is assumed by analogy.[4] A Stern–Volmer treatment (plot of $1/\phi$ vs. concentration of anthracene quencher) at initial absorbed light intensity of 3 $\times$ 10^{-7} einstein min gave a reasonable straight line over the range 1.5–10 $\times$ 10^{-5} M anthracene with a slope of 7 $\times$ 10^4 M^{-1}. However, it should be emphasized that this result may be fortuitous. In the present case, the effect of quencher in reducing the instantaneous concentration of triplet states is comparable to reducing light intensity and thus increasing quantum yield. The observed result will be the sum of this effect plus the usual effect of the quencher in reducing quantum yield.

(8) The intermediacy of these radicals is supported by a number of experimental results including ESR spectra, CIDNP experiments,[3d,e] and minor products observed in special cases. No CIDNP effect could be detected with aromatic aldehydes.[9] It might be noted that the transient reported[3d] in the CIDNP spectrum of camphorquinone and acetaldehyde has been shown[9] to be acetyl chloride presumably formed via reaction of intermediate acetyl radicals with carbon tetrachloride, the solvent employed in these experiments.

(9) M. Cocivera, personal communication.

(10) Unequivocal support for the occurrence of reaction 4 derives from the observation that irradiation of BOD and benzaldehyde in the presence of deuterium oxide to partial completion afforded recovered benzaldehyde enriched in deuterium. From kinetic analysis, k_4 is suggested to be three to four times larger than k_5.

(11) The results presented in Table I establish that $k_5 > k_8$; extrapolation to even higher light intensities suggests that reaction 6 may be unimportant.

(12) The feasibility of addition of aroyl radicals to BOD was established by experiments in which cyclohexane solutions containing benzoin isopropyl ether, a known[13] precursor of benzoyl radicals, and BOD were irradiated at 366 nm (>99% of light absorbed by the benzoin ether). The only addition product formed was keto ester 1. A similar result was obtained using benzoyl radicals generated by thermolysis of di-*tert*-butyl peroxide in the presence of benzaldehyde and BOD. The reversibility of this addition reaction is suggested but has not been established experimentally.

(13) F. D. Lewis, R. T. Lauterback, H. G. Heine, W. Hartmann, and H. Rudolph, *J. Am. Chem. Soc.*, **97**, 1519 (1975), and refences therein.

(14) Formation of 1 via its enol 4 is energetically reasonable and consistent with stereochemistry observed in reactions of camphorquinone.[3c]

(15) An alternative reaction of 3, abstraction of hydrogen from aldehyde, would produce 1 plus an aroyl radical resulting in a chain reaction. This is not consistent with the data presented in Table I.

(16) J. M. Ben-Bassat, M.Sc. Thesis, Technion, 1969.

Mordecai B. Rubin,* Shai Inbar

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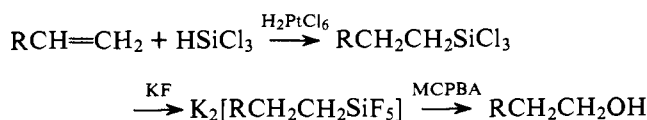*Technion-Israel Institute of Technology, Haifa, Israel*

Organofluorosilicates in Organic Synthesis. 2. A Convenient Procedure for Preparing Primary Alcohols from Olefins. A Novel Facile Oxidative Cleavage of Carbon–Silicon Bonds by *m*-Chloroperoxybenzoic Acid[1]

Sir:

It has long been recognized that "silicon–alkyl and, particularly, silicon–aryl bonds are fairly resistant to oxidative cleavage, and appropriately substituted organic groups attached to silicon may be oxidized without cleavage of the silicon–carbon bonds".[2]

However, we have found that silicon–carbon bonds in organopentafluorosilicates[3] are easily cleaved by the action of *m*-chloroperoxybenzoic acid (MCPBA) to afford the corresponding alcohols in high yields. This reaction provides the first method for the direct introduction of an oxygen functionality into an organic group via cleavage of the silicon–carbon bond,[4] and makes possible a simple and practical procedure for the conversion of olefins into primary alcohols.[7]

$$RCH{=}CH_2 + HSiCl_3 \xrightarrow{H_2PtCl_6} RCH_2CH_2SiCl_3$$

$$\xrightarrow{KF} K_2[RCH_2CH_2SiF_5] \xrightarrow{MCPBA} RCH_2CH_2OH$$

In contrast to reactions with NBS,[1] reactions of organopentafluorosilicates with MCPBA were greatly dependent upon the nature of the reaction media. Thus, yields of 1-octanol produced in the reaction of $K_2[C_8H_{17}SiF_5]$ with MCPBA varied with solvent as follows: THF, trace; EtOH, MeCN, dioxane, ~30%; benzene, 45%; diglyme, 60%; DMF, 82%.

