[Contribution from the Department of Chemistry, Purdue University, West Lafayette, Ind.]

The Synthesis of Cyclic Silicon Systems

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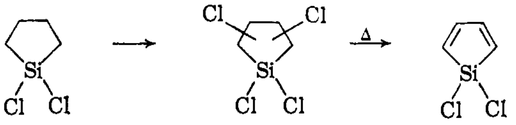
Chlorination of 1,1-dichlorosilacyclopentane by sulfuryl chloride in the presence of benzoyl peroxide leads to a mixture of β- and α-monochloro isomers in a ratio of 4:1. Dehydrohalogenation of these monochloro isomers by quinoline, pyrolysis, and ferric chloride has been studied. Quinoline treatment results predominantly in ring opening with the formation of 3-butenyltrichlorosilane. The ferric chloride method results in a minimum of ring opening, the principal reaction products being 1,1-dichlorosila-2-cyclopentene and 1,1-dichlorosila-3-cyclopentene. A very satisfactory synthesis of highly pure 1,1-dichlorosila-2-cyclopentene has been developed which involves the cyclization of *cis*-4-chloro-1-trichlorosilyl-1-butene by magnesium in diethyl ether. Dichlorination of 1,1-dichlorosilacyclopentane with sulfuryl chloride and peroxide results in a complex mixture, two components of which have been identified by their n.m.r. spectra as 1,1,3,4-tetrachlorosilacyclopentane and 1,1,3,3-tetrachlorosilacyclopentane. Pyrolysis of the mixture resulting from dichlorination results in the formation of many products. One of these (obviously the result of ring opening) is 1,3-butadienyltrichlorosilane. While several other products from this pyrolysis have been separated and identified, no trace of 1,1-dichlorosilacyclopentadiene has been detected thus far, contrary to our earlier reports. Hence all previous claims of compounds derived from this substance must be withdrawn.

It was reported previously[1] that a substantial amount of the experimental work from our laboratory[2] which supported the idea of aromaticity in certain cyclic silicon systems could not be duplicated when we attempted an extension of this work.

In the interim we have repeated all of the experiments previously reported[2] where possible, and, in so doing, have examined many of them in much greater detail. We are recording our revised results in this paper.[3]

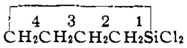
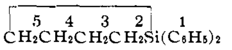
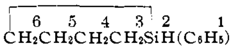
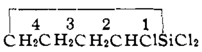
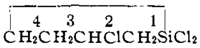
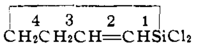
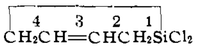
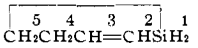
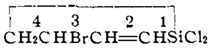
The ultimate goal of this work was to prepare silacyclopentadiene (from the reduction of 1,1-dichlorosilacyclopentadiene) and to test whether the anion derived from this material showed any evidence of aromatic stabilization. The approach chosen to achieve this objective was: (1) dichlorination of 1,1-dichlorosilacyclopentane and (2) pyrolysis of the dichlorination product to form 1,1-dichlorosilacyclopentadiene.



Chlorination of 1,1-Dichlorosilacyclopentane.—The dichlorination of 1,1-dichlorosilacyclopentane was carried out stepwise, such that monochloro isomers could be first isolated and identified. When 1,1-dichlorosilacyclopentane was treated with sulfuryl chloride (1:1 mole ratio) in the presence of benzoyl peroxide, a 48% yield of pure monochlorinated product was obtained boiling rather sharply at 70–71° (15 mm.), 183.5–185.5° (atm. pressure). Despite this rather sharp boiling point, a vapor phase chromatogram of the product[4] showed that it consisted of a mixture of α- and β-isomers in a ratio of 1:4, respectively. Positive identification of these two monochloro isomers was achieved through their n.m.r. spectra (Table I) after prior separation and purification by preparative scale v.p.c. Previous work[5,6] on the chlorination of 1,1-dichlorosilacyclopentane (without the obvious benefits of v.p.c. as an analytical tool) had reported the formation of β-isomer exclusively. Apparently the boiling points of the α- and β-isomers differ only slightly from one another since an attempted separation of the two compounds by distillation through a Todd fractionating column resulted in only a slight change in isomer ratio.

Table I

N.m.r. Spectra of Various Cyclic Silanes[a,b] (τ-Values)

(1)	 $\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2SiCl_2$	8.22 (H^2 and H^3 multiplet), 8.89 (H^1 and H^4 multiplet)
(2)	 $\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2Si(\overset{1}{C_6H_5})_2$	2.65 (H^1 multiplet), 8.19 (H^3 and H^4 quintet), 8.91 (H^2 and H^5 multiplet)[c]
(3)	 $\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2Si\overset{2}{H}(\overset{1}{C_6H_5})$	2.62 (H^1 multiplet), 5.49 (H^2 quintet), 8.28 (H^4 and H^5 quintet), 9.08 (H^3 and H^6 mu t plet)[d]
(4)	 $\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}HClSiCl_2$	6.40 (H^1 triplet), 8.02 (H^2 and H^3 multiplet), 8.80 (H^4 multiplet)
(5)	 $\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}HCl\overset{1}{C}H_2SiCl_2$	5.55 (H^2 quintet), 8.30 (H^1, H^3, and H^4-multiplet)
(6)	 $\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H=\overset{1}{C}HSiCl_2$	2.88 (H^2 two triplets), 3.88 (H^1 two triplets), 7.36 (H^3 multiplet), 8.73 (H^4 multiplet)
(7)	 $\overset{4}{C}H_2\overset{3}{C}H=\overset{2}{C}H\overset{1}{C}H_2SiCl_2$	4.05 (H^2 and H^3 triplet), 8.18 (H^1 and H^4 doublet)
(8)	 $\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H=\overset{2}{C}HSi\overset{1}{H_2}$	3.15 (H^3 two triplets), 4.10 (H^2 two triplets), 5.80 (H^1 septet), 7.40 (H^4 multiplet); 9.02 (H^5 multiplet)
(9)	 $\overset{4}{C}H_2\overset{3}{C}HBr\overset{2}{C}H=\overset{1}{C}HSiCl_2$	2.82 (H^2 two doublets), 3.76 (H^1 two doublets), 5.00 (H^3 multiplet), 8.02 (H^4 multiplet)

[a] These spectra were determined in carbon tetrachloride solution with tetramethylsilane as an internal standard. A Varian A-60 n.m.r. spectrometer was employed. Chemical shifts are measured to the estimated center of a singlet or multiplet. [b] In the case of each of the spectra listed in this table, the peak areas were quite consistent with the proton assignments made. [c] This compound was prepared by Dr. G. M. Stanton by treating 1-phenylsilacyclopentane with phenyllithium. See D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **80**, 2677 (1958). [d] Prepared by Dr. G. M. Stanton. The method of preparation and physical constants are correctly described: *ibid.*, **84**, 4730 (1962).

