Mechanistic Studies of a Linear Trisazoalkane, a New Azimine, and a Bicyclic Triaziridine. Azoalkane Homolysis into Seven Fragments

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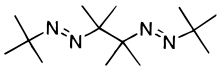
An aliphatic azo compound containing three azo groups (**1**) has been prepared by IF_5 oxidation of β-azoamine **3**. The thermolysis kinetics of this vicinal trisazoalkane were investigated above 155 °C, leading to a rate constant only 5.5 times faster than that of the simple model, azo-*tert*-butane. Because thermolysis to form seven stable products proceeds stepwise, the rate is hardly affected by the high exothermicity of the overall reaction (−93.4 kcal/mol). Oxidation of amine **3** also afforded a cyclic azimine **5** that underwent photolysis to yield a highly strained triaziridine **9** plus an unusual triazane **10**, whose structures were elucidated by detailed NMR studies. On standing at ambient temperature, **9** reverted to **5** with a half-life of about an hour.

While a number of bisazoalkanes appear in the literature,[1] very few compounds containing three aliphatic azo moieties have been reported.[2] The high stability of vicinal bisazoalkane **6**[1,3] encouraged us to examine the related



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trisazoalkane **1**, whose highly exothermic decomposition could produce seven fragments. In the course of synthesizing **1**, we encountered a cyclic azimine **5** that closed photochemically to a highly strained triaziridine.

Taking advantage of Ciganek's valuable transformation[4] of nitriles to *tert*-alkylamines, we converted the known cyanoazoalkane **2**[5] to β-azoamine **3**. Prolonged reaction times led to formation of acetone *tert*-butyl hydrazone, which presumably arose by scission[4] of the iminyl anion from addition of one methyl group to **2**. Since this hydrazone was not readily separable from **3**, the reaction conditions were carefully controlled to minimize its yield, even though a good deal of **2** remained unreacted. Treatment of **3** with sulfuryl chloride[6] afforded sulfamide **4**, which was oxidized by the nonaqueous hypochlorite-base method[7] to yield azimine **5**. At −78 °C, addition of IF_5[8,9] to **3** afforded **1** as a stable, light yellow solid in 32% yield but addition of **3** to IF_5 at higher temperatures led only to **5**.

Table 1. Thermolysis Activation Parameters of Selected Azoalkanes

compound	solvent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol[a]	k_{rel}[a]
ATB[b]	Ph_2O-iq[c]	42.1	16.3	34.7	1.0
6[d]	toluene	35.2 ± 0.3	2.8 ± 0.6	33.9	2.4
1	decane	35.8 ± 0.2	5.8 ± 1.5	33.2	5.5

[a] At 180.0 °C. [b] Data from ref 10. [c] iq is isoquinoline. [d] Data from ref 1.

Thermolysis of 1. A solution containing 0.124 mmol of **1** in 1.5 mL of decane was heated at 170 °C for 10 h, yielding 97.5% of the nitrogen expected from loss of 3 equiv of N_2. Thermolysis kinetics of **1** in degassed decane were carried out in sealed 1 cm Pyrex cuvettes, which were thermolyzed in a regulated oil bath and monitored by UV spectroscopy. Seven temperatures between 155 and 182 °C were employed, giving clean first-order kinetics and a linear Eyring plot (ρ = 0.999). The activation parameters are compared with those of **6** and azo-*tert*-butane (ATB) in Table 1.

To probe the thermolysis mechanism of **1**, a solution of 10 mg of **1** and 12 mg of thiophenol in 0.5 mL of

