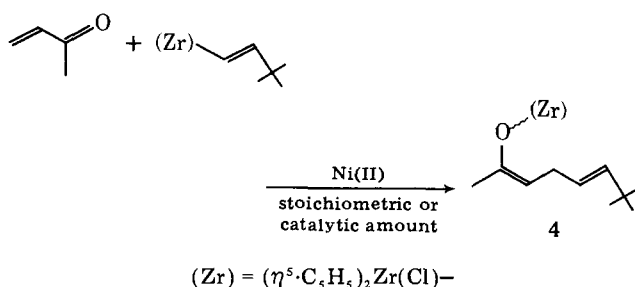


with no discernible reductive cleavage of the ethereal unit. This result, of special importance for the preparation of prostaglandin analogues,¹⁰ stands in marked contrast to reports concerning the preparation using organoaluminum hydrides of precursors of vinylic copper(I) species employed in copper(I)-based syntheses of similar compounds.¹⁰

It has been noted that Ni(AcAc)₂ will catalyze the conjugate addition of (CH₃)₃Al to several unsaturated ketones with varying degrees of success.^{4,5} This reported system is believed to proceed through a nickel(0) catalyst. The structure of the active catalyst in the Zr–Ni route described herein is not yet known. It is apparent, though, that in this latter system nickel(II) and *not* nickel(0) partakes. Conversion of nickel(II) to nickel(0) would be accomplished with concomitant oxidative coupling of vinylic units to dienes, and, although in all cases investigated a small amount of such dimer is observed, we note that the use of Ni(AcAc)₂ as a *stoichiometric* reagent, under the same conditions noted above, gives rise to essentially the same high yields of conjugate addition products as were observed in Ni-catalyzed procedures. Were nickel(0) the active catalytic form, these stoichiometric procedures should lead, contrary to observation, to high yields of dimers (dienes) and to essentially no conjugate addition product. It is interesting to note here that the reaction of dialkylvinylalanes, Ni(AcAc)₂, and α,β -unsaturated ketones does give rise to some product of conjugate addition of the vinylic group; however, this product is formed in low yield and then only as one component of a complex mixture of by-products resulting from either 1,2 or 1,4 addition of either the alkenyl or alkyl group of the mixed alane.^{11,12}

The initial product of conjugate addition involving either catalytic or stoichiometric amounts of Ni(AcAc)₂, prior to hydrolysis, is the zirconium *O*-enolate (as evidenced, for example, clearly by the NMR spectrum of 4).¹³ Hydrolysis yields the observed ketone. For 2-methylcyclopent-2-enone, trans stereochemistry of groups on the C₅ ring is assigned based on analogy to cuprate chemistry in which workup under the conditions described herein also gives the thermodynamically preferred product.¹⁴



The scope of Ni(AcAc)₂-catalyzed conjugate addition of alkenyl zirconium compounds is now being explored with regard to types of substrates amenable to this procedure. The nature of the catalytically active species in this sequence is also being examined.¹²

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- Ni(AcAc)₂, dried by heating to 98 °C in vacuo for 24 h, is soluble in THF.
- In no case were products of 1,2 addition observed; a small amount of the product of reductive coupling (diene) is always noted (in this example, 3% (by mmole) by VPC). A direct comparison of the Ni and Cu transmetalation routes can be obtained from the following data: for conjugate addition of the (3,3-dimethyl-1-butenyl) group to methyl vinyl ketone vs. dimerization of that group to (*E,E*)-2,2,7,7-tetramethyl-3,5-octadiene, the Ni(AcAc)₂-catalyzed route gave >95% ketone and <1% diene (by mmole), whereas the stoichiometric CuOTf procedure^{2a} afforded 73% ketone and 11% diene (by mmole) (determined by VPC). For cyclic enones, these yield differences are even more dramatic.
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- NMR for 4 prepared by nickel catalysis (in C₆D₆; δ , multiplicity, H): 6.0 (s, 10), 5.2–5.5 (m, 2), 4.1 (t, 1, *J* = 7 Hz), 2.7 (m, 2), 1.6 (s, 3), 0.9 (s, 9). All spectral lines are significantly broadened in the presence of a stoichiometric amount of nickel(II).
- We thank W. Krol and P. Demou (Yale University) for obtaining a 270-MHz NMR spectrum of this compound (J_{H_a,H_b} = 11.2 Hz, J_{H_1,H_2} = 17 Hz, J_{H_1,H_3} = 7 Hz).
- Alfred P. Sloan fellow, 1976–.