When 1,1-dichlorosilacyclopentane was treated with two equivalents of sulfuryl chloride in the presence of benzoyl peroxide, a complex product mixture resulted. This was arbitrarily divided into three fractionation

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(1) R. A. Benkeser and G. M. Stanton, *J. Am. Chem. Soc.*, **85**, 834 (1963).

(2) R. A. Benkeser, *et al.*, *ibid.*, **84**, 4723, 4727 (1962). A preliminary announcement of this work appeared: *ibid.*, **83**, 3716, 5029 (1961).

(3) All physical constants listed in our earlier work[2] should be ignored in favor of those reported in this paper.

(4) We have found that chlorosilanes can be analyzed quite easily by v.p.c. *provided* the column is first conditioned by the prior injection of several samples of silicon tetrachloride or other volatile chlorosilanes. We are greatly indebted to Dr. A. Torkelson of the General Electric Co. for supplying us with this information.

(5) V. F. Mironov and V. V. Nepomnina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (Engl. trans.), 1188 (1959).

(6) A. D. Petrov, N. P. Smetankina, and G. I. Nikishin, *ibid.*, 1414 (1958).

TABLE II

N.M.R. SPECTRA OF VARIOUS STRAIGHT-CHAIN OLEFINIC AND DIENYLSILANES[a,b] (τ-VALUES)

(1) $\overset{4}{C}H_2{=}\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}H_2SiCl_3$	4.12 (H^3 multiplet), 4.97 (H^4 multiplet), 7.66 (H^2 multiplet), 8.53 (H^1 multiplet)
(2) $\overset{5}{C}H_2{=}\overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{Si}H_3$	4.15 (H^4 multiplet), 5.02 (H^5 multiplet), 6.50 (H^1 triplet), 7.80 (H^3 quartet), 9.15 (H^2 multiplet)
(3) $\overset{4}{C}H_2{=}\overset{3}{C}H\overset{2}{C}H{=}\overset{1}{C}HSiCl_3$	2.8–4.7 (H^1, H^2, H^3, H^4 complex pattern)
(4) $\overset{5}{C}H_2{=}\overset{4}{C}H\overset{3}{C}H{=}\overset{2}{C}H\overset{1}{Si}H_3$	3.0–5.0 (H^2, H^3, H^4, H^5 complex pattern), 6.15 (H^1 doublet)
(5) $ClC\overset{4}{H_2}C\overset{3}{H_2}\overset{2}{C}H{=}\overset{1}{C}HSiCl_3$ (*cis*)	3.25 (H^2 two triplets), 4.12 (H^1 two triplets), 6.42 (H^4 triplet), 7.15 (H^3 multiplet, $J_{H^1H^2} = 14$
(6) $ClC\overset{4}{H_2}C\overset{3}{H_2}\overset{2}{C}H{=}\overset{1}{C}HSiCl_3$ (*trans*)	3.30 (H^2 two triplets), 4.13 (H^1 two triplets), 6.35 (H^4 triplet), 7.28 (H^3 multiplet), $J_{H^1H^2} = 18$
(7) $(\overset{3}{C}H_2{=}\overset{2}{C}H)_2\overset{1}{Si}H_2$	4.00 (H^2 and H^3 multiplet), 5.85 (H^1 triplet)
(8) $(\overset{3}{C}H_2{=}\overset{2}{C}H)_3SiH^1$	4.00 (H^2 and H^3 multiplet), 5.65 (H^1 broad singlet)

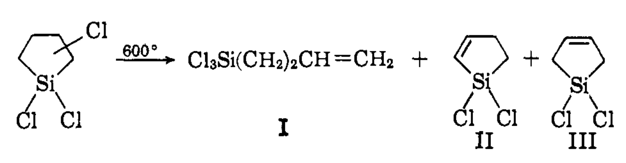
[a] These spectra were determined in carbon tetrachloride solution with tetramethylsilane as an internal standard. A Varian A-60 n.m.r. spectrometer was employed. Chemical shifts are measured to the estimated center of a singlet or multiplet. [b] In the case of each of the spectra listed in this table, the peak areas were quite consistent with the proton assignments made.

cuts, the bulk of the material boiling at 85–95° (10 mm.). The first two cuts analyzed correctly for dichlorination product while the third cut had a higher chlorine content.

Two products were isolated in a pure state from the dichlorination reaction. These materials were tentatively identified by their n.m.r. spectra as 1,1,3,3-tetrachlorosilacyclopentane and 1,1,3,4-tetrachlorosilacyclopentane.

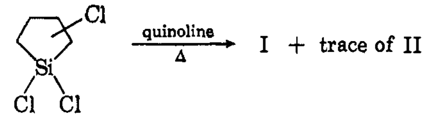
It becomes clear that dichlorination of 1,1-dichlorosilacyclopentane is a complex reaction and numerous products are formed. From the 80–20 isomer ratio obtained from monochlorination, it is probably safe to conclude that all six positional isomeric dichlorination products are produced at least to some extent. We have been successful in identifying two of these six.

Chemistry of Monochlorination Products of 1,1-Dichlorosilacyclopentane.—When the 80–20 (β to α) monochloro isomer mixture was pyrolyzed at 600°, essentially three products were produced. These were identified by their n.m.r. spectra (Tables I and II) as 3-butenyltrichlorosilane (I), 1,1-dichlorosila-2-cyclopentene (II), and 1,1-dichlorosila-3-cyclopentene (III) in a ratio of 5:4:1, respectively.



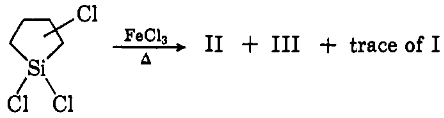
When this pyrolysate mixture was treated with lithium aluminum hydride, again a three-component mixture was obtained, from which sila-2-cyclopentene was isolated by vapor phase chromatography. Its elemental analysis and n.m.r. spectrum (Table I) clearly established its identity.

When the monochlorinated isomer mixture was refluxed with quinoline, a product resulted consisting almost exclusively of 4-trichlorosilyl-1-butene (20 parts) contaminated with a small amount of 1,1-dichlorosila-2-cyclopentene[7] (1 part).



