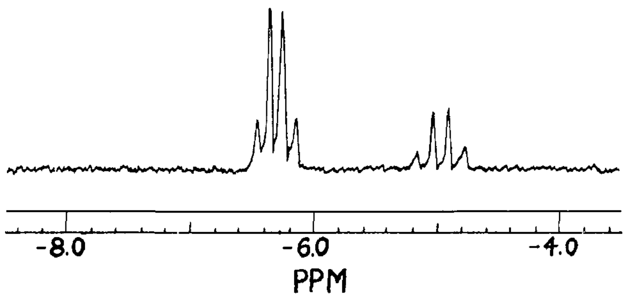

Figure 1. ^1H nmr spectrum of $CF_3CH_2N_2^+$ (and some $CF_3CH_2OSO_2F$) in FSO_3H at −60°.

$$CF_3CHN_2 \xrightarrow[-60^\circ]{FSO_3H} CF_3CH_2N_2^+SO_3F^- \xrightarrow[-N_2]{\text{warming}} CF_3CH_2OSO_2F$$

Nmr spectra were recorded on a Varian Model A-60-A spectrometer and a Varian Model A56-60A spectrometer using TMS and fluorotrichloromethane, respectively, in capillary tubes as external references.

The ^1H nmr spectrum of trifluoromethyldiazomethane in FSO_3H at −60° (Figure 1) exhibits a quartet at −6.3 ppm, $J_{HF} = 6.1$ cps, which we assign to the 2,2,2-trifluoroethyldiazonium ion. There is also a smaller quartet at −5.0 ppm, $J_{HF} = 7.5$ cps, due to the presence of some 2,2,2-trifluoroethyl fluorosulfate[8] formed during the mixing and transferring processes.

After the evolution of nitrogen had been effected by warming the sample, the spectrum was again recorded at −60° (Figure 2). The quartet at −6.3 ppm has completely disappeared, while the quartet assigned to the reaction product at −5.0 ppm has grown in size.

Trifluoromethyldiazomethane itself shows a quartet in the ^1H spectrum at −4.6 ppm ($CDCl_3$), $J_{HF} = 4.0$ cps, and a doublet in the ^{19}F spectrum at +54.45 ppm ($CDCl_3$).

The ^{19}F nmr spectrum of trifluoromethyldiazomethane in FSO_3H at −60° complements the ^1H spectrum. It shows the diazonium ion as a triplet at +64.58 ppm, $J_{HF} = 6.1$ cps, and the fluorosulfate as a triplet of doublets at +75.76 ppm and a quartet at −36.98 ppm. We have assigned the −36.98-ppm quartet, $J_{FF} = 2.5$ cps, to the fluorine attached to sulfur and the +75.76-ppm pattern to the trifluoromethyl group. In the latter pattern the vicinal hydrogen–fluorine coupling, $J_{HF} = 7.5$ cps, is again apparent, and long-range fluorine–fluorine coupling,[9] $J_{FF} = 2.5$ cps, is seen as well. Again, warming and nitrogen evolution led to the disappearance of the +64.58 triplet assigned to the diazonium ion.

We find no evidence from the ^{19}F spectrum for the protonation of the diazo compound at the terminal nitrogen leading to the stable cationic species I under these conditions.[10]

$$CF_3CH{=}\overset{+}{N}{=}NH$$

I

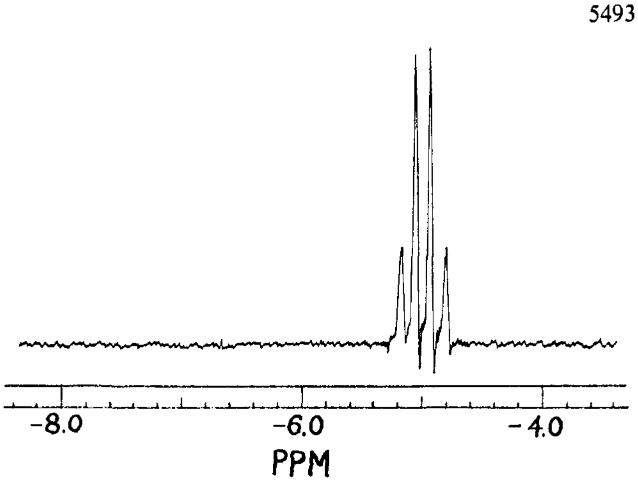

Figure 2. ^1H nmr spectrum of $CF_3CH_2OSO_2F$ in FSO_3H at −60°.

