mol. wt., 897.8. Found: B, 3.51; C, 77.04; Cl, 0.00; N, 4.85; Si, 9.19; mol. wt., 881.2. Calcd. for $B_3[Si(C_6H_5)_3]_3N_3(C_6H_5)_3$: B, 2.99; C, 79.76; Cl, 0.00; N, 3.88; Si, 7.77; mol. wt., 1084. Found: B, 3.02; C, 79.70; Cl, 0.00; N, 3.98; Si, 7.50; mol. wt., 1052.

In addition to the method of synthesis and analysis, the assignment of a substituted borazine structure to these compounds is supported by the molecular weights, determined cryoscopically in benzene, and by certain features of their infrared spectra in carbon tetrachloride. The salient features are: bands in the 7μ region characteristic of the borazine ring[3]

N-Trimethyl compound:	6.94 (s)	7.02 (ms)	7.27 (s)
N-Triphenyl compound:	6.68 (ms)	7.00 (s)	7.35 (vs)

Both compounds have absorption at 14.4 μ which is due to a monosubstituted phenyl group.[4] Also, the C–H band at about 3.5 μ is diffuse and seems to be characteristic of the triphenylsilyl group.[5]

Both compounds react with moist air, but do not take up dry oxygen at room temperature or at 160°. Reaction with bromine proceeds readily in carbon tetrachloride and at room temperature, producing triphenylbromosilane as the only soluble product (identified by infrared spectrum and bromine analysis) and a precipitate which does not exhibit the borazine ring frequency in a KBr pellet infrared spectrum. This suggests that ring cleavage had occurred.

(3) W. C. Price, R. P. B. Fraser, T. S. Robinson and H. C. Longuet-Higgins, *Disc. Faraday Soc.*, **9**, 131 (1950).

(4) H. M. Randall, "Infrared Determination of Organic Structures," D. Van Nostrand Co., New York, N. Y., 1949.

(5) The authors found that the infrared spectrum of hexaphenyldisilane had this same flattening effect.

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RECEIVED DECEMBER 11, 1959

THE SYNTHESIS AND STRUCTURE OF BIS-(CYCLOPENTADIENYLNICKEL)-ACETYLENE

Sir:

The first synthesis of an acetylene complex of nickel is herein reported, bis-(cyclopentadienylnickel)-acetylene being a product of the reaction between nickelocene and acetylene. Alkyne metal complexes in which the alkyne as such is bonded via its π electron system have been reported with the cobalt[1] and iron carbonyls[2] and various derivatives of platinum.[3,4] Recently certain alkyne nickel complexes have been reported as the products of reaction between alkynes and dicyclopentadienyldinickel dicarbonyl.[5] The isolation of bis-(cyclopentadienylnickel)-acetylene through a different route represents the first member of this novel series of nickel alkyne complexes.

(1) H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, H. R. Markby and I. Wender, THIS JOURNAL, **76**, 1457 (1954); **78**, 120 (1956).

(2) W. Hubel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959).

(3) S. V. Bukhovets and K. A Molodava, *Zhur. Neorg. Khim.*, **2**, 776 (1957); S. V. Bukhovets and N. K. Pukhova, *ibid.*, **3**, 1714 (1958).

(4) J. Chatt, C. A. Rowe and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957); J. Chatt, L. A. Duncanson and R. G. Guy, *Chem. and Ind.*, 430 (1959).

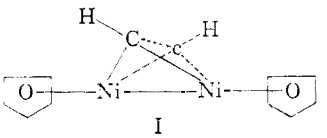
(5) J. F. Tilney-Bassett and O. S. Mills, THIS JOURNAL, **81**, 4757 (1959).

Bis-(cyclopentadienylnickel)-acetylene was prepared by contacting 18 g. of nickelocene dissolved in tetrahydrofuran with acetylene at 180 p.s.i. and 80° for 15 hours. The reaction mixture was filtered and the solvent was removed at reduced pressure. Fractional vacuum sublimation of the dark green residue resulted in a recovery of 5.5 g. (30%) of unreacted nickelocene and the isolation of a less volatile dark green crystalline solid which crystallized from petroleum ether at −60° as light green lustrous plates m.p. 143–144° (dec.).

Anal. Calcd. for $(C_6H_6Ni)_2$; C, 52.7; H, 4.39; Ni, 42.9. Found: C, 52.3; H, 4.49; Ni, 42.6.

