When the precipitate, which was a mixture of "White Salt" [the bis enolate of 2,4,6,8-tetrakis(methoxycarbonyl)bicyclo[3.3.0]octane-3,7-dione[10]] and sodium sulfite, was acidified with dilute acid, the product did not precipitate and had to be extracted with large volumes of ether. A better procedure was found to be grinding the precipitate with 1 equiv of concentrated hydrochloric acid followed by filtration. With all of these precautions, a 71% yield of product was obtained. This good yield of highly deuterated material is attributable to the use of preformed dimethyl sodio-3-oxoglutarate, which condenses with glyoxal-d_2 much faster than it induces the 1,2 hydride shift of glyoxal[11] or the H–D exchange of glyoxal bisulfite.

Experimental Section

Melting points were measured with a Thomas-Hoover apparatus and are uncorrected. Mass spectra were obtained with an AEI MS9 instrument.

Glyoxal-d_2 Bis(sodium bisulfite)-*O*-d_2. A 26.5-g (99.7 mmol) quantity of glyoxal bis(sodium bisulfite) dissolved in 120 mL of D_2O (99.8%) was held at 100 ± 0.5 °C in a 200-mL three-necked flask fitted with a reflux condenser and two rubber septa. Two temperature-controlling thermometers[12] inserted through the septa were connected to relays wired in series with the oil bath maintaining the temperature. A gas-inlet tube on the condenser admitted a static nitrogen atmosphere. Samples (0.50 mL) of the magnetically stirred solution were withdrawn periodically and added to 5.0 mL of a stock solution prepared by dissolving 10 g of phenylhydrazine hydrochloride and 12 g of sodium acetate in 200 mL of water. The yellow solids were filtered off after being allowed to stand overnight in sealed 25-mL Erlenmeyer flasks, washed with 5 mL of water, and then dissolved in 15 mL of boiling ethanol in the same flasks. After the mixture cooled, the solvent was evaporated in a vacuum desiccator to give the osazones, which were weighed to obtain the yields shown in Figure 1 and analyzed by mass spectroscopy (15 eV, 140–150 °C). After 39 h the bright yellow reaction mixture was allowed to cool, its mass was reduced to 40 g on a high-vacuum rotary evaporator, and it was refrigerated to give 12.5 g (46%) of white crystals, which were isolated by filtration under nitrogen, washed with two 5-mL portions of D_2O, and dried under vacuum. After correction for the 10 mL of solution removed as samples, the yield was 50%. The yield of phenyl osazone from a sample of this material was 99%.

2,4,6,8-Tetrakis(methoxycarbonyl)bicyclo[3.3.0]octane-3,7-dione-*1,5*-d_2. Dimethyl 3-oxoglutarate (31.0 g, 178 mmol) in 200 mL of methanol was treated with 35.0 mL of 5.00 M NaOH (175 mmol) and, after 15 min, with 12.1 g (44.8 mmol) of glyoxal bis(sodium bisulfite)-d_4 (95% deuterated). The temperature was raised from 35 to 65 °C, and the reaction mixture was stirred *mechanically* for 24 h. Filtration gave 24 g of white solid which was ground to paste with 15 mL of water, using a *silver* spatula. (A purple color developed when an ordinary metal one was used.) Acidification with 15 mL of concentrated HCl and further grinding gave a white gum that was dried by pressing it on a sintered glass frit with the aid of suction. Further drying under vacuum over phosphorus pentoxide yielded 9.29 g of white solid, mp 98–100 °C. An additional 2.56 g (71% total) was harvested by continuous extraction of the aqueous filtrate with ether. Hydrolysis and decarboxylation according to the literature procedure[13] produced bicyclo[3.3.0]octane-3,7-dione-*1,5*-d_2, which mass spectroscopic analysis showed to be 93% deuterated. The deuterium contents were calculated by using the formula % $d = 100(d_1 + 2d_2)/2(d_0 + d_1 + d_2)$ where d_1 and d_2 are the intensities of the molecular ions of the monodeuterated and dideuterated compounds, corrected for natural isotopic abundance (M + 1 and M + 2).

