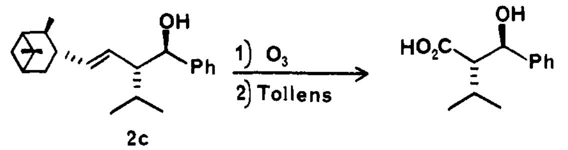
Table I. Optically Active Threo Homoallylic Alcohols **2** from Propargylic Acetates **3**

config of $3^{a,c}$	R	R′	R″	% yield^d of 2	% ee of **2**	threo/erythro^f	config of **2**	entry
S	*n*-C_5H_{11}	cyclohexyl	CH_3	76	50.2^e	96/4	*S,R*	a
R	*i*-Pr	cyclohexyl	Ph	70	60^b	99/1	*R,R*^{g}	b
S	*n*-C_5H_{11}	isopinocampheyl	*i*-Pr	63	80^a	96/4	*S, R*	c
S	*n*-C_5H_{11}	isopinocampheyl	*n*-C_5H_{11}	62	85^a	96/4	*S,R*	d
S	*n*-C_5H_{11}	isopinocampheyl	Ph	72	79^a	98/2	*S,S*^{g}	e

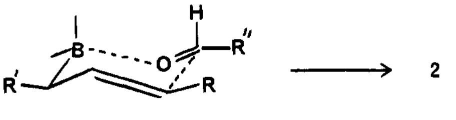
[a] Optical purities determined by 90-MHz ^{1}H NMR spectroscopy with tris[*d,d*-dicampholylmethanato]europium(III). [b] Shift reagent used is tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium(III). [c] All % ee >99% except for **3b**, which is 90% ee. [d] All yields are isolated. [e] Determined by HPLC separation of the ester from (*S*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride.[11] [f] Determined via ^{13}C NMR comparison with threo/erythro mixtures. [g] Note change in priority: phenyl > alkyl.

our results, **2c** was converted to *threo*-1-isopropyl-2-hydroxyhydrocinnamic acid via ozonolysis followed by Tollens oxidation (eq 3).[7] The structure of this acid has previously been unambiguously determined.[8] The relative amounts of threo to erythro **2a**–**2e** were determined by comparison of the 22.6-MHz ^{13}C spectra of **2a**–**2e** and of a mixture of threo and erythro **2a**–**2e**.[9] The ratios in **2a** were further confirmed by VPC and in **2b** by ^{1}H NMR spectroscopy. The absolute configuration was determined by mechanistic considerations of the established "chair" transition state[6] for allylborane condensations with the assumption that all groups occupy an equatorial position as depicted in eq 4. The absolute configuration was further confirmed by comparison of the NMR spectrum in the presence of chiral shift reagents to the NMR spectrum of similar compounds of known configuration in the presence of chiral shift reagents. The trans geometries of **2a**–**2e** were determined by ^{1}H vinyl coupling constants (15.3–15.6 Hz), IR data, and ^{13}C calculations.[10] It should be noted that Yamamoto[6i] obtains cis olefins from condensations of α-silyl- or α-stannyl-substituted crotylboranes with aldehydes and that Hoffmann[6f] obtains predominately cis products from condensations with esters of 1-butenyl-3-boronic acid. Presumably steric factors in their examples force R′ into an axial position.



2c

(3)



(4)

The enantiomeric purity of the final product **2** is essentially the same as the enantiomeric purity of the allylborane **1**. Thus the chirality of the boron–carbon bond of **1** is transferred to the two new centers of **2** with essentially 100% efficiency. Since the loss of enantiomeric purity occurs during the transformation of **4** to **1**, development of more efficient processes for preparing enantiomerically enriched allylboranes should led to an additional increase in the enantiomeric purity of the final product. In a previous study in our laboratories[3] it was found that the enantiomeric enrichment of allylborane **1** (and hence the alcohol **2**) increased with the steric bulk of the migrating species R′. Table I illustrates that a large increase in % ee is obtained by using isopinocampheyl as the migrating species, instead of cyclohexyl. The increased % ee is evidently due to steric effects and not to the chirality of the isopinocampheyl group. Thus when diisopinocampheylborane is used with racemic acetate, the allylborane is racemic at the boron–carbon bond as shown by oxidation of the allylborane to an alcohol that is racemic at the alcohol center.

