unperturbed fragment results are to be expected (even if the structure of the molecule remains unaltered). There is a "direct" inductive effect on the polarity of the CH and C'H' bonds involved in the coupling that has been considered by Hiroike[10] and by Ranft.[11] Introduction of reasonable inductive parameters into their treatment indicates that the "direct" term is relatively small. However, there is an additional effect that arises through the substituent-induced changes in hybridization[12] of the HCC'H' fragment carbon atoms. If the structure of the molecule is assumed constant, an estimate of the carbon atom hybridization can be obtained from J_{CH} coupling measurements[13] and an appropriately modified fragment calculation can be performed. The values found can be written $J_{HH'}(cis) \cong J^u_{HH'}(cis)(1 - 0.60\Delta X)$, $J_{HH'}(trans) \cong J^u_{HH'}(trans)(1 - 0.25\Delta X)$ for CH_2CHX, and $J_{HH'}(av) \cong J^u_{HH'}(av)(1 - 0.07\Delta X)$ for CH_3CH_2X, where $J^u_{HH'}$ refers to the unperturbed fragment and $\Delta X = X - X_H$. These results for the substituent effects are in qualitative agreement with the available experimental data.[3a,7,14]

Bond Angle Dependence.—The vicinal couplings are expected to depend significantly on the angles θ and θ' [$\theta = \angle HCC'$, $\theta' = \angle CCH'$] of the HCC'H' fragment, even when the orbitals point along the bond direction and the bond lengths remain unchanged. Fragment-model calculations show that $J_{HH'}$ should decrease for most dihedral angles as θ and θ' increase. For $105° \leq \theta,\theta' \leq 115°$, we find that A, B, and C of eq. 1 are given *approximately* by $A \cong 4.2 - 0.1(\Delta\theta + \Delta\theta')$, $B = -0.5 - 0.05(\Delta\theta + \Delta\theta')$, and $C = 4.4 - 0.12(\Delta\theta + \Delta\theta')$, where $\Delta\theta = \theta - 110°$, $\Delta\theta' = \theta' - 110°$. Corresponding results for the ethylenic system are $J_{HH'}(cis)$ equals 16, 6.1, 2.1 for ($\theta = \theta'$) angles of $110°$, $120°$, $130°$, respectively.[15] Bond angle changes of $J_{HH'}$ in the calculated direction were noted some years ago by Pople, Bernstein, and Schneider[16] and have been emphasized recently by a number of workers.[3b]

Bond Length Dependence.—For constant bond angles and hybridization, the vicinal σ-bond coupling is expected to be a function of the C–C bond length (R), a decrease of the coupling being produced by an increase in the bond length. For ethylenic systems, for example, the fragment calculations yield an almost linear dependence of the form $J_{HH'}(cis) \cong J^u_{HH'}(cis)$ $[1 - 2.9(R - 1.35)]$ for R in the range 1.35–1.55 Å., in qualitative agreement with experiment.[17]

In addition to the factors discussed in detail, other molecular properties (*e.g.*, exchange integral variation, molecular vibrations,[18] ΔE variation, changes in π-bonding[19]) can influence vicinal coupling constants under appropriate conditions. Also, it is likely that the various perturbations affect the coupling through a

combination of the mechanisms that have been isolated earlier for convenient description.[20]

Any structural analysis based on the dihedral-angle dependence of vicinal coupling constants must take account of their variation as a function of other aspects of the molecular environment. Until extensive studies have been made to ascertain the quantitative details of these relationships, the most reliable results are to be expected from the comparison of closely related species. The introduction of empirical parameters to adjust the theoretical formulas for a particular series of compounds can be helpful in this regard.[2] Furthermore, it is best if the solution to the structural problem under consideration depends not on the exact values of coupling constants, but only on the fact that certain couplings are "large" rather than "small," or *vice versa*. Certainly with our present knowledge, the person who attempts to estimate dihedral angles to an accuracy of one or two degrees does so at his own peril.

(20) This means of course, that experimental attempts to test the theoretical results must use care to isolate the variables under consideration.

