($J_{PH\,trans}$ = 100, $J_{PH\,cis}$ = 25 Hz); **9**, δ -7.0 ($J_{PH\,trans}$ = 82, $J_{PH\,cis}$ = 25 Hz). In contrast, **1** and **2** react with $(Ph_3P)_3RuHCl(CO)$ in toluene at 60 °C to form $(Ph_3P)_4Ru_2HCl_2(CO)_2^+$, purified as the Ph_4B^- salt **11**. The ^{1}H NMR spectrum of this compound reveals a triplet of triplets, δ -13.2, J_{PH} = 43, 11 Hz, indicative of a hydride bridging two $(Ph_3P)_2RuCl(CO)$ units. Protonation of the polyhydride $(Ph_3P)_3OsH_4$ with **1** produces stereochemically nonrigid $(Ph_3P)_4OsH_3^+HC(SO_2CF_3)_2^-$ (**12**), $\delta(^1H)$ (27 °C) -9.83 (J_{PH} = 20 Hz, binomial pentet). Its $\{^1H\}^{31}P$ NMR spectrum at $\leq$-80 °C discloses two resonances at δ -9.4 and 40.7 in a 3:1 ratio, consistent with a static structure in which osmium is surrounded by a tetrahedron of phosphorus atoms with terminal hydride ligands positioned on the triangular faces of the OsP_4 core.[8]

In conclusion, we find that bis((perfluoroalkyl)sulfonyl)alkanes and -amines are unique and useful reagents for the synthesis of cationic organometallic compounds. Sulfonic acids having long perfluoroalkyl groups are especially useful in preparation of salts that have high solubility in aromatic hydrocarbons. Extension to other classes of organometallic compounds is under investigation as is the chemistry of the cationic materials reported here.

Acknowledgment. We are grateful to Robert Koshar, 3M Industrial and Consumer Sector Research Laboratory, for gifts of fluorochemical acids, and to the staff of the 3M Analytical and Properties Research Laboratory for spectroscopic and analytical data. L.H.P. is also acknowledges support by the National Science Foundation (Grant CHE-81-08490) of his contribution to this research.

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[8] The crystal structure of **12** will be reported elsewhere. Preliminary results confirm the presence of a slightly distorted OsP_4 tetrahedron.

Mechanism of Amination of Organolithiums by Alkoxyamines: Use of a Geometrical Test for Displacements on Heteroatoms

Peter Beak,* Anwer Basha, and Bruce Kokko

Department of Chemistry
University of Illinois at Urbana—Champaign
Urbana, Illinois 61801

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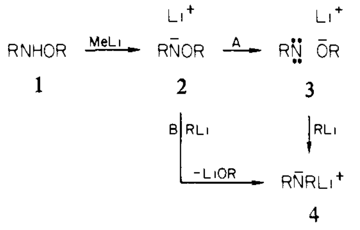
Alkoxyamine derivatives bearing at least one proton on nitrogen can be activated by methyllithium to give species that react with organolithium reagents to provide amines in synthetically useful yields as shown in eq 1.[1-3] The mechanism of the reaction has

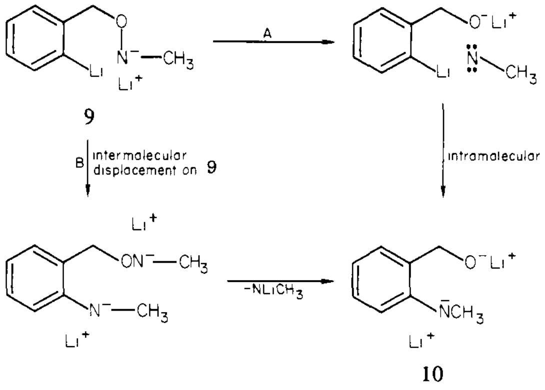
$$\mathrm{RLi} \xrightarrow[\text{2. } H_3O^+]{\text{1. RONHR-}CH_3Li} \mathrm{RNHR} \qquad (1)$$

not been determined. In this communication we report observations that support a process of displacement by the nucleophilic organolithium on the nitrogen of a lithium alkoxyamide in a transition state that has bond angles characteristics of an S_N2 reaction. The present results illustrate an approach, suggested by work done by Eschenmoser on nucleophilic displacements on carbon and by Kampmeier on radical displacements on sulfur, that should be generally useful for establishing the stereochemistry of displacements on atoms that do not maintain chirality.[4-6]

