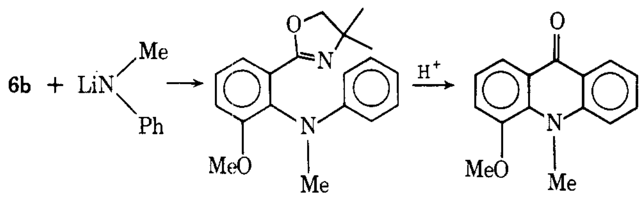
hanced by strong chelation of the lithium cation. This mode of entry would be relatively free of nonbonded interactions thus allowing bulky amino substituents easy access to the sp^2 carbon at the ortho position. There exists the remote possibility that these displacements as well as those previously reported[2] using alkyl metallics are proceeding via an electron-transfer process and this aspect is currently under investigation.

An interesting example which may have considerable potential in heterocyclic syntheses is given by the reaction of **6b** with the lithio salt of *N*-methylaniline. The adduct **9** was formed in 50% yield (+50% recovery of **6b**) which gave, after acidic hydrolysis, the acridone **10** (mp 91 °C, 40%)[6] and the expected uncyclized benzoic acid (25%).



9 **10**

These preliminary results indicate that the amination of *o*-(methoxyaryl)oxazolines may provide additional methodology to aromatic substitution and further studies in this respect are in progress.

Acknowledgment. The authors wish to express their gratitude to the Army Research Office (Durham) for financial support of this work.

References and Notes

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(2) A. I. Meyers and E. D. Mihelich, *J. Am. Chem. Soc.*, **97**, 7383 (1975).
(3) A number of nucleophilic reagents have been surveyed in addition to alkyl and aryl metallics and the results to date indicate that enamines, thiolates, enolates, and other "soft" anions fail to substitute the methoxyl group. The reactions observed with these nucleophiles are those which cleave the methyl-oxygen bond. Details of these reactions will be reported in the full account of this work.
(4) The oxazolines **6a** and **6b** were prepared from the corresponding *o*-methoxybenzoic acids, thionyl chloride, and 2-amino-2-methylpropanol as described previously [A. I. Meyers et al., *J. Org. Chem.*, **39**, 2787 (1974)].
(5) At this time, the only lithio amine which failed to displace the methoxy group is 2,2,6,6-tetramethylpiperidine.
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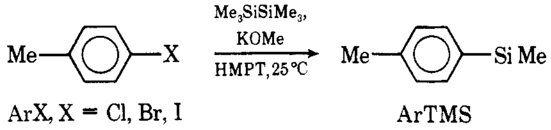
Trimethylsilyl Anions. Direct Synthesis of Trimethylsilylbenzenes

Summary: The reaction of aryl halides with hexamethyldisilane and potassium methoxide (or sodium methoxide or methyllithium) in hexamethylphosphoric triamide (HMPT) affords the corresponding trimethylsilyl-substituted benzene and some reduction product.

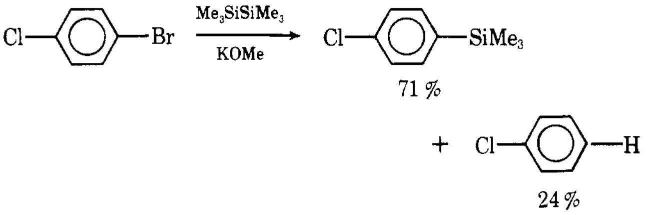
Sir: Silyl anions are highly reactive nucleophiles and one-electron-transfer reagents.[1,2] The synthetic utility of trimethylsilylpotassium,[2g,h] -sodium,[2d] and -lithium,[2j] (TMSK, TMSNa, TMSLi, respectively) has increased owing to recently reported convenient methods of in situ generation from the reaction of hexamethyldisilane and potassium methoxide, sodium methoxide, and methyllithium, respectively. The reaction of silyl anions and aromatic halides has been known in the literature for over 20 years but the chemistry reported to date has not been very clean.[2a,d] We report a mild one-step procedure at 25 °C for the conversion of aryl halides to trimethylsilylbenzenes, formally a trimethylsilyldehalogenation on an aromatic compound.[3] Trimethylsilyl-substituted benzenes are very useful intermediates for directing specific mild electrophilic substitution on carbon as shown in the work of Eaborn and coworkers.[4]

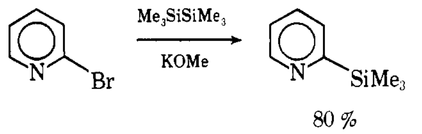
Reaction of aryl halides, ArX (X = Cl, Br, I), with hexamethyldisilane and KOMe (or NaOMe or MeLi) in anhydrous HMPT at 25 °C under argon for 3 h affords the corresponding substitution product ArSiMe$_3$ (92–63%) and some reduction product ArH (4–26%) depending mostly on the choice of aryl halide. Typical yields are shown in Table I.