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Mercury-Sensitized Photodissociation of the Silicon–Silicon Bond. Synthesis of Methylfluorodisilanes via a Disilane “Metathesis” Reaction

Sir:

Photochemically induced reactions of silicon compounds in which a silicon atom is a distinct component of a chromophore remain rather few in number. Many Si–X bonds exhibit characteristic ultraviolet absorption maxima at wavelengths shorter than 2200 Å¹ and are thus inaccessible as chromophores with more commonly employed sources of ultraviolet radiation. Important exceptions are for X = Hg,^{2,3} and Si for polysilanes.⁴ Kumada^{5,6} and Sakurai⁷ have established that linear and cyclic polyalkylated polysilanes undergo effective elision of a silylene under the influence of UV radiation;⁸ however, simple alkyl-, fluoro-, or chlorodisilanes are impervious to direct photolysis under comparable conditions. The difference in behavior between disilanes and polysilanes on direct photolysis is comprehensible on the basis of the well-documented bathochromic shift of absorption maxima in linear permethylated polysilanes on increasing chain length.⁹

An alternative to direct photolysis which has proven very useful for Si–H bond dissociation is mercury-sensitized photolysis at 2537 Å.^{10,11} We wish to report here the facile homolytic dissociation of silicon–silicon bonds in simple methyl- and fluorodisilanes under conditions of mercury-sensitized photolysis and specific, high yield synthetic routes to the (largely unknown) representatives of the class of disilanes Si₂Me_xF_{6-x}, 1 ≤ x ≤ 5.

Our initial interest lay in the cophotolysis of hydrogen-bearing monosilanes with disilanes in the hope that S_H2 reactions at the Si–Si bond would provide synthetic pathways to new mixed disilanes. Indeed, such reactions proved to be

Table I. ^{19}F NMR Spectral Parameters for Methylfluorodisilanes

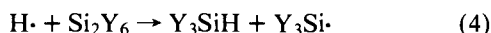
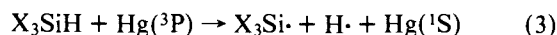
Compd	$\delta_{\text{SiMe}_2\text{F}}^a$	δ_{SiMeF_2}	δ_{SiF_3}	$^3J_{\text{HF}}^{b,c}$	$^3J_{\text{FF}}^{b,c}$	$^1J_{\text{SiF}}^{b,c}$	$^2J_{\text{SiF}}^d$
$\text{Me}_3\text{SiSiMe}_2\text{F}$	175.7			8.57		307.1	26.7
$\text{Me}_3\text{SiSiMeF}_2$		132.8		8.12		347.7	29.6
$\text{Me}_3\text{SiSiF}_3$			122.7	0.9 ^e			
$\text{Me}_2\text{FSiSiMe}_2\text{F}$	176.0			8.93	9.02	302.8	35.08
$\text{Me}_2\text{FSiSiMeF}_2$	176.3	133.9		8.33 (SiMeF ₂)	9.63	341.8 (SiMeF ₂)	39.4 (SiMeF ₂)
$\text{Me}_2\text{FSiSiF}_3$	173.0		124.3	8.15	9.85	296.2 (SiMe ₂ F)	56.6 (SiMe ₂ F)
						368.4 (SiF ₃)	42.4 (SiF ₃)
$\text{MeF}_2\text{SiSiMeF}_2$		133.7		8.03	13.13	334.2	53.8
$\text{MeF}_2\text{SiSiF}_3$		131.9	125.7	7.41	14.80		

^a Chemical shift in parts per million upfield from CFCl_3 . ^b Coupling constant in hertz. ^c Sign of J very likely positive; see ref 20–22. ^d Sign of $^2J_{\text{SiF}}$ likely negative. ^e $^4J_{\text{HF}}$.

effective means for synthesizing methylfluorodisilanes; reactions such as eq 1 and 2 typically¹² proceeded to give yields¹³ of from 40–70% of the mixed disilane. The only other products of appreciable abundance were the symmetrical disilane resulting from self-coupling of the radicals derived from the monosilane, and the monosilane which formally results from recombination of a hydrogen atom with the radical derived from the disilane. For example, the reaction of Me_2SiFH with Si_2F_6 generated $\text{Me}_2\text{SiFSiF}_3$ in 66% yield,¹³ $(\text{Me}_2\text{SiF})_2$ (34%), and lesser amounts of SiF_3H , H_2 , and SiF_4 .



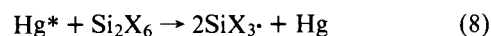
On the assumption that the initial step in these monosilane/disilane reactions is Si–H bond homolysis (eq 3), the formation of the observed mixed disilanes can be rationalized as occurring via $\text{S}_{\text{H}2}$ attack on the Si–Si bond by hydrogen atoms and/or silyl radicals (eq 4–6). An alternative mode of initiation is attack on the Si–Si bond by excited mercury atoms (eq 7). Such a pathway seemed highly unlikely for polyfluorodisilanes, given the characterization of $\text{Hg}(^3\text{P})$ as a distinctly electrophilic species.¹⁴



To explore the possibility of attack of excited mercury atoms on Si–Si bonds, we photolyzed two disilanes under conditions¹² comparable with those employed for the monosilane/disilane reactions. To our considerable surprise, an equimolar mixture of Si_2F_6 and $(\text{Me}_2\text{SiF})_2$ underwent a 40% conversion to $\text{SiF}_3\text{SiMe}_2\text{F}$ when photolyzed for 20 min. Production of the tetrafluorodisilane was nearly quantitative. Repetition of the experiment with other pairs of symmetrical methyl- and fluorodisilanes established the general nature of the reaction: in each case the asymmetric mixed disilane was formed in high yield.