Scheme I

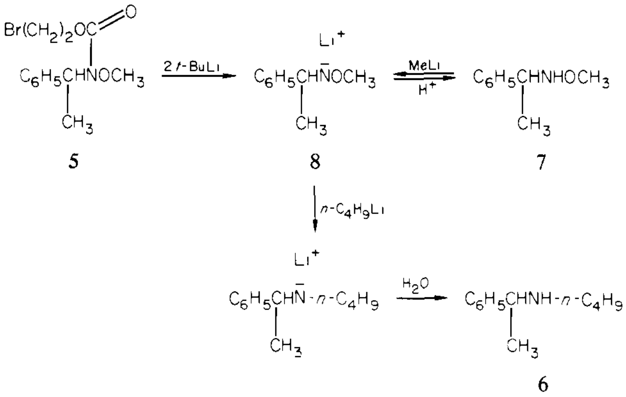


Scheme II



Two possible mechanisms for the amination are outlined in Scheme I. Initial deprotonation of the alkoxyamine **1** to **2** could be followed by loss of lithium methoxide to produce a nitreneoid **3**, which, by addition of an organolithium, would give the lithium amide product **4** as illustrated for pathway A. Alternatively, direct displacement on the initially formed anion **2** by the organolithium could be envisioned as shown for pathway B.

We have confirmed that reaction proceeds via a lithium alkoxyamide by formation of that intermediate by two different paths. Treatment of the bromocarbamate **5** with 2 mol of *tert*-butyllithium at -78 °C followed by *n*-butyllithium, warming to -15 °C, and addition of water provides the amine **6** in 64% yield. If an acid quench is added after the reaction with *tert*-butyllithium, the alkoxyamine **7** is obtained in 80% yield. The amine **6** is also obtained in 68% yield when **7** is treated with methyllithium prior to addition of *n*-butyllithium. These results rule out direct reaction of **7** and support the intermediacy of **8**.[7]



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[1] Sheverdina and Kocheshkov (Sheverdina, N. I.; Kocheshkov, Z. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1938**, **8**, 1825) first reported the use of methoxyamine with 2 equiv of organolithium to provide amines. For representative cases, see: Gilman, H.; Ingham, R. *J. Am. Chem. Soc.* **1953**, *75*, 4843. Acton, E. M.; Silverstein, R. M. *J. Org. Chem.* **1959**, *24*, 1487. Silver, M. W. *J. Am. Chem. Soc.* **1961**, *83*, 3487. Yamada, S. I.; T.; Shiorri, Oguri, T. *Chem. Pharm. Bull.* **1975**, *23*, 167. Erdik, E. **1975**, *Commun. Fac. Sci. Univ. Ankara, Ser. B.* **1980**, *26*, 83; *Chem. Abstr.* **1981**, *95*, 115634*p*. Wakefield, B. J. "Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1974; p 215.

[2] (a) Beak, P.; Kokko, B. J. *J. Org. Chem.* **1982**, *47*, 2822. (b) Beak, P.; Kokko, B. J. *Tetrahedron Lett.* **1983**, 561. (c) Quirk, R. P.; Chung, P. L. *Polymn. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, in press.

[3] For recent developments with other aminations, see: Reed, J. N.; Snieckus, V. *Tetrahedron Lett.* **1983**, 3795. Boche, G.; Bernheim, M.; Niessner, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 53. Trost, B. M.; Pearson, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 1054.

[4] Tenud, L.; Faroog, S.; Seible, J.; Eschenmoser, A.; *Helv. Chim. Acta.* **1970**, *53*, 2059.

[5] Kampmeier, J. A. *ACS Symp. Ser.* **1978**, *No.* **69**. Kampmeier clearly noted the potential of this approach for determining the geometry of displacement at heteroatoms that do not maintain chirality.

