tion and rearrangement of these nitritoammine complexes. Other metal systems are also being investigated to see whether additional examples of linkage isomerism can be obtained.

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RECEIVED DECEMBER 28, 1959

PREPARATION OF TETRABORON SILICIDE, B_4Si

Sir:

Much effort is being expended today in the search for high temperature, oxidation resistant materials. In this respect, we wish to report for the first time the preparation in large quantities of a new silicide of boron, tetraboron silicide, B_4Si.[1]

The question of compound formation in the system boron–silicon has been reviewed recently by Cline[2] in his paper on investigations of B_6Si. We have not observed any evidence to date for the existence of B_3Si as first reported by Moissan and Stock[3] and more recently by Samsonov and Latysheva.[4] Only the presently reported B_4Si[5] and the known B_6Si have been found.

B_4Si is prepared by heating the elements in an inert atmosphere at temperatures not exceeding 1370°. Above this temperature, B_4Si is thermally unstable; and the interesting phase transformation $B_4Si \rightarrow B_6Si$ is now being studied.

Amorphous boron of 83 to 95% purity has been used, each material giving the identical product. Crystalline silicon of 98% purity was used. An intimate mixture of 500 g. of 86.6% boron[6] (40 moles) and 574 g. of 98% silicon,[7] +200 mesh, (20 moles) was placed in a large metallurgical fire clay crucible of the sillimanite type[8] and heated in an electrical resistance-type furnace in argon atmosphere to 1370° over 4–5 hours, soaked at 1370° for 2–3 hours, and furnace cooled.

The product consisted of a glassy, slag-like top and an inner, black friable core. The latter was powdered readily and sieved through a 325 mesh screen, the fine portion being shown by X-ray powder diffraction patterns to be B_4Si plus traces of B_6Si. Tetraboron silicide is readily distinguishable from hexaboron silicide by its X-ray powder pattern,[5] the six strongest lines (d Å.) and respective intensities being: 4.15, 30; 2.75, 90; 2.67, 100; 1.606, 50; 1.582, 30; 1.510, 30. Chemical analysis of the fine fraction showed B, 60.6%; Si, 36.8%, and Mg, 0.65%. The B/Si molar ratio is 4.28, slightly larger due to the presence of traces of B_6Si than the expected value of 4.00 required for B_4Si. Yields of B_4Si of 50–80%, based on boron, have been achieved by proper choice of reaction conditions. It seems very likely that B_4Si completely free of B_6Si can be prepared by the reaction of the elements in inert atmosphere for periods longer than 2–3 hours at temperatures below 1370° and above about 1200°. Such studies are now in progress.

B_4Si is highly oxidation resistant due to the formation of a protective boron–silicon–oxygen coating which first forms upon exposure of the material to air at elevated temperatures. Shapes fabricated from B_4Si by powder metallurgical techniques have withstood oxidation in air for over 100 hours at 1370° and showed excellent thermal shock resistance, no cracks being observed when pieces were removed from 1370° to room temperature numerous times. The ceramic properties of B_4Si are now being investigated.

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RECEIVED DECEMBER 30, 1959

(1) The writer prefers the nomenclature "tetraboron silicide" in contrast to "silicon tetraboride" in consistency with the boron–carbon system in which B_4C is called "boron carbide."

(2) C. F. Cline, *J. Electrochem. Soc.*, **106**, 322 (1959).

(3) H. Moissan and A. Stock, *Compt. rend.*, **131**, 139 (1900).

(4) G. V. Samsonov and V. P. Latysheva, *Doklady Akad. Nauk S.S.S.R.*, **105**, 499 (1955), *Chem. Abstr.*, **50**, 7639h (1956).

(5) V. I. Matkovich, *Acta. Cryst.* (1959). The complete crystal structure of B_4Si has been submitted for publication.

(6) From F. W. Berk and Co., Wood-Ridge, N. J., and Metalsalts Corp., Hawthorne, N. J.

(7) Union Carbide Metals Co.

(8) Denver Fire Clay Co., Denver, Colo.

REARRANGEMENT AND FRAGMENTATION REACTIONS IN CARBENOID DECOMPOSITION OF DIAZO HYDROCARBONS

Sir:

Tosylhydrazones of aliphatic aldehydes and ketones react with bases in aprotic solvents to give diazo compounds.[1,2] The diazo compounds undergo thermal carbenoid decomposition[1,2] with loss of nitrogen to yield olefins derived from hydrogen-migration and cyclopropanes by intramolecular-insertion.[1] Carbon-skeleton rearrangement did not occur appreciably even in systems involving *tert*-butylcarbenes. Rearrangement in carbenoid decomposition of diazo ketones is quite common, however.[3]

It is now reported that cyclopropanecarboxaldehyde tosylhydrazone[4] reacts with sodium methoxide in diethyl Carbitol or N-methylpyrrolidone at 180°[5a] to yield (Equations 1–2) cyclobutene (60, 67%)[5b] by *ring-expansion*, ethylene (13, 10%) and acetylene (13, 10%) by *carbon-skeleton fragmentation*, and 1,3-butadiene (4.5, 7%) by *ring-rupture*.[6a,b] Methylenecyclopropane was not detected.[6b] Formation of cyclobutene is thus a prime example of extensive carbon-skeleton rearrangement in a simple carbenoid system.[7] De-

(1) L. Friedman and H. Shechter, THIS JOURNAL, **81**, 5512 (1959); L. Friedman, Ph.D. Dissertation, The Ohio State University, 1959.

