resulting oil was recrystallized from low-boiling petroleum ether, yielding 4.64 g (35%): mp 43–44 °C; ^{1}H NMR ($CDCl_3$) δ 2.27 (br s, 2 H), 3.72 (s, 3 H), 7.30 (s, 10 H); IR ($CHCl_3$) 3390, 3310, 3080, 3060, 2990, 2950, 1730, 1600 cm^{-1}.

A small sample was converted to the hydrochloride salt: mp 216–218 °C (lit. mp 216–218 °C).[7]

3-*tert*-Butyl-5,5-diphenyl-2,4-imidazolidinedione. To a stirred mixture of 1.6 g (0.33 mol) of NaH in 30 mL of THF was added 5.47 mL (0.048 mol) of *tert*-butyl isocyanate and 3.85 g (0.016 mol) of α,α-diphenylglycine methyl ester. The mixture was heated at reflux for 16 h. Toluene (20 mL) was added and the excess *tert*-butyl isocyanate, THF, and most of the toluene were distilled. The remaining material was dissolved in ether, and water was added to quench the excess NaH. The water layer was extracted with ether, and the combined organics were washed with water, dried ($MgSO_4$), and concentrated. Recrystallization from toluene yielded 2.08 g (42%) of **1a**: mp 193–193.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 9 H), 7.34 (s, 10 H); IR ($CHCl_3$) 3440, 3080, 3060, 2995, 2970, 2930, 2900, 1780, 1715 cm^{-1}.[8]

Anal. Calcd for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08. Found: C, 74.05; H, 6.55; N, 8.98.

1-Adamantyl Isocyanate. To a stirred, ice cooled solution of 15.0 g (0.15 mol) of phosgene in 150 mL of toluene was added dropwise 30.0 g (0.38 mol) of pyridine followed by 14.2 g (0.094 mol) of 1-adamantanamine in 200 mL of ether, and the mixture was stirred for 30 min. An additional 50 mL of toluene was added and the mixture was stirred overnight. The reaction mixture was filtered and the filtrate was poured into ice–water. The aqueous layer was washed several times with ether and dried ($MgSO_4$), and the solvent was removed in vacuo. The remaining solid was recrystallized from pentane to yield 7.36 g (44%); mp 145–147 °C (lit. mp 144–145 °C).[9]

***tert*-Octyl Isocyanate.** Following the procedure for the preparation of 1-adamantyl isocyanate, the desired product was obtained in 24% yield as a colorless liquid: bp 137–143 °C; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9 H), 1.40 (s, 6 H), 1.50 (s, 2 H); IR (film) 2260 cm^{-1} (N=C=O). A small sample was converted into the urea with gaseous ammonia: mp 86–87 °C.

Anal. Calcd for $C_9H_{20}N_2O$: C, 62.79; H, 11.70; N, 16.26. Found: C, 62.83; H, 11.80; N, 16.20.

3-*tert*-Octyl-5,5-diphenyl-2,4-imidazolidinedione (1b). Following the procedure for the preparation of **1a**, 1.25 g (0.03 mol) of NaH, 3.50 g (0.02 mol) of *tert*-octyl isocyanate, and 3.00 g (0.0125 mol) of diphenylglycine methyl ester gave 1.80 g (39% of **1b** from ethanol): mp 180–181 °C; ^{1}H NMR ($CDCl_3$) δ 0.8 (s, 9 H), 1.65 (s, 6 H), 1.9 (s, 2 H), 7.3 (s, 10 H).

Anal. Calcd for $C_{23}H_{28}N_2O_2$: C, 75.79; H, 7.74; N, 7.69. Found: C, 76.02; H, 7.69; N, 7.81.