This procedure thus makes available a "one-pot" method (starting from the propargylic acetate) for carbon–carbon bond formation that is both enantio- and diastereoselective. The selectivity is for threo isomers, which nicely compliments the many existing methods for generating erythro isomers. The homoallylic alcohols formed can be cleaved to form aldol-type products, which we are currently studying as possible precursors to natural products.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Committee on Research, University of California, Riverside, for support of this research.

Registry No. 1a, 81206-09-9; **1b**, 81206-10-2; **1c**, 81206-11-3; **2a**, 81206-12-4; **2b**, 81206-13-5; **2c**, 81206-14-6; **2d**, 81206-15-7; **2e**, 81206-16-8; **3a**, 54315-38-7; **3b**, 81206-17-9; dicyclohexylborane, 1568-65-6; diisopinocamphenylborane, 24041-59-6; acetaldehyde, 75-07-0; benzaldehyde, 100-52-7; 2-methylpropanol, 78-84-2; hexanal, 66-25-1.

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(7) Barua, R. K.; Barua, H. B. *Biochem. J.* **1964**, *92*, 21c.

(8) Mulzer, J.; Zippel, M.; Bruntrup, G.; Segner, J.; Finke, J. *Liebigs Ann. Chem.* **1980**, 1108.

(9) Mixtures were prepared by Jones oxidation followed by lithium aluminum hydride reduction of **2a**–**2e**.

(10) Silverstein, R. M.; Bassler, C. G.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; pp 260–264.

(11) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

Polymerization of Ethylene by an Alkylidene Hydride Catalyst

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In spite of the fact that transition-metal-catalyzed polymerizations of ethylene and propylene were discovered more than 25 years ago, surprisingly little is known about the most important step in the polymerization reaction, the mechanism of forming the carbon–carbon bond.[1] There is overwhelming evidence that the polymerization process consists of what is overall "insertion" of an olefin into a metal–alkyl bond or, perhaps more accurately, migration of the alkyl to a coordinated olefin. Yet a nagging question is why do the vast majority of *isolable* metal alkyl complexes not react with ethylene readily, while many which are presumably prepared in situ (using a main-group alkylating agent) react rapidly to produce ethylene oligomers or polymers? We report here what we believe to be the first example of a well-characterized ethylene polymerization catalyst, one that happens to be slow enough so that polymer-chain growth can be monitored and that does not require a Lewis Acid cocatalyst. The fact that the catalyst is an alkylidene hydride complex should justify a reevaluation of the possible mechanisms for polymerizing ethylene and propylene.

Tantalum neopentylidene hydride complexes have been prepared by reducing tantalum(V) neopentyl complexes by two electrons.[2] We discovered that although one of these, $Ta(CHCMe_3)(H)L_3Cl_2$

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(1) Boor, John, Jr. "Ziegler-Natta Catalysts and Polymerizations"; Academic Press: New York, 1979.

(2) Fellmann, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6608.

