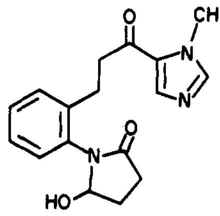
gam in aqueous tetrahydrofuran,[7] gave a mixture of two compounds which were separated by preparative plate chromatography on silica gel (9:1 CH_3CN–CH_3OH eluent). The less mobile of the two products, obtained in 64% yield at 0° as an off-white foam,[8,9] showed nmr behavior ($CDCl_3$) which implied structure VII: δ 2.12 (2 H, m), 2.65 (2 H, m), 3.50 (3 H, s), 4.50 (4 H, broad; collapses to 1 H, m, upon addition of D_2O), 6.5–7.2 (6 H, m) ppm. The more mobile compound, produced in 39% yield at 60°,[8] exhibited nmr behavior ($CDCl_3$) which led to the assignment of structure VIII: δ 2.08 (2 H, m), 2.82 (2 H, m), 3.58 (3 H, s), 4.42 (2 H, m; collapses to 1 H, d of d, J = 5, 7 Hz, upon addition of D_2O), 6.4–7.3 (6 H, m) ppm. The tetrahydroquinoline structure of VIII was further substantiated by its conversion, upon treatment with 10% Pd–C and sulfur in refluxing xylene for 2 days,[10] to isomacrorine (IX), in 57% yield. This sample exhibited mass spectral and ultraviolet behavior as reported,[11,12] and melted at 105–107° (lit.[12] mp 110°). Thus, this work constitutes a new synthesis of isomacrorine.[13]

Amino alcohol VII proved to be the key to the synthesis of dehydroisolongistrobine, for in its production from VI, the carbonyl group had been rendered incapable of intramolecular cyclization to a dihydroquinoline system. Compound VII, admixed with 1 equiv of pyridine in methylene chloride, was treated at 0° with an equivalent amount of β-carbomethoxypropionyl chloride[14] to produce, after plate chromatography on silica gel (9:1 CH_3CN–CH_3OH eluent), hydroxyamido ester X as an off-white foam in 63% yield.[15] Upon oxidation of X with Cornforth's reagent (CrO_3 in aqueous pyridine)[16] and plate chromatography on silica gel (9:1 CH_3CN–CH_3OH eluent), the beautifully crystalline ketone XI, mp 119–120.5° (CH_2Cl_2–hexane), was obtained in 43% yield.[17]

When XI was heated *in vacuo* above its melting point for 5 min, III was obtained in 83% yield as splendid white needles mp 130.5–131.5° (lit.[1] mp 131°, nmp 130–131.5°[18]) from methylene chloride–hexane.[19] Uv and nmr spectra were in agreement with those reported[1] for dehydroisolongistrobine. The infrared spectra of natural and synthetic samples of the alkaloid were identical, showing bands at 1780 (weak), 1710 (very strong),[20] and 1665 (strong) cm^{-1}. It should be noted that only the 1710-cm^{-1} band was reported by Arndt, *et al.*[1] In addition, mass spectra of natural and synthetic samples of dehydroisolongistrobine run under identical conditions were the same. Prominent peaks were observed at *m/e* 311 (parent), 110, 109, and 82.

On the basis of this work, structure III is firmly established for dehydroisolongistrobine, in preference to I. Furthermore, structure XII, rather than the previously proposed structure II, is strongly indicated for isolongistrobine, on the basis of the now-substantiated 5-[β-(*o*-anilino)propionyl]-1-methylimidazole skeleton and the spectral and chemical data reported by the original workers.



XII

Further work on these alkaloids is in progress in our laboratories.

Acknowledgments. One of us (M. A. W.) thanks the NSF for a predoctoral fellowship (1969–1971). Thanks are also due to W. J. Pegg and G. W. Busby III for determination of mass spectra. Elemental analyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

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(7) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **86**, 1639 (1964).

(8) At 0°, the ratio of VII to VIII was greater than 2:1; at 60°, *ca.* 1:1.

(9) Exact mass measurement of parent peak of VII. Calcd for $C_{13}H_{17}N_3O$: 231.1372. Found: 231.1378.

(10) *Cf.* H. S. Blair, M. Crawford, J. M. Spence, and V. R. Supanekar, *J. Chem. Soc.*, 3313 (1960); M. Crawford and V. R. Supanekar, *ibid.*, 2380 (1964).

(11) V. P. Joynt, R. R. Arndt, A. Jordaan, K. Biemann, and J. L. Occolowitz, *J. Chem. Soc. B*, 980 (1966).

(12) R. R. Arndt, A. Jordaan, and V. P. Joynt, *J. Chem. Soc., Suppl. 2*, 5969 (1964).

(13) *Cf.* A. Jordaan, V. P. Joynt, and R. R. Arndt, *J. Chem. Soc. B*, 3001 (1965).

(14) "Organic Syntheses" Collect. Vol III, Wiley, New York, N. Y., 1955, p 169.

