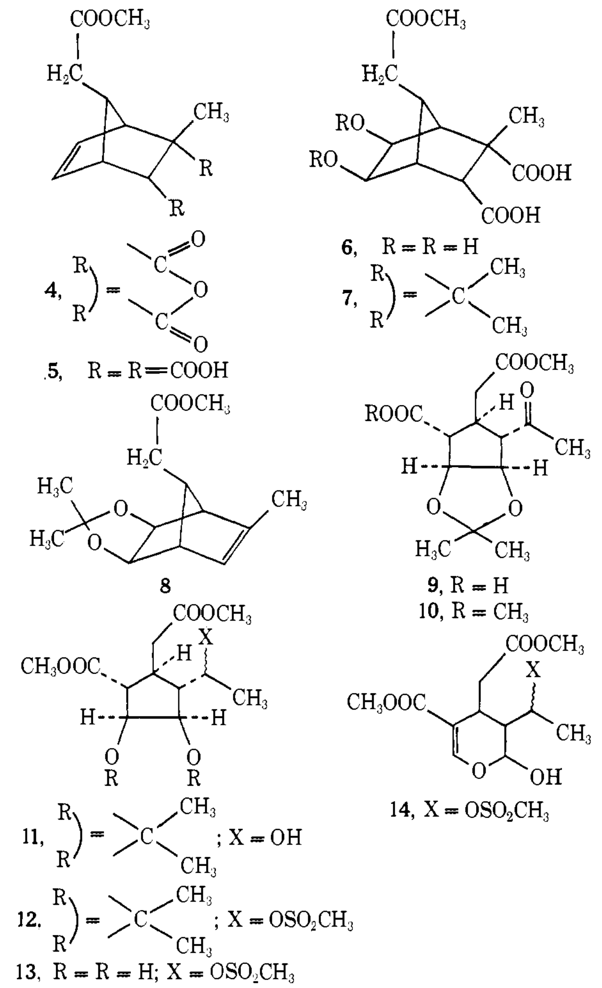
Chart I



pyridine gave, again in nearly quantitative yield, the mesylates **12**: nmr ($CDCl_3$) δ 1.33, 1.50 (2 s, 6, CCH_3), 1.50 and 1.55 (d, J = 6 Hz, 3, SO_3CHCH_3), 3.00 and 3.03 (s, 3, CH_3SO_3). The mixture of mesylates crystallized on standing; recrystallization afforded one of the diastereomers in pure form, mp 102-103°.[6] Hydrolysis of the latter with 60% formic acid followed by oxidation of the resultant glycol **13** with periodate (pH 6-7) afforded an isomerically pure mesylate **14** in 20% yield: mp 107-111°;[6] nmr ($CDCl_3$) δ 1.58 (d, J = 6.5 Hz, 3, $CHCH_3$), 3.02 (s, 3, O_3SCH_3), 3.70, 3.74 (2 s, 6, OCH_3), 5.62-5.82 (m, 1, OCHO), 7.55 (s, 1, OCH=). Heating **14** in an aqueous pyridine solution resulted in the formation of *dl*-methyl elenolate as an oil, identical by ir, uv, and nmr spectroscopy with the oily, chromatographically highly purified material obtained from natural elenolic acid on treatment with diazomethane. The synthetic material crystallized on standing to give isomerically pure racemic material, mp 93-98°. The natural material has not yet been obtained in crystalline form. The transformation of the mixture of mesylates **12** to methyl elenolate of the same purity as that from the single isomer of **12** could be carried out without isolation of intermediates in an overall yield of 30%.

The formal synthesis of calcium elenolate (**1**) was completed by the hydrolysis of natural methyl elenolate with 0.1 *N* sulfuric acid at 80-90° followed by treatment of the free acid with calcium carbonate.

Acknowledgment. We wish to thank Dr. W. A. Struck and associates for analytical and spectral data and L. M. Reinecke for vpc analyses.

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Received July 2, 1973

Dynamic Stereochemistry of Triarylsilanes[1]

Sir:

In connection with our recent studies of isomerism and isomerization in propeller-like molecules,[2] we noted with interest a report that the mesityl groups of trimesitylfluorosilane (**1**) are "... nicht mehr frei drehbar,"[3] as indicated by the doubling of the ortho methyl group resonance in the ambient temperature ^1H nmr spectrum. Additionally, Gilman and coworkers had previously reported the isolation of four crystalline stereoisomers of tetra-*o*-tolylsilane.[4] These two reports led to the expectation that the isolation of torsional isomers of triarylsilanes, such as trimesitylsilane (**2**), might be possible at ambient temperatures.