The possibility that the disilane “metathesis” occurs via a bimolecular redistribution reaction between two disilane molecules (one of which would presumably have been activated by Hg^*) was discredited by an experiment in which a small amount of the radical trap nitric oxide was included in a mixture of Si_2F_6 and Si_2Me_6 . Very little $\text{Me}_3\text{SiSiF}_3$ was formed; the major products of the reaction were the disiloxanes $\text{SiF}_3\text{OSiF}_3$, $\text{SiF}_3\text{OSiMe}_3$, and $\text{Me}_3\text{SiOSiMe}_3$.¹⁵ We must accordingly conclude that the primary process in the disilane/disilane reactions is the attack of Hg^* on a Si–Si bond to give two silyl radicals (eq 8). Reactions in the monosilane/disilane and disilane/disilane systems occur at comparable rates. Eq

8 may therefore be of importance in the former series and eq 5 may serve as a chain-propagation step in both series.



Some hydrogen atoms were apparently generated in disilane/disilane reactions in which Si_2Me_6 was a component. Small amounts of H_2 , Me_3SiH , and a liquid residue of low volatility can all be attributed to C–H bond dissociation. However, Gunning and Strausz¹⁰ have shown that the presence of fluorine in alkylsilanes exerts a powerful deactivating influence with respect to attack of C–H bonds by $\text{Hg}(^3\text{P})$ atoms. Such behavior apparently extends to alkylidilanes: C–H bond dissociation appears to be unimportant in photochemistry of $(\text{Me}_2\text{SiF})_2$ and $(\text{MeSiF}_2)_2$, at least on the time scale (≤ 1 h) employed in this work.

Surprisingly little is known about methylfluorodisilanes. The only representatives of the class of compounds $\text{Si}_2\text{Me}_x\text{F}_{6-x}$, $1 \leq x \leq 5$, at all well known are $\text{Si}_2\text{Me}_5\text{F}$ and $(\text{SiMe}_2\text{F})_2$.¹⁶ 1,1,2-Trimethyltrifluorodisilane has been reported to be a minor product in the reaction of 1,1,2,2-tetramethyldisilacycloheptane with H_2SO_4 followed by $\text{NH}_4\text{F}\cdot\text{HF}$.¹⁷ No properties of the molecule were related. The other five methylfluorodisilanes in the above series have apparently not been previously reported. Once the symmetrical species $(\text{Me}_2\text{SiF})_2$ and $(\text{MeSiF}_2)_2$ have been prepared,¹⁸ either the monosilane/disilane or disilane/disilane schemes provide access to all other methylfluorodisilanes. Isolation of new disilanes was readily effected by preparative scale gas chromatography. A 10-ft, $\frac{3}{8}$ -in. column (10% OV-101 on 60/80 mesh Chromosorb G) comfortably separated nonisomeric members of the series.

All methylfluorodisilanes were fully characterized by ^{19}F , ^1H , and, in some instances, by ^{29}Si NMR spectra. Heteronuclear and homonuclear decoupling were employed and ^{29}Si satellite spectra analyzed where appropriate. The symmetrical compounds $(\text{Me}_2\text{SiF})_2$ and $(\text{MeSiF}_2)_2$ were assigned as $[\text{A}_3\text{A}'_3\text{X}]_2$ and $[\text{A}_3\text{XX}']_2$ ¹⁹ spin systems, respectively. All other disilanes exhibited simple first-order spectra. Data obtained from fluorine NMR spectra are enumerated in Table I.

