

The transformation of the diene IV to a ten-membered carbocycle (V) was accomplished photochemically using the now well known photofission of 1,3-cyclohexadiene systems.^{9,10} The irradiation of IV was carried out in methanol solution at -18° under an argon atmosphere using a low-pressure mercury discharge tube [Hanovia type SC-2537, 96.5% of total ultraviolet (*ca.* 10 w.) emitted at 2537 Å.] and a filter of chlorine gas at 1 atm. All but 25 cm.² of the surface area of the light source was masked and the source, filter, and quartz jacket were surrounded by the externally cooled solution of diene IV. Spectroscopic analysis of the cold solutions at several minute intervals during irradiation indicated the gradual appearance of a strong absorption peak at 211 m μ and the diminution of the original diene band at *ca.* 265 m μ . After about an hour a photostationary state was reached in which the ratio of the optical density at 211 m μ to that at 265 m μ was 3.4 (initial value, 0.1); *ca.* 50–55% of diene IV remained in the steady-state mixture which resulted under the conditions of the experiment.

The other component of the mixture is considered to be triene V both on the basis of existing analogy and because of the subsequent conversion to dihydrocostunolide (I). Inspection of models indicates that the geometry of triene V is not such as to allow extensive π -conjugation and so the occurrence of the main absorption maximum at 211 m μ rather than at longer wave length is not regarded as inconsistent with this structure.

Hydrogenation of the solution from photolysis over Raney nickel at -18 to -15° afforded a mixture from which dihydrocostunolide I was obtained by chromatography on silicic acid in the cold (temperature programmed between -23 and $+5^\circ$) followed by recrystallization from *n*-hexane-ether (10% yield based on the amount of diene actually transformed on photolysis). The synthetic material had m.p. 76.5–78.0° (undepressed upon admixture with an authentic sample),¹¹ $[\alpha]_D +110.8^\circ$ (chloroform), and n.m.r. peaks at 1.19 δ (3H, doublet, $J = 6.5$ c.p.s.), 1.40 δ (3H, doublet, $J \cong 1.5$ c.p.s.), 1.67 δ (3H, doublet, $J \cong 1.0$ c.p.s.), 4.39 and 4.52 δ (2H, multiplet), and 4.75 δ (1H, multiplet), identical with those exhibited by natural I. The synthetic and natural specimens showed identical infrared and ultraviolet (ϵ 10,300 at 207 m μ) spectra.

When cold (-18°) methanolic solutions of triene V were warmed to 25° , a transformation occurred (half-life *ca.* 15 min. at $+25^\circ$) to give a diene stereoisomeric with IV, m.p. 69.5–70.5°, $[\alpha]_D^{25} +375^\circ$ (chloroform), ultraviolet max. 265 m μ (ϵ 4800, methanol), n.m.r. peaks at 0.98 δ (3H, singlet), 1.15 δ (3H, doublet, $J = 7$ c.p.s.), 1.95 δ (3H, singlet), 3.79 δ (1H, ABC triplet), and a series due to three olefinic protons at 5.2 to 6.0 δ . This diene is regarded as a *cis*-fused $\Delta^{1,3}$ -diene. Because of the instability of intermediate triene V, this substance has not been isolated. It is noteworthy that the irradiation of the *cis* isomer of IV does not produce the peak at 211 m μ .

The photolysis of bi- or polycyclic dienes as exemplified by IV represents another route to medium-ring

(9) The classical case of such a reaction is the formation of precalciferol from ergosterol in the light-promoted synthesis of vitamin D. See (a) E. Havinga, R. J. de Kock, and M. P. Rappoldt, *Tetrahedron*, **11**, 276 (1960), and previous papers; (b) L. Velluz, B. Goffinet, and G. Amiard, *ibid.*, **4**, 241 (1958); (c) H. H. Inhoffen, *Fort. Chem. org. Naturstoffe*, **17**, 70 (1959).

(10) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959); D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, **1** (1960).