(11) Arcus, C. L.; Jackson, B. A. *Chem. Ind. (London)* **1964**, 2022.
(12) This arrangement ensured that if one relay became stuck in the closed position, the oil bath temperature would not rise above the desired value; since the other relay would still control it. If one stuck in the open position, the oil bath would cool off; thus no product would be lost due to overheating. If the bath temperature is increased so that vigorous boiling sets in, the yield is decreased.
(13) Vossen, G. Dissertation, University of Bonn, 1910. Yates, P.; Hand, E. S.; French, G. B. *J. Am. Chem. Soc.* **1960**, *82*, 6347.

Registry No. Glyoxal-d_2 bis(sodium bisulfite)-*O*-d_2, 78529-84-7; dimethyl 3-oxoglutarate, 1830-54-2; 2,4,6,8-tetrakis(methoxycarbonyl)bicyclo[3.3.0]octane-3,7-dione-*1,5*-d_2, 78529-85-8; bicyclo[3.3.0]octane-3,7-dione-*1,5*-d_2, 78515-15-8.

Bicyclo[1.1.0]butanes. Reactions with Cyclic Azo Compounds†

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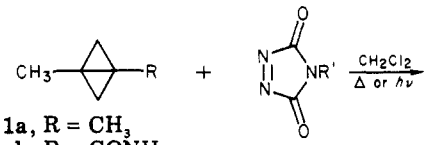
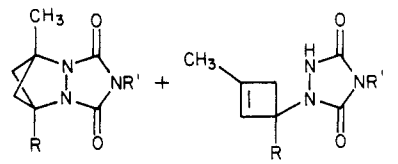
Received February 25, 1981

Although bicyclo[1.1.0]butanes (1) undergo addition reactions with olefins,[1a–d] dienes,[1b] alkynes,[2] and ketones,[1b] they have not been observed to react with azo compounds. We report here the addition of cyclic azo species to bicyclobutanes 1. Thermal and, in certain cases, photochemical reactions of 1 with 1,2,4-triazoline-3,5-diones (2) give [2 + 2] cycloadducts 3 and ene products 4 (Table I). Compounds 3 are the first examples of 2,3-diazabicyclo[2.1.1]hexanes. Only the related etheno-bridged species **5a**,[3a] **5b**,[3b] and the monoaza analogue 6[3c–e] have been reported.

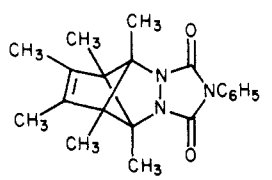


1a, R = CH_3
b, R = $CONH_2$
c, R = CO_2CH_3
d, R = CN

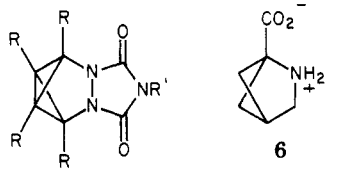
2a, R′ = C_6H_5
b, R′ = CH_3



3 **4**



5a



5b, R = CF_3
R′ = CH_3, C_6H_5

6

Total yields of products are moderate to good, and the ratios of the products (3/4) are highly dependent on the bicyclobutane substituent R. Thus, **1a** (R = CH_3) yields exclusively ene product; **1d** (R = CN) yields only cycloadduct. Between these limits, varying mixtures of 3 and 4 are obtained.

The reaction of bicyclobutane with benzyne,[2d] the reaction of **1a** with ethylene at elevated temperatures,[1b] and the reaction of 1-cyanobicyclobutane with tricyanoethylene[1d] are the only other known cases in which bicyclobutanes give both ene and cycloaddition products.

We also observed a dramatic effect of the substituent R on the relative reactivity of the bicyclobutanes. The following qualitative (thermal) order of reactivity is found: **1a > 1b > 1c ≫ 1d**. The range of reactivity, from seconds

† Contribution No. 2889.