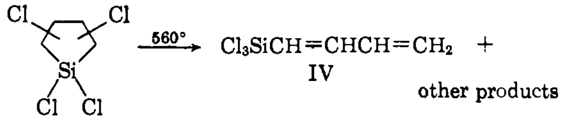
When the 4-trichlorosilyl-1-butene obtained from this reaction was reduced with lithium aluminum hydride, 4-silyl-1-butene was obtained in 55% yield. Its elemental analysis and n.m.r. spectrum (Table II) clearly established its identity.

When the monochlorinated isomer mixture derived from 1,1-dichlorosilacyclopentane was heated with catalytic quantities of ferric chloride, very little ring opening occurred. The product consisted mainly of 1,1-dichlorosila-2- and -3-cyclopentene in a ratio of 3:2.



It becomes immediately clear from the above results that a *minimum* of ring opening occurs in the method employing catalytic quantities of ferric chloride, while a *maximum* of ring opening occurs in the quinoline treatment. One must remember that in all of these experiments an 80–20 β- to α-monochloro isomer mixture was used. There can be little doubt that the β-isomer will be more susceptible to ring opening than the α-. In a subsequent paper we plan to contrast the reactivity of these two isomers.

Pyrolysis of Dichlorination Products of 1,1-Dichlorosilacyclopentane.—When the dichlorinated material obtained from 1,1-dichlorosilacyclopentane was pyrolyzed at 560°, a very complex mixture of products resulted as adjudged by v.p.c. analysis. One predominant component of this mixture was separated and identified by n.m.r. (Table II) as 1,3-butadienyltrichlorosilane (IV).

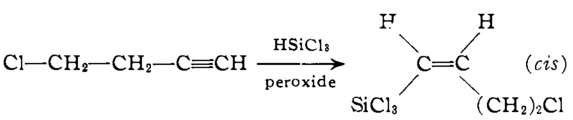


In still another pyrolysis attempt, a portion of the product was reduced with lithium aluminum hydride. Again, gas chromatography showed a complex mixture, from which 3-butenylsilane, 1,3-butadienylsilane, and sila-2-cyclopentene could be separated and identified by their n.m.r. spectra.

An authentic sample of 1,3-butadienylsilane (V) was obtained for comparison purposes by reducing 1,3-butadienyltrichlorosilane with lithium aluminum hydride. Its n.m.r. spectrum is listed in Table II.

$$Cl_3SiCH{=}CH{-}CH{=}CH_2 \xrightarrow{LiAlH_4} \underset{V}{H_3Si{-}CH{=}CH{-}CH{=}CH_2}$$

Independent Synthesis of 1,1-Dichlorosila-2-cyclopentene.—In order to obtain an authentic sample of 1,1-dichlorosila-2-cyclopentene for comparison purposes, the following independent synthesis was devised and successfully carried out.



(1)

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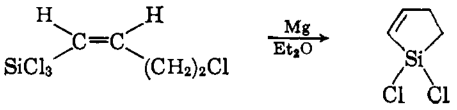
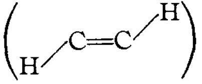
[7] These results are in essential agreement with those of Mironov and Nepomnina; see ref. 5.



(2)

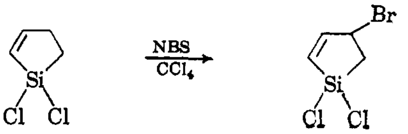
Earlier work[8] from our laboratory had established that peroxide-catalyzed additions of trichlorosilane to monosubstituted acetylenes usually proceeds in a predominantly *trans* fashion to yield *cis* product. This same generalization was found to hold when 4-chloro-1-butyne was treated with trichlorosilane in the presence of benzoyl peroxide (eq. 1). The product could be separated by careful fractionation into two components which were identified both by their n.m.r. and infrared spectra as the *cis* and *trans* isomers of 4-chloro-1-trichlorosilyl-1-butene in a ratio of 4:1, respectively.[9]

Spectral data on each of the two components isolated from this reaction made the *cis–trans* assignments rather straightforward. One component showed an infrared peak[10] at 985 cm.$^{-1}$ while the other did not. This absorption is commonly attributed to a *trans*  hydrogen arrangement on a vinyl group. Likewise the n.m.r. coupling constant of the two vinyl hydrogens on this compound was of the order of 18, while the other isomer had a coupling constant of about 14 (see Table II). Both of these values lie nicely in the range designated for *cis–trans* pairs.[11]

An isomeric mixture of *cis-* and *trans*-4-chloro-1-trichlorosilyl-1-butene was treated with excess methylmagnesium iodide. An isomeric mixture of *cis-* and *trans*-4-chloro-1-trimethylsilyl-1-butene was obtained which gave a correct elemental analysis, thus confirming the composition of these structures.

The ring closure shown in eq. 2 was quite successfully achieved in a solvent of diethyl ether.[12] The best yield of 1,1-dichlorosila-2-cyclopentene (51%) was obtained when pure *cis*-4-chloro-1-trichlorosilyl-1-butene was used as starting material. The yield dropped to 42% when a 3:1 *cis–trans* isomer mixture was employed. Interestingly, a 20% yield of product could still be obtained when pure *trans*-4-chloro-1-trichlorosilyl-1-butene was used as starting material. Quite obviously the *trans* isomer must first isomerize to *cis* before it can undergo cyclization. This was evidenced by the very slow rate of the cyclization in the case of the *trans* compound.

1,1-Dichlorosila-2-cyclopentene was found to react readily with N-bromosuccinimide forming a compound to which we have assigned the structure 1,1-dichloro-3-bromosila-2-cyclopentene (VI) based upon its infrared and n.m.r. spectra (see Tables I and III). The infrared absorption at 6.41 μ for VI clearly places the double bond in 2- rather than 3-position (compare entries 3 and 4, Table III). Likewise the vinylic H in position "3" appearing as a pair of doublets is highly suggestive of structure VI.