DEPARTMENT OF CHEMISTRY MARTIN KARPLUS
AND IBM WATSON LABORATORY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

The Nature of "Silirene" Compounds

Sir:

In 1961 Vol'pin and his co-workers reported the synthesis of a compound with an empirical formula $C_{16}H_{16}Si$ (I), which they supposed to have the novel "silirene" structure (II).[1-3] We have found that compound I actually has a molecular weight twice that reported by Vol'pin.[4] The compound probably has the six-membered ring structure III. The same

II III IV
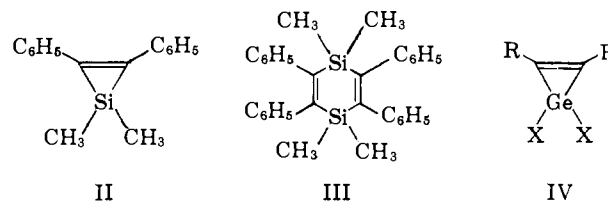
workers also reported three-membered ring structures (IV) for the related germanium compounds.[2,3,5] These compounds have recently been shown to be dimers of this structure, in mass spectrometric studies by Johnson and Gohlke,[6] who also suggested that the three-ring structures advanced for the silicon compounds might be incorrect. Thus the heterocyclic three-membered ring system containing a metalloid atom, theoretically rationalized by Vol'pin and his co-workers,[2,7] has yet to be demonstrated.

A modification of the method of synthesis used by the previous workers led to a 10-fold increase in the yield of I. A suspension of 10 g. (0.43 g.-atom) of sodium was prepared in a solution of 27 ml. (0.22 mole) of dimethyldichlorosilane in 500 ml. of xylene. At

(10) E. Hiroike, *J. Phys. Soc. Japan*, **15**, 270 (1960).

(11) J. Ranft, *Anal. Phys.*, **8**, 322 (1961); **9**, 124 (1962).

(12) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(13) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959); J. M. Shoolery, *ibid.*, **31**, 1427 (1959); M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci.*, **45**, 1269 (1959); C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962); *Discussions Faraday Soc.*, **34**, 52 (1962).

(14) R. E. Glick and A. A. Bothner-by, *J. Chem. Phys.*, **25**, 362 (1956); T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962); J. S. Waugh and S. Castellano, *J. Chem. Phys.*, **35**, 1900 (1961).

(15) See also, H. S. Gutowsky and A. L. Porte, *ibid.*, **35**, 839 (1961).

(16) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 195; see also R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 905 (1961); J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

(17) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1963). The change in the π-bond contribution is expected to be very small in the compounds studied.

(18) See R. W. Lenz and J. P. Heeschen, ref. 2; H. S. Gutowsky, V. D. Mochel, and B. G. Sommers, *J. Chem. Phys.*, **36**, 1153 (1962).

(19) M. Karplus, *ibid.*, **33**, 1842 (1960).

(1) M. E. Vol'pin, Yu. D. Koreshkov, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1355 (1961).

(2) M. E. Vol'pin, Yu. D. Koreshkov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, **18**, 107 (1962).

(3) L. A. Leites, V. G. Dulova, and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 731 (1963).

(4) Preliminary mass spectrometric investigations of I by D. Weyenberg and A. P. Bey appear to confirm the dimeric molecular weight for I (private communication from Dr. Weyenberg).

(5) M. E. Vol'pin and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1903 (1960); M. E. Vol'pin, V. G. Dulova, and D. N. Kursanov, *ibid.*, 727 (1963); M. E. Vol'pin and D. N. Kursanov, *Zh. Obshch. Khim.*, **32**, 1455 (1962).

(6) F. Johnson and R. S. Gohlke, *Tetrahedron Letters*, 1291 (1962).

