# Thermolysis of Allylic Azoalkanes

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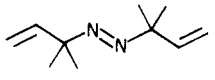
The synthesis and thermolysis kinetics of five new allylic azoalkanes are described in detail. The effect of one and two bridgehead vinyl groups (compounds **3** and **4**) on the rate of nitrogen loss from 2,3-diazabicyclo-[2.2.2]oct-2-ene suggests that **3** decomposes by simultaneous but asynchronous C–N bond stretching. On the other hand, the symmetrical compounds **1** and **4** probably follow the synchronous bond-breaking pathway. Thermolysis rates for three allylic azoalkanes (**5**, **6**, and **9**) were found to be very similar to that of known compound **2**. Thus neither considerable geometric distortion of the olefin nor addition of alkyl groups beyond two has much effect on allylic radical stability. The similarity of **2** and **9** may arise from a previously predicted saturation effect.

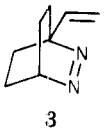
Azoalkanes are the cleanest and most convenient precursors for a wide variety of radicals and biradicals.[1-3] Although a few azoalkanes which produce allylic radicals have been prepared,[4-7] the radicals and most of the azo compounds were acyclic. The present report deals with two new kinds of allylic azoalkanes: derivatives of 2,3-diazabicyclo[2.2.2]oct-2-ene (**1**) and cycloalkenyl analogues of **2**.

**1**

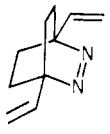


**2**

One of us noted recently[8] that compound **1** is much more stable thermally than its 10 kcal mol$^{-1}$ strain energy would predict. An attempt to probe its decomposition mechanism did not provide a conclusive answer because the effect of bridgehead methyl groups was found to be anomalously small. To circumvent this problem, we have now prepared bicyclic azoalkanes **3** and **4**, in which thermolysis should



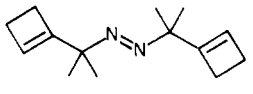
**3**



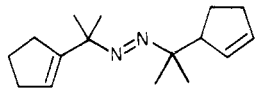
**4**

be markedly accelerated by the bridgehead vinyl groups. It was expected that application of the Ramsperger criterion[4-10] would distinguish stepwise from simultaneous C–N bond rupture. Product and photochemical studies on **3** and **4** will be reported separately.[11]

The second set of compounds (**5** and **6**) to be discussed

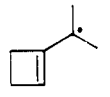


**5**

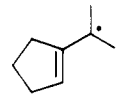


**6**

here was designed to estimate the stability of radicals **7** and **8**. Our interest in the related methyl ketones,[12] the

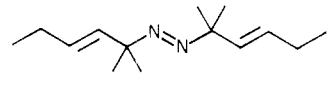


**7**



**8**

possibility that formation of **7** might be accelerated by strain relief, and our experience in synthesizing allylic azoalkanes[5] led us to these particular compounds. Since the activation energy for thermolysis of RN=NR is linearly related to the C–H bond dissociation energy of hydrocarbon RH,[13,14] decomposition rates of **2**, **5**, **6**, and reference compound **9** should reflect the relative stability of the resulting allylic radicals.



**9**

## Synthesis of Compounds

Bridgehead-substituted bicyclic azoalkanes are quite uncommon substances[3,8,15] partly because appropriate cyclohexa-1,3-diene precursors are not easily prepared. The synthesis of **3** was achieved as shown in Scheme I, starting with 2-phenethyl alcohol. The Diels–Alder reaction using *N*-methyltriazolinedione (MTD) was carried out on the distilled dienol mixture (**10** and **11**) resulting from Birch reduction and double bond equilibration. Catalytic hydrogenation followed by potassium *tert*-butoxide induced elimination of the tosylate **14** yielded **15**, which was converted to the desired azoalkane by hydrolysis and oxidation.[16]

Attempts to prepare **4** by an analogous route were unsuccessful on account of the undesirable physical properties of the dienediol mixture (high-boiling, viscous, hygroscopic oil). Therefore, a new synthesis was devised, as shown in Scheme II. Following a model procedure for cyclohexanone,[17] we were able to find reaction conditions which would allow direct preparation of **17** from cyclohexane-1,4-dione (cf. Experimental Section). The Diels–Alder reaction with MTD proceeded smoothly to give **18**, which

(1) Koenig, T. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1.
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(6) Crawford, R. J.; Ohno, M. *Can. J. Chem.* **1974**, *52*, 3134.
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(11) Engel, P. S.; Nalepa, C. J.; Leckonby, R. A.; Chae, W. K. *J. Am. Chem. Soc.*, in press.
(12) Engel, P. S.; Schexnayder, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 145.
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(14) Engel, P. S.; Dalton, A. I.; Shen, L. *J. Org. Chem.* **1974**, *39*, 384.
(15) Luttke, W.; Schabacker, V. *Justus Liebigs Ann. Chem.* **1966**, *698*, 86.
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(17) Wadsworth, W. S.; Emmons, W. D. "Organic Syntheses", Collect. Vol. V; Wiley: New York, 1973; p 547.

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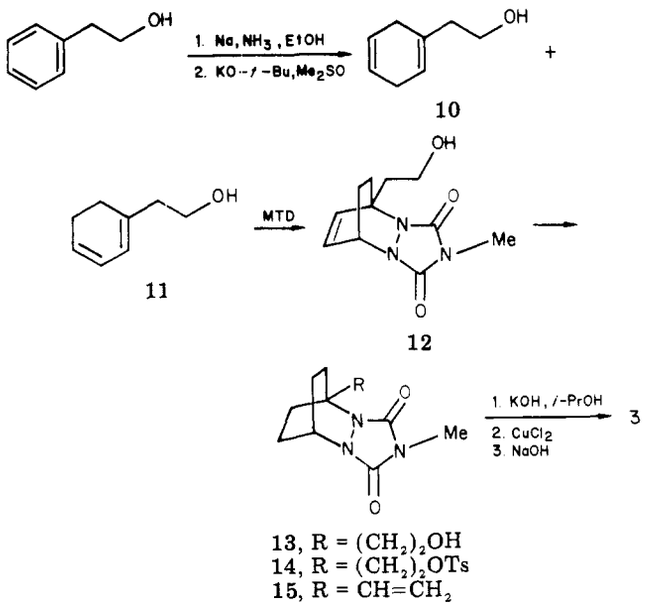
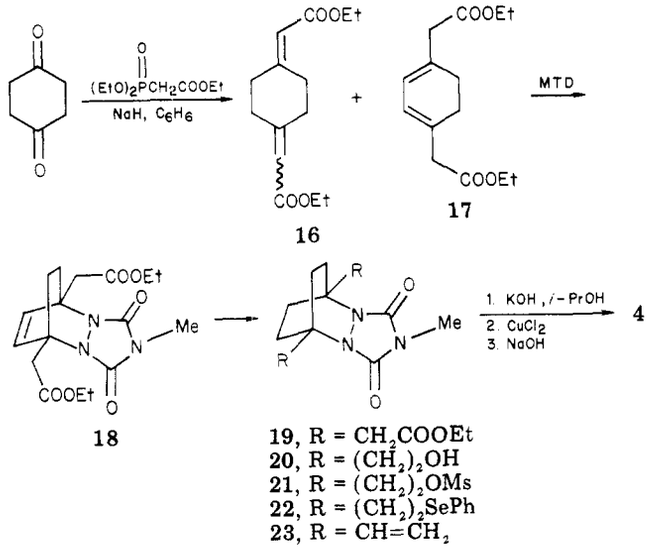
Scheme I



