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Studies of Boranes. XXVIII. Reactions of Hexaborane(12)[1]

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Reaction of hexaborane(12) with liquid deuteriodiborane(6) at −30° yielded 1,1,4,4-tetradeuteriohexaborane(12). Further reaction with liquid deuteriodiborane(6) at room temperature resulted in the complete deuteration of hexaborane(12). The proton magnetic resonance spectrum at 100 MHz contains evidence for two sets of nonequivalent protons in the two BH_2 groups present in the compound in contrast to only one set found in the 60-MHz spectrum. There is no evidence for boron exchange between hexaborane(12) and liquid ^{10}B-diborane(6) at −30°. Hexaborane(12) was found to be moderately stable in the liquid phase at room temperature and in the gas phase at higher temperatures but decomposes rapidly in the liquid phase at 100°. Trimethylamine and propionitrile gave diborane and pentaborane(9) derivatives when they reacted with hexaborane.

Introduction

Studies of many boranes have been hindered by the difficulty of isolating them in significant quantities. Hexaborane(12) has been prepared by several methods, all of which yield only small amounts. Stock and Siecke[2,3] made the first report of a hexaborane(12) but later withdrew the report. Mass spectral evidence for hexaborane(12) has been reported by several groups,[4,5] but only a few chemical and physical studies of the compound have been made.[6-9] We therefore undertook additional studies of the thermal stability and chemical reactivity of hexaborane(12) including isotopic exchange studies.

Experimental Section

Methods.—Standard high-vacuum techniques were used in this investigation and have been treated elsewhere.[3,10] Separation of hydride mixtures was frequently accomplished with the aid of a low-temperature fractional distillation column.[11]

The hydrogen–deuterium analyses of the partially deuterated compounds prepared during this study were obtained by pyrolyzing the samples and analyzing the mass spectrum of the resulting hydrogen. This method has been previously reported.[12]

Some of the reactions described below were carried out in liquid diborane(6) at room temperature. Pure diborane has a vapor pressure of approximately 11 atm at −30° and reaches its critical pressure below room temperature although solutions retain a liquid phase at room temperature. Because of the high pressures involved, extreme caution was used during these experiments The reactions were carried out in Pyrex bombs and medium-walled nmr tubes.

Spectroscopic Techniques.—The ^{11}B nuclear magnetic resonance spectra were obtained with a Varian Associates HA-60-IL high-resolution spectrometer at 19.3 MHz. The ^{1}H and ^{2}D nuclear magnetic resonance spectra were obtained using a Varian Associates HA-100 high-resolution spectrometer at 100 and 15.31 MHz, respectively. Standard Varian variable-temperature probe accessories were used for obtaining spectra at low temperatures. The ^{11}B chemical shift values are reported relative to boron trifluoride diethyl etherate and were measured by the external standard technique using boron trichloride. Proton chemical shifts are reported relative to tetramethylsilane using benzene as the standard. Mass spectra were obtained using a Consolidated Electrodynamics Corp. Model 21-620A spectrometer.

Preparation of Starting Materials.—Hexaborane(12) was prepared by the method of Gaines and Schaeffer[7] and was purified before use by several distillations into a U tube cooled to −63°.[7] The preparations of $^{10}B_2H_6$ and B_2D_6 are described elsewhere.[12,13]

Reaction of B_6H_{12} with B_2D_6 at −30°.—A 0.28-mmol sample of B_6H_{12} and 3.2 mmol of B_2D_6 (85% D) were sealed in a medium-walled nmr tube at −196°. The ^{11}B nmr spectrum of the mixture was monitored as the reaction mixture warmed between −35 and −31°, when the triplet at δ −9.9 ppm collapsed to a singlet. After freezing to −196°, the nmr tube was opened to a vacuum line through a U trap on the bottom of which a second nmr tube was attached. The nmr tube and trap were kept at −80° so that the B_2D_6 passed through but the deuterated hexaborane(12) stopped. The hexaborane was then sealed into the nmr tube. The ^{11}B nmr spectrum of the deuterated hexaborane(12) at 19.3 MHz has two doublets centered at −23.0 and 21.8 ppm with J = 160 cps and a singlet at −9.5 ppm. The ^{1}H nmr of the deuterated hexaborane(12) was obtained at 100 MHz and is discussed below. The hydrogen–deuterium analyses of the recovered B_2D_6 and hexaborane(12) gave 80.9 and 24.6% deuterium, respectively. Thus, an average of 3.65 hydrogen atoms per molecule was exchanged by deuterium.

