REACTION OF B-(1-ALKENYL)-DIALKYLBORANES WITH ISOCYANATES†

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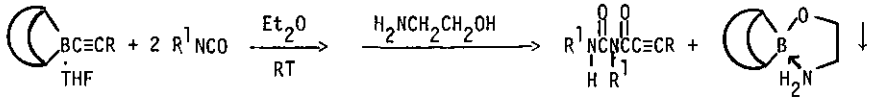
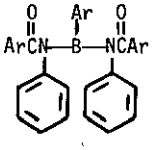
9-(1-Alkenyl)-9-borabicyclo[3.3.1]nonanes [9-(1-alkenyl)-9-BBN], easily prepared by hydroboration of the corresponding alkynes with 9-borabicyclo-[3.3.1]nonane (9-BBN), undergo remarkably facile reaction with two equivalents of isocyanates to give the intermediates (6), which on hydrolysis, provide in excellent yield *N,N'*-disubstituted *N*-(2-alkenoyl)-ureas. *B*-(1-Octenyl)-dicyclohexylborane reacts with aliphatic and aromatic isocyanates to furnish the novel heterocycle (11), which on hydrolysis yields *N,N'*-disubstituted *N*-(3-cyclohexylnonanyl)-ureas. *B*-(1-Alkenyl)disiamylboranes are inert towards isocyanates.

Recently we described the reaction of 9-(1-alkynyl)-9-borabicyclo[3.3.1]nonanes with isocyanates to provide, after protonolysis, the corresponding *N,N'*-disubstituted *N*-(2-alkynyl)-ureas (1).[1]



(1)

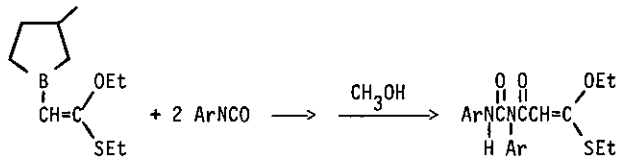
We noted in that article that the course of the reaction of organoboranes with isocyanates is critically dependent on the type of organoborane utilized.[2] For example, trialkylboranes do not react with isocyanates under normal conditions, while triarylboranes react with two equivalents of isocyanates to provide diamidoboranes (2).



(2)

†Cordially dedicated to Prof. Dr. Tetsuji Kametani on the occasion of his retirement.

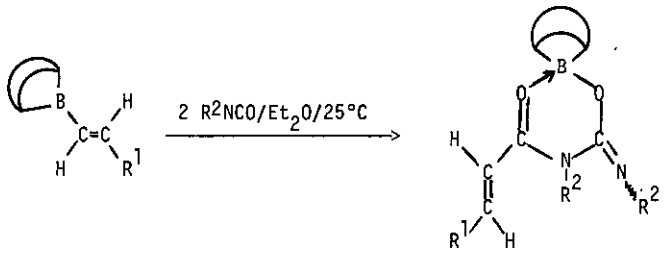
Although Mikhailov had observed that the alkenyldialkylborane (3) reacted to provide the substituted urea derivative (4),[3] no experimental details were published. Moreover, to our knowledge, the method was only utilized to prepare a single compound. Consequently, we set out to explore the



(3) (4)

reaction in greater detail to elucidate the structure of the intermediate formed and to establish that the method was indeed general for a variety of alkenyldialkylboranes and isocyanates.

Initially our study concentrated on the 9-(1-alkenyl)-9-borabicyclo[3.3.1]nonanes [9-(1-alkenyl)-9-BBN] (5). We discovered that the reaction proceeded with remarkable ease in diethyl ether, (EE), to provide excellent yields of the intermediate (6), which precipitates in most cases from the reaction mixture as a yellow solid (Table I).



(5) (6)

TABLE I. The Intermediate (6)

R^1	R^2	Isolated yield %	mp °C	^{11}B nmr ppm
3-Chloro-*n*-propyl	Phenyl	80	124-126	+ 8.3
n-Butyl	Phenyl	80	128-130	+ 7.4
tert-Butyl	Phenyl	93	178-180	+ 9.6
n-Butyl	*n*-Butyl	—	—	+10.2
n-Butyl	Cyclohexyl	80	138-140	+ 7.5
n-Butyl	1-Naphthyl	90	129-131	+ 8.6

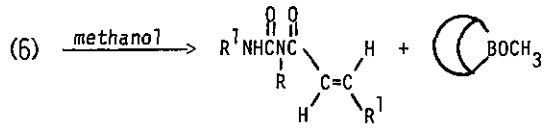
The intermediate was hydrolyzed with excess methanol; the solid product (7) then crystallizes out as a colorless solid in essentially quantitative yield. When the product is highly soluble in methanol, it is isolated by pumping off the volatiles under reduced pressure (0.1 mm Hg) (Table II).