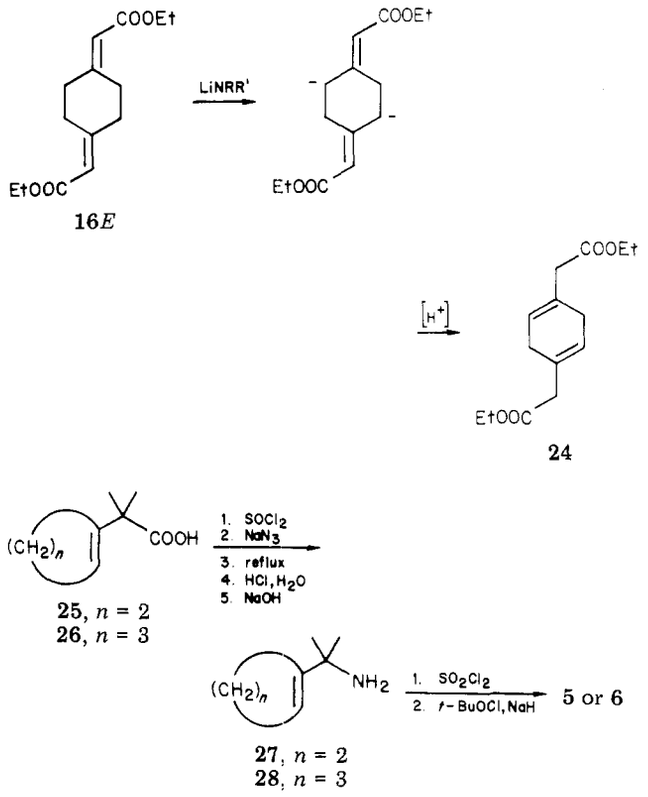

Scheme II



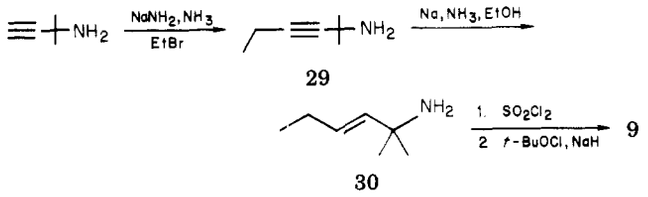

was hydrogenated to **19**. Reduction with lithium borohydride, formation of mesylate **21**, and selenoxide elimination[18] gave **23**. Conversion of this intermediate to azo compound **4** was achieved as in the case of **15**.[16]

An interesting sidelight of this route is that preparation of **16** by the literature procedure[17] gave a separable mixture of the *E* and *Z* isomers, whose structure was apparent from their NMR spectra. Treatment of **16*Z*** with lithium cyclohexylisopropylamide in THF at −78 °C yielded exclusively **17** on workup whereas similar treatment of **16*E*** produced the 1,4-diene **24**. Thus, anion formation occurs anti to the carbethoxyl group, even when two negative charges must be placed on adjacent carbons, as in **16*Z***. This higher acidity of the protons anti to the carbethoxyl group is probably electronic in origin and could be synthetically useful.

For the synthesis of **5** and **6**, carboxylic acids **25** and **26**, which had been made previously in our laboratory,[12] were converted by the Curtius reaction to amines **27** and **28**.




2-Amino-2-methyl-3-hexene (**30**) was prepared from 1,1-dimethylpropargylamine by alkylation and reduction. The azo compounds were prepared by oxidation of sulfamides using Timberlake's modification[19] of Ohme's hypochlorite–base procedure.[20]




## Results

Decomposition of **3** and **4** in xylene was monitored by UV spectroscopy, providing the kinetic data shown in Table I. Compounds **5**, **6**, and **9** were thermolyzed in *n*-decane by using a constant-volume kinetic apparatus to follow nitrogen evolution. As a control, kinetics were redetermined on known[5] azoalkane **2**. The rate data and calculated activation parameters are displayed in Table II.

Decomposed solutions of **5** and **6** were each found by capillary GC/MS to contain four hydrocarbon dimers. Because these compounds were only partially separated on preparative GC columns, their structural assignment could not be secured with certainty. From our previous experience with such dimers however,[22,23] we know that tail–tail (tt) products[24] give the largest molecular ions and that more head–tail (ht) products are formed than head–head (hh). The tt dimer in the present case should consist of equal amounts of the two diastereomers.[25,26] Comparing

(18) Sharpless, K. B.; Young, M. W.; Lauer, R. F. *Tetrahedron Lett.* **1973**, 1979. Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697. Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22.

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(23) Engel, P. S.; Bishop, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 2148.
(24) "Head" refers to the dimethyl end of the allylic radicals.

Table I. Rate Constants and Activation Parameters for Bicyclo[2.2.2]azoalkanes

| compd | temp, °C | $10^4k$, $s^{-1}$ | $\Delta H^{\ddagger}$ [a] | $\Delta S^{\ddagger}$, eu | $\Delta G^{\ddagger}$ (150 °C)[a] |
|---|---|---|---|---|---|
| 1 | ~245 | | 45.0 ± 0.2[b] | 10.6 ± 0.4[b] | 40.5 |
| | | | 43.5 ± 0.03[c] | 8.4 ± 0.1 | 39.9 |
| 3 | 131.37 | 1.351 | 34.2 ± 0.8 | 7.7 ± 2.0 | 30.9 |
| | 135.13 | 2.182 | | | |
| | 138.79 | 2.866 | | | |
| | 143.84 | 5.097 | | | |
| | 147.71 | 7.369 | | | |
| | 151.71 | 11.21 | | | |
| 4 | 88.85 | 0.697 | 28.8 ± 0.3 | 1.5 ± 0.8 | 28.2 |
| | 92.51 | 1.094 | | | |
| | 98.83 | 2.060 | | | |
| | 102.75 | 3.130 | | | |
| | 108.81 | 5.876 | | | |
| | 113.59 | 10.02 | | | |
| | 117.93 | 14.71 | | | |

[a] In kcal $mol^{-1}$. [b] Reference 8. [c] Reference 21.

Table II. Rate Constants and Activation Parameters for Four Azo Compounds

| compd | temp, °C | $10^4k$, $s^{-1}$ | $\Delta H^{\ddagger}$ [a] | $\Delta S^{\ddagger}$, eu | $\Delta G^{\ddagger}$ (100 °C)[a] |
|---|---|---|---|---|---|
| 5 | 39.21 | 1.286 | 26.8 ± 0.3 | 9.2 ± 1.0 | 23.4 |
| | 44.97 | 2.820 | | | |
| | 50.71 | 5.678 | | | |
| | 55.43 | 10.53 | | | |
| | 58.95 | 17.62 | | | |
| | 63.74 | 31.66 | | | |
| | 63.88 | 32.13 | | | |
| 6 | 39.21 | 0.9981 | 27.9 ± 0.6 | 12.2 ± 1.9 | 23.3 |
| | 44.89 | 2.091 | | | |
| | 49.52 | 4.593 | | | |
| | 55.42 | 8.976 | | | |
| | 58.95 | 15.28 | | | |
| | 63.76 | 27.88 | | | |
| 9 | 39.25 | 0.5329 | 27.5 ± 0.5 | 9.7 ± 1.5 | 23.9 |
| | 44.89 | 1.107 | | | |
| | 49.52 | 2.256 | | | |
| | 55.40 | 4.868 | | | |
| | 58.95 | 7.584 | | | |
| | | | 26.1 ± 0.8[b] | 5.0 ± 2.5[b] | 24.2 |
| 2 | 44.90 | 0.6735 | 25.6 ± 0.3 | 3.4 ± 0.8 | 24.3 |
| | 49.53 | 1.272 | | | |
| | 55.44 | 2.631 | | | |
| | 58.95 | 4.058 | | | |
| | 63.74 | 7.045 | | | |

