$ReSnPh_2H$ (oil); **3**, $[(OC)_5Mn]_2SnH_2$ (yellow, mp 89–92°); **4**, $[(OC)_5Re]_2SnH_2$ (yellow, mp 94–97°); **5**, $[(OC)_5Mn]_3SnH$ (orange, mp 127–130°); **6**, $(OC)_5MnGePh_2H$ (oil); and **7** $(OC)_5ReGePh_2H$ (white, mp 47–49°). The Ge derivatives **6** and **7** are more stable toward heat and O_2 than the Sn compounds **1–5**. The stability of such tin hydrides appears to be sensitive to the nature of the attached transition metal, and our attempts to prepare tin hydrides containing Co, Mo, W, or Fe substituents were unsuccessful.

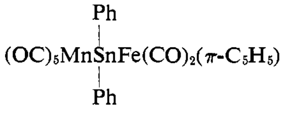
Coupling reactions of transition metal substituted silicon, germanium, and tin hydrides have not been previously reported.[9] Having these transition metal–tin hydrides in hand, we first examined tin–tin coupling reactions modeled after those in eq 1 and 2. Both procedures afforded complex, often intractable, mixtures. Careful analysis of these reactions (*cf.* eq 5)

$$(OC)_5MnSnPh_2H + Et_2NSnPh_3 \longrightarrow Et_2NH + Ph_3SnSnPh_3 + Ph_3SnMn(CO)_5 + \text{unidentified products} \quad (5)$$

indicated varying degrees of disproportionation about tin. However, reactions of these tin hydrides with binuclear metal carbonyls were more successful and in some cases selectively afforded metal oligomers. For example the dihydride **3** reacts with $Co_2(CO)_8$ under ambient conditions forming the pentametallic derivative **8** (eq 6). Similarly at 90° the monohydride **1** reacts with the dimeric iron complex **9** to form the trimer **10** (eq 7).

$$\underset{\mathbf{3}}{H_2Sn[Mn(CO)_5]_2} + Co_2(CO)_8 \xrightarrow{25°} \underset{\mathbf{8}}{[(OC)_4Co]_2Sn[Mn(CO)_5]_2} \quad (6)$$

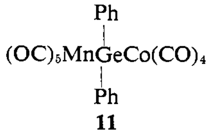
$$HSnPh_2[Mn(CO)_5] + \underset{\mathbf{9}}{[\pi\text{-}C_5H_5Fe(CO)_2]_2} \xrightarrow{90°}$$



$$(OC)_5Mn\overset{Ph}{\underset{Ph}{Sn}}Fe(CO)_2(\pi\text{-}C_5H_5) \quad (7)$$

10

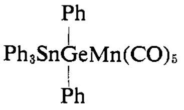
The moderate thermal instability of these tin hydrides limits the scope of this sort of reaction. For example $Mn_2(CO)_{10}$ fails to react with the dihydride **3** up to 120° at which point **3** undergoes self-coupling forming cyclic oligomers of the type $[Sn[Mn(CO)_5]_2]_n$. Because of this thermal instability we turned our attention to the more robust metal substituted germanium hydrides. $Co_2(CO)_8$ reacts with **6** affording the trimer **11** in high yield (eq 8). These germanium hydrides can



$$\underset{\mathbf{6}}{HGePh_2[Mn(CO)_5]} + Co_2(CO)_8 \xrightarrow{25°} (OC)_5Mn\overset{Ph}{\underset{Ph}{Ge}}Co(CO)_4 \quad (8)$$

11

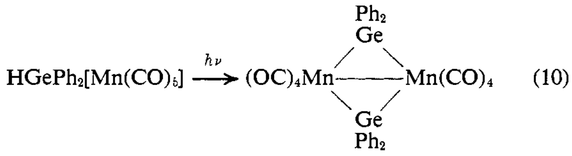
also be coupled with tin amido derivatives as illustrated in the formation of **12** (eq 9). When irradiated the



$$Et_2NSnPh_3 + HGePh_2[Mn(CO)_5] \xrightarrow{25°} Ph_3Sn\overset{Ph}{\underset{Ph}{Ge}}Mn(CO)_5 \quad (9)$$

12

manganese substituted germanium hydride **6** undergoes related self-coupling affording the dimer **13**[10] (eq 10)

