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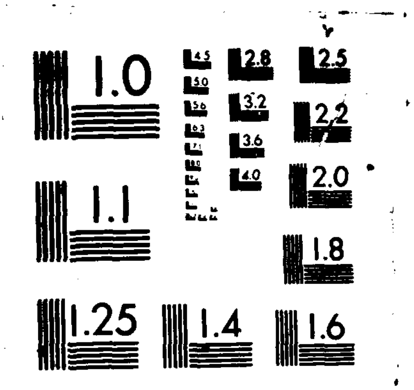

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SYNTHESIS AND REACTIONS OF SILANES CONTAINING TWO TRIFLATE GROUPS*

by

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1,2-Bis(trifluoromethanesulfonyloxy) tetramethyldisilane (1) and dimethylsilyl-bis(trifluoromethanesulfonate) (2) were prepared via displacement of phenyl, chloro, and methyl groups in the corresponding mono, and disilanes. Phenyl groups were displaced more rapidly than chloro and methyl groups. The unreacted groups were strongly deactivated by the presence of triflate group at the same silicon atom. The deactivation was much weaker when triflate group was present at the adjacent silicon atom. Alcohols and amines reacted more rapidly with ditriflates than with monotriflates.

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SYNTHESIS AND REACTIONS OF SILANES CONTAINING TWO TRIFLATE GROUPS*

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Abstract

1,2-Bis(trifluoromethanesulfonyloxy)tetramethyldisilane (1) and dimethylsilyl-bis(trifluoromethanesulfonate) (2) were prepared via displacement of phenyl, chloro, and methyl groups in the corresponding mono, and disilanes. Phenyl groups were displaced more rapidly than chloro and methyl groups. The unreacted groups were strongly deactivated by the presence of triflate group at the same silicon atom. The deactivation was much weaker when triflate group was present at the adjacent silicon atom. Alcohols and amines reacted more rapidly with ditriflates than with monotriflates.

Introduction

Silanes with trifluoromethanesulfonate (triflate) leaving groups are the most versatile silylating reagents [1]. Trimethylsilyl triflate has been a few orders of magnitude more reactive than the classical silylating reagent, trimethylsilyl chloride [2]. The reactivity of the triflate derivative is similar to the perchlorate and the iodide which have the disadvantages as an explosive (perchlorate) and a light sensitive (iodide) compound.

Triflate groups have been introduced to silanes in different reactions [1]. Initially, silver triflate had been reacted with trimethylchlorosilane and, in addition to the insoluble silver chloride, the trimethylsilyl triflate was formed [3]. Later, trifluoromethanesulfonic acid was used and found to react readily with chloro [4], [5], aryl [6], and alkyl [7] groups.

The preparation of linear and cyclic compounds containing a di- or polysilane linkage requires the use of difunctional disilanes. Different 1,2-dichlorosilanes, although successfully used in various chemical reactions, have limited synthetic application because of their relatively low reactivity.

We report here the preparation and some chemical reactions of a new compound, a disilane containing two triflate groups, 1,2-bis(trifluoromethanesulfonyloxy)-tetramethyldisilane (1) and a simple method of synthesis of dimethylsilyl-bis(trifluoromethanesulfonate) (2).

We are interested in the preparation of new high molecular weight polysilanes [8]. The severe reactions conditions of a typical reductive coupling of dichlorosilanes with sodium allow only alkyl and aryl substituents at the silicon atom. Rapid and quantitative displacement of aryl groups and formation of the reactive polysilanes opens a synthetic avenue to new polysilanes. The studies reported below describe our model studies with mono and disilanes

Results and Discussion

1. Relative rates of displacement of chloro and phenyl groups.

Rapid and quantitative formation of trimethylsilyl triflate from trimethylchlorosilane and trimethylphenylsilane indicated higher reactivity of chloro and phenyl than methyl groups towards triflic acid. The relative rates of the displacement of phenyl and chloro substituents was not known.