[a] In kcal $mol^{-1}$. [b] Reference 5.

these expectations to the data in Table III, we find a nicely consistent assignment in the case of **5** if peak 1 is hh, 2 is ht, and 3 and 4 are meso and *dl* tt dimers. Irradiation of 2-methyl-2-(1-cyclobutenyl)-3-butanone[12] gave the same pattern of four GC peaks as thermolysis of **5**. Separation of the products from **6** was achieved only with great difficulty on capillary GC columns. Since molecular ions were extremely weak from all of these compounds, we are unable to make even tentative structural assignments. That the four GC peaks were the dimers ($m/e$ 218) is confirmed by the base peak at $m/e$ 109 for all of them.

Table III. Products from 5 and 6

| precursor | peak no. | $t_R$, h | % total | $M^{+}\cdot$/base, %[b] |
|---|---|---|---|---|
| 5[a] | 1 | 1.80 | 13 | 0.1 |
| | 2 | 1.93 | 55 | 0.0 |
| | 3 | 2.20 | 16 | 6.6 |
| | 4 | 2.35 | 16 | 9.2 |
| 6[c] | 1 | 1.70 | 14 | |
| | 2 | 1.76 | 20 | |
| | 3 | 1.84 | 16 | |
| | 4 | 1.91 | 50 | |

[a] Column was 250 ft × 0.01 in., SF-96, at 90 °C. [b] Intensity ratio of molecular ion to base peak at 70 eV. [c] Column was 250 ft × 0.01 in., OV-17, at 125 °C.

## Discussion

Following our earlier discussion[8] of the bridgehead methyl homologues of **1**, we calculate predicted and observed relative rate constants for simultaneous and stepwise C–N bond rupture of **3** and **4**. If $k_{rel}$ for **1** is 1.0 and that for **3** is $n$, the simultaneous mechanism predicts that $k_{rel}$(**4**) will be $n^2$ whereas the stepwise mechanism predicts that $k_{rel}$(**4**) = $2n - 1$. Since $k_{rel}$(**3**) = $n$ = 6.0 × $10^4$ at 150 °C, we obtain the following values for $k_{rel}$(**4**) [mechanism ($k_{rel}$(**4**))]: simultaneous (3.6 × $10^9$), stepwise (1.2 × $10^5$), observed (1.5 × $10^6$). The observed rate for **4** is over three orders of magnitude slower than expected on the basis of simultaneous C–N bond rupture, but it is 12-fold faster

(25) Bartlett, P. D.; McBride, J. M. *Pure Appl. Chem.* **1967**, 89.
(26) Greene, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867.

than the stepwise mechanism predicts.

Another way to view the results is in terms of the generalized Polanyi equation[4] $E_a = \alpha D(R\text{–}H) + \alpha' D(R'\text{–}H) - C$, where $E_a$ is the activation energy for azoalkane thermolysis, $D(R\text{–}H)$ and $D(R'\text{–}H)$ are the bond dissociation energies of the corresponding hydrocarbons, and $C$ is a constant. Letting $E_a = \Delta H^{\ddagger}$ and $\alpha + \alpha' = 1.0$, we obtain for the bicyclic azoalkanes:

$$1:\ 44.2 = \alpha(94.5) + \alpha'(94.5) - C$$

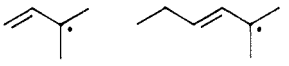
$$3:\ 34.2 = \alpha(94.5) + \alpha'(78.4) - C$$

$$4:\ 28.8 = \alpha(78.4) + \alpha'(78.4) - C$$

These equations lead to the values $C = 50$ kcal mol$^{-1}$ and $\alpha = 0.36$, implying that breaking of the stronger C–N bond is not as advanced in the transition state as breaking of the weaker bond. Indeed, this so-called "asynchronous mechanism" is consistent with the results for most acyclic azoalkanes[3,5,10] and pyrazolines.[6,7] It will be noted, however, that any values of $\alpha$ and $\alpha'$ are satisfactory in the equations for **1** and **4**. Since these symmetrical compounds need not decompose by the same mechanism as **3**, real evidence for asynchronous decomposition exists only for the unsymmetrical azoalkane. Incorporation of bridgehead methyl groups into **1** is a less drastic structural modification than the use of vinyl groups, and the results of such a study[8] were marginally in favor of synchronous C–N bond cleavage. Secondary deuterium isotope effect studies in symmetrical acyclic,[27] cyclic,[7,28] and bicyclic[29] azoalkanes are also in accord with the synchronous mechanism, though a recent theoretical calculation[30] on pyrazoline pointed toward stepwise cleavage as the lowest energy process. In our view, the experimental results for the present compounds and most azoalkanes studied previously are best accommodated if symmetrical compounds cleave synchronously and unsymmetrical compounds cleave asynchronously.

Since the decrease in $\Delta H^{\ddagger}$ caused by introducing $\alpha$-methyl groups is much smaller in **1** than in acyclic azoalkanes,[8] it is of interest to make the same comparison by using vinyl groups. The first vinyl group lowers the $\Delta H^{\ddagger}$ of **1** by 10.0 kcal mol$^{-1}$, but its effect in azoisopropane is 15.1 kcal mol$^{-1}$.[5] Similarly, the second vinyl group lowers $\Delta H^{\ddagger}$ by an additional 5.4 kcal mol$^{-1}$ in **3** vs. **4**, but the change is 6.9 kcal mol$^{-1}$ in the acyclic $\alpha,\alpha$-dimethylallyl analogues. Regardless of whether $\Delta H^{\ddagger}$ or $\Delta G^{\ddagger}$ (150 °C) is employed, the effect of $\alpha$-vinyl groups on **1** is about 75% of that found in the acyclic series. The discrepancy between bicyclic and acyclic azoalkanes widens when dealing with bridgehead phenyl groups.[31,32] Paquette and Leichter[31] attributed the poor rate-enhancing effect of bridgehead phenyl to geometric constraints which prevent full utilization of the benzyl resonance energy in the transition state for thermolysis. On account of its lower steric requirements, vinyl is expected to be less sensitive to such constraints, in accord with experiment. An additional point of interest is that the $\Delta H^{\ddagger}$ difference between **1** and **3** is close to the allyl stabilization energy (SE = 11.4 kcal mol$^{-1}$ [33]); however, the difference between **1** and **4** is less than 70% of two allyl SE's.

The second question posed at the outset of this work was whether radicals **7** and **8** differ in stability from **31** and **32**.