VI

TABLE III

INFRARED SPECTRA OF VARIOUS CYCLIC SILANES[a]

(1)	Silacyclopentane	3.4, 3.5, 4.66, 6.90, 7.07, 9.3, 10.5, 11.34, 12.0, 13.30
(2)	1,1-Dichlorosilacyclopentane	3.4, 6.8, 7.1, 8.0, 9.3, 11.7, 13.6
(3)	1,1-Dichlorosila-2-cyclopentene	3.34, 3.44, 3.52, 6.40, 6.96, 7.15, 7.57 8.71, 9.11, 10.14, 11.20, 12.04, 13.25
(4)	1,1-Dichlorosila-3-cyclopentene	3.30, 3.45, 6.20, 7.15, 8.27, 9.10, 10.60, 12.25, 13.75
(5)	1,1-Diphenylsilacyclopentane[b]	3.30, 3.45, 3.50, 6.99, 8.99, 9.00, 9.30, 9.77, 11.75, 12.55
(6)	1-Phenylsilacyclopentane[c]	3.30, 3.45, 3.55, 4.7, 7.0, 8.95, 9.25, 10.65, 11.4, 11.7, 12.75
(7)	Sila-2-cyclopentene	3.35, 3.45, 3.52, 4.7, 6.39, 6.93, 7.1, 7.59, 8.74, 9.09, 10.13, 10.4, 11.5, 14.2
(8)	1,1-Dichloro-3-bromosila-2-cyclopentene	3.30, 3.40, 6.41, 7.14, 7.58, 8.15, 8.42, 8.66, 9.09, 9.86, 10.77, 11.19, 12.01, 12.47, 12.73, 13.18

[a] These data were obtained from a Perkin–Elmer Model 221 spectrophotometer. [b] This compound was prepared by Dr. G. M. Stanton by treating 1-phenylsilacyclopentane with phenyllithium; n^{20}_{D} 1.5868; see D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **80**, 2677 (1958). [c] See footnote *c* in Table I.

Divinylsilane.—The preparation of divinylsilane from the reaction of vinylmagnesium bromide with vinyltrichlorosilane was also carried out and an analytically pure sample of this material was obtained for the first time. The infrared and n.m.r. spectra of this compound are listed in Tables II and IV.

TABLE IV

INFRARED SPECTRA OF VARIOUS STRAIGHT-CHAIN OLEFINIC AND DIENYLSILANES[a]

(1)	3-Butenyltrichlorosilane	3.22, 3.33, 3.40, 6.03, 6.88, 7.02, 7.15, 10.06, 10.90, 12.9, 14.2
(2)	3-Butenylsilane	3.25, 3.35, 3.42, 4.63, 6.06, 6.90, 7.05, 7.11, 10.06, 10.8, 14.5
(3)	1,3-Butadienyltrichlorosilane	3.25, 3.35, 6.09, 6.34, 9.92, 10.79, 12.25
(4)	1,3-Butadienylsilane	3.25, 3.35, 4.65, 6.11, 6.37, 9.91, 10.8, 12.04
(5)	Divinylsilane	3.26, 3.31, 3.35, 3.38, 4.65, 6.25, 7.10, 9.91, 10.42, 10.6, 11.8

[a] These data were obtained from a Perkin–Elmer Model 221 spectrophotometer.

Spectral Data.—Tables I to IV list the n.m.r. and infrared spectra of all the compounds reported in this paper.

Conclusions.—It is now clear that the dichlorination of 1,1-dichlorosilacyclopentane leads to a complex mixture of products. It is not surprising that pyrolysis of such a mixture should compound the complexity of the products. Our repeated efforts to isolate a sample of 1,1-dichlorosilacyclopentadiene from the complex pyrolysis products have thus far met failure. Likewise, reduction of the pyrolysate with lithium aluminum hydride in the hope of simplifying the purification procedure has failed to yield any compound identifiable as silacyclopentadiene. While it is entirely possible that such cyclic dienes may be present in minor amounts or have transient existence in the complex py-

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(8) R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Am. Chem. Soc.*, **83**, 4385 (1961).

(9) No attempt was made to determine whether the *trans* isomer (which is presumably the more thermodynamically stable) was arising from isomerization of the *cis* form.

(10) A peak in the 965–985 cm.$^{-1}$ region is considered of diagnostic value for a *trans* ethylene. See N. Sheppard and D. M. Simpson, *Quart. Rev.* (London), **6**, 1 (1952); B. Loev and C. R. Dawson, *J. Am. Chem. Soc.*, **78**, 1180 (1956).

(11) See L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 85.

(12) When tetrahydrofuran was tried as a solvent, only a low yield of 1,1-dichlorosila-2-cyclopentene could be realized.

rolysis mixtures we are dealing with, they have thus far escaped our detection.[13]

While we are continuing to work in this area, it is clear that our earlier claims[2] concerning the existence of aromatic silicon systems must be considered premature in view of our current results.

Experimental

Monochlorination of 1,1-**Dichlorosilacyclopentane.**[14]—In a 200-ml. round-bottomed flask were placed 101 g. (0.65 mole) of 1,1-dichlorosilacyclopentane, 81 g. (0.60 mole) of sulfuryl chloride, and 1 g. of benzoyl peroxide. The flask was heated to initiate the reaction and then cooled with ice water until the vigorous reaction subsided. The mixture was then heated until the evolution of gases ceased (2–5 hr.). Gas chromatographic analysis (16 ft. silicone oil column, 130°, 15 p.s.i.) of the crude reaction product showed, in addition to starting material, two product peaks of 80 and 20%, respectively. Distillation of the reaction mixture on a Todd column yielded 60 g. (48%) of pure monochlorinated product boiling at 70–71° at 15 mm. Vapor phase chromatographic analysis of this material showed the same two product peaks in a 4:1 ratio.

Anal. Calcd. for $C_4H_7SiCl_3$: C, 25.35; H, 3.72; Cl, 56.11. Found: C, 25.57; H, 3.97; Cl, 56.50.

Titration of this monochlorinated isomer mixture for hydrolyzable chlorine[15] with standard sodium hydroxide indicated the mixture to be 80% β- and 20% α-chloro compound.

Separation of these two isomers was accomplished by preparative scale gas chromatography (Autoprep, $^3/_8$ in. × 20 ft. S.E. 30 column, 145°).

1,1,2-Trichlorosilacyclopentane (comprising 20% of isomer mixture) was identified by its n.m.r. spectrum (see Table I).

Anal. Calcd. for $C_4H_7SiCl_3$: C, 25.35; H, 3.72; Cl, 56.11. Found: C, 25.51; H, 4.00; Cl, 56.30.

The 1,1,3-trichlorosilacyclopentane (80% of isomer mixture) could also be characterized by its n.m.r. spectrum (Table I).

Anal. Calcd. for $C_4H_7SiCl_3$: C, 25.35; H, 3.72; Cl, 56.11. Found: C, 25.70; H, 3.74; Cl, 55.92.

