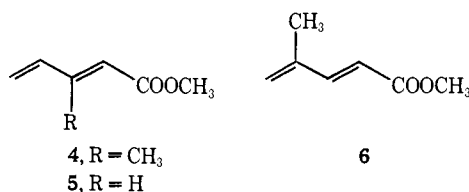


-78° for 3 hr, cooling again to -90° , and quenching with methanol afforded after work-up (addition of aqueous ammonium chloride, vacuum concentration, extraction with ether, and distillation) analytically pure *cis* adduct 2:⁴ bp $62-63^{\circ}$ (0.6 mm); ir max (neat) 1725 cm^{-1} in $>90\%$ yield; less than 0.1% of the (*Z*) isomer of 2⁵ as determined by vpc analysis; adduct with maleic anhydride, mp 112° . Exposure of 2 to 0.1% methanolic hydrochloric acid at 25° for 1 hr resulted in cleavage of the trimethylsilyl ether and lactonization to form in high yield the desired lactone 3,⁴ ir max (neat) 1750 cm^{-1} , as a colorless liquid (evaporatively distilled at $80-85^{\circ}$ (0.01 mm)).

The reaction of vinylcopper reagents with methyl propynoate and methyl 2-butyrate also proceeded smoothly. In these cases good results were obtained using either 1.1 equiv of the reagent $\hat{V}_2\text{CuLi}$ (\hat{V} = vinyl) or 2 equiv of the reagent $\hat{V}\text{Cu}$ (from $\hat{V}\text{Li}$ or $\hat{V}\text{MgCl}$), although the latter generally afforded somewhat higher yields. Thus, addition of methyl 2-butyrate to vinylcopper (generated from 2 equiv of vinyl-lithium and 2 equiv of cuprous iodide under N_2 , -78° , 40 min), quenching with methanol at -78° , and isolation as indicated above for 2 afforded stereospecifically methyl 3-methyl-*trans*-2,4-pentadienoate (4)⁴ as a colorless liquid, ir max (neat) $1729, 1654\text{ cm}^{-1}$, in 74% yield (isolated). Also prepared in a similar manner were 5 (85% yield, identical with an authentic sample⁶) and 6⁴ (isopropenylcopper as reagent, 63% yield).⁷



The ready availability of vinylcopper reagents in pure stereoisomeric form, the stereospecificity and directional specificity of the vinylcopper-ynoic ester addition to form 1,3-dienes in a single step, and the importance of such dienes to synthesis as Diels-Alder components all contribute to the proposition that the route to conjugated dienes which is outlined above will prove to be highly useful.

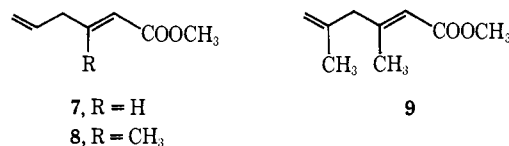
An analogous process for the stereospecific generation of 1,4-dienes starting with allylcopper reagents has also been demonstrated. Thus, reaction of 2 equiv of allylcopper⁸ in ether at -78° under N_2 with methyl propynoate for 2 hr followed by the usual work-up gave methyl *trans*-2,5-hexadienoate (7)⁴ as a colorless liquid: ir max (neat) $1730, 1662, 990, 910\text{ cm}^{-1}$. Similarly prepared were 8⁴ (70%) and 9⁴ (65%), from methyl 2-butyrate and allylcopper or methallylcopper, respectively.

(5) The (*Z*) isomer of 2 was obtained by preparative vpc separation of a mixture of (*E*)- and (*Z*)-2 which resulted from reaction at 0° after an initial period at -78° (see ref 1).

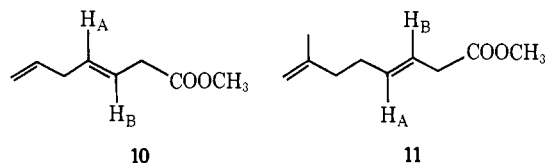
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(7) For related reactions of monoalkylcopper with nonconjugated acetylenes, see J. F. Normant and M. Bourgain, *Tetrahedron Lett.*, 2583 (1971).