3-Adamantyl-5,5-diphenyl-2,4-imidazolidinedione (1c). Following the procedure for the preparation of **1a**, from 1.0 g (0.015 mol) of NaH, 4.00 g (0.023 mol) of adamantyl isocyanate, and 2.00 g (0.008 mol) of diphenylglycine methyl ester was obtained 1.00 g (31% of **1c** from ethanol): mp 217–219 °C; ^{1}H NMR ($CDCl_3$) δ 1.6–2.4 (adamantyl ring, 15 H), 2.75 (s, 10 H).

Anal. Calcd for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25. Found: C, 77.72; H, 6.75; N, 7.19.

***N*-(*tert*-Butylcarbamoyl)glycine Ethyl Ester (3d).** To a slurry of 1.5 g (0.031 mol) of NaH in 50 mL of ether was added 4.2 g (0.03 mol) of glycine ethyl ester hydrochloride (**2d**), and the mixture was stirred for 1 h at room temperature. *tert*-Butyl isocyanate (3.3 mL, 0.03 mol) was added, and the mixture was heated at reflux for 16 h. Water was added and the aqueous layer was extracted with 10 mL of ether. The combined organics were washed with 2 × 20 mL of water, dried ($MgSO_4$), and concentrated. The solid was recrystallized from ether–hexane to yield 2.94 g of **3d** (48.5%): mp 81–82 °C; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3 H), 1.30 (s, 9 H), 3.81 (d, 2 H), 4.07 (q, 2 H), 5.10 (br s, 1 H), 5.43 (br s, 1 H); IR ($CHCl_3$) 3410, 2940, 2905, 2850, 1740, 1670 cm^{-1}; mass spectrum, *m/e* 202.

Anal. Calcd for $C_9H_{18}N_2O_3$: C, 53.45; H, 8.97; N, 13.85. Found: C, 53.54; H, 8.97; N, 13.81.

The reaction was repeated with a twofold excess of NaH producing **1d** in 45% yield.

3-*tert*-Butyl-2,4-imidazolidinedione (1d). Following the procedure for the preparation of **1a**, 1.0 g (0.021 mol) of NaH and 2.63 g (0.014 mol) of **3d** yielded 1.1 g (50% of **1d** from ether–hexane): mp 99–100 °C; ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 9 H), 3.72 (s, 2 H); IR ($CHCl_3$) 3680, 3600, 3450, 2950, 2920, 2860, 1750, 1700 cm^{-1}.

Anal. Calcd for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.94. Found: C, 53.73; H, 7.70; N, 17.83.

Rearrangement of Diphenylglycine Methyl Ester. Diphenylglycine methyl ester (0.48 g, 2 mmol) was dissolved in 5 mL of THF and added to 0.10 g (2 mmol) of NaH in 5 mL of THF. After heating at reflux for 1 h, cooling to room temperature, and quenching with 3 mL of water, the THF was removed in vacuo. The solid was dissolved in ether, washed with water, dried ($MgSO_4$), and concentrated. The solid recrystallized from ethanol yielded 0.35 g (73%) of **6**: mp 149–150 °C; ^{1}H NMR ($CDCl_3$) δ 3.64 (s, 3 H), 5.40 (br s, 1 H), 5.98 (d, 1 H), 7.21 (s, 10 H); IR 3445, 3080, 3030, 2995, 1730 cm^{-1}.

Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.48; H, 6.20; N, 5.65.

Acknowledgment. Support for this research by the Louisiana Board of Regents is gratefully acknowledged.

Registry No. **1a**, 93504-25-7; **1b**, 93504-27-9; **1c**, 93504-26-8; **1d**, 93099-59-3; **2d**, 623-33-6; **3d**, 93504-28-0; **6**, 14983-80-3; 5,5-diphenylhydantoin, 57-41-0; diphenylglycine, 3060-50-2; α,α-diphenylglycine methyl ester, 93504-23-5; α,α-diphenylglycine methyl ester hydrochloride, 93504-24-6; *tert*-butyl isocyanate, 1609-86-5; 1-adamantanamine, 768-94-5; phosgene, 75-44-5; 1-adamantyl isocyanate, 4411-25-0; *tert*-octylamine, 107-45-9; *tert*-octyl isocyanate, 1611-57-0.