(11) We thank Dr. S. C. Bhattacharyya and Dr. V. Herout for samples of natural costunolide from which authentic dihydrocostunolide was prepared.

compounds; moreover, it makes available for study the unusual triene system exemplified by V and related structures.

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Triphenyl(bipyridyl)siliconium Ion

Sir:

Although siliconium ions occasionally have been postulated as intermediates in reactions of organosilicon compounds,¹ stable tricoordinate organosiliconium ions analogous to carbonium ions are unknown. Previous attempts have been made to obtain such species by a variety of methods, but heretofore always unsuccessfully.² We now wish to report the preparation of the compounds triphenyl(bipyridyl)silicon iodide (I) and bromide (II), which dissociate in dichloromethane solution to yield the stable pentacoordinate ion $\text{Ph}_3\text{Si}(\text{bipy})^+$.

Triphenylsilylosilane, also previously unreported, was obtained by the method of Fritz and Kummer,³ from iodine and triphenylsilane in refluxing ethyl iodide. After completion of the reaction the product crystallized from the cooled solution as a pale pink solid, m.p. 154–156°. *Anal.* Calcd. for $\text{C}_{18}\text{H}_{15}\text{SiI}$: C, 55.81; H, 3.88. Found: C, 55.72; H, 3.66. Addition of an equimolar amount of 2,2'-bipyridine to a freshly prepared solution of triphenylsilylosilane in dichloromethane produced a bright yellow color. Evaporation of the solvent yielded a solid which was recrystallized from additional dichloromethane to give I as pale yellow prisms with m.p. 174–175°. *Anal.* Calcd. for $\text{C}_{28}\text{H}_{23}\text{N}_2\text{SiI}$: C, 61.88; H, 4.24; I, 23.39; N, 5.16; Si, 5.16. Found: C, 61.44; H, 4.39; I, 24.01; N, 5.14; Si, 5.13. Unlike triphenylsilyl iodide, compound I is hydrolyzed only slowly by moist air.

In acetonitrile solution, I shows ultraviolet absorption bands characteristic of the bipyridyl moiety^{4,5} at 2450 and 3030 Å. The position of these bands indicates that the nitrogen atoms are in the *cis* configuration, *i.e.*, both coordinated to the silicon atom.⁵ The infrared spectrum of a dichloromethane solution of I is complex, but contains no bands attributable to N–H, O–H, or siloxane absorption. Comparative infrared spectral studies show that I is free of admixture with the two most probable hydrolysis products, 2-(2'-pyridyl)pyridinium iodide and hexaphenyldisiloxane.

(1) F. C. Whitmore, L. H. Sommer, and J. R. Gould, *J. Am. Chem. Soc.*, **69**, 1976 (1947); L. H. Sommer, D. L. Bailey, J. R. Gould, and F. C. Whitmore, *ibid.*, **76**, 801 (1954); L. H. Sommer and F. J. Evans, *ibid.*, **76**, 1186 (1954); M. Kumada, J. Nakajima, M. Ishikawa, and Y. Yamamoto, *J. Org. Chem.*, **23**, 292 (1958); L. H. Sommer and G. A. Baughman, *J. Am. Chem. Soc.*, **83**, 3346 (1961); unpublished studies by L. H. Sommer and collaborators.

(2) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, p. 114; M. E. Peach and T. C. Waddington, *J. Chem. Soc.*, 1238 (1961); H. Gilman and G. E. Dunn, *Chem. Rev.*, **52**, 77 (1953); G. A. Russell, *J. Am. Chem. Soc.*, **81**, 4831 (1959); U. Wannagat and F. Brandmair, *Z. anorg. allgem. Chem.*, **280**, 223 (1955); U. Wannagat and W. Liehr, *Angew. Chem.*, **69**, 783 (1957); J. Y. Corey and R. C. West, *J. Am. Chem. Soc.*, **85**, 2430 (1963); R. H. Flowers, R. J. Gillespie, and E. A. Robinson, *Can. J. Chem.*, **41**, 2464 (1963).