In general we find that (1) the ratio of substitution/reduction increases in the direction I < Br < Cl; (2) this ratio is relatively insensitive to the choice of metal cation; (3) the rates of reaction appear to decrease in the direction I, Br > Cl; (4) substitution occurs exclusively on the carbon bearing the halogen substituent; (5) the ratio of substitution/reduction increases as substituent position on the aromatic ring changes from ortho > meta > para;[5] (6) yields and substitution/reduction ratios are sensitive to temperature.[6]

Differences in reactivity of the halogen substituent could be distinguished on the same molecule. 1-Bromo-4-chlorobenzene reacts with hexamethyldisilane and KOMe to afford reaction mostly (>95%) at the carbon bearing bromine.[7] Substitution also occurs in heteroaromatic molecules, for example, 2-bromopyridine. No reduction product was found in this case.





The mechanisms of these reactions are not yet known. In a formal sense, the silylated product is derived from a nucleophilic aromatic substitution reaction. At least four mechanisms can be considered: (1) the aryne mechanism, (2) direct nucleophilic substitution (S$_N$Ar), (3) halogen–metal interchange to afford an ArM (M = K, Na, Li) intermediate, (4) radical-anion chain reaction (S$_{RN}$1).[8] The aryne pathway can be excluded based on the stereochemical results. Concerted nucleophilic displacement at aromatic carbon is more difficult to eliminate,[8b] especially in view of the strong nucleophilicity of silyl anions. However, this S$_N$Ar mechanism is seldom encountered with unactivated aryl halides and requires a second competing pathway for reduction product. Quenching the reaction mixture of iodobenzene and TMSK with D$_2$O after 5 min affords reduction product (benzene) with 30% d_1 incorporation.[9] This is permissive evidence that at least

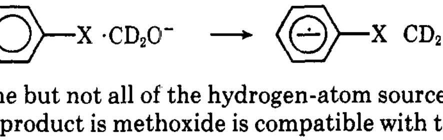
Table I. Reactions of Trimethylsilyl Anions with Aryl Halides

Reagent	ArX	ArTMS	ArH	Total[a] yield, %	ArTMS/ ArH
Me_3SiK[b]	Cl	86	5	91	17
	Br	92	7	99	13
	I	68	26	94	2.6
Me_3SiNa[c]	Cl	87	5	92	17
	Br	91	8	99	11
	I	70	27	97	2.6
Me_3SiLi[d]	Cl	69	4	73	17
	Br	84	7	91	12
	I	63	26	89	2.4

[a] Percent yield based on aryl halide determined by VPC analysis after workup (20 ft × ⅛ in. 10% SE-30; internal standard, decane). [b] Generated by the reaction of hexamethyldisilane and potassium methoxide in HMPT at 25 °C. [c] Generated by the reaction of hexamethyldisilane and sodium methoxide in HMPT at 25 °C. [d] Generated by the reaction of hexamethyldisilane and methyllithium in HMPT/Et_2O at 0 °C, then allowed to warm to 25 °C.[2j]

part of the reaction may be proceeding via a phenylpotassium intermediate.[2a] Whether this phenyl anion comes from nucleophilic attack of silyl anion on halogen or from the reduction of phenyl radical by silyl anion cannot be distinguished at this time.

The relative rates with regard to halogen substitution and the observation of reduction product are reminiscent of other aromatic nucleophilic substitution reactions proposed to proceed by radical-chain mechanisms.[8] Sakurai has shown that trimethylsilyl anion is a convenient one-electron donor.[2e] Replacement of CH_3OK with CD_3OK[10] in the reaction of iodobenzene and hexamethyldisilane affords reduction product with 64% d_1 incorporation,[9] consistent with the chain-carrying properties ascribed to methoxide found in the growing list of aromatic free radical-chain mechanisms.[8,11] The observation that some but not all of the hydrogen-atom source in the reduction product is methoxide is compatible with the finding that, for the cases using TMSLi, which contains no methoxide owing to the method of generation, reduction product is still observed. Further investigations will be necessary before these reactions are fully understood.[12] However, it appears from the present deuterium incorporation data that the iodobenzene reaction with TMSK may involve *at least* two aromatic intermediates, phenyl radical and phenyl anion.