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Effect of Oxidized States of Heteroatoms and of Orthogonal π Systems on Radical Stabilities

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The rates of thermal decomposition of azo compounds of structure **1** are known to be sensitive to the nature of the substituent.[1] These rates have been used to assess incipient radical stabilities for which absolute thermodynamic stabilities are difficult or impossible to obtain.[2] Several addition compounds have been analyzed here in an attempt to understand the effect of oxidized states of heteroatoms (**1b,d,f**) and secondly to evaluate the influence of orthogonal π systems (**1m**).

We have previously noted that the influence of a π system adjacent to a radical center is the most significant factor in providing an enhanced rate of decomposition.[3] Furthermore, groups like nitriles, esters, and ketones which are carbanion-stabilizing groups also show pronounced radical stabilization. The effects of sulfur substituents are somewhat harder to rationalize, for with the exception of **1g**, the others (**1h–j**) all show negative activation entropies. This is unexpected for a fragmentation process where presumably three fragments are generated in the transition state.[2] Nonetheless, the stabilization of sulfur toward radical centers appears to be the result of better lone pair

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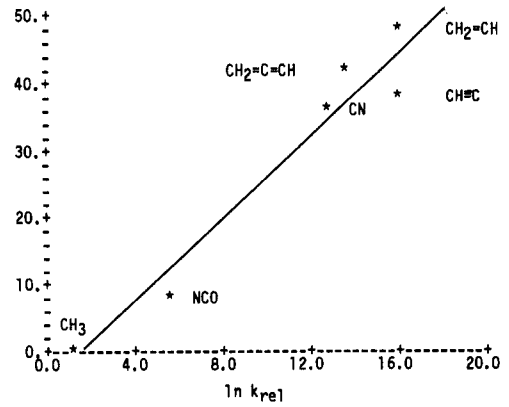


Figure 1. Plot of percent spin density on atom 3 (calculated by INDO) vs. ln k_{rel}. Percent spin density for CH_3 is assumed to be 0.

interaction with the carbon p orbital for sulfur than for oxygen. This explanation appears to negate any d orbital participation.[4] In an oxidized state the sulfur lone pairs would no longer be available and any stabilization due to this interaction should be reduced. Indeed, this is borne out experimentally as a rate diminution of approximately 2000 is observed between **1j** and **1b** and for **1i** and **1d**. This trend is opposite to what is observed in anion stabilization, at least as measured by hydrocarbon acidities.[5] The phosphorus effect is difficult to interpret without a lower oxidation state model for comparison. We were unable to prepare such a derivative and simply report it (**1f**) as a derivative that displays a moderate rate enhancement.

The allenyl compound **1m** is interesting to compare with the isocyanate **1e** which we previously found to be less labile than expected.[6] The difference in rate, a factor of almost 10^4, may be the result of an inductive effect of the two heteroatoms in **1e**, or, more likely, a difference in the resonance effect of the C=C=C vs. the N=C=O bonds.[7] In any event, it is clear that the pure carbon π system is superior. This we conclude because the allenyl **1m** and vinyl **1n** are so similar in rate. It is also interesting to note that a plot of log k_{rate} vs. % spin density at atom 3 for $(CH_3)_2C_1X_2{=}Y_3$ INDO calculations) shows some degree of linearity (Figure 1). This might be expected as the extent of delocalization should parallel radical stability and hence show the expected enhanced rates.

The syntheses of the sulfonyl derivatives in good yields were accomplished by oxidation of the known sulfur derivatives with *m*-chloroperbenzoic acid. The preparation of **1m** was not as straightforward and at least six different routes were abandoned before **1m** was prepared in an overall yield of 1.5% by the route shown in Scheme I.