When the crude monochlorination reaction product was distilled on a Todd column at atmospheric pressure (see ref. 6), there was obtained, in addition to starting material, a mixture of the trichlorosilacyclopentanes boiling at 183.5–185.5°. This material was collected as six separate fractions, each of which contained both the α- and β-isomers. The first fraction contained 17% α and the last 27% α. Each fraction was slightly contaminated with minor amounts of two lower boiling components. From their v.p.c. retention times, it is possible that these latter two contaminants were 1,1-dichlorosila-2-cyclopentene and 1,1-dichlorosila-3-cyclopentene.

Pyrolysis of the Monochlorination Products of 1,1-**Dichlorosilacyclopentane.**—A sample of 92 g. of the trichlorosilacyclopentane isomer mixture (80% β, 20% α) was passed through a 10 in. column packed with glass beads at 600° in a nitrogen stream. Considerable gas evolution was noted and 73 g. of liquid product was trapped in Dry Ice. Distillation resulted in 53 g. of a clear liquid boiling at 135–150°. Analysis of this material by v.p.c. (8 ft. XF-1150 cyanosilicone column, 100°, 8 p.s.i.) disclosed three main peaks. Only partial separation of these materials could be achieved on a Todd column, but pure samples were collected by v.p.c. Elemental analyses and n.m.r. spectra (see Tables I and II) established the identity of these three products as 3-butenyltrichlorosilane, 1,1-dichlorosila-2-cyclopentene, and 1,1-dichlorosila-3-cyclopentene in a distribution of 5:4:1.

Anal. Calcd. for $C_4H_7SiCl_3$ (3-butenyltrichlorosilane): C, 25.34; H, 3.72; Cl, 56.11. Found: C, 25.69; H, 3.98; Cl, 56.44. Calcd. for $C_4H_6SiCl_2$ (1,1-dichlorosila-3-cyclopentene): C, 31.38; H, 3.95; Cl, 46.31. Found: C, 31.77; H, 4.29; Cl, 46.16. Calcd. for $C_4H_6SiCl_2$ (1,1-dichlorosila-2-cyclopentene): C, 31.38; H, 3.95; Cl, 46.31. Found: C, 31.21; H, 4.08; Cl, 46.29.

Sila-2-cyclopentene.—Reduction of 17 g. of the distilled pyrolysate (b.p. 135–150°) with 6.8 g. (0.18 mole) of lithium aluminum hydride in dry diglyme yielded 4.7 g. of product boiling at 57–66°. Analysis of the product by v.p.c. (30 ft. Apiezon L column, 51°, 12.5 p.s.i.) showed this product to be a mixture of two major components in approximately equal amounts, contaminated by a minor amount of a third component. Based upon the identification of the pyrolysate (see above), these three components were assumed to be 3-butenylsilane, sila-2-cyclopentene, and sila-3-cyclopentene (minor component). One of the two major peaks was separated by gas chromatography and identified by n.m.r. (see Table I) as sila-2-cyclopentene, $n^{25}\text{D}$ 1.4565, b.p. (Siwoloboff) 71°.

Anal. Calcd. for C_4H_8Si: C, 57.06; H, 9.57. Found: C, 57.08; H, 9.43.

Reaction of Monochlorinated 1,1-**Dichlorosilacyclopentane with Quinoline.**—In a 50-ml. flask was placed 5 g. (0.026 mole) of monochlorinated 1,1-dichlorosilacyclopentane (80–20 isomer mixture) and 25 ml. of quinoline. The mixture was refluxed (oil bath, 210°) overnight. Analysis of the reaction mixture by gas chromatography (10 ft QF-1 column, 10 p.s.i., 100°) showed 3-butenyltrichlorosilane (see Table II for n.m.r. spectrum) and 1,1-dichlorosila-2-cyclopentene in a ratio of approximately 20 to 1. Distillation of the reaction mixture through a microcolumn yielded 2.5 g. (50%) of product boiling at 140–160°. Analysis of the distilled product by v.p.c. again showed contamination of 3-butenyltrichlorosilane by about 5% 1,1-dichlorosila-2-cyclopentene.

Reaction of Monochlorinated 1,1-**Dichlorosilacyclopentane with Ferric Chloride.**—A mixture of 45 g. (0.24 mole) of monochlorinated 1,1-dichlorosilacyclopentane and 0.1 g. of ferric chloride was refluxed for 10 hr. (oil bath temperature was about 200°).

Analysis of the crude reaction mixture by v.p.c. (8 ft XF-1150 cyanosilicone column, 100°) showed the presence of 3-butenyltrichlorosilane, 1,1-dichlorosila-3-cyclopentene, and 1,1-dichlorosila-2-cyclopentene in an approximate ratio of 1:8:12. The crude mixture was distilled on a Todd column and three fractions were collected: (1) b.p. below 138.5° (12 g.) consisting of 2 parts 1,1-dichlorosila-3-cyclopentene and 1 part 1,1-dichlorosila-2-cyclopentene; (2) b.p. 138.5–143° (4 g.), 1 part 1,1-dichlorosila-3-cyclopentene and 5 parts of 1,1-dichlorosila-2-cyclopentene; (3) b.p. 143° (8 g.), 1,1-dichlorosila-2-cyclopentene. All fractions were contaminated with small amounts of 3-butenyltrichlorosilane.

3-Butenylsilane.—To 1.4 g. (0.04 mole) of lithium aluminum hydride in 50 ml. of dry diglyme was added slowly 5 g. (0.026 mole) of 4-trichlorosilyl-1-butene (from the quinoline treatment of monochlorinated 1,1-dichlorosilacyclopentane). This mixture was stirred at 20° for 2 hr. under nitrogen pressure. The volatile product was removed from the reaction mixture under vacuum and condensed in a Dry Ice trap. Distillation of this material yielded 1.2 g. (55%) of 3-butenylsilane, boiling at 53–54° ($n^{25}\text{D}$ 1.4050). An analytical sample was prepared by gas chromatographic purification (30 ft. Apiezon L column, 51°, 12.5 p.s.i.) to remove a small amount of sila-2-cyclopentene.

Anal. Calcd. for $C_4H_{10}Si$: C, 55.73; H, 11.69. Found: C, 55.86; H, 11.67.