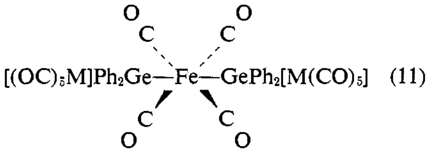


13

which is thought to have the indicated bicyclic structure because of the similarity of its infrared spectrum with that of the structurally characterized silicon analog.[11]

The most interesting reaction is that of $Fe_2(CO)_9$ with **6** and **7** affording the metallic pentamers **14a,b** under mild conditions (eq 11). These new metallic

$$2HGePh_2[M(CO)_5] + Fe_2(CO)_9 \longrightarrow$$



14a, M = Mn
b, M = Re

oligomers **8–14** have been characterized by elemental analyses, vibrational spectroscopy, and molecular weight measurements. A trans configuration about iron is most consistent with the ν_{CO} region in the ir spectra of **14a,b**. If this steric assignment (which is currently being examined by X-ray diffraction) is correct, this reaction (eq 11) takes on great importance because difunctional germanium hydrides may react with $Fe_2(CO)_9$ forming linear intermetallic polymers. The apparent transoid nature of the germanium–iron bond forming reaction augers well for directing linear polymerization, avoiding the formation of cycles. We plan to test this hypothesis.

Acknowledgment. This work was supported by ARPA Contract No. N00014-67-A-0112-0056 and National Science Foundation Grant No. GP20273X.

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[9] The following reaction has been observed

$$2HCl_2SiMn(CO)_5 + Mn_2(CO)_{10} \longrightarrow Cl_2Si[Mn(CO)_5]_2$$

J. K. Hoyano and W. A. G. Graham, unpublished results.

[10] Previously prepared by heating Ph_2GeH_2 with $Mn_2(CO)_{10}$ at *ca.* 160°. Note that in reactions of this type transition metal substituted germanium hydrides cannot be isolated (see ref 4b).

[11] G. L. Simon and L. F. Dahl, *J. Amer. Chem. Soc.*, **95**, 783 (1973), and references cited therein.

[12] National Research Council of Canada Postdoctoral Fellow.

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Photochemical Sigmatropic Rearrangement of Boron. Interconversions of Allyl(amino)boranes *via* Occurrence of a 1,3-Aminoboryl Shift

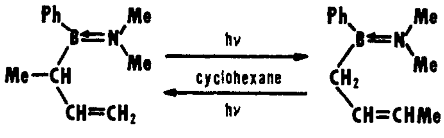
Sir:

One of the more ubiquitous photochemical rearrangement pathways is the 1,3-sigmatropic shift, quantum mechanically and geometrically allowed in the excited state for a suprafacial transfer with configurational retention at the migrating center. Although the actual stereochemistry remains invisible when the migrating group is a π bond and although intimate radical-pair mechanisms rather than concerted reorganizations appear involved in many cases, this formal $[_{\pi}2_s + {}_{\sigma}2_s]$

rearrangement of 1,4-bichromophoric compounds is of wide occurrence and utility. β,γ-Unsaturated ketones, β-diketones, and enol esters are among the common photochemical reactants in these 1,3 shifts;[1] however, the closely related 1,4-dienes are intriguingly less prone to this rearrangement mode than to the 1,2 shift (di-π-methane reaction).[2] The commonly accepted rationalization of this discrepancy has been that an n–π^* excited state was typically involved in the 1,3 shifts, and that the electronic distribution in π–π^* states of 1,4-dienes was only favorable to the 1,2 shift.

We have uncovered in allyl(amino)boranes—isoelectronic, polar-π-bond analogs of 1,4-dienes—a photochemical reaction which is at the present unique: the 1,3 shift of an aminoboryl fragment to give an isomeric allyl(amino)borane. We believe this finding, the very first photochemical migration reaction of boron,[3] suggests that the photochemical reactivity patterns of 1,4-dienes and other 1,4-bichromophoric systems (*e.g.*, β,γ-unsaturated ketones) may be repeated in molecules of quite disparate electronic configurations. Additionally, it becomes clear that the photochemical 1,3 shift is not the exclusive domain of n–π^* singlet states.

