Thermolysis of Geminal Bisazoalkanes. Stabilization of a Carbon-Centered Radical by the Azo Substituent

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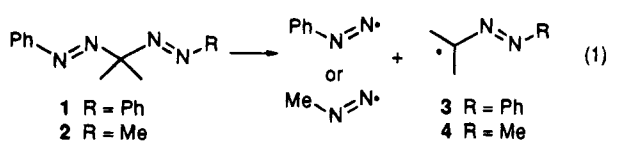
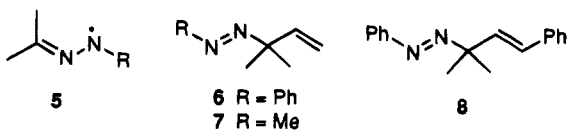
Two geminal bisazoalkanes (**1** and **2**) have been employed to generate a radical center next to the azo group. The 8.0 kcal/mol lower $\Delta G^{\ddagger}$ for thermolysis of **1** and **2** relative to model compounds **6** and **7** is dissected into a 1 kcal/mol contribution from ground state elevation of **1** and **2** and at least 2.6 kcal/mol from phenyl stabilization of radical **3**. Any extra stabilization of the aliphatic 2,3-diazaallyl radical (**4**) relative to α,α-dimethylallyl amounts to no more than 4.4 kcal/mol. Finally, γ-phenyl conjugation of the α,α-dimethylallyl radical stabilizes it by 4.5 kcal/mol.

Thermolysis of azoalkanes is facilitated by radical stabilizing groups on the α-carbon atom;[1] in fact, the rate of this reaction serves as a good quantitative measure of radical stability.[2] When the activation energies for azoalkane homolysis are plotted against the most recent values of the bond dissociation energy (BDE) for the corresponding hydrocarbons, the result is a straight line of slope 1.03 and correlation coefficient of 0.983.[3] Although azoalkanes have been widely used to generate free radicals,[2] the effect of the azo substituent on an adjacent radical center (α-azo radicals) has received little attention. Azoalkanes are better α-hydrogen atom donors to the trichloromethyl radical than are the corresponding olefins,[4] and gas phase decomposition of simple azoalkanes gives minor products arising from attack at the α-hydrogen of the starting material.[5] A few azoalkanes undergo homolysis of the C–C bond adjacent to the azo group instead of the usual C–N homolysis.[6–10] Using vicinal bisazoalkanes, we have recently determined that any extra stabilization of a radical center by the azo group relative to a vinyl group amounts to no more than 3.1 kcal/mol.[11]

In this report, we consider the thermolysis of geminal bisazoalkanes **1** and **2**. While C–N cleavage of the symmetrical compound **1** gives α-azo radical **3**, there are two possible cleavages in **2**, yielding either **3** or **4** (cf. eq 1). Only two *gem*-bisazoalkanes have appeared in the literature previously,[12,13] and studies of their decomposition are competely lacking. Although the term "α-azo radical" shows the relationship of the radical to its precursors, these species are better described as hydrazonyl radicals (**5**).[11,14] Oxidation of hydrazones[15–17] produces hydrazonyl radicals that dimerize reversibly[10,11,18,19] and can be observed by ESR spectroscopy.[20,21] Model azo compounds **6**–**8** were also studied in an effort to sort out the effect of phenyl groups on the stability of allylic and hydrazonyl radicals.





Results

Synthesis of Compounds. The geminal bisazoalkanes **1** and **2** were prepared from benzenediazonium tetrafluoroborate and acetone phenylhydrazone (APH) or acetone methylhydrazone (AMH), respectively.[12] Such reactions usually fail when aldehyde hydrazones are used because the bisazo products tautomerize to formazans.[12,22] The *gem*-dimethyl group of our compounds serves to prevent this undesired reaction. The known allylic azoalkanes **6**[23–25] and **7**[26] were made by oxidation of the appropriate urea and sulfamide, respectively.