By analogy with acetyltriphenylsilane[5] and related compounds,[2] **2** is presumed to have a propeller (C_3) conformation in the ground state. Such a conformation is chiral and therefore capable of existing in two enantiomeric forms. In addition, each ring carries two diastereotopic ortho methyl groups: one proximal to the hydrogen on silicon and the other distal. In the absence of rotation about the carbon-silicon bonds, the two diastereotopic methyl groups would be expected to give rise to two separate signals in the ^1H nmr spectrum.

Trimesitylsilane was prepared by the action of excess mesityllithium on trichlorosilane in refluxing benzene for 45 hr. At ambient temperatures, the para and ortho methyl groups each appeared as a singlet in the ^1H nmr spectrum (Table I); upon cooling, however, the ortho methyl signal broadened and ultimately split

Table I. Properties[a] of Triarylsilane Derivatives

Compd no.	Mp, °C	$\Delta G^{\ddagger}_T$ (T, °C),[b] kcal/mol	$\Delta\nu$, Hz[c]	Chemical shifts[d] (δ, ppm from TMS) *p*-Me	*o*-Me
1	192-193[e]			2.23	2.04[f]
2	197-198	10.9 (−47)	23.0	2.19	2.06
3	150.5-151.5	12.1 (−24)	24.5		2.12[f]
4	143-145	12.5 (−13)	25.3		2.18
5	151.5-153.5	11.1 (−43)	22.3		2.12

[a] All compounds were recrystallized to constant melting point and gave satisfactory elemental analyses. Mass spectra were consistent with the assigned structures. Nmr spectra were recorded on a Varian A-60A spectrometer. [b] Free energy of activation for enantiomerization by a two-ring flip pathway. [c] Separation, at the slow exchange limit, of the ortho methyl signals. [d] Data refer to *ca.* 10% solutions in CS_2 with *ca.* 1% TMS as internal standard, at ambient probe temperature (*ca.* 37°). [e] Lit.[3] 193-193.5°. [f] Center of a doublet, $^5J_{HF}$ = 2.7 Hz.

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(1) This work was supported by the National Science Foundation (GP-30257).

(2) D. Gust and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 1535 (1973).

(3) N. Wiberg and B. Neruda, *Chem. Ber.*, **99**, 740 (1966).

(4) G. N. R. Smart, H. Gilman, and H. W. Otto, *J. Amer. Chem. Soc.*, 77, 5193 (1955).

(5) For X-ray structure see P. C. Chieh and J. Trotter, *J. Chem. Soc.*, 1778 (1969).

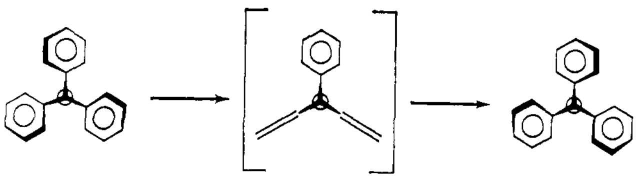

Figure 1. Schematic representation of the two-ring flip mechanism for a triarylsilane, looking along the Si–H bond.

into the expected doublet ($\Delta\nu$ 23.0 Hz). The Gutowsky–Holm approximation[6] yielded a rate constant k_c for exchange of magnetic environments of the ortho methyl groups of 50.6 sec^{-1} at the coalescence temperature (−47°).

Isomerization of triarylsilane derivatives may be interpreted in terms of an extension of the flip mechanisms postulated by Kurland, *et al.*, for triarylcarbenium ions.[2,7] Studies in analogous systems[8] indicate that the two-ring flip is the stereoisomerization pathway of lowest energy. In this mechanism, two aryl rings rotate through two planes perpendicular to the reference plane defined by the three carbon atoms attached to silicon and the third ring rotates through an orientation in which the normal to the ring which passes through the carbon atom attached to silicon lies in a plane perpendicular to the reference plane and containing the C–Si bond (Figure 1). Assuming that the triarylsilanes discussed herein also isomerize by this mechanism, the rate of enantiomerization equals $3k_c$. Thus, the free energy of activation for enantiomerization of **2** by a two-ring flip mechanism is $\Delta G^{\ddagger}_{-47}$ 10.9 kcal/mol, as calculated from the Eyring equation.