Reaction between B_6H_{12} and B_2D_6 at Room Temperature.—A 0.26-mmol sample of B_6H_{12} and 2.82 mmol of B_2D_6 (81%) were sealed into a medium-walled nmr tube and warmed to room temperature for 2 hr. Subsequently, the diborane was removed at −80° and the remaining sample was sealed into another nmr tube. The ^{11}B nmr spectrum showed only three singlets at −23.8, −9.9, and 21.5 ppm. Hydrogen–deuterium analyses were obtained for both diborane and hexaborane(12) and yielded 72.9 and 68.3%, respectively, indicating a compound with the average composition $B_6H_{0.8}D_{11.2}$.

Rearrangement of Deuterium in 1,1,4,4-$B_6H_8D_4$.—1,1,4,4-Tetradeuteriohexaborane(12) was prepared by allowing 0.87 mmol of B_6H_{12} and 8.9 mmol of B_2D_6 (73% D) to react for 2 hr at −30° in a 5-ml Pyrex bomb with a break-tip. The reaction vessel was cooled to −196° and opened to a high-vacuum line, B_2D_6 was removed, and 1,1,4,4-$B_6H_8D_4$ was condensed into an nmr tube. There was no significant rearrangement during the transfer because the distance through which the vapor had to

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[1] Part XXVII: P. C. Keller and R. Schaeffer, *Inorg. Chem.* **9**, 390 (1970).

[2] A. Stock and W. Siecke, *Chem. Ber.*, **57**, 566 (1924).

[3] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[4] S. G. Gibbins and I. Shapiro, *J. Amer. Chem. Soc.*, **82**, 2968 (1960).

[5] T. P. Fehlner and W. S. Koski, *ibid.*, **86**, 1012 (1964).

[6] D. F. Gaines and R. Schaeffer, *Proc. Chem. Soc.*, 267 (1963).

[7] D. F. Gaines and R. Schaeffer, *Inorg. Chem.*, **3**, 438 (1964).

[8] C. A. Lutz, D. A. Phillips, and D. M. Ritter, *ibid.*, **3**, 1191 (1964).

[9] S. R. Gunn and J. H. Kindsvater, *J. Phys. Chem.*, **70**, 1114 (1966).

[10] R. T. Sanderson, "High Vacuum Manipulation of Volatile Compounds," Wiley, New York, N. Y., 1948.

[11] J. Dobson and R. Schaeffer, *Inorg. Chem.*, **8**, 2183 (1969).

[12] R. Maruca, J. D. Odom, and R. Schaeffer, *ibid.*, **7**, 412 (1968).

[13] D. B. MacLean, J. D. Odom, and R. Schaeffer, *ibid.*, **7**, 408 (1968).

pass was short (less than 15 cm) and the sample, while in condensed phases, was kept below the rearrangement temperature. The migration of the deuterium atoms was followed by ^{2}D nmr at 15.31 MHz. Because the ^{2}D nmr signal is very weak, the signal to noise ratio made it difficult to obtain reproducible spectra; therefore, at least three spectra were obtained at each temperature. Spectra were observed at −20, −10, −5, 0, and 20°. At −35° only one peak could be seen but when the sample was warmed to −20°, a shoulder appeared about 1 ppm downfield from the original peak. As the sample was warmed to −10°, the downfield peak became more pronounced, at times appearing to be almost as strong as the original peak. Another signal, which was 3.7 ppm upfield from the first peak, appeared at −5° and continued to grow until it reached the height of the center peak at +5°. There was no further change as the sample was warmed to 20°.

Attempted Reaction of B_6H_{12} with $^{10}B_2H_6$ at −30°.—A 1.6-mmol sample of B_6H_{12} and 9.3 mmol of $^{10}B_2H_6$ (92% ^{10}B) were sealed into a 5-ml Pyrex bomb with a break-tip and allowed to warm slowly to −80° for 25 min and then to −30° for about 4 hr. Diborane and hexaborane were recovered quantitatively by fractionation, and mass spectrometric analysis of the recovered B_2H_6 showed no decrease in ^{10}B content. The ^{11}B nmr spectrum and mass spectrum of the recovered hexaborane(12) were identical with the spectra of the original sample.

