

"soluble"-ribonucleic acid. The partition chromatographic procedure has the great advantage of simplicity.

Experiments are underway to improve and extend these results.

Acknowledgment.—This work was supported in part by a grant from the National Science Foundation.

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RECEIVED SEPTEMBER 19, 1960

THE STRUCTURE OF THE $B_3H_8^-$ ION

Sir:

An X-ray diffraction crystal structure study of the diammoniate of tetraborane, $B_4H_{10} \cdot 2NH_3$, conducted at room temperature as well as at -100° shows that the crystals are orthorhombic with room temperature unit cell parameters $a = 9.25$, $b = 9.42$ and $c = 8.23$ Å. The space group is $Pbnm$ and the cell contains four formula units.

Analysis of the two independent sets of diffraction data comprising 433 and 534 reflections, respectively, confirms the ionic structure $[(H_3N)_2BH_2]^+ [B_3H_8]^-$.¹ Fig. 1(a) is a composite electron density map of the $B_3H_8^-$ ion, for which several different structures have been proposed,¹⁻⁵ including the

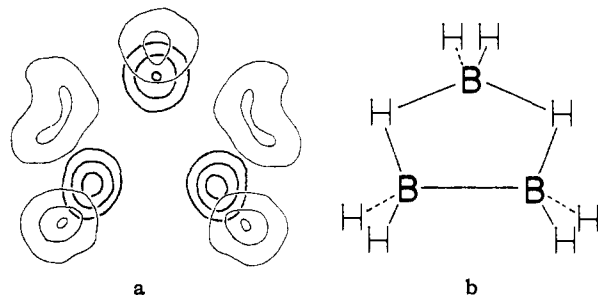


Fig. 1(a).—Composite electron density map of $B_3H_8^-$; heavy contours are at intervals of $2.5 \text{ e.}\text{\AA}^{-3}$. Light contours showing the hydrogen atoms in a difference Fourier synthesis are drawn at intervals of $0.24 \text{ e.}\text{\AA}^{-3}$. The three "regular" hydrogen atoms behind the boron plane have been omitted. (b) Schematic representation of the $B_3H_8^-$ ion.

one supported by our results.¹⁻³ The boron atoms form an isosceles triangle of 1.80 Å. base and 1.77 Å. sides, the latter being B-H-B bridges. Each boron atom has two "regular" (*i.e.*, non-bridge) hydrogens on opposite sides of the boron plane. All B-H_{regular} distances are in the range 1.05–1.20 Å. Approximate bridge B-H distances are $B_{\text{apex}}\text{-H}_{\text{bridge}} = 1.5$ Å. and $B_{\text{base}}\text{-H}_{\text{bridge}} = 1.2$ Å. The bridge hydrogen atom appears somewhat elongated at both temperatures. The over-all

(1) G. Kodama, R. W. Parry and J. C. Carter, *THIS JOURNAL*, **81**, 3534 (1959).

(2) W. N. Lipscomb, *J. Phys. Chem.*, **62**, 381 (1958).

(3) W. N. Lipscomb in "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1959, pp. 132–133.

(4) W. D. Phillips, H. C. Miller and E. L. Muetterties, *THIS JOURNAL*, **81**, 4496 (1959).

(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 378.

agreement is $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.084$ and 0.077 for observed reflections at -100° and room temperature, respectively.

The ion as shown in Fig. 1 has a vertical mirror plane demanded by the space group. Another mirror plane in the plane of the boron triangle is satisfied within experimental error. Thus the ion apparently has C_{2v} symmetry. The alternative space group $Pbn2_1$, in which the ion would lack a mirror plane, is ruled out by the failure of least squares refinement to yield significantly different parameters.

We are indebted to Dr. Goji Kodama for providing us with samples of the compound. The work was conducted, in part, under a grant from the National Science Foundation and, in part, under Contract AF33(616)-5874 with the U. S. Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

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RECEIVED SEPTEMBER 24, 1960

CARBENE BY THE DEHYDROHALOGENATION OF METHYL CHLORIDE

Sir:

Carbene, CH_2 , is formed by photolysis or pyrolysis of ketene^{1a,b,c} and diazomethane,^{1c,d,e} and presumably as a zinc iodide complex² from methylene iodide and zinc-copper couple. Recently it was reported that trimethylaminemethylene³ is also a source of carbene.