(3) G. Fritz and D. Kummer, *Z. anorg. allgem. Chem.*, **304**, 322 (1960).

(4) P. E. Fielding and R. J. W. LeFevre, *J. Chem. Soc.*, 1811 (1951).

(5) K. Nakamoto, *J. Phys. Chem.*, **64**, 1420 (1960); R. H. Linnell and A. Kaczmarczyk, *ibid.*, **65**, 1196 (1961).

The equivalent conductance for I and for 2-(2'-pyridyl)pyridinium iodide are plotted *vs.* the square root of concentration in Fig. 1. At equal molar concentrations, the conductance of I is slightly higher than that of the salt (bipyH)⁺I⁻, strongly suggesting that I is also completely dissociated in this solvent.⁶ The siliconium ion must be pentacoordinate, and as such represents the first known pentacoordinate species for silicon bonded to three organic groups.⁷ The three

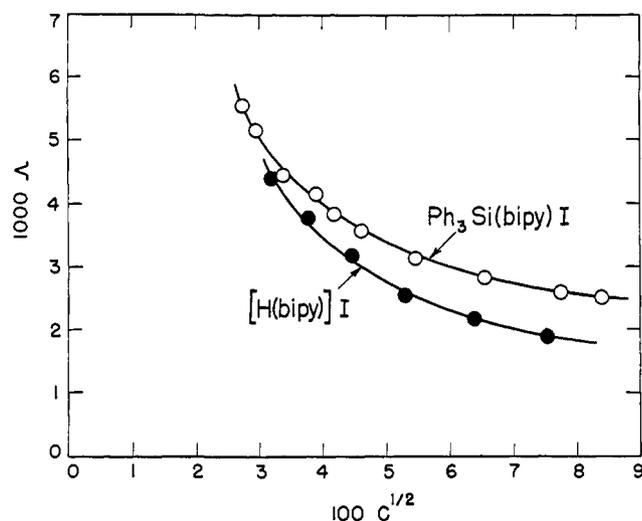


Fig. 1.—Equivalent conductance *vs.* square root of concentration for 2-(2'-pyridyl)pyridinium iodide and for triphenyl(bipyridyl)siliconium iodide in dichloromethane solution.

phenyl groups and two nitrogens of the bipyridyl probably are in a trigonal bipyramidal arrangement about the silicon atom. Because the bipyridyl group occupies adjacent positions in octahedral coordination, the structure shown in Fig. 2 seems most reasonable for the ion, but alternate structures cannot yet be excluded. At present it is not known whether the solid compounds I and II exist as ionic compounds of ions like those of Fig. 2, or whether they contain hexacoordinated molecular species, Ph₃Si(bipy)X, but structural studies on I are in progress.

Triphenylbromosilane and 2,2'-bipyridine in dichloromethane give Ph₃Si(bipy)Br (II), a white solid similar in properties to I. However, no reaction has been observed between triphenylchlorosilane and 2,2'-bipyridine under similar conditions. Triorganosilicon bromides with fewer than three aryl groups (*e.g.*, PhMe₂SiBr) appear to give complexes with 2,2'-bipyridine that are similar to II, but the adducts formed from the corresponding iodides are less stable than I, if they are formed at all.

The chelate-stabilized siliconium ions reported above are very different in properties from carbonium ions such as Ph₃C⁺, but find a close analogy in the chelated boronium ions reported by Davidson and French.⁸ However, stabilized onium ions of this sort seem to be more readily prepared for boron than for silicon.⁹

(6) Compound I was recovered quantitatively from the solutions used for conductance studies, indicating that very little if any hydrolysis could have taken place.

(7) Pentacoordinate species are probable intermediates in many displacement reactions occurring at silicon, and the pentacoordinate triphenylsiliconium ion may be considered as a model for these intermediates. See C. Eaborn, *ref. 2*, pp. 103–113; J. R. Chippenfield and R. M. Prince, *J. Chem. Soc.*, 3567 (1963).

