the resulting two diols to (−)-(*S*)-2-phenyl-2-butanol and (−)-(*R*)-2-phenylpropionic acid (hydratropic acid).[13] Rearrangement of **3** utilized the procedure of Kagan.[4] The optical purity of **3** and **5** was established by using the europium chemical shift reagent "Eu-Opt" (Ventron, Beverly, Mass.) in CCl_4 solvent.
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Coupling Constants between Directly Bonded Silicon Atoms

Sir:

The recent widespread availability of pulsed Fourier transform (FT) NMR has resulted in a substantial surge of activity related to direct observation of the silicon-29 nucleus at its 4.7% natural abundance. To date, however, no reports of coupling between directly bonded silicon nuclei have appeared in the literature; the only silicon-silicon coupling constant which has been reported[1] is J_{SiOSi} for $(Me_3SiO)_4Si$. We wish to report the first examples of directly bonded Si-Si coupling constants for some linear and neopentyl disilanes and polysilanes.[2]

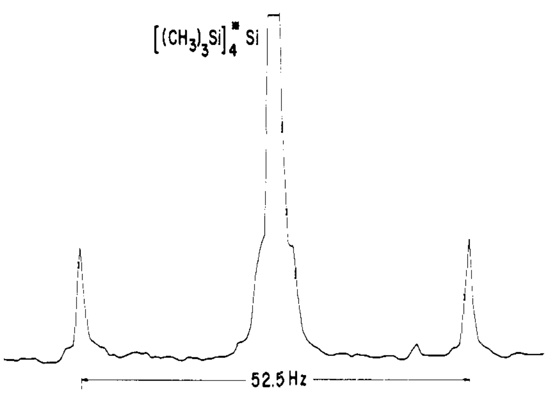

Figure 1. Silicon-29 NMR spectrum of the central silicon in $[(CH_3)_3Si]_4Si$.

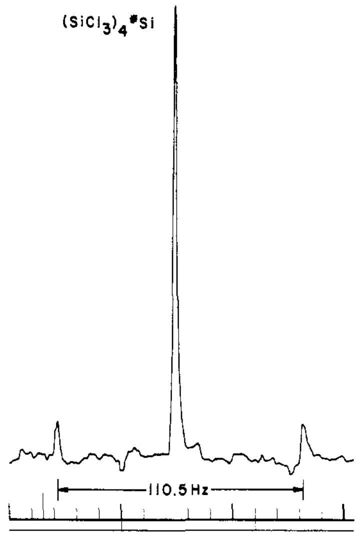

Figure 2. Silicon-29 NMR spectrum of the central silicon in $(SiCl_3)_4Si$.

Parameters related to ^{29}Si NMR for the compounds selected for this study are presented in Table I. The spectra of the central silicons in $(Me_3Si)_4Si$ (**1**) and $(Cl_3Si)_4Si$ (**10**) are shown in Figures 1 and 2. All spectra except that for **10** were obtained with complete proton decoupling (where appropriate) on Varian XL-100-15 NMR spectrometers operating in the FT mode at 19.9 MHz for ^{29}Si. The spectrum of **10** was obtained on a JEOL-FT-1A (^{29}Si at 19.8 MHz) instrument. A small amount of $Cr(acac)_3$ was added to each sample to shorten the long silicon spin-lattice relaxation times and suppress the negative NOE arising from proton decoupling.[4] The Si-C coupling constants of **9** were confirmed in the ^{13}C spectrum obtained on a Varian CFT-20 spectrometer operating in the FT mode at 20 MHz for ^{13}C. First order (or nearly so) spectra were obtained for

Table I. Silicon-29 Chemical Shifts and Coupling Constants[a]