Dichlorination of 1,1-**Dichlorosilacyclopentane.**—In a 500-ml. flask were combined 86.2 g. (0.56 mole) of 1,1-dichlorosilacyclopentane, 172.4 g. (1.28 moles) of sulfuryl chloride, and 2 g. of benzoyl peroxide. The mixture was heated to initiate the reaction and then cooled with ice water to control the vigorous reaction which ensued. The mixture was then heated for 10 hr. until the evolution of gases had ceased. Distillation of the mixture on a Todd column gave, after removal of a lower boiling forerun, three fractions: (1) b.p. 80–85° (10 mm.), 1 g.; (2) b.p. 85–95° (10 mm.), 52 g.; (3) b.p. 95–100° (10 mm.), 5 g. The yield of dichlorinated material based on fraction 2 was 41%.

Anal. Calcd. for $C_4H_6SiCl_4$: C, 21.45; H, 2.69; Cl, 63.31. Found (fraction 1): C, 21.61; H, 3.00; Cl, 63.19; (fraction 2): C, 21.24; H, 2.81; Cl, 63.25; (fraction 3): C, 19.98; H, 2.35; Cl, 66.43.

Attempted Identification of Dichlorinated 1,1-**Dichlorosilacyclopentanes.**—The forerun obtained from the dichlorination of 1,1-dichlorosilacyclopentane (b.p. 61–85° (10 mm.)) was refractionated and a cut boiling at 48–50° (9 mm.) was obtained. Likewise the second fraction obtained previously (b.p. 85–95° (10 mm.)) was refractionated and a cut boiling at 59–61° (3 mm.)

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[13] Since our original publications[2] there have been two independent claims made for the synthesis of 1,1-dimethylsilacyclopentadiene. See J. Goubeau, T. Kalmar, and H. Hofmann, *Ann.*, **659**, 39 (1962); O. M. Nefedov and M. N. Manakov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, **No. 4**, 769 (1963). Both of these laboratories resorted to catalytic dehydrogenation of 1,1-dimethylsilacyclopentane.

[14] R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).

[15] L. H. Sommer and F. C. Whitmore, *ibid.*, **68**, 485 (1946).

was obtained. Analysis by v.p.c. (DEGS, 4 ft. column, 130°) indicated the two new fractions were essentially pure.

An n.m.r. spectrum of the cut boiling at 48–50° (9 mm.) showed a triplet at 7.28 τ, a singlet at 7.14 τ, and a triplet at 8.39 τ (relative intensities of 1:1:1). The cut boiling at 59–61° (3 mm.) showed two multiplets at 5.41 and 8.04 τ, respectively (relative intensities of 1:2). These spectra are quite consistent with the structural assignment of 1,1,3,3-tetrachlorosilacyclopentane (48–50° (9 mm.)) and 1,1,3,4-tetrachlorosilacyclopentane (59–61° (3 mm.)).

Pyrolysis of the Dichlorination Products of 1,1-Dichlorosilacyclopentane. Preparation of 1,3-Butadienyltrichlorosilane.—A sample of 105 g. of the dichlorinated product (b.p. 80–95° (10 mm.)) obtained from 1,1-dichlorosilacyclopentane was added dropwise onto a 9 in. vertical glass column packed with 5 mm. glass beads in a slow nitrogen stream. The glass tube (1 in. diameter) was surrounded by a 12 in. electric furnace heated to 560°. The dark-colored pyrolysate was collected in a Dry Ice trap. Analysis of this material by vapor phase chromatography (DEGS column) disclosed a great number of peaks. Vacuum distillation of the pyrolysate at 2.5 mm. through a short column resulted in the collection of the following cuts: (1) 14 g. boiling below room temperature, (2) 14 g. boiling at 48–60°, and (3) 32 g. boiling at 60–120°. The predominant component of the second cut was 1,3-butadienyltrichlorosilane identified by its analysis and n.m.r. spectrum (see Table II).

Anal. Calcd. for $C_4H_5SiCl_3$: C, 25.61; H, 2.69; Cl, 56.72. Found: C, 25.89; H, 2.91; Cl, 57.00.

A vapor phase chromatogram of the third cut showed a great number of peaks indicating a very complex mixture.

In another run, 66 g. of dichlorinated product was pyrolyzed in a similar fashion. Distillation of the pyrolysate again resulted in three cuts: (1) b.p. 50–57° (28 mm.), 8 ml.; (2) b.p. 45–52° (13 mm.), 2 ml.; (3) b.p. 58–74° (13 mm.) 10, ml.

Fraction 3 (10 g.) dissolved in 20 ml. of dry diglyme was treated with 3.8 g. of lithium aluminum hydride in 70 ml. of dry diglyme. The reaction was kept at 20° under nitrogen and was allowed to stir for 2 hr. The volatile products were pulled off from the reaction mixture under vacuum and condensed in a Dry Ice trap. There was obtained 2 g. of product which, by gas chromatography, was shown to be a four-component mixture. Separation of the mixture by v.p.c. (30 ft. Apiezon L column, 51°, 12 p.s.i.) was achieved. Three of the four components were positively identified as 3-butenylsilane, 1,3-butadienylsilane, and sila-2-cyclopentene, by a comparison of the n.m.r. and infrared spectra with authentic samples. The fourth component was not positively identified.

1,3-Butadienylsilane.—A total of 121 g. (0.54 mole) of dichlorinated 1,1-dichlorosilacyclopentane was pyrolyzed at 580° as previously described. The pyrolysate was distilled and 11 g. boiling at 60–70° (32 mm.) was collected in addition to other cuts. Analysis by v.p.c. showed that this fraction consisted of about 90% 1,3-butadienyltrichlorosilane. This material was reduced with 3.1 g. (0.08 mole) of lithium aluminum hydride in 70 ml. of dry diglyme as described previously and 1.4 g. of product was obtained. Purification by v.p.c. (16 ft. silicone oil column, 38°, 12 p.s.i.) yielded pure 1,3-butadienylsilane, $n^{23}D$ 1.4555, b.p. 58° (see Table II for n.m.r. spectrum).

Anal. Calcd. for C_4H_8Si: C, 57.06; H, 9.57. Found: C, 56.70; H, 9.87.

Hydrosilylation of 4-Chloro-1-butyne.—To a 500-ml. 3-neck flask, equipped with thermometer and Friedricks condenser connected to a Dry Ice trap and a mercury bubbler were added 35 g. (0.4 mole) of 4-chloro-1-butyne,[16] 108 g. (0.8 mole) of trichlorosilane, 105 g. (1.2 moles) of cyclohexane (freshly distilled from sodium), and 6.4 g. (0.026 mole) of benzoyl peroxide. The mixture was refluxed for 72 hr., then solvent and excess trichlorosilane were removed on a steam bath under water aspirator pressure. Distillation of the residue gave 28 g. (33%) of a *cis–trans* mixture of 4-chloro-1-trichlorosilyl-1-butenes boiling at 94–99° (4.5 mm.).