Experimental Section

***N,N'*-Bis[dimethyl(methylsulfonyl)methyl]diazene (1b) and *N,N'*-Bis[dimethyl(phenylsulfonyl)methyl]diazene (1d).** These compounds were prepared in 93% and 69% yields, respectively, by oxidation with *m*-chloroperbenzoic acid. For example, to 3.1 g (15 mmol) of *N,N'*-bis[dimethyl(methylthio)-methyl]diazene[1] dissolved in 75 mL of $CHCl_3$ and cooled to 0 °C was added dropwise 13 g (60 mmol) of 85% MCPBA in 100 mL of $CHCl_3$. The reaction mixture was stirred for 3 h at room temperature, washed with 5% bicarbonate (5 × 50 mL), dried over $MgSO_4$, filtered, and concentrated. Sulfone **1b** was recrystallized from CH_2Cl_2–ether: mp 166–167 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.66 (s, 12 H) and 3.00 (s, 6 H); UV ($CHCl_3$) λ_{max} 382 nm (ϵ 26.5).

Anal. Calcd for $C_8H_{18}N_2O_4S_2$: C, 35.51; H, 6.72; N, 10.41. Found: C, 35.76; H, 6.71; N, 10.36.

Sulfone **1d** was recrystallized from hexane–$CHCl_3$: mp 209–210 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 12 H) and 7.4–8.0 (m, 10 H); UV ($CHCl_3$) λ_{max} 375 nm (ϵ 31.3).

Anal. Calcd for $C_{18}H_{22}N_2S_2O_4$: C, 54.80; H, 5.62; N, 7.10; S, 16.25. Found: C, 54.94; H, 5.66; N, 7.15; S, 16.31.

Rate constants are in s^{-1}. For **1b**: 165.2 °C (1.42×10^{-4}) 170.3 °C (2.05×10^{-4}), 175.9 °C (3.47×10^{-4}), 179.6 °C (5.47×10^{-4}), and 186.0 °C (1.07×10^{-3}). For **1d**: 154.8 °C (1.46×10^{-4}), 159.85 °C (2.26×10^{-4}), 165.2 °C (3.54×10^{-4}), 170.4 °C (6.44×10^{-4}), and 175.7 °C (1.25×10^{-3}).

***N,N'*-Bis[dimethyl(diethoxyphosphinyl)methyl]diazene (1f).** Compound **1f** was prepared according to Levin[8] in 31%

Scheme I

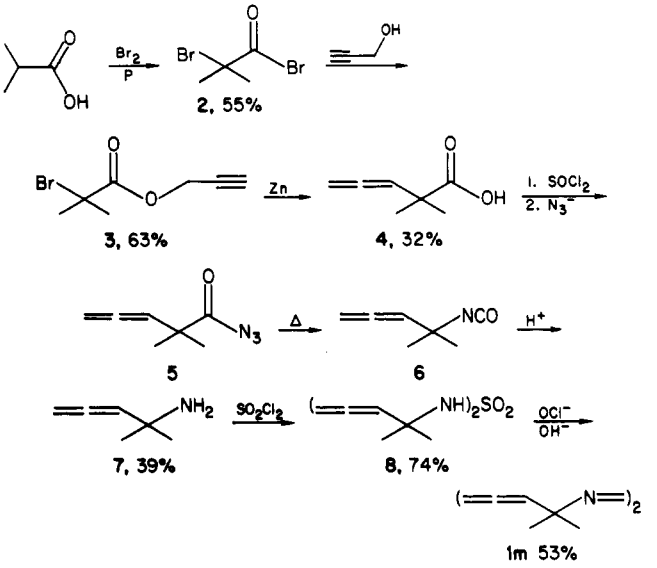
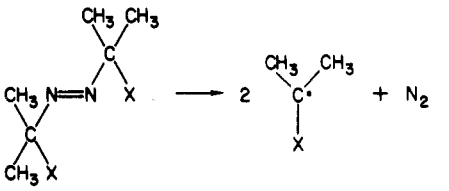