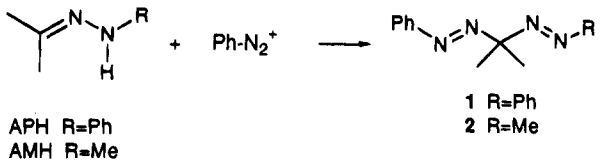


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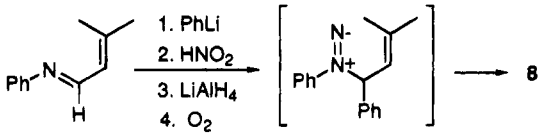
Table 1. Activation Parameters for Thermolysis of Selected Azoalkanes

compd	solvent	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}(298)$[a]	temp range, °C
1	Ph_2O	29.3 ± 0.6	12.6 ± 1.7	25.5	60.8–68.9
1	C_6H_6	24.9 ± 0.2	−0.3 ± 0.5	25.0	49.1–68.6
1	C_6H_6 + PhSH	25.3 ± 0.2	1.0 ± 0.5	25.0	49.1–68.6
2	xylene	25.9 ± 0.2	8.9 ± 0.7	23.2	30.5–41.2
6	Ph_2O	37.3 ± 0.5	12.6 ± 1.3	33.5	146.7–164.4
7[b]	*p*-diisopropyl-benzene	35.3 ± 1.0	13.6 ± 2.5	31.2	114.6–133.3
8	C_6D_6	29.7 ± 0.3	2.1 ± 0.9	29.0	97.5–121.6

[a] kcal/mol. [b] Reference 26.

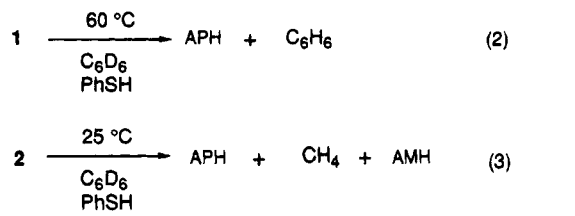
Because conventional routes to **8** were unsuccessful, we employed the [2,3]-sigmatropic shift of allylic l,l-diazene **10**.[24,25] Surprisingly, the two olefinic hydrogens of **8** occur at the same chemical shift in both C_6D_6 and $CDCl_3$ but a $^1H-^{13}C$ HETCOR spectrum verified the structure.



9 **10**

Thermolysis of 1, 2, and 6–8. Thermolysis of **1** in benzene for 7 h at 80 °C gave nitrogen in 98% yield, but a similar experiment with **2** afforded N_2 in only 87% yield, probably because **2** is labile and it partially decomposed during weighing. The rates of nitrogen evolution for both compounds and for model compound **6** were determined at several temperatures, leading to the activation parameters shown in Table 1. Because the $\Delta S^{\ddagger}$ obtained by N_2 evolution rates for **1** came out unexpectedly high and because the temperature range employed was only 8 °C, we repeated the kinetic study with and without added thiophenol over a 19 °C range, monitoring by UV spectroscopy. Without PhSH, a small, unidentified 414 nm band remained at $t = \infty$, but only an absorption tail was observed in the presence of PhSH. The first-order plots without PhSH were linear only when the residual absorbance was subtracted from each reading; moreover, this treatment led to much better agreement between the activation parameters calculated with and without PhSH than did the treatment where the infinity point was not subtracted (cf. Table 1). All three series of kinetic runs for **1** in Table 1 gave similar values of $\Delta G^{\ddagger}$ but the lower $\Delta S^{\ddagger}$ figures are preferred because the temperature range was larger in these series. Disappearance of **8** was monitored by UV spectroscopy with results also included in Table 1.

Although the thermolysis products from **1** and **2** were complex in the absence of a radical scavenger, inclusion of thiophenol in the initial degassed solution allowed NMR identification of the major products shown in eqs 2 and 3. The formation of methane from **2** was further verified by GC. While the dominant product from **2** was APH, a miniscule GC peak was observed at the correct retention time for AMH. Thus heating **2** with thiophenol at 39.3 °C showed APH and AMH in a 3610:1 ratio after correction for response factors. This ratio is important for assessing the relative cleavage rate of the two bonds from nitrogen to the central carbon of **2**; however, the amount of AMH is so small that it could merely be residual starting material from the synthesis of **2**.



Discussion

In light of recent evidence favoring stepwise azoalkane homolysis,[24,27–33] we suggest that C–N bond cleavage takes place in **1** and **2** to produce $^{\bullet}CMe_2N{=}NPh$ (**3**) plus phenyldiazenyl and methyldiazenyl radicals, respectively. The hydrazonyl radical **3** abstracts hydrogen exclusively on N,[11] while the diazenyl radicals lose nitrogen to give phenyl or methyl radicals which then abstract hydrogen from thiophenol.