TABLE II. *N,N'*-Disubstituted *N*-(2-Alkenoyl)-ureas (7)

R^1	R^2	Yield[a] %	mp or bp[b] °C	Molecular Formula	Elemental Analysis, % Calculated C	H	N	Cl	Found C	H	N	Cl
3-Chloro-*n*-propyl	Phenyl	70	85-86	$C_{19}H_{19}N_2O_2Cl$	66.6	5.6	8.2	10.3	66.4	5.5	8.1	10.4
n-Butyl	Phenyl	75	74-75	$C_{20}N_{22}N_2O_2$	74.5	6.9	8.7	—	74.4	6.7	8.6	—
tert-Butyl	Phenyl	94	125-126	$C_{20}H_{22}N_2O_2$	74.5	6.9	8.7	—	74.7	6.8	8.5	—
n-Butyl	*n*-Butyl	70	130/0.1 mm Hg	$C_{16}H_{30}N_2O_2$	68.0	10.7	9.9	—	68.2	10.6	9.7	—
n-Butyl	Cyclohexyl	65[c]	95-96	$C_{20}H_{34}N_2O_2$	71.8	10.2	8.4	—	72.0	10.3	8.2	—
n-Butyl	1-Naphthyl	85	119-120	$C_{28}H_{26}N_2O_2$	79.6	6.2	6.6	—	79.5	6.3	6.6	—

[a]Refers to pure, recrystallized (or distilled) product. Satisfactory spectral data (ir, ^{1}H nmr) were obtained for all compounds.

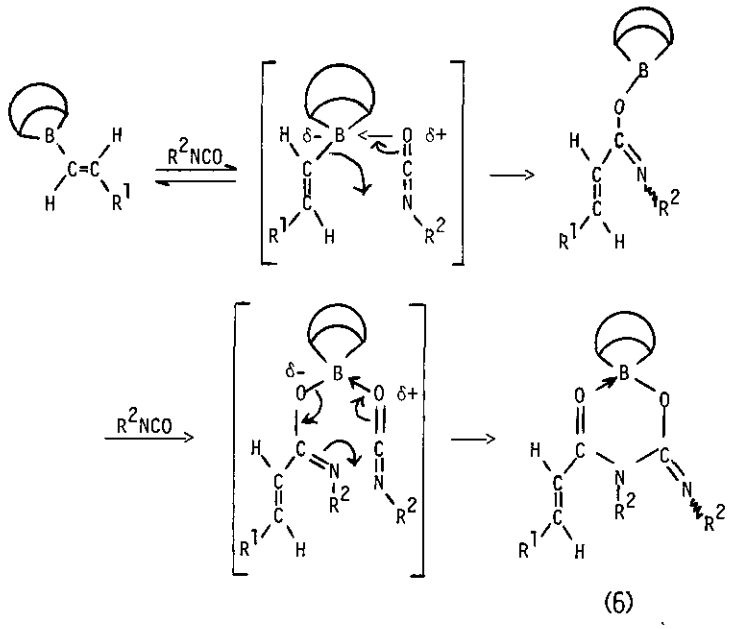
[b]Solid products were recrystallized from methanol. [c]Isolated by pumping off 9-methoxy-9-borabicyclo[3.3.1]nonane (8) at 0.1 mm Hg. Recrystallized from petroleum ether (bp 40-60°C).



(7) (8)

The stereochemistry of the alkenyl group transferred is predefined by the hydroboration reaction, and strict retention of stereochemistry is observed by all spectral data. Reaction with both equivalents of isocyanate is virtually instantaneous. Thus the reaction of 9-(1-hexenyl)-9-BBN (5, R^1 = n-C_4H_9) with one equivalent of phenylisocyanate, followed by methanolysis, affords 1-hexene (48% by glc analysis), the urea derivative (7) (R^1 = n-C_4H_9, R^2 = C_6H_5), and methoxy-9-borabicyclo[3.3.1]-nonane (8) as the only isolated products.