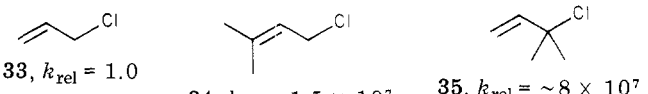


31 32

The rate differences between **2**, **5**, **6**, and **9** are small (cf. Table II); hence, considerable angle distortion of the $\sigma$ system has no great effect on the ability of a double bond to stabilize an adjacent radical center. Radical **7** is formed a bit more readily than **8**, possibly because converting the strained double bond in **5** to a partial double bond is more favorable than this process in the less strained homologue **6**. Our original idea that radical stability might be responsible for the different amounts of photochemical $\alpha$ cleavage in the previously studied ketones[12] seems to have little merit. This reaction of $\beta,\gamma$-unsaturated ketones is under investigation by others.[34]

Comparison of the product distribution from **5** with that from **2** (hh:ht:tt = 16:30:54)[23] reveals some factor disfavoring tt product in **5**. Whether this results from greater steric hindrance to recombination at the tail end of **7** or from lower spin density at that position cannot be determined at present.

Azoalkane **9** was prepared as a strain-free model for compounds **5** and **6**. However, comparison of **9** with **2** turned out to be the most interesting one because the ethyl group in **9** accelerates its thermolysis by only 78% relative to **2**. Since a methyl group on the double bond of propene decreases its allylic C–H bond dissociation energy (BDE) by 3.4 kcal mol$^{-1}$,[35] one would expect the ethyl group in **32** to have a similar effect. Azoalkane **9** should therefore decompose much faster than **2**. Solvolysis of allylic chlorides **33–35** also shows the expected trend; that is, $\gamma$-methyl



33, $k_{rel} = 1.0$ 34, $k_{rel} = 1.5 \times 10^7$ 35, $k_{rel} = \sim 8 \times 10^7$

groups accelerate cation formation nearly as much as $\alpha$-methyl groups.[36] Why then is radical formation aided by $\alpha$- but not by $\gamma$-alkyl groups? A possible explanation lies in our choice of compounds and in a "saturation effect".

In 1973, the stabilization energies (SE) of allyl, 2-butenyl, and **31** were taken to be 9.6, 12.6, and 13.1 kcal mol$^{-1}$.[37] Whereas the first two values suggest that alkyl groups stabilize allylic radicals, the small difference between 12.6 and 13.1 casts considerable doubt on this idea. On the other hand, more recent work[38] assigns the SE of **31** as 16.7 kcal mol$^{-1}$, thus supporting alkyl stabilization of allyl radicals. It was predicted[37] that substitution of the first hydrogen by alkyl would have a much more pronounced effect than introduction of further substituents. A variant of this idea will explain the present results; namely, the first two alkyl groups are much more effective than the third. Although the uncertainty in allylic SE's[33,38] leaves room for such a postulate, testing it would require thermolysis studies of various azo-2-propenes which lack $\alpha$-methyl groups.[4] Unfortunately, such compounds tautomerize readily, complicating interpretation of their decomposition kinetics.

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(28) Al-Sader, B. H.; Crawford, R. J. *Can. J. Chem.* **1968**, *46*, 3301.
(29) Snyder, J. P.; Olsen, H., unpublished results.
(30) Hiberty, P. C.; Jean, Y. *J. Am. Chem. Soc.* **1979**, *101*, 2538.
(31) Paquette, L. A.; Leichter, L. M. *J. Org. Chem.* **1974**, *39*, 467.
(32) Evnin, A. B.; Arnold, D. R.; Karnischky, L. A.; Strom, E. *J. Am. Chem. Soc.* **1970**, *92*, 6218.
(33) Rossi, M.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1230.
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## Experimental Section

Elemental analyses were performed by Elek Microanalytical Laboratories, Torrance, CA. High-resolution mass spectra were run on a CEC 21-110C, and GC/MS data were collected by using a Finnigan Model 3300 mass spectrometer. Melting points were taken on a Mel-Temp in capillary tubes and are uncorrected. NMR spectra were run in $CDCl_3$ usually on a Varian EM-390 spectrometer but occasionally on a Perkin-Elmer R-12 or a Varian XL-100; chemical shifts are expressed as $\delta$ values. IR spectra were taken on a Beckman IR8 and IR20 while UV spectra were recorded on a Cary 17 spectrometer.

THF and pentane were dried over $K_2CO_3$ and then distilled under $N_2$ from Na and $LiAlH_4$, respectively. $Me_2SO$ was dried by distillation from $CaH_2$ at 25 mm. *N*-Methyltriazolinedione (MTD) was prepared in EtOAc by the published procedure[39] except that unreacted *N*-methylurazole was removed by filtration, and excess *tert*-butyl hypochlorite was removed by rotary evaporation.

**1-(2-Hydroxyethyl)cyclohexa-1,4-diene (10).**[40] In a dry, 5-L, three-necked, round-bottom flask equipped with a powerful mechanical stirrer, dry ice condenser, and nitrogen- and gas-inlet tubes was condensed 2.5–3 L of $NH_3$ at −78 °C. The gas-inlet tube was replaced with an addition funnel. A 74.4-g sample (0.610 mol) of phenethyl alcohol followed by 138 g (3.00 mol) of absolute EtOH was then added at a slow rate to keep the liquid $NH_3$ from boiling excessively. Over 1.5 h, 85.1 g (3.70 g-atom) of sodium metal was added in ~0.3 $cm^3$ pieces. The deep blue solution was stirred at −78 °C for 6 h; 800 mL of water was then added dropwise over 1.25 h. The reaction mixture was allowed to warm to 0 °C, and the product was carefully extracted with two portions of ether. The ether solution was dried with $K_2CO_3$, filtered, and concentrated to give 35.5 g of a colorless oil. The ammonia solution was extracted after 12 h with three more portions of ether. The combined extracts were dried, filtered, and concentrated to provide an additional 38.0 g of crude product. The product was vacuum distilled through a 12-cm metal helices packed column to give 69.2 g (91.5%) of **10** as a clear oil, bp 57–63 °C (0.3 mm). Analysis by GC (0.125 in. × 6 ft, 10% XF-1150 on Chromosorb W, 100 °C) showed 5% starting material and 5% impurities. NMR $\delta$ 2.15 (t, 2 H, $J$ = 7 Hz), 2.60 (s, 4 H), 3.29 (br s, 1 H), 3.60 (t, 2 H, $J$ = 7 Hz), 5.43 (br s, 1 H), 5.63 (s, 2 H).

**1-(2-Hydroxyethyl)cyclohexa-1,3-diene (11, Isomer Mixture).** In a 500-mL round-bottom flask equipped with a condenser and a nitrogen inlet was placed 69.2 g (0.558 mol) of **10** in 250 mL of dry $Me_2SO$. A 10.0-g (89.3 mmol) sample of KO-*t*-Bu was then added, and the reaction was stirred at room temperature overnight. GC analysis of worked up aliquots (XF-1150 column as in the previous reaction) indicated only partial isomerization, so 5.0 g (44.6 mmol) of KO-*t*-Bu was added, and the reaction mixture was heated at 60 °C for 2 h. GC analysis showed ~50% **11**, 25% **10**, 15% isomeric 1,3-diene, and 10% aromatic compound. Since further heating increases aromatization at the expense of **11**, the mixture was poured at this point into 1 L of ice–water plus 100 mL of saturated aqueous NaCl. The product was extracted with three portions of ether. The ether solution was dried with $K_2CO_3$, filtered, and concentrated to yield 65.3 g of oil. NaCl was added to the water solution, which was then extracted twice with ether. The extract was dried, filtered, and concentrated to give 5.8 g of a yellow oil. The fractions were combined, and the product was vacuum distilled through a heated 15-cm metal helices packed column. The fractions that had bp 52–54 °C (0.25 mm), 54.2 g (73.6%), were substantially enriched in the desired isomer (**11**) and were used for the next reaction. NMR $\delta$ 2.04–2.50 (m), 2.60–2.79 (m), 2.95–3.16 (m), 3.54–3.90 (m), 5.48–5.97 (m).