In accord with our previous treatment[24] of the energetics of decomposition of **6** and **7**, we assume that the barrier ($\Delta G^{\ddagger}_D$) to homolytic loss of nitrogen from the phenyldiazenyl radical is 8.9 kcal/mol while that for the methyldiazenyl radical is 6.6 kcal/mol. If diazenyl–allyl radical pair recombination proceeds with a negligible activation energy,[34] the observed $\Delta G^{\ddagger}$ for azoalkane thermolysis ($\Delta G^{\ddagger}_{obs}$) is simply $\Delta G^{\ddagger}_D$ plus the energy needed to break the first C–N bond (ΔG_1). The figure 24.6 kcal/mol has already been suggested[24] for ΔG_1 of $RN{=}NCMe_2CH{=}CH_2$ thermolysis, and we shall adopt this value for **6** and **7**. Although recent evidence suggests that $\Delta G^{\ddagger}_D$ for $CH_3N{=}N^{\bullet}$ may be less than 6.6 kcal/mol,[35,36] the exact value is not important in the present treatment because only azoalkanes giving the same diazenyl fragment will be compared. Our implicit assumption that the barrier to recombination of diazenyl with alkyl radicals is less than that for fragmentation of the diazenyl radicals is supported by the formation of "turn-around" azoalkanes when one R group is allylic.[24]

Stepwise homolysis and the activation free energy for each step are shown in eqs 4–9 for the compounds listed in Table 1. We have used the $\Delta G^{\ddagger}_{obs}$ for each azo compound and the assumed $\Delta G^{\ddagger}_D$ values to calculate ΔG_1 for the initial C–N cleavages, since $\Delta G_1 = \Delta G^{\ddagger}_{obs} - \Delta G^{\ddagger}_D$. Because **1** is a symmetrical compound, we applied a statistical correction to its rate constant.[37] The ΔG_1 in eq 8 is a minimum value calculated by converting the maximum yield of AMH relative to APH (2.77×10^{-4}) to a free energy difference at 25 °C. The resulting $\Delta\Delta G^{\ddagger}$ of

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(37) Since two identical C–N bonds can break initially in **1**, the observed rate is twice as fast as if only one such bond cleaved. We calculate that $\Delta G^{\ddagger}$ for **1** would be 0.4 kcal/mol higher, or 25.5 kcal/mol, if this statistical advantage were absent.

4.9 kcal/mol was added to the observed $\Delta G^{\ddagger} = 23.2$ kcal/mol for **2** → Me•, giving $\Delta G^{\ddagger} > 28.1$ kcal/mol for **2** → Ph•.

$$\underset{\mathbf{6}}{\mathrm{PhN{=}NCMe_2CH{=}CH_2}} \xrightarrow{24.6} \mathrm{PhN{=}N^{\bullet} + {}^{\bullet}CMe_2CH{=}CH_2} \xrightarrow{8.9} \mathrm{Ph^{\bullet} + N_2} \quad (4)$$

$$\underset{\mathbf{1}}{\mathrm{PhN{=}NCMe_2N{=}NPh}} \xrightarrow{16.6} \mathrm{PhN{=}N^{\bullet} + {}^{\bullet}CMe_2N{=}NPh} \xrightarrow[\mathbf{3}]{8.9} \mathrm{Ph^{\bullet} + N_2} \quad (5)$$

$$\underset{\mathbf{7}}{\mathrm{MeN{=}NCMe_2CH{=}CH_2}} \xrightarrow{24.6} \mathrm{MeN{=}N^{\bullet} + {}^{\bullet}CMe_2CH{=}CH_2} \xrightarrow{6.6} \mathrm{Me^{\bullet} + N_2} \quad (6)$$

$$\underset{\mathbf{2}}{\mathrm{MeN{=}NCMe_2N{=}NPh}} \xrightarrow{16.6} \mathrm{MeN{=}N^{\bullet} + {}^{\bullet}CMe_2N{=}NPh} \xrightarrow[\mathbf{3}]{6.6} \mathrm{Me^{\bullet} + N_2} \quad (7)$$

$$\underset{\mathbf{2}}{\mathrm{MeN{=}NCMe_2N{=}NPh}} \xrightarrow{>19.2} \mathrm{PhN{=}N^{\bullet} + {}^{\bullet}CMe_2N{=}NMe} \xrightarrow[\mathbf{4}]{8.9} \mathrm{Ph^{\bullet} + N_2} \quad (8)$$