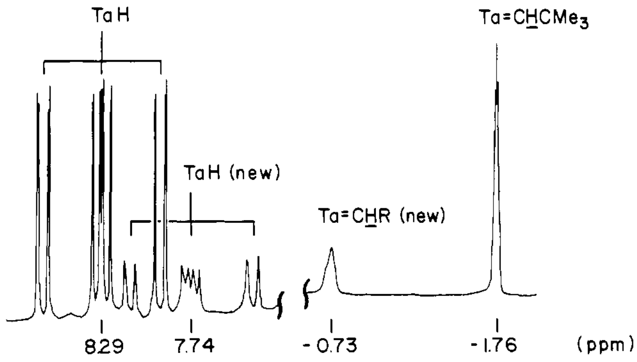


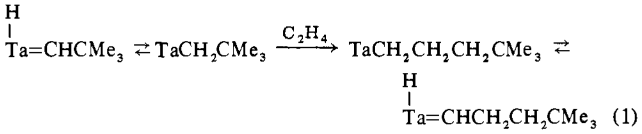
Figure 1. 270-MHz ^{1}H NMR spectrum of a sample of Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$I$_2$ in C$_6$D$_6$ after reaction with 1 equiv of ethylene in toluene at 0 °C (PMe$_3$ resonances omitted; ratio of Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$I$_2$ to Ta(CHR)(H)(PMe$_3$)$_3$I$_2$ is approximately 3:1).

(L = PMe$_3$), did react with ethylene readily, no product of rearrangement[3] or metathesis[3] of an intermediate α-*tert*-butyltantalacyclobutane complex was observed.[4] High-boiling organic products were formed, but we could not obtain consistent results. Only when we prepared the analogous diiodide did we observe a consistent and reproducible reaction with ethylene.[5]

Green Ta(CHCMe$_3$)(H)L$_3$I$_2$ reacts with 1-5 equiv of ethylene in toluene to yield a thermally stable species whose ^{1}H NMR spectrum shows a new alkylidene α-proton signal at −0.73 ppm and a new hydride signal at 7.74 ppm (Figure 1). A significant amount (~50%) of Ta(CHCMe$_3$)(H)L$_3$I$_2$ remains. When C$_2$D$_4$ is used the new alkylidene α-proton signal and the new hydride signal are absent in the ^{1}H NMR spectrum, but new signals for D$_\alpha$ and TaD can be observed at −0.81 and 7.70 ppm in the ^{2}H NMR spectrum. When mixtures of Ta(CHCMe$_3$)(H)L$_3$I$_2$ and Ta(CHR)(H)L$_3$I$_2$ are hydrolyzed with CF$_3$CO$_2$H or HCl, the expected amount of neopentane is produced by hydrolysis of the Ta(CHCMe$_3$)(H)L$_3$I$_2$ in the mixture (checked separately) while hydrocarbons produced by hydrolysis of Ta(CHR)(H)L$_3$I$_2$ in the mixture are the linear hydrocarbons Me$_3$C(CH$_2$CH$_2$)$_n$CH$_3$ where n = 1–5. This result suggests that Ta(CHR)(H)L$_3$I$_2$ is Ta[CH(CH$_2$CH$_2$)$_n$CMe$_3$](H)L$_3$I$_2$ formed by reaction of Ta(CHCMe$_3$)(H)L$_3$I$_2$ with n equiv of ethylene. On the basis of mass balance[6] Ta[CH(CH$_2$CH$_2$)$_n$CMe$_3$](H)L$_3$I$_2$ is the only product of the reaction between Ta(CHCMe$_3$)L$_3$I$_2$ and ethylene.[7] The absence of significant amounts of hexane, octane, etc. in the hydrolysis products suggests that chain transfer to give Ta[CH(CH$_2$CH$_2$)$_n$CH$_3$](H)L$_3$I$_2$ is not appreciable under these conditions.