Table I. Rates of Decomposition of Azoalkanes



1

1	rel rate, 100 °C	$\Delta H^{\ddagger}$, kcal/mol[a]	$\Delta S^{\ddagger}$ [a]	ref
a CH_3	1.0			*b*
b CH_3SO_2	9.2	38.6 ± 2.5[c]	10.8 ± 5.0[c]	this work
c CH_3O	1.1 × 10			*b*
d $C_6H_5SO_2$	3.2 × 10	38.0 ± 2.3[c]	11.9 × 5.2[c]	this work
e O=C=N	3.3 × 10^2			*d*
f $(C_2H_5O)_2P(O)$	5.6 × 10^2	33.3 ± 1.0[e]	6.6 ± 2.3[e]	this work
g $CH_3C(O)S$	6.3 × 10^2			*b*
h N≡CS	3.8 × 10^3			*d*
i C_6H_5S	7 × 10^3			*f*
j CH_3S	1.9 × 10^4			*b*
k N≡C	2.9 × 10^5			*b*
l C_6H_5CO	1.1 × 10^6			*g*
m CH_2=C=CH	2.0 × 10^6	30.9 ± 1.6[h]	14.7 ± 4.4[h]	this work
n CH_2=CH	8.8 × 10^6			*i*
o HC≡C	9.7 × 10^6			*i*

[a] Determined from measured rates over a range of 25 ° for at least five different temperatures. [b] Reference 1. [c] In diphenyl ether. [d] Reference 6. [e] In hexadecane. [f] Ohno, A.; Ohnishi, Y. *Tetrahedron Lett.* **1969**, 4405. [g] Reference 3. [h] In cumene. [i] Engel, P. S.; Bishop, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 2148.

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yield: ^{1}H NMR ($CDCl_3$) δ 1.45 (d, 12 H), 1.31 (t, 12 H), 4.22 (m, 8 H). Rate constants in s^{-1} 135.1 °C (1.64×10^{-4}), 140.15 °C (2.64×10^{-4}), 145.1 °C (4.75×10^{-4}), 150.3 °C (7.40×10^{-4}), and 155.14 °C (1.21×10^{-3}).

2-Propynyl 2-Bromo-2-methylpropanoate (3). To a solution of the α-bromoisobutyryl bromide (**2**) (103 g, 0.45 mol) in 200 mL of anhydrous ether cooled to 0 °C under nitrogen was added a solution of 30.0 g (0.53 mol) of propargyl alcohol and 43 g (0.53 mol) of pyridine in 150 mL of dry ether. The reaction mixture was allowed to warm to room temperature and to stir overnight. The product mixture was washed with water (2 × 50 mL), 5% bicarbonate (3 × 75 mL)8 5% HCl (2 × 50 mL), and brine (50 mL), dried over $MgSO_4$, and concentrated. Distillation provided 65 g (0.32 mol, 63%) of the ester: bp 84–87 °C (20 mm) [lit.[9] bp 59–60 °C (3 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 6 H), 2.17 (t, 1 H), 4.71 (d, 2 H); IR (neat) 3290, 2180, 1735 cm^{-1}.