0022-3263/81/1946-4090$01.25/0

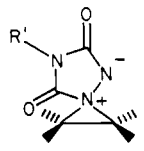
Table I. Addition Reactions of 1 and 2[a]

reactants	product(s)[b]	reaction conditions
1a, 2a	4a, R = CH_3, R′ = C_6H_5	mixing (seconds), 25 °C, CH_2Cl_2
1a, 2b	4b, R = CH_3, R′ = CH_3	mixing (seconds), 25 °C, CH_2Cl_2
1b, 2a	3a, R = $CONH_2$, R′ = C_6H_5; 4c, R = $CONH_2$, R′ = C_6H_5 (60/40)[c]	7 min, 25 °C, CH_2Cl_2
1b, 2b	3b, R = $CONH_2$, R′ = CH_3; 4d, R = $CONH_2$, R′ = CH_3 (55/45)[c]	4 min, 25 °C, CH_2Cl_2
1c, 2a	3c, R = CO_2CH_3, R′ = C_6H_5; 4e, R = CO_2CH_3, R′ = C_6H_5 (80/20)[c]	40 min–1 h, 25 °C, CH_2Cl_2
1d, 2a	3d, R = CN, R′ = C_6H_5	5 h, *hν*, CH_2Cl_2; 3–5 days, 50 °C, CH_2Cl_2
1d, 2b	3e, R = CN, R′ = CH_3	2 h, *hν*, CH_2Cl_2

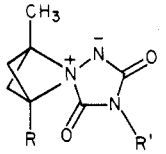
[a] All new compounds gave satisfactory elemental analyses (C, H, N; 0.4%). [b] Relative crude amounts determined by ^1H NMR spectroscopy. [c] Cyclobutenes determined by ^1H NMR spectroscopy but not further characterized.

to days, is surprisingly large (Table I). If azo attack occurs from the bottomside (endo) of the bicyclobutane, which is the case for attack of olefins[1b,4] and of benzyne[2d] on bicyclobutanes, the steric effects of substituents R should be negligible, assuming that R does not alter the flap angle significantly.

Two possible electronic arguments may explain these results. Greene[5] suggested that the reaction of **2** with olefins proceeds via a dipolar intermediate **7**, which then



7

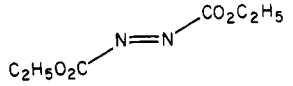


8

collapses either to an ene product or to a diazetidine. If a similar species, e.g., **8**, occurs in the reaction (possibly exo attack) of bicyclobutanes with **2**, substituents R can markedly influence the rate of reaction by their stabilization (R = electron donor) or destabilization (R = electron acceptor) of the positive nitrogen center. The increasing reactivities of **1** indeed follow in the order of decreasing Hammett σ_p values for R.[6]

An alternative, albeit simplistic, explanation also suggests a correlation of reactivity with the electron acceptor ability of R. As electron withdrawal from the bicyclobutane C_1–C_3 bond increases (CN > CO_2CH_3 > $CONH_2$ > CH_3), the bond lengthens. Such lengthening relieves, to some extent, ring strain[7] and should increase the bicyclobutane stability (or lower its reactivity) as is observed. At this time, we do not have any experimental evidence which allows us to distinguish between these possible alternatives.

In contrast to the thermal reactions of **1** with **2**, bicyclobutanes do not react with diethyl azodicarboxylate (**9**) at temperatures up to 110 °C. Prolonged irradiation



9

of a mixture of **1d** and **9** with a medium-pressure mercury lamp at 254 nm leads only to yellow tars. Presumably the thermal reaction is exceedingly slow owing to the trans geometry of **9**. Photochemical equilibration to give *cis*-**9** is rapid at 254 nm, but if any reaction products are formed, they are rapidly decomposed under these reaction conditions.

Experimental Section

Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were obtained on a Perkin-Elmer 157 infrared spectrophotometer. Proton NMR spectra (90 MHz) were taken at ambient temperature with Me_4Si as internal standard on a Varian EM-390 instrument, unless otherwise indicated. ^{13}C NMR spectra (relative to Me_4Si) were obtained on a Bruker WH-90 spectrometer.

