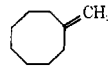
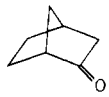
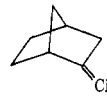
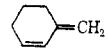
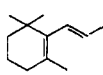
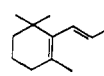
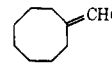
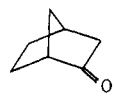
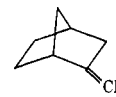
Table I. Conversion of Carbonyl Compounds to Olefins

Entry	Carbonyl compound	Sulfoximine	Yield of adduct, %	Olefin	Yield, %
1	$CH_3(CH_2)_{14}C(=O)CH_3$	4	90	$CH_3(CH_2)_{14}C(=CH_2)CH_3$	90
2	$CH_3(CH_2)_{14}C(=O)CH_3$	4	*a*	$CH_3(CH_2)_{14}C(=CH_2)CH_3$	85
3	$CH_3(CH_2)_6CHO$	4	50	$CH_3(CH_2)_6CH=CH_2$	60
4	$CH_3(CH_2)_8CHO$	4	80	$CH_3(CH_2)_8CH=CH_2$	70
5	PhCHO	4	90	$PhCH=CH_2$	60
6	$CH_3(CH_2)_3C(=O)(CH_2)_5CH_3$	4	90	$CH_3(CH_2)_3C(=CH_2)(CH_2)_3CH_3$	80
7		4	*a*		73
8		4	75		85
9		4	50		82
10		4	89		50
11		4	85		93
12	$CH_3(CH_2)_8CHO$	5	60	$CH_3(CH_2)_5CH=CHCH_3$ cis–trans mixture	60
13	$CH_3(CH_2)_4CHO$	5	75	$CH_3(CH_2)_4CH=CHCH_3$ 60% trans 40% cis	100
14	$CH_3(CH_2)_2CHO$	6	78	$CH_3(CH_2)_2CH=CH(CH_2)_2CH_3$ 64% trans 36% cis	78
15		5	85		70
16		5	75	 78%-22% mixture	65

[a] Not isolated.

three asymmetric centers and hence the possibility that the adduct as produced is a mixture of four diastereomers. This provides for the intriguing and potentially useful possibility that the individual diastereomers, upon separation and reduction, could provide pure samples of cis or trans olefins. At this juncture we have not achieved this goal. We have, in several cases (entires 14 and 16), separated and purified what we believe to be single diastereomers. However, upon reduction the purified diastereomers resulted in cis/trans mixtures, albeit enriched in a single isomer (as compared with the direct reduction of the original diastereomeric mixture). Our efforts along these lines are continuing.

The sulfoximines (**4**, **5**, **6**), dissolved in THF (30 mmol/100 ml), were treated at 0° with 1 equiv of *n*-butyllithium. The carbonyl compounds, dissolved in THF, were added to the reagent, and the reaction mixture was maintained at 0° for 1 hr, then allowed to warm to room temperature over 1 additional hr (with conjugated substrates, the reaction mixtures were maintained constantly at 0° for 2–4 hr).[12] Acetic acid (30–45 equiv) diluted with an equal volume of water was added to the reaction mixture followed by addition of 10–15 g-atom equiv of aluminum amalgam. The reactions, run at room temperature, were monitored by thin-layer chromatography; typically, reductive elimination was complete in 4 hr. The olefins were isolated and purified by extraction with pentane and washing the pentane extract with 20% aqueous sodium hydroxide[13] followed by distillation or chromatography. The yields reported in Table I are for isolated and purified materials.

(12) When the β-hydroxysulfoximines were isolated, the reaction mixtures were quenched at this point with 10% aqueous ammonium chloride; the adducts were extracted into methylene chloride, washed with water, dried, and purified, if desired, by chromatography on silica gel. The crude or purified adducts were dissolved in THF and reduced as described without isolation.

(13) To remove thiophenol produced by reduction of *N*-methylbenzenesulfinamide.

Carl R. Johnson,* James R. Shanklin, Robert A. Kirchhoff
Department of Chemistry, Wayne State University
Detroit, Michigan 48202
Received May 18, 1973

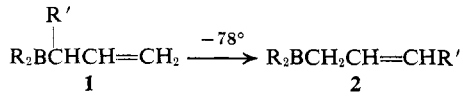
Thermal Isomerization of But-1-en-3-yl(dimethylamino)ethylborane. The Reluctant 1,3-Sigmatropic Shift of Boron in an Unusually Stable Allylborane

Sir:

The high reactivity of allylboranes with a host of diverse nucleophiles under generally mild conditions has been widely exploited in organic synthesis.[1] There