[6] For generalizations, see: Baldwin, J. E.; Lusch, M. J. *Tetrahedron* **1982**, *19*, 2939 and references cited therein.

[7] The conversion of **5** to **8** presumably involves bromine lithium exchange followed by loss of ethylene and carbon dioxide. The later loss could occur slowly to release small amounts of **8** for reaction during the warming period.

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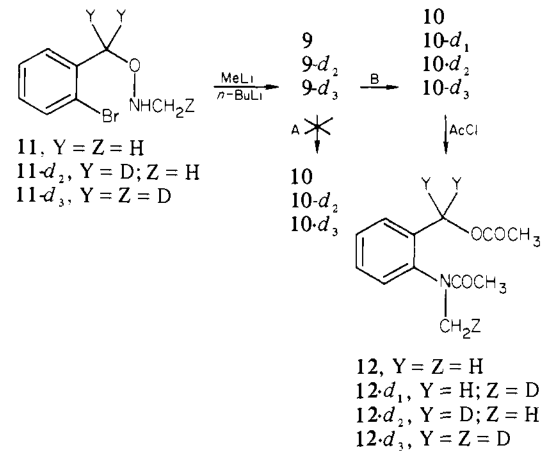
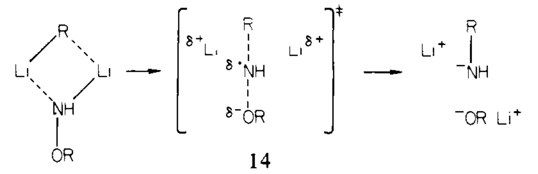
Scheme III



A distinction between possibilities A and B in Scheme I may be made on the basis of differences expected for each path in the conversion of **9** to **10** in Scheme II. The nitrenoid reaction of A would be expected to proceed without rigid geometrical requirement and should occur intramolecularly. Our earlier work on the conversion of *N*-(2-(2-bromophenyl)ethyl)methoxyamine to *N*-acetylindoline shows that intramolecular reaction is possible in an exocyclic mode.[2b,8] If the conversion of **9** to **10** proceeds by the direct displacement of path B a transition state in which the entering and leaving groups would be at 180° would be expected. That reaction would be of prohibitively high energy in the endocyclic mode in a five-membered ring, and an intermolecular reaction would be observed.[4-6]

The reaction of **11** to give **12** proceeds in 13% yield presumably via **9** and **10**.[9] The distinction between the intramolecular and intermolecular possibilities can be made by the double-labeling experiment shown in Scheme III. Thus a 51:18:31 mixture of **9**, **9**-d_2, and **9**-d_3 was generated from a 51:18:31 mixture of **11**, **11**-d_2, and **11**-d_3.[9] An intramolecular reaction would give **10**, **10**-d_2, and **10**-d_3 and subsequently **12**, **12**-d_2, and **12**-d_3 in a 51:18:31 ratio. Intermolecular reaction would give **10**, **10**-d_1, **10**-d_2, and **10**-d_3 and subsequently **12**, **12**-d_1, **12**-d_2, and 12-d_3 in a 35:16:33:15 ratio. The ratio of **12**, **12**-d_1, **12**-d_2, and **12**-d_3 obtained is 35 (±5):18 (±5):30 (±5):17 (±5) in accord with path B.[9] These observations may be taken to suggest that displacement of the alkoxy group requires bond angles that are characteristic of a concerted bimolecular substitution on a first-row element.[4-6,10]

Formally the displacement process of path B involves reaction of two anionic species, an interaction that should be repulsive.[11] However, organolithiums are generally aggregated, and a reasonable pathway involving associated species can be envisioned. In the simplest case, a dimer **13** in which the entering carbon is disposed on the back side of the nitrogen and the nitrogen oxygen bond is polarized, leading to transition state **14**, can be suggested.



13

14

This appears to be another case in which a proximity effect operating in a lithium complex provides access to a novel reaction pathway.[12] The implication of these results, that other nucleophilic reactions may take place via formal dianions and that the geometry of nucleophilic substitutions at heteroatoms can be established by this approach, are under study.