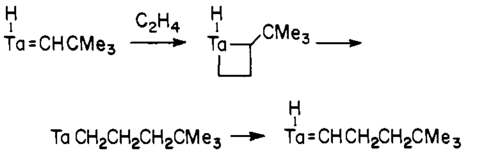
When Ta(CHCMe$_3$)(H)L$_3$I$_2$ in toluene is treated with excess ultrapure ethylene at 1 atm, a solid begins to separate from solution after approximately 15 min. Treating a 0.30-g sample of Ta(CHCMe$_3$)(H)L$_3$I$_2$ with ethylene for 2 days yielded a pale green solid that weighed 1.05 g. The filtrate absorbed little additional ethylene, but when the thoroughly rinsed pale green solid was suspended in fresh toluene and exposed to ethylene, it *continued to take up ethylene*, although at less than 25% of the initial rate. After an additional 2 days under ethylene its weight had increased to 1.20 g. We propose that the pale green solid in part consists of a living polymer, Ta[CH(CH$_2$CH$_2$)$_n$CMe$_3$](H)L$_3$I$_2$. Stirring a 0.77-g sample of the green polymer in toluene under molecular hydrogen (30 psi) for 1 day gave 0.70 g of a white polymer and an orange solution.[9] A field-desorption mass spectrum[10] of the white organic polymer (dissolved in hot mesitylene) showed that only 10–20% of the chains have the alkane empirical formula, C$_n$H$_{2n+2}$. The majority of the chains are olefinic (C$_n$H$_{2n}$), presumably the result of chain transfer. Further evidence that chain transfer has occurred is the fact that the fraction of the polymer that contains on the order of 50–70 carbon atoms is approximately a 1:1 mixture of odd-carbon and even-carbon chains. By starting with Ta(CDCMe$_3$)(D)L$_3$I$_2$ we have shown that all the patterns for odd-carbon chains are shifted up by 2 mass units in the FD mass spectrum of the white polymer. Therefore, the odd-carbon chains probably contain the five carbon atoms of the original neopentylidene ligand while the even-carbon chains are authentic linear polyethylene.

There are two ways of viewing the reaction between Ta(CHCMe$_3$)(H)L$_3$I$_2$ and ethylene. The one shown in eq 1 (non-



$$\overset{H}{\overset{|}{Ta}}{=}CHCMe_3 \rightleftarrows TaCH_2CMe_3 \xrightarrow{C_2H_4} TaCH_2CH_2CH_2CMe_3 \rightleftarrows \overset{H}{\overset{|}{Ta}}{=}CHCH_2CH_2CMe_3 \quad (1)$$

essential ligands omitted) contains in part the classical Cossee-type step[11] where ethylene "inserts" into the tantalum(III)–neopentyl and subsequent tantalum(III)–alkyl bonds. The alkyl complexes are in equilibrium with the preferred tantalum(V) alkylidene hydride complexes. That Ta(CHCMe$_3$)(H)L$_3$I$_2$ and (presumably) Ta(CH$_2$CMe$_3$)L$_3$I$_2$ do interconvert has been shown by magneitzation transfer experiments. The alternative shown in eq 2



(2)

is analogous to that proposed recently by Ivin, Rooney, and Green[12] to explain the stereoselective polymerization of propylene by Ziegler–Natta catalysts. We do not think it will be easy to distinguish between these two possibilities, if it is possible at all. But since alkylidene ligands in other tantalum(V) complexes react extremely rapidly with olefins[3,13] and since there are few examples of isolable metal alkyl complexes that react rapidly with ethylene,[14]

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[3] Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1440.

[4] Fellmann, J. D. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1980.

[5] Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$I$_2$ was prepared by treating Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$Cl$_2$ with Me$_3$SiI. Anal. Calcd for TaC$_{14}$H$_{38}$P$_3$I$_2$: C, 22.90; H, 5.18. Found: C, 22.44; H, 5.14. ^{1}H NMR (C$_6$D$_6$) δ 8.29 (dddd, 1, J_{HP} = 18, 92, 104 Hz, J_{HH} = 1.5 Hz, TaH), 1.82 (d, 9, J_{HP} = 9 Hz, PMe$_3$); 1.54 (d, 9, J_{HP} = 3 Hz, PMe$_3$), 1.51 (d, 9, J_{HP} = 2 Hz, PMe$_3$), 0.95 (s, 9, CHC*Me*$_3$), −1.76 (m, 1, C*H*CMe$_3$); ^{13}C NMR (C$_6$D$_6$, gated {^{1}H}) δ 221.1 (d, J_{CH} = 71 Hz, *C*HCMe$_3$), 46.7 (s, CH*C*Me$_3$), 32.9 (q, J_{CH} = 127 Hz, CHC*Me*$_3$), 25.4 (qd, J_{CP} = 27, J$_{CH}$ = 133 Hz, PMe$_3$), 23.2 (qd, J_{CP} = 29, J$_{CH}$ = 131 Hz, PMe$_3$), 19.3 (qd, J_{CP} = 25, J_{CH} = 129 Hz, PMe$_3$); ^{31}P NMR (C$_6$D$_6$) δ −29.0 (m, P$_A$P$_B$), −43 (m, P$_C$).