Table I. Oxidative Cleavage of $K_2[RSiF_5]$ by MCPBA in DMF[a]

Olefin	R in $K_2[RSiF_5]$	Product	Yield, %[b]
$n\text{-}C_6H_{13}CH{=}CH_2$	$n\text{-}C_8H_{17}\text{–}$	$n\text{-}C_8H_{17}OH$	82
$n\text{-}C_8H_{16}$[c]	$n\text{-}C_8H_{17}\text{–}$	$n\text{-}C_8H_{17}OH$	68
$n\text{-}C_{10}H_{21}CH{=}CH_2$	$n\text{-}C_{12}H_{25}\text{–}$	$n\text{-}C_{12}H_{25}OH$	75
$MeO_2C(CH_2)_8\text{-}CH{=}CH_2$	$MeO_2C\text{-}(CH_2)_{10}\text{–}$	$MeO_2C(CH_2)_{10}\text{-}OH$	77

			54

			22

$C_6H_5\text{–}$[d]		C_6H_5OH	64[e]

a Carried out on a 3-mmol scale in the same manner as described in the text. *b* Isolated yield by distillation, based on the silicate, unless otherwise noted. *c* An isomeric mixture of internal and terminal olefins. *d* Prepared from commercial $C_6H_5SiCl_3$. *e* Determined by GLC.

Interestingly, the yield of 1-octanol was improved up to 70% by the addition of an equimolar amount of 18-crown-6 to a reaction mixture in benzene. However, the most convenient and practical solvent is still DMF. It should also be mentioned that the presence of extra lithium or potassium fluoride almost completely inhibits the oxidation reaction, the reason for which is not clear. Other peroxides examined, such as peroxyacetic acid in acetic acid and *tert*-butyl hydroperoxide in diglyme or hydrogen peroxide, gave mainly octyltrifluorosilane rather than the octanol.

A typical procedure is given for the preparation of methyl 11-hydroxyundecanoate from methyl 10-undecenoate. $K_2[MeO_2C(CH_2)_{10}SiF_5]$ was prepared by the platinum-catalyzed hydrosilylation of methyl 10-undecenoate with trichlorosilane followed by treatment with potassium fluoride in water.[3] The silicate (1.20 g, 3.0 mmol), MCPBA (80% pure) (0.81 g, 3.6 mmol as active oxygen), and dry DMF (10 mL) were combined and stirred at room temperature for 6 h. The mixture changed gradually to an almost homogeneous solution. After the addition of ether, the mixture was washed successively with water (once), 20% sodium bisulfite (twice), and saturated sodium bicarbonate (twice), dried over sodium sulfate, and evaporated. Bulb-to-bulb distillation of the residue gave 0.50 g (77% yield based on the silicate) of pure methyl 11-hydroxyundecanoate.[8]

Representative results summarized in Table I were obtained under similar conditions. Primary alcohols were obtained in high yields, the secondary alcohol yield being much lower. The phenyl–silicon bond in $K_2[PhSiF_5]$ is also cleaved to form phenol. While many advantages mentioned in the previous paper[1] also apply to the present reaction, the following particular points deserve further comment. (1) The MCPBA cleavage of, at least, the primary alkyl–silicon bond in silicates proceeds much faster than the epoxidation of double bonds, as indicated by the selective preparation of 4-(2-hydroxyethyl)cyclohexene from 4-vinylcyclohexene. This opens a new route to unsaturated primary alcohols from various polyenes. (2) Since the platinum-catalyzed hydrosilylation of internal olefins forms primary alkyl–silicon compounds exclusively,[9] the present procedure provides a novel route to primary alcohols from a mixture of positional isomers of olefins. This is exemplified by the result given for $n\text{-}C_8H_{16}$ in Table I.

Mechanistic studies and additional synthetic applications of the present oxidation reaction are now in progress.

