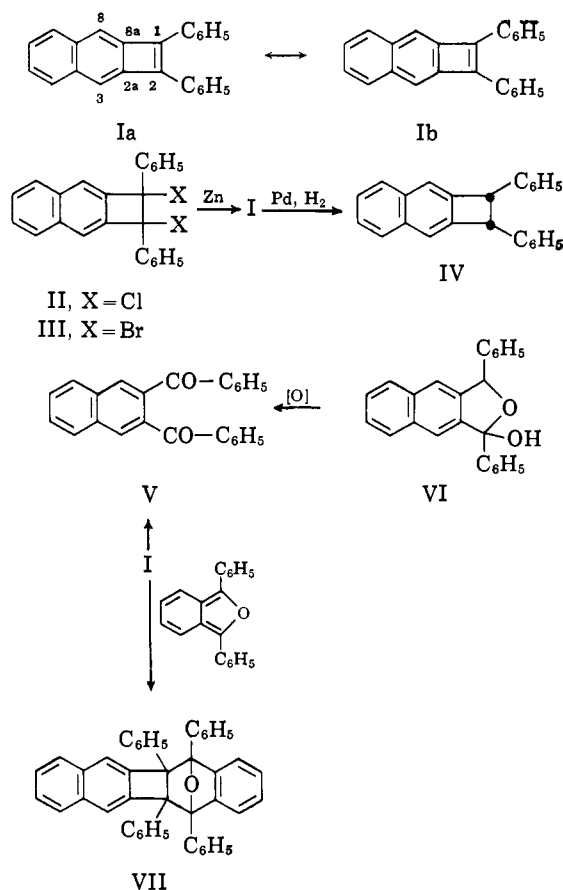


Compound I is a reactive dienophile and adds readily to 1,3-diphenylisobenzofuran to give, in 85% yield, a colorless adduct, m.p. 296–297°; the structure VII is assigned tentatively to this adduct. In the crystalline state I has remained unchanged for several weeks at room temperature in the presence of air and ordinary laboratory illumination; molten I retains its blood red color on heating up to about 260°, at which temperature the melt fades to a yellow color.

It is well known that the α,β -bonds of naphthalene have appreciably more double bond character than the β,β -bonds.⁶ This factor might be expected to exert a stabilizing effect on hydrocarbon I, since it should operate to diminish the cyclobutadienoid character of the four-membered ring by increasing the single bond character of the 2a–8a bond. Evidence that bonds 2a–3 and 8–8a in I are fixed to a remarkable degree as in Ia comes from the n.m.r. spectrum of I. In addition to 14 protons in the usual aromatic region, two protons appear as a sharp peak at 6.50 δ ; the position of these protons, undoubtedly those at C-3 and C-8, is very near to that (6.55 δ) of the olefinic protons of *cis*-stilbene.^{7,8}



The correlation of the observed properties of I with molecular orbital calculations for this molecule will be awaited with considerable interest.

A study of the chemistry of I as well as its saturated precursors is continuing. Among the problems under investigation are dimerization and cycloadditions of I, and the possibility of converting I to a stable dianion or dication.⁹

(6) E.g., see L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 880

(7) Spectrum No. 305, Varian Associates N.M.R. Spectra Catalogue.

(8) By contrast, in the spectrum of IV, no vinylic protons appear at higher field than the phenyl protons at 6.94 δ .

(9) Melting points are uncorrected. Satisfactory analyses were obtained for all new compounds. Due to the relative importance of hydrocarbon I, analytical results for this compound are recorded here. Calcd. for $C_{24}H_{18}$: C, 94.70; H, 5.30. Found: C, 94.41; H, 5.21.

