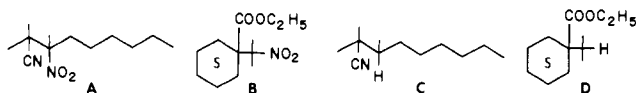


Table I. The Replacement of the Nitro Group by Hydrogen at 25°C^a

A	Solvent	Reaction time, h	Yield, % ^b
H	HMPA	8	94
CN	DMF	15	91
C ₆ H ₅ C(=O)-	DMF	18	76
C ₆ H ₅ SO ₂ -	DMF	8	83
3,5-(CF ₃) ₂	DMF	20	84
CN	HMPA	16 ^c	82
C ₆ H ₅ C(=O)-	HMPA	12 ^c	80
C ₆ H ₅ SO ₂ -	HMPA	10 ^d	80
3,5-(CF ₃) ₂	HMPA	16 ^c	77

Nitro compd	Solvent	Reaction time, h	Product	Yield, % ^b
<i>tert</i> -Nitrooctane	HMPA	46	Isooctane	55
1-Nitroadamantane	HMPA	42 ^e	Adamantane	71
A ^f	Me ₂ SO	17	C ^f	92
1	Me ₂ SO	10	2	91
B ^f	Me ₂ SO	24	D ^f	83

^aAll reactions were carried out with exposure to two 20-W ordinary fluorescent lights unless otherwise noted. ^bPure, isolated, product. ^cIn total darkness. ^dRoom light. ^eAt 100 °C. ^fFor structures A-D, see below.



with water and dried (MgSO₄), and the solvent was removed. This gave 8.09 g of a yellow oil which was dissolved in an ethyl ether-pentane mixture (1:3) and passed through a column of silica gel (90%)–silver nitrate (10%). Removal of solvents followed by distillation at 7 mm gave 7.05 g (91% yield) of pure 2, bp 84–86 °C.¹⁴

Acknowledgment. We thank the National Science Foundation and Hoffmann-La Roche, Inc., for generous support.

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- The sodium salt of methyl mercaptan is prepared as follows. Under N₂ 9.20 g (0.40 mol) of sodium is added to 350 mL of freshly distilled 2-propanol. The mixture is refluxed until the reaction is complete (~5 h) after which heating is discontinued; the flask is promptly fitted with a Dry Ice condenser and 25 g (0.52 mol) of methyl mercaptan is passed in. 2-Propanol is then removed under reduced pressure at 30–35 °C. When the solution becomes

viscous ~250 mL of cyclohexane is added and the solvents are removed under reduced pressure. Two additional 250-mL portions of cyclohexane are added and the azeotrope is repeated. The resulting white solid is subjected to a vacuum of ~1 mm for 0.5 h (rotary evaporator) and then the free-flowing white powder is transferred to a sintered-glass funnel (protected by an N₂ blanket), and washed with a total of 500 mL of anhydrous ethyl ether. The solid, still moist with ether, is transferred to a round-bottom flask which is evacuated to ~1 mm and heated at 55–60 °C for ~15 h (rotary evaporator). The product, a finely divided, free-flowing white powder, is stored under N₂. It has a neut equiv of 71, calcd 70. Presumably, replacement of nitro by hydrogen would also occur with salt prepared in situ, but this has not yet been tried.

- (13) We thank the Crown-Zellerbach Corp. for a generous supply of Me₂SO.
 (14) Satisfactory elemental analyses and NMR spectra were obtained for all new compounds.

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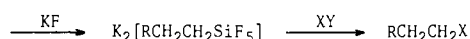
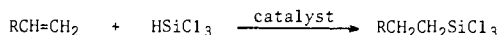
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Organofluorosilicates in Organic Synthesis. 1. A Novel General and Practical Method for Anti-Markownikoff Hydrohalogenation of Olefins via Organopentafluorosilicates Derived from Hydrosilylation Products

Sir:

The addition of silicon hydrides to olefins and acetylenes has become one of the most important methods of forming silicon-carbon bonds.¹ While alkenylsilanes thus obtained have recently been recognized as useful intermediates in various organic syntheses,² use of *alkylsilanes* has been rather limited. The major reason for this situation is that there has been virtually no method for transformation of the *alkyl*-silicon bonds into functional groups.