[6] In a typical experiment, Ta(CHCMe$_3$)(H)(PMe$_3$)$_3$I$_2$ (0.3 g, 0.41 mmol) was treated with 2 equiv of ethylene in toluene. The volatiles were removed in vacuo. An ^{1}H spectrum of the green oily residue in C$_6$D$_6$ showed the new complex to be present in 50% yield. The mixture was then dissolved in toluene and treated with 2.8 mmol of CF$_3$CO$_2$H, and the volatiles were removed in vacuo for examination by GLC; CMe$_4$ = 0.174 mmol (85% of theory), C$_7$ = 0.046, C$_9$ = 0.019, C$_{11}$ = 0.047, C$_{13}$ = 0.053, C$_{15}$ = 0.017; total = 0.182 mmol (89% yield). The identity of the first four new alkanes (C$_7$, C$_9$, C$_{11}$, C$_{13}$) were confirmed by GLC/mass spectroscopy. The mass spectra of the first two (C$_7$ and C$_9$) were identical with those of authentic Me$_3$CCH$_2$CH$_2$CH$_3$ and MeCCH$_2$CH$_2$CH$_2$CH$_2$CH$_3$.

[7] Under some conditions we have observed formation of complexes of the type Ta(CHR′)(CH$_2$PMe$_2$)L$_2$I$_2$ (R′ = CMe$_3$, etc.). Ta(CHCMe$_3$)(CH$_2$PMe$_2$)L$_2$Br$_2$ was the first complex of this type to be prepared (by treating Ta(CH$_2$CMe$_3$)$_3$Br$_2$ with PMe$_3$[8]). This type of species will be discussed in detail elsewhere.

[8] Rupprecht, G. A. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1979.

[9] Ta(CHCMe$_3$)(H)L$_3$Cl$_2$ reacts with molecular hydrogen to give green [TaL$_2$Cl$_2$H$_2$]$_2$.[4] Ta(CHCMe$_3$)(H)L$_3$I$_2$ reacts with H$_2$ to give an analogous compound that is orange. We assume that the metal is removed from the living polymer upon treating it with H$_2$. (Addition of molecular hydrogen is the favored means of restricting polymer chain length in Ziegler–Natta catalyst systems.[1])

[10] Beckey, H. D. "Principles of Field Ionization and Field Desorption Mass Spectrometry"; Pergamon Press: New York, 1977.

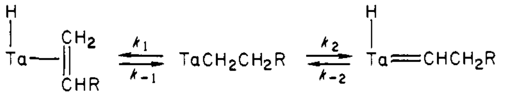
[11] Cossee, P. *J. Catal.* **1964**, *3*, 80–88.

[12] Ivin, R. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604–606.

[13] (a) Fellmann, J. D.; Schrock, R. R.; Rupprecht, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5752. (b) Schrock, R. R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73–83. (c) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558.

we feel that the second alternative is more plausible.

One of the most interesting aspects of the mechanism shown in eq 2 is the last step, an α-elimination reaction to give the new alkylidene hydride complex.[17] We want to point out that our results do not *necessarily* imply that β elimination to give an olefin hydride intermediate is relatively slow. It is possible that although $K_2 > K_1$ (where $K_2 = k_2/k_{-2}$ and $K_1 = k_1/k_{-1}$), k_1 is still greater than k_2 (eq 3), i.e., β elimination is still faster. If this is true, it



$$\mathrm{H{-}Ta{-}(CH_2{=}CHR)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{TaCH_2CH_2R} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{H{-}Ta{=}CHCH_2R} \qquad (3)$$

must also be true that the olefin hydride complex is *relatively* stable toward displacement of $CH_2{=}CHR$ by ethylene under the reaction conditions that we employed here. Chain transfer is most likely a result of an occasional displacement of $CH_2{=}CHR$ from the olefin hydride complex.