Compound	A, δ	B, δ	Solvent	$\lvert {}^1J_{SiSi} \rvert$	$^1J_{Si^AC}$	$^1J_{Si^BC}$
$(Me_3Si^A)_4Si^B$ (**1**)	−9.8	−135.5	$CDCl_3$	52.5	44.7	—
$(Me_3Si^A)_2Si^BMe_2$ (**2**)	−16.1 (−15.93)[b]	−48.7 (−48.45)[b]	$CDCl_3$	73.2	43.8	37.0
$Me_3Si^ASi^BMe_2H$ (**3**)	−18.9	−39.1	Acetone-d_6	84.6	44.6	43.8
$Me_3Si^ASi^BMe_2Ph$ (**4**)	−19.3	−21.7	Acetone-d_6	86.1	44.1	44.8
$Me_3Si^ASi^BPh_3$ (**5**)	−18.4	−20.2	$CDCl_3$	86.5	*[c]	*[c]
$Me_3Si^ASi^BMe_2Cl$ (**6**)	−18.2	+22.8	$CDCl_3$	94.0	46.2	45.9
$(Me_3Si^ASi^BMe_2)_2NH$ (**7**)	−22.0	−5.4	C_6D_6	96.0	42[c]	46.6
$Me_3Si^ASi^BMe_2F$ (**8**)	−22.5	+34.0	C_6D_6	98.7 ($^1J_{SiF}$ = 306.8, $^2J_{SiF}$ = 26.7)	*[c]	47.9
$(Me_3Si^ASi^BMe_2)_2O$ (**9**)	−23.1	+5.2	$CDCl_3$	103.4	43.8	48.0
$(Cl_3Si^A)_4Si^B$ (**10**)	+3.5	−80.0	$CDCl_3$	110.5	—	—
$(MeO)_3Si^ASi^BPh_3$ (**11**)	−45.9	−29.2	$CDCl_3$	160.0	—	*[c]
$(Cl_3Si^A)_2Si^BCl_2$ (**12**)	−3.5	−7.2	C_6D_6	186	—	—

[a] All chemical shifts are given in ppm relative to internal tetramethylsilane (Me_4Si) except for **10** and **12** which are relative to external Me_4Si. Negative values correspond to upfield shifts. Coupling constants are given in Hz. Silicon–silicon couplings from all ^{29}Si spectra except those of **4**, **5**, and **12** were determined from satellites of both Si^A and Si^B lines to an estimated accuracy of ±0.5 Hz. Spectra of **1** and **10** were first order; all the rest were assigned as AB spin systems. Only the two central lines of the quartet were observed for $^1J_{SiSi}$ of **4**, **5**, and **12** (estimated accuracy for **4** and **5** is 0.5 Hz; for **12**, ±2 Hz). [b] Literature values from ref 3. [c] Assignments for $^1J_{SiC}$ not clear.

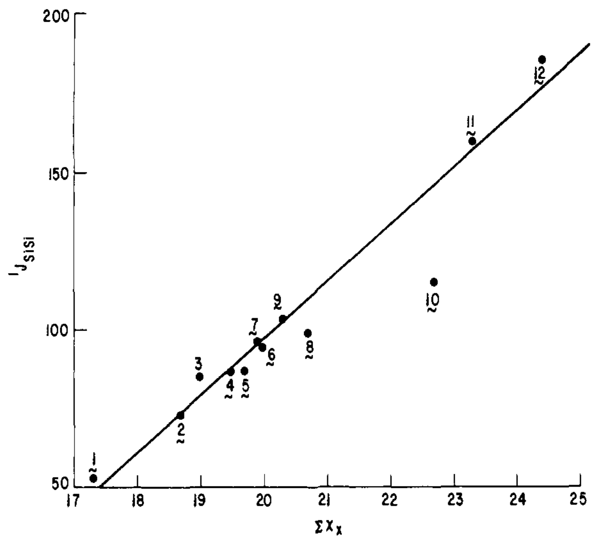

Figure 3. Plot of $|^1J_{SiSi}|$ vs. the sum of the substituent electronegativities for **1–12.** χ_x values are from ref 1 except that for $SiCl_3$, which is taken from ref 18. The value for Me_3Si was used for $(Me_3Si)_3Si$, Ph_3Si, and $(Cl_3Si)_3Si$. Me_2SiX groups were approximated by Me_3Si (e.g., χ_x for Me_3SiO was used for the $Me_3SiSiMe_2O$ substituent). The value for Cl_3Si was used for $(MeO)_3Si$.