(2) Similar conclusions have been reached by J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

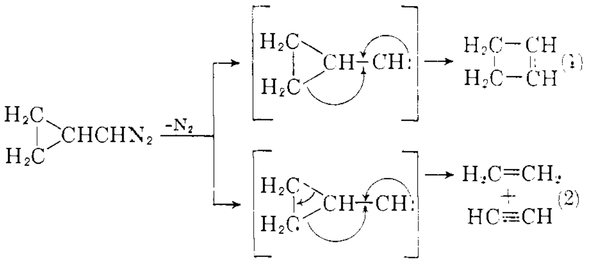
(3) W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, Chapter 2, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 38.

(4) All tosylhydrazones gave satisfactory analyses.

(5) (a) The tosylhydrazones and sodium methoxide were added to the solvent at 25°, allowed to stand for a few minutes and then heated at 180°. Decomposition is complete in less than 5 min. (b) The tosylhydrazones decompose to hydrocarbons in excellent yields; the percentages reported herein are actual product compositions.

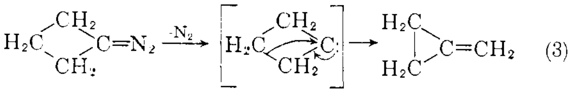
(6) (a) The hydrocarbons were analyzed, separated, and identified by gas-chromatographic and subsequent infrared methods; comparisons were made with authentic samples. (b) Minor amounts of other hydrocarbons also were obtained.

(7) (a) L. Hellerman and R. L. Garner, THIS JOURNAL, **57**, 139 (1935), report that thermal decomposition of 1-diazo-2,2,2-triphenylethane gives triphenylethylene. It is thus apparent that phenyl migration occurs in triphenylmethylcarbene systems. (b) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958), raise the question that reaction of 1,1-dibromocyclopropanes with magnesium or sodium to give allenes may involve carbenoid processes.



composition of cyclopropyldiazomethane to ethylene and acetylene can occur by requisite shifts of electrons and bond breaking. It has not been established whether butadiene is formed directly in decomposition of the tosylhydrazone or by subsequent decomposition of cyclobutene. The ability of a cyclopropylcarbenyl system to undergo ring-expansion is also illustrated in the base-catalyzed reaction of cyclopropyl methyl ketone tosylhydrazone in diethyl Carbitol to give 1-methyl-1-cyclobutene (92%); vinylcyclopropane (1%), isoprene (2%), methylacetylene (3%) and ethylene (3%) also were formed.

Carbenoid decomposition of cyclobutanone tosylhydrazone[4] in diethyl Carbitol or N-methylpyrrolidone is of significance in that *ring-contraction* (Equation 3) to give methylenecyclopropane (79, 80%) occurs[8]; *hydrogen-migration* to yield cyclobutene (18, 20%) and formation of 1,3-butadiene (2, 1%) are minor reactions. These results are to be contrasted with that from cyclopentanone tosylhydrazone[4] in which cyclopentene (94%) is the major product.



We wish to acknowledge the assistance of Dr. R. R. Hopkins, Whiting Research Laboratories, Standard Oil Company (Ind.).

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[8] The yields of the principal carbenic products from cyclopropanecarboxaldehyde and cyclobutanone tosylhydrazones as reported in Abstracts of Papers, 136th Meeting of the American Chemical Society, Atlantic City, N. J., 1959, p. 4, are in error and should be reversed.

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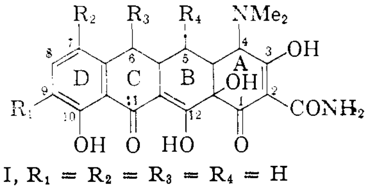
RECEIVED DECEMBER 21, 1959

FURTHER 6-DEOXYTETRACYCLINE STUDIES: EFFECT OF AROMATIC SUBSTITUENTS ON BIOLOGICAL ACTIVITY

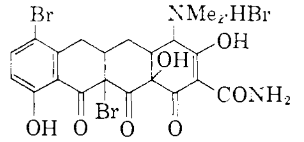
Sir:

The stability of 6-deoxytetracyclines[1] to acid has made feasible, for the first time, chemical substitution of the phenolic D-ring in the tetracycline series. Interesting structure-activity relationships have been observed with the derivatives thus obtained.



