with aqueous acetic acid.[5b] Pure bradykinin (610 mg., 51% of the material liberated from the solid support) was obtained from the major Sakaguchi positive peak.

The product was homogeneous and indistinguishable from authentic bradykinin[7] by paper electrophoresis and paper chromatography (detected by ninhydrin and Sakaguchi reagents): R_{arg} 0.62 (0.1 M pyridine acetate, pH 5.0); R_{glu} 1.38 (formic acid–acetic acid–H_2O, 1.5:1:100, pH 2.1); R_f 0.50 (propanol–H_2O, 2:1); R_f 0.49 (sec-butyl alcohol–formic acid–H_2O, 100:16:16); R_f 0.26 (isoamyl alcohol–pyridine–H_2O, 35:35:30); $[\alpha]^{25}D$ −76.5° (c 1.37, 1 N acetic acid). Amino acid ratios were: arg, 1.90; pro, 2.71; phe, 2.04; gly, 1.00; ser, 1.01.

Anal. Calcd. for $C_{50}H_{73}O_{11}N_{15} \cdot 3CH_3CO_2H$: C, 54.2; H, 6.9; N, 16.9. Found: C, 54.3; H, 6.9; N, 17.2.

The synthetic bradykinin possessed the full biological activity of the natural hormone. It was compared quantitatively with an authentic standard in the isolated rat uterus assay and in the rat duodenum assay. Over the range of 10^{-10} to 10^{-9} g./ml., the two preparations were equally active in both tests.

The over-all yield of biologically active bradykinin was 32%. The total time required for the synthesis starting with t-BOC amino acids and ending with chromatographically pure bradykinin was 8 days.

(7) Obtained through the courtesy of Dr. E. D. Nicolaides, Parke, Davis & Company, Ann Arbor, Michigan.
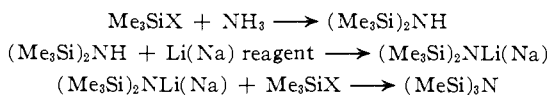
THE ROCKEFELLER INSTITUTE   R. B. MERRIFIELD
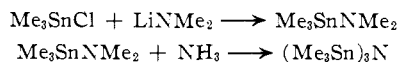NEW YORK 21, NEW YORK

Preparation of Tris(trimethylsilyl)- and Tris(trimethylstannyl)amines

Sir:

It is reported in the literature[1–3] that attempts to prepare tris(trimethylsilyl)amine directly by reaction of trimethylchlorosilane with ammonia failed, even at 500° with pyridine as solvent. Successful preparations of this material[2,3] and of the analogous tin compound, tris(trimethylstannyl)amine,[4] have required at least two steps, one of which involved the preparation of an N-lithio or N-sodio intermediate.

$$Me_3SiX + NH_3 \longrightarrow (Me_3Si)_2NH$$
$$(Me_3Si)_2NH + Li(Na)\ reagent \longrightarrow (Me_3Si)_2NLi(Na)$$
$$(Me_3Si)_2NLi(Na) + Me_3SiX \longrightarrow (MeSi)_3N$$

The tin compound has been prepared as follows.

$$Me_3SnCl + LiNMe_2 \longrightarrow Me_3SnNMe_2$$
$$Me_3SnNMe_2 + NH_3 \longrightarrow (Me_3Sn)_3N$$

The purpose of this paper is to describe a simple, convenient, one-step synthesis of these materials by the use of the novel new reagent, lithium nitride (I).[5] It has been found that a slurry of lithium nitride in tetrahydrofuran (THF) will react with trimethylchlorosilane (IIa) and trimethylchlorostannane (IIb) to give the corresponding tris(trimethylmetallo)amine (IIIa,b)

(1) R. O. Sauer and R. H. Hasek, J. Am. Chem. Soc., **68**, 241 (1946).
(2) U. Wannagat and H. Niederprum, Angew. Chem., **71**, 574 (1959).
(3) J. Goubeau and J. Jimenez-Barbera, Z. anorg. allgem. Chem., **303**, 217 (1960).
(4) K. Jones and M. F. Lappert, Proc. Chem. Soc., 358 (1962).
(5) Commercially available from Foote Mineral Company, Philadelphia 44, Pennsylvania.

in good yield. Koenig and co-workers[6] reported that lithium nitride reacts "with organotin halides, which presumably reacted metathetically, since the lithium halide separated" but did not indicate the nature of the other product.

$$Li_3N + 3Me_3MCl \longrightarrow (Me_3M)_3N + LiCl$$

I   II   III

a, M = Si; b, M = Sn
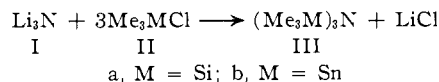
The general procedure used was as follows. To a slurry of 0.05 mole of I in 50 ml. of dry THF, maintained under an atmosphere of dry nitrogen, was added dropwise, with stirring, a solution of II, 0.15 mole in 50 ml. of THF, over a period of 1 hr. Care was exercised during the addition due to the extremely exothermic nature of the reaction. After the addition was completed the reaction mixture was heated at reflux for 2 hr. The major portion of the THF was removed by distillation, 150 ml. of petroleum ether (b.p. 30–60°) was added to the concentrate, and the mixture filtered to remove insoluble LiCl. The filtrate was concentrated and the residue distilled to give the desired product. The silyl compound (IIIa) was obtained in 72% yield and was identified by comparison of its infrared[3] and n.m.r.[7] spectra with values published in the literature and its elemental analysis and molecular weight. The stannyl compound (IIIb) was obtained in 59% yield and was identified by a comparison of its boiling point, 84° (.40 mm.), with the value published in the literature and by the determination of its molecular weight. Anal. Calcd: 505. Found: 515, 519. The n.m.r. of IIIb exhibited only a single peak, 11.0 c.p.s. downfield from tetramethylsilane (CCl_4 solution) consistent with its structure. No attempts were made to optimize the yields of these reactions.

It is expected that the reaction of lithium nitride with haloorganometallo compounds will be a general reaction and will be applicable to the preparation of a wide variety of other tris(organometallo)amines of the group III, IV, V, and VI elements. Work is proceeding along these lines.

(6) P. E. Koenig, et al., J. Org. Chem., **26**, 4777 (1961).
(7) H. Schmidbaur, J. Am. Chem. Soc., **85**, 2336 (1963).

POLYMER BRANCH   W. L. LEHN
NONMETALLIC MATERIALS DIVISION
AIR FORCE MATERIALS LABORATORY
U. S. AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Large Salt Effects and Mechanism in Acetone and Ether[1,2]

Sir:

Salt effects on rate of ionization of organic substrates can become enormous in poorly ionizing solvents.[3] In this communication we call attention to the magnitude and specific pattern of such salt effects on ionization of p-methoxyneophyl p-toluenesulfonate[3] (ROTs) and the spirodienyl p-nitrobenzoate[4] (I-OPNB). Some mechanistic features of salt-promoted ionization are also discussed.

Salt effects on rate of ionization of ROTs in acetone,[3] measured by acid production, are moderately large. Addition of 0.05 M LiClO$_4$ increases the rate by a factor of 3.4. With I-OPNB first-order rate constants for production of HOPNB and tetralin show much greater

(1) Research supported by the National Science Foundation.
(2) Research sponsored by the U. S. Army Research Office (Durham).
(3) S. Winstein, S. Smith, and D. Darwish, J. Am. Chem. Soc., **81**, 5511 (1959).
(4) E. C. Friedrich and S. Winstein, Tetrahedron Letters, **No. 11**, 475 (1962).