Reaction between B_6H_{12} and B_2H_6 at Room Temperature.—A 1.26-mmol sample of B_6H_{12} and 13.7 mmol of B_2H_6 were sealed into a 5.6-ml Pyrex bomb with a break-tip and warmed to room temperature for 47 hr. After freezing to −196°, the reaction was opened to a vacuum line where the products were separated. The following products were recovered: H_2 (1.26 mmol), B_2H_6 (13.15 mmol), B_4H_{10} (0.11 mmol), B_5H_9 (0.24 mmol), B_6H_{12} (0.49 mmol), B_9H_{15} (0.10 mmol), and $B_{10}H_{14}$ (0.03 mmol). A yellow solid residue of 31.2 mg was also obtained but was not further analyzed. Tetraborane(10) was identified by its mass spectrum and the other less volatile boranes were identified by their ^{11}B nmr spectra.

Thermal Stability of B_6H_{12} at Room Temperature.—A 0.49-mmol sample of B_6H_{12} was sealed into a 100-ml bulb with a break-tip and warmed to room temperature. After 3 hr a small amount of a yellow liquid was evident in the bottom of the flask. After 21 hr the flask was opened to a high-vacuum line and the volatile components were removed and separated. The fraction which stopped at −63.5° was identified as hexaborane(12) by its vapor pressure of 17.5 mm at 0° (lit.[8] 17.1 mm (0°)) and was recovered in 87% yield. Traces of H_2, B_2H_6, B_4H_{10}, and B_5H_9 were also obtained.

Decomposition of Gaseous B_6H_{12} at 145°.—A 0.70-mmol sample of B_6H_{12} was passed from a U trap at −30°, through a trap at 145°, and into a trap at −196°. A 6-cm long section of 2-mm i.d. capillary connected the second and third traps instead of the usual 12-mm tubing so that the pressure of B_6H_{12} in the hot zone would approach the vapor pressure of B_6H_{12} at −30°. The small amount of hydrogen that was produced by the pyrolysis was continuously removed and measured in a calibrated automatic Toepler system. Only 0.01 mmol of hydrogen was evolved. The ^{11}B nmr spectrum of the pyrolysis product at −80° contained peaks attributable to B_6H_{12} with a small amount (less than 5%) of B_5H_9.

Decomposition of Liquid B_6H_{12} at 100°.—A sample of B_6H_{12} was sealed into an nmr tube, heated in a steam bath for 5 min, and then frozen to −196°. A white solid dissolved into a yellow liquid when the sample was warmed to room temperature. The ^{11}B nmr spectrum of the pyrolysis product had peaks attributable to B_5H_9 (δ 12.4 and 53.1 ppm, lit.[14] δ 12.7 and 51.8 ppm) and to $B_{10}H_{14}$ (δ 34.9 ppm, lit.[15] δ 34.9 ppm). The ^{11}B nmr spectrum in the range from −16 to 0 ppm was broad and could be attributed to $B_{10}H_{14}$ in the sample.

Critical Temperature of B_2H_6.—Approximately 2 mmol of diborane was sealed into a medium-walled nmr tube and allowed to warm in a stirred water bath from 6° to its critical temperature. A thermometer was placed beside the nmr tube and the sample was observed over a period of 2 hr as the temperature slowly rose. The temperature at which the meniscus between the liquid and vapor disappeared was 15.8° (lit.[16] T_c 16.7 ± 0.2°).

Reaction between B_6H_{12} and Excess $(CH_3)_3N$.—Hexaborane(12) (0.36 mmol) and trimethylamine (3.06 mmol) were condensed into a 50-ml reaction flask equipped with a Fisher–Porter valve. The mixture was warmed to 0° for 4 hr; then the excess $(CH_3)_3N$ (2.05 mmol) was removed. $(CH_3)_3N \cdot BH_3$ (15.1 mg, 0.21 mmol) was sublimed from the residue and identified by its mass spectrum. The nonvolatile residue was not further studied.