**1-(2-Hydroxyethyl)-4-methyl-2,4,6-triazatricyclo[5.2.2.0$^{2,6}$]undec-8-ene-3,5-dione (12).** In a 250-mL round-bottom flask equipped with an addition funnel and stirring bar was placed 54.2 g (0.437 mol) of diene mixture (mostly **10** and **11**) in 100 mL of distilled EtOAc. *N*-Methyltriazolinedione solution[39] was added dropwise at 0 °C, and the extent of reaction was followed by GC. Part way through the addition, the product precipitated. The reaction mixture was vacuum filtered after GC showed no **11** remaining. The filtrate was concentrated and diluted with a small amount of ether. When the filtrate was cooled, more product precipitated; this was added to the other crop, and the whole was recrystallized from acetone: total conversion 30.3 g (29.3%) of a white solid. A pure sample had mp 112.5–113 °C. NMR $\delta$ (100 MHz) 1.43–1.68 (m, 2 H), 2.15–2.54 (m, 4 H), 2.99 (s, 3 H), 3.18 (br s, 1 H), 4.02 (d of t, 2 H, $J$ = 6.5, 1.5 Hz), 4.84–4.98 (br s, 1 H), 6.37 (AB portion of ABX, 2 H, $J_{AB}$ = 8 Hz).

Anal. Calcd for $C_{11}H_{15}N_3O_3$: C, 55.69; H, 6.37. Found: C, 55.89; H, 6.45.

**1-(2-Hydroxyethyl)-4-methyl-2,4,6-triazatricyclo[5.2.2.0$^{2,6}$]undecane-3,5-dione (13).** In a 500-mL round bottom flask was placed 31.0 g (0.131 mol) of Diels–Alder adduct **12** in 406 mL of absolute EtOH. A 201.6-mg sample of 10% palladium on carbon was then added, and the flask was attached to an atmospheric-pressure hydrogenation apparatus. The contents were stirred vigorously at 0 °C, whereupon 3.22 L of $H_2$ was absorbed. The solution was then filtered and concentrated; yield 31.4 g (100%) of a white solid. A sample that was recrystallized from cyclohexane had mp 117–118 °C. NMR $\delta$ 1.66–2.16 (m, 8 H), 2.34 (t, 2 H, $J$ = 7 Hz), 3.07 (s, 3 H), 3.89 (t, 2 H, $J$ = 7 Hz), 4.34–4.46 (br s, 1 H).

Anal. Calcd for $C_{11}H_{17}N_3O_3$: C, 55.21; H, 7.16. Found: C, 55.36; H, 7.11.

**1-[2-(Tosyloxy)ethyl]-4-methyl-2,4,6-triazatricyclo[5.2.2.0$^{2,6}$]undecane-3,5-dione (14).** In a 250-mL round bottom flask was placed 33.9 g (0.142 mol) of **13** in 150 mL of freshly distilled pyridine. The mixture was cooled to 0 °C and 36.0 g (0.189 mol) of pure *p*-toluenesulfonyl chloride was added. A salmon pink color was evident after a short time, and the flask filled with long white needle crystals of pyridine hydrochloride. After 22 h at 0 °C, the reaction mixture was poured into 600 mL of ice-water, and the product was extracted with four portions of $CH_2Cl_2$. The pink $CH_2Cl_2$ solution was washed with 2 M HCl until the water washings had pH 2. The now off-white solution was dried with $K_2CO_3$, filtered, and concentrated. Removal of solvent at 0.3 mm left 55.7 g (99.9%) of a very viscous yellow oil containing a trace of $CH_2Cl_2$. Crystallization occurred on standing: mp 87–90 °C; NMR $\delta$ 1.69–2.28 (m, 8 H), 2.28–2.67 (m, 2 H), 2.46 (s, 3 H), 3.02 (s, 3 H), 4.36 (br s, 1 H), 4.34 (t, 2 H, $J$ = 6 Hz), 7.44 (d, 2 H, $J$ = 8 Hz), 7.89 (d, 2 H, $J$ = 8 Hz); MS (70 eV) $m/e$ (rel intensity) 393 ($M^+$, 1), 221 (M − TsO, 6), 116 (97), 107 (58), 106 (97), 91 (100), 79 (83), 78 (45), 67 (24), 65 (28), 41 (37), 39 (22).

**1-Vinyl-4-methyl-2,4,6-triazatricyclo[5.2.2.0$^{2,6}$]undecane-3,5-dione (15).** In a dry, 500-mL, three-necked, round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and condenser was placed 11.2 g (28.5 mmol) of crude tosylate **14** in 330 mL of very dry benzene. A 11.2-g (0.100 mol) sample of KO-*t*-Bu was then added, and the bright yellow reaction mixture was stirred at 25 °C for 24 h. It was then poured into 400 mL of water. The phases were separated, and the water solution was extracted twice with $CH_2Cl_2$. The combined organic layers were dried with $K_2CO_3$, filtered (with difficulty), and concentrated. Recrystallization of the beige solid from cyclohexane afforded 4.6 g (72%) of product **15**: mp 93–94 °C dec; NMR $\delta$ 1.72–2.27 (m, 8 H), 3.10 (s, 3 H), 4.42 (br s, 1 H), 5.22 (d, 1 H, $J$ = 18 Hz), 5.30 (d, 1 H, $J$ = 10 Hz), 6.61 (dd, 1 H, $J$ = 11, 18 Hz).

Anal. Calcd for $C_{12}H_{15}N_3O_2$: $m/e$ 221.1164 ($M^{+\cdot}$). Found: $m/e$ 221.1174.

**1-Vinyl-2,3-diazabicyclo[2.2.2]oct-2-ene (3).** A dry, 100-mL, three-necked, round-bottom flask was equipped with a reflux condenser, $N_2$ inlet, addition funnel, and magnetic stirring bar. The flask was then charged with 15 mL of *i*-PrOH (previously refluxed over and distilled from CaO). To this was added 1.16 g (20.6 mmol) of solid KOH. After the KOH had dissolved, the temperature of the solution was slowly raised to 50 °C, and 1.00 g (4.52 mmol) of **15** in 10 mL of dry *i*-PrOH was added dropwise. As the reaction ensued, a white precipitate began to form. The mixture was heated at reflux for 24 h under $N_2$. The cooled reaction mixture was filtered, and the solid was washed with *i*-PrOH. The combined filtrate and washings were rotoevaporated to dryness, yielding a yellow oil. This oil was dissolved in 30 mL

(39) Cookson, R. C.; Gupta, S. S.; Stevens, I. D. R.; Watts, C. T. *Org. Synth.* **1971**, *51*, 121.

(40) This procedure is adapted from the Birch reduction of cumene. See: Benkeser, R. A.; Burrows, M. L.; Hazdra, J. J.; Kaiser, E. M. *J. Org. Chem.* **1963**, *28*, 1094.

of $H_2O$ and carefully neutralized (pH 7) with 6 M HCl. This solution was extracted with 3 × 30 mL of $CH_2Cl_2$. The combined organic phases were dried ($K_2CO_3$), filtered, and concentrated to yield the *N*-methylurea as a thick semisolid.

To form the cuprous chloride complex of **3**, we first equipped a 100-mL round-bottom flask with a magnetic stirring bar and an addition funnel. The flask was charged with a solution of 2.63 g (0.155 mol) of $CuCl_2 \cdot 2H_2O$ in 10 mL of $H_2O$. To this vigorously stirred solution was added dropwise 5 mL of a solution prepared by dissolving the crude *N*-methylurea in 15 mL of $H_2O$. During the addition, the reaction mixture turned dark green, and then a red precipitate appeared. After the 5-mL aliquot had been added (~30 min), the mixture was filtered and the solid washed with 15 mL of $H_2O$. The combined green filtrate and washings were returned to the reaction flask, and another 5-mL aliquot of urea solution was added. After the combined brick red cuprous chloride complex was dried in a desiccator, the total yield was 0.458 g (43%). The green aqueous filtrates could be extracted with $CH_2Cl_2$ to recover 0.45 g (40%) of the starting material (**15**).

To a 100-mL beaker containing 30 mL of concentrated $NH_4OH$ was added the dried cuprous chloride complex of **3** in small portions with stirring. The light blue solution turned green as the complex dissolved. The solution was then extracted with 2 × 60 mL of $CH_2Cl_2$. The combined organic phases were washed with 2 × 100 mL of saturated NaCl solution and dried ($K_2CO_3$). The solution was filtered and the solvent carefully distilled off at atmospheric pressure. The yellow oily residue was molecularly distilled [35–40 °C (1 mm)] to yield the desired azo compound, 0.118 g (20% based on **15**), as a clear oil: NMR $\delta$ 1.1–1.8 (m, 8 H), 5.1–5.6 (m, 3 H), 6.6 (dd, 1 H, $J$ = 11, 18 Hz); UV $\lambda_{max}$ 381 nm ($\epsilon$ 238).

**1,4-Bis(carbethoxymethylene)cyclohexa-1,3-diene (17).** A dry, 500-mL, three-necked, round-bottom flask equipped with a powerful mechanical stirrer and an addition funnel was charged with 22 g (0.46 mol) of 50% NaH in mineral oil. The oil was removed by washing with dry benzene, and 100 mL of benzene was added. To this stirred mixture was added dropwise over 45 min 100 g (0.446 mol) of triethyl phosphonoacetate with ice-bath cooling. Vigorous evolution of hydrogen occurred. The mixture was then stirred for 1 h at 25 °C until hydrogen evolution ceased. To this nearly clear solution was added dropwise over 30 min 23.8 g (0.22 mol) of 1,4-cyclohexanedione in 125 mL of benzene. During the addition, the temperature was maintained at 40 °C by using an ice bath. After approximately 75% of the ketone has been added, a gummy dark brown material (sodium diethyl phosphate) formed, which in some instances made agitation difficult. Heating briefly to 60 °C alleviated this problem. After addition of the dione was complete, the mixture was stirred for 30 min at 80 °C. The solution was cooled to 25 °C, and the supernatant was decanted. The residue was washed with hot benzene several times, and the combined benzene solution was concentrated on the rotovap: yield 50 g (93.4%) of **17**; NMR $\delta$ 1.20 (t, 6 H, $J$ = 7 Hz), 2.20 (s, 4 H), 3.05 (s, 4 H), 4.10 (q, 4 H, $J$ = 7 Hz), 5.70 (s, 2 H).

Anal. Calcd for $C_{14}H_{20}O_4$: $m/e$ 252.1361 ($M^+\cdot$). Found: $m/e$ 252.1340.

If this reaction was carried out according to the procedure for cyclohexanone,[17] there was isolated a mixture of **16*E*** and **16*Z***. After evaporation of the benzene solvent, the resulting oil (**16**) was allowed to stand in the refrigerator. The *E* isomer which crystallized out was isolated and recrystallized from hexane and then from methanol: mp 77–78.5 °C; NMR (**16*E***) $\delta$ 1.26 (t, 6 H, $J$ = 7 Hz), 2.38 (t, 4 H, $J$ = 7 Hz), 3.01 (t, 4 H, $J$ = 7 Hz), 4.08 (t, 4 H, $J$ = 7 Hz), 5.64 (s, 1 H). The mother liquor was enriched in the *Z* isomer, but this compound could not be completely purified because it was an oil: NMR (**16*Z***) $\delta$ 1.29 (t, 6 H, $J$ = 7 Hz), 2.45 (s, 4 H), 3.06 (s, 4 H), 4.24 (q, 4 H, $J$ = 7 Hz), 5.80 (s, 2 H).

**1,4-Bis(carbethoxymethylene)cyclohexa-1,4-diene (24).** Lithium isopropylcyclohexylamide was prepared at −78 °C under $N_2$ by adding dropwise 3.45 mL of 2.3 M *n*-BuLi (7.94 mmol) in hexane to 1.12 g (7.94 mmol) of isopropylcyclohexylamine in 10 mL of anhydrous THF. After addition was complete, the solution was stirred for 15 min, and then 1 g (3.97 mmol) of diester **16*E*** in 3 mL of THF was added dropwise to the mixture at −78 °C. After the mixture was stirred at −78 °C for 2.5 h, the reaction was quenched with 20% HCl and extracted with ether and chloroform. The extracts were dried over $MgSO_4$, and the solvent was evaporated. The resulting white solid (mp 42–44 °C) was recrystallized from *n*-hexane to give pure 1,4-diene **24**: NMR $\delta$ 1.27 (t, 6 H, $J$ = 7 Hz), 2.73 (s, 4 H), 2.98 (s, 4 H), 4.13 (q, 4 H, $J$ = 7 Hz), 5.59 (s, 2 H). The same procedure starting from **16*Z*** afforded **17** in 94% yield.

**1,7-Bis(carbethoxymethylene)-4-methyl-2,4,6-triazatricyclo[5.2.2.0$^{2,6}$]undec-8-ene-3,5-dione (18)** was prepared from a 56-g portion of diene **17** in the same manner as **12** (see above). The MTD solution[39] was added with stirring until the red color persisted. Recrystallization from EtOAc gave 30 g (0.082 mol, 37.3%) of adduct **18**: mp 110.5–111.5 °C; NMR $\delta$ 1.27 (t, 6 H, $J$ = 7 Hz), 1.70 (m, 2 H), 2.30 (m, 2 H), 2.90 (s, 3 H), 3.62 (4 H, AB, $J$ = 17 Hz), 4.15 (q, 4 H, $J$ = 7 Hz), 6.50 (s, 2 H).

**1,7-Bis(carbethoxymethylene)-4-methyl-2,4,6-triazatricyclo[5.2.2.0$^{2,6}$]undecane-3,5-dione (19)** was prepared in the same manner as **13** (see above): yield 97.7% of white crystals, mp 107.5–109 °C; NMR 1.25 (t, 6 H, $J$ = 7 Hz), 2.10 (m, 8 H), 2.97 (s, 3 H), 3.12 (s, 4 H), 4.13 (q, 4 H, $J$ = 7 Hz); MS $m/e$ (rel intensity) 367 (5), 322 (5), 279 (18), 165 (50), 119 (35), 116 (27), 105 (33), 91 (77), 29 (100).

Anal. Calcd for $C_{17}H_{25}N_3O_6$: $m/e$ 367.1743 ($M^+\cdot$). Found $m/e$ 367.1752.

**1,7-Bis(2-hydroxyethyl)-4-methyl-2,4,6-triazatricyclo[5.2.2.0$^{2,6}$]undecane-3,5-dione (20).** A 1000-mL, three-necked, round-bottom flask was equipped with a reflux condenser, nitrogen-inlet tube, magnetic stirrer, and addition funnel. Under $N_2$, the flask was charged with $LiBH_4$ (6.59 g, 0.302 mol) and 200 mL of dry THF. In a separate flask, a 38.5-g (0.105 mol) portion of **19** was dissolved in 50 mL of THF, and the solution was flushed with nitrogen. This slightly cloudy solution was syringed into the addition funnel and then added to the hydride dropwise over a 30-min period. The resulting mixture was refluxed for 5 h, cooled in an ice bath, and quenched with 5% HCl. This solution was saturated with $K_2CO_3$, causing the organic layer to separate. The aqueous layer was continuously extracted for 48 h with $CHCl_3$. The combined organic layer was evaporated to yield 25.3 g (0.09 mol, 85.7%) of diol **20**: mp 141–142 °C; NMR $\delta$ 1.90 (m, 8 H), 2.30 (t, 4 H, $J$ = 7 Hz), 3.00 (s, 3 H), 3.40 (br s, 2 H), 3.85 (t, 4 H, $J$ = 7 Hz); MS $m/e$ (rel intensity) 283 (43), 238 (10), 220 (5), 185 (22), 180 (42), 168 (38), 116 (41), 107 (52), 105 (86), 93 (47), 91 (72), 79 (78), 41 (95), 31 (100).

Anal. Calcd for $C_{13}H_{21}N_3O_4$: $m/e$ 283.1532 ($M^+\cdot$). Found: $m/e$ 283.1545. Calcd for $C_{13}H_{21}N_3O_4$: C, 55.11; H, 7.47. Found: C, 54.82; H, 7.40.

**1,7-Bis[2-(mesyloxy)ethyl]-4-methyl-2,4,6-triazatricyclo[5.2.2.0$^{2,6}$]undecane-3,5-dione (21).** To an approximately 0.2 M solution of diol **20** (20 g, 0.071 mol in 350 mL of $CH_2Cl_2$) containing triethylamine (21.5 g, 0.212 mol) at 0–5 °C was added methanesulfonyl chloride (18.4 g, 0.16 mol) over 20 min.[41] Stirring for an additional 30 min in the ice bath completed the reaction. The first batch of white crystalline product was filtered off, and the mother liquor was washed in succession with ice-cold water, cold 10% HCl, saturated $NaHCO_3$, and saturated NaCl. The organic layer was evaporated to dryness, and the residue was combined with the first batch of product. Recrystallization from $CHCl_3$ afforded 30.2 g (0.069 mol, 97%) of **21**: mp 179–181 °C; NMR $\delta$ 1.95 (m, 8 H), 2.5 (t, 4 H, $J$ = 7 Hz), 2.95 (s, 3 H), 3.00 (s, 6 H), 4.50 (t, 4 H, $J$ = 7 Hz).

**1,7-Divinyl-4-methyl-2,4,6-triazatricyclo[5.2.2.0$^{2,6}$]undec-8-ene-3,5-dione (23).** Diphenyl diselenide (16.2 g, 52 mmol) was dissolved in 100 mL of absolute ethanol. $NaBH_4$ (4.7 g, 124 mmol) was added in batches while the mixture was stirred, until the bright yellow solution turned colorless (**Caution:** exothermic hydrogen evolution). After addition of 20 g (45.6 mmol) of **21**, the reaction mixture was gently refluxed for 5 h. The solution of selenide **22** was cooled, and 100 mL of THF was added. An 80-mL portion of 50% $H_2O_2$ was then added at 0 °C over 1 h. The resulting mixture was stirred for 3 h at 25 °C and then gently refluxed overnight. After the solution was cooled to 25 °C, it was diluted with 100 mL of water and then extracted with ether and $CHCl_3$. The combined organic phase was washed several times

(41) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

with aqueous $Na_2CO_3$, dried over $Na_2SO_4$, and evaporated to dryness. The resulting solid was purified by silica gel column chromatography and recrystallization to give 8.0 g (53%) of white, crystalline **23**: mp 111.5–113 °C; NMR δ 2.00 (m, 8 H), 2.97 (s, 3 H), 5.10 (d, 2 H, $J$ = 9 Hz), 5.26 (d, 2 H, $J$ = 4 Hz), 6.50 (dd, 2 H, $J$ = 18, 10 Hz); MS $m/e$ (rel intensity) 247 (2), 219 (9), 180 (32), 167 (22), 161 (28), 133 (63), 132 (88), 105 (60), 91 (79), 79 (63), 67 (43), 41 (100).

Anal. Calcd for $C_{13}H_{17}N_3O_2$: $m/e$ 247.1321 ($M^+$·). Found: $m/e$ 247.1309. Calcd for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93. Found: C, 63.14; H, 6.95.

**1,4-Divinyl-2,3-diazabicyclo[2.2.2]oct-2-ene (4)** was prepared from **23** by the same procedure[16] used to convert **15** to **3** (see above). Concentration of the $CH_2Cl_2$ solution of **4** gave a pale yellow oil, which yielded white crystals on sublimation: yield 32.3% overall, mp 31–32 °C; NMR δ 1.50 (m, 8 H), 5.40 (m, 4 H), 6.60 (dd, 2 H, $J$ = 12, 18 Hz); UV (hexane) $\lambda_{max}$ 382 nm (ε 142); MS, no $M^+$·, $m/e$ 134 (loss of $N_2$).

Anal. Calcd for $C_{10}H_{14}$: $m/e$ 134.1096. Found: $m/e$ 134.1089.

**2-(Cyclobut-1-enyl)-2-aminopropane (27) and 2-(Cyclopent-1-enyl)-2-aminopropane (28).** The appropriate 2-methyl-2-(cycloalk-1-enyl)propanoic acids[12] were converted to acid chlorides by addition of the carboxylic acid to refluxing $SOCl_2$. Following the procedure of Smith,[42] we dissolved the acid chloride (36.9 mmol) in 125 mL of acetone. The solution was cooled to −78 °C and stirred vigorously with a magnetic stirrer while a solution of 3.0 g (46.2 mmol, 25% excess) of $NaN_3$ dissolved in a minimal amount of $H_2O$ was added dropwise at a slow rate. The mixture was then stirred for 1 h as it warmed to ambient temperature. Excess $H_2O$ was then added to dissolve the resulting precipitate. After removal of the acetone on a rotary evaporator, the solution was extracted with benzene and dried over $Na_2SO_4$. This solution, which had been added to more benzene to bring the total volume to 175 mL, was refluxed for 1–4 h until the azide disappeared, as determined by IR (2140 $cm^{-1}$). A 100-mL portion of 20% HCl was added, and the mixture was stirred until the isocyanate disappeared (24 h), again monitoring by IR (isocyanate 2260 $cm^{-1}$). The aqueous layer was made basic with concentrated NaOH and was extracted twice with ether. The combined ether extracts were rotary evaporated, whereupon the amine was dried over $K_2CO_3$. Compounds **27** and **28** were then distilled, bp 45–47 °C (35 nm) and 56–58 °C (15 mm), respectively. The yield of **27** was 50% and that of **28** was 58%. **27**: NMR ($CCl_4$) δ 1.15 (s, 2 H), 1.30 (s, 6 H), 2.45 (m, 4 H), 5.75 (s, 1 H). **28**: NMR ($CCl_4$) δ 1.00 (m, 2 H), 1.20 (s, 6 H), 2.15 (m, 6 H), 5.46 (t, 1 H).

**2-Amino-2-methylhex-3-yne (29)** was prepared by a modification of the procedure of Campbell and Campbell.[43] A 5-L, three-necked, round-bottom flask was equipped with a Claisen adaptor, addition funnel, dry ice–acetone condenser, $N_2$ inlet, and Hirshberg stirrer. The flask was cooled to −78 °C, and 2000 mL of $NH_3$ was condensed into it. After addition of a catalytic amount of $FeCl_3$, Na (55.2 g, 2.4 mol) was added in chunks; the solution was allowed to turn from deep blue to gray after each piece was added. The amine (199.5 g, 2.4 mol) was then added dropwise. After the solution had stirred for 5 h, ethyl bromide (326.9 g, 3.0 mol) was added dropwise, and the solution was allowed to stir overnight. $NH_4OH$ (400 mL) was then added, followed by 500 mL of $H_2O$. The dry ice condenser was replaced by a drying tube, and the solution was allowed to warm to ambient temperature. The mixture was filtered to remove the catalyst and then extracted with ether. The organic layer was washed with $H_2O$ and dried over $K_2CO_3$. Distillation under $N_2$ through a 6-in. glass helices packed column gave the desired product in 50% yield: bp 132–134 °C; NMR δ 1.1 (t, 3 H), 1.3 (s, 6 H), 1.5 (s, 2 H), 2.1 (q, 2 H).

**2-Amino-2-methylhex-3-ene (30)** was prepared by the method of Campbell and Eby[44] with the following modifications. After the addition of the $NH_4OH$ and $H_2O$, the solution was extracted with ether. The organic layer was rinsed with $H_2O$ and saturated NaCl solution and dried over $K_2CO_3$. Ether was removed by rotary evaporation to give a 50% yield of colorless amine: NMR δ 0.9 (t, 3 H), 1.1 (s, 6 H), 1.4 (s, 2 H), 1.9 (m, 2 H), 5.4 (m, 2 H).

**Conversion of Amines to Sulfamides.** All amines were converted to sulfamides with sulfuryl chloride and triethylamine in $CH_2Cl_2$, according to the published procedure.[45] The sulfamide from **27**, after recrystallization from hexane, exhibited the following properties: mp 123.5–124.2 °C; NMR δ 1.70 (s, 12 H), 2.45 (m, 8 H), 4.30 (m, 2 H), 5.85 (t, 2 H).

Anal. Calcd for $C_{14}H_{24}N_2O_2S$: C, 59.12; H, 8.51. Found: C, 58.84; H, 8.49. The sulfamide from **28** was recrystallized from a mixture of hexane and EtOAc: mp 131–133 °C; NMR δ 1.50 (s, 12 H), 1.88 (m, 4 H), 2.32 (m, 8 H), 4.10 (br s, 2 H), 5.50 (m, 2 H).

Anal. Calcd for $C_{16}H_{28}N_2O_2S$: C, 61.50; H, 9.03. Found: C, 61.57; H, 9.10. The sulfamide from **30**, after recrystallization from hexane, had mp 105.9–106.2 °C. Anal. Calcd for $C_{14}N_{28}N_2O_2S$: 288.1871. Found: 288.1863. NMR δ 0.96 (t, 6 H), 1.41 (s, 12 H), 2.0 (m, 4 H), 5.5 (m, 4 H).

**Synthesis of Azoalkanes.** Compounds **5**, **6**, and **9** were prepared according to Timberlake[19] except that, after addition of *tert*-butyl hypochlorite, the solution was stirred for 5 h at 0 °C. The azoalkanes were purified by column chromatography on Florisil (100–200 mesh) using pentane as eluent; fractions were monitored by UV: **5** (pentane) 368 nm; **6** (pentane) 367 nm; **9** (pentane) 367 nm. NMR: **5** δ 1.23 (s, 12 H), 2.33 (m, 8 H), 5.71 (s, 2 H); **6** δ 1.13 (s, 12 H), 1.76 (m, 4 H), 2.18 (m, 8 H), 5.40 (m, 2 H); **9** δ 0.95 (t, 6 H), 1.38 (s, 12 H), 2.1 (m, 4 H), 5.9 (m, 4 H).

**Kinetics.** Disappearance of compounds **3** and **4** was monitored in sealed, degassed, square Pyrex cells at 381 nm. The cells were placed in a small, thermostated oil bath in the compartment of a Cary 17 spectrometer. Absorbance as a function of time was converted to first-order plots, which were fitted by a least-squares computer program. Nitrogen evolution from **2**, **5**, **6**, and **9** was monitored on an automated, constant-volume, variable-pressure apparatus.[14] In both kinetic methods, the temperature was regulated by a Bayley controller and was measured with a platinum resistance thermometer and potentiometer.

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**Registry No.** **1**, 3310-62-1; **2**, 71647-31-9; **3**, 71647-32-0; **4**, 71647-33-1; **5**, 71647-34-2; **6**, 71647-35-3; **9**, 71647-36-4; **10**, 71647-37-5; **11**, 71647-38-6; **12**, 71647-39-7; **13**, 71647-40-0; **14**, 71647-41-1; **15**, 71647-42-2; (*E*)-**16**, 71647-43-3; (*Z*)-**16**, 71647-44-4; **17**, 71647-45-5; **18**, 71647-46-6; **19**, 71647-47-7; **20**, 71647-48-8; **21**, 71647-49-9; **22**, 71647-50-2; **23**, 71647-51-3; **24**, 71647-52-4; **25**, 54683-89-5; **26**, 16642-54-9; **27**, 71647-53-5; **28**, 71647-54-6; **29**, 66227-20-1; **30**, 71647-55-7; MTD, 13274-43-6; phenethyl alcohol, 60-12-8; *p*-toluenesulfonyl chloride, 98-59-9; *i*-PrOH, 67-63-0; *N*-methylurea, 598-50-5; chloro(2,3-diazabicyclo[2.2.1]hept-2-ene-$N^2$)copper homopolymer, 71647-03-5; triethyl phosphonoacetate, 867-13-0; 1,4-cyclohexanedione, 637-88-7; sodium diethyl phosphate, 2870-30-6; lithium isopropylcyclohexylamide, 32400-20-7; methanesulfonyl chloride, 124-63-0; diphenyl diselenide, 1666-13-3; 2-methyl-2-(cyclobut-1-enyl)propanoyl chloride, 71647-56-8; 2-methyl-2-(cyclopent-1-enyl) propanoyl chloride, 71647-57-9; ethyl bromide, 74-96-4; 1,1-dimethylpropargylamine, 2978-58-7; bis[2-methyl-2-(cyclobut-1-enyl)propylamino] sulfone, 71647-58-0; bis[2-methyl-2-(cyclopent-1-enyl)propylamino] sulfone, 71647-59-1; bis[2-methyl-2-hex-3-enylamino] sulfone, 71647-60-4.

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