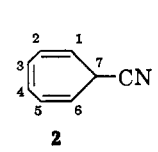
caradiene (**3**, 41% yield) and 1,4-dimethyl-7,7-dicyanonorcaradiene (**4**, 39% yield). Isomer **3**, m.p. 123–



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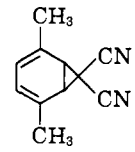

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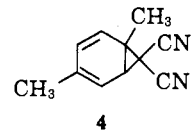
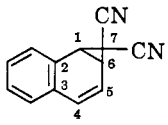


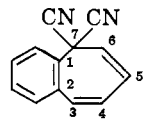
4

124°, absorbs at 279 mμ (ε 4900) and 238 mμ (ε 3290) in the ultraviolet spectrum; its n.m.r. spectrum shows singlets at τ 7.87 (methyl groups), 6.78 (protons on C-1 and C-6), and 3.81 (olefinic protons). The second isomer, **4**, was obtained in only 90% purity, m.p. 91–95°, λ_{max} 276 mμ (ε 2540) and 235 mμ (shoulder, ε 1850). Its n.m.r. spectrum exhibits a singlet at τ 8.27 (C-1 methyl), a doublet (J = 1 c.p.s.) centered at 7.97 (C-4 methyl), a doublet ($J_{5,6}$ = 6 c.p.s.) centered at 6.88 (proton on C-6), and the olefinic protons as an AB quartet (doublet components centered at τ 3.63 and 3.96, $J_{2,3}$ = 10 c.p.s.; protons on C-2 and C-3) superimposed on further bands (proton on C-5). Both isomers rearranged on heating to 2,5-xylylmalononitrile, m.p. 56–58°, which was degraded to 2,5-xylylacetic acid by acid-catalyzed hydrolysis and decarboxylation.

Thermal decomposition of dicyanodiazomethane in naphthalene resulted in the formation of three isomers of $C_{13}H_8N_2$, assigned structures **5**, **6**, and **7** on the basis of spectral evidence. The main product 7,7-dicyano-



5



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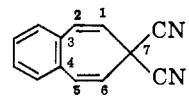

7

2,3-benzonorcaradiene (**5**, m.p. 126–127°), obtained in 50% yield, shows maxima at 227 mμ (ε 25,200) and 272 mμ (ε 7900) in the ultraviolet spectrum. Its n.m.r. spectrum displays the aromatic protons as a multiplet at τ 2.2–2.7, the olefinic protons as a doublet centered at 3.03 and a quartet centered at 3.77 ($J_{4,5}$ = 10 c.p.s.), the proton on C-1 as a doublet centered at 6.20, and the proton at C-6 as a quartet centered at 6.65 ($J_{1,6}$ = 9 c.p.s.). The mixture of **6** and **7** was isolated in 12% yield. The ultraviolet spectrum of 7,7-dicyano-1,2-benzocyclohepta-1,3,5-triene (**6**, m.p. 87–88°; λ_{max} 277 mμ (ε 8000); λ_{min} 243 mμ (ε 2600)) is almost superimposable on that of 1,2-benzocyclohepta-1,3,5-triene[8] (λ_{max} 275 mμ (ε 7400); λ_{min} 243 mμ (ε 2900)). The n.m.r. spectrum of **6** shows only aromatic and olefinic protons, the highest-field signal being a doublet centered at τ 4.12, probably due to the proton adjacent to the dicyanomethylene group. The ultraviolet spectrum of 7,7-dicyano-3,4-benzocyclohepta-1,3,5-triene (**7**, m.p. 85–90°, λ_{max} 228 mμ (ε 45,700) and 257 mμ (ε 5900)) is again almost identical with that of the parent 3,4-benzocyclohepta-1,3,5-triene[8] (λ_{max} 228 mμ (ε 44,000) with a shoulder at 256 mμ (ε 5200)). The n.m.r. spectrum of **7** shows the aromatic protons as a barely split singlet at τ 2.39 and the olefinic protons as two doublets centered at 2.89 and 3.93, respectively ($J_{1,2}$ = 10 c.p.s.). The two dicyanobenzocycloheptatrienes **6** and **7** probably were formed by the addition of dicyanocarbene to the 1,9 and 2,3 bonds of naphthalene, followed by rearrangement of the *o*-quinonoid norcaradienes to the more stable benzocycloheptatrienes.[9] To our knowledge this represents the first example of a carbene addition to bonds other than the 1,2 bond in naphthalene.