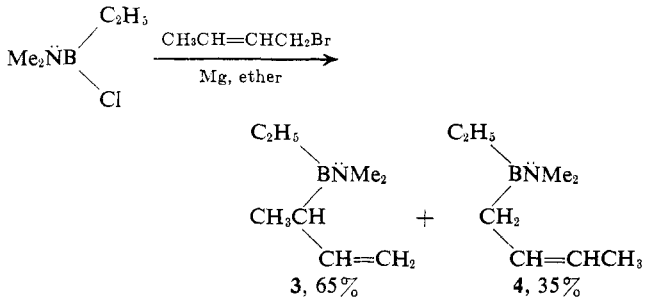
(1) For a recent review, see B. M. Mikhailov, *Organometal. Chem. Rev., Sect. A*, **8**, 1 (1972).

is, however, the attendant problem limiting synthetic utility that allylboranes are prone to allylic rearrangement, so much so that α-substituted allylboranes spontaneously rearrange to the thermodynamically favored straight-chain, internal-olefin isomer (**1** → **2**).



Attempts to synthesize allylboranes with branching at the α-carbon yield only the straight-chain isomer even at $-78°$.[2]

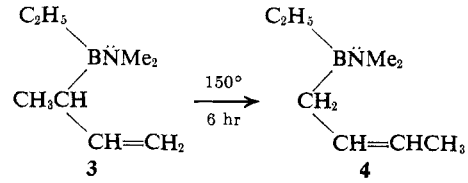
Formally, the rearrangement is a 1,3-sigmatropic shift of boron, but its facility is in contrast to the scarcity and energetic stringency of 1,3 shifts of carbon centers.[3,4] It thus seemed worthwhile to prepare and study allylboranes in which the 1,3 shift was sufficiently retarded to allow the branched-chain isomers chemically useful lifetimes. This report describes the preparation and thermal chemistry of but-1-en-3-yl-(dimethylamino)ethylborane (**3**), an unusually stable allylborane.



But-1-en-3-yl(dimethylamino)ethylborane (**3**) was synthesized by a modification of the general method of Niedenzu and Dawson.[5,6] Reaction of chloro(dimethylamino)ethylborane and the Grignard reagent from 1-bromo-2-butene gave a 50% yield of a 65:35 mixture of **3** and its straight-chain isomer, but-2-en-1-yl(dimethylamino)ethylborane (**4**). Separation of the isomeric boranes was accomplished by spinning-band distillation (20 mm), taking fractions of bp 57–60° (**3**) and 62–64° (**4**). The α-methylallyl- and crotylboranes **3** and **4** are easily distinguished by their pmr spectra. At 60 MHz (CCl_4), **3** had resonances at δ 5.85 (H_x, eight lines, J_{ax} = 17.6 Hz, J_{bx} = 9.6, J_{mx} = 6.8), 4.77 (H_a and H_b, mult, J_{ab} = 1.5 Hz), 2.78 (6 H, s), 2.11 (1 H_m, pentet, J = 7.0 Hz), 0.98 (3 H, d, J = 7.0 Hz), and 0.81 (5 H, broad singlet, with downfield shoulder); **4** had absorptions at δ 5.33 (2 H, mult), 2.78 (6 H, s), 2.00 (2 H, mult), 1.60 (3 H, d), and 0.84 (5 H, broad singlet, with downfield shoulder).

The existence of **3** as a stable isomer is in itself noteworthy, considering the spontaneous rearrangements of branched-chain allyldialkylboranes. The closest reported resemblance to the stability of **3** is found in di-*n*-hexyl (but-1-en-3-yl)boronate (**5**),[7] which is semi-stable at room temperature, isomerizing over a period of weeks. On a qualitative scale it thus appears that one amino substituent is as effective as two alkoxy groups in quenching the proclivity of allylic boron to a 1,3 shift.

In sealed tubes at 150°, thermal isomerization of **3** to **4** was complete in several hours. The reaction was quantitative and absolutely clean; there were no detectable side products or polymerization. Monitoring by nmr (*vide supra*) was particularly convenient; ir analysis indicated formation of **4** as a cis–trans isomer mixture by the appearance of vinylic bending absorptions at both 710 and 962 cm^{-1} as the 895 and 997 cm^{-1} bands of **3** disappeared.



The isomerization was shown to obey strict first-order kinetics, with the equilibrium totally in favor of the crotylborane **4** at all temperatures studied. In typical kinetic runs, 300-mg samples of **3**, either neat or in a solvent, were sealed under argon in Pyrex nmr tubes.[8] Tubes were immersed in a constant-temperature bath, and the proportions of **3** and **4** at various times were determined after quenching the reaction by immersing the tube in ice water and then analyzing by pmr spectroscopy.[9] The kinetic data at five temperatures (multiple runs, at least six points, two-plus half-lives per run) are summarized for the neat isomerization in Table I. Runs in methylcyclohexane gave comparable results.

