

Laser Initiated Thermal Synthesis of Triethylborane

ANTONIO BARRIOLA, CARLOS MANZANARES I* and JUAN CARLOS DE JESUS

Departamento de Quimica, Universidad Simon Bolivar, Apartado 80659, Caracas 1081, Venezuela

Received October 24, 1984

Olefin hydroboration with diborane has been extensively studied in the liquid phase in the presence of a catalytic ether solvent or similar weak base [1, 2]. In transmetalation experiments, $B(C_2H_5)_3$ has been prepared by treating KBF_4 or BF_3 with $Al(C_2H_5)_3$ [3, 4]. Little work has been done involving the gas phase. Previous experiments in the gas phase have not proved successful for the preparation of trialkylboron compounds [5, 6] in general, requiring elevated temperatures, long time intervals and producing low yields of the trialkylborane. Under carefully controlled conditions, simple alkenes in the presence of diborane in excess react in the gas phase to give mono and dialkylboranes in yields of around 60% and 35%, respectively [7]. Other experiments in the gas phase have used Group VIII metals as catalysts to obtain $B(C_2H_5)_3$ [8].

The photoinitiation of thermal explosions using infrared lasers to affect chemical reactions in the gas phase has been used successfully in several reactions. For example, SF_6 in mixtures with polyatomic molecules [9], the isomerization of methyl isocyanide [10], the combustion of CH_4-O_2 mixtures using SF_6 as a resonant absorber [11], the irradiation of ethyl iodide [12] and the single pulse irradiation of NH_3-O_2 mixtures [13]. The processes occur due to the high temperatures that can be obtained in a very short time which are sufficient to trigger a thermal explosion.

Because of the low yields and long time intervals required by the standard thermal synthesis of $B(C_2H_5)_3$ from gaseous B_2H_6 and C_2H_4 , the idea of the present study was to develop a convenient method of synthesis in the gas phase using an infrared source to initiate the reaction. In this paper the laser induced synthesis of $B(C_2H_5)_3$ is reported. Gas phase mixtures of B_2H_6 and C_2H_4 of different compositions are irradiated with a cw CO_2 laser. By tuning the laser frequency to coincide simultaneously with the bands of fundamental frequencies ν_{14} of B_2H_6 and ν_7 of C_2H_4 , a thermal explosion is initiated.

The reaction results in the complete disappearance of the B_2H_6 from the mixture and the formation of $B(C_2H_5)_3$ in yields of up to 91%. The whole process occurs within the first second of irradiation.

Experimental

Diborane was synthesized using methods described in the literature [14] and purified by trap-to-trap distillation ($-80^\circ C$ to $-190^\circ C$) in a vacuum system. B_2H_6 was separated first from noncondensable H_2 using a liquid nitrogen trap at $-190^\circ C$ and subsequent pumping. This was followed by several dry ice-acetone ($-80^\circ C$) to liquid nitrogen transfers to remove higher boron hydrides. Infrared spectra of the purified diborane did not indicate the presence of impurities. C_2H_4 (99.98% purity from Matheson) was used without further purification.

The cell used was designed for vacuum operation and quick disassembly and cleaning. It was made of pyrex with a volume of 225 cm^3 equipped with a cold finger. KBr windows were attached to the cell with epoxy adhesive. The cell was vacuum leak checked prior to use, purged with a 50–100 Torr of B_2H_6 , reevacuated and charged with the desired $B_2H_6-C_2H_4$ mixture sample. Pressures were measured with a Hg manometer. The cell fitted directly into the sample compartment of a Perkin-Elmer infrared spectrophotometer model 735B. Infrared spectra could be conveniently recorded prior to and following irradiation, as well as during various phases of the separation of the volatile components generated. The analysis of the reaction mixture after the irradiation indicated the formation of H_2 , total disappearance of B_2H_6 , remains of C_2H_4 in excess, small amounts of a solid polymeric material and liquid $B(C_2H_5)_3$. A vacuum system with sections of calibrated volume was utilized subsequent to the irradiations to determine the amounts of the individual components.

Separation of the volatile components was achieved by immersion of the reaction cell cold finger in different low temperature baths. The total pressure following irradiation was first determined by expansion into a calibrated volume. The reaction cell cold finger was then immersed in liquid nitrogen which condensed all components except H_2 . The hydrogen was then pumped away. The cold finger was then allowed to warm up to room temperature and the pressure in the calibrated volume was measured. The difference between this pressure and the pressure found immediately following irradiation yields the H_2 pressure. Repeating this procedure first with a toluene-liquid nitrogen ($-95^\circ C$)

*Research Fellow, 1983–1985, Department of Chemistry, Northwestern University, Evanston, Ill. 60201, U.S.A.

TABLE I. Irradiation of $B_2H_6-C_2H_4$ Mixtures with a cw CO_2 Laser.