The isomers **5**, **6**, and **7** provide good models for the 7,7-dicyanonorcaradiene and 7,7-dicyanocycloheptatriene systems. The n.m.r. spectra of **6** and **7** show that the protons on C-1 and C-6 in the hypothetical 7,7-dicyanocycloheptatriene would be expected to absorb at *ca.* τ 4, whereas these signals in **1**, **3**, and **4** actually occur at τ 6.5 to 7, as predicted on the basis of the spectrum of **5**. Solubility difficulties prevented the determination of the n.m.r. spectrum of **1** at temperatures below −70°, so that the possibility cannot be excluded that in solution **1** is in equilibrium with a small amount of the valence-tautomeric 7,7-dicyanocycloheptatriene. Structure determination by X-ray diffraction[10] corroborates the assignment of the norcaradiene structure to crystalline **3**.

Details of these and other reactions of dicyanodiazomethane will be reported shortly.

(8) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

(9) The adduct of dicyanocarbene to the 9,10 bond of naphthalene could not be found among the products. If formed at all, it may have rearranged to **6** during the isolation procedures; such a rearrangement has been observed in the case of the related 1,6-oxido[10]annulene [E. Vogel, M. Biskup, W. Pretzer, and W. A. Böll, *Angew. Chem.*, **76**, 785 (1964); F. Sondheimer and A. Shani, *J. Am. Chem. Soc.*, **86**, 3168 (1964)].

(10) C. J. Fritchie, to be published.

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Received November 19, 1964

Photoinduced Nucleophilic Substitution in Polyhedral Boranes

Sir:

The polyhalogenated derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are remarkably inert toward nucleophiles.[1] They are, however, photolytically unstable and easily undergo photoinduced nucleophilic substitution when irradiated in the presence of a suitable anion. This reaction, unprecedented in boron chemistry,[2] makes it possible to prepare many hitherto inaccessible polyhedral boranes and is the subject of this communication.

When an aqueous solution 0.07 *M* in $B_{12}Br_{12}^{2-}$ and 1.7 *M* in potassium cyanide was irradiated with a low-pressure mercury lamp for 4 days at room temperature, a 56% yield of $B_{12}Br_3(CN)_9^{2-}$, precipitated as the cesium salt, was obtained. The structure assignment rests on analysis (*Anal.* Calcd. for $C_9B_{12}Br_3Cs_2N_9 \cdot H_2O$:

(1) W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).

(2) Some analogy for it may be found in photochemical solvolyses of nitrophenyl phosphates and sulfates [E. Havinga, R. O. de Jongh, and W. Dorst, *Rec. trav. chim.*, **75**, 378 (1956)], benzylic chlorides and acetates [H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 915 (1963)], nitrophenyl trityl ethers [H. E. Zimmerman and S. Somasekhara, *ibid.*, **85**, 922 (1963)], as well as the photoinduced displacement of nitrite ion from various aromatic nitro compounds by hydroxide ion or pyridine [see V. Gold and C. H. Rochester, *Proc. Chem. Soc.*, 403 (1960); R. L. Letsinger and O. B. Ramsay, *J. Am. Chem. Soc.*, **86**, 1448 (1964); and R. M. Johnson and C. W. Rees, *Proc. Chem. Soc.*, 213 (1964)].