We have studied by ^{1}H NMR the reaction of a mixture of chloro- and phenyltrimethylsilane (10:1 molar ratio) with 1 equivalent of the triflic acid in CH_2Cl_2 solvent at 20 ^{0}C. After 1 minute the complete disappearance of the signal of trimethylphenylsilane (0.299 ppm) and the formation of trimethylsilyl triflate (0.526 ppm) was found. The signal of the chloride (0.467 ppm) remained unchanged. This indicates at least 200 times higher reactivity of the phenyl group in comparison with the chloro derivative. Displacement of the phenyl group proceeding via benzenonium cation [9] proceeds readily in the presence of triflic acid which is the strongest protonic acid known.

Silanes containing two electron withdrawing groups are more reactive (and thermodynamically less stable) than compounds possessing one electron withdrawing group. Therefore the prediction of the pathway of the reaction between triflic acid and dimethylphenylchlorosilane was more difficult. In Fig. 1a the ^1H NMR spectrum of the unreacted silane (0.712 ppm and the A_2B_2C aromatic pattern) is shown. After reaction with one equivalent of the triflic acid, the sharp singlet of benzene (7.4 ppm) and a new singlet of methyl groups in the dimethylchlorosilyl triflate at 0.861 ppm was formed (Fig. 1b). No signal of the dimethylphenylsilyl triflate (0.823 ppm) was found. This result indicates that phenyl group is displaced much more rapidly than the chlorine atom:

$$\text{Ph-SiMe}_2\text{-Cl} + \text{HOSO}_2\text{CF}_3 \rightarrow \text{CF}_3\text{SO}_2\text{O-SiMe}_2\text{-Cl} + \text{C}_6\text{H}_6 \qquad (1)$$

Formation of the dimethylchlorosilyl triflate is probably kinetically controlled. Similar result was found in the reaction of the triflic acid with the methylphenyldichlorosilane. In that case phenyl group was again preferentially displaced in spite of the presence of two chloro atoms and methyldichlorosilyl triflate (1.176 ppm) was formed.

2. Preparation of Dimethylsilyl bis(trifluorometanesulfonate) (2)

Reaction of diphenyldimethylsilane (0.609 ppm) with 1 equivalent of triflic acid yielded immediately phenyldimethysilyl triflate (0.823 ppm). Addition of the second equivalent of the acid led to the formation of 2. The displacement of the second phenyl group was much slower and the reaction was completed after 1 hour at room temperature ($[HOSO_2CF_3]_0$=0.40 mol/L). After 2 minutes nearly equal proportion of mono and ditriflate were observed.

Dimethyldichlorosilane reacted with triflic acid much slower than diphenyldimethylsilane. Under similar conditions the rection of the second equivalent of the acid with dimethylchlorosilyl triflate was completed after 24 hours. Displacement of the methyl group in trimethylsilyl triflate was not observed after a few days at room temperature. However, at higher temperatures dimethylsilylbis(fluorosulfonate) was found in a similar reaction[10].

3. Synthesis of 1,2-Bis(trifluoromethanesulfonyloxy)-tetramethyldisilane (1)

Reaction of 1 equivalent of triflic acid with 1,2-diphenyltetramethyl disilane led to a mixture of the unreacted disilane, 1, and monotriflate. This result indicates that the second phenyl group in the disilane is deactivated less by the triflate group than the second group in the monosilane. In Fig. 2 the dependence of the composition of the reaction mixture on the ratio of the acid to the initial disilane is shown. The experimental points fit very well with the theoretically calculated curves for the eight times higher reactivity of the first phenyl group relative to the second ($k_1/k_2 = 8$):

$$CF_3SO_2OH + Ph\text{-}SiMe_2\text{-}SiMe_2\text{-}Ph \xrightarrow{k_1} CF_3SO_2O\text{-}SiMe_2\text{-}SiMe_2\text{-}Ph + PhH \qquad (2)$$

$$CF_3SO_2OH + CF_3SO_2O\text{-}SiMe_2\text{-}SiMe_2\text{-}Ph \xrightarrow{k_2} CF_3SO_2O\text{-}SiMe_2\text{-}SiMe_2\text{-}OSO_2CF_3 + PhH$$

For the monosilane the reaction proceeds as a two-step process, allowing the separation of the monotriflate after addition of 1 equivalent of the acid. Under similar conditions 13% of the unreacted disilane and 13% of the ditriflate were present in the reaction with the disilane. Thus, taking into account the statistical factor (two phenyl groups in the diphenyldisilane) the presence of the triflate group at the neighboring silicon atom weakly deactivates the adjacent phenyl group (4 times).