Reaction between B_6H_{12} and CH_3CH_2CN.—A 0.27-mmol sample of B_6H_{12} was sealed into an nmr tube with an excess of CH_3CH_2CN. As the mixture was warmed to room temperature, a vigorous reaction occurred and the solution became yellow. The only peaks in the ^{11}B nmr spectrum were those attributable to B_5H_9. No attempt was made to identify products by other techniques.

Reaction between B_6H_{12} and Br_2.—An nmr tube to which a standard taper joint was attached was flushed with dry nitrogen, 0.29 mmol of Br_2 in pentane solution was added, the tube was connected to a vacuum line, and 0.29 mmol of B_6H_{12} was added. The ^{11}B nmr spectrum of the mixture at room temperature showed only B_6H_{12}. After 1 hr at room temperature, the solution became yellow, a small amount of white solid formed, and the ^{11}B nmr spectrum developed a small peak at δ −40.1 ppm (lit.[15] for BBr_3, δ −40.1 ppm). The BBr_3 signal continued to increase over a period of 15 hr after which there was no further change. There was no evidence that any substituted borane was produced.

Discussion

The ^{11}B nmr spectrum of the reaction product between hexaborane(12) and deuteriodiborane(6) at −30° indicates that deuteration occurs solely at the BH_2 sites with reasonable rate at that temperature. The doublets, which are due to the two magnetically nonequivalent BH groups in the compound, are not affected under these conditions. However, when the reaction was allowed to proceed at room temperature, the exchange was complete and the ^{11}B nmr spectrum collapsed to three singlets. Since the hydrogen–deuterium analysis of the product from the exchange at room temperature yields a compound with a molecular formula of $B_6H_{0.8}D_{11.2}$, it is obvious that exchange also occurs with the bridge hydrogens. Although the ^{11}B nmr spectrum at 32 MHz (Figure 1) is consistent with the spectrum obtained at 19.3 MHz, there are additional signals in the ^{1}H nmr spectrum at 100 MHz which are

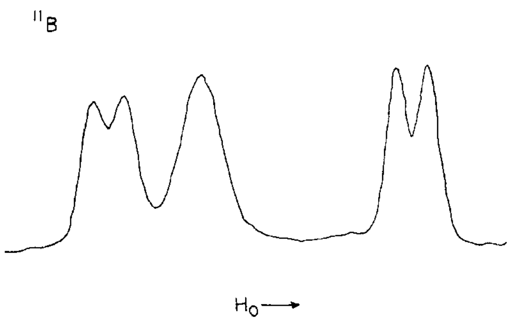

Figure 1.—The 32-MHz ^{11}B nmr spectrum of 1,1,4,4-$B_6H_8D_4$.

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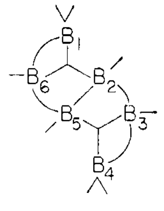
(14) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **81**, 4496 (1959).

(15) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1933 (1959).

(16) A. E. Newkirk, *J. Amer. Chem. Soc.*, **70**, 1978 (1948).

not evident in the 60-MHz spectrum.[7] The assignment of the new peaks permits a refinement of the structure which was previously proposed by Gaines and Schaeffer and which is consistent with the 4212 formulation (I) proposed by Lipscomb.[17]



I

The peaks labeled a and b in the ^1H nmr spectrum (Figures 2 and 3) may be attributed to the protons on the 3,6 borons and the 2,5 borons, respectively, and are the same as the 60-MHz proton spectrum. However, there are two separate quartets of proton signals, labeled c and c′, which may be attributed to the protons on the 1,4 borons. The correctness of this assignment is demonstrated by the ^1H nmr spectrum at 100 MHz of the hexaborane(12) which has undergone exchange with deuteriodiborane(6) at −30°. In this spectrum both of the quartets disappear after the exchange.