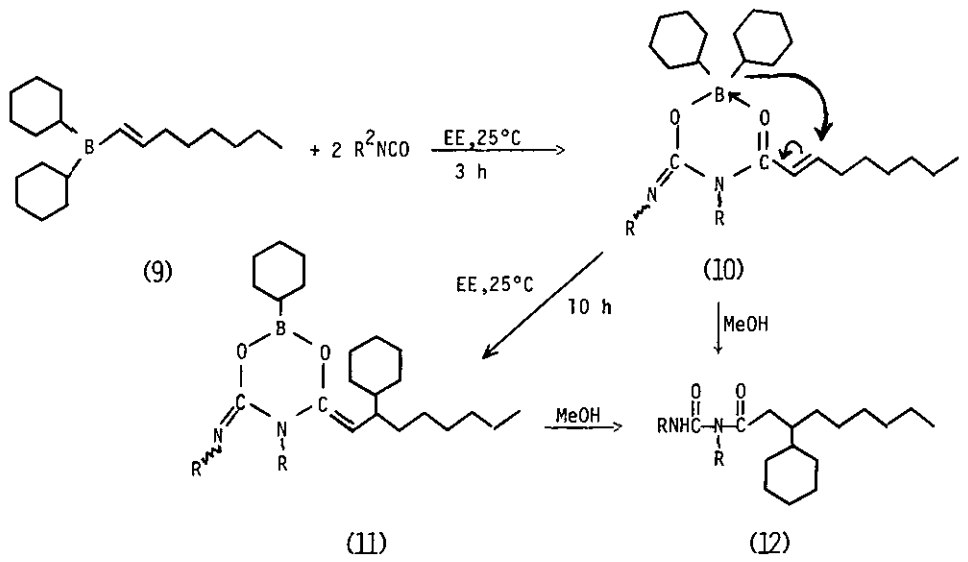
The mechanism of the reaction can be envisioned as an initial 1,2-addition of 9-(1-alkenyl)-9 BBN to the isocyanate, followed by rapid addition of a second equivalent of isocyanate through a six-membered transition state. In most cases, the intermediate (6) immediately precipitates out of the solution as a yellow solid.



(6)

Internal 9-alkenyl-9-BBN and *B*-alkenyldisiamylboranes do not react with isocyanates under the experimental conditions. *B*-Alkenyldicyclohexylboranes react differently with isocyanates. For example, *B*-(1-Octenyl)-dicyclohexylborane (9) reacts with two equivalents of isocyanate to give the intermediate (10), which is converted into the novel heterocyclic compound (11). Both the intermediate (10), as well as the heterocyclic compound (11), give, on hydrolysis with methanol, the

N,N'-disubstituted *N*-(3-cyclohexylnonanoyl)-urea (12).



R = Ph-, *n*-Bu

Experimental Section

The ir spectra were recorded on a Perkin-Elmer 700 spectrophotometer. The ^{1}H nmr spectra were recorded on a Varian T-60 (60 MHz) spectrometer and all of the chemical shifts are relative to TMS (0 ppm). The ^{11}B nmr spectra were recorded on a Varian FT-80A (80 MHz) spectrometer and all chemical shifts are relative to BF_3·EE (0 ppm). The microanalyses were performed by the Purdue Microanalytical Laboratory.

N,N'-Diphenyl-*N*-(4,4-dimethyl-2-heptenoyl)-urea (7, R^1 = *t*-C_4H_9, R^2 = C_6H_5); Typical Procedure.