A Signer molecular weight determination of 290 supported the above written empirical formula. The total yield of product was 6.3 g. (48%).

The product exhibits moderate solubility in saturated hydrocarbons but is very soluble in all other common organic solvents. Oxidatively, it appears to be more stable than nickelocene and it can be handled readily in air for short periods of time. The infrared spectrum of the material contains bands characteristic of a π bonded cyclopentadienyl metal grouping. Magnetic susceptibility measurements[6] indicate that the product is diamagnetic which suggests that nickel has attained rare gas electronic structure. On the basis of the above data, Structure I corresponding to bis-(cyclopentadienylnickel)-acetylene is proposed in which acetylene is bonded via four π electrons to a binuclear cyclopentadienyl nickel system. The



I

exact orientation of the acetylene carbons relative to the binuclear nickel bonding is unknown. However, in view of the recent X-ray studies by Sly[7] with the binuclear cobalt carbonyl complex of diphenylacetylene, the bonds probably are at right angles. The proposed structure is in agreement with the structures of the alkyne nickel complexes as outlined by Tilney-Bassett and Mills.

The extension of the above reaction to substituted alkynes will be discussed in forthcoming publications.

(6) We are indebted to Dr. Stanley Kirschner of Wayne State University for carrying out the magnetic measurements.

(7) W. G. Sly, THIS JOURNAL, **81**, 18 (1959).

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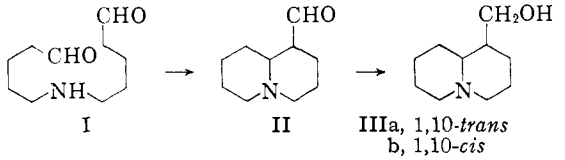
RECEIVED NOVEMBER 19, 1959

SYNTHESIS OF THE LUPININE SYSTEM PATTERNED AFTER THE BIOGENETIC SCHEME OF SCHÖPF AND ROBINSON

Sir:

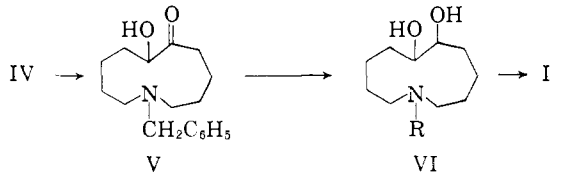
Consideration of structural relationships leads to the inference that the simple lupin alkaloids (III) arise in nature by Mannich cyclization of the amine dialdehyde I, formed in the plant by



I II IIIa, 1,10-*trans* b, 1,10-*cis*

decarboxylative deamination, and coupling, of two molecules of lysine.[1] We wish to report the realization of this ring-closure in the laboratory, and the reduction of the product (II) to *dl*-epilupinine (IIIa).

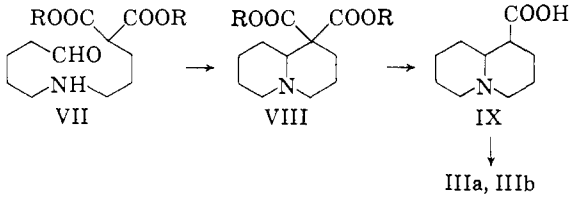
Acyloin ring-closure[2] of diethyl N-benzyl-N,N-bis-(ω-*n*-valerate) (IV) (b.p. 180–184° (0.6 mm.)) afforded N-benzyl-azacycloundecan-6-ol-7-one (V) (b.p. 172° (0.2 mm.)), which (without deliberate purification of intermediates) was reduced with lithium aluminum hydride to VI (R = benzyl), and then hydrogenolyzed catalytically to the



V VI

secondary amine (VI, R = H). The debenzylated diol was allowed to stand for one day at room temperature in dilute solution with periodic acid at *p*H 5. Under these conditions normal periodate cleavage to the dialdehyde I was followed by cyclization; lithium aluminum hydride reduction of unisolated II afforded *dl*-epilupinine (IIIa).[3]

Lupinine, the less stable epimer (IIIb), can be synthesized by a modification of the above approach. The amorphous quinolizidine-1,1-dicarboxylic acid (VIII, R = H) was prepared by three methods, each of which proceeds by way of VII, or an equivalent[4]: (a) selective two-mole hydrogena-



VII VIII IX

tion of the betaine X (dec. 130–135°), carried out in methanol over nickel in the presence of one equivalent of hydrochloric acid[5]; (b) mercuric acetate dehydrogenation of γ-piperidyl-*n*-propylmalonic ester XI (b.p. 134–135° (0.2 mm.), and then saponification of the resulting bicyclic ester VIII (R = C_2H_5) (b.p. 133–134° (1.0 mm.)); and (c) alkylation of Δ^1-piperideine trimer with γ-bromo-*n*-propylmalonic ester, and subsequent hydrolysis.