compounds **1**, **2**, **6**, **8**, and **10**. The remainder of the compounds investigated comprised AB spin systems. Compound **1** was kindly provided by Dr. G. C. Levy; **10** was generated from the mercury-sensitized photolysis of trichlorosilane;[5] **12** was a commercial sample which required extensive purification via high vacuum fractionation, and the others were synthesized by standard literature procedures.[6]

It is not obvious which other one-bond couplings should serve as appropriate analogues for those presented here. A substantial number of $^1J_{CC}$ values are now known.[7] Earlier workers[8] considered variations in J_{CC} to be well accounted for by simple bond hybridization arguments. More recent contributions[9] have indicated that substituent inductive and polarization phenomena and steric effects should be considered as well. Theoretical calculations[10-12] have been generally successful in rationalizing trends in values of $^1J_{CC}$. However, these calculations have usually considered only the Fermi contact contribution to the coupling and have invoked the "mean excitation energy" approximation. Calculations of J_{CC} utilizing the finite perturbation treatment at the INDO level of approximation which explicitly include contributions from orbital and spin dipolar terms have recently appeared.[13-14] These indicate that the contributions from the orbital term are substantial when the coupled carbons are π-bonded, and are relatively important in three-membered rings. The spin dipolar term is apparently small except for acetylenic carbons.[13] Even at this higher level of sophistication, however, calculated values for some very simple species such as C_2H_4 or CH_3CHO differ appreciably from experimental values.[13] Theoretical reckoning with $^1J_{SiSi}$ values may be more difficult yet: orbital and spin dipolar terms may well be more important than for C–C couplings, and successful calculations may require the inclusion of π-symmetry orbitals in both ground and excited states in the Fermi contact term and d orbitals in the orbital term.

Several workers have recently reported and/or discussed $^1J_{SiC}$ couplings. Levy, White, and Cargioli[15] obtained values for several organosilicon compounds and observed a rough proportionality between the magnitude of J_{SiC} and "s character of the carbon nucleus". Kovacevic and Maksic[16] were able to correlate these data well with bond hybridization parameters, despite some rather extensive approximations, in a theoretical treatment employing approximate MO calculational methods (featuring the maximum overlap approximation) for the Fermi contact term.

Recently, Harris and Kimber[1] have presented additional $^1J_{SiC}$ couplings and have also suggested that the Fermi contact term is likely dominant for this interaction. For a series of Me_3SiX species, these authors established linear correlations between $^1K_{CC}$ and $^1K_{SiC}$ (where K is the reduced coupling constant: $K_{AB} = (4\pi^2 J_{AB})/h\gamma_A\gamma_B$) and between $^1K_{SiC}$ and the electronegativity of X. Their data further suggest that $^1J_{SiC}$ is universally negative ($^1K_{SiC}$ is therefore positive) for these species, based on a relative sign determination for Me_4Si.

We find a good linear correlation (correlation coefficient $r = 0.95$) between the $|^1J_{SiSi}|$ values reported here and the sum of the electronegativities of the eight substituents on the coupled silicons.[17] (However, given the considerable uncertainty involved in estimating group electronegativities, we must conclude that the quality of the correlation is to some extent fortuitous.) The correlation is presented graphically in Figure 3. A second correlation which is free from assumptions or parameter estimations is a linear relationship ($r = 0.95$) between $|^1J_{SiSi}|$ and $^1J_{Si^BC}$ for the pentamethyldisilanyl species $Me_3Si^ASi^BMe_2X$. These observations strongly suggest that the contributing factors most important for $^1J_{SiC}$ remain most influential for $^1J_{SiSi}$, and it seems likely that the Fermi contact term is dominant for both. Since $^1K_{CC}$ and $^1K_{SiC}$ are both positive and none of the $^1J_{SiSi}$ values presented here is near zero, we suggest that the sign of $^1K_{SiSi}$ (and therefore $^1J_{SiSi}$) is positive in these species.