(8) J. M. Davidson and C. M. French, *ibid.*, 114 (1958); J. M. Davidson and C. M. French, *Chem. Ind. (London)*, 750 (1959).

(9) J. E. Douglas, *J. Am. Chem. Soc.*, **84**, 121 (1962).

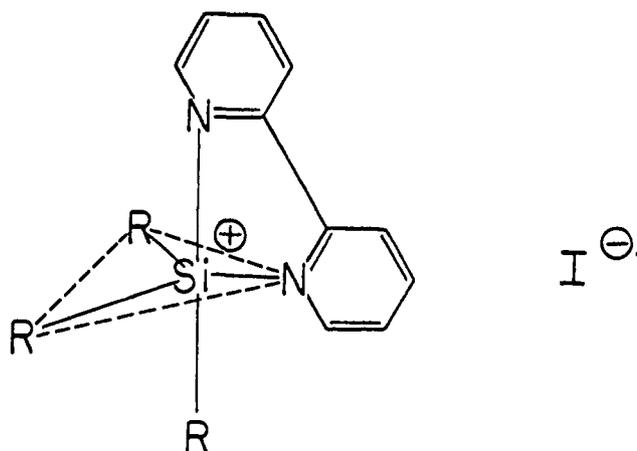


Fig. 2.—Proposed structure for triphenyl(bipyridyl)siliconium ion.

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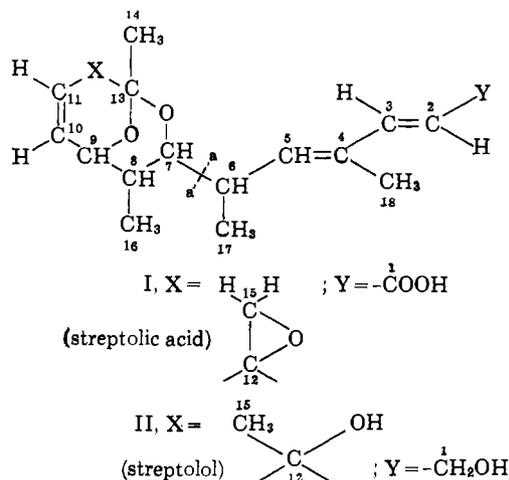
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Streptolydigin. I. Streptolic Acid

Sir:

We wish to present evidence which assigns structure I to streptolic acid, C₁₈H₂₄O₅, m.p. 168–170°, [α]_D²⁶ +147° (*c* 1.22, in 95% ethanol) [*Anal.* Found: C, 67.36; H, 7.59; C-CH₃, 15.69; neut. equiv., 318], the principal chloroform-soluble product of periodate oxidation of the sodium salt, C₃₂H₄₃N₂NaO₉, m.p. 225°, [α]_D²⁶ +153° (*c* 1.35, in chloroform) [*Anal.* C, 61.54; H, 7.26; N, 4.22] of the antibiotic streptolydigin.¹



Streptolic acid consumes 4 moles of hydrogen over platinum oxide or palladium-barium sulfate in ethanol, indicating four reducible functions in the acid. One of these is the terminal epoxide group A, which gives positive epoxide tests² and is confirmed by a pair of n.m.r. doublets (*J* = 5.2 c.p.s.) at τ 6.98 and 7.17; the latter are lost (and replaced by a new methyl singlet at τ 8.58) on lithium aluminum hydride reduc-

(1) T. E. Eble, C. M. Large, W. H. DeVries, G. F. Crum, and J. W. Shell, *Antibiot. Ann.*, 893 (1955–1956). These authors assigned the formula C₃₂H₄₆N₂O₉ to streptolydigin, but our analytical values fit just as well for the presently indicated C₃₂H₄₃N₂O₉.

(2) R. Fuchs, R. C. Waters, and C. A. VanderWerf, *Anal. Chem.*, **24**, 1514 (1952); W. C. J. Ross, *J. Chem. Soc.*, 2257 (1950).