(8) Prepared from 1 equiv of allylmagnesium chloride and 1 equiv of cuprous iodide in ether at -30 to -40° for 2 hr (deep red color).



Finally, another and related stereospecific approach to 1,4- and 1,5-dienes was developed based on the addition of copper reagents to 2,4-pentadienoic ester derivatives. Reaction of vinylcopper and methallylcopper at -78° with methyl *trans*-2,4-pentadienoate followed by quenching at -78° with methanol and isolation as outlined above afforded in good yield the *trans*-diene esters 10⁴ and 11,⁴ respectively [ir max (neat) for 10, $1750, 1640, 990, 910, 972$; for 11, $1750, 1640, 972, 890\text{ cm}^{-1}$]. In these instances the protonation of



the intermediate (allylic) organocopper species occurs specifically α to the ester carbonyl. The assignment of *trans* geometry about the disubstituted double bond is indicated by the characteristic infrared absorption for 10 and 11 at 977 cm^{-1} and by $J_{\text{H}_A\text{H}_B} = 16\text{ Hz}$ (nmr in presence of $\text{Eu}(\text{fod})_3$).

The examples recorded above illustrate a number of effective stereospecific operations which can be used to good advantage in synthesis. The processes are also quite versatile, since the intermediate organocopper species can be quenched in ways other than by protonation, for example, by alkylation,^{1,9,10} halogenation,¹ or oxidative coupling,¹¹ the latter leading in a very simple way to rather complex polyenes.¹²

Acknowledgment. This work was assisted financially by grants from the National Science Foundation and the National Institutes of Health.

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 Received February 26, 1972

Photochemical Interconversion of the Geometrical Isomers of Aminoboranes

Sir:

We wish to report that the interconversion of geometrical isomers is a significant primary photoprocess in aminoboranes.¹ This previously undiscerned reaction is of fundamental interest by virtue of its superficial parallels to and mechanistic differences from the corresponding transformation in olefins. It is of practical

(1) Presented in part by K. G. Hancock, D. A. Dickinson, and A. K. Uriarte at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract ORGN-143.

importance for its effect on other potential and actual photochemical reaction pathways in aminoboranes^{1,2} and homologous boron–nitrogen chromophores.³

While photochemical *cis*–*trans* isomerization is well documented in olefin photochemistry,⁴ the corresponding photochemical isomerization about the boron–nitrogen “double bonds” of aminoboranes has not been reported, although aminoboranes are isoelectronic and essentially isosteric⁵ counterparts of similarly substituted olefins. The simple expectation that an analogous *cis*–*trans* photoisomerization reaction should exist in boron–nitrogen photochemistry has been difficult to verify experimentally. The low boron–nitrogen π bond order is reflected in the low barrier to rotation about the B–N π bond in aminoboranes. Depending upon electronic and steric substituent effects, these barriers are in the 10–26 kcal mol⁻¹ range, generally allowing rapid thermal equilibration of *cis* and *trans* isomers in solution near room temperature.^{6,8} However, irradiation of aminoborane solutions at lower temperatures, where thermal isomerization is retarded, permits the optical process to predominate and allows detection of the otherwise invisible photoisomerization phenomenon.

Irradiation of a 0.10 *M* methylcyclohexane solution of *trans*-(benzylmethylamino)benzylphenylborane (**1**)⁸ either at 2537 Å in a Rayonet reactor or with a Corex-D filtered mercury arc for 10 min at –22°⁹ produced an aminoborane isomer mixture containing about 15% of *cis*-(benzylmethylamino)benzylphenylborane (**2**). The composition of the mixture was determined by monitoring the N-benzylic proton nmr resonances at δ 4.20 for **1** and 4.47 for **2**. During the same time period, thermal isomerization accounted for only *ca.* 3% net conversion of the *trans*-aminoborane **1** to the *cis* isomer **2**. Under these same irradiation conditions, attainment of a photostationary state consisting of **2** and **1** in a *cis*:*trans* ratio of 0.91 required only 2 hr. In contrast, to reach a thermal equilibrium mix-