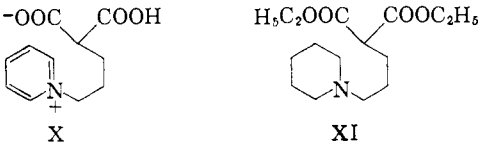
(1) (a) C. Schöpf, E. Schmidt and W. Braun, *Ber.*, **64**, 683 (1931); (b) R. Robinson, "The Structural Relations of Natural Products," Oxford University Press, London, 1955, p. 74.

(2) N. J. Leonard, R. C. Fox and M. Ōki, THIS JOURNAL, **76**, 5708 (1954).

(3) Identified by analysis, melting point, mixed melting point and infrared comparison.

(4) The corresponding, cyclic alkanolamine, enamine or iminium salt.

(5) *Cf.* C. Schöpf, G. Herbert, R. Rausch and G. Schröder, *Angew. Chem.*, **69**, 39 (1957).



X XI

Decarboxylation of crude VIII (R = H), when carried out in refluxing 20% hydrochloric acid, gave mono acid IX, which was converted to the ethyl ester (b.p. 154–155° (20 mm.)); hydride reduction of the latter afforded a mixture consisting of approximately 20% *dl*-lupinine[3] and 80% *dl*-epilupinine.[3] On the other hand, heating of the fused diacid at 165° induced formation of monoacid which was converted as above to a mixture composed of approximately 50% each of the two alkaloids in the racemic form.[6]

Discussion of the biogenetic and mechanistic aspects of these results will be presented subsequently.

Acknowledgment.—The authors are indebted to Professors C. Schöpf (Darmstadt) and V. Boekelheide (Rochester) for samples of *dl*-lupinine and epilupinine, and to the National Institutes of Health for financial support (Grant RG-3892).

(6) Where possible, and except as indicated, satisfactory analyses of substances reported herein have been secured.

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LABORATORY REALIZATION OF THE ROBINSON-SCHOPF SCHEME OF ALKALOID SYNTHESIS. THE PYRROLIZIDINE ALKALOIDS[1]

Sir:

The early suggestions of Robinson[2] as to possible reaction sequences which can lead to the formation of alkaloids have stimulated laboratory syntheses under mild conditions, examination of the applicability of the postulates to plant alkaloid biogenesis, and logical argumentation in structure elucidations.[3–7] A scheme for the biogenesis of lupinine has been proposed by Schöpf[8–10] and Robinson[3] based on the over-all sequence: 2 lysine → δ,δ'-imino-bis-valeraldehyde → 1-hydroxymethylquinolizidine, and for the biogenesis of the ring-homologous moiety of the *Senecio* alkaloids,[3,10] on the sequence: 2 ornithine →

(1) This investigation was supported in part by the Marsh Fund of the National Academy of Sciences and in part by a research grant (USPHS-RG5829) from the National Institutes of Health, Public Health Service.

(2) R. Robinson, *J. Chem. Soc.*, **111**, 876 (1917).

(3) R. Robinson, "The Structural Relations of Natural Products," Oxford University Press, London, 1955; see especially pp. 72–78.

(4) R. Robinson, *J. Roy. Soc. Arts*, **96**, 795 (1948).

(5) G. K. Hughes and E. Ritchie, *Revs. Pure and Appl. Chem. (Aust.)*, **2**, 125 (1952).

(6) C. Schöpf, *Angew. Chem.*, **50**, 779, 797 (1937).

(7) E. Leete, "The Use of Isotopes in the Study of Alkaloid Biogenesis," Chap. VIII in "The Biogenesis of Natural Substances," edited by M. Gates, Interscience Publishers, Inc., New York, in press. The authors are grateful to Dr. Leete for providing this chapter in manuscript form.

(8) C. Schöpf, E. Schmidt and W. Braun, *Ber.*, **64**, 683 (1931).

(9) C. Schöpf, *IX International Congress of Pure and Applied Chemistry (Madrid)*, **5**, 189 (1934).

(10) C. Schöpf, *Chimia Switz.*, **2**, 206, 240 (1948).