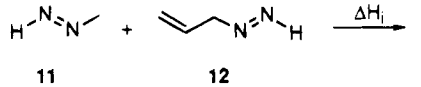
$$\underset{\mathbf{8}}{\mathrm{PhN{=}NCMe_2CH{=}CHPh}} \xrightarrow{20.1} \mathrm{PhN{=}N^{\bullet} + {}^{\bullet}CMe_2CH{=}CHPh} \xrightarrow{8.9} \mathrm{Ph^{\bullet} + N_2} \quad (9)$$

Equations 4–9 reveal sizeable variations in the ease of breaking the first C–N bond of azoalkanes. For example, initial cleavage of **1** is 8.0 kcal/mol more facile than that of **6** (cf. eqs 4 and 5); the same value is obtained by comparing **2** with **7** (cf. eqs 6 and 7). Since both sets of reactions give a common radical (PhN=N• and MeN=N•, respectively), **3** must be more stable than the dimethylallyl radical, ignoring any ground state energy differences (see below). One might hope to estimate the effect of phenyl conjugation on **3** from its effect on an allylic radical. Comparison of eqs 4 and 9 implies that phenyl stabilizes the dimethylallyl radical by 4.5 kcal/mol, in reasonable agreement with the 5.4 kcal/mol found for allyl versus 1-phenylallyl.[38] The 0.9 kcal/mol difference can be attributed to the fact that the stabilization due to phenyl is generally smaller in an already stabilized radical.[39] Unfortunately, because of the high spin density on nitrogen,[20,21] the phenyl group may stabilize radical **3** more than it stabilizes dimethylallyl. It then becomes necessary to eliminate the effect of phenyl conjugation, which might be done by considering eq 8. Comparison of eqs 4 and 8 shows that in the purely aliphatic series, α-azo radical **4** is less than 5.4 kcal/mol more stable than dimethylallyl. Although an accurate value for this stability difference would be highly desirable, the present data allow us to deduce only a maximum, as will be discussed further below. Also of interest is the phenyl stabilization energy of an α-azo radical, a figure shown by comparing eqs 5 and 8 to equal at least 2.6 kcal/mol.

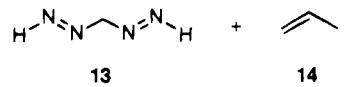
Since the ground state energy of radical precursors can be just as important as product radical stabilization in its effect on $\Delta G^{\ddagger}$,[40–42] we must determine whether two azo groups on the same carbon atom elevate the ground state of **1** and **2**. For example, the gem azo groups in **1** and **2** could suffer a repulsive interaction that accounts for part of the $\Delta G^{\ddagger}$ difference between eqs 4 and 5, eqs 6 and 7, or eqs 4 and 8. In other cases, this "geminal effect" can result in ground state stabilization or destabilization amounting to more than 10 kcal/mol.[43]

An experimental approach to this problem would require a value of ΔH_i for the isodesmic reaction 10. Making use of the identity reaction 11, we may deduce the desired bond dissociation energy difference, $D_4 - D_1$, from measurable quantities D_2 and D_3 by the simple equation $D_4 - D_1 = D_2 - D_3 - \Delta H_i = 8.0$ kcal/mol $- \Delta H_i$. In view of the errors inherent in determinations of $\Delta H^{\ddagger}$,[44] we have assumed that $D_2 - D_3$ equals the difference in activation free energy between **1** and **6**. Unfortunately, determination of ΔH_i requires the heat of formation (ΔH_f) of the four compounds shown in eq 10 (Scheme 1). Of these, the most troublesome is **1**, whose instability precludes meaningful calorimetric work. Even if ΔH_f(**1**) could be measured, each ΔH_f in eq 10 would have enough uncertainty that ΔH_i would not be very reliable. We therefore turned to theoretical calculations to evaluate ΔH_i.

