CO2 LASER INDUCED SYNTHESIS OF TRIALKYLBORANES

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INTRODUCTION.

In an earlier work[1], we described the laser induced synthesis of $B(C_2H_5)_3$ from gaseous B_2H_6 and C_2H_4 . Gas phase mixtures of diborane and envlene of different compositions were irradiated with a CW CO₂ laser and by tuning the laser frequency to the P(20) line at 944.2 cm⁻¹, a thermal explosion was initiated resulting in the formation of $B(C_2H_5)_3$ in yields up to 91%. We now report similar results using a pulsed CO₂ laser and irradiating B_2H_6 /alkene mixtures where the system is energized by selective excitation of B_2H_6 , alkene or SF₆

In this paper the results of a study of the laser induced reaction of B_2H_6 with $CH_2=CH_2$, $CH_2=CH-CH_3$, $CH_2=CH-C(CH_3)_3$ and cyclohexene are reported and also in the continuation of the studies about the behavior of boron hydrides to the CO_2 laser radiation [2], we report that tetraborane (B_4H_{10}) decomposes to diborane when irradiated with a CW CO_2 laser tuned to the R(20) line at 975.8 cm⁻¹. Mixtures of B_4H_{10}/C_2H_4 react explosively giving polymeric material, hydrogen, and traces of triethylborane.

EXPERIMENTAL SECTION.

A pulsed CO_2 TEA laser (Lumonics Ltd., Model 203-2) was used in the diborane/alkene mixtures irradiations. The P(20) line at 944.2 cm⁻¹was used and the laser beam size was 0.7 cm in diameter. No focusing techniques were utilized. The measurement of the energy output and laser fluences were made with a ratiometer Laser Presicion, Model Rj-7200 provided with a RjP-735 Pyroelectric Probe.

In the irradiation of B_4H_{10} , B_4H_{10}/C_2H_2 , and B_4H_{10}/C_2H_4 mixtures an Advanced Kinetics Model MIRL-50 grating tuned CW CO₂ laser was used. The maximun power was 5.2 W and the intensity 13.8 W/cm². Beam diameter was 0.7 cm and irradiation times were 5 min. In all cases the laser was tuned to the R(20) line at 975.8 cm⁻¹. No focusing techniques were utilized.

Diborane and tetraborane were synthetized using methods described in the literature [3,4] and purified by trap to trap distillation. Acetylene (C_2H_2) , ethylene (C_2H_4) , propylene (C_3H_6) , and Sulfur hexafluoride (SF_6) were purchased from Matheson Co. and all were used without further purification. 3,3-Dimethyl-l-butene (Neohexene, C_6H_{12}) and cyclohexene (C_6H_{10}) were purchased from Aldrich Chemical Co., and were purified by distillation.

The procedure employed for the handling and manipulation of the reagents and products were the same as described in the previous paper [1]. A cylindrical infrared cell, fabricated from pyrex glass and equiped with NaCl windows on both ends, was used as the reaction vessel. The volume of the cell was 60.0 cm^3 and the path length was 12.0 cm. The reaction products were analyzed using a Perkin-Elmer infrared spectrophotometer model 735B and a Nuclear Magnetic Resonance Spectrometer Varian, model T60 for hydrogen. The products for the 1:3 ratio mixtures were further analyzed by oxydizing the trialkylboranes to the corresponding alcohol [5], and employing a Gas Cromatograph Hewlett-Packard 584-A equiped with a Cabowax 20M, 10% Cromosorb N column (l= 20 meters) which allowed the separation and identification of the alcohols.



removal of the unreacted C_3H_6 and the H_2 generated from the irradiated sample.



RESULTS AND DISCUSSION.

Table I shows the total and partial pressures for the diborane/alkene mixtures before irradiation. Also listed in Table I are the mass of the trialkylborane and percentage yield obtained for each composition after irradiation of the sample mixture. The table also shows the number of pulses, and the corre-sponding fluences for each experiment.

IRRADIATION OF DIBORANE/ETHYLENE MIXTURES.

 $B_2H_6/CH_2=CH_2$ mixtures were irradiated with a pulsed CO_2 laser tuned to the P(20) line at 944.2 $\rm cm^{-1}$, obtaining similar result to the one reported in the previous work [1]. The reaction is complete and occurs after one single shot provided that we have total pressures above 100 torr and fluences bigger than 0.05 J/cm^2 .

IRRADIATION OF DIBORANE/PROPYLENE MIXTURES.

