

trum of 9,9-dimethyl-10,10-diphenyl-9,10-dihydro-10,9-borazarophenanthrene (VI) in the region $>320 \mu$. Since the ultraviolet spectrum of III appears to bear a closer resemblance to that of VI than to that of V, this implies that the aluminum and nitrogen centers in III are tetracoordinated also. Whether the degree of association (x) of aluminazarophenanthrene units in III is variable⁸ or whether the attractive possibility of a compact dimer unit ($x = 2$) is realized⁹ remains to be resolved.

The foregoing study enhances the feasibility of synthesizing other pseudophenanthrene systems by treating suitable 2-substituted biphenyls (HO-, HS-, HP(R)-, etc.) with group III organometallics. These extrapolations are receiving our earnest attention.

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(8) A. W. Laubengayer, K. Wade, and G. Lengnick, *Inorg. Chem.*, **1**, 632 (1962).

(9) Cf. J. I. Jones and W. S. McDonald, *Proc. Chem. Soc.*, 366 (1962).

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A New Carborane, $B_9C_2H_{11}$, and Its Derivatives

Sir:

In recent months a great deal of interest has developed with regard to the carboranes *o*-,¹ *m*-,² and *p*-³ $B_{10}C_2H_{12}$, $B_9C_2H_7$,⁴ $B_4C_2H_5$,⁵ $B_4C_2H_6$,^{6b,c} and $B_3C_2H_5$.^{4c} We have recently prepared a new carborane, $B_9C_2H_{11}$, and representative C-alkyl, C-aryl, and C,C'-dialkyl derivatives. These carboranes were obtained in moderate to high yields by pyrolysis of the corresponding $B_9C_2H_{13}$ derivatives⁶ at 110–150° in a suitable organic solvent. The $B_9C_2H_{13}$ intermediates were generated *in situ* by treating the cesium or potassium salts of the proper $B_9C_2H_{12}^-$ ion⁶ with polyphosphoric acid in the presence of solvent. At temperatures above 100°, hydrogen is briskly evolved and the resulting carborane is separated by distillation *in vacuo*. Table I presents representative yield and characterization data. The $B_9C_2H_{11}$ carboranes survive brief exposure to moist air.

(1) (a) C. C. Clark, U. S. Patent 3,062,756 (Nov. 6, 1962); (b) T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963); (c) H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963); (d) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963); (e) S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963); (f) R. P. Alexander and H. Schroeder, *ibid.*, **2**, 1107 (1963); (g) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963); (h) M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1115 (1963); (i) D. Grafstein, J. Bobinski, J. Dvorak, J. E. Paustian, H. P. Smith, S. Karlan, C. Vogel, and M. M. Fein, *ibid.*, **2**, 1125 (1963); (j) D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, **2**, 1120 (1963); (k) J. A. Potenza and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 1874 (1964).

(2) (a) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963); (b) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).

(3) S. Papetti and T. L. Heying, *J. Am. Chem. Soc.*, **86**, 2295 (1964).

(4) (a) R. A. Beaudet and R. L. Poynter, *ibid.*, **86**, 1258 (1964); (b) T. P. Onak, F. J. Gerhart, and R. E. Williams, *ibid.*, **85**, 3378 (1963); (c) I. Shapiro, C. D. Good, and R. E. Williams, *ibid.*, **84**, 3837 (1962).

(5) T. P. Onak, R. E. Williams, and H. G. Weiss, *ibid.*, **84**, 2830 (1962); see also footnote 6 in that paper.

(6) R. A. Wiesboeck and M. F. Hawthorne, *ibid.*, **86**, 1642 (1964).

TABLE I

YIELD AND CHARACTERIZATION DATA FOR $B_9C_2H_9RR'$ SPECIES

R	R'	M.p., °C.	Yield, %	Analysis, %					
				Calcd.			Found		
				C	H	B	C	H	B
H	H	212–213	22	18.13	8.37	73.50	18.40	8.64	73.44
CH ₃	H	84–84.5	60	24.59	8.94	66.46	24.66	8.90	66.63
CH ₃	CH ₃	57–58	75	29.92	9.42	60.66	30.17	9.61	60.38
C ₆ H ₅	H	37–37.8	57	46.07	7.25	46.69	46.87	7.57	46.14

Aside from the elemental analyses obtained, each carborane described in the table exhibited the parent peaks in its mass spectrum which coincided with the assigned empirical formulas containing a random distribution of ¹⁰B and ¹¹B isotopes in their natural abundance.