Deactivation is much stronger in the reaction with hexamethyldisilane and 1,2-dichlorotetramethyldisilane. In both systems reaction with one equivalent of the acid lead to monotriflate while the second triflate group is incorporated only at higher temperature. Pentamethyldisilyl triflate has been recently described in literature [11]. The first methyl group was displaced rapidly at 0 ^{0}C. We found that the second group is removed only at 60 ^{0}C.

1 was separated by vacuum distillation (bp= 92^{0}C/ 10 mm). The preparative yield was above 70% in the reaction with all discussed disilanes.

4. Reactions of Ditriflates.

Silyl triflates are powerfull silylating reagents. We have studied the reactions of ditriflates with different nucleophilic reagents such as alcohols and amines. Ditriflates reacted rapidly with methyl, ethyl, isopropyl, tertbutyl, allyl, and 2,2,2-trifluoroethyl alcohol:

$$CF_3SO_2O\text{-}SiMe_2\text{-}SiMe_2\text{-}OSO_2CF_3 + 2\ ROH + 2B: \rightarrow RO\text{-}SiMe_2\text{-}SiMe_2\text{-}OR + 2BH^+,\ OSO_2CF_3{}^-$$

$R= CH_3\text{-}, C_2H_5\text{-}, (CH_3)_3C\text{-}, CH_2{=}CH\text{-}CH_2\text{-}, CF_3CH_2\text{-}$,

(3)

The reactivity of ditriflates is higher than that of monotriflates. Thus, when the mixture of trimethylsilyl triflate and 2 (3:1) reacted with 1 equivalent of methanol in the presence of triethylamine only dimethylmethoxysilyl triflate (0.514 ppm) was formed. 1 has been also found to be more reactive than disilylmonotriflate.

Reactions of ditriflates with alcohols are catalyzed by amines which act as proton traps. Best results were obtained with hindered pyridines 2,6-ditertbutylpyridine and 2,6-ditertbutyl-4-methylpyridine. Due to steric hindrances they do not react with the silyl group directly. The unsubstituted pyridine reacted with triflates forming silylated pyridinium salts which were insoluble in methylene chloride and chloroform. This resembles the behavior of a monotriflate [12]. The pyridinium salts of 1 were soluble in nitromethane. The ^1H NMR spectra of the mixture of pyridine and ditriflate (1:1 molar ratio) showed a broad singlet of all methyl groups in ditriflate at 0.3 ppm and signals of pyridine shifted downfield by approximately 0.2 ppm. This indicates a rapid exchange of the pyridine between all silyl triflate groups. The signal of methyl groups shifted downfield with an increasing concentration of pyridine and at a ratio larger than 2:1, a narrow singlet at 0.21 ppm was found. At still higher concentration of pyridine, the aromatic signals move upfield indicating again rapid exchange between free and complexed pyridine.

Secondary amines are more basic than pyridine. Thus, the addition of two equivalents of diethylamine to ditriflate (1:1 molar ratio) yields an equimolar mixture of protonated amine and 1-diethylamino-2-trifluoromethanesulfonyloxytetramethyldisilane:

$$CF_3SO_2O\text{-}SiMe_2\text{-}SiMe_2\text{-}OSO_2CF_3 + 2HNEt_2 \rightarrow Et_2N\text{-}SiMe_2\text{-}SiMe_2\text{-}OSO_2CF_3 + Et_2NH_2^+CF_3SO_3^- \quad (4)$$

The excess of diethylamine led to 1,2-disilyldiamines:

$$CF_3SO_2O\text{-}SiMe_2\text{-}SiMe_2\text{-}OSO_2CF_3 + 4HNEt_2 \rightarrow Et_2N\text{-}SiMe_2\text{-}SiMe_2\text{-}NEt_2 + 2\ Et_2NH_2^+CF_3SO_3^-$$

Methyl groups bound to the silicon atoms in diamine absorb at higher field (0.154 ppm) than in monotriflate (0.322 and 0.587 ppm). The excess of diethylamine exchanges with the protonated amine.