Anal. Calcd. for $C_4H_6SiCl_4$: C, 21.45; H, 2.70; Cl, 63.31. Found: C, 21.68; H, 2.68; Cl, 63.00.

Vapor phase chromatographic analysis (3 ft. PMPE column, 100°) disclosed that the above product was a 70:30 *cis–trans* isomer mixture.

Separation and Identification of *cis*- and *trans*-4-Chloro-1-trichlorosilyl-1-butenes.—In another hydrosilylation run the product was carefully separated into five fractions on a Todd column at 1 mm.: (1) 35–47.5°, 3 ml.; (2) 47.5–50°, 16.9 ml.; (3) 50°, 37 ml.; (4) 50.5–54°, 8.5 ml.; (5) 54–55°, 5.5 ml.

The vapor phase chromatograms (3 ft. PMPE column, 100°) of the first two fractions were virtually identical, showing but one peak. Fractions 3–5 showed the development of a second, closely-spaced peak with a somewhat longer retention time. In fraction 5 this second peak had assumed a ratio of 8:1 over the first peak. Subsequent v.p.c. separation of the two components (10 ft. preparative PMPE column, 130°) permitted infrared (*trans* isomer showed a peak at 985 cm.$^{-1}$ which was absent in the *cis* compound) and n.m.r. determinations (see Table II) which confirmed the identity of the first peak as the *cis* isomer and the second peak as the *trans* isomer. The *cis*:*trans* ratio in this run was about 4:1 and the over-all yield was 31%.

4-Chloro-1-trimethylsilyl-1-butenes.—Seven grams (0.31 mole) of an isomeric mixture of *cis*- and *trans*-4-chloro-1-trichlorosilyl-1-butene was treated with 0.5 mole of methylmagnesium iodide. After 0.5 hr. the mixture was hydrolyzed with aqueous 10% sulfuric acid. After the usual work-up, distillation gave 2.4 g. (50%) of an isomeric mixture of *cis*- and *trans*-4-chloro-1-trimethylsilyl-1-butene boiling at 151–152°.

Anal. Calcd. for $C_7H_{15}SiCl$: C, 51.67; H, 9.28; Cl, 21.79. Found: C, 52.02; H, 9.38; Cl, 21.41.

1,1-Dichlorosila-2-cyclopentene.—Ten grams (0.41 g.-atom) of magnesium was placed in a carefully dried 500-ml. 3-neck flask fitted with a dropping funnel, condenser, and stirrer. To this flask were added 100 ml. of anhydrous ether and 4 drops of methyl iodide. While this mixture was refluxing, 14 g. (0.062 mole) of *cis*-4-chloro-1-trichlorosilyl-1-butene, diluted with about five times its volume of ether, was added dropwise with stirring. The solution turned cloudy after 15 min. and a dark brown color developed over a period of 1.5 hr. After a reflux time of 4 hr., petroleum ether (35–38°) was added. The mixture was filtered and evaporated to about a 100-ml. volume under reduced pressure and filtered again. It was then evaporated to about 10 ml. and refiltered. Distillation of the final filtrate (deep red-brown color) gave 4.9 g. (51%) of 1,1-dichlorosila-2-cyclopentene boiling at 42° (17.5 mm.). A v.p.c. analysis of this material indicated a minimum purity of over 95%. A very minor contaminant appeared to be 1,1-dichlorosila-3-cyclopentene. An infrared spectrum of the major product as well as its v.p.c. retention time agreed with an authentic sample of 1,1-dichlorosila-2-cyclopentene prepared from the pyrolysis of monochlorinated 1,1-dichlorosilacyclopentane.

In another run, 35 g. of 3:1 *cis-trans*-olefin mixture of 4-chloro-1-trichlorosilyl-1-butene was cyclized in a similar fashion. Ten grams of magnesium and 150 ml. of ether were used. The reflux time was 6 hr. There was obtained 10 g. (42%) of 1,1-dichlorosila-2-cyclopentene boiling at 142–144°.

In still another run, the cyclization was attempted with 12 g. (0.05 mole) of pure *trans*-4-chloro-1-trichlorosilyl-1-butene. The reaction proceeded much more slowly, and only a 20% yield of product was realized after 4 hr.

1,1-Dichloro-3-bromosila-2-cyclopentene.—A mixture of 7.3 g. (0.047 mole) of 1,1-dichlorosila-2-cyclopentene and 8.3 g. of N-bromosuccinimide (0.047 mole) in 50 ml. of carbon tetrachloride was refluxed for 12 hr. Distillation yielded 7 g. (59%) of product boiling at 66–70° (3 mm.). The infrared and n.m.r. spectra of this product are listed in Tables I and III.

Anal. Calcd. for $C_4H_5BrCl_2Si$: C, 20.71; H, 2.17; Br, 34.45; Cl, 30.56. Found: C, 20.82; H, 2.42; Br, 34.56; Cl, 30.41.

Divinylsilane.—Vinyl bromide (Matheson, 140 g., 1.3 moles) was condensed in a large test tube immersed in a Dry Ice–acetone bath protected by a drying tube. Tetrahydrofuran (100 ml.) was added to the vinyl bromide and this solution was then added with stirring to 38 g. (1.6 g.-atom) of magnesium in 1000 ml. of dry tetrahydrofuran in a 2-l., 3-neck flask equipped with an addition funnel and a Dry Ice condenser and protected from the atmosphere by a drying tube.

The vinyl Grignard was then added to 320 g. (2 moles) of vinyltrichlorosilane (redistilled, b.p. 87–88°) in 500 ml. of dry ether with stirring in a 3-l. flask equipped with a stirrer, addition funnel, and water condenser. The reaction mixture was filtered from the salts, solvent distilled off, and 500 ml. of dry pentane added to precipitate additional salts. This was filtered, and the pentane removed by distillation. The 200 g. of chlorovinyl-

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[16] G. Eglington and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950).

silanes so obtained was then added to 76 g. (2 moles) of lithium aluminum hydride in 750 ml. of dry diglyme in a 3-neck flask equipped with a stirrer, condenser, and addition funnel. The reaction mixture was kept at 20–25°. The volatile vinylsilanes were then removed from the reaction mixture under vacuum and condensed in a Dry Ice trap. The volatile material (52 g.) was distilled on a Todd column. Eleven fractions were collected, but none of these gave an analytically pure sample of divinylsilane. Pure divinylsilane ($n^{19}\text{D}$ 1.4180) was obtained from one of the fractions (b.p. 41–42°) by gas chromatography (16 ft. silicone oil column at room temperature).