Before Irradiation				After Irradiation		Weight	% Yield
P(B_2H_6) (Torr)	P(C_2H_4) (Torr)	Composition	P(total) (Torr)	P(H_2) (Torr)	P(C_2H_4) (Torr)	B(C_2H_5) ₃ (mg)	B(C_2H_5) ₃
24.5	295.5	1:12	320	18	169	67.7	91
32	288	1:9	320	39	140	55.8	56
46	274	1:6	320	86	127	48.2	34
80	240	1:3	320	172	105	36.0	14.5
69	386	1:6	455	130	188	63.9	30
23	137	1:6	160	37	65	25.0	34.5

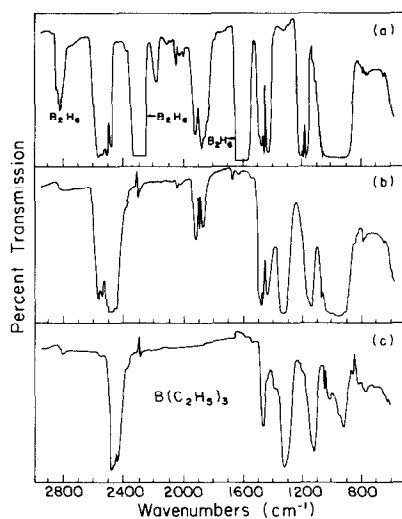


Fig. 1. Infrared transmission spectra of the $B_2H_6-C_2H_4$ mixture (1:6) (a) before irradiation, (b) immediately following irradiation with the P(20) line of the $10.6\ \mu m$ CO_2 laser transition ($944.21\ cm^{-1}$), and (c) after removal of the unreacted C_2H_4 and the H_2 generated from the irradiated sample.

slush allowed the pressure of residual C_2H_4 to be determined. At this point only $B(C_2H_5)_3$ and boron hydride polymer remained in the cold finger. The $B(C_2H_5)_3$ was distilled *in vacuo* into a preweighed sample tube immersed in liquid N_2 . The weight was then determined gravimetrically. Infrared spectra and boiling point ($0\ ^\circ C$) determination of the crystalline liquid indicated the presence of pure $B(C_2H_5)_3$ in the tube.

An Advanced Kinetics model MIRL-50 grating tuned CO_2 laser was used to irradiate the gas samples. In all cases the laser was tuned to the P(20) line of the $10.6\ \mu m$ transition ($944.21\ cm^{-1}$). The power was $5.3\ W$ and the intensity $13.8\ W/cm^2$. Beam diameter was $0.7\ cm$ and irradiation times were always $2\ s$. No reaction ever occurred when the power of the laser was below $5\ W$.

Results and Discussion

The infrared absorption spectrum of the mixture $B_2H_6-C_2H_4$ (1:6) prior to irradiation with the CO_2 laser is displayed in Fig. 1a. The spectrum of the mixture after irradiation is shown in Fig. 1b. It can be observed in this figure that the strong bands corresponding to B_2H_6 have disappeared (see Figs. 1a and 1b). Figure 3c corresponds to the spectra of the fraction collected at $-95\ ^\circ C$. Clear features corresponding to the pure product $B(C_2H_5)_3$ are shown. All the bands in the spectra of Fig. 3c have been reported previously by W. J. Lehmann *et al.* [15] in a study of the characteristic frequencies of triethylborane. Absorption due to CH stretching frequencies in the $2800-2900\ cm^{-1}$ range, HCH bending frequencies around $1471\ cm^{-1}$, and B-C stretching frequency at $1120\ cm^{-1}$ confirm the presence of pure $B(C_2H_5)_3$.

Table I shows the initial pressures, composition, and total pressures of the mixtures of B_2H_6 and C_2H_4 before irradiation. Also listed in Table I are the pressure of unreacted C_2H_4 remaining in the cell, the pressure of H_2 formed, the mass of liquid $B(C_2H_5)_3$ and the percentage yield obtained for each composition after irradiation of the sample mixture. Upon examination of these data several trends are noticed. At fixed total pressure ($320\ Torr$) of $B_2H_6-C_2H_4$ mixtures, the amount of polymeric material and H_2 increase as the mole fraction of B_2H_6 increases in the mixture. Several experiments were done using a 1:1 mixture which produced mainly H_2 , polymeric material and small amounts of $B(C_2H_5)_3$. The situation is reversed when the mole fraction of B_2H_6 is decreased. For a $B_2H_6-C_2H_4$ (1:6) mixture, the product inside the cell is a yellowish liquid. After purification, a small amount of boron hydride polymer remained in the cell and crystalline liquid $B(C_2H_5)_3$ was obtained. For a mixture of composition 1:12 the product in the cell is a crystalline liquid with no visible signs of the polymer. If the composition is fixed (1:6), the yield of $B(C_2H_5)_3$