(15) Physical data for X: ir (NaCl plate) 3300 (very broad), 1735, 1665, and 1530 cm^{-1}; mass spectrum (70 eV) *m/e* 111, 125, and 345 (parent).

(16) R. H. Cornforth, J. W. Cornforth, and G. Popjak, *Tetrahedron*, **18**, 1351 (1962).

(17) Physical data for XI: ir (KBr) 3330, 1735, 1665, 1660, and 1530 cm^{-1}; nmr ($CDCl_3$, 100 MHz) δ 2.83 (4 H, s), 2.99 (2 H, t, J = 6 Hz), 3.26 (2 H, t, J = 6 Hz), 3.73 (3 H, s), 3.92 (3 H, s), 7.0–7.9 (6 H, m), and 8.96 (1 H, broad s) ppm; uv (MeOH) λ_{max} 254 nm (ϵ 16,100) shifted to 232 nm (ϵ 15,900) in acid; mass spectrum (70 eV) *m/e* 82, 83, 109, 110, 234, 256, and 343 (parent). *Anal.* Calcd for $C_{18}H_{21}N_3O_4$: C, 62.96; H, 6.16; N, 12.24. Found: C, 62.77; H, 6.22; N, 12.33.

(18) We are grateful to Dr. A. Jordaan for a sample of dehydroisolongistrobine from natural sources, which we recrystallized twice (mp 130.5–131.5°).

(19) *Anal.* Calcd for $C_{17}H_{17}N_3O_3$: C, 65.58; H, 5.50; N, 13.50. Found: C, 65.48; H, 5.47; N, 13.37.

(20) The 1780–1710-cm^{-1} doublet is characteristic of *N*-arylsuccinimides: K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 47; M. A. Wuonola, unpublished observations.

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A New Synthesis of Internally Substituted Alkyl Silanes

Sir:

Previous methods for preparing internally substituted alkyl silanes include the coupling of branched organometallics with the appropriate silicon compound,[1] as well as peroxide[2] and base-catalyzed[3] addition of $\equiv$SiH to internal olefins. The methods are tedious, some requiring long reaction times, and generally do not produce the alkyl silanes in good yield.

Hydrosilylation of olefins with trichlorosilane, catalyzed by transition metals on various supports or

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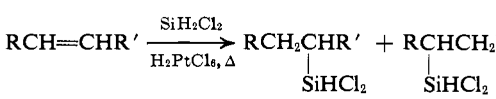
(1) For typical examples, see J. W. Jenkins and H. W. Post, *J. Org. Chem.*, **15**, 552 (1950).

(2) C. A. Burkhard and R. H. Krieble, *J. Amer. Chem. Soc.*, **69**, 2687 (1947); J. C. Saam and J. L. Speier, *ibid.*, **80**, 4104 (1958).

(3) R. A. Pike, *J. Org. Chem.*, 27, 2186 (1962).

chloroplatinic acid, has proved to be an excellent synthetic route to the formation of a carbon–silicon bond. With internal olefins, however, the terminal adduct is usually the major product[4] in such reactions.

We have discovered that dichlorosilane[5] (H_2SiCl_2) adds directly to internal olefins when catalyzed by chloroplatinic acid to give internally substituted alkyl silanes in excellent yields. Significantly no bond migration[6] occurs with dichlorosilane[7] in contrast to similar reactions with trichlorosilane and chloroplatinic[8] acid.



$$RCH{=}CHR' \xrightarrow[H_2PtCl_6,\,\Delta]{SiH_2Cl_2} \underset{SiHCl_2}{RCH_2\underset{|}{C}HR'} + \underset{SiHCl_2}{R\underset{|}{C}HCH_2R'}$$

Table I lists typical results for such dichlorosilane additions.

Table I. Chloroplatinic Acid-Catalyzed Addition of Dichlorosilane to Internal Olefins

Olefin[a]	Temp, °C (time, hr)	Products[b] (% distribution)	Bp, °C (mm)	Yield, %
2-Heptene	150 (8)	2-$C_7H_{15}SiCl_2H$ (64) 3-$C_7H_{15}SiCl_2H$ (36)	55–60 (5)	81
2-Heptene	110 (8)	As above		51
2-Hexene	140 (8)	2-$C_6H_{13}SiCl_2H$ (66) 3-$C_6H_{13}SiCl_2H$ (34)	48–51 (7.5)	89
2-Hexene	72–74 (24)	As above		26
3-Hexene[c]	150 (8)	3-$C_6H_{13}SiCl_2H$[d]	50–55 (12)	56
3-Hexene[c]	150 (24)	3-$C_6H_{13}SiCl_2H$[d]	47–51 (9)	88
2-Pentene	128–130 (8)	2-$C_5H_{11}SiCl_2H$ (69) 3-$C_5H_{11}SiCl_2H$ (31)	131–136 (740)	92

[a] Pure mixtures of cis and trans. [b] All compounds gave acceptable elemental analyses and nmr spectra. [c] Contained 6% 2-hexene as an impurity. [d] Contained 4% 2-$C_6H_{13}SiCl_2H$.