2,2-Dimethyl-3,4-pentadienoic Acid (4). The general method of Walker and Baldwin was used.[9,10] Activated zinc dust (45 g) was placed in flame-dried glassware with 90 mL of dry benzene under argon gas. The stirred suspension was heated to reflux and 10.2 g (50 mmol) of ester **3** in 60 mL of dry benzene was slowly added over a time period of 1.5 h. After addition, heating was maintained for 2 h. The product mixture was then cooled to room temperature and 50 mL of 6 M sulfuric acid was added. After 1 h the unreacted zinc was filtered and the acidic layer was removed and extracted with ether (3 × 30 mL). The combined organic phases were then washed with saturated bicarbonate (4 × 40 mL) and water (30 mL). The basic extracts were made acidic with concentrated sulfuric acid and extracted with ether (4 × 30 mL). The etheral solution was dried over $MgSO_4$, filtered, and concentrated to a clear light yellow liquid. Distillation provided 2.0 g (16 mmol, 32%) of the colorless product: bp 81–84 °C (2 mm) [lit.[10] 66–70 °C (0.8 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 6 H), 4.83 (d, 2 H), 5.41 (t, 1 H), 11.63 (br, 1 H); IR (neat) 1950 and 1710 cm^{-1}.

1,1-Dimethyl-2,3-butadienylamine·Hydrochloride (7). To dry glassware was added a mixture of 5.8 g (46 mmol) of allenic acid **4**, 30 mL of $CHCl_3$, and dropwise 8.0 g (67 mmol) of thionyl chloride. After stirring at reflux for 8 h, the solvent and unreacted $SOCl_2$ were distilled from the acyl chloride, which was used without further purification in the next step: ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 6 H), 4.9 (d, 2 H), 5.3 (t, 1 H); IR (neat) 1955 and 1790 cm^{-1}.

Sodium azide (6.0 g, 92 mmol) was added portionwise to a solution of the previously prepared acyl chloride in 20 mL of acetone cooled to 0 °C. Sufficient water was added to dissolve the NaN_3 and the mixture was stirred for 1 h. The reaction mixture was then poured into a separatory funnel and extracted with ether (4 × 30 mL). The etheral solution was dried over $MgSO_4$, filtered, and concentrated to the acyl azide, a clear liquid; IR (neat) 2125, 1958, and 1680 cm^{-1}. The acyl azide was taken up in benzene and stirred under reflux for 18 h. An infrared spectrum of a concentrated 1-mL aliquot of the product solution indicated the azide had completely decomposed to isocyanate; IR (neat) 2255 and 1958 cm^{-1}. Hydrolysis of the isocyanate to the amine was accomplished by heating the benzene solution with 10% HCl for 12 h. The reaction mixture was then cooled to room temperature, the aqueous layer drawn off, and the organic layer extracted with 5% HCl (3 × 10 mL). The combined acidic extracts were made basic by the addition of K_2CO_3 and then extracted with CH_2Cl_2 (5 × 30 mL). Continuous extraction for 24 h of the aqueous phase with CH_2Cl_2 provided an additional small amount of amine. The amine **7** was purified as the hydrochloride salt (2.12 g, 18 mmol; 39% based on the starting allenic acid) by recrystallization from ethanol–ethyl acetate: mp 171–172 °C; ^{1}H NMR ($CDCl_3$) δ 1.57 (s, 6 H), 5.0 (d, 2 H), 5.43 (t, 1 H), 8.50 (br, 3 H; exchangeable with D_2O); IR ($CHCl_3$) 3380 and 1950 cm^{-1}.

Anal. Calcd for $C_6H_{12}NCl$: C, 53.95; H, 8.99; N, 10.50. Found: C, 54.15; H, 9.15; N, 10.35.

***N,N'*-Bis(1,1-dimethyl-2,3-butadienyl)sulfamide (8).** The amine hydrochloride **7** (1.0 g, 8.4 mmol) was taken up in 5 mL of 10% NaOH and the free amine was extracted with CH_2Cl_2 (5 × 5 mL). The solution was dried over KOH for 2 h, decanted into a dry flask containing 0.85 g (8.4 mmol) of triethylamine under argon, and cooled to −30 °C. A solution of 0.57 g (4.2 mmol) of sulfuryl chloride in 20 mL of CH_2Cl_2 was added slowly over approximately 30 min. After addition the reaction was kept at dry ice temperature for 2 h and then allowed to warm to room temperature and stir overnight. The product mixture was washed with 5% HCl (3 × 20 mL), dried over $MgSO_4$, filtered, and concentrated to a white solid, which was recrystallized from pentane to give 0.84 g, (3.1 mmol, 74%): mp 69–70 °C; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 12 H), 4.32 (br, 2 H), 4.90 d, 2 h), 5.48 (m, 2 H).