(7) M. E. Vol'pin and D. N. Kursanov, *Zh. Obshch. Khim.*, **32**, 1137 (1962).

reflux temperature, a solution of 20.0 g. (0.12 mole) of diphenylacetylene in 100 ml. of xylene was added over a period of 1 hr. with vigorous stirring. The mixture was refluxed for 2 hr. after addition was complete, then filtered and concentrated. Hexane was added to dissolve by-products, and the crude product was filtered. Purification by recrystallization from toluene and vacuum sublimation yielded 1.2 g. of I (5% based on diphenylacetylene), m.p. 329–330° (lit.[1] 324–328°). *Anal.* Calcd. for $C_{32}H_{32}Si_2$: C, 81.4; H, 6.78. Found: C, 81.3; H, 6.71. The infrared spectral features and chemical properties agree with those reported by the earlier workers.[1,2] The analytical data eliminate from consideration the five-membered ring "silole" structure also suggested as a possibility for I.[5]

Determination of the molecular weight by the Rast method in camphor gives, as Vol'pin and his co-workers state,[2] a value of about 240. (The calculated mol. wt. for I is 236.) However, the Rast method is known to be unreliable for silicon compounds, and in this instance its use led directly to the incorrect structural assignment. The low solubility of I in many organic solvents makes determination of its molecular weight by usual methods difficult. Therefore, the technique of vapor phase osmometry, which has been found to give excellent results for other high molecular weight organosilicon compounds,[8] was employed. By this method we find the molecular weight of I to be 475 (average of six determinations ranging from 453 to 506, benzene solution). A dimeric structure is therefore indicated.

Structure III is favored over less-symmetrical alternatives because the tetra-*p*-tolyl analog of I, prepared in an analogous manner from di-*p*-tolylacetylene, shows only one sharp n.m.r. resonance peak for the tolyl-methyl protons, at τ 7.70. An equivalent magnetic environment for the four methyl groups is indicated, consistent with a structure of type III. *Anal.* Calcd. for $C_{36}H_{40}Si_2$: C, 81.8; H, 7.62; mol. wt., 529. Found: C, 82.6; H, 7.71; mol. wt., 510 (average of three determinations in benzene).

Compound I and its tetra-*p*-tolyl analog are rather unreactive toward many of the usual reagents which add to carbon-to-carbon double bonds (Br_2 in CCl_4, $KMnO_4$ in acetone, H_2/Pt). The low reactivity can be attributed in part to steric hindrance to the attacking reagent and perhaps in part to delocalization of the olefinic π-electrons by participation of 3d-orbitals of silicon in the π-bonding.[9]

Acknowledgments.—This research was supported by a grant from the Air Force Office of Scientific Research of the Air Research and Development Command. The authors are grateful to Dr. F. Johnson for an extensive discussion of this problem.

(8) H. Gilman and G. L. Schwebke, *J. Am. Chem. Soc.*, **85**, 1016 (1963); "Advances in Organometallic Chemistry," Vol. I, in press.

(9) L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *J. Am. Chem. Soc.*, **76**, 1613 (1954); E. Larsson, *Chalmers Tek. Hogskol. Handl.*, **25**, 115 (1951).

DEPARTMENT OF CHEMISTRY   ROBERT WEST
UNIVERSITY OF WISCONSIN   ROBERT E. BAILEY
MADISON 6, WISCONSIN

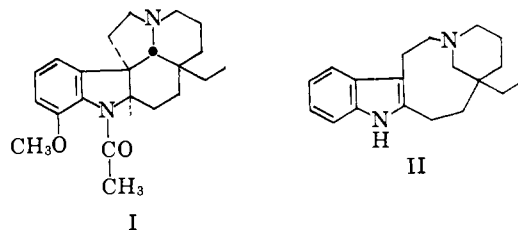## The Total Synthesis of *dl*-Aspidospermine and of *dl*-Quebrachamine

Sir:

The alkaloid aspidospermine, isolated from *Aspidosperma quebracho blanco*, has been shown to have structure I by a combination of degradative[1] and X-ray[2]

(1) H. Conroy, P. R. Brooks, and Y. Amiel, *Tetrahedron Letters*, **No. 11**, 4 (1959); G. F. Smith and J. T. Wróbel, *J. Chem. Soc.*, 1463 (1960).