Anal. Calcd. for C_4H_8Si: C, 57.06; H, 9.57. Found: C, 57.47; H, 9.67.

There was also isolated by gas chromatography a material which appeared to be ethylvinylsilane (probably caused by an ethyl halide impurity in the starting vinyl bromide).

The later fractions from the distillation proved to be trivinylsilane (b.p. 89.5°, $n^{20}\text{D}$ 1.4475). See Table II for the n.m.r. spectrum of this compound.

Acknowledgment.—The authors are grateful to Dr. John Hooz and Dr. Garth M. Stanton for their technical assistance. We are also deeply indebted to Mr. William Baitinger for obtaining the n.m.r. spectra and to Dr. C. S. Yeh and her staff for all the microanalyses.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

Alkaloid Studies. XLVI.[1] The Alkaloids of *Aspidosperma obscurinervium* Azembuja. A New Class of Heptacyclic Indole Alkaloids[2]

BY KEITH S. BROWN, JR.,[3] AND CARL DJERASSI

RECEIVED JANUARY 30, 1964

From *A. obscurinervium* bark extract there was isolated (+)-aspidocarpine (Ia), (+)-aspidolimine (Ib), a new alkaloid of the methoxyindole type, and four new alkaloids (dihydroobscurinervine, IIa; obscurinervine, IIb; dihydroobscurinervidine, IIc; and obscurinervidine, IId) representative of a new class of heptacyclic indole alkaloids. The structures were assigned on the basis of analysis, infrared, ultraviolet, n.m.r., and mass spectra of the parent alkaloids and of a variety of chemical transformation products. Dihydroobscurinervidinol (IIIu) and dihydroobscurinervinol (IIIt) were synthesized from depropionylaspidoalbine (IVb) by addition of iodopropanol and iodobutanol, respectively, followed by cyclization of the more polar isomer of each addition pair through its monobrosylate, and lithium aluminum hydride reduction of the ether linkage. Neblinine, an alkaloid isolated from *A. neblinae* Monachino, could be shown to be 15-demethoxyobscurinervidine (IIe). Dihydroneblininane (IIIz) and its C-22 epimer were synthesized from deacetylaspidocarpine (Ic) and the configuration of the natural isomer at position 22 established by n.m.r. measurements. The configuration at position 4 in the original series of alkaloids II–IIg was assigned by three independent and mutually consistent n.m.r. comparisons.

In connection with our investigation of the indole alkaloids of Brazilian *Aspidosperma* species,[4] the bark of *A. obscurinervium* Azembuja was extracted with ethanol[5] and the basic portion of the extract partitioned between benzene and dilute acetic acid. The latter fraction contained (+)-aspidocarpine (Ia)[6–8] in a very high yield (3.5% of the ethanol extract), (+)-aspidolimine (Ib, 0.025%),[7,9] and a new alkaloid of the methoxyindole type (0.5%) whose structure is currently under investigation. The former fraction (benzene-soluble acetates) contained four closely related bases: dihydroobscurinervine (IIa, 0.06%), obscurinervine (IIb, 0.07%), dihydroobscurinervidine (IIc, 0.01%), and obscurinervidine (IId, 0.03%). These were assigned the unusual heptacyclic constitutions on the basis of the evidence described below.

The four bases IIa–IId showed an ultraviolet spectrum very similar to that of O-methyl-N-ethylaspidoalbinol (VIb),[10] while the infrared spectrum indicated the presence of a strained carbonyl function (1750 cm.$^{-1}$). The mass spectra of the alkaloids (Fig. 1) showed a diagnostic and exceedingly simple pattern, with the only significant peaks arising from loss of methyl and carbon monoxide (from all four molecular ions) and ethyl (from the molecular ions of IIa and IIb only); small peaks were also present at *m/e* 244 (in all four spectra and unaffected by catalytic deuteration of the 6,7 double bond; ion a), 260 (IIa and IIb; ion f), and 246 (IIc and IId; ion c).[11,12a] The molecular ion peaks (IIa, *m/e* 440 = $C_{25}H_{32}N_2O_5$; IIb, *m/e* 438 = $C_{25}H_{30}N_2O_5$; IIc, *m/e* 426 = $C_{24}H_{30}N_2O_5$; IId, *m/e* 424 = $C_{24}H_{28}N_2O_5$) confirmed the formulas indicated by analysis, and led to a simplification of the picture confirmed by hydrogenation of IIb to IIa, and IId to IIc. Also implied in the mass spectra was the conclusion that the obscurinervine and obscurinervidine pairs differed only in the presence of an easily expelled ethyl group in the former, replaced by a methyl group in the latter, probably attached to the aromatic portion of the molecules.

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[1] Part XLV: J. A. Joule and C. Djerassi, *J. Chem. Soc.*, in press.

[2] Partial support was provided by the National Institutes of Health (Grant No. GM-11309) of the U. S. Public Health Service.

[3] National Institutes of Health Postdoctorate Fellow, 1963.

[4] For most recent reference on this work, see J. M. Ferreira, B. Gilbert, R. J. Owellen, and C. Djerassi, *Experientia*, **19**, 585 (1963).

[5] We thank Dr. B. Gilbert, Universidade do Brasil, Rio de Janeiro, for the collection and initial extraction of the bark, which was collected 8 km. north of Manaus, Amazonas. Thanks are due to Dr. W. Rodrigues for locating this tree.

[6] S. McLean, K. Palmer, and L. Marion, *Can. J. Chem.*, **38**, 1547 (1960).

[7] Identity was established by infrared and ultraviolet spectra, optical rotation, and a mixture melting point with an authentic sample of the compound.

[8] The configurations of all compounds in this paper are relative and not absolute.

[9] H. Schmid and M. Pinar, *Helv. Chim. Acta*, **45**, 1283 (1962); B. Gilbert, J. A. Brissolese, J. M. Wilson, H. Budzikiewicz, L. J. Durham, and C. Djerassi, *Chem. Ind.* (London), 1949 (1962).

[10] C. Djerassi, L. D. Antonaccio, H. Budzikiewicz, J. M. Wilson, and B. Gilbert, *Tetrahedron Letters*, 1001 (1962).

[11] For reasons explained in H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, we are fixing the charge on nitrogen in molecular ions, followed by homolytic cleavages in all cases, to give ions in which the charge is also localized.

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