A dry, 50-ml centrifuge tube capped with a rubber septum and equipped with a magnetic stirring bar was flushed with dry nitrogen. The tube was charged with 9-(3,3-dimethyl-1-hexenyl)-9-BBN (5, R^1 = *t*-C_4H_9; 2.1 g, 10 mM) dissolved in dry ethyl ether (8 ml). Phenylisocyanate (2.4 g, 20 mM) was added dropwise and the stirring continued for 6 h. The yellow solid was separated by centrifugation, washed with *n*-pentane (2 x 10 ml) and dried to give the adduct (6, R^1 = *t*-C_4H_9, R^2 = C_6H_5); 4.1 g (93%), mp 178-180°C. The adduct (2.2 g, 5 mM) was taken in a 50-ml centrifuge tube and methanol (5 ml) was added with stirring. The yellow adduct went into solution, and after 1 h, the crude urea derivative precipitated out. The reaction mixture was cooled to 0°C to insure complete precipitation and the product was separated from the mother liquor, which contained 9-methoxy-9-BBN (8), by centrifugation. The product was crystallized from a minimum amount of methanol, 1.5 g (94%), mp 125-126°C. (Found: C, 74.7; H, 6.8; N, 8.5. $C_{20}H_{22}N_2O_2$ requires C, 74.5; H, 6.9; N, 8.7); ir (KBr) 3200, 2940, 1710, 1640, 1600, 1580 and 1500 cm^{-1}; ^{1}H nmr $CDCl_3$) δ 0.92 (s, 9H, *t*-

C_4H_9); 5.5 (d, J = 16 Hz, 1H, olefinic); 7.0-7.8 (m, 11H, aromatic and olefinic); and 11.6 (s, 1H, NH).

Reaction of *B*-(1-Octenyl)-dicyclohexylborane (9) with Phenyl Isocyanate. With the usual experimental setup, *B*-(1-octenyl)-dicyclohexylborane (2.88 g, 10 mM) in EE (8 ml) was mixed with phenyl isocyanate (2.4 g, 20 mM) at 25°C. After 3 h, a yellow solid precipitated out of solution. The solid was separated by centrifugation, washed with *n*-pentane (2 x 5 ml) and dried to give the intermediate (10), 3.7 g (70%), mp 129-131°C. ^{1}H nmr ($CDCl_3$) δ 0.8-2.3 (m, 35H); 5.6 (d, J = 16 Hz, 1H, olefinic), and 7.2 (m, 11H, aromatic and olefinic). When the above reaction mixture was stirred for 10 h without isolating the intermediate (10), a clear, colorless solution resulted. The intermediate (11) was isolated by pumping off the solvent, 4.5 g (85%), mp 105-107°C, ^{1}H nmr ($CDCl_3$) δ 0.86-2.0 (m, 35H); 3.13 (d, J = 12 Hz, 1H, olefinic) and 7.3 (m, 10H, aromatic). The intermediate (11) (2.6 g, 5 mM) was stirred with methanol (5 ml) for 1 h. Excess methanol and dimethoxycyclohexylborane were pumped off at reduced pressure (0.1 mm Hg, 50°C). The crude *N,N'*-diphenyl-*N*-(3-cyclohexylnonanoyl)-urea (12, R = C_6H_5) was recrystallized from petroleum ether (bp 40-60°C), 1.65 g (75%), mp 103-104°C. (Found: C, 77.7; H, 8.6; N, 6.4. $C_{28}H_{38}N_2O_2$ requires C, 77.4; H, 8.8; N, 6.4); ir (KBr) 3200, 1690, 1640, 1570, 1520, 1130, and 730 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.9-2.3 (m, 27H), 7.0-7.7 (m, 10H, aromatic), and 11.7 (s, 1H, NH).

Reaction of *B*-(1-Octenyl)-dicyclohexylborane (9) with *n*-Butylisocyanate. With the regular experimental setup, *B*-(1-octenyl)-dicyclohexylborane (2.88 g, 10 mM) in EE (8 ml) was mixed with *n*-butylisocyanate (1.98 g, 20 mM) at 25°C. The reaction mixture developed a yellow color, and after stirring for 24 h, the solution became almost colorless. Methanol (5 ml) was added to the reaction mixture and the stirring continued for one hour more. Excess methanol and dimethoxycyclohexylborane were pumped off at reduced pressure (0.1 mm Hg, 50°C) to give pure *N,N'*-di-*n*-butyl-*N*-(3-cyclohexylnonanoyl)-urea (12, R = n-C_4H_9), 3.6 g (90%), bp 180-182°C (0.1 mm Hg). (Found: C, 73.11; H, 11.8; N, 7.0. $C_{24}H_{46}N_2O_2$ requires C, 73.0; H, 11.7; N, 7.1); ir (neat) 3250, 1710, 1650, 1540, 1450, and 1120 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.87-2.2 (m, 41H), 3.0-3.3 (m, 4H).

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References

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