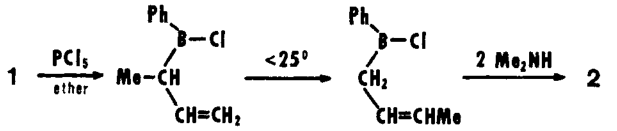
The direct photolysis of but-1-en-3-yl(dimethylamino)phenylborane (**1**)[4] in cyclohexane leads to the reversible formation of the isomeric allyl(amino)borane but-2-en-1-yl(dimethylamino)phenylborane (**2**), formally *via* a 1,3-aminoboryl shift. The photochemical stationary state is reached after *ca.* 100 hr of irradiation and consists of **1** and **2** in a 40:60 mole ratio. Other than surprisingly small amounts of polymer,[5] not yet completely characterized, the but-1-en-3-yl- and crotyl(amino)boranes **1** and **2** are the sole photoproducts.



1 **2**

The synthesis of **1**, which had not been reported previously, was accomplished by modification of the general method of Niedenzu and Dawson.[8,9] Treatment of chloro(dimethylamino)phenylborane with the Grignard reagent prepared from 3-bromo-1-butene and magnesium gave a 59% yield of butenyl(dimethylamino)phenylboranes as an *ca.* 85:15 mixture of **1** and **2**, bp 65–67° (0.5 mm). Because of rearrangement of the Grignard reagent,[10] the same 85:15 mixture of **1**:**2** was obtained starting with 1-bromo-2-butene as well. Although branched isomer **1** could not be freed of straight-chain isomer **2**, pure crotyl(amino)borane **2** could be prepared unambiguously from **1** by two convenient methods.

Reaction of **1** with phosphorus pentachloride[11] in either diethyl ether or carbon tetrachloride gave the corresponding but-1-en-3-yl(chloro)phenylborane (**3**), which isomerized rapidly at room temperature to but-2-en-1-yl(chloro)phenylborane (**4**). Without isolation, crotylchloroborane **4** was treated with 2 equiv of dimethylamine to give **2**. The thermodynamically more stable straight-chain isomer **2** was also prepared in quantitative yield by thermolysis of **1** in a sealed tube at 150°.[12]



3 **4**

Irradiation of a 1.6 *M* solution of **1** (85% **1**, 15% **2**) in degassed cyclohexane-d_{12} at 254 nm for 25 hr resulted in a 50:50 mixture of **1**:**2**. Photolysis for 100 hr produced the 40:60 stationary state of **1**:**2**. Similarly, irradiation of a degassed cyclohexane-d_{12} solution of **2** at 254 nm for 81 hr gave the same 40:60 steady-state mixture of **1**:**2**. The course of the reaction could be monitored by changes in the infrared, uv, and nmr spectra of the isomers. But-1-en-3-ylborane **1** had characteristic ir (neat) 1405 (ν_{B-N}) and 890 cm^{-1}; uv (cyclohexane) λ_{max} 276 nm (ϵ 265), 269 (ϵ 376), and 262 (ϵ 374), ϵ_{254} = 255; nmr (C_6D_{12}, 60 MHz) δ 7.25 (s, 5 H), 5.93 (m, 1 H_x, J_{ax} = 18.0 Hz, J_{bx} = 10.0, J_{mx} = 7.3), 4.92 (m, H_a and H_b, J_{ax} = 18.0 Hz, J_{bx} = 10.0, J_{ab} = 1.5), 2.98 and 2.67 (s, 3 H each), 2.42 (quintet, 1 H_m, J = 7.0 Hz), 0.99 (d, 3 H, J = 7.0 Hz). Crotylborane **2** had ir (neat) 1410 (ν_{B-N}) and 960 cm^{-1}; uv (cyclohexane) λ_{max} 276 nm (ϵ 293), 269 (ϵ 378), and 262 (ϵ 340), ϵ_{254} = 522; nmr (C_6D_{12}) δ 7.31 (s, 5 H), 5.42 (m, 2 H), 2.98 and 2.78 (s, 3 H each), 2.0 (d, 2 H, J = 5.0 Hz), 1.65 (m, 3 H).

The quantum yield for disappearance of **1**, extrapolated to zero conversion, was 0.15, while the figure for **2** at zero reaction was 0.051. Using extinction coefficients measured for **1** and **2** at 254 nm of 255 and 522, respectively, the ratio of **1** to **2** at the photostationary state can be calculated (eq 1).[15] The calculated

$$[\mathbf{1}]/[\mathbf{2}] = \Phi_{2\rightarrow1}\epsilon_2/\Phi_{1\rightarrow2}\epsilon_1 \qquad (1)$$

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[1] (a) See, for example, R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966; (b) an excellent recent compendium of references to the 1,3 shift in β,γ-unsaturated ketones is: K. N. Houk, D. J. Northington, and R. E. Duke, Jr., *J. Amer. Chem. Soc.*, **94**, 6233 (1972).