Acknowledgment. We are grateful to the National Science Foundation and the National Institute of Health for support of this work.

Registry No. 11, 88703-76-8; **12**, 88703-77-9.

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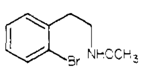
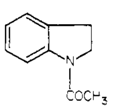
(8) The yield of ii from i for material that is spectroscopically uncontaminated is 78%, but losses on purification provide 42% of analytically pure ii. The expected products of intermolecular reaction of i are not observed.



i



ii

(9) The alkoxyamine **11** was prepared from *o*-bromobenzyl alcohol by the sequence of (1) hydroxyphthalamide, triphenylphosphine, and diethylazidodicarboxylete (65%), (2) hydrazine (98%), and (3) formaldehyde and pyridine–borane (66%). The structure of **12** was verified by independent synthesis from *o*-aminobenzyl alcohol by treatment with (1) acetyl chloride (56%) and (2) methyl iodide (35%). The intermediates were characterized by ^{1}H NMR, IR, and analysis, and **11** and **12** were characterized also by mass spectrometry. Deutrated **11** was prepared by reduction of *o*-bromobenzoic acid with lithium aluminum deuteride and by the use of pyridine–borane-d_3 in the third step of the synthesis of **11**. The deuterium composition of labeled reactants and products were determined by mass spectrometry. Details are available: Kokko, B. J. Ph. D. Thesis, University of Illinois, 1983, University Microfilms, Ann Arbor, Michigan.

(10) In the reaction via path B the loss of $LiNCH_3$ presumably occurs to provide **10**. The low yield of **12**, which may reflect the difficulty of amination ortho to a bulky group on an aromatic ring as well as the incursion of side reactions, does not compromise the mechanistic conclusions. Reaction via path A might be expected to produce methylnitrene, which would rearrange to methylene imine. Reactions of *N*-methylmethoxyamine give only methylamine products.[2b]

(11) It should be noted however, that M. Anbar and G. Yagel (Anbar, M.; Yagel, G. *J. Am. Chem. Soc.* **1982**, *84*, 1790) have reported a direct nucleophilic displacement on the chloramine anion.

(12) For diverse examples, see: Beak, P.; Hunter, J. E.; Jun, Y. M. *J. Am. Chem. Soc.* **1983**, *105*, 6350. Meyers, A. I.; Pansgrau, P. D. *Tetrahedron Lett.* **1983**, 4935. Comins, D.; Brown, J. D. *Ibid.* **1983**, 5465. Richey, H. G.; Heyn, A. S.; Erickson, W. F. *J. Org. Chem.* **1983**, *48*, 3821 and references cited therein.

Homo-Diels-Alder Reaction of Tricyclo[5.3.1.0^{4,9}]undeca-2,5-diene: A Molecule with Unusually Strong Through-Space Interaction in a 1,4-Cyclooctadiene System

Ryohei Yamaguchi,* Masakazu Ban, and
Mituyosi Kawanisi*

Department of Industrial Chemistry
Faculty of Engineering, Kyoto University
Kyoto 606, Japan

Eiji Ōsawa,* Carlos Jaime,[1] and Andrzej B. Buda[1]

Department of Chemistry, Faculty of Science
Hokkaido University, Sapporo 060, Japan

Shunji Katsumata

Institute of Applied Electricity
Hokkaido University, Sapporo 060, Japan

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The [2 + 2 + 2] cycloaddition of a 1,4-diene with a dienophile is a symmetry-allowed reaction[2] and has been known as the homo-Diels–Alder reaction for 25 years.[3] In contrast with the Diels–Alder reaction where a large variety of 1,3-diene systems

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(1) Hokkaido University Postdoctoral Fellow.

(2) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim, 1970; pp 101.

(3) Recent leading references on this subject: (a) Fickes, G. N.; Metz, T. E. *J. Org. Chem.* **1978**, *43*, 4057–4061 and references cited therein. (b) Jenner, G.; Papadopoulos, M. *Tetrahedron Lett.* **1982**, *23*, 4333–4336.

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