The 2,2,2-trifluoroethyl fluorosulfate has been isolated from its FSO_3H solution by adding a 2,2,4-trimethylpentane solution of the diazo compound to FSO_3H at −78° and subsequently distilling the solution. Sodium fluoride was added to the distillation flask. The fluorosulfate was characterized by infrared and nmr spectra and elemental analysis. 2,2,2-Trifluoroethyl fluorosulfate, bp 81–82° (750 torr), has a quartet in its ^1H nmr spectrum (CCl_4) at −5.0 ppm, $J_{HF} = 7.4$ cps. Its infrared spectrum exhibits intense absorption peaks at 6.86, 7.8, 8.13, 8.46, 9.6, and 11.8 μ, which we have assigned to SO_2, CF_3, and SF absorptions.[11]

Anal.[12] Calcd for $C_2H_2F_4O_3S$: C, 13.19; H, 1.10; F, 41.74; S, 17.61. Found: C, 13.40; H, 1.20; F, 42.05; S, 17.90.

Preliminary deuterium exchange experiments have indicated that complete hydrogen exchange occurs in the perchloric acid catalyzed hydrolysis of trifluoromethyldiazomethane to 2,2,2-trifluoroethanol.

Further experiments testing the stability of simple alkyldiazonium ions in other systems are in progress.

Acknowledgment. We are grateful to Professor George Olah for his encouragement and the use of his Varian Model A56-60A spectrometer for the ^{19}F spectra, to M. B. Comisarow and D. H. O'Brien for running the ^{19}F spectra, and to Dr. George Slomp and F. A. MacKellar of the Upjohn Company, Kalamazoo, Mich., for their assistance in obtaining the ^1H nmr spectra. This work was partially supported by grants from the Research Corporation and the Undergraduate Research Participation Program of the National Science Foundation.

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(8) For an analogous formation of a fluorosulfate in FSO_3H solution see G. A. Olah, R. D. Chambers, and M. B. Comisarow, *J. Am. Chem. Soc.*, **89**, 1268 (1967).

(9) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Inc., New York, N. Y., 1966, pp 879–880.

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(11) M. Lustig and G. H. Cady, *Inorg. Chem.*, **2**, 388 (1963).

(12) By Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

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(14) Undergraduate Research Participant, National Science Foundation Undergraduate Research Participation Program, 1966–1967.

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Stereochemistry of the Formation and Thermal Rearrangement of β-Ketosilanes

Sir:

We wish to report that β-ketosilanes on prolonged heating at temperatures of 80–175° are converted into

Table I. Thermal Isomerization of β-Ketosilanes

Compound	Conditions	Products	Yield,[a] %
Ph_3SiCH_2COPh	Cyclohexane, 81°, 18 hr	$Ph_3SiOCPh{=}CH_2$	10[b]
	Cyclohexane, 81°, 72 hr	$Ph_3SiOCPh{=}CH_2$	30[b]
	Toluene, 110°, 18 hr	$Ph_3SiOCPh{=}CH_2$	100
(+)-1-$NpPhMeSiCH_2COPh$	Toluene, 110°, 52 hr	(−)-1-$NpPhMeSiOCPh{=}CH_2$	100
Me_3SiCH_2COMe	Neat,[c] 140°, 36 hr	$Me_3SiOCMe{=}CH_2$	100
Me_3SiCH_2COPh	Neat,[c] 100°, 24 hr	$Me_3SiOCPh{=}CH_2$	16
	Neat,[c] 150°, 36 hr	$Me_3SiOCPh{=}CH_2$	100
Ph_3SiCH_2COMe	Xylene,[c] 175°, 18 hr	$Ph_3SiOCMe{=}CH_2$	100
Ph_3GeCH_2COPh	Xylene, 140°, 36 hr	$Ph_3GeO\text{-}CPh{=}CH_2$	0[b]

[a] Yields were estimated from nmr or by isolation. [b] Ketone recovered in good yield. [c] Sealed vial.