Table I. Kinetic Analysis of Thermal Isomerization of But-1-en-3-yl(dimethylamino)ethylborane

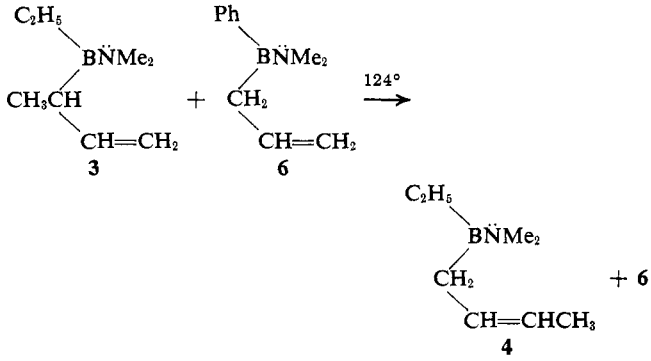
T, °C	k, sec^{-1}	$\tau_{1/2}$, hr
148.0 ± 0.2	1.34 (±0.14) × 10^{-4}	1.4
136.0 ± 0.2	5.23 (±0.10) × 10^{-5}	3.7
123.5 ± 0.2	1.81 (±0.11) × 10^{-5}	10.6
114.0 ± 0.2	1.02 (±0.03) × 10^{-5}	18.8
101.0 ± 0.1	3.08 (±0.11) × 10^{-6}	62.3

From the linear Arrhenius plot the activation energy E_a was determined to be 24.6 kcal/mol; $\Delta H^{\pm}$ was 23.9 kcal/mol, and at 100°, $\Delta G^{\pm}$ and $\Delta S^{\pm}$ were 31.6 kcal/mol and −20.6 eu, respectively.

The unimolecular kinetics of the **3** → **4** isomerization are compatible with, but not demanding of an intramolecular rearrangement mechanism. However, thermolysis at 124° of an equimolar mixture of **3** and allyl-(dimethylamino)phenylborane (**6**)[6] gave only **6** (for which the 1,3 shift is degenerate) and **4**. The absence of any radical coupling products and of crossover products allyl(dimethylamino)ethylborane (**7**) and but-

(2) G. S. Zweifel, personal communication.
(3) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).
(4) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.
(5) K. Niedenzu and J. W. Dawson, *J. Amer. Chem. Soc.*, **82**, 4223 (1960).
(6) Satisfactory spectral data and analyses were recorded for new compounds, the details to be reported later in full.
(7) J. Blais, J. Soulié, and P. Cadiot, *C. R. Acad. Sci., Ser. C*, **271**, 589 (1970).
(8) Controls run with added precleaned Pyrex wool demonstrated the absence of surface catalysis. However, these reactions were particularly prone to catalysis by trace impurities, so that scrupulous purification was necessary in order to obtain reproducible kinetic data.
(9) The vinylic region of the pmr spectrum proved most convenient; averages of five integrations were used to compute isomer distributions, and results agreed with distributions calculated from other resonance lines.

2-en-1-yl(dimethylamino)phenylborane (**8**)[10] rules out alternative intermolecular mechanisms and unequivocally establishes the intramolecularity of the 1,3-aminoboryl shift.[11]



Considering the substantial negative $\Delta S^{\ddagger}$ and an E_a well below reasonable estimates of the allylic B–C bond energy,[12-14] a concerted reorganization mechanism such as one involving a four-electron, five-orbital transition state (Figure 1) is suggested.

Mikhailov has reported[1] that the so-called "permanent allylic rearrangement" of allylboranes to symmetrical structures with equivalent α- and γ-carbons in the allylic moiety is inhibited by amines and THF. The **3** → **4** isomerization can be similarly, but not dramatically, retarded. At 101°, the rearrangement of **3** is 3.5 times slower in pyridine than in methylcyclohexane. With lower concentrations of pyridine in methylcyclohexane quenching was negligible. Further inhibition of the isomerization with stronger Lewis bases (*e.g.*, diazabicyclo[2.2.2]octane) was not possible. Dioxane was even less effective as a quencher; less than a 10% rate reduction was noted in dioxane relative to methylcyclohexane.

Unlike allyldialkylboranes, however, the α-methylallyl(amino)borane **3** is subject to Lewis acid catalysis. Addition of 10% by weight of anhydrous $ZnCl_2$ caused complete isomerization of **3** in 24 hr at 101° (*ca.* tenfold acceleration), but with some accompanying decomposition. Anhydrous $MgCl_2$ increased the rate at 101° twofold. Similar catalysis has been observed only for the allylboronate **5**,[7] leading to the conclusion that Lewis-acid catalysis depends on reducing the electron-donor substituent's stabilizing influence.