The infrared spectrum of the parent $B_9C_2H_{11}$ contained a B–H stretching band at 3.88 μ and a C–H stretching band at 3.27 μ . Although the ¹¹B n.m.r. spectra of $B_9C_2H_{11}$ and its alkyl and aryl derivatives have not been unequivocally interpreted, the spectra obtained at 60 Mc./sec.⁷ are consistent with an eleven-particle icosahedral fragment related to $B_9C_2H_{12}^-$,⁶ $B_{11}H_{14}^-$,⁸ and $B_{11}H_{13}^{2-}$.⁸ Degradation of the C-phenyl and C,C'-dimethyl derivatives with a palladium catalyst and propionic acid at the reflux temperature was quite vigorous and afforded toluene (7% yield) and ethane (67% yield), respectively. The similar degradation of the C-phenyl derivative of *o*- $B_{10}C_2H_{12}$ produced only ethylbenzene (21% yield). Thus, the chemical evidence available suggests that the carbon atoms in $B_9C_2H_{11}$ are not near neighbors and that carborane formation is accompanied by rearrangement of the carbon atoms.⁹

Additional evidence suggests that the gross structural features present in $B_9C_2H_{12}^-$ are retained in $B_9C_2H_{11}$. Treatment of the $B_9C_2H_{11}$ carboranes described above with a variety of ligands produced monoadducts of the general formula $B_9C_2H_{11}(\text{ligand})$ which are iso-electronic with $B_9C_2H_{12}^-$. Representative ligands include triphenylphosphine (m.p. for the C-phenyl derivative, 255° dec. *Anal.* Calcd. for $B_9C_{26}H_{30}P$: C, 66.32; H, 6.42; B, 20.68. Found: C, 65.78; H, 6.79; B, 22.62) and triethylamine (m.p. for the C-phenyl derivative, 157–159° dec. *Anal.* Calcd. for $B_9C_{14}H_{30}N$: C, 54.28; H, 9.77; B, 31.44. Found: C, 52.57; H, 9.89; B, 32.24). Titration of $B_9C_2H_{10}-(C_6H_5)$ with methoxide ion in methanol was typical for a strong acid and 1 equiv. of base was consumed (equiv. wt., 206.8; theory, 208.6).

Further studies are in progress and will be reported at a later date.

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(7) N.m.r. spectra of the ¹¹B nucleus at 60 Mc./sec. were obtained by Mr. E. A. Pier at Varian Associates, Palo Alto, Calif.

(8) V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).

(9) This argument assumes that the formation of $B_9C_2H_{12}^-$ from *o*- $B_{10}C_2H_{12}$ (ref. 6) retains the near neighbor relationship of the carbon atoms present in the starting material.

and Mr. P. F. Stokely for the equivalent weight determination.

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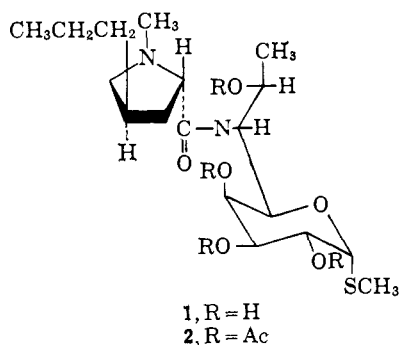
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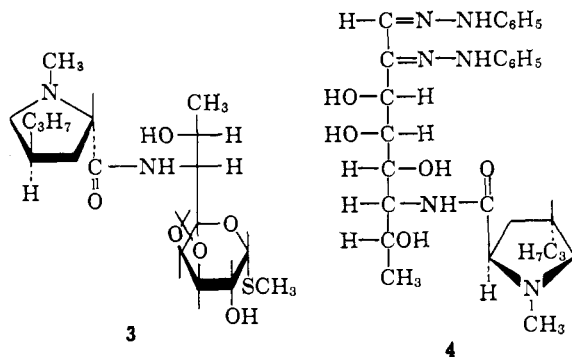
Chemical Studies on Lincomycin. I. The Structure of Lincomycin

Sir:

The antibiotic lincomycin¹⁻⁵ has been found to have structure 1 as shown by the following data. Linco-



mycin, $C_{18}H_{34}N_2O_6S$, contains one N-methyl, two C-methyls, one basic function, $pK_a' = 7.5$, and gives a negative iodoform test.⁶ The infrared absorption is indicative of a monosubstituted amide (1530 and 1640 cm^{-1}). A tetraacetate, 2, and isopropylidene lincomycin, 3, could be prepared. Aqueous 2 *N* acid liberated methanethiol and another fragment isolated as the phenylsazone 4, $C_{29}H_{42}N_6O_5$.



A vigorous acid hydrolysis freed an amino acid, 5, $C_9H_{17}NO_2$. Preliminary comparisons with L-hygric acid and n.m.r. studies suggested an *n*-propylhygric acid. Rotational shifts on acidification suggested the L-series.⁷ Synthesis from 4-keto-L-proline⁸ placed the

(1) D. J. Mason, A. Dietz, and C. De Boer, *Antimicrobial Agents Chemotherapy*, 554 (1962).

