

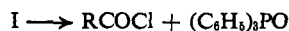
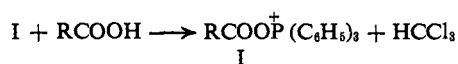
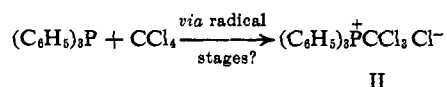
The reaction is obviously a several-step process, and it is suggested that initially formation of II (triphenyltrichloromethylphosphonium chloride) occurs, with further reaction yielding chloroform and the ion I. Other examples of this reaction are given in Table I.

Table I

Acid	Halides, ^a bp, °C	Derivative, mp, °C
Acetic	50-53	Anilide, 114-115
Propionic	80-84	Anilide, 100-102
<i>n</i> -Butyric	101-107	<i>p</i> -Toluidide, 57-59
Phenylacetic	206-211	Anilide, 110-112
Benzoic	195-200	Anilide, 163-165
Chloroacetic	106-109	Anilide, 127-128
<i>n</i> -Heptylic	123-125	<i>p</i> -Toluidide, 78-79
Pelargonic	210-218	<i>p</i> -Toluidide, 81-82
2,3-O-Isopropylidene-glyceric	80-83° (20 mm)	

^a Confirmed by comparison by gas-liquid partition chromatography and by spectral comparison with authentic material.

Work is proceeding to elucidate the reaction details and to determine its scope and limitations.



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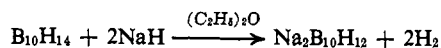
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Preparation and Properties of Sodium Decaborate(12,2-)¹

Sir:

We wish to report the preparation of sodium decaborate(12,2-), Na₂B₁₀H₁₂. Several previous investigations²⁻⁴ have demonstrated the initial reaction of sodium hydride with decaborane(14) in ethyl ether to yield NaB₁₀H₁₃, but evidence of a second acid hydrogen on the B₁₀H₁₃⁻ anion reacting with NaH was not presented. We have found that the reaction with excess sodium hydride proceeds slowly in ethyl ether with liberation of hydrogen and formation of the salt Na₂B₁₀H₁₂. The over-all reaction is



The reaction could be accelerated by warming to 45°; this was accomplished in a stainless steel bomb reactor. Starting with 7.9 mmoles of NaH and 0.90 mmole of B₁₀H₁₄, 89% of the hydrogen expected for formation of

(1) Research supported by the American Cancer Society (Grant T-325) and National Institutes of Health (Grant CA-08222-01A1).

(2) J. J. Miller and M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 4501 (1959).

(3) N. J. Blay, R. J. Pace, and R. L. Williams, *J. Chem. Soc.*, 3416 (1962).

(4) W. V. Hough and L. J. Edwards, Abstracts, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., 1958, p 28L.

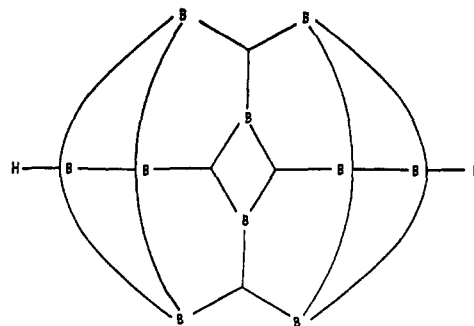


Figure 1. Proposed structure of 0822 B₁₀H₁₂²⁻ (a terminal H on each boron atom is omitted).

Na₂B₁₀H₁₂ was evolved in 68 hr. In separate experiments it was shown that the reaction proceeds, although very slowly, even at 0°. Approximately 75% of the expected hydrogen was evolved in 6 days at 0° when excess NaH was used.

Sodium decaborate(12,2-) is a white solid insoluble in ethyl ether. This allows easy separation from NaB₁₀H₁₃, which is highly soluble in ethyl ether. When slightly less than two formula weights of sodium hydride was used per mole of decaborane(14), the reaction allowed to continue until hydrogen evolution ceased, and the resulting mixture filtered and washed with ethyl ether, solid nonsolvated Na₂B₁₀H₁₂ was obtained. The only previous report of a B₁₀H₁₂²⁻ species is that of the solvated Grignard reagent, B₁₀H₁₂²⁻(MgX)₂·(C₂H₅)₂O, which was characterized by analysis.⁵

Analytical results on sodium decaborate(12,2-) and its molecular weight obtained by freezing-point depression in liquid ammonia support the formula Na₂B₁₀H₁₂. *Anal.* Calcd for Na₂B₁₀H₁₂: Na, 27.6; B, 65.1; H, 7.28; mol wt, 166. Found: Na, 25.4; B, 67.9; H, 7.49; mol wt, 180 ± 20.

The infrared spectrum shows strong ν(B-H) bands at 2440, 2380, and 2310 cm⁻¹ but no absorption in the region 2000 to 1700 cm⁻¹ generally ascribed to bridging hydrogens. The description provided by the valence theory proposed by Lipscomb⁶ would be 0822, which is shown as a planar projection in Figure 1. In three dimensions, the boron atoms differ little in location from those in B₁₀H₁₄.

Further support of the close structural relationship of the ion to decaborane(14) may be drawn from the results of the reaction of Na₂B₁₀H₁₂ with dilute aqueous HCl at 100°. The principal product of this reaction is decaborane(14), which was obtained in 67% yield. Na₂B₁₀H₁₂ was found to be hygroscopic and decomposed on handling in moist air, apparently because of the ready protonation of the anion to yield B₁₀H₁₃⁻ or B₁₀H₁₄. The salt is stable for at least several days at room temperature in a dry inert atmosphere.

(5) B. Siegel, J. L. Mack, J. V. Lowe, Jr., and J. Gallagher, *J. Am. Chem. Soc.*, **80**, 4523 (1958).

(6) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

(7) P. H. W. appreciates financial support by the Astronuclear Laboratory of the Westinghouse Electric Corporation under its Doctoral Assignment Program.

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