It is now reported that carbene is formed by the dehydrohalogenation (α -elimination) of methyl chloride with strong bases. Thus, methyl chloride reacts with phenyl sodium in the presence of carbene-acceptors, such as cyclohexene, isobutylene and *cis*-2-butene to give norcarane, 1,1-dimethylcyclopropane and *cis*-1,2-dimethylcyclopropane, respectively.⁴ Apparently carbene generated in this manner undergoes stereospecific *cis* addition.⁵ There was no evidence of carbon-hydrogen bond insertion. Methyl chloride (1 mole) was passed into a suspension of phenylsodium (*ca.* 1 mole) in hexadecane (100 ml. and cyclohexene (130 ml.) maintained below 40° (external cooling) to give after carbonation, norcarane (3.2%), benzene (19%), toluene (41%), ethylbenzene (1.9%), *n*-propylbenzene (0.1%), isopropylbenzene (0.08%), benzoic acid (3.0%)

(1) (a) T. G. Pearson, R. H. Purcell and G. S. Saigh, *J. Chem. Soc.*, 409 (1938); (b) M. Burton, T. W. Davis, A. Gordon and H. A. Taylor, *THIS JOURNAL*, **63**, 1956 (1941); (c) H. M. Frey and G. B. Kistiakowsky, *ibid.*, **79**, 6373 (1957); (d) H. Staudinger and R. Endle, *Chem. Ber.*, **46**, 1437 (1913), and earlier papers; (e) F. O. Rice and A. C. Glasebrook, *THIS JOURNAL*, **55**, 4329 (1933); **56**, 2381 (1943).

(2) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(3) V. Franzen and G. Wittig, *Angew. Chem.*, **72**, 417 (1960).

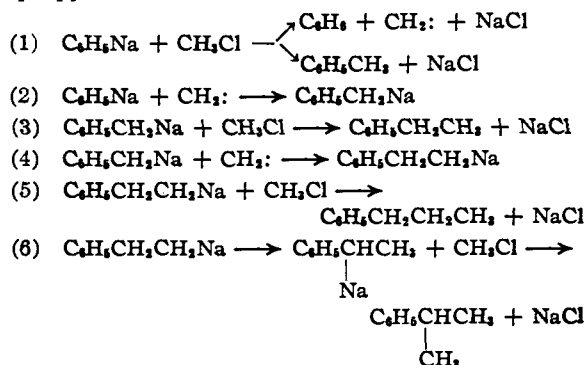
(4) Products were characterized and identified by the usual physical properties and/or gas-chromatographic and infrared comparisons with authentic samples.

(5) W. von E. Doering and P. M. LaFlamme, *THIS JOURNAL*, **78**, 5447 (1956); P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); W. von E. Doering, R. G. Laughlin, R. G. Buttery and N. Chaudhuri, *ibid.*, **78** 3224 (1956); F. A. L. Anet, R. F. W. Bader and A. Van der Auwera, *ibid.*, **82**, 3217 (1960).

and traces of phenylacetic acid. Ethylene and minor amounts of ethane also were obtained.

In a similar experiment employing *cis*-2-butene, *cis*-1,2-dimethylcyclopropane was obtained in 1% yield as the sole cyclic product. This exclusive *cis* addition is consistent with properties previously reported for carbene.⁵

Benzene and toluene are formed by hydrogen-metal interchange and S_N2 displacement of phenylsodium with methyl chloride, respectively. It is proposed that ethylbenzene, propylbenzene and isopropylbenzene are formed as outlined



Under the described experimental conditions benzylsodium is *not* formed by hydrogen-metal interchange of phenylsodium with toluene.⁶

The formation of carbene from methyl chloride thus bears formal resemblance to the preparation of dihalocarbenes^{7a} and chlorocarbene^{7b} from the corresponding haloforms and methylene chloride, respectively.

(6) Compare H. Gilman, H. A. Facevitz and O. Baine, *THIS JOURNAL*, **63**, 1514 (1940).

(7) (a) J. Hine, *ibid.*, **72**, 2438 (1950); J. Hine and A. M. Dowell, Jr., **76**, 2688 (1954); (b) G. L. Closs and L. E. Closs, *ibid.*, **81**, 4996 (1959).