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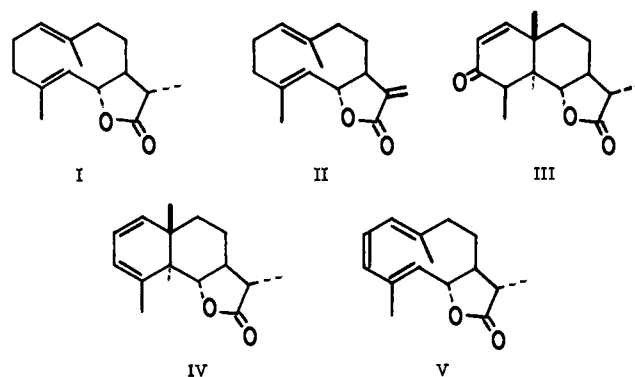
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RECEIVED OCTOBER 21, 1963

Total Synthesis of Dihydrocostunolide

Sir:

The natural sesquiterpenes of the cyclodecane series are noteworthy because of their role as possible biogenetic links between farnesol and the polycarbocyclic sesquiterpenes.¹ In addition, the novel structures of these compounds are interesting to the chemist who seeks to extend synthetic methodology. We describe here a short synthesis of the medium-ring sesquiterpene lactone dihydrocostunolide (I) by a new approach



which also would seem to be applicable to other sesquiterpenoid structures. Dihydrocostunolide was first obtained by catalytic hydrogenation of the related natural product costunolide (II).² However, more recent studies indicate that dihydrocostunolide is also a naturally occurring substance.³

The point of origin for this synthesis was the keto lactone (III), readily available from santonin⁴ by known procedures.⁵ Reduction of III with aluminum isopropoxide in isopropyl alcohol gave the corresponding unsaturated alcohol as a mixture of epimers, oxidation of which (manganese dioxide) regenerated the starting ketone. The mixture of epimeric alcohols was dehydrated by heating with 2.8 parts of neutral alumina (Woelm, activity I), which previously had been treated with 2% of pyridine^{6,7} at 230°, in a slow stream of nitrogen to give the diene IV, m.p. 95–97°, $[\alpha]^{25}_D + 70.5^\circ$ (chloroform), infrared max. 1785, 1640 cm^{-1} , ultraviolet max. (methanol) 262 $m\mu$ (ϵ 4900). *Anal.* Found: C, 77.71; H, 8.80.⁸

(1) For recent reviews see F. Šorm, *Fort. Chem. org. Naturstoffe*, **19**, 1 (1961); T. G. Halsall and D. W. Theobald, *Quart. Rev. (London)*, **16**, 1 (1962).

(2) A. S. Rao, G. R. Kelkar, and S. C. Bhattacharyya, *Tetrahedron*, **9**, 275 (1960), and earlier papers.

(3) A. S. Rao, A. Paul, Sadgopal, and S. C. Bhattacharyya, *ibid.*, **13**, 319 (1961).

(4) Previously made by total synthesis by Y. Abe, T. Harukawa, H. Ishikawa, T. Miki, M. Sumi, and T. Toga, *Proc. Japan Acad.*, **28**, 425 (1952); **29**, 113 (1953); **30**, 116, 119 (1954).

(5) See (a) W. Cocker and T. B. H. McMurry, *J. Chem. Soc.*, 4549 (1956); (b) J. B. Hendrickson and T. L. Bogard, *ibid.*, 1678 (1962); (c) M. Yanagita and A. Tahara, *J. Org. Chem.*, **20**, 959 (1955).

(6) E. von Rudloff, *Can. J. Chem.*, **39**, 1860 (1961).

(7) L. Beránek, M. Kraus, K. Kochloeff, and V. Bažant, *Collection Czech. Chem. Commun.*, **25**, 2513 (1960).

(8) This diene has also been prepared from III by Prof. G. Büchi and Dr. D. W. Hutchinson using different procedures for reduction and elimination (personal communication from Dr. Büchi).

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 $\text{Ph}_3\text{Si}(\text{bipy})^+$.

Triphenyliodosilane, 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 triphenyliodosilane 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).