In view of this surprisingly low value, it was decided to reinvestigate the ^{1}H nmr spectrum of **1**. This compound, prepared from **2** by bromination in CCl_4 followed by treatment of the resulting mixture of halides with aqueous HF in ethanol, did indeed exhibit a para methyl singlet and an ortho methyl doublet at ambient temperature, as reported.[3] However, at lower temperatures, the doublet collapsed and split into an upfield singlet and a downfield doublet partially obscured by the para methyl signal. This behavior suggested that the doublets were due to long-range H–F coupling; spectra run at both 60 and 100 MHz, as well as fluorine decoupling and INDOR experiments,[9] confirmed this suggestion. In order to facilitate line-shape analysis, the spectroscopically irritating para methyl absorption was eliminated as follows. Tris(2,6-xylyl)fluorosilane (**3**) was synthesized by a route analogous to that for **1**, and its temperature dependent ^{1}H nmr spectrum was measured (Figure 2). Spectra were calculated using DNMR2[10] which matched the observed spectra at various temperatures, and the rates obtained were used to determine a barrier of $\Delta G^{\ddagger}_{-24}$ 12.1 kcal/mol for enantiomerization. Similarly, tris(2,6-xylyl)chlorosilane (**4**), prepared by treatment of the corresponding silane (**5**) with sulfuryl chloride, exhibited a barrier of $\Delta G^{\ddagger}_{-13}$ 12.5 kcal/mol, as compared to $\Delta G^{\ddagger}_{-43}$ 11.1 kcal/mol for **5**.

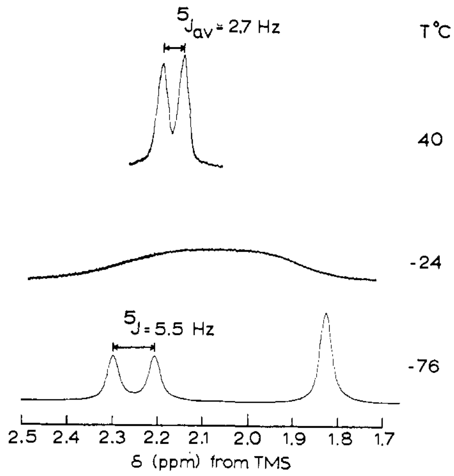

Figure 2. Temperature-dependent ^{1}H nmr spectrum of tris(2,6-xylyl)fluorosilane (**3**) in CS_2 solution.

It is thus clear that barriers to enantiomerization in trimesitylsilanes are much too low to permit facile resolution. This result brings into question the reported[4] isolation of diastereomeric tetra-*o*-tolylsilanes. This question is laid to rest in the communication immediately following.[11]

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(6) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(7) R. J. Kurland, I. I. Schuster, and A. K. Colter, *J. Amer. Chem. Soc.*, 87, 2279 (1965).

(8) See ref 2 and references cited therein.

(9) We thank Mr. D. F. Hillenbrand, University of Wisconsin, Madison, Wisconsin, for performing the INDOR and corroborative ^{19}F decoupling experiments.

(10) G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969).

(11) M. G. Hutchings, C. A. Maryanoff, and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 7158 (1973).

(12) NIH Postdoctoral Fellow, 1972–1973.

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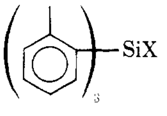
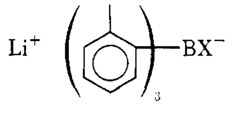
Received July 11, 1973

Dynamic Stereochemistry of Tetraarylsilanes and Borate Salts

Sir:

In the preceding communication,[1] a question was raised concerning a report[2] claiming the isolation of different conformational stereoisomers of tetra-*o*-tolylsilane (**1a**) at ambient temperatures. We now wish to report results, part of an ongoing study of hindered rotation in tetraaryl molecules of type Ar_4Z, which have the effect of invalidating the earlier claim.[2]





1a, X = o-tolyl
b, X = chlorine
c, X = fluorine
d, X = 1-naphthyl
e, X = o-anisyl

2a, X = o-tolyl
b, X = o-anisyl

The ^{1}H nmr spectrum of **1a** (mp 228–230°)[3] in $CDCl_3$–CS_2 shows the methyl group as a sharp singlet

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(1) R. J. Boettcher, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 7157 (1973).

(2) G. N. R. Smart, H. Gilman, and H. W. Otto, *J. Amer. Chem. Soc.*, 77, 5193 (1955).

(3) Compound **1a**[4] was prepared from *o*-tolyllithium and **1b** (3% yield), **1c** (67% yield), or tetramethoxysilane (9% yield).

(4) All compounds exhibited analytical and spectral data consistent with the given structural assignments.