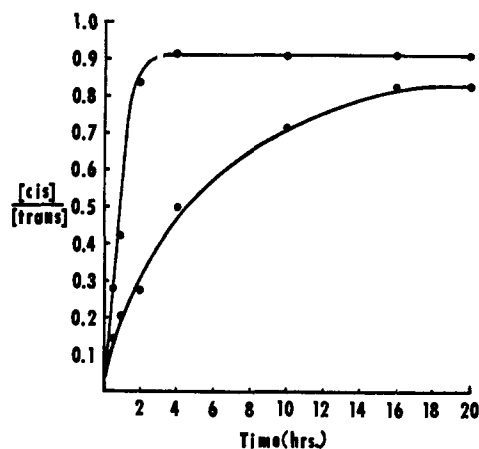
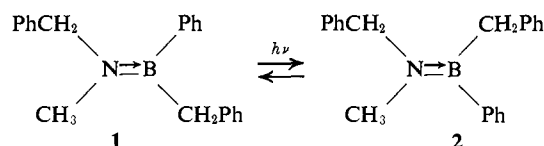


Figure 1. Comparison of photochemical (upper) and thermal (lower) equilibrations of 0.10 *M* *trans*-(benzylmethylamino)benzylphenylborane (**1**) to the *cis* isomer **2** as functions of time at 2537 Å and –22° in methylcyclohexane.

ture of **2** and **1** in a *cis*:*trans* ratio of 0.83 ± 0.05 required *ca.* 18 hr at –22° (see Figure 1).



The quantum yield for the *trans*–*cis* photoisomerization of **1** to **2** is 0.36 ± 0.07 at 2537 Å and –22°. Concurrent thermal and photochemical reversions of **2** to **1** made it necessary to extrapolate quantum yields obtained at 10–40% concentrations of the *cis* isomer back to zero conversion. Interestingly, the quantum efficiency for photoisomerization about the B–N double bond of aminoboranes is comparable in magnitude to values previously determined in stilbenes and piperlynes (Φ *ca.* 0.4–0.5)⁴ and, more recently, about the C–N double bond of oxime ethers ($\Phi = 0.43$ –0.48).¹⁰

The ratio of *cis* and *trans* isomers at the photostationary state is given by the following expression (eq 1).⁴

$$\frac{[\text{cis}]}{[\text{trans}]} = \frac{\Phi_{t \rightarrow c} \epsilon_t}{\Phi_{c \rightarrow t} \epsilon_c} \quad (1)$$

Unlike the stilbenes,⁴ whose *cis* isomers have molar absorptivities diminished by steric inhibitions to conjugation, there apparently are no large differences in the absorption spectra of the *trans* and *cis* isomers of simple aminoboranes. At –22° and 255 nm, extinction coefficients were determined to be 950 cm² mol⁻¹ for *trans* isomer **1** and, by difference, 860 for the *cis* isomer **2**. Use of eq 1 thus allows estimation of the quantum yield for the reverse isomerization, **2** to **1**, as *ca.* 0.4 at 2537 Å and –22°. In light of the close similarity of the thermal and photochemical equilibrium isomer ratios, it is not surprising that photoisomerization of aminoboranes has escaped previous detection. Rapid unimolecular thermal equilibration can normally easily undo any photochemical isomerization that has been accomplished. Although the 0.36 *trans*–*cis* quantum efficiency is reasonably high, significant optical pumping in uncrowded aminoboranes—limited *a priori* by expected similarities in absorptivity

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(7) A rotational barrier of 40.7 kcal in aminoborane was calculated by *ab initio* methods.

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(9) Internal temperatures of solutions were monitored during photolyses with an iron–constantan thermocouple; control experiments demonstrated the absence of any catalytic effect.

and reactivity—will therefore be possible only at low temperatures, low substrate concentrations, and high levels of photon flux.