the isomeric siloxyalkenes in high yield,[1] as shown in Table I, although the analogous germanium compounds fail to rearrange.[3]

$$\mathrm{R_3SiCH_2COR'} \xrightarrow{\Delta} \mathrm{R_3SiOCR'{=}CH_2}$$

The rearrangement occurs with high stereospecificity since (+)-α-(1-naphthylphenylmethylsilyl)acetophenone[6] ((+)-1-naphthylphenylmethylphenacylsilane), I, $[\alpha]_D$ +25.6° (chloroform), rearranged during 52-hr heating in toluene to give a quantitative yield of (−)-α-(1-naphthylphenylmethylsiloxy)styrene,[6] II, $[\alpha]_D$ −47.1° (chloroform).

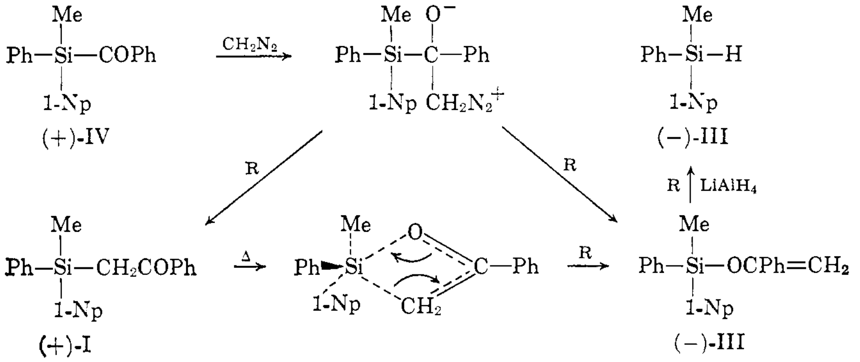

Figure 1. Stereochemistry of ketosilanes and siloxystyrenes.

The above findings are obviously closely related to our recently published observations that many acylsilanes[7] when treated with diazomethane yield a mixture of the homologous β-ketosilane and its isomeric siloxyalkene.[8]

$$\mathrm{R_3SiCOR' + CH_2N_2 \longrightarrow R_3SiCH_2COR' + R_3SiOCR'{=}CH_2}$$

The stereochemistries of these latter reactions are highly pertinent to this study. When (R)-(+)-benzoyl-1-naphthylphenylmethylsilane,[9] IV, $[\alpha]_D$ 6.05° (benzene), was treated with cold ethereal diazomethane in the dark over 14 days, it gave on work-up 67% (+)-α-(1-naphthylphenylmethylsilyl)acetophenone as an oil, $[\alpha]_D$ 25.6° (chloroform), which on crystallization gave solid material, mp 54–56°, $[\alpha]_D$ 27.1° (chloroform), and 33% (−)-α-(1-naphthylphenylmethylsiloxy)styrene, $[\alpha]_D$ −43.9° (chloroform), as an oil. Reduction of the latter compound with lithium aluminum hydride in ether, a reaction which with silyl ethers is well established as occurring with retention of configuration,[10,11] gave (−)-1-naphthylphenylmethylsilane, $[\alpha]_D$ −30.8° (cyclohexane). Taking into account the optical purity of the starting benzoylsilane[9] (90%) these data indicate that the formation of siloxystyrene occurred with complete retention of configuration at the asymmetric silicon center, a result that parallels the related silylcarbinol to silyl ether rearrangement.[11]

The reaction of benzoylsilane IV leading to β-ketosilane I may also be expected to occur with retention of configuration at silicon, by analogy with Gutsche and Chang's study of the ring expansion of (−)-2-methylcyclohexanone with diazomethane.[12] To date, the only evidence of the stereochemistry and thus the absolute configuration of (+)-α-(1-naphthylphenylmethylsilyl)acetophenone (I) comes from ORD comparison of this compound with that of its (+)-germanium

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(1) Related rearrangements of trialkylsilylacetones catalyzed by mercuric iodide or trialkylsilyl iodides have recently been described by Litvinova, *et al.*[2]

(2) O. V. Litvinova, Yu. I. Baukov, and I. F. Lutsenko, *Dokl. Akad. Nauk SSSR*, **173**, 578 (1967).