In order to avoid excessive computation times, the phenyl and methyl groups in the components of eq 10 were replaced by hydrogen, leading to eq 12. All calcula-



11 **12**



13 **14** (12)

tions were performed using the GAUSSIAN 92 program system,[45] optimizing geometries of **11**–**13**[46] at the Hartree–Fock 6-31G** level. For each species, the equilibrium structure was confirmed to be a local minimum by performing a vibrational analysis at the optimized geometry and verifying that all of the normal mode frequencies were real. The calculated structure of methyldiazene (**11**) reproduced that found by McKee[14] and was very close to the one reported by Tomasic and Scuseria.[47] Using the //HF/6-31G** geometries, we refined our estimate of ΔH_i by performing single-point energy cal-

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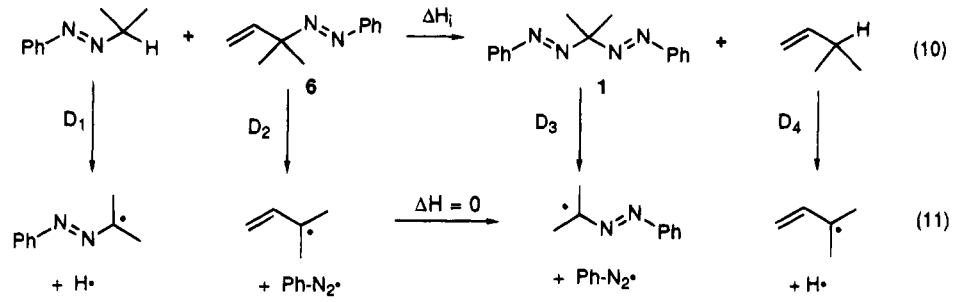
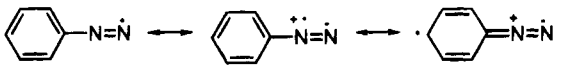
Scheme 1



culations with the extended 6-311G** basis set and also by including electron correlation effects through a fourth-order Moller–Plesset correlation energy correction (MP4) with a 6-31G** basis. We were encouraged by the fact that the variation in ΔH_i from one level of treatment to another was only 0.8 kcal/mol. Our best estimate of 1.02 kcal/mol for ΔH_i (at zero Kelvin) is from the MP4/6-31G**//HF/6-31G** calculation and includes zero-point energy corrections.

Ignoring the gem dimethyl group and applying this ΔH_i to eqs 10 and 11 gives $D_4 - D_1 = 7$ kcal/mol. Part of this difference is due to the phenyl group, as shown by comparison of eqs 5 and 8. Phenyl stabilization amounts to at least 2.6 kcal/mol, but we cannot deduce an exact value because the yield of AMH from **2** is so small. This limitation, which arises because eq 7 is much more important than eq 8, might be overcome if a purely aliphatic gem bisazoalkane could be studied. Unfortunately, such compounds are unknown and are not likely to be accessible by the approach used here, which relies on diazonium ion chemistry. Any extra stabilization of **4** relative to dimethylallyl must therefore be no more than 4.4 kcal/mol. In earlier work,[11] we concluded that D_4 minus the C–H BDE of *t*-BuN=NCMe$_2$H was less than 81.7 − 78.6 = 3.1 kcal/mol.

It is of interest that thermolysis of **2** leads mainly or perhaps only to one of the two possible fragmentation modes, shown in eq. (7). Since the odd electron of the diazenyl radical may be stabilized by resonance[48] (**15**), the dominance of eq 7 must arise from still greater phenyl stabilization of the diazaallylic radical.



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In summary, we have found that geminal bisazoalkanes undergo thermolysis to α-azo radicals at moderate temperatures. The major product from both **1** and **2** was acetone phenylhydrazone, showing in the case of **2** that the aliphatic azo linkage is far more labile than the aromatic one. By assuming stepwise thermolysis, we have deduced from the activation parameters that radical **3** is 7 kcal/mol more stable than 1,1-dimethylallyl (i.e. $D_4 - D_1 = 7$ kcal/mol) and that γ-phenyl conjugation stabilizes the 1,1-dimethylallyl radical by 4.5 kcal/mol. Because loss of phenyldiazenyl from **2** was below our detection limit, we can only say that aliphatic α-azo radical **4** is less than 4.4 kcal/mol more stable than dimethylallyl and that phenyl stabilizes the α-azo radical by at least 2.6 kcal/mol. Ab initio theoretical calculations show that ground state elevation due to two azo groups on the same carbon amounts to only 1 kcal/mol.