Anal. Calcd for $C_{12}H_{20}N_2O_2S$: C, 56.22; H, 7.88; N, 10.93. Found: C, 56.39; H, 7.71; N, 10.79.

***N,N'*-Bis(1,1-dimethyl-2,3-butadienyl)diazene (1m).** A two-phase mixture of hexane and a solution of 60 mL of bleach and NaOH (1.80 g) was cooled to 0 °C. The sulfamide **8** (0.50 g, 2 mmol) and 3 drops of Aliquot 336 (phase-transfer catalyst) were added to the mixture. After 6 h at 0 °C, the reaction had reached completion as evidenced by the disappearance of the starting material. The two layers were separated and the hexane solution was washed with water (30 mL), 5% HCl (2 × 15 mL), and water (10 mL), followed by drying over $MgSO_4$. The solution was then passed through a short column of Florisil. Removal of the solvent under vacuum provided 0.10 g (1.1 mmol, 53%) of the diazene, a light yellow liquid. Further purification was accomplished via sublimation: ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 12 H) 4.79 (d, 4 H), 5.39 (t, 2 H); ^{13}C NMR ($CDCl_3$) 25.46, 68.48, 96.96, 206.6 ppm; IR (neat) 1950 cm^{-1}; UV (cyclohexane) λ_{max} 364 (ϵ 38.7).

Registry No. **1b**, 93605-35-7; **1d**, 93605-36-8; **1f**, 7336-02-9; **1m**, 93605-37-9; **2**, 20769-85-1; **3**, 40630-86-2; **4**, 4058-53-1; **4** (acid chloride), 93605-44-8; **5**, 93605-40-4; **6**, 93605-41-5; **7**·HCl, 93605-42-6; **8**, 93605-43-7; ·$C(CH_3)_2SO_2CH_3$, 4853-78-5; ·$C(CH_3)_2SO_2C_6H_5$, 93605-38-0; ·$C(CH_3)_2P(O)(C_2H_5O)_2$, 85971-71-7; ·$C(CH_3)_2CH{=}C{=}CH_2$, 93605-39-1; ·$CH{=}CH_2$, 2669-89-8; ·CN, 2074-87-5; ·C≡CH, 2122-48-7; ·NCO, 22400-26-6; ·CH_3, 2229-07-4; $HC{\equiv}CCH_2OH$, 107-19-7; *N,N'*-bis[dimethyl(methylthio)methyl]diazene, 40889-01-8; *N,N'*-bis[dimethyl(phenylthio)methyl]diazene, 26307-20-0.

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Cycloadditions of 5-Nitropyrimidines with Ynamines. Synthesis and Crystal Structure of a 2,2a-Dihydroazeto[2,3-*d*]-3,5-diazocine, a Novel Heterocycle[1]

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In a previous paper we have reported that 5-nitropyrimidine is able to undergo [4 + 2]-cycloaddition reactions with electron-rich enamines.[2] This reaction proceeds through an addition of the enamine to the 1 and 4 positions of the pyrimidine, followed by loss of HCN and amine, resulting in formation of 2,3,5-trisubstituted pyridine derivatives. In contrast, the cycloaddition of the ynamine 1-(diethylamino)propyne with methyl pyrimidine-5-carboxylate takes place across C-2 and C-5 to afford, after

(1) Part 32 on Ring transformations of heterocycles with nucleophiles; for part 31, see: Smit P.; Stork G. A.; van der Plas, H. C. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 453.
(2) Charushin, V. N.; van der Plas, H. C. *Tetrahedron Lett.* **1982**, *23*, 3965.

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