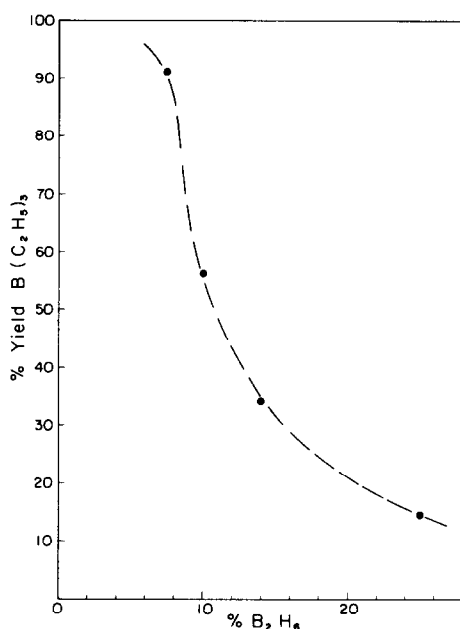
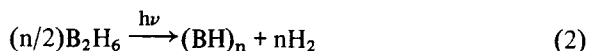
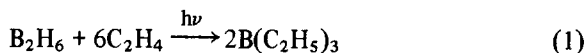


Fig. 2. Triethylborane percentage yield obtained after purification of the irradiated sample as a function of the percentage of B₂H₆ in the mixture B₂H₆-C₂H₄ before irradiation. Power was 5.3 W and intensity 13.8 W/cm². Irradiation time was 2 s. Total pressure 320 Torr.

is around 34% for a total pressure of 320 Torr. An increase in the total pressure to 455 Torr for a mixture of the same composition (1:6) results in a decrease (30%) of the yield of B(C₂H₅)₃. In Fig. 2 the percentage yield of B(C₂H₅)₃ is calculated from the number of moles of product obtained after purification and eqn. (1) is plotted as a function of the B₂H₆ mole fraction in the mixture before irradiation. A dramatic increase in the percentage yield of B(C₂H₅)₃ is obtained by decreasing the mole fraction of B₂H₆. In particular the 1:12 mixture produces a 91% yield with minimal formation of H₂ and traces of boron hydride polymer. Although the microscopic reaction is complex and out of the scope of this report, the results suggest that there is a competition between the following reactions:



The formation of B(C₂H₅)₃ from reaction (1) of boron hydride polymer and H₂ from reaction (2) can be controlled by changing the composition of B₂H₆ in the mixture.

In summary, a convenient method of synthesis and purification of triethylborane from gaseous diborane and ethylene mixtures is reported. An infrared cw CO₂ laser was used to initiate a thermal explosion which results in high yields of the product in a very short reaction time.

Acknowledgements

This work was supported by the Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT) of Venezuela under grants S1-1290 and S1-970. The authors gratefully acknowledge the assistance of the Chemistry Department at Northwestern University, Ill., U.S.A. for typing the manuscript.

References

- 1 H. C. Brown, 'Boranes in Organic Chemistry', Cornell Univ. Press, Ithaca, New York, 1972.
- 2 H. C. Brown, 'Hydroboration', Benjamin, New York, 1962.
- 3 R. Köster, *Liebigs Ann.*, **618**, 31 (1958).
- 4 H. Nöth and W. Storch, *Synth. Inorg. Met.-Org. Chem.*, **1**, 197 (1971).
- 5 D. T. Hurd, *J. Am. Chem. Soc.*, **70**, 2053 (1948).
- 6 F. G. A. Stone and W. A. G. Graham, *Chem. Ind. (London)*, 1181 (1955).
- 7 H. Hasso Lindner and T. Onak, *J. Am. Chem. Soc.*, **88**, 1886 (1966).
- 8 T. Matsuda and T. Tanaka, *Kokai Tokkyo Koho*, **79**, 39021 (1979).
- 9 S. H. Bauer, E. Bar-Ziv and J. A. Haberman, *IEEE J. Quantum Electron.*, **QE-14**, 237 (1978).
- 10 D. S. Bethune, J. R. Lankard, M. M. T. Loy, J. Ors and P. P. Sorokin, *Chem. Phys. Lett.*, **57**, 479 (1978).
- 11 R. A. Hill and G. A. Laguna, *Opt. Commun.*, **32**, 435 (1980).
- 12 J. C. Bellows and F. K. Fong, *J. Chem. Phys.*, **63**, 3035 (1975).
- 13 C. T. Lin and C. A. Bertran, *J. Phys. Chem.*, **82**, 2299 (1978).
- 14 W. L. Jolly, 'The Synthesis and Characterization of Inorganic Compounds', Prentice, New Jersey, 1970.
- 15 W. J. Lehmann, C. O. Wilson Jr. and I. Shapiro, *J. Chem. Phys.*, **28**, 777 (1958).