Experimental Section

General. The following instrumentation was employed in this study. NMR spectroscopy: JOEL FX-90Q, Bruker AF-250, Bruker AF-500, solvent $CDCl_3$. UV spectroscopy: Cary 17. Nitrogen yields: vacuum line with Toepler pump, gas buret, and GC interface.[11] Gas evolution kinetics: homemade constant volume, variable pressure automated kinetics apparatus.[49] Melting points (uncorrected): Mel-Temp apparatus. HPLC: Beckman 342 system with a model 165 dual variable wavelength detector.

2,2-Bis(phenylazo)propane (1). A mixture of 25 mL of concd HCl and 15 mL of water was cooled in an ice–salt bath. A 10.3 g (0.11 mol) portion of freshly distilled aniline was slowly added with stirring. The aniline was diazotized by the slow addition of 7.6 g of $NaNO_2$ as a saturated aqueous solution while maintaining the temperature below 5 °C. In a second flask, a solution of 15 g (0.10 mol) of freshly prepared acetone phenylhydrazone, 80 mL of DMF, and 40 mL of pyridine was cooled in the ice–salt bath. The benzenediazonium chloride solution was slowly added with stirring to the phenylhydrazone while keeping the temperature below 10 °C. After addition was complete, the mixture was stirred in the cold for 15 min, and the orange solid product was filtered off rapidly. Low-temperature (−78 °C) recrystallization from methanol gave 10.2 g (40%) of greenish yellow product. Mp. 40 °C dec. UV (hexane) $\lambda_{max} = 412$ nm, $\epsilon = 393$. ^{1}H NMR: 1.58 (s, 6H); 7.50 (m, 6H); 7.81 (m, 4H). ^{13}C NMR: 23.04, 96.84, 122.43, 128.93, 130.82, 151.84. Anal. Calcd for $C_{15}H_{16}N_4$: C, 71.4; H, 6.39; N, 22.2. Found: C, 71.09; H, 7.02; N, 21.88.

2-(Phenylazo)-2-(methylazo)propane (2). Into a 250 mL round bottom flask fitted with a cooled addition funnel were placed 2.25 g of acetone methylhydrazone, 2.64 g of triethylamine, and 80 mL of DMF. The solution was cooled to −15 °C, and a solution of 5.01 g of benzenediazonium fluoroborate[50] in 40 mL of DMF was placed into the addition funnel which was also held at −15 °C. The diazonium salt was added to the stirred hydrazone solution over 40 min, and the mixture was then stirred for 1 h. The crude reaction mixture was poured into an ice-cold mixture of 100 mL of hexane and 100 mL of water. The hexane layer was separated, washed with ice water, and dried over K_2CO_3. The solvent was removed with a vacuum pump and trap while the product was kept around 0 °C. The remaining orange oil (1.79 g) was shown by NMR to contain 64% of the desired product. Purification was effected using preparative HPLC on a cold (~5 °C) silica gel column eluting with 10% EtOAc in hexane. The greenish-yellow oil exhibited a UV maximum at 410 nm (hexane) but was too unstable for ε determination and elemental analysis. ^{1}H NMR: 1.42 (s, 6H); 3.96 (s, 3H); 7.49 (m, 3H); 7.78 (m, 2H). ^{13}C NMR: 22.80, 57.45, 96.27, 122.41, 128.88, 130.86, 151.68.

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***N*-(1,1-Dimethylallyl)-*N'*-phenylurea**. To a stirred solution of 3.15 g (37 mmol) of 2-amino-2-methyl-3-butene[26] in 100 mL of hexane under nitrogen was slowly added 4.42 g (37 mmol) of phenyl isocyanate in 10 mL of benzene. The white slurry was stirred at ambient temperature for 2 h and the collected solid was recrystallized from toluene and dried under vacuum. Yield: 6.5 g (86%). Mp 121–122 °C. ^{1}H NMR: 1.36 (s, 6H); 5.10 (m, 2H); 6.00 (m, 1H); 7.28 (m, 5H). Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.71. Found: C, 70.89; H, 8.25; N, 13.98.