(3) While rearrangements involving silicon–oxygen bond formation are frequently observed, as with silylcarbinols[4] or acylsilanes,[5] in all cases the germanium analogs have failed to rearrange.

(4) A. G. Brook, C. M. Warner, and M. E. McGriskin, *J. Am. Chem. Soc.*, **81**, 981 (1959).

(5) A. G. Brook and N. V. Schwartz, *J. Org. Chem.*, **27**, 2311 (1962).

(6) Acceptable analyses and spectra have been obtained for all new compounds.

(7) We now favor use of the term "acylsilane" in lieu of "α-silyl ketone" to designate compounds with the structure R_3SiCOR.

(8) A. G. Brook, W. W. Limburg, D. M. MacRae, and S. A. Fieldhouse, *J. Am. Chem. Soc.*, **89**, 704 (1967).

(9) A. G. Brook and W. W. Limburg, *ibid.*, **85**, 832 (1963); A. G. Brook, C. M. Warner, and W. W. Limburg, *Can. J. Chem.*, **45**, 1231 (1967).

(10) L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Am. Chem. Soc.*, **86**, 3776 (1964), and references cited therein.

(11) A. G. Brook and C. M. Warner, *Tetrahedron Letters*, **18**, 815 (1962).

(12) C. D. Gutsche and C. T. Chang, *J. Am. Chem. Soc.*, **84**, 2263 (1962); C. Djerassi, B. F. Burrows, C. Overberger, T. Takakoshi, C. D. Gutsche, and C. T. Chang, *ibid.*, **85**, 949 (1963).

analog,[13] which was synthesized with known configuration by a route involving unambiguous stereochemistry.[14]

However, preliminary rate studies carried out on α-(triphenylsilyl)acetophenone have shown that the thermal rearrangement cleanly follows first-order kinetics for more than three half-lives (90% completion). Hence the isomerization must be intramolecular, involving a four-center transition state, and the rearrangement of (+)-I to (−)-II must lead to retention of configuration at silicon.[15,16]

Thus, as shown in Figure 1, since (−)-siloxystyrene (II) may arise directly from (+)-benzoylsilane (IV) with retention of configuration, or indirectly *via* formation of (+)-silylacetophenone (I) and its subsequent thermal rearrangement, both the formation and rearrangement of I must also involve retention of configuration. Consequently all three compounds must have the same relative configuration at the asymmetric silicon center.

It might be asked whether the siloxyalkene which was isolated as one of the products from the reaction of diazomethane with benzoylsilane arose, not as a direct product of the reaction, but instead from the sequence of reactions acylsilane → β-ketosilane → siloxyalkene. That this is not possible follows from observation of the progress of the reaction of the acylsilane with diazomethane at 5° by both nmr and infrared spectroscopy which showed that the ratio of siloxyalkene to β-keto silane formed was independent of the reaction time, as would be required if both products arose from a common intermediate.

Attempts to effect this rearrangement by photochemical methods did not succeed because the reaction took alternative pathways leading to dimerization and photoreduction products. These will be described later, as will our further studies now in progress.

Acknowledgment. We acknowledge support of this research by a grant from the National Research Council of Canada and by a Fellowship to W. W. L. by Dow Corning Silicones of Canada.

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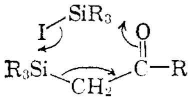
[13] Both + enantiomers show virtually identical single positive Cotton curves down to about 320 mμ, at which point absorption interferes.

[14] A. G. Brook and D. M. MacRae, unpublished results.

[15] There is ample precedent that four-center reactions involve retention of configuration—*e.g.*, the reduction of alkoxysilanes with lithium aluminum hydride[10] and the Wittig reaction.[17]

[16] The catalyzed and therefore bimolecular reactions of Litvinova[2] undoubtedly involve six-center transition states such as



which would also be expected to involve retention of configuration.

[17] A. Bladé-Font, C. A. VanderWerf, and W. E. McEwen, *J. Am. Chem. Soc.*, **82**, 2396 (1960).

[18] Dow Corning Silicones of Canada Fellow, 1961–1962.