Bicyclo[1.1.0]butanes. Compounds **1a–d** were prepared according to literature procedures.[8]

Azo Compounds. Compounds **2a** and **2b** were prepared according to literature procedures[9] from commerically available 4-phenylurazole[10a] and 4-methylurazole.[10b] Diethyl azodicarboxylate was obtained commercially.[9a]

Addition Reactions of Bicyclo[1.1.0]butanes (1) with Diones 2. The general procedures for both thermal and photochemical syntheses of **3** and/or **4** are illustrated below for compounds **3c** and **3d**. Physical properties of **3a–e** and **4a–e** are listed below. All recrystallizations are from CCl_4.

a. Thermal Synthesis. Methyl 2,3,6,7-Tetrahydro-7-methyl-1,3-dioxo-2-phenyl-5,7-methano-1*H*,5*H*-pyrazolo[1,2-*a*][1,2,4]triazole-5-carboxylate (3c). A solution of 0.63 g (5.0 mmol) of **1c** and 0.87 g (5 mmol) of **2a** in 25 mL of CH_2Cl_2 was stirred at 25 °C. After 1 h, the decolorized solution was stripped, and the yellow gum (1.4 g, **3c** + **4e**) was repeatedly washed with petroleum ether until washes were colorless. Recrystallization from CCl_4 gave **3c** (0.76 g, 64%): mp 86–90 °C; IR (Nujol) 1725 (C=O), 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 1.80 (s, 3, CH_3), 2.14, 2.36 (AB m, 4, CH_2, J_{AB} = 5.3 Hz), 3.82 (s, 3, OCH_3), 7.50 (m, 5, ArH); ^{13}C NMR ($CDCl_3$) δ 15.75 (CCH_3), 49.31 (CH_2), 55.59 (OCH_3), 56.22 (CCH_3), 72.37 (C-CO_2CH_3), 113.23 (Ar, C-2), 117.57 (Ar, C-4), 129.95 (Ar, C-3), 152.62 (Ar, C-1), 158.41 (CO), 169.58 (CO_2CH_3); mass spectrum (high resolution) calcd 301.1062, found 301.1080.

Anal. Calcd for $C_{15}H_{15}N_3O_4$: C, 59.79; H, 5.02; N, 13.95. Found: C, 59.39; H, 4.95; N, 14.15.

b. Photochemical Synthesis. 2,3,6,7-Tetrahydro-7-methyl-1,3-dioxo-2-phenyl-5,7-methano-1*H*,5*H*-pyrazolo-

(1) (a) Blanchard, E. P., Jr.; Cairncross, A. *J. Am. Chem. Soc.* **1966**, *88*, 487. (b) Cairncross, A.; Blanchard, E. P., Jr. *Ibid.* **1966**, *88*, 496. (c) Rifi, M. *Ibid.* **1967**, *89*, 4442. (d) Hall, H. K., Jr.; Ykman, P. Y. *J. Polym. Sci. C, Polym. symp.* **1976**, *54*, 373.

(2) (a) Pomerantz, M. *J. Am. Chem. Soc.* **1966**, *88*, 5349. (b) Pomerantz, M.; Gruber, G. W.; Wilbe, R. N. *Ibid.* **1968**, *90*, 5040. (c) Pomerantz, M.; Wilbe, R. N. *Tetrahedron Lett.* **1969**, *463*. (d) Pomerantz, M.; Wilbe, R. N.; Gruber, G. W.; Roy, U. *J. Am. Chem. Soc.* **1972**, *94*, 2752.

(3) (a) Lemal, D. M.; Lokensgard, J. P. *J. Am. Chem. Soc.* **1966**, *88*, 5934. (b) Kobayashi, Y.; Nakano, T.; Shirahashi, K., Takeda, A.; Kimadaki, I. *Tetrahedron Lett.* **1980**, 4615. (c) Bell, E. A.; Qureshi, M. V.; Pryce, R. J.; Janzen, D. H., Lemke, P.; Clardy, J. *J. Am. Chem. Soc.* **1980**, *102*, 1409. (d) Pirrung, M. C. *Tetrahedron Lett.* **1980**, 4577. (e) Hughes, P.; Martin, M.; Clardy, J. *Ibid.* **1980**, 4579.

(4) Gassman, P. G. *Acc. Chem. Res.* **1971**, *4*, 128 and references therein.

(5) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6384.

(6) CH_3, σ_p = –0.17; $CONH_2$, σ_p = 0.36; CO_2CH_3, σ_p = 0.45; CN, σ_p = 0.66. See Hansch, C.; Leo, A. "Substituent Constants for Correlation Analysis in Chemistry and Biology"; Wiley: New York, 1979.