Experimental

All reactions were carried out in an argon atmosphere in flame-dried glassware. All the reagents were freshly distilled and dried over CaH_2 in an argon atmosphere. ^1H NMR spectra were recorded using 300 MHz GE and 80 MHz IBM instruments in $CDCl_3$, CD_3NO_2 and CD_2Cl_2 solutions using the signal of CH_2Cl_2 (5.32 ppm) as the reference. Elemental analysis were performed by MicAnal (Tuscon, Ar)

Synthesis of 1.

A. From 1,2-dichlorotetramethyldisilane and triflic acid.

Trifluoromethanesulfonic acid (5.09 g, 34 mmol) was added dropwise to 1,2-dichlorotetramethyldisilane (3.16 g, 17 mmol) at room temperature. The reaction mixture was heated to 60^0C for 12 hours. After that time no further HCl was evolved. The product was distilled directly from the reaction mixture to afford 5.65 g (80% yield) of 1, bp=92 ^0C (10 mm). ^1H NMR: singlet at 0.771 ppm, ^{13}C NMR: -0.5, and 119.2 ppm. Anal. Calcd for $C_6H_{12}F_6O_6S_2Si_2$: C, 17.39; H, 2.92; S, 15.47. Found: C, 17.01; H, 2.98; S, 15.16

B. From 1,2-diphenyltetramethyldisilane and triflic acid.

Trifluoromethanesulfonic acid (3.39 g, 23 mmol) was added dropwise at -23^0C to 1,2-diphenyltetramethyldisilane (3.06 g, 11.5 mmol) dissolved in 15 mL of CCl_4 . After the addition was completed the reaction mixture was stirred for 2 hours at room temperature and distilled using Vigreaux column to yield 72% (3.37 g) of 1

C. From hexamethyldisilane and triflic acid.

The reaction was performed in the way analogous to A yielding 81% of 1.

Reactions of 1 with different nucleophiles.

A. Allyl alcohol.

To the mixture of 0.95 g (16 mmol) of the allyl alcohol and 1.65 g (16 mmol) of the triethylamine in 10 mL of CH_2Cl_2, 3.37 g (8 mmol) of **1** was added at 0 ^{0}C. The mixture was stirred for 1 h at 0 ^{0}C and for an additional 12 hours at room temperature. After aqueous work-up and drying, the residue was distilled to yield 1,2-diallyloxytetramethyldisilane[13] in 46% yield.

B. Methanol

This reaction was performed in the identical way as described above. The preparative yield of 1,2-dimethoxytetramethyldisilane [14] was only 34%. However, the NMR spectra of the reaction mixture using triethylamine or 2,6-di-tert-butylpyridine show only the presence of 1,2-dialkoxytetramethyldisilane.

C. Diethylamine

This reaction was carried out in an NMR tube in the presence of 2,6-di-tert-butylpyridine. Chemical shift of **1** (0.76 ppm) did not shift after addition of two equivalents of the pyridine. Two new signals at 0.59 and 0.32 ppm (1:1 ratio) ascribed to the monotriflated amine were found after addition of the first equivalent of the diethylamine. After addition of the second equivalent of the diethylamine, half of **1** was converted to the monoamine (no diamine was found). Two triplets at 1.05 and 1.39 and two quartets at 2.85 and 3.05 ppm were assigned to methyl and methylene groups in the monoamine and the protonated diethylamine. After addition of four equivalents of the diethylamine, 1,2-bis(diethylamino)tetramethyldisilane 0.15 (s), 1.00(t), and 2.80 ppm(q) was found. Triflic acid was exclusively complexed by the diethylamine (3.05 and 1.39 ppm). The hindered pyridine was not protonated under this reaction conditions.

D. Pyridine

Addition of one eqivalent of the unsubstituted pyridine to **1** in $CDCl_3$ led to the precipitation of the complex with pyridine. In CD_3NO_2 the complex is soluble and the broad singlet at 0.27 ppm indicates the rapid exchange of pyridine with **1**. This signal shifts upfield to 0.21 ppm after addition of a second equivalent of pyridine. Pyridine absorbs at approximately 0.2 ppm downfield indicating complexation. An excess of pyridine exchanges with the complex leading to the upfield shift of the pyridine and has no effect on the absorption of the methyl groups.

Synthesis of **2** .