C, 12.2; H, 0.23; B, 14.6; Br, 27.0; Cs, 29.9; N, 14.2. Found: C, 12.2; H, 0.40; B, 14.2; Br, 26.5; Cs, 29.6; N, 14.2); the B^{11} n.m.r. spectrum[3] which shows only two peaks at +27.5 and +33.0 p.p.m. with relative areas of 3:9; and the infrared spectrum which shows nitrile absorption at 2200 cm.$^{-1}$ and is otherwise simple with strong bands at 1142, 1115, 980, 950, and 920 cm.$^{-1}$. The species $B_{12}Cl_5(CN)_7^{2-}$ was obtained in analogous fashion from $B_{12}Cl_{12}^{2-}$. *Anal.* Calcd. for $Cs_2B_{12}C_7Cl_5N_7$: C, 11.1; B, 17.2; Cl, 23.5; N, 13.0. Found: C, 11.1; B, 17.3; Cl, 24.1; N, 12.8.

By contrast, $B_{10}Cl_{10}^{2-}$ was much less reactive and under comparable conditions yielded a mixture of $B_{10}Cl_9CN^{2-}$, $B_{10}Cl_8(CN)_2^{2-}$, and $B_{10}Cl_7(CN)_3^{2-}$ from which the first two species were isolated. *Anal.* Calcd. for $CCs_2B_{10}Cl_9N$: C, 1.67; B, 15.0; Cl, 44.3; N, 1.94. Found: C, 2.04; B, 14.9; Cl, 44.3; N, 1.65. Calcd. for the tetramethylammonium salt of $B_{10}Cl_8(CN)_2^{2-}$, $C_{10}H_{24}B_{10}Cl_{10}N_4$: C, 20.4; H, 4.06; B, 18.3; Cl, 48.0; N, 9.47. Found: C, 20.3; H, 4.38; B, 18.1; Cl, 47.8; N, 8.66. While the stereochemistry of the $B_{10}Cl_8(CN)_2^{2-}$ compound was not established, its infrared spectrum was strikingly different from that of $B_{10}Cl_8(CN)_2^{2-}$ prepared by exhaustive chlorination of $B_{10}H_8(CN)_2^{2-}$ containing 1,10-cyano groups.[4] The reactivity seems thus to be the inverse of that observed in the case of electrophilic substitution.

The reaction is thought to proceed through a photo-induced heterolysis of the boron–halogen bond resulting in an electron-deficient species. This reacts with a suitable base to regenerate the dianion bearing at this point a new substituent, *viz.*

$$B_{12}X_{12}^{2-} \xrightarrow{h\nu} B_{12}X_{11}^{-} + X^{-} \xrightarrow{Z^{-}} B_{12}X_{11}Z^{2-}$$

The above scheme is in accord with the finding that when $B_{12}Br_{12}^{2-}$ is irradiated in the presence of chloride ion or $B_{12}Cl_{12}^{2-}$ in the presence of bromide ion, halogen exchange takes place, the former being seven times faster than the latter. This is in line with bromine being (1) a better departing ion and (2) a better stabilizer of the electron-deficient intermediate through forms such as $(B_{12}Br_{10}\not\ni)^{2-}Br^{+}$. Furthermore, irradiation of $B_{12}Br_{12}^{2-}$ in the presence of N_3^-, OCN^-, and other anions has yielded appropriately substituted derivatives.

The details of this work will be described in a forthcoming publication.

(3) The B^{11} n.m.r. spectrum was determined at 19.25 Mc. and the chemical shifts are referred to external methyl borate.

(4) W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 115 (1964).

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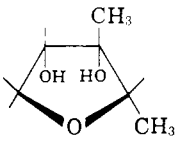
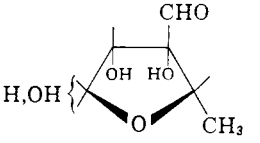
Streptomycin. II.[1] Streptose

Sir:

A unique feature in the determination of the structure of the potent antibacterial substance streptomycin is that the central carbohydrate fragment, streptose, has never been isolated as a degradation product. Through studies of the chemistry and properties of various derivatives and transformation products of streptose, its structure was established[2] in 1946 to be a 2,3,4-trihydroxy-3-C-formylvaleraldehyde. The absolute stereochemistry of streptose was established to be (*R*) (L) at C-4[3] and (*S*) (D) at C-2.[4] Because dideoxydihydrostreptose (**1**) enhanced the acidity of boric acid solutions,[5] the hydroxyl groups at C-2 and C-3 of **1** were presumed to be *cis* oriented and the configurations at C-2 and C-3 of streptose were presumed to be similar. Consequently, streptose was assigned the structure 3-C-formyl-5-deoxy-L-lyxofuranose (**2**). We report total syntheses of streptose and several derivatives and transformation products of streptose that fully substantiate the assigned structures.



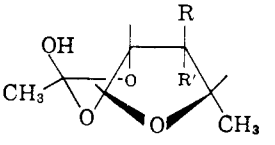
1



2

Potassium permanganate hydroxylation of 2,3-dimethyl-2,5-dihydrofuran[6] gave a 50% yield of a mixture of *cis*-diols, whose composition (g.l.c.) was approximately 1:2[7] *dl*-dideoxydihydrostreptose (**1**)[9] and an isomer (**3**). Synthetic *dl*-dideoxydihydrostreptose, m.p. 62.0–62.2°, had infrared and n.m.r. spectra identical with those of a naturally derived sample[10] (**1**) and identical g.l.c. behavior. The *dl* isomer **3**, m.p. 58.5–59.5°, had markedly different infrared and n.m.r. spectra and different g.l.c. behavior.

Oxidation of 1,2-O-isopropylidene-5-deoxy-β-L-arabinofuranose[11] (**4**), using dicyclohexylcarbodiimide, pyri-



4, R = —OH, R′ = H
5, R,R′ = =O
6, R = —CH=CH$_2$, R′ = —OH
7, R = —CH$_2$OH, R′ = —OH
10, R = —CHO, R′ = —OH

dinium phosphate, and dimethyl sulfoxide,[12] gave sirupy 1,2-O-isopropylidene-5-deoxy-β-L-*threo*-pentofuranos-3-ulose (**5**), $[\alpha]_D$ +76°, characterized as a crystalline oxime, m.p. 104–105.5°, $[\alpha]_D$ −10°. Reaction of the ketone **5** with vinylmagnesium bromide gave 1,2-O-isopropylidene-3-C-vinyl-5-deoxy-β-L-lyxofuranose (**6**),[13] m.p. 67.5–68.5°, $[\alpha]_D$ +21°. Ozonol-

(1) J. R. Dyer and A. W. Todd, *J. Am. Chem. Soc.*, **85**, 3896 (1963), is regarded as paper I of this series.

(2) R. U. Lemieux and M. L. Wolfrom, *Advan. Carbohydrate Chem.*, **3**, 337 (1948), and references cited therein.

(3) J. Fried, D. E. Walz, and O. Wintersteiner, *J. Am. Chem. Soc.*, **68**, 2746 (1946).

(4) M. L. Wolfrom and C. W. DeWalt, *ibid.*, **70**, 3148 (1948).

(5) N. G. Brink, F. A. Kuehl, Jr., E. H. Flynn, and K. Folkers, *ibid.*, **68**, 2405 (1946).

(6) E. E. Schweizer, *ibid.*, **86**, 2744 (1964).

(7) This is to be anticipated since *cis* hydroxylations of olefins by potassium permanganate are known to proceed predominantly from the less sterically hindered side.[8]

(8) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 358.

(9) Satisfactory analytical results were obtained for all new compounds reported.

(10) We are grateful to Mr. R. K. Chawla for the preparation of an authentic sample of this substance.

(11) P. A. Levene and J. Compton, *J. Biol. Chem.*, **116**, 189 (1936).

(12) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963).

(13) If the Grignard reagent adds to the less sterically hindered side of **5**, as would be anticipated,[14] the desired *lyxo*, rather than *arabino*, configuration results. G.l.c. analysis of the crude product failed to reveal any other component with a retention time comparable to that of **6**.

(14) Ref. 9, p. 69.