3-Methyl-3-(phenylazo)-1-butene (6).[23-25] Under nitrogen, 150 mL *of tert*-butyl alcohol, 1.79 g (16.0 mmol) of potassium *tert*-butoxide, and 2.42 g (11.9 mmol) of the above urea were stirred for 25 min. While the reaction temperature was maintained below 26 °C, a 2.6 g (24.0 mmol) portion of *tert*-butyl hypochlorite was slowly added to the stirred slurry. The mixture was stirred at ambient temperature until all of the suspended urea was consumed. The solution was added to 100 mL of pentane and 200 mL of ice water. The pentane layer was washed with ice water, dried over K_2CO_3, and carefully rotary evaporated. The residual greenish-yellow oil weighed 1.22 g (59.1%). ^{1}H NMR: 1.44 (s, 6H); 5.20 (m, 2H); 6.18 (m, 1H); 7.42 (m, 3H); 7.66 (m, 2H).

3-Methyl-1-phenyl-3-(phenylazo)-1-butene (8). Into a round bottom flask equipped with a Dean–Stark trap was placed 6.9 g of aniline, 6.23 g of 3-methyl-2-butenal, and 100 mL of benzene. The mixture was stirred and refluxed for 2 h to remove about 1.4 mL of water. An oily brown product (11.7 g, 99%) was obtained after the solvent was removed. Because attempted vacuum distillation led to decomposition, the crude Schiff base was used directly in the next step. ^{1}H NMR (250 MHz): δ 1.96 (3H, d, J = 1.0 Hz), 2.01 (3H, d, J = 1.1 Hz), 6.22 (1H, m), 7.38–7.08 (5H, m), 8.36 (1H, d, J = 9.6 Hz).

A solution of 1.57 g bromobenzene in 30 mL dry THF was cooled to −78 °C under nitrogen. A 12 mL portion of *tert*-butyl lithium (1.7 M in pentane) was slowly dropped into the solution with stirring over 15 min. After the reaction was stirred at −78 °C for about 1 h, the above Schiff base (1.59 g in 15 mL of THF) was added, and the reaction was stirred at −78 °C for another 1.5 h before it was warmed up to room temperature. TLC (20% EtOAc, 80% hexane) showed only one major product (R_f = 0.8). The crude amine (98% yield) was purified by column chromatography on silica gel, eluting with 5% EtOAc/95% hexane. ^{1}H NMR (250 MHz): δ 1.80 (3H, d, J = 1.2 Hz), 1.87 (3H, d, J = 1.3 Hz), 4.05 (1H, br s), 5.15 (1H, d, J = 8.7 Hz), 5.38 (1H, m), 6.60 (2H, dd, J_1 = 7.5 Hz, J_2 = 1 Hz), 6.74 (1H, t, J = 7.3 Hz), 7.47–7.15 (7H, m); ^{13}C NMR (250 MHz): δ 18.38, 25.54, 56.40, 113.22, 117.13, 126.24, 126.71, 127.33, 128.48, 128.79, 134.12, 143.70, 147.36. MS (70 eV): *m/e* (relative abundance) 77 (8.7), 91 (12), 93 (13), 105 (8), 115 (11), 117 (30), 129 (15), 130 (18), 149 (17), 150 (100), 151 (25), 237 (8).

A 2.1 g portion of the above amine and 25 mL of 95% EtOH was cooled to 0–4 °C. Concentrated HCl (2.6 mL) was added with mechanical stirring, resulting in a brown slush. A 1.3 g portion of $NaNO_2$ in 4 mL of water was slowly added, maintaining the temperature below 4 °C. After addition, the reaction was stirred at 4 °C for 30 min. The brown-black solution was washed sequentially with 25 mL of water, 5% aqueous $NaHCO_3$, and water. The solution was dried over K_2CO_3 and rotary evaporated to yield fairly pure product according to TLC and NMR. The brown oil was purified by column chromatography on silica gel, eluting with 20% EtOAc in hexane. The nitrosamine was obtained as a light yellow solid, mp 28–30 °C, in 67.6% yield. As is usual for nitrosamines,[51] the ^{1}H NMR was complex because both syn and anti forms were present. ^{1}H NMR (500 MHz) major isomer: 1.562 (3H, d, J = 1.15), 1.637 (3H, d, J = 0.90), 5.383 (1H, dm, J = 8.7), 7.041 (2H, d, J = 7.5), 7.123 (1H, d, J = 9.3), 7.166–7.265 (10 H, m). The minor isomer (12%) showed distinguishable peaks at 1.762 (3H, d, J = 1.2), 1.754 (3H, d, J = 1.25), 5.646 (1H, dm, J = 9.4), 6.622 (2H, m). Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.75; H, 6.82; N, 10.53. Found: C, 76.85; H, 7.06; N, 10.43.