A. From dichlorodimethylsilane and triflic acid.

Trifluoromethanesulfonic acid (5.09 g, 34 mmol) was added dropwise to the dichlorodimethylsilane (2.101 g, 17 mmol) at room temperature. The resulting mixture was heated to 60^0C for 12 hours until no further hydrogen chloride was evolved. The product was distilled at 66-68^0C (10 mm) to afford 5.11 g (85%) of **2**.

B. From diphenyldimethylsilane and triflic acid.

Trifluoromethanesulfonic acid (0.070g, 0.47 mmol) was added dropwise to diphenyldimethylsilane (0.050 g, 0. 235 mmol) dissolved in 1 mL of $CDCl_3$. ^{1}H NMR showed quantitative formation of **2** (0.91 ppm) and complete disappearance of diphenyldimethylsilane (0.61 ppm).

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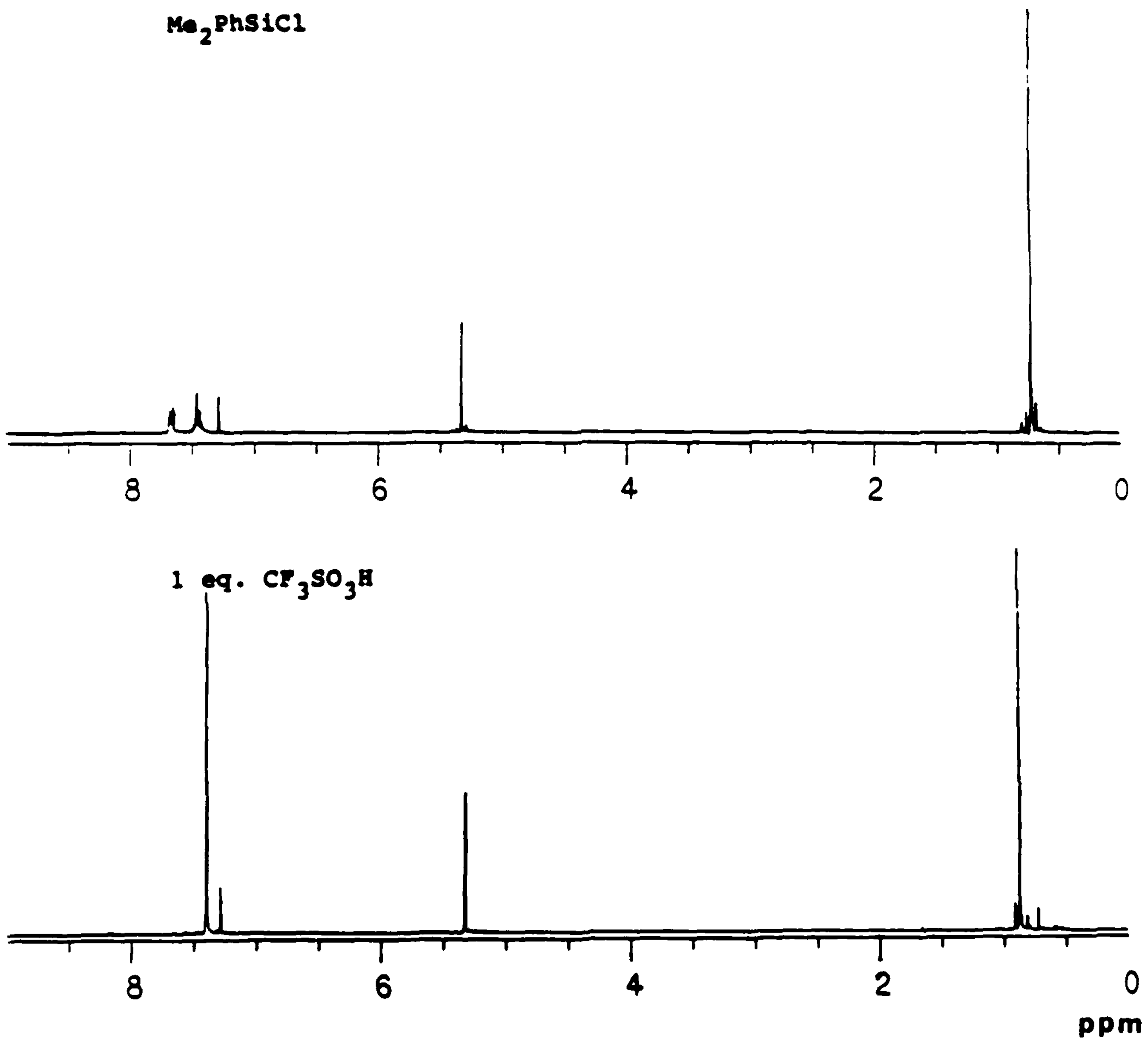
Captions for Figures