I, $R_1 = R_2 = R_3 = R_4 = H$
II, $R_2 = Br, R_1 = R_3 = R_4 = H$
III, $R_1 = NO_2, R_2 = Br, R_3 = R_4 = H$
IV, $R_2 = NO_2, R_1 = R_3 = R_4 = H$
V, $R_1 = NO_2, R_2 = R_3 = R_4 = H$
VI, $R_1 = NH_2, R_2 = R_3 = R_4 = H$
VII, $R_2 = NH_2, R_1 = R_3 = R_4 = H$
VIII, $R_1 = NO_2, R_3 = CH_3, R_2 = H, R_4 = OH$

6-Demethyl-6-deoxytetracycline[1] [I, m.p. of the hydrochloride, 224–225°, dec.; $[\alpha]^{25}D$ ($C = 1$ in 0.01*N* HCl) −102°; *Anal.* Found for $C_{21}H_{22}N_2O_7 \cdot HCl$: C, 55.64; H, 5.35; N, 6.35; Cl, 7.79] was chosen for initial studies in this area. Compound I shows *in vitro* antibacterial activity[2] (Table I) essentially equivalent to that of tetracycline. Bromination of I (bromine in trifluoroacetic acid) results in the *substance* IX.



IX

[λ_{max}^{KBr} 5.72 μ; *Anal.* Found for $C_{21}H_{20}N_2O_7Br_2 \cdot HBr$: N, 4.15; Br, 38.0] which on heating in the reaction solution is converted to *7-bromo-6-deoxy-6-demethyltetracycline* [II, m.p. of the hydrobromide, 241–243°, dec.: $\lambda_{max}^{(MeOH-0.01N\ HCl)}$ 268 mμ, log ε 4.30; 345 mμ, log ε 4.12; 365 mμ, log ε 4.12; $\lambda_{max}^{(MeOH-0.01N\ NaOH)}$ 243 mμ, log ε 4.23; 382 mμ, log 4.10. *Anal.* Found for $C_{21}H_{21}N_2O_7Br \cdot HBr \cdot H_2O$: C, 42.59; H, 4.21; N, 4.90; Br, 27.10] a compound with somewhat enhanced *in vitro* antimicrobial activity. Nitration of II (70% HNO_3-concd. H_2SO_4) yields *7-bromo-9-nitro-6-demethyl-6-deoxytetracycline*[3] [III, $\lambda_{max}^{(MeOH-0.01N\ HCl)}$ 263 mμ, 370 mμ, $\lambda_{max}^{(MeOH-0.01N\ NaOH)}$ 239 mμ, 285 mμ, 446 mμ] which is relatively inactive.[2]

Direct nitration[4] of I (70% HNO_3-concd. H_2SO_4) results in a mixture from which a *7-nitro compound*[3] [IV, m.p. 218°, dec., λ_{max}^{KBr} 6.54, 7.46 μ; $\lambda_{max}^{(MeOH-0.01N\ HCl)}$ 263 mμ, log ε 4.30; 354 mμ, log ε 4.11; $\lambda_{max}^{(MeOH-0.01N\ NaOH)}$ 243 mμ, log ε 4.17; 255 mμ, log ε 4.16; 280 mμ, log ε 4.07; 385 mμ, log ε 4.17; *Anal.* Found for $C_{21}H_{21}N_3O_9 \cdot HCl \cdot 2H_2O$: C, 47.27; H, 5.00; N, 7.80] and a *9-nitro compound*[3] [V, m.p. 215°, dec., λ_{max}^{KBr} 6.62, 7.42 μ; $\lambda_{max}^{(MeOH-0.01N\ HCl)}$ 263 mμ, log ε 4.42; 360 mμ, log ε 4.26; $\lambda_{max}^{(MeOH-0.01N\ NaOH)}$ 242 mμ, log ε 4.30; 283 mμ, log ε 4.16; 352 mμ, log ε 4.02; 424 mμ, log ε 4.05; *Anal.* Found for $C_{21}H_{21}N_3O_9 \cdot HCl \cdot 2H_2O$: C, 47.63; H, 4.60; N, 7.96] have been isolated.

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[1] C. R. Stephens, K. Murai, H. H. Rennhard, L. H. Conover and K. J. Brunings, THIS JOURNAL, **80**, 5324 (1958).

[2] Activity comparisons herein are based on the standard oxytetracycline biological assay (*cf.* R. C. Kersey, *J. Am. Pharm. Assoc.*, **39**, 252 (1950), against *Klebsiella pneumoniae.* The same relationships do not necessarily hold with other microörganisms.

[3] Structural assignments rest on interpretation of absorption spectra, polarographic studies, oxidative degradation, etc. The 9-nitro tetracyclines show characteristic ultraviolet absorption at unusually long wave length in alkaline solution—a phenomenon which greatly facilitates their identification. We wish to express our gratitude to L. L. Ciaccio and associates foi the polarographic investigation.

[4] A preliminary report on a similar nitration has appeared in the patent literature without structural assignment of the products (*cf.* South African Patent Application No. 1415/59).