[2] For leading references, see H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, **94**, 6208 (1972).

[3] A 1,3 shift of a diarylboron moiety was suggested in one postulated mechanism for the photochemistry of tetraarylborates, but no distinction was made between equally allowed thermal and photochemical processes: P. J. Grisdale, J. L. R. Williams, M. E. Glogowski, and B. E. Babb, *J. Org. Chem.*, **36**, 544 (1971).

[4] For facilitation of visual analogy to π bonds in olefins and carbonyls, we have retained in structures here the N$\rightleftarrows$B coordinate-covalent notation, despite misleading charge-distribution implications (*cf.* ref 20 and 21).

[5] Photochemical reactions of aminoboranes[6] and bis(amino)diborane(4)s[7] have been reported to be accompanied by considerable (up to 30%) polymerization.

[6] K. G. Hancock and D. A. Dickinson, *J. Amer. Chem. Soc.*, **95**, 280 (1973).

[7] K. G. Hancock and A. K. Uriarte, submitted for publication.

[8] K. Niedenzu and J. W. Dawson, *J. Amer. Chem. Soc.*, **82**, 4223 (1960).

[9] Satisfactory spectral data and analyses were recorded for new compounds, the details to be reported later in full.

[10] W. G. Young, S. Winstein, and A. N. Prater, *J. Amer. Chem. Soc.*, **58**, 289 (1936).

[11] L. F. Hohnstedt, J. P. Brennan, and K. A. Reynard, *J. Chem. Soc. A*, 2455 (1970).

[12] This thermal 1,3-sigmatropic shift of boron has no close parallel in the chemistry of 1,4-dienes and/or β,γ-unsaturated ketones, but is common in allylboranes.[13] The intriguing mechanistic implications of a detailed study of the thermal shift are reported separately.[14]

[13] B. M. Mikhailov, *Organometal. Chem. Rev., Sect. A*, 1 (1972).

[14] K. G. Hancock and J. D. Kramer, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, 1973, ORGN-94.

[15] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

ratio of 41:59 is in excellent agreement with the experimentally determined 40:60 steady state. The quantum yields for the 1,3-aminoboryl shift are only slightly lower than those measured for the formally analogous 1,3-acyl shifts of β,γ-unsaturated ketones.[16] That the 1,3-shift quantum yields are not higher can probably be attributed to efficient deactivation by the invisible photochemical geometrical isomerization about the boron–nitrogen bond, recently demonstrated to be an important photochemical process in similar aminoboranes.[17]

Attempts to sensitize the 1,3-aminoboryl shift with fluorene (E_T = 68 kcal mol^{-1})[18] failed. However, irradiation of **2** in chlorobenzene (E_T = 82 kcal mol^{-1})[19] at 254 nm (chlorobenzene absorbing *ca.* 85% of incident light) resulted in formation of very small amounts of **1** and a new photoproduct not yet identified. These experiments indicate that the 1,3-aminoboryl shift, like the analogous 1,3 shift in β,γ-unsaturated ketones, is a singlet-state process.

The fact that allyl(amino)boranes, which are isoelectronic with 1,4-dienes, undergo a 1,3 shift that is analogous to the reactivity of β,γ-unsaturated ketones (among others) rather than of 1,4-dienes suggests some interesting inferences about the relative importance of various factors determining photochemical reaction mechanisms. Extended Hückel and *ab initio* calculations indicate the B–N bond in aminoboranes has a net polarization in the sense $B^{\delta+}$–$N^{\delta-}$,[20,21] paralleling the charge distribution in a carbonyl. Photochemical aminoboron–carbon cleavage in the 1,3 shift thus closely resembles the carbonyl–carbon α-cleavage step of a β,γ-unsaturated ketone, despite the absence of strictly nonbonding electrons and n–π^* states in the aminoborane. Although it is thus clear that the aminoborane excited singlet in the 1,3 shift is surely not n–π^*, both π–π^* and σ–π^* singlets are compatible with present data. Calculations on simple aminoboranes in fact predict S_1 to be σ–π^*.[20,21] The corresponding σ-HOMO in allyl(amino)borane would be largely B–C bonding so that α cleavage (α to boron) and a 1,3 shift would be probable in the σ–π^* state. Thus, a general reactivity parallel may exist between ketone n–π^* singlets and σ–π^* aminoborane singlets.[22] Alternatively, mixing of the B–N π system with the π systems of the allyl and/or phenyl moieties may cause the π–π^* state to drop below σ–π^* in allyl(amino)boranes.[23] In this case, the difference in reactivity between a π–π^* 1,4-diene singlet and an allyl(amino)borane π–π^* singlet seems most likely due to the known preference of olefinic π–π^* singlets for a 90°-twisted geometry, an arrangement expected to favor the 1,2 bonding (di-π-methane reaction) observed in 1,4-dienes over the nonobserved 1,3 bonding. In contrast, calculations on aminoboranes predict no such predilection for excited-state twisting.[20,21]