A typical procedure is as follows. To 1.91 g (0.027 mol) of potassium methoxide[13] in 50 mL of anhydrous HMPT[14] under argon at 25 °C was added 3.12 g (0.018 mol) of *p*-bromotoluene followed by 4.38 g (0.029 mol) of hexamethyldisilane.[15] The yellow reaction mixture was allowed to stir for 6 h. Aqueous NH_4Cl (5%) was added to the reaction mixture and this was extracted twice with pentane. The pentane layers were combined and dried (Na_2SO_4). Distillation under reduced pressure afforded 2.46 g (82% isolated yield) of *p*-tolyltrimethylsilane, 99.6% pure by vapor phase chromatography (VPC).[17]

Acknowledgment. The authors are grateful to the National Science Foundation (MPS 75-06776) for their generous support of this work. We appreciate stimulating discussions with Professor David A. Evans.

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(4) For a review of this field, see C. Eaborn, *J. Organomet. Chem.*, **100,** 43 (1975).

(5) For example, the reaction of *o*-, *m*-, and *p*-bromotoluene with TMSK afforded substitution/reduction ratios of 3, 10, and 13, respectively.

(6) As the temperature is raised above 25 °C the yields and ratio of substitution/reduction decreases. If the reaction is run at 0 °C in HMPT/Et_2O (10:1 ratio), the substitution/reduction ratio apparently increases although the mass balance (yield) of the substitution product does not increase significantly.

(7) Benzene, 1-bromo-4-trimethylsilylbenzene, and bromobenzene were not observed in the reaction mixture (<1%) under analytical conditions (VPC) independently shown to separate authentic mixtures. Trimethylsilylbenzene and 1,4-bis(trimethylsilyl)benzene were observed in 1 and 2% yields, respectively.

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(9) Determined by the Caltech Analytical Facility on a Du Pont 21-492B mass spectrometer.

(10) Made from CD_3OD (Aldrich) and potassium hydride.

(11) In the cases using potassium and sodium methoxide, *p*-methoxytoluene was never observed in the products under VPC conditions capable of detecting <1% of this compound.

(12) For recent work on the reactions of trialkylstannyllithium, and -sodium with aryl halides, see J. P. Quintard, S. Hawrette, and M. Pereyre, *J. Organomet. Chem.*, **112,** C11 (1976), and H. G. Kuivila and K. R. Wursthorn, *J. Organomet. Chem.*, **105,** C6 (1976), respectively.

(13) Obtained from Alfa.

(14) Distilled from lithium wire under reduced pressure and redistilled from CaH_2. HMPT was handled with the precautions appropriate to a potential carcinogen.

(15) Hexamethyldisilane was prepared by the method of Gilman.[16]

(16) H. Gilman, K. Shiina, D. Aoki, B. Gaj, D. Wittenberg, and T. Brennan, *J. Organometal. Chem.*, **13,** 323 (1968).

(17) 20 ft × ⅛ in. SE-30, flame ionization detector, electronic integration.

(18) National Science Foundation Predoctoral Fellow, 1973–1976.

(19) Alfred P. Sloan Research Fellow, 1977–1979.

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Synthesis of Cycloalkenes by Intramolecular Titanium-Induced Dicarbonyl Coupling

Summary: Cycloalkenes of ring size 4–16 are prepared in good yield by treatment of dicarbonyl compounds with a reagent prepared from $TiCl_3$/Zn–Cu.

Sir: We have reported recently that ketones and aldehydes can be reductively coupled to olefins by treatment with low valent titanium.[1-3] The intermolecular version of this reaction works best when identical carbonyl species are coupled to give symmetrical olefins,[2] but we have also demonstrated that, in

$$R_2C{=}O \xrightarrow{Ti^0} \left\{ \begin{array}{c} {}^-O \quad O^- \\ | \qquad | \\ R_2C{-}CR_2 \end{array} \right\} \longrightarrow R_2C{=}CR_2$$