We report here the first general and practical method for preparing alkyl halides from alkyl-silicon compounds, as outlined in the following equation. This sequence of reactions represents our initial results concerning transformation of



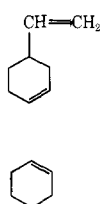
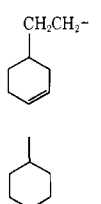
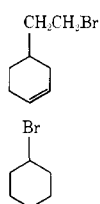
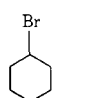
(XY = Cl₂, Br₂, I₂, NBS)

carbon-silicon bonds into functional groups via organopentafluorosilicates which contain a doubly negatively charged hexacoordinate silicon atom, M₂[RSiF₅],³ the reactivities of which are expected to be quite different from those of neutral tetracoordinate organosilanes.⁴

In contrast to the complete inertness of tetracoordinate alkylsilanes towards halogenolysis,⁵ alkylpentafluorosilicates have been found to react almost spontaneously (exothermically) with halogen,⁶ forming alkyl halides in high yields. Organopentafluorosilicates also undergo a rapid reaction with NBS to give alkyl bromides. Representative results are summarized in Table I. The high yields of primary alkyl halides should particularly be noted, because these procedures provide a new convenient route to anti-Markownikoff hydrohalogenation of olefins under neutral reaction conditions.⁷ Another significant feature is that the reaction with NBS can tolerate certain functional groups,⁷ as shown by two examples in Table I. The nature of the reaction medium does not significantly affect the yield, although aliphatic hydrocarbon and alcoholic solvents seem less favorable. The yield dropped with secondary alkyl groups. Unfortunately, NCS gave mainly an organotri-fluorosilane rather than an organic chloride.

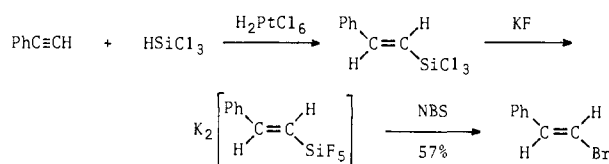
The present methodology, of course, applies to the regio- and

Table I. Cleavage Reactions of $K_2[RSiF_5]$ by Halogens and NBS^a

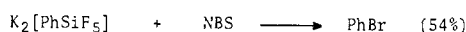
Olefin	R in $K_2[RSiF_5]$	XY (solvent) ^b	Product	Yield, % ^c
$n-C_8H_{17}CH=CH_2$	$n-C_8H_{17}-$	Cl_2 (CCl_4) ^d	$n-C_8H_{17}Cl$	73
		Br_2 (CCl_4) ^d	$n-C_8H_{17}Br$	69
		I_2 (CCl_4) ^d	$n-C_8H_{17}I$	73
		NBS (C_6H_6)	$n-C_8H_{17}Br$	77 (99)
		NBS (CCl_4)		(99)
		NBS (THF)		(98)
		NBS (Et_2O)		73 (91)
		NBS (hexane)		(78)
		NBS (MeOH)		(72)
		NBS (C_6H_6)		75
$n-C_{10}H_{21}CH=CH_2$ $MeO_2C(CH_2)_8CH=CH_2$	$n-C_{12}H_{25}-$ $MeO_2C(CH_2)_{10}-$	NBS (C_6H_6)	$n-C_{12}H_{25}Br$	86
		NBS (C_6H_6)	$MeO_2C(CH_2)_{10}Br$	84
		NBS (Et_2O)		84
		NBS (C_6H_6)		54
	CH_2CH_2- 	NBS (THF)		37
				

^a Carried out on a 5-mmol scale for isolation of the product and on a 1-mmol scale for GLC determination of yields. ^b Reactions with NBS were carried out at room temperature for 2 h. ^c Isolated yield. Yields determined by GLC are given in parentheses. ^d Halogen in CCl_4 was added dropwise at 0 °C until a slight color of halogen remained.