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Phosphaboranes and Carbaphosphaboranes

Sir:

In the past few years there have been several reports concerning slightly distorted icosahedral boranes containing one or two heteroatoms in the cage. The first series of these molecules to appear in the literature was 1,2-, 1,7-, and 1,12-dicarbaclovododecaborane(12).[1–3] More recently brief communications concerning the $B_{11}H_{11}CH^-$ ion[4] and the $B_{10}H_{10}SBC_6H_5$ molecule[5] have appeared in the literature. All of these molecules are isoelectronic with the $B_{12}H_{12}{}^{2-}$ ion. In certain cases[3,6,7] either X-ray or ^{11}B nmr studies have indicated that these molecules are best described as distorted icosahedra.

This communication concerns the formation, characterization, and preliminary chemistry of 1,2-$B_{10}H_{10}CHP$ (I), 1,7-$B_{10}H_{10}CHP$ (II), and $B_{11}H_{11}PC_6H_5$ (III). Slow addition of a 5% heptane solution of phosphorus trichloride to a slurry of $Na_3B_{10}H_{10}CH\cdot 2THF$[8] in heptane at reflux produced 1,2-$B_{10}H_{10}CHP$, mp 349–350°, in moderate yield. *Anal.* Calcd for $B_{10}H_{10}CHP$: C, 7.41, H, 6.4, P, 19.1, mol wt, 162. Found: C, 7.50, H, 6.84, P, 20.0; mol wt, 165 (cryoscopic in benzene). This compound is a white sublimable solid with an odor reminiscent of carborane ($B_{10}H_{10}C_2H_2$). The mass spectrum of I at low electron voltage (13 ev) cuts off at *m/e* 164 corresponding to the $^{12}C_1H_{11}{}^{11}B_{10}{}^{31}P_1{}^+$ ion. The ^{11}B nmr spectrum (32 Mc) of I is consistent with a 1:1:2:2:2:2 pattern expected for 1,2- or 1,7-$B_{10}H_{10}CHP$. Complete interpretation of the spectrum was not possible because of extensive overlap of the individual doublets. That the carbon and phosphorus atoms are *ortho* in I is suggested by the method of synthesis which formally involves insertion of a phosphorus atom into the open, carbon-containing pentagonal face of the $B_{10}H_{10}CH^{3+}$ ion to complete the distorted icosahedron. The proton nmr of I contains a broad doublet at τ 7.85 with a 14-cps splitting attributed to $^{31}P-^{1}H$ coupling.

Heating I at 485° for 10 hr produced a new isomer (II), mp 325–327°, in 55% yield. Gas chromatographic analysis indicated that II was at least 98% pure. The ^{11}B nmr spectrum of II was too complex to be consistent with the two doublets expected for 1,12-$B_{10}H_{10}H_{10}CHP$. The ^{1}H nmr spectrum of II contained a broad singlet (CH) at τ 7.52 with no observable $^{31}P-^{1}H$ coupling. The nmr spectra suggest that II is best represented as 1,7-$B_{10}H_{10}CHP$ (Figure 1). This isomerization therefore appears to follow the rearrangement mechanism proposed by Lipscomb.[9]

The chemical properties of the carbaphosphaboranes are in some respects similar to the respective carborane analogs. Metalation of II with butyllithium and then reaction with methyl iodide produced 1,7-$B_{10}H_{10}C(CH_3)P$. An extensive derivative chemistry of the analogous 1-lithio-*m*-carborane has been reported.[10] Reaction of I with excess bromine and aluminum chloride gave, as the ultimate product, 1,2-$B_{10}Br_3H_7CHP$.

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[1] T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).

[2] D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

[3] S. Papetti and T. L. Heying, *J. Am. Chem. Soc.*, **86**, 2295 (1964).

[4] W. H. Knoth, *ibid.*, **89**, 1274 (1967).

[5] E. L. Muetterties, "The Chemistry of Boron and Its Compounds," John Wiley and Sons, Inc., New York, N. Y., 1967, p 657.

[6] J. A. Potenza and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1917 (1966).

[7] J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1673 (1964).

[8] This solvated salt is obtained as a precipitate from the reaction of $B_{10}H_{12}CN(CH_3)_3$ with sodium metal in tetrahydrofuran.

[9] W. N. Lipscomb, *Science*, **153**, 373 (1966).

[10] T. P. Onak, *Advan. Organometal. Chem.*, **3**, 335 (1965).