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Bis(2-diphenylphosphinoethyl)amine. A Flexible Synthesis of Functionalized Chelating Diphosphines[1]

Sir:

Chelating diphosphines are an important class of ligand in inorganic and organometallic chemistry. Applications of these materials in areas such as asymmetric synthesis and catalysis by polymer-bound metals increasingly require incorporation of diphosphine units into complicated organic structures. The most commonly used methods for synthesis of polydentate phosphines involve the introduction of multiple individual phosphine units into a precursor, ordinarily by displacement of halides or tosylates by diphenylphosphide ion or by addition of diphenylphosphine to activated olefins.[2] These syntheses suffer from unpredictable yields and incompatibility with many functional groups. Here we outline an alternative and widely applicable synthetic method in which the chelating diphosphine moiety is introduced as a unit, taking advantage of the highly reliable coupling of amines with carbonyl halides, anhydrides, active esters, and isocyanates (eq 1).
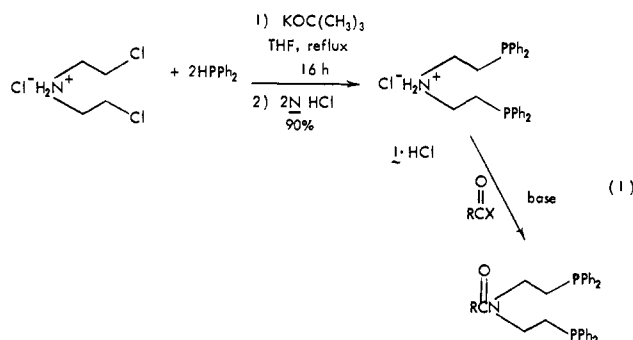

Table I. Functionalized Diphosphines Derived from **1**[a]

Compd	Structure	Reacting group	Yield, %
2		RCOCl or (RCO)$_2$O, CH$_2$Cl$_2$, Et$_3$N	> 95
3		RCOCl, Pyr, THF	50[b]
4		ROCOCl, THF (n = 12, 16), CH$_2$Cl$_2$ (n = 110), Et$_3$N	(high)[c]
5		R(COCl)$_2$, CH$_2$Cl$_2$, Et$_3$N	70
6		Anhydride, THF, Et$_3$N	96
7		Anhydride, BuLi, THF[d]	85[d]
8		Anhydride, CH$_3$CN, Et$_3$N	95[e]
9		, DMF, Et$_3$N	84
10		PhN=C=O, CH$_2$Cl$_2$, Et$_3$N	93

[a] Except where indicated, **1** was allowed to react with 1 equiv of the derivatizing agent for 15 h at room temperature. Yields are based on **1** unless noted otherwise. Satisfactory elemental analyses were obtained for compounds **2, 3, 7, 9,** and **10.** Compounds **4** and **8** were intrinsically heterogeneous, and were amenable only to spectroscopic characterization, although elemental analysis afforded the approximate degree of substitution in **8.** Compounds **5** and **6** were characterized spectroscopically. [b] The **1** involved in this reaction was generated directly by reaction of LiPPh$_2$[3] and HN(CH$_2$CH$_2$Cl)$_2$ and was acylated in situ. The yield is based on HPPh$_2$. [c] The starting materials for these preparations were commercial monomethyl polyethylene glycols. The average degree of polymerization of these materials is indicated by n. Reactions were carried out at room temperature for these durations: n = 12, 16 h; n = 16 and 110, 1 h. The product yield was difficult to estimate accurately, but essentially all of the **1** was converted to a water-soluble derivative. [d] Compound **1** was converted to LiN(CH$_2$CH$_2$PPh$_2$)$_2$ by reaction with butyllithium, before addition of camphoric anhydride. [e] Prepared by reaction of poly(methyl vinyl ether–*co*–maleic anhydride) with quantities of **1** sufficient to consume between 10 and 50% of the anhydride moieties. The initial product was a pink gum, insoluble in acetonitrile, which contained the major part of the **1** added. This gum was suspended in a 1:1 mixture of ~0.1 N aqueous HCl and acetonitrile and refluxed for 30 min to hydrolyze remaining anhydrides. The resulting white solid was dried at ~0.5 Torr.

The central intermediate in this scheme, bis(2-diphenylphosphinoethyl)amine (**1**) was prepared and isolated as a