(2) J. F. D. Mills and S. C. Nyburg, *ibid.*, 1458 (1960).

evidence. In the short time since the determination of its structure, it has become apparent that aspidospermine is a member of a large class of indole alkaloids based on the same general skeleton, while others [*e.g.*, quebrachamine (II)] are simply related to the group.[3]

I   II

We have now succeeded in achieving the total synthesis of *dl*-aspidospermine, as well as that of *dl*-quebrachamine.

Reaction of the pyrolidine enamine of butyraldehyde with methyl acrylate, followed by aqueous acetic acid hydrolysis at room temperature, gave a 67% yield of methyl 4-formylhexanoate (III), b.p. 95–98° (10 mm.).[4] This was once more submitted to the enamine alkylation reaction, using the pyrolidine enamine of III and methyl vinyl ketone. Treatment of the reaction mixture, following initial condensation, with hot acetic acid resulted in cyclization to the desired 4-ethyl-4-(2-carbomethoxyethyl)-2-cyclohexenone (IV), b.p. 105° (0.05 mm.) λ_{max}^{EtOH} 226 mμ (ϵ 12,300), in 48% yield.

Reaction of the unsaturated keto ester IV with aqueous ammonia at room temperature led to the bicyclic keto lactam V as a mixture of *cis* and *trans* epimers.

There was good reason to believe that with either the *cis* or the *trans* bicyclic ketolactam V, the Fischer indole synthesis[5] would involve the enamine tautomer of the phenylhydrazone with the double bond parallel to the ring junction[6] and would thus lead, even in the *cis* case, to the undesirable linear system of VI.

III   IV   V
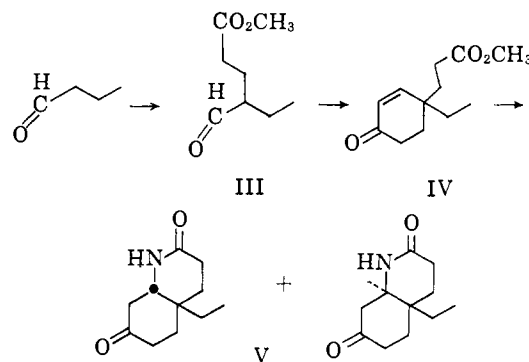
In fact, cyclization of the *o*-methoxyphenylhydrazones derived from V in the presence of hot acetic acid gave two crystalline tetracyclic lactams, m.p. 269–271° and m.p. 237°, in about 15% yield each. These lactams represent the two possible stereoisomers of the linear

(3) *Cf.* K. Biemann, M. Friedmann-Spiteller, and G. Spiteller. *Tetrahedron Letters*, **No. 14**, 485 (1961); K. Biemann and G. Spiteller, *ibid.*, **No. 9**, 299 (1961); C. Djerassi, H. Budzikiewicz, and J. M. Wilson, *ibid.*, **No. 6**, 235 (1962); M. Plat, J. Le Men, M.-M. Janot, J. M. Wilson, H. Budzikiewicz, L. Durham, Y. Nakagawa, and C. Djerassi, *ibid.*, **No. 7**, 271 (1962); C. Djerassi, L. D. Antonaccio, H. Budzikiewicz, J. M. Wilson, and B. Gilbert, *ibid.*, **No. 22**, 1001 (1962); H. K. Schnoes, A. L. Burlingame, and K. Biemann, *ibid.*, **No. 22**, 993 (1962); C. Djerassi, A. A. P. G. Archer, T. George, B. Gilbert, and L. D. Antonaccio, *Tetrahedron*, **16**, 212 (1961); S. McLean, K. Palmer, and L. Marion, *Can. J. Chem.*, **38**, 1547 (1960); C. Djerassi, H. W. Brewer, H. Budzikiewicz, O. O. Orazi, and R. A. Corral, *Experientia*, **18**, 113 (1962).

(4) Satisfactory analyses have been obtained for all key intermediates.

(5) The mechanism of the Fischer indole synthesis has been discussed by R. B. Carlin and E. E. Fisher, *J. Am. Chem. Soc.*, **70**, 3421 (1948).

(6) *Cf.* bromination and oxidation of 10-methyl-*cis*-2-decalone, M. Yanagita and K. Yamakawa, *J. Org. Chem.*, **22**, 291 (1957).