(2) R. R. Herr and M. E. Bergy, *ibid.*, 560 (1962).

(3) L. J. Hanka, D. J. Mason, M. R. Burch, and R. W. Treick, *ibid.*, 565 (1962).

(4) C. N. Lewis, H. W. Clapp, and J. E. Grady, *ibid.*, 570 (1962).

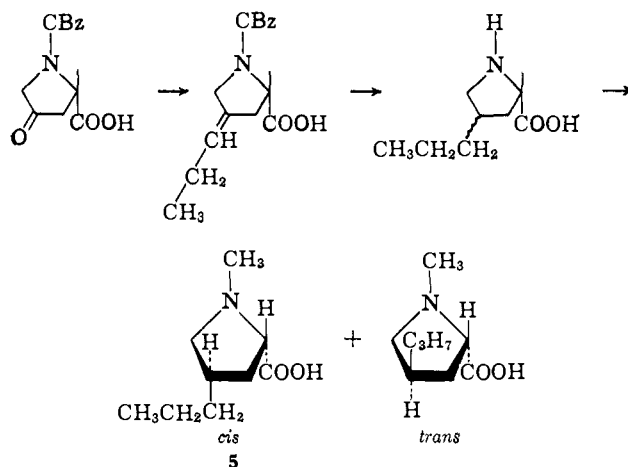
(5) G. K. Daikos, *et al.*, *ibid.*, 197 (1963); W. J. Holloway, *et al.*, *ibid.*, 200 (1963); J. Harnecker, *et al.*, *ibid.*, 204 (1963); E. W. Walters, *et al.*, *ibid.*, 210 (1963); J. C. Trakas and H. B. Lind, *ibid.*, 216 (1963).

(6) Although the negative iodoform test denied the presence of a methylcarbinol (*cf.* ref. 1), subsequent n.m.r. and chemical studies proved the iodoform test to be anomalous.

(7) J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1961, p. 83.

(8) A. A. Patchett and B. Witkop, *J. Am. Chem. Soc.*, **79**, 185 (1957).

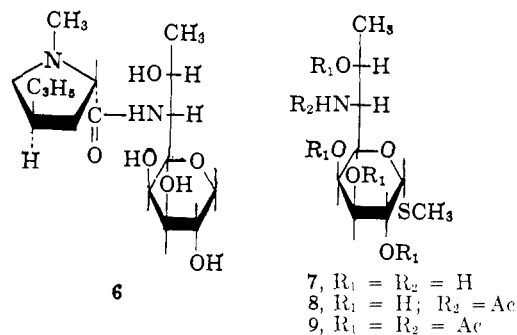
n-propyl group at C-4 and confirmed the L-configuration. The amide of one of the two diastereomers so



formed was found to be identical with that obtained from lincomycin. Oxidation⁹ of 5 to (*R*)(+)-propylsuccinic acid showed it to be *trans*-L-4-*n*-propylhygric acid.

Lincomycin and its acetonide (3) took up 4 and 2 moles of periodate, respectively. Its nickel desulfurization product, $C_{17}H_{32}N_2O_6$, 6, consumed 2 moles, liberating 1 mole of formic acid.

Hydrazinolysis cleaved 1 into 5 as the hydrazide and compound 7, $C_9H_{18}NO_3S$, methyl α -thiolincosaminide. The base 7, $pK_a' = 7.5$, containing no amide, gave a negative iodoform test⁶ and consumed 5 moles of periodate. Acylation of 7 with the propyl carbonate mixed anhydride of 5, both natural and synthetic, yielded crystalline 1 as the hydrochloride. Two acetyl derivatives, 8 and 9, were obtained. The n.m.r. spectrum of 7, in addition to suggesting galactose stereochemistry and an axial methylthio function,¹⁰ displayed a distinct doublet of doublets centered at δ 3.3, $J = 10.5$ and 3.0 c.p.s., suggesting, in contradiction to the earlier iodoform data, that the hydrogen on the carbon bearing nitrogen was split by only two hydrogens. Therefore, the amine was not adjacent to the terminal methyl group.



Conversion of 8 to acetonide (10), hydrazinolysis to 11, followed by oxidation, first with periodate, then with nitric acid, afforded mucic acid, confirming the galactopyranose configuration. Borohydride reduction of the above periodate product (not isolated), hydrolysis with

(9) A. Neuberger, *J. Chem. Soc.*, 429 (1945); G. W. Kenner, J. S. Dalby, and R. C. Sheppard, *ibid.*, 4387 (1962).

(10) A complete discussion of the n.m.r. spectrum will be the subject of a later communication.