As shown in Table I mixtures of $B_2H_6/CH_2=CH-CH_3$ were irradiated with a pulsed CO_2 laser tuned to the P(20) line at 944.2 cm⁻¹. In all cases tripropylborane was obtained in yields up to 60%. The infrared absorption spectrum of the mixture B_2H_6/C_3H_6 (1:3) prior to the irradiation with the CO₂ laser is displayed in Figure 1A. The spectrum of the mixture after irradiation is shown in Figure 1B. It can be observed in this figure that the strong bands corresponding to the diborane have disappeared. Figure 1C correspods to the spectra of the fraction collected at -80°C, mainly the $B(C_{1}H_{7})_{1}$. Absortion due to the CH stretching frequencies in the 2959-2725 cm^{-1} range, HCH bending frequencies around 1470 -1475 cm⁻¹, and B-C stretching frequency at 1250 confirm the presence of $B(C_3H_7)_3$. All the bands in the spectrum of Figure 1C have been reported previously by M. D. Rushdy and M. A. Wahab [6] in an IR study of tri n-propylborane. The NMR spectrum taken from a sample was similar to the one reported by L. H. Long and M. G. H. Wallbridge [7] for the trialkylborane.

Upon examination of the data in Table I we can see that the higher the B_2H_6/C_3H_6 ratio the bigger the yield and the lower the fluence threshold needed to initiate the reaction. Moreover, in the 1:10 ratio mixture it was necessary to add a sensitizer (SF_6) in order to have some appreciable reaction. For better characterization of the trialkylboranes formed, the reaction products were oxidized with alkaline hydrogen peroxide to get the corresponding alcohol, which isolated and characterized resulted in 1-propanol and 2-propanol in a ratio of 96 to 4, very similar proportion to the one reported in the liquid phase [8]. This suggests to us that in the gas phase the boron atom prefers to attach to the less substituted of the two olefinic carbon atoms of the double bond (see scheme below). Similar results have been reported elsewhere for the hydroboration of olefins in liquid phase [9].

IRRADIATION OF DIBORANE/NEOHEXENE MIXTURES.

As in the previous case the main product in the irradiation of $B_2H_6/$ $CH_2 = CH - C(CH_3)_3$ mixtures is the trialkylborane $B[CH_2CH_2C(CH_3)_3]_3$. The compound is a white solid very reactive in air, highly soluble in ethereal solvents and partly soluble in chloroform. The infrared absortion spectrum of the mixture B_2H_6/C_6H_{12} (1:3) before and after irradiation are dispayed in Figure 2A and 2B. Figure 2C corresponds to the spectra of the fraction remaining in the cell after removal of the unreacted reagents and the hydrogen generated from the irradiated sample. The group of signals show a very similar pattern to the one founded for the tripropylborane and triethylborane. Also the proton NMR spec-trum shows a couple of signals in the 1.2 and 0.9 ppm region (relative to TMS) suggesting that the compound is mainly the corresponding trialkylborane: $B[CH_2CH_2C(CH_3)_3]_3$. Further oxidation with alkaline hydrogen peroxide resulted in a 97% yield of the primary alcohol.

In Table I we see a similar trend compared to the B_2H_6/C_3H_6 mixture, that is, the bigger the ratio mixture the higher the percentage yield and the lower the fluence threshold. We also note that it is necessary to add SF₅ to the mixture in order to have some appreciable reaction. The longer the alkene chain the less reactive to the IR radiation is the mixture, therefore we will need more energy to be applied to the system or distribute it more efficiently as it happens when we use the sensitizer.

Scheme of reaction for diborane/alkene mixtures in gas phase, under IR laser Radiation.

 $\frac{1}{2}B_2H_6 + 3CH_2 \approx CHR$ \xrightarrow{h} $B(CH_2CH_2R)_3$ (preferred pathway) $B[CH(CH_3)R]_3$

IRRADIATION OF DIBORANE/CYCLOHEXANE MIXTURES.

The irradiation of the $B_2H_6/cyclohexane$ mixtures gave tri-cyclohexilborane as the main product. The white solid compound was identified by its IR (Strong bands at: 2910, 2849, 1550, 1450, and 1400 cm⁻¹; weak bands in 1150-1200 cm⁻¹ region) and proton NMR spectra (Sharp signal at 1.4 ppm and broad signal in the 1.2-2.0 ppm region (relative to TMS)). In this system it was necessary to warm up the reaction cell to about 60°C because the lower vapor pressure of the cyclohexene. The induced chemical reaction is not accomplished in one single shot, and as shown in Table I several shots were needed in order to have an appreciable quantity of the tricyclohexilborane.

IRRADIATION OF TETRABORANE.