At the moment, we lean toward the hypothesis that the reordering of energy levels occasioned by the electronegativity effects in the B–N bond makes aminoboranes more analogous to ketones than to olefins. However, we are presently exploring the full scope of allylborane photochemistry, including identification of excited states.

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

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[16] See, for example, K. G. Hancock and R. O. Grider, *Tetrahedron Lett.*, 1367 (1972).

[17] K. G. Hancock and D. A. Dickinson, *J. Amer. Chem. Soc.*, **94**, 4396 (1972).

[18] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

[19] S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964).

[20] R. Hoffmann, *J. Chem. Phys.*, **40**, 2474 (1964).

[21] D. R. Armstrong, B. J. Duke, and P. G. Perkins, *J. Chem. Soc. A*, 2566 (1969).

[22] Another example of the σ–π^* aminoborane–n–π^* ketone analogy may be found in comparing biacetyl and bis(amino)diborane(4) photochemistry.[7]

[23] Conjugation of an aminoborane with a carbon π system has been shown to cause raising of a π-MO energy and lowering of the B-σ-HOMO energy. With strong interaction, inversion of σ and π levels will occur.[24]

[24] A. K. Uriarte and K. G. Hancock, *Inorg. Chem.*, in press.

[25] National Defense Education Act (Title IV) Fellow at the University of California, Davis.

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Received November 10, 1972

Participation of an sp Hybrid Center in the Di-π-methane Rearrangement[1]

Sir:

In an extension of our studies on the di-π-methane rearrangement[2] we have investigated *cis*- and *trans*-1,5-diphenyl-3-methyl-3-methoxy-1-penten-4-yne (**1**), in which the di-π moieties bound to the sp^3 center are styryl and phenylethynyl groups. Our objective was to assess the migratory potential of an sp center and to evaluate the effect of C-1 stereochemistry on the reaction course.[3]

The enyne **1b** was prepared by addition of phenylethynylmagnesium bromide to benzalacetone and subsequent etherification of the resulting alcohol.[4] The cis isomer **1a** was obtained from **1b** by acetophenone-sensitized photoisomerization (at 350 nm).[5a] The assignment of cis and trans stereochemistry is based upon infrared and 100-MHz pmr data.[5b] A 10.30-μ band characteristic of trans 1,2-disubstituted alkenes appears in the infrared spectrum of **1b** and is absent in that of **1a**.[6a] Trans vicinal coupling constants for vinyl protons in isomeric 1,2-disubstituted alkenes are generally larger than their cis counterparts as is the case for **1a** and

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[1] Presented in part by J. Perreten and G. W. Griffin at the 27th Southwestern Regional Meeting of the American Chemical Society, San Antonio, Tex., Dec 1–3, 1971, Abstract No. 238.

[2] B. Halton, M. Kulig, M. A. Battiste, J. Perreten, D, M. Gibson, and G. W. Griffin, *J. Amer. Chem. Soc.*, **93**, 2327 (1971).

[3] An independent investigation of the effect of stereochemistry of a methyl group at C-1 on the rearrangement was recently reported. See H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6267 (1970).

[4] Satisfactory analyses and mass spectra were obtained on all compounds with the exception of **2b**.

[5] (a) Irradiations were conducted in a Rayonet RPR-100 reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 8-W 254- or 350-nm lamps; (b) pmr spectra were recorded on a Varian HA-100 instrument.

[6] (a) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 25; (b) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, England, 1969, p 301; (c) *ibid.*, p 286.