Acknowledgment. We thank the National Science Foundation (Grant CHE 79 05307 to R.R.S.) and, in part, the National Institutes of Health (Research Grant RR00317 to Professor K. Biemann) for support of this research. We also thank Professor Mark Wrighton for suggesting the FD mass spectroscopic analysis and Dr. Catherine Costello for her cooperation in obtaining the FD mass spectrum.

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(14) An example of a complex that reacts slowly with ethylene in a manner consistent with ethylene "insertion" into the metal–alkyl bond is $Co(\eta^5\text{-}C_5H_5)(PPh_3)Me_2$.[15] There are some less well-studied examples.[1] A recent report[16] of the stepwise reaction of a metal–alkyl complex $(Lu(\eta^5\text{-}C_5Me_5)_2R)$ with an olefin (propylene) is the only other example of observed polymer growth at a well-characterized metal center. It is an especially important observation since it can be argued that propylene inserts into a metal–alkyl bond (the Cossee mechanism), not a metal–alkylidene bond.

(15) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 3973.

(16) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337–339.

(17) The recently observed equilibrium between $Ta(CHCMe_3)(C_2H_5)L_2Cl_2$ and $Ta(CH_2CMe_3)(C_2H_4)L_2Cl_2$ ($L = PMe_3$)[18] is an example of α elimination competing successfully with β elimination.

(18) Fellmann, J. D.; Schrock, R. R.; Traficante, D. D. *Organometallics* **1982**, *1*, 481.

Photochemistry of 2,3-Diazabicyclo[2.1.1]hex-2-ene. β C-C Cleavage to a Stereorandom Triplet Biradical

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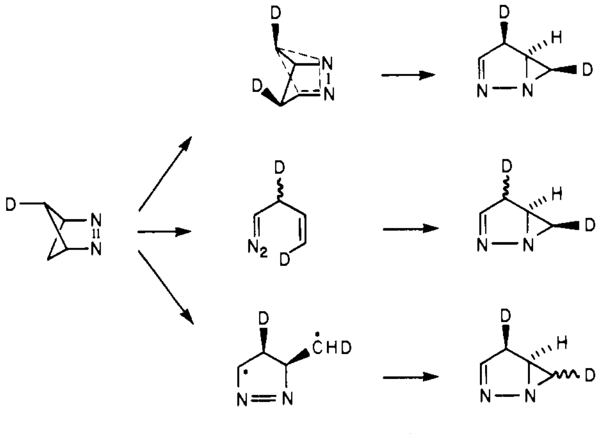
Received November 20, 1981

The photochemistry of 1,2-diazenes (azo compounds) has been intensively studied because of its potential synthetic utility,[1] the unique dependencies on structural variations,[2] and the theoretical interest in this simple chromophore.[3,4] We describe herein the photochemistry of 2,3-diazabicyclo[2.1.1]hex-2-ene (**1**),[5] the smallest and most strained member of the series of homologous bicyclic azoalkanes. This simple compound displays a rich and varied photochemistry that is quite different from that of related compounds.

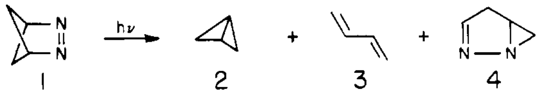
Table I. Product Yields from Photolysis of 1

conditions	2	3	4
direct, 25 °C	55	17	28
direct, −100 °C	23	13	64
sensitized, 25 °C	6	10	84