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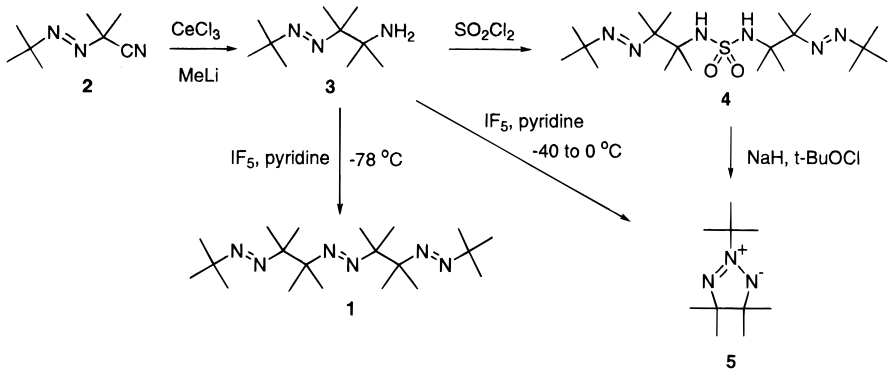
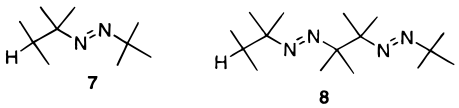
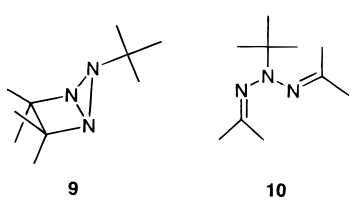


benzene was thermolyzed for various times at 153.56 °C. GC/MS analysis revealed both **7** and **8**, and the structure of **7** was confirmed by comparison with an authentic sample.



The Chemistry of Azimine 5. The unexpected azimine **5** turned up in oxidation both of the sulfamide **4** and of the azoamine **3** at warmer temperatures. This compound was a stable liquid whose high-resolution EI mass spectrum gave the formula $C_{10}H_{21}N_3$ and whose UV showed a band at 288 nm ($\epsilon = 2500$), similar to that seen in other azimines.[11−13] The ^{1}H NMR spectrum of **5** exhibited only two singlets at 1.02 and 1.47 ppm in the ratio of 4:3. In the ^{15}N−^{1}H HETCOR spectrum, the larger singlet at 1.02 ppm correlated with the ^{15}N signal at 294.9 ppm relative to NH_3 while the smaller ^{1}H singlet at 1.47 ppm correlated with the ^{15}N signal at 326.5 ppm, which must therefore be the central azimine nitrogen. An unequivocal proof of structure followed from single-crystal X-ray diffraction studies of the stable picrate salt of **5** (mp 129.5 °C) and of the HI salt, which was isolated as crystals from IF_5 oxidation of **3**.

Azimines are known to proceed photochemically to triaziridines.[14] We irradiated **5** in hexane at 313 nm and 0 °C in an attempt to form anti triaziridine **9** and/or its syn isomer. The characteristic 288 nm band of **5** diminished rapidly, leaving a weaker 270 nm band. As the solution stood in a thermostated cell holder at 23.4 °C, the 288 nm band gradually reappeared. Since there was no isosbestic point, the 270 nm band is not due to a triaziridine but instead must represent another photochemical product, probably triazane **10** (see below). The kinetics of the regeneration of **5** were determined by subtracting the immediate postirradiation spectrum from each spectrum obtained as the solution aged. This correction led to an array of azimine spectra over time with an invariant λ_{max} of 288 nm, which reappeared with a rate constant of 3.84×10^{-4} s^{-1} at 23.4 °C.



The photochemical ring closure of **5** could also be monitored by ^{1}H NMR. Irradiation (313 nm) of **5** in $CDCl_3$ below 0 °C decreased its two singlets at 1.02 and 1.47 ppm and caused the appearance of two sets of three singlets each, with the peaks of each set in the ratio 3:2:2. The larger of these sets (0.93, 1.04, and 1.24 ppm) was assigned to the anti triaziridine **9** while the smaller one (1.01, 1.83, and 1.87 ppm) was assigned to triazane **10**. Both **9** and **10** proved to be thermally labile, with **9** disappearing much faster than **10**. Monitoring the 0.93 ppm singlet of **9** in the NMR probe at a temperature of 24.4 °C led to a disappearance rate constant of 2.05×10^{-4} s^{-1} ($\rho = 0.999$). The sum of the NMR peak areas of **5** (*t*-Bu at 1.47 ppm) and **9** (*t*-Bu at 0.93 ppm) gave a value that rose by less than 3% as >90% of **9** disappeared, indicating that the only fate of **9** is reversion to **5**. The reappearance rate of **5** based on its 1.47 ppm singlet was 1.90×10^{-4} s^{-1}, but this value is less reliable than the disappearance rate of **9** because the infinity point was estimated. The two-fold discrepancy between the UV and NMR regeneration rate of **5** is attributed to the different solvents used and possible temperature measurement errors.