In a typical experiment, 0.10 mol of 2-heptene and 50 μl of chloroplatinic acid in isopropyl alcohol (0.10 g of $H_2PtCl_6 \cdot 6H_2O$ in 2 ml of isopropyl alcohol) were placed in a stainless steel bomb and cooled to −78°. Dichlorosilane (0.20 mol, 14.2 ml) was condensed in a calibrated tube at −78° and then distilled into the bomb under dry nitrogen after which the bomb was heated in an oil bath at 150° for 8 hr. Upon cooling, the excess dichlorosilane was vented and the bomb washed with dry pentane. Solvent removal followed by distillation afforded 16.1 g (81%) (bp 55–60° at 5.0 mm) of a mixture of 2- (64%) and 3- (36%) heptyldichlorosilane: nmr (CCl_4–TMS) δ 0.73–1.87 multiplet and two unresolved singlets (SiH) at δ 5.42 (64%) and 5.48 (36%). *Anal.* Calcd for $C_7H_{16}SiCl_2$: C, 42.20; H, 8.10; Si, 14.10; Cl, 35.60. Found: C, 42.30; H, 8.27; Si, 14.01; Cl, 35.81.

Authentic samples of 1-, 2-, and 3-heptyldichlorosilane were prepared for comparison purposes by treating the appropriate Grignard reagent derived from the isomerically pure 1-, 2-, and 3-bromoheptanes with excess trichlorosilane. The nmr spectrum of 1-heptyldichlorosilane thus prepared showed a triplet for SiH at δ 5.5, while the authentic 2- and 3-heptyl isomers showed unresolved singlets for SiH at δ 5.42 and 5.48, respectively. These differences in chemical shift for the silanic protons proved a valuable diagnostic in analyzing the isomeric mixtures depicted in Table I. Based on the results in Table I the silicon atom of dichlorosilane attached itself preferentially to the less hindered carbon atom, thus favoring formation of the 2 over the 3 isomer by a ratio of about 2:1. Further substantiation for the assignments of the chemical shifts of the silanic protons was forthcoming from the reaction between 3-hexene and dichlorosilane where only the 3 isomer can result (Table I). The nmr spectrum of the product again showed an unresolved singlet for Si–H at δ 5.48.

To establish whether impurities, surreptitiously introduced from the metal of the stainless steel bomb, were responsible for the failure to obtain terminal adducts with dichlorosilane, 2-heptene was treated with trichlorosilane in the same bomb and under identical reaction conditions (chloroplatinic acid, 110°, 8 hr). *n*-Heptyltrichlorosilane was obtained in this case in 83% yield. Clearly the mechanism[9] suggested for trichlorosilane additions requires some modification in the case of similar dichlorosilane additions.

A new area of organosilicon chemistry is now open since, for the first time, internally substituted alkyl silanes can be prepared in convenient quantities by a direct and economical route. Studies are continuing in our laboratory on the stereochemistry of dichlorosilane additions as well as its addition to dienes. Preliminary studies indicate that monoadducts derived from diene substrates can be made to undergo intramolecular cyclizations. Details of these experiments will be published shortly.

Acknowledgment. We wish to thank the National Science Foundation for its financial support of this work.

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(4) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Amer. Chem. Soc.*, **79**, 974 (1957).

(5) Obtained from Union Carbide Corp., Sistersville, W. Va.

(6) With 2-butene some terminal adduct could be obtained if the reaction were carried out at lower temperatures. The results in Table I would indicate that the rate of internal addition is increased by higher reaction temperatures.

(7) We have obtained some preliminary evidence that monochlorosilane also can be made to add to internal olefins without rearrangements.

(8) While chloroplatinic acid was initially introduced into the bomb, one is not justified in assuming that it *must* be the active catalyst in these reactions. Decomposition to other active platinum species may well have occurred under the reaction conditions employed. Blank runs made in the absence of initially added chloroplatinic acid gave little or no product, clearly indicating the catalytic effect of some form of platinum.

(9) A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, **87**, 16 (1965).

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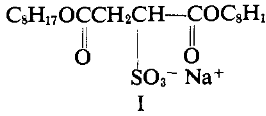
Catalysis in Water Pools

Sir:

Octane solutions of di-2-ethylhexyl sodium sulfosuccinate (I) dissolve remarkable amounts of water (50 mol/mol of solute).[1] Thus, a 0.1 *M* solution of the sulfosuccinate in octane can incorporate nearly 10% water. This solubilized water is confined in spherical



$$C_8H_{17}O\underset{O}{\underset{\|}{C}}CH_2\underset{SO_3^-\,Na^+}{\underset{|}{C}H}{-}\underset{O}{\underset{\|}{C}}OC_8H_{17}$$

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(1) W. I. Higuchi and J. Misra, *J. Pharm. Sci.*, **51**, 455 (1962).