(7) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.

(8) **1a**, Griesbaum, K.; Butler, P. E. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 444. **1b**, ref 1a. **1c**, Hall, H. K., Jr.; Smith, C. D.; Blanchard, E. P., Jr.; Cherkofsky, S. C.; Sieja, J. B. *J. Am. Chem. Soc.* **1971**, *93*, 121. **1d**, ref 1a.

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

(10) (a) From Aldrich Chemical Co. (b) From TransWorld Chemicals.

[1,2-*a*][1,2,4]triazole-5-carbonitrile (3d). A solution of **1d** (0.43 g, 4.55 mol) and **2a** (0.79 g, 4.55 mmol) in methylene chloride (25 mL) was irradiated for 5 h with a 275-W GE sunlamp. When the initial ruby red solution had faded to pale yellow, the solvent was removed under reduced pressure. A yellowish glassy solid was obtained and repeated recrystallizations from hot carbon tetrachloride gave 0.58 g (40%) of **3d**: mp 103–105 °C; IR (Nujol) 2250 (C≡N), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ 1.85 (s, 3, CH_3), 2.20, 2.43 (AB m, 4, CH_2, $J_{AB} \approx 6$ Hz), 7.46 (s, 5, ArH); mass spectrum (high resolution) calcd 268.0990, found 268.0959.

Anal. Calcd for $C_{14}H_{12}N_4O_2$: C, 62.68; H, 4.53; N, 20.59. Found: C, 62.86; H, 4.93; N, 20.89.

2,3,6,7-Tetrahydro-7-methyl-1,3-dioxo-2-phenyl-5,7-methano-1*H*,5*H*-pyrazolo[1,2-*a*][1,2,4]triazole-5-carboxamide (3a): mp 121–125 °C; IR (Nujol) 3465, 3450, 1740, 1725 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.85 (s, 3, CH_3), 2.48 (m, 4, CH_2), 3.85 (br s, 2, NH_2), 7.50 (m, 5, ArH). Isolated yield = 48%.

2,3,6,7-Tetrahydro-7-methyl-1,3-dioxo-2-methyl-5,7-methano-1*H*,5*H*-pyrazolo[1,2-*a*][1,2,4]triazole-5-carboxamide (3b): mp 46–50 °C; IR (Nujol) 3400, 1705, 1725 cm^{-1}; ^1H NMR (acetone-d_6) δ 1.82 (s, 3, CH_3), 2.44 (m, 4, CH_2), 3.15 (s, 3, NCH_3), 3.90 (br s, 2, NH_2). Isolated yield = 35%.

2,3,6,7-Tetrahydro-7-methyl-1,3-dioxo-2-methyl-5,7-methano-1*H*,5*H*-pyrazolo[1,2-*a*][1,2,4]triazole-5-carbonitrile (3e): mp 162–164 °C; IR (Nujol) 2250, 1740 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ 1.81 (s, 3, CH_3), 2.25, 2.48 (AB m, 4, CH_2, $J_{AB} \approx 6$ Hz), 3.07 (s, 3, NCH_3); ^{13}C NMR ($CDCl_3$) δ 15.47 (CCH_3), 26.06 (NCH_3), 48.48 (CH_2), 55.57 (CCH_3), 71.95 (CCN), 118.16 (CN), 159.38 (CO); mass spectrum (high resolution) calcd 206.0803, found 206.0802. Yield = 25%.

2-(1,3-Dimethylcyclobuten-3-yl)-4-phenyl-1*H*,2*H*-1,2,4-triazole-3,5-dione (4a): mp 50–52 °C; IR (Nujol) 3350, 1745, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (s, 3, CH_3), 1.80 (d, 3, CH_3, $J \approx 1.5$ Hz), 2.15, 2.42 (AB m, 2, CH_2, $J_{AB} \approx 14$ Hz), 4.85 (br s, 1, NH), 5.95 (m, 1, CH), 7.41 (m, 5, ArH). Isolated yield = 62%.

2-(1,3-Dimethylcyclobuten-3-yl)-4-methyl-1*H*,2*H*-1,2,4-triazole-3