technique being required. We have recently found a very simple method to prepare hexamethyldisilane, the requisite precursor to trimethylsilylsodium.[2]

(b) Only very small amounts of both substrates and solvent are required in the operation.

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[1] Silyl Anions. IV. For part III, see ref 2.

[2] H. Sakurai and A. Okada, *J. Organometal. Chem.*, 36, C13 (1972).

[3] Presented in part at the 3rd International Symposium on Organosilicon Chemistry as a plenary lecture by H. S., Madison, Wisc., Aug 21, 1972, and at the 11th Electron Spin Resonance Symposium, Kanazawa, Japan, Oct 8, 1972, Abstracts, p 38.

[4] (a) H. Sakurai, A. Okada, M. Kira, and K. Yonezawa, *Tetrahedron Lett.*, 1511 (1971); (b) H. Sakurai and A. Okada, *J. Organometal. Chem.*, 35, C13 (1972).

[5] All esr spectra were taken with a Varian Associates E-12 spectrometer.

[6] W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, 463, 1 (1928).

[7] (a) S. I. Weissman, J. Townsend, D. E. Paul, and G. E. Pake, *J. Chem. Phys.*, 21, 2227 (1953); (b) T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend, and S. I. Weissman, *J. Phys. Chem.*, 57, 504 (1953); (c) D. Lipkin, D. E. Paul, J. Townsend, and S. I. Weissman, *Science*, 117, 534 (1953).

[8] (a) D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, 82, 2771 (1960); (b) M. T. Melchior and A. H. Maki, *J. Chem. Phys.*, 34, 471 (1961).

[9] K. H. Hauser, A. Habich, and V. Franzen, *Z. Naturforsch. A*, 16, 836 (1961).

[10] (a) I. Bernal, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.*, 37, 1489 (1962); (b) P. H. Rieger and G. K. Fraenkel, *ibid.*, 37, 2795 (1962); (c) *ibid.*, 37, 2811 (1962); P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 85, 683 (1963).

[11] (a) P. B. Ayscough and R. Wilson, *Proc. Chem. Soc. (London)*, 229 (1962); (b) *J. Chem. Soc.*, 4412 (1963); (c) P. B. Ayscough, F. B. Sargent, and R. Wilson, *ibid.*, 5418 (1963).