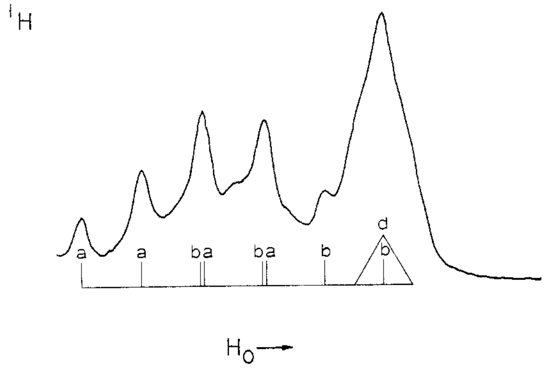


Figure 2.—The 100-MHz ^1H nmr spectrum of 1,1,4,4-$B_6H_8D_4$.

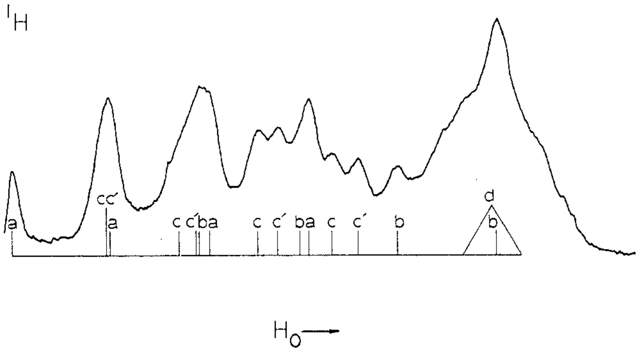
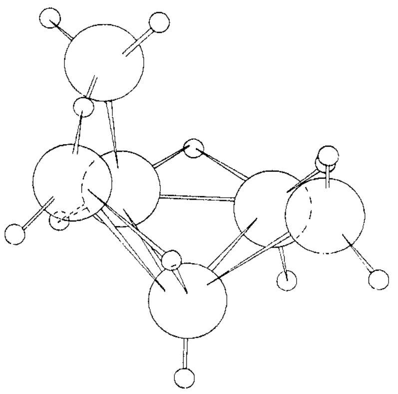


Figure 3.—The 100-MHz ^1H nmr spectrum of B_6H_{12}.

The nonequivalence of the protons on the 1,4 borons can be explained in terms of the originally proposed structure (II). It can be seen that one proton from the 1 boron and one from the 4 boron will protrude toward the center of the icosahedral fragment and one proton from each is located away from the center. The two sets are nonequivalent. Although one might expect to see some evidence for coupling between the protons on the same boron atom, line widths of the proton signals due to the boron–proton coupling are so broad that this effect may not be seen. Another possibility is that the proposed structure is not correct and that the two boron atoms are not magnetically equivalent. If this is the case, the two triplets in the ^{11}B nmr spectrum are so close that they are indistinguishable. Thus, although a definite assignment cannot be made for c and c′, the nonequivalence of the protons in the BH_2 groups of hexaborane(12) has been definitely established. Decoupling experiments, in which ^{10}B and ^{11}B are irradiated, should be helpful in further clarifying the structure. Pertinent nmr constants are collected in Tables I and II.



II

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF HEXABORANE(12)

		BH		BH₂		BHB
^1H	δ^a (±0.1), ppm	−4.75	−1.76	−3.80	−3.58	+0.52
	J (±3), cps	159	159	120	135	

[a] With reference to $Si(CH_3)_4$.

TABLE II

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF 1,1,4,4-TETRADEUTERIOHEXABORANE(12)

		BH		BD₂	BHB
^1H	δ^a (±0.1), ppm	−4.78	−1.74		+0.51
	J (±3), cps	158	158		
^{11}B	δ^b (±0.5), ppm	−24.3	+22.7	−10.1	
	J (±3), cps	155	160		

[a] With reference to $Si(CH_3)_4$. [b] With reference to $BF_3 \cdot O(C_2H_5)_2$.

An attempt was made to follow the rearrangement of deuterium from the 1,4 borons in 1,1,4,4-tetradeuteriohexaborane(12) by observing the ^2D nmr spectra at 15.3 MHz of this compound between −35° and room temperature. Although the signal to noise ratio was low, it was possible to distinguish some of the deuterium resonances as the atoms migrated. The first evidence for rearrangement as the temperature of the sample was

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[17] W. N. Lipscomb, *J. Phys. Chem.*, **65**, 1064 (1961), and references therein.

raised was the appearance of a shoulder 1 ppm downfield from the original signal and was due to deuterium migrating to the 3,6 borons. At −5° a signal appeared 3.7 ppm upfield from the original peak and was ascribed to deuterium in the bridge positions. No evidence was seen in these spectra for migration to the 2,5 borons. A ^{2}D nmr spectrum of the product of exchange between hexaborane(12) and deuteriodiborane(6) at room temperature was made and gave qualitative evidence for exchange at all positions; however, the chemical shifts of the peaks were not measured.