The other irradiation product of **5** exhibited chemical behavior consistent with its structural assignment as **10**. After 36 min irradiation of **5**, the photolyzate was quickly filtered through Celite and silica gel to remove cloudiness. This treatment destroyed **10** and converted it to acetone, which was obvious from its 2.09 ppm ^{1}H singlet and its 205.74 ppm ^{13}C peak. Continued irradiation at 0 °C caused the buildup of both **9** and **10**. The thermolysis of **10** was monitored by its 1.83 ppm NMR singlet, leading to a rate constant of 1.03×10^{-5} s^{-1}. After several days at room temperature, the NMR spectrum of the product mixture from **5** exhibited many peaks whose origin could have been **10**.

The assignment of structure to the two photoisomers, while seemingly easy, required a careful analysis of the ^{1}H, ^{13}C, and ^{15}N correlated NMR spectra. First we note that the spectra of both **9** and **10** exhibit the same symmetry. There are two different methyl resonances (six

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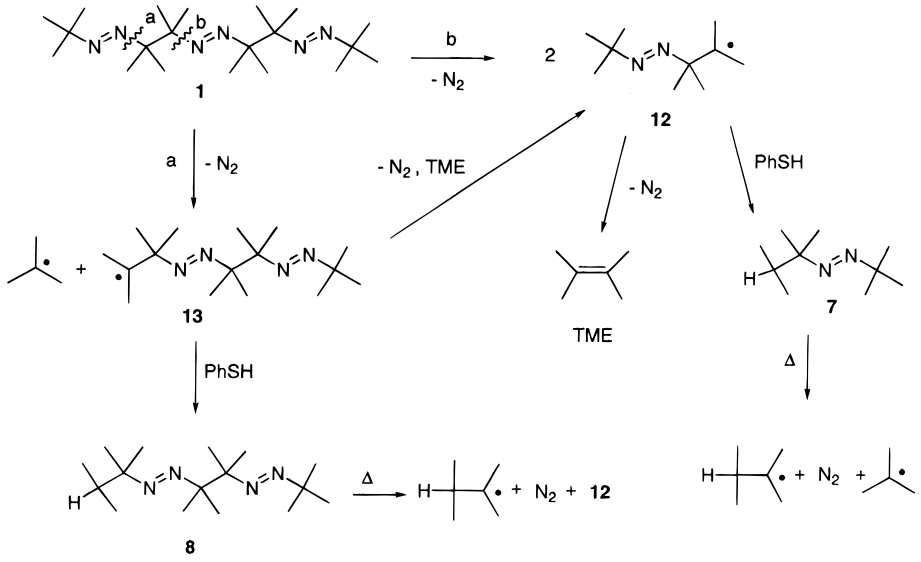
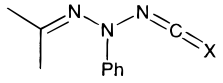
Scheme 1. Thermolysis of 1 with PhSH



hydrogens total in each), one *tert*-butyl proton resonance, ^{13}C peaks for the methyl and *tert*-butyl groups, two quaternary methyl signals in the intensity ratio 2:1, and two nitrogen resonances in the ratio of 2:1. Triaziridine **9** exhibited ^{15}N chemical shifts similar to those of related triaziridines,[15] and its configuration was assigned as anti on the basis of the absence of any NOE between the *tert*-butyl and ring methyl groups. The signals in each isomer, **9** and **10**, were correlated by direct and long-range 2D heteronuclear NMR.[16] In **10**, the nitrogen signal of intensity 2 at 179.7 ppm and the quaternary carbon of intensity 2 at 165.57 ppm are in the chemical shift range expected for the N=C group. The details of the correlated spectra verify the structures assigned to **9** and **10**, which are fully rationalized elsewhere.[16] An online search of Beilstein uncovered only two compounds (**11a**,**b**), whose structure resembles **10**.[17]