A 0.5 g portion of LAH and 100 mL of dry ether were refluxed for 1 h under N_2 and then cooled to 0 °C. The above nitrosamine (1.3 g) in 20 of mL dry ether was slowly dropped into the stirred LAH solution. The reaction was stirred at 0 °C for 1 h and at room temperature for 12 h. TLC (silica gel, 10% EtOAc in hexane) revealed many products (nitrosamine R_f = 0.5; **8**, R_f = 0.8) A 2 mL portion of 3 N NaOH was used to destroy excess LAH, and the yellow solution was extracted with ether, which was then removed by rotary evaporation. The crude product (1.2 g) was purified by silica gel column chromatography (hexane eluent), and the first yellow fraction was the desired compound. Air oxidation presumably converted the 1,1-disubstituted hydrazine to **10**, which spontaneously rearranged to **8**. Yield 0.18 g (22%) of pure **8**. ^{1}H NMR (250 MHz): δ 1.56 (6H, s), 6.57 (2H, s, both olefinic H's), 7.47–7.25 (8H, m), 7.72–7.68 (2H, m). ^{13}C NMR (250 MHz): δ 25.15, 71.02, 121.83, 126.17, 127.14, 127.93, 128.26, 128.67, 129.96, 134.88, 136.99. UV (hexane): λ_{max} = 410 nm, ϵ = 121.5. Anal. Calcd for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19: Found: C, 81.53; H, 7.45; N, 11.40.

Kinetics. A 0.99 M solution of the azo compounds in the solvents shown in Table 1 was placed in the automated gas evolution kinetics apparatus.[49] Pressure–time data were treated with a first order kinetics computer program, giving the following results (compound, method, solvent, temp, °C, 10^4k, s^{-1}): **1**, N_2 evolution, Ph_2O, 60.85, 2.57; 62.00, 2.97; 64.83, 4.45; 68.85, 7.34. **1**, UV, C_6H_6, 49.14, 0.776; 55.74, 1.91; 61.62, 3.73; 68.64, 7.38. **1**, UV, C_6H_6 with 0.0075 M PhSH, 49.14, 0.798; 55.74, 1.86; 61.62, 3.72; 68.64, 7.68. **2**, N_2 evolution, xylene, 30.49, 1.19; 35.89, 2.55; 37.90, 3.33; 39.14, 4.03; 41.21, 5.31. **6**, N_2 evolution, Ph_2O, 146.68, 1.85; 150.00, 2.79; 154.97, 4.54; 158.44, 6.57; 166.42, 14.7. **8**, UV, C_6H_6, 97.47, 0.669; 102.73, 1.37; 109.11, 2.46; 114.58, 4.58; 121.38, 8.69. **8**, NMR, C_6D_6, 121.32, 10.0; 121.61, 9.41. Correlation coefficients of the first order plots were uniformly above 0.997.

Product Studies. A solution of 14.4 mg (0.0758 mmol) of **2** and 20.4 mg (0.185 mmol) of thiophenol in 0.5 mL of C_6D_6 was sealed into a NMR tube filled with a 7/25 standard taper joint. The tube was allowed to stand in the dark at ambient temperature for 20 h while the course of the reaction was monitored by NMR spectroscopy. The starting materials disappeared smoothly and the characteristic acetone phenylhydrazone peaks grew in. NMR (C_6D_6): 1.08 (s, 3H), 1.78 (s, 3H), 7.10 (m, 5H). A peak for methane appeared at δ = 0.16 ppm while those for PhSSPh were at 7.4 (m, 4H) and 6.9 (m, 6H). After thermolysis was complete, the tube was placed on the vacuum line and the gaseous products were collected with a Topler pump and gas buret. The total gas yield (CH_4 and N_2) was 173%. A similar experiment employed 25.5 mg (0.101 mmol) of **1**, 35.9 mg (0.326 mmol) of PhSH, and 0.5 mL of C_6D_6. The sealed tube was heated at 60 °C for 8 h, again monitoring the course of the reaction by NMR. Although no gas yield was determined for this particular sample, a separate experiment showed it to be 98%.

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