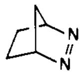
Scheme I



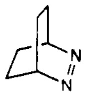
Photolysis of **1** in benzene or cyclohexane produces bicyclo-[1.1.0]butane (**2**), butadiene (**3**), and 1,2-diazabicyclo[3.1.0]-hex-2-ene (**4**) in overall quantitative yield.[6] Table I shows that the relative yields are dependent on temperature and spin multiplicity. We have determined the quantum yield[7] for overall decomposition of **1** upon direct photolysis at 25 °C to be 0.45 ± 0.05, and thus **1** is not a "reluctant" azoalkane.[8] The next higher homologue **5** also loses N_2 efficiently, but the next symmetrical homologue **6** is quite photoinert.[8] Fluorescence is observed for **1** with $\lambda_{max} = 337$ nm (hexane), and a near mirror image relationship with the absorption spectrum, as expected for such a rigid structure.[3]



1 2 3 4



5



6

The most surprising feature of the photochemistry of **1** is the formation of the nitrogen-retained product **4**. It is the parent of a ring system that has recently been the subject of several studies,[9] and its structure was assigned on the basis of spectral data.[10] One can envision three different routes to **4**. It is formally related to **1** by a [1,3]-sigmatropic shift, and such a photochemically allowed, concerted reaction seems plausible, at least upon direct excitation.

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(1) Adam, W.; DeLucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762–779.

(2) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99–150.

(3) Mirbach, M. J.; Liu, K.-C.; Mirbach, M. F.; Cherry, W. R.; Turro, N. J.; Engel, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 5122–5129.

(4) Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1978**, *100*, 2639–2642.

(5) Chang, M. H.; Dougherty, D. A. *J. Org. Chem.* **1981**, *46*, 4090–4092.

(6) Photolyses were carried out in Pyrex vessels using either a 450-W Hanovia medium-pressure mercury lamp or a 1000-W Oriel Xe arc. Products were analyzed by a combination of NMR spectroscopy, GC, and HPLC, and control experiments demonstrate that all products are stable to the various reaction conditions.

(7) Quantum yields were determined by using **5** as an actinometer ($\Phi = 1.0^2$) in photolyses to low conversion. Identical results were obtained whether monochromatic or broad-band irradiation was used.

(8) See, for example, ref 2 and Engel et al. (Engel, P. S.; Nalepa, C. J.; Leckonby, R. A.; Chae, W.-K. *J. Am. Chem. Soc.* **1979**, *101*, 6435–6437).

(9) (a) Nishizawa, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1980**, *102*, 1776–1777. (b) Padwa, A.; Ku, H. *Tetrahedron Lett.* **1980**, *21*, 1009–1012. (c) Miyashi, T.; Fujii, Y.; Nishizawa, Y.; Mukai, T. *J. Am. Chem. Soc.* **1981**, *103*, 725–727. (d) Padwa, A.; Rodriquez, A. *Tetrahedron Lett.* **1981**, *22*, 187–190.

(10) ^{1}H NMR (500 MHz; coupling constants from extensive decoupling and complete spectral simulation; n = *endo*; x = *exo*; $CDCl_3$): δ 7.29 (H3), 3.06 (H4x), 3.03 (H4n), 2.71 (H5), 2.29 (H6x), 1.11 (H6n); J (in Hz) H4n–H4x = 18, H4x–H5 = 7, H4n–H5 = 3, H6n–H6x = 1.5, H5–H6x = 7, H5–H6n = 5, H3–H4n = H3–H4x = H3–H6n = 1.2, H3–H6x = 1.5, H4x–H6n = H4n–H6n = 0.6. ^{13}C NMR ($CDCl_3$) δ 36.78 (CH), 39.05 (CH_2), 39.76 (CH_2), 158.88 (C=N). IR (CCl_4) 3050, 3000, 2930, 2840, 1595, 1435, 1295, 1260 cm^{-1}. UV (hexane) 210 (ϵ 1295), 243 nm (ϵ 645). Mass spectrum: calcd for $C_4H_6N_2$, 82.0531; found, 82.0529, 82 (17), 55 (100), 54 (86), 53 (77), 41 (15), 40 (11).

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