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Stereoelectronic Effects in the Reactions of Phosphate Diesters. Ab Initio Molecular Orbital Calculations of Reaction Profiles

Sir:

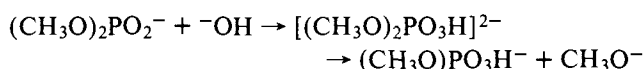
We have recently suggested that the selective weakening of P–O ester bonds which are trans, antiperiplanar (app) to lone pairs on directly bonded oxygen atoms may provide an important basis for further understanding enzymatic and nonenzymatic reactions of phosphate esters. Thus, we have suggested that a significant portion of the 10⁶–10⁸-fold rate acceleration of five-membered cyclic phosphates relative to acyclic phosphates derives from this stereoelectronic effect. We have also indicated that the preferential cleavage of yeast

phenylalanyl transfer RNA by pancreatic ribonuclease A at only two positions along the chain originates from this stereoelectronic effect.¹

These conclusions were based upon molecular orbital calculations on O₁–P–O₂ structural fragments in phosphate diesters and pentavalent oxyphosphoranes. As has recently been demonstrated,^{2–5} when the O₁ atom lone pair is app to the P–O₂ bond, the P–O₁ bond is strengthened (shown by an increase in the P–O₁ Mulliken overlap population) and the P–O₂ bond is weakened (shown by a decrease in the P–O₂ Mulliken overlap population).

Previous molecular orbital studies on this stereoelectronic effect have only utilized overlap population changes or bond length changes as a measure of the potential difference in reactivity of various conformations.^{1–4} In this communication we wish to present the first ab initio molecular orbital study on a stereoelectronically controlled reaction surface.

Shown in Figure 1 is the reaction profile for the base-catalyzed hydrolysis of dimethyl phosphate in two different ester conformations:



The points comprising the profile were computed with the Gaussian 70 series of programs, utilizing the minimal, STO-3G basis set.⁶ Geometry optimization for the dimethoxyphosphorane structures shown in Figure 1 was performed in essentially the same fashion as that previously reported for dimethyl phosphate. All nonhydrogen bond lengths and bond angles MeO_a–P–O[–], MeO_a–P–O_eMe, and [–]O–P–O_eCH₃ in the approximately trigonal-bipyramidal, D_{3h}, structures were optimized. C_s symmetry for the array of five oxygens and phosphorus was assumed throughout the reaction profile. (Thus colinear [–]OH attack and MeO[–] leaving were assumed.) Extensive geometry optimization on the structure with d_{P–OH} = 2.5 Å was also performed for the t_g–g conformation. The geometries for other reaction intermediates were obtained by interpolation. The same geometric parameters were assumed for the [–]OH attack reaction pathway involving the g,t,t intermediate. Geometries for the methoxide displacement re-

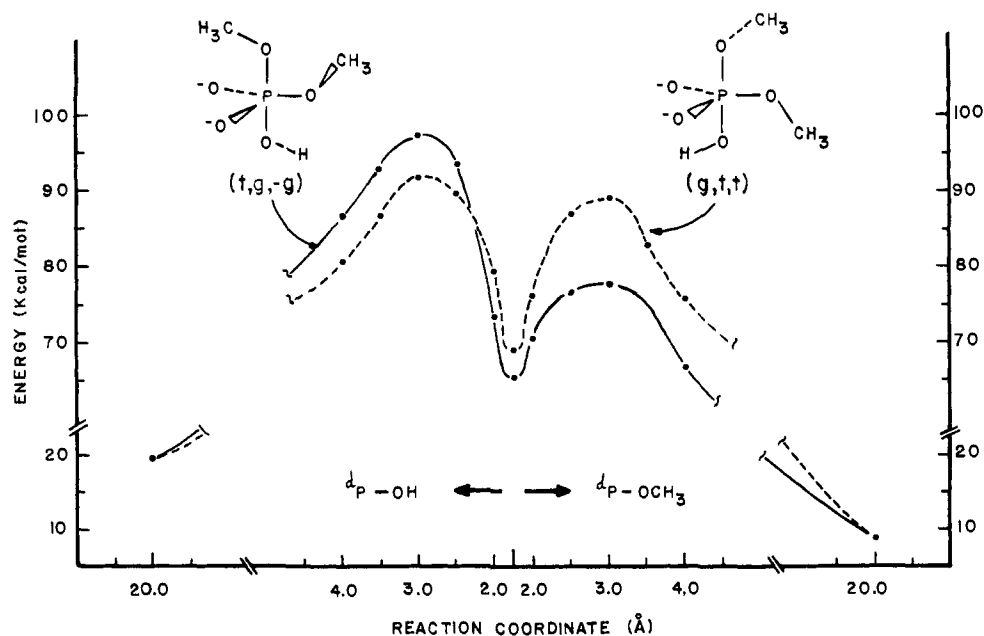


Figure 1. Reaction profiles for hydroxide-catalyzed hydrolysis of dimethyl phosphate in two different conformations. Torsional angles about the P–OMe bonds for the two phosphorane intermediates 1 and 2 are defined by the MeOPMe structural fragment, and the torsional angle about the P–OH bond is defined by the MeO_ePOH fragment. Conformers are defined by the following order for the torsional angles: apical ester, equatorial ester, and apical P–OH bonds. The reaction coordinate is defined by the P–OH distance (*d*_{P–OH}) and P–OMe distance (*d*_{P–OMe}) for the attack and displacement steps, respectively.