stereoselective preparation of alkenyl halides from acetylenes, as exemplified by the following conversion:^{8,9}



The phenyl-silicon bond in a phenylpentafluorosilicate is also cleaved by NBS:



A wide applicability of the present procedures is apparent from the foregoing results. In addition to the mildness of reaction conditions, high yields of products, high regio- and stereoselectivity, and functional group compatibility, the following features and advantages deserve comment. (1) Organopentafluorosilicates can easily be prepared directly from organotrichlorosilanes obtained by the hydrosilylation of olefins.^{3,4d,f,g,10} (2) A regioselectivity and a stereoselectivity of the hydrosilylation have been well established.¹ (3) Various kinds of catalysts exhibiting different selectivities for the hydrosilylation have been discovered.^{1,11} (4) A ready accessibility of less expensive, air-stable trichlorosilane enables a large scale preparation, in comparison with similar conversions using organoboron, -aluminum, or -zirconium compounds.⁷ (5) In contrast to air-sensitive organoboron or -aluminum analogues, organopentafluorosilicates are air stable and hence no special precaution in handling is necessary (a beaker reaction is all right). (6) Fluorosilicates, either the starting material or the reaction by-product,¹² are almost insoluble in common organic solvents. Therefore, the desired organic product can be separated by simple filtration only.

Preparation of 1-bromooctane from 1-octene provides a typical procedure. 1-Trichlorosilyloctane (24.8 g, 0.10 mol), prepared by the hydrosilylation of 1-octene with trichlorosilane in the presence of chloroplatinic acid as catalyst,¹³ was added dropwise to a stirred solution of potassium fluoride (100 g, 1.72 mol) in distilled water (200 mL) at 0 °C. The resulting white precipitate was filtered, washed successively with cold water-ethanol, ethanol, and diethyl ether, and dried in a vacuum desiccator and weighed 27.8 g (88.5% yield). $K_2[C_8H_{17}SiF_5]$ (1.50 g, 4.78 mmol), NBS (0.90 g, 5.05 mmol), and benzene (10 mL) were combined. An exothermic

reaction started almost immediately. After 2-h standing (or stirring) at room temperature, hexane (20 mL) was added. The mixture was filtered and the insoluble white precipitate washed with hexane. The filtrate and the washings were combined, washed with water, dried (Na_2SO_4), and evaporated. The residue was distilled (Kuegelrohr) to give 0.71 g (77% yield) of 1-bromooctane,¹⁴ >98% pure by GLC.

The present development suggests the possibility that (1) transformation of carbon-silicon bonds into many other functional groups may be achieved by the action of appropriate reagents on organopentafluorosilicates, and (2) the hydrosilylation, in the 30th year of its discovery,¹⁵ may prove to be an attractive alternative to so far developed hydrometalations in synthetic organic chemistry. Investigations are continuing on the extension, refinement, and application of the promising procedure reported here.

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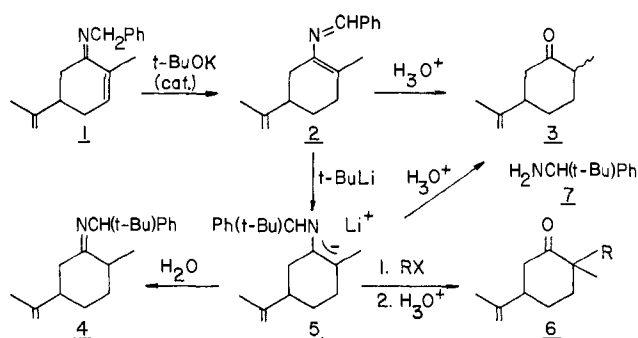
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Regiospecific Generation of Lithoenamines from α,β -Unsaturated Imines. An Alternative Method for Reduction-Alkylation of Enones

Sir:

The demonstration¹ that ketone enolates can be regiospecifically generated from the dissolving metal reduction of enones has further enhanced the importance and utility of these organometallic intermediates in synthesis.² However, the adaptability of this reductive method to the preparation of regiospecifically alkylated ketones is often attenuated by the intrinsic reactivity of the enolate³ and its facile equilibration via proton transfer.⁴ Furthermore, since enolates generated in this fashion are more efficiently alkylated in a solvent other than liquid ammonia, a solvent exchange is frequently necessitated.⁵ In principle, these chemical and operational problems which lead to the formation of polyalkylated products, substrate over-reduction, and diminished regioselectivity could be circumvented by reduction of the imine derivatives of enones to the corresponding metalloenamines, intermediates of demonstrated versatility in synthesis.⁶ Our preliminary study of methods for effecting this unprecedented reduction-alkylation, processes which additionally represent the first ex-

Scheme I



amples of regiocontrolled metalloenamine preparations, is described herein.

The present study is based on the finding⁷ that enones can be reduced to the corresponding ketones in yields of 40–77% via N -alkenylimine intermediates (Scheme I, $1 \rightarrow 2 \rightarrow 3$). Our anticipation that these intermediates could be nucleophilically trapped in situ, thereby regiospecifically generating metalloenamines, prompted our examination of this approach to the aforementioned objective.

Alkenylimine 2 is obtained in essentially quantitative yield by treatment of imine 1 with potassium *tert*-butoxide in anhydrous tetrahydrofuran (THF) at ambient temperature. When *tert*-butyllithium is added to the solution of imine 2, metalloenamine 5 is readily formed as indicated by its conversion upon protonation (H_2O) to imine 4 and transformation (aqueous acid) to ketone 3 in >90% overall yield (distilled).^{8,9} Comparison of this result with the yield obtained using the previously reported imine isomerization-hydrolysis sequence (77%)⁷ or enone metal-ammonia reduction (66%,¹⁰ 61%^{4b}) illustrates the efficiency of this new variant. The crucial application of this concept to the reduction-alkylation objective was realized by the sequential addition of methyl iodide and aqueous acid to metalloenamine 5, thereby providing the regiospecifically alkylated ketone 6 ($\text{R} = \text{CH}_3$) in an isolated yield of 93%. Trapping of imine 2 has also been effected with *sec*-BuLi, *n*-BuLi, and PhLi with only slight variation in overall efficiency ($1 \rightarrow 6$ ($\text{R} = \text{CH}_3$); *sec*-BuLi, 90%; *n*-BuLi, 84%; and PhLi, 90%).

The regioselectivity of the above alkylation is contrasted and synthetically complemented by the finding⁶ that alkylation of metalloenamines derived from unsymmetrically substituted imines using conventional deprotonation procedures occurs preferentially or exclusively at the less substituted carbon center. For example, in contrast to the exclusive formation of ketone 6 ($\text{R} = \text{CH}_3$) noted above, 2,6-dimethyl-3-isopropenylcyclohexanone is the main product obtained when metalloenamine 5 is heated under reflux (THF, 16 h) with 0.1 mol equiv of water and the resulting mixture submitted to standard alkylation and hydrolysis procedures.¹¹ The regioselectivity of the present method is further demonstrated with imines 8 and 10 (Table I), which would be expected to provide a common mixture of alkylated products if metalloenamine equilibration were to occur. Upon examination, imines 8 and 10 are cleanly converted to ketones 9 and 11, respectively, without any evidence of crossover. Finally, reduction-alkylation of imine 12, a system which tests equilibration between a primary and tertiary center, provides ketone 13. Similarly, imine 14 is regiospecifically converted to 3,3-dimethyl-2-butanone.¹²

The efficiency and regiospecificity of this one-flask reduction-alkylation method is augmented by the ease with which it is performed as typified in the following procedure. Thus, imine 1 (13.2 mmol) is added dropwise (1 min) to a stirred solution (ambient temperature) of potassium *tert*-butoxide (1.4 mmol) in anhydrous THF (43 mL). After 30 min, the solution is cooled to -78°C and treated with *tert*-butyllithium (20.5