A plot of δ_{Si^B} vs. $|^1J_{SiSi}|$ in the $Me_3Si^ASi^BMe_2X$ series reveals a rather poor correlation between the two parameters. A similar observation was reported by Harris and Kimber[1] for δ_{Si} vs. $^1J_{SiC}$ in various Me_3SiX species.

We are aware of only one calculated value for $^1J_{SiSi}$: for Si_2H_6 the coupling was calculated by Cowley and White[19] (using an LCAO-SCF calculation which included only the Fermi contact contribution) to be +10.3 Hz. Extrapolation of our data to Si_2H_6 predicts the value of $|^1J_{SiSi}|$ to be ca. 40-45 Hz.

We are presently investigating systems suitable for relative sign determinations.

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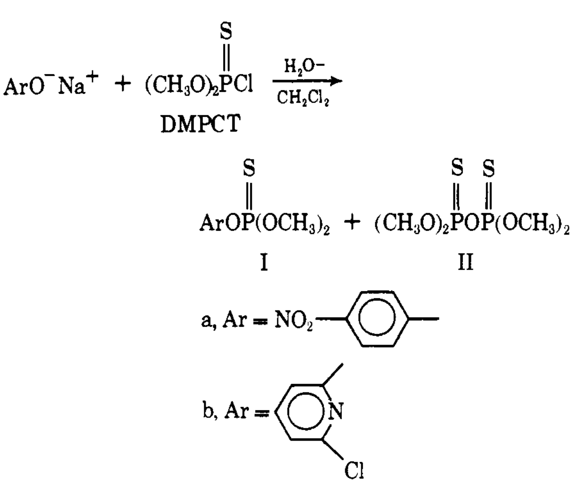
Cocatalysis of Phenolate Phosphorylation in Biphasic Media

Sir:

Acyl transfer reactions between a basic, anionic nucleophile in aqueous medium and a hydrolyzable acyl compound in a nonpolar solvent are inhibited by the mutual insolubilities of the reagents as well as the sensitivity of the acyl compound to the alkaline aqueous environment. In particular, thiophosphorylation of moderately nucleophilic phenolates or pyridinates by dialkylthiophosphoryl chlorides in such a biphasic medium is a slow and inefficient process in which the major products may be those of hydrolysis rather than esterification (eq 1). We now present data on several approaches to catalysis of this process including: (1) activation of the acylating agent (nucleophilic catalysis),[1] (2) activation of the nucleophile (phase transfer catalysis)[2] (PTC), and (3) a combination of (1) and (2) in which both rates and product selectivity are enhanced by the unique interaction of intermediates generated from both reactants.

We initially investigated the formation of methyl parathion (Ia) by rapidly stirring a refluxing 0.15 M solution of dimethylphosphorochloridothionate (DMPCT) in methylene chloride with an excess of aqueous sodium *p*-nitrophenolate.[3] That this uncatalyzed reaction has negligible synthetic utility is shown by its slow rate ($t_{1/2}$ ~30 h) and final product distribution of 40% Ia and 60% of DMPCT hydrolysis products, mainly tetramethylthiopyrophosphate(II).