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RECEIVED SEPTEMBER 7, 1960

A CONVENIENT NEW SYNTHESIS OF BIS-(TRIFLUOROMETHYL)-MERCURY¹

Sir:

We have found that tris-(trifluoromethyl)-phosphine reacts with mercuric oxide at 100° to form nearly one Hg(CF₃)₂ per two (CF₃)₃P consumed. This new synthesis of bis-(trifluoromethyl)-mercury seems to be more convenient than the earlier photochemical and amalgam methods² if it is considered that (CF₃)₃P is an easily isolated by-product of the synthesis of the chemically versatile trifluoromethyl-iodo-phosphines.^{3,4}

The direct removal of a CF₃ group from (CF₃)₃P by mercuric oxide is unusual because most tertiary

(1) This research was supported by the United States Air Force under subcontracts of Prime Contract AF 33(616)-5435 and 6913, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

(2) H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 2953 (1949).

(3) F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *ibid.*, 1568 (1953).

(4) A. B. Burg, W. Mahler, A. J. Bilbo, C. P. Haber and D. L. Her-ring, *THIS JOURNAL*, **79**, 247 (1957).

phosphines under similar conditions would be oxidized to the corresponding phosphine oxides. One reason for the present result may be the relative weakness of attachment of the CF₃ group to phosphorus, as shown by the manner of decomposition of the trifluoromethyl-bromophosphoranes.⁵

The non-volatile by-product of the HgO-(CF₃)₃P reaction has not been investigated fully, but decidedly does not include the diphosphorane (CF₃)₂POP(CF₃)₂,⁶ which might reasonably have been expected. Instead, it might be a mercury salt formulated either as Hg[-PO(CF₃)₂]₂ or as Hg[-OP(CF₃)₂]₂, from which, however, the corresponding phosphinous acid (CF₃)₂POH⁶ was not liberated by hydrogen chloride.

In the first experiment 0.964 mmole of (CF₃)₃P and 0.761 mmole of HgO were heated in a sealed tube for 36 hr. at 100°, after heating at 60° had proved ineffective. The tube was opened to the high-vacuum system, with recovery of 0.590 mmole of (CF₃)₃P (mol. wt. 238.0, as calcd.) and 0.180 mmole of Hg(CF₃)₂. The latter was analyzed by bromination to CF₃Br and HgBr₂, showing 40.3% CF₃ (calcd., 40.76) and 58.3% Hg (calcd., 59.24). The yield of Hg(CF₃)₂ represented 96% of the consumed (CF₃)₃P, in terms of the equation 2(CF₃)₃P + 2HgO → Hg(CF₃)₂ + "Hg[OP(CF₃)₂]₂." The unused HgO presumably was coated with the non-volatile byproduct, explaining the cessation of the reaction.

Another experiment employed a large excess of mercuric oxide, with the result that all of the 1.000 mmole sample of (CF₃)₃P was consumed during 22 hr. at 100°. In this case the yield of Hg(CF₃)₂ was 0.421 mmole, or 84%.

(5) A. B. Burg and J. E. Griffiths, *ibid.*, **82**, 3514 (1960).

(6) J. E. Griffiths and A. B. Burg, *ibid.*, **82**, 1507 (1960).

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RECEIVED SEPTEMBER 2, 1960

DIBUTYL ACETYLENEBORONATE¹

Sir:

Dibutyl acetyleneboronate, HC≡CB(OC₄H₉)₂, represents a new class of organoboron compounds, the α,β-acetylenic boronic esters.² It is also a useful reagent for preparing new types of unsaturated boronic esters inaccessible by classical methods.

Addition of 0.5 mole of ethynylmagnesium bromide³ in 600 ml. of tetrahydrofuran to 63 ml. of trimethyl borate in 600 ml. of ether at -70° (± 2°) then addition of 20 ml. of hydrochloric acid and 35 ml. of phosphoric acid in 250 ml. of water

(1) Supported by National Science Foundation Grant G-9916.

(2) The only closely related compounds reported in the literature appear to be (diethylamino)-diethynylboron, complexes of triethynylboron and triphenylethynylboron with Lewis bases, and salts of tetraethynylboron and related anions: E. C. Ashby and W. E. Foster, Abstracts of Papers, 133rd Meeting, American Chemical Society, San Francisco, April, 1958, p. 36L; U. Krueke, *Z. Naturforsch.*, **11b**, 606, 676 (1956); V. A. Sazonova and N. Ya. Kronrod, *J. Gen. Chem. U.S.S.R.* (English translation), **26**, 2093 (1956); G. Wittig and P. Raff, *Ann.*, **873**, 195 (1951).

(3) L. Skattebol, E. R. H. Jones and M. C. Whiting in "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1959, vol. 39, p. 56.