Finally, considerable thermal stability is clearly conferred upon terminal-olefin allylborane isomers by π-electron-donor substitution at boron. Quantitatively, the activation energy for a 1,3 shift of boron is apparently increased in **3** relative to **1** by *ca.* the π energy of the N⇄B bond. Thus, for allyldialkylboranes **1**, activation energies of *ca.* 10 kcal/mol were found by nmr.[1] The N⇄B rotational barrier for *sec*-butyl(dimethylamino)phenylborane (**9**), a close saturated analog

(10) K. G. Hancock and J. D. Kramer, *J. Amer. Chem. Soc.*, **95**, 3425 (1973); 5% of **8** was easily detectable in a control experiment.

(11) Alternative crossover experiments involving labeling of the amino function are vitiated by transamination reactions which occur at these temperatures.

(12) In the absence of precise thermochemical data, a rough estimate for the allylic carbon–boron bond energy would be *ca.* 68 kcal/mol, based on the well-established resonance energy of the allylic radical[13] and the B–C bond energy in trialkylboranes.[14]

(13) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 5420 (1964).

(14) E. L. Muetterties, Ed., "The Chemistry of Boron and Its Compounds," Wiley, New York, N. Y., 1967.

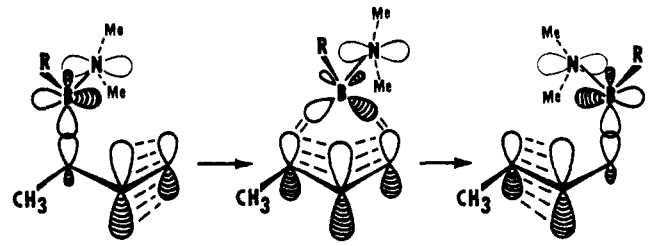


Figure 1. Concerted mechanism for the 1,3-aminoboryl shift.

of **3**, has been determined as 15 kcal/mol.[15] The agreement between the sum of these values and the experimental E_a of 25 kcal/mol is quite satisfactory.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 5860-AC3), is gratefully acknowledged.

(15) (a) T. Totani, H. Watanabe, and M. Kubo, *Proc. Colloq. AMPERE (At. Mol. Etud. Radio Elec.)*, **13**, 366 (1964); (b) H. Watanabe, T. Totani, K. Tori, and T. Nakagawa, *ibid.*, **13**, 374 (1964).

Kenneth G. Hancock,* James D. Kramer
Department of Chemistry, University of California
Davis, California 95616
Received June 7, 1973

Multiconfigurational Aspects of the Metastable Triplet State of Cyclopentanone[1]

Sir:

We have recently described some anomalies[2] in the paramagnetism of triplet cyclopentanone and have suggested[2b] their possible connection with the ring scission which copiously occurs *via* this state.[3] Tacit in our discussion was the assumption that the paramagnetism we had observed arose from a single electronic configuration. In this communication we develop magnetic and optical evidence that triplet cyclopentanone consists, in fact, of several distinct electron–nuclear configurations which interconvert, even at liquid helium temperatures, at rates exceeding 10^3 sec^{-1}. Convergence both of photochemical and spectroscopic interest on such features imparts urgency to our results, and we report them briefly here.

Neat cyclopentanone samples prepared for our previous work exhibited not only the usual triad[4] of zero-field resonances clearly identifiable[2a] with cyclopentanone but also two additional weaker triads (Figure 1(a)) whose PMDR spectra[5] were quite different from the phosphorescence[6,7] of cyclopentanone. Not understanding their origin, we made no mention of them. Since that time we have performed experiments in which

(1) Work supported by the National Science Foundation and the U. S. Army Research Office (Durham).

(2) (a) A. L. Shain, W.-T. Chiang, and M. Sharnoff, *Chem. Phys. Lett.*, **16**, 206 (1972); (b) A. L. Shain and M. Sharnoff, *ibid.*, **16**, 503 (1972).

(3) P. Dunion and C. N. Trumbore, *J. Amer. Chem. Soc.*, **87**, 4211 (1965).

(4) R. W. Brandon, R. E. Gerkin, and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 447 (1962).

(5) D. S. Tinti, M. A. El-Sayed, A. H. Maki, and C. B. Harris, *Chem. Phys. Lett.*, **3**, 343 (1969).

(6) S. R. La Paglia and B. C. Roquitte, *J. Phys. Chem.*, **66**, 1739 (1962).

(7) W. D. Chandler and L. Goodman, *J. Mol. Spectrosc.*, **35**, 232 (1970).