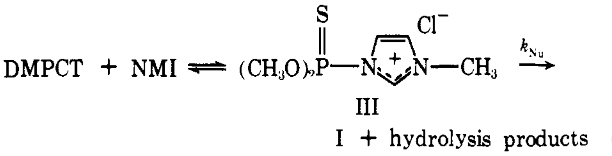


$$\mathrm{ArO^-Na^+} + \underset{\text{DMPCT}}{(\mathrm{CH_3O})_2\overset{\text{S}}{\overset{\|}{\mathrm{P}}}\mathrm{Cl}} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{H_2O-}} \underset{\text{I}}{\mathrm{ArO}\overset{\text{S}}{\overset{\|}{\mathrm{P}}}(\mathrm{OCH_3})_2} + \underset{\text{II}}{(\mathrm{CH_3O})_2\overset{\text{S}}{\overset{\|}{\mathrm{P}}}\mathrm{O}\overset{\text{S}}{\overset{\|}{\mathrm{P}}}(\mathrm{OCH_3})_2} \quad (1)$$

a, Ar = NO_2—

b, Ar =

The addition of 1% (1.5×10^{-3} M) of the nucleophilic catalyst, N-methylimidazole (NMI), greatly increased the reaction rate ($t_{1/2}$ ~1.5 h) but considerable hydrolysis (20%) was still evident. This rate increase clearly implicates the formation of the reactive intermediate III,[4] which is partitioned between the two nucleophiles (eq 2). This reaction is very sensitive to stirring rate and, as with a similar nucleophilic catalysis reaction in a biphasic system,[5] may be largely interfacial in nature.



(2)

Catalysis can also be accomplished with organosoluble quaternary ammonium (Q^+) salts, the first example of PTC applied to phosphorylation. Addition of 1% of tetra-*n*-butylammonium bisulfate (TBAB) gives 91% of ester Ia with $t_{1/2}$ of ~4 h. Unlike the NMI catalyzed process, but as generally found for PTC reactions,[6] the rate is insensitive to stirring beyond ~100 rpm.

Combining both catalysts, 1% each of NMI and TBAB, provides a unique cocatalytic effect in which the rate enhancement of the nucleophilic catalyst and the product specificity of the phase transfer catalyst are both combined and even surpassed ($t_{1/2}$ ~ 1.2 h, % I = 95). The most plausible explanation for this previously unobserved phenomenon is that an additional mechanistic pathway has been made available; the activated electrophilic intermediate III can now react directly with the activated nucleophile, the quaternary ammonium phenate IV, as it is extracted into the organic layer (eq 3). The rate constant for such a reac-

$$\underset{(\mathrm{aq})}{\mathrm{ArO^-Na^+}} + \underset{(\mathrm{aq})}{\mathrm{Q^+HSO_4^-}} \rightleftharpoons \underset{\substack{(\mathrm{org})\\ \mathrm{IV}}}{\mathrm{ArO^-Q^+}} + \underset{(\mathrm{aq})}{\mathrm{NaHSO_4}}$$

$$(\mathrm{Q^+} = n\text{-}\mathrm{Bu_4N^+})$$

$$\underset{(\mathrm{org})}{\mathrm{III} + \mathrm{IV}} \xrightarrow{k_{\mathrm{cocat}}} \mathrm{I} + \mathrm{NMI} + \mathrm{Q^+Cl^-} \qquad (3)$$

Table I. Pseudo-First-order Rate Constants (k_{obsd}) for Uncatalyzed, Individually Catalyzed, and Cocatalyzed Aqueous 0.8 M Sodium 2-(6-chloropyridinolate) and 0.2 M DMPCT in CH_2Cl_2 at 25° and 500 rpm.

	$k_{\mathrm{obsd}} \times 10^4$, s^{-1} [a]						
	Catalyst[b]		Cocatalyst				
[Cat], M	TBAB	NMI	[TBAB] = [NMI]	[TBAB] (0.01 M NMI)	[TBAB] (0.02 M NMI)	[NMI] (0.01 M TBAB)	[NMI] (0.02 M TBAB)
0.000	0.046	0.046	0.046	3.0	6.3	0.6	1.0
0.002	—	—	0.7	—	—	—	—
0.005	—	—	1.8	3.3	—	2.5	—
0.010	0.6	3.0	4.5	4.5	7.8	4.5	4.8
0.020	1.0	6.3	10.1	4.8	10.1	7.8	10.1
0.030	1.2	8.7	22	6.7	—	—	—

[a] All ±10%. [b] Individual catalysts.