In other set of related experiments tetraborane $(B_4H_{10}, 10 \text{ torr})$ was irradiated with a CW CO₂ laser tuned to the R(20) line at 975.8 cm⁻¹ during five minutes, resulting in a low decomposition (10%) to diborane (B_2H_6) , polymeric material, and hydrogen. Although the thermal reaction of tetraborane results in the formation of higher boron hydrides [10], no higher molecular boron hydrides were detected in these experiments. The low pressure employed and the lack of heating of the cell walls probably inhibited the formation of other boron hydrides.

IRRADIATION OF TETRABORANE/ACETYLENE MIXTURES.

 B_4H_{10}/C_2H_2 in different ratios were irradiated with a continous CO_2 laser tuned to the R(20) line at 975.8 cm⁻¹ and employing powers in the 3.8 to 2.7 range (see Table 2). In all cases there was an explosive reaction causing the complete dissapareance of the tetraborane and the formation of hydrogen and a dusty brown polymeric material (Strong IR band in 3100-2900 and 2700-2600 cm⁻¹) which was not further characterized. We found the same results when irradiated with a CO_2 pulsed laser tuned to the P(20) line at 944.2 cm⁻¹. We can notice in Table 2 that when the total pressure of the irradiated system was below 100 torr in order to have reaction it was necessary to add SF₆ and tune to the P(20) line at 944.2 cm⁻¹. We have also found that the diborane/acetylene mixtures are highly explosives when submitted to the infrared laser radiation, therefore we favor the mechanistic view that tetraborane irradiated with a CO_2 infrared laser

decomposes to diborane which reacts violently with acetylene giving polymeric material and hydrogen.

IRRADIATION OF TETRABORANE/ETHYLENE MIXTURES.

Employing similar conditions to the ones reported in the previous experiments, B_2H_6 /CH₂=CH₂ mixtures react explosively under the CW or pulsed CO₂ laser radiation giving hydrogen, polymeric material, and traces of triethylborane (see Table 3), suggesting that under the action of the IR radiation, tetraborane decomposes to diborane which further reacts with ethylene giving the trialkylborane.

CONCLUSIONS.

We have found a fast and convenient way of synthetizing trialkylboranes. With this method we avoid the use of solvents and tedious ways of isolating the desired reaction product. Although this method only efficiently works with those alkenes with low molecular weight and therefore high vapor pressures, with the use of specially designed high temperature infrared cells it is possible to synthetize higher molecular trialkylboranes.

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Table I.Irradiation of B₂H₆/alkene mixtures with a CO₂ pulsed Laser tuned to the P-20 line (944.2 cm⁻¹). A: diborane/propylene, B: diborane/3,3-dimethyl-1-butene, C: diborane/ cyclohexene.

			Partia.	Press.(forr)				
System	^B 2 ^H 6 ^{/alkene} ratio	Total Press (Torr)	^B 2 ^H 6	Alkene	SF ₆	BR ₃ weight (mg)	% yield	Number of pulses	Fluence (J/cm ²)
1 A	1:10	365	33	322	10	11.7	38		
2 A	1:6	356	52	304		20.7	44	1	0.10
3 A	1:3	360	90	270		24.7	60	1	0.08
4 B	1:10	366	33	323	10	Traces		415	0.16
5 B	1:6	360	50	300	10	22.0	26	8	0.08
6 B	1:3	375	90	270	15	64.0	83	1	0.04
7 C	1:10	164	14	140	10	7.0	29	530	0.14
8 C	1:6	156	22	124	10	20.0	57	320	0.11
9 C	1:3	150	37	103	10	21.4	75	31	0.09

Table 2. Irradiation of $B_{\mu}H_{10}/C_{2}H_{2}$ mixtures with a CW CO₂ Laser.

Exp.	Partial Pressures (Torr)				Line (10.6 µm)	Power (Watts)	
	^B 4 ^H 10	^С 2 ^Н 2	SF ₆	^H 2			
1	90	90		334	R-20	3.8	
2	186	93		491	R-20	3.2	
3	123	47		326	R-20	4.0	
4	25	25	10	108	P-20	3.0	
5	37	13	10	240	P-20	3.0	
6	25	50	10	97	P-20	2.8	
7	25	75	10	106	P-20	2.7	

Table 3. Irradiation of B_4H_{10}/C_2H_4 mixtures with a CW CO₂ Laser tuned to 975.8 cm⁻¹.

Exp.	Part	ial Press	Power	
	^B 4 ^H 10	^с 2 ^н 4	н2	(Watts)
1	33	97	141	3.2
2	47	93	135	3.1
3	70	70	124	3.0

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