Although the hydrogens on the 1,4 borons of hexaborane(12) have been shown to undergo exchange with deuterium in deuteriodiborane(6) at −30°, the mechanism of exchange does not involve exchange of the 1,4 borons with the diborane. After 2 hr under identical conditions, both B_6H_{12} and ^{10}B-enriched diborane(6) were recovered unchanged.

Earlier studies of hexaborane(12) claimed that it has low stability but later reports have demonstrated that the compound is reasonably thermally stable up to room temperature in the liquid phase and is even more stable in the vapor phase at higher temperatures. The present study confirms these later reports completely. Hexaborane(12) was recovered in 87% yield when the liquid and a substantial amount of its vapor were kept for 24 hr at room temperature. This observation is consistent with an earlier study which reported a 98.5% recovery when liquid hexaborane(12) was kept at 25° for 3 hr.[8] When the vapors were passed through a hot zone at 145°, similar results were obtained but only a 37% recovery of hexaborane(12) was obtained when it was dissolved in a large excess of liquid diborane(6) for 47 hr. There was no evidence for pentaborane(11) in the ^{11}B nmr spectra of any of the products. This is in contrast to earlier decomposition studies in which the products were examined gas chromatographically. The use of extreme conditions on liquid hexaborane(12) (100° for 5 min) resulted in the complete destruction of that compound.

The critical temperature of diborane(6) has been previously reported to be 16.7 ± 0.2°. Since we have reported several experiments here and elsewhere in liquid diborane(6) above that temperature, we felt obliged to check the critical temperature. The present measurement, 15.8°, was in close approximation to the previously reported value. However, the volume of the liquid present in the high-pressure experiments at room temperature makes it apparent that diborane(6) and hexaborane(12) form a liquid solution under these conditions.

The reactions between hexaborane(12) and both trimethylamine and propionitrile are consistent with the previously reported reaction with dimethyl ether.[7] In all three cases, the attack by a base results in the elimination of a BH_3 group. In the trimethylamine reaction, the ratio of amine reacted to hexaborane(12) was 2.86 and trimethylamine–borane was recovered. A trimethylamine adduct with pentaborane(9) has been previously reported and was possibly the nonvolatile residue obtained in this reaction.[18] Thus the probable reaction might be written

$$3(CH_3)_3N + B_6H_{12} \longrightarrow B_5H_9\cdot 2(CH_3)_3N + (CH_3)_3N\cdot BH_3$$

The reaction of hexaborane(12) with propionitrile follows a similar path with the borane being split into pentaborane(9) and diborane(6); however, in this case, the nitrile probably reacts with the diborane(6) fragment. Diborane(6) and propionitrile have been reported to form an adduct which decomposes violently at 20° to give hydrogen and unidentified solids and decomposes at −10° to 0° to give N′,N″,N‴-tri-*n*-propylborazine.[19] Since no attempt was made to moderate the hexaborane(12) reaction, it may be assumed that the decomposition took the former path. Thus, it appears that the initial reaction between hexaborane(12) and bases is the cleavage of hexaborane(12) into pentaborane(9) and borane(3) fragments.

An attempt to prepare a monobrominated hexaborane(12) by direct bromination was unsuccessful. The only product which could be detected by ^{11}B nmr was boron tribromide. This result is in contrast to direct bromination of both tetraborane(10) and pentaborane(9).[20,21] It is possible that a brominated species was prepared but was unstable under the conditions used and was subject to decomposition and further bromination. Reactions at lower temperatures over a longer period of time may yield the desired product.

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[18] A. B. Burg, *J. Amer. Chem. Soc.*, **79**, 2129 (1957).

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[21] R. Schaeffer, J. N. Shoolery, and R. Jones, *J. Amer. Chem. Soc.*, **80**, 2670 (1958).