Fig.1. ^{1}H NMR spectrum of dimethylphenylchlorosilane (0. 25 mol/L) (a), and after reaction with 1 equivalent of triflic acid in $CDCl_3$ at 20 ^{0}C (b).

Fig.2 Calculated (curves) and experimental proportions of 1,2-diphenyltetramethyldisilane (●), monotriflate (■) and ditriflate (○) at different $[acid]_0/[disilane]_0$ ratios. Calculations were performed assuming $k_1/k_2=8$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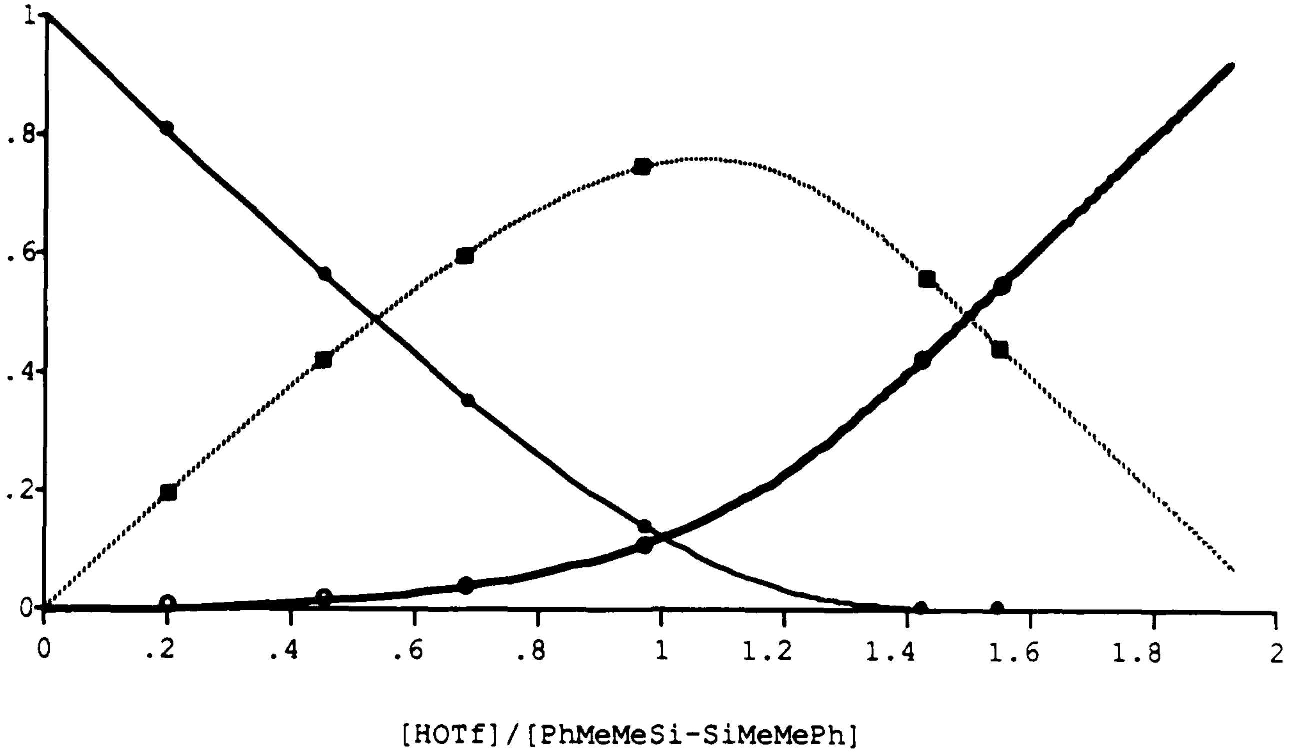
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