Nevertheless, efficient photoisomerization about the B–N bond of aminoboranes and homologs is clearly important as an effective, though virtually invisible, energy dissipation mechanism. Such “free rotor” effects are known to limit the photoreactivity of 1,4-dienes^{11,12} and β,γ -unsaturated ketones.^{13,14} Analogous photochemical boron–nitrogen free rotors are evidently partly responsible for the only moderately quantum-efficient boron–carbon cleavage reactions in aminoboranes such as **1**,^{1,2} and may also play a role in photoreactions of B–N diene analogs.^{3,15}

The parallel between aminoborane photoisomerizations and analogous transformations in olefins, imines, and β,γ -unsaturated ketones, however, is apparently only superficial. Whereas triplet states (mostly $\pi-\pi^*$) are the “free rotors” in most cis–trans photoisomerizations, photoinduced rotation about the boron–nitrogen bond in aminoborane **1** evidently occurs in an excited singlet state.¹⁶ Conversion of **1** to **2** photochemically could not be quenched by piperylene, nor could the conversion be sensitized under a variety of conditions: in chlorobenzene ($E_T = 82$ kcal/mol) at 2537 Å; in toluene with 0.06 M xanthone ($E_T = 74$ kcal/mol) at 3500 Å; or in toluene with 0.25 M phenanthrene ($E_T = 62$ kcal/mol) at 3500 Å.

Photochemical cis–trans isomerization in aminoboranes appears to be general,¹ and additional experiments are in progress to probe in detail the electronic distribution of this apparently anomalous singlet-state¹⁶ “free rotor.”

Acknowledgment. Financial support by the Research Corporation and by the Petroleum Research Fund of the American Chemical Society (No. 5860-AC3) is gratefully acknowledged.

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(16) The excitation could be either electronic or vibronic; the possible intermediacy of a vibrationally “hot” ground state either instead of or subsequent to involvement of the electronically excited singlet state is a detail still under study.

(17) Petroleum Research Fund Predoctoral Fellow, 1971–1973.

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Pyrolytic Conversion of Bicyclo[4.2.0]octatrienes to Cyclooctatetraenes. The Tetracyclo[3.2.0.0^{2,8}.0^{5,7}]octene Pathway of Thermal Bond Reorganization

Sir:

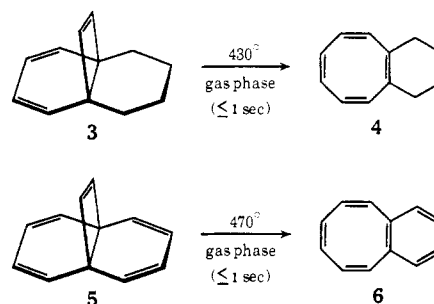
Alicyclic molecules endowed with appreciable degrees of unsaturation usually possess the capability for thermal bond reorganization. In fact, pyrolytic interconversions, in tandem with photoisomerizations, have comprised the chief means for elucidation of the interrelationships of many (CH)_n hydrocarbons, particularly

those with the empirical formulas (CH)₁₀^{1,2} and (CH)₁₂.³ However, only scattered reports of thermal rearrangements in the (CH)₈ series have appeared.^{4–7} Cyclooctatetraene (**1**), for example, affords styrene, benzene, ethylene, acetylene, and under suitable conditions, dihydropentalene at elevated temperatures.^{4,6} Although the role played by bicyclo[4.2.0]octatriene (**2**)⁸ in the



thermal degradations of **1** remains elusive, we have concerned ourselves with the possibility that preformed derivatives of **2** might exhibit previously unrecognized thermal rearrangement by one or more low activation energy pathways which are inaccessible or invisible when starting from **1**.⁹

Gas-phase experiments with the readily accessible unsaturated propellanes **3** and **5**¹⁰ provided immediate indication of skeletal rearrangement. Pyrolysis of **3** at 430° (2.5 mm) in a flow system¹¹ under nitrogen (contact time ≤ 1 sec) resulted in >95% conversion to cyclooctatetraene **4**¹² (60% isolated). Similar treatment of **5** gave benzocyclooctatetraene (**6**)^{12,13} in 53%



isolated yield as the only product. Leaving aside for the moment the question of mechanism, these observations assume particular significance when viewed as the pyrolytic isomerization of a 1,4-disubstituted cyclooctatetraene to the corresponding 1,2 isomer. The actual operation of such a skeletal rearrangement gains

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