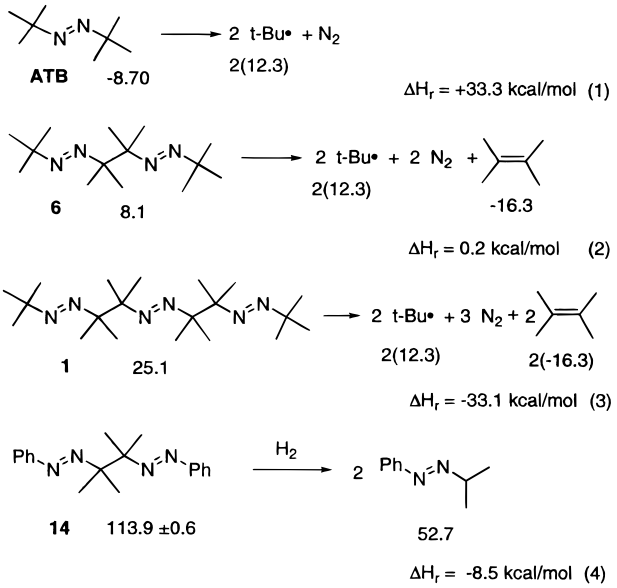
11 a X = O
11 b X = S

Discussion

Thermolysis studies of **1** demonstrated that despite the presence of three azo groups, this compound is very stable at ambient temperature. On a statistical basis, **6** should decompose twice as fast as ATB, and **1** should proceed at three times the rate of ATB. The fact that the decomposition rates of **6** and **1** were faster than these figures is attributed to a higher ground-state energy caused by greater steric crowding.[18,19]

The formation of azoalkanes **7** and **8** in the thermolysis of **1** with thiophenol shows that both radicals **12** and **13** are intermediates; that is, homolysis proceeds stepwise. Breaking bond **a** in Scheme 1 affords a *tert*-butyl radical plus β-azo radical **13**, which fragments to **12**, while initial cleavage of bond **b** leads directly to two molecules of **12**. These β-azo radicals are already known to undergo rapid fragmentation to tetramethylethylene (TME), nitrogen, and a *tert*-butyl radical.[3]

The overall thermolysis of **1** into seven fragments is considerably exothermic. Whereas fragmentation of ATB is endothermic by 33.3 kcal/mol (eq 1), **6** is nearly thermoneutral (eq 2) and **1** releases 33.1 kcal/mol (eq 3). The major fate of *tert*-butyl radicals is disproportionation to isobutane plus isobutene, a reaction that liberates 60.3 kcal/mol. Combining this figure with ΔH_r of reactions 1 and 3, we find that thermolysis of **1** to seven stable products liberates 93.4 kcal/mol, more than three times as much energy as thermolysis of azo-*tert*-butane to yield isobutane plus isobutene ($\Delta H_r = -27.0$ kcal/mol.) Extrapolation of eqs 1−3 indicates that each additional *t*-Bu-N=N−CMe_2 group renders homolysis more exothermic by ~33 kcal/mol. *It is important to note that the stepwise nature of these thermolyses masks most of the effect of exothermicity on the activation enthalpy.*



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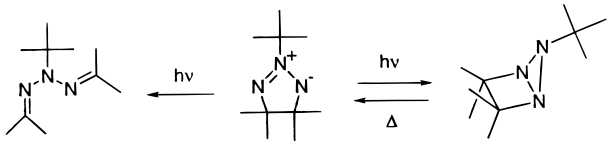
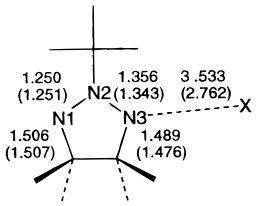
Scheme 2. Photochemical and Thermal Reactions of 5 and 9



10 **5** **9**

The reaction enthalpies in eqs 1−3 were determined from the known ΔH_f of ATB[10] and *t*-Bu•,[20] the experimental value for tetramethylethylene,[21] and the calculated ΔH_f of **1** and **6**. To obtain the latter, we assume that the heat of hydrogenation of each quaternary C−C bond of **1** and **6** equals that of **14**, which is −8.5 kcal/mol (cf. eq 4).[1] ΔH_f of *t*-Bu-N=N-i-Pr is calculated as the average of the values for ATB and azoisopropane.[10]

A possible mechanism for the formation of azimine **5** during the synthesis of **1** is halogenation of the amino group of **3** or of the sulfamide nitrogen of **4** followed by displacement of the halogen by the azo group. However, since no mechanistic studies have been carried out, we cannot rule out **9** as an intermediate in the formation of **5**.[22] The new azimine afforded both a picrate and a hydrogen iodide salt, selected bond lengths of which are shown below. Those of the iodide are listed above those of the picrate, which are in parentheses. The N1−N2



bond is shorter than the N2−N3 bond, indicating protonation of N3 and a double N1−N2 bond. The N3−X bond length is greater in the iodide (X = I) than in the picrate (X = O), presumably an effect of atomic size. On account of the net positive charge on the azimine moiety, the ^{1}H NMR chemical shifts of the picrate and iodide lie downfield from those in free **5**. The observation that the spectrum of the salts consists only of two singlets implies a plane of symmetry due to rapid exchange of the proton from N1 to N3.

A plausible mechanism for the reactions of azimine **5** is shown in Scheme 2. Irradiation of **5** affords **9**, a reaction that can be classified as an allowed disrotatory process.[23] Triazane **10** might arise directly by photolysis of **5** or by thermolysis of the exceedingly strained and undetected syn isomer of **9**. If this syn triaziridine is an intermediate, its rapid thermal ring opening to **10** is analogous to a known minor reaction of bicyclo[2.1.0]-pentane, conversion to 1,4-pentadiene.[24] Attempts to model the syn isomer calculationally led to a spontaneous *tert*-butyl flip to the thermodynamically more stable **9**. The only observed thermal reaction of **9** is simply reversion to **5**, a process found in other triaziridines.[11] This ring opening is much more facile than the conversion of bicyclo[2.1.0]pentane to cyclopentene, which proceeds through an unstabilized 1,3-biradical.

DFT calculations on the opening of **9** to **5** indicated a reaction exothermicity of 45 kcal/mol and a low activation energy. A large number of attempts to locate the TS for the ring-opening process led to many structures meeting the requirement of a single imaginary frequency. However, these invariably reflected pseudorotations of the five-membered ring or one or more of the seven methyl groups. The PE surface for the ring opening was very flat with each of these TS's appearing as pimples on the surface. Subsequently, to approximate the TS for the bond-breaking process, a series of 30 structures was generated by a relaxed potential energy in which the breaking N−N bond was extended from 1.5 to 2.15 Å in small increments (ca. 150 h CPU time). A possible maximum in the energy was found at or near 1.780 Å, corresponding to a structure whose central nitrogen had progressed only slightly toward planar. This proved not to be a true TS, but the energy was assumed to be close to that of the desired structure. The approximate activation enthalpy was 11.0 kcal/mol, which is lower than the 22.4 kcal/mol calculated from the disappearance rate of **9** at 24.5 °C with an assumed activation entropy of zero.

In summary, trisazoalkane **1** undergoes exothermic thermolysis to seven fragments. Despite its ∼65 kcal/mol greater thermodynamic driving force for homolysis than that of the simple model, azo-*tert*-butane, its rate is not even six times faster than that of ATB. A byproduct of the synthesis, azimine **5**, rearranged to **9** on irradiation, and this strained bicyclic triaziridine reopened to **5** with a half-life of about an hour at ambient temperature. Another irradiation product of **5** was found to be the triazane **10**, a member of a rare class of compounds.

Experimental Section

General. ^{1}H NMR spectra were run at 250 MHz in $CDCl_3$ unless otherwise specified. Other general procedures were as described earlier.[25]

2-(*tert*-Butylhydrazo)-2-cyanopropane[5] was prepared by adding acetone (4.2 mL, 0.057 mol) dropwise to a stirred solution of *t*-$BuNHNH_3Cl$ (7.15 g, 0.057 mol) and NaCN (2.81 g, 0.057 mol) in 20 mL of deionized water. The flask was stoppered, and the mixture was stirred overnight, whereupon the product separated an oil. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layer was dried over Na_2SO_4. The solvent was removed by rotary evaporation, leaving a yellow oil (yield > 95%). ^{1}H NMR δ 1.03 (s, 9H), 1.41 (s, 6H).

2-*tert*-Butylazo-2-cyanopropane (2)[5] was made by adding 132 mL of commercial bleach (5.25% NaOCl) over a period of 1 h to 3.6 g (0.023 mol) of ice cold 2-(*tert*-butylhydrazo)-2-cyanopropane with stirring. The ice bath was removed, and the reaction mixture was stirred for an additional 3 h. After collection of the upper layer consisting of product **2**, the aqueous layer was extracted with ether. The combined organic layer was washed with 1% HCl, followed by two portions of saturated $NaHCO_3$ and one of deionized water. The organic layer was dried over Na_2SO_4, and the ether was rotary evaporated, leaving a pale yellow oil (yield > 90%). ^{1}H NMR δ 1.22 (s, 9H), 1.61 (s, 6H). ^{13}C NMR ($CDCl_3$) 25.03, 26.41, 67.36, 67.76, 120.5. IR 2991, 2240, 2220, 1463, 1364, 1224 cm^{-1}.

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2-Amino-2,3-dimethyl-3-(*tert*-butylazo)butane (3). The method was modified from Ciganek[4] and Imamoto.[26] Cerium chloride heptahydrate[27] (10 g) was quickly ground to a fine powder in a warm, oven-dried mortar. The powdered $CeCl_3$ was transferred into a 250 mL flask containing a magnetic stirring bar and a three-way stopcock. The flask was evacuated to 0.2 mmHg and was gradually heated in a 100 °C oil bath without magnetic stirring for 2.0 h. Then the bath temperature was raised to 150 °C, the $CeCl_3$ was dried with magnetic stirring for another 1 h, and the sublimed solids were returned into the flask by frequent tapping. The vacuum was replaced by argon gas while the flask was still hot. The flask was first cooled in the air and then in an ice bath; then cool, freshly distilled, dry THF (100 mL) was added. After the suspension was stirred at room temperature overnight, the flask was cooled to −78 °C and 1 equiv of CH_3Li (1.6 M in Et_2O) was added. The mixture was stirred for 1−1.5 h at −78 °C; then the bath temperature was raised to −65 °C. 2-*tert*-Butylazo-2-cyanopropane **2** (0.25 equiv) was added, and stirring was continued for 1.5 h at −65 °C. Concentrated NH_4OH (30 mL) was added, and the mixture was allowed to warm to room temperature. The cerium slurry was filtered and washed with ether. The solvent was removed by rotary evaporation, and 5 mL of 5% aqueous HCl was added with stirring to the crude product. The mixture was extracted with ether to remove unreacted **2**. Concentrated aqueous NaOH was added very slowly to the remaining aqueous solution in an ice bath until the pH rose to 9. The azoamine was extracted with ether and dried over K_2CO_3. Removal of the solvent by rotary evaporation left **3** as a yellow oil in 30% yield. ^{1}H NMR δ 1.04 (s, 6H), 1.13 (s, 6H), 1.17 (s, 9H). ^{13}C NMR ($CDCl_3$) 20.39, 26.19, 26.77, 54.69, 66.91, 73.03. IR 3369, 3286, 2967, 1698, 1462, 1358, 1205, 804 cm^{-1}. HRMS CI$^+$ (M + H) 186.197 03, calcd 186.197 02. UV λ_{max} = 372 nm.

2,3-Dimethyl-3-(*tert*-butylazo)but-2-yl sulfamide (4) was made according to Stowell's method.[6] A 1 g portion of 2-amino-2,3-dimethyl-3-(*tert*-butylazo)butane **3** in 2 mL of dry pentane was cooled in an ice bath under N_2. SO_2Cl_2 (109 μL) in 0.2 mL of pentane was added over a period of 30 min. After removal of the ice bath, the mixture was stirred for 2 h. Deionized water (0.5 mL) and ether (2 mL) were added slowly, and mixture was stirred for 5 min. The organic layer was washed with 5% aqueous HCl and brine. Removal of the solvent yielded a light yellow solid, which was recrystallized from pentane. Yield 48%. ^{1}H NMR δ 1.06 (s, 6H), 1.18 (s, 9H), 1.46 (s, 6H) ^{13}C NMR ($CDCl_3$) 20.37, 22.61, 26.65, 61.85, 67.60, 73.44. HRMS CI$^+$ (M + 1H) 433.331 62, calcd 433.332 47.

Azimine 5. An 8 mg portion of a 50% dispersion of NaH in mineral oil (167 μmol) was rinsed with pentane and stirred with 0.5 mL of dry pentane. Sulfamide **4** (25 mg, 57.8 μmol) in 0.2 mL of dry pentane was added slowly to the ice cold NaH suspension. The mixture was stirred at room temperature for 4 h and then recooled to 0 °C. *tert*-Butyl hypochlorite (15 μL, 126 μmol, in 25 μL of pentane) was added dropwise, the temperature was allowed to rise to ambient, and the mixture was stirred overnight. Water was added very slowly to destroy the excess NaH. The pentane layer was separated, dried over Na_2SO_4, and carefully concentrated by microdistillation. Pure **5** was obtained by silica gel chromatography, eluting with 1:4 Et_2O:pentane. Yield 60%.

In an alternate procedure, **5** was made by adding 1 mL of dry pyridine and 1.35 g of IF_5 to 8 mL of dry CH_2Cl_2 under argon. The solution was stirred for 40 min at −78 °C. Azoamine **3** (1.0 g) in 3 mL of CH_2Cl_2 was added at −40 °C, and the mixture was stirred for 20 min. The temperature was allowed to rise to 0 °C, and stirring was continued for 2 h. Water (3 mL) was added dropwise, and the mixture was stirred until all of the precipitate had dissolved. The organic layer was washed with 5% HCl and then 5% $NaHSO_3$. CH_2Cl_2 was evaporated, and the oily product was stored at −5 °C overnight. The yellow HI salt of **5** (160 mg) crystallized out of the oil. After filtration, the mother liquor was added to 10 mL of CH_2Cl_2 and washed with 3 × 5 mL brine. The solvent was removed and the residue subjected to silica gel chromatography, yielding 760 mg (85%) of liquid azimine **5**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (s, 12H), 1.47 (s, 9H). ^{13}C NMR ($CDCl_3$) 19.14, 27.98, 64.41, 69.18. These ^{1}H and ^{13}C δ's differ slightly from those in the Supporting Information, which were obtained at 250 MHz. ^{15}N NMR ($CDCl_3$ solvent, δ relative to NH_3) 294.9, 326.5. IR 2973, 2934, 1514, 1448, 1415, 1363, 1226, 1213, 1167 cm^{-1}. UV λ_{max} = 288 nm, ϵ = 2500. HRMS EI$^+$ 183.1732, calcd 183.1732. HI salt: ^{1}H NMR δ 1.41 (s, 12H), 1.85 (s, 9H).

Picrate of 5. In a 3 mL conical vial, 0.3 mL of a saturated solution of picric acid in 95% EtOH was added to 15 mg of azimine **5** in 0.3 mL of 95% EtOH. The vial was equipped with a condenser, and the mixture was refluxed for 1 min. The solution was cooled slowly to room temperature. Needlelike yellow crystals were collected by vacuum filtration. The crystals were further purified by recrystallization from 95% EtOH. Mp 129.5 °C. ^{1}H NMR 1.31 (12H), 1.75 (9H), 8.91 (2H).

Trisazoalkane 1 was made according to a modified procedure of Timberlake.[9] A 100 mL flask charged with 1.6 g of **3**, 9.2 mL of dry pyridine (freshly distilled from CaH_2), and 30 mL of dry CH_2Cl_2 was quickly connected to a 20 mL funnel equipped with a septum and an argon balloon. An IF_5 solution (19 mL of 3.5 g of IF_5 in 25 mL of CH_2Cl_2) was quickly syringed into the funnel. The IF_5 solution was added over 4 h at −78 °C, and the resulting solution was stirred for 5.5 h at −78 °C. The bath temperature was raised slowly to −50 °C, 2 mL of ethanol was added dropwise, and the bath temperature was raised to −10 °C over 15 min. Water (5 mL) was added dropwise, and the mixture was stirred for 10 min; then, the mixture was poured into ice water. The organic layer was washed successively with 5% HCl, 5% $NaHSO_3$, and brine; then it was dried over Na_2SO_4. Following removal of the solvent, silica gel chromatography with 5% ether in pentane afforded **1** as a yellow solid. Recrystallization from MeOH and Et_2O (9:1) gave light yellow flakes in 32% yield. Mp 75 °C. ^{1}H NMR (C_6D_6) δ 1.21 (18H), 1.29 (12H), 1.34 (12H). ^{1}H NMR ($CDCl_3$) δ 1.106 (12H), 1.133 (12H), 1.158 (18H). ^{13}C NMR ($CDCl_3$) 20.76, 20.87, 26.80, 66.69, 72.67, 73.67. HRMS CI$^+$ (M + 1H) 367.35454, calcd 367.35492. UV (λ_{max} = 374 nm, ϵ = 55). 150 mg of **5** was obtained as a byproduct in this reaction.

Thermolysis Products of 1. The ^{1}H NMR spectrum of thermolyzed samples of **1** in C_6D_6 exhibited major peaks for isobutane (0.863 d, 10H, J = 6.6 Hz; 1.637 dectet, 1H, J = 6.6 Hz), isobutene (1.596 t, 6H, J = 1.15 Hz; 4.750 sept, 2H, J = 1.14 Hz), and tetramethylethylene (1.618 s), as judged by comparison with authentic samples. An unidentified doublet appeared at 0.964 ppm, J = 6.8 Hz. In a separate experiment, a benzene solution containing 0.055 M **1** and 0.23 M thiophenol was placed into three tubes, which were degassed and sealed. After heating for a known time, the tubes were opened and analyzed by GC using an internal standard. The times (min) and concentrations (M) of **7** and **8** (M) were 262, 0.0020, 0.0010; 501, 0.0020, 0.00067; 1366, 0.0013, 0.000065.

Nitrogen Yield of 1. A solution of 15.1 mg of **1** in 1.5 mL of decane was subjected to four freeze−thaw degas cycles at 77 K below 10^{-4} mmHg. The tube was sealed under vacuum and was heated at 170 °C for 10 h. After the tube was broken under vacuum, the evolved gases were collected using a Töpler pump with a liquid nitrogen trap to retain any condensable gases. The nitrogen, which was quantified in a gas buret, corresponded to a yield of 97.5%.

Thermolysis Kinetics of 1. The disappearance rate of **1** was monitored by UV using a HP-8452 diode array spectrometer. The temperatures (°C) and rate constants (s^{-1}) are as follows: 155.49, 8.81×10^{-5}; 157.42, 1.04×10^{-4}; 161.97, 1.74×10^{-4}; 169.85, 3.33×10^{-4}; 173.92, 4.90×10^{-4}; 178.62, 8.07×10^{-4}; 182.45, 1.16×10^{-3}. These values were used in the Eyring equation to obtain the activation parameters in Table 1.

Irradiation Products of 5. A solution of **5** cooled below 0 °C was irradiated with 313 nm light from a 500 W high-pressure mercury lamp through a potassium chromate filter

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solution. The irradiation in pentane (10 mL) employed 50 mg of **5**. For the NMR experiment, a solution of 90 mg of **5** in 0.4 mL of $CDCl_3$ was monitored by periodic spectra taken as quickly as possible to avoid reversion of **9** to **5**. Triaziridine **9** ^{1}H NMR (400 MHz, $CDCl_3$) 0.93 (9H), 1.04 (6H), 1.24 (6H). ^{13}C NMR 20.16, 21.80, 23.70, 54.96, 64.19. ^{15}N NMR versus NH_3 148.6, 154.0. Triazane **10** ^{1}H NMR 1.01 (9H), 1.83 (6H), 1.87 (6H). ^{13}C NMR 18.9, 24.3, 24.5, 60.44, 165.57. ^{15}N NMR versus NH_3 179.7, 340.7.

Theoretical Calculations. All calculations were carried out with Gaussian 98.[28] The structures of **5** and **9** were initially minimized at the HF/3-21G* level. Such minimizations routinely required 4−6 h on a Dec-Alpha 500 MHz workstation. The relaxed potential energy scan (30 data points) was also carried out at this level. All structures were then reoptimized at the Becke3LYP/6-31G* level following a suggestion from Professor Paul v. R. Schleyer.[29]

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Supporting Information Available: A table of SPARTAN quantum chemical results, X-ray crystallography data for the picrate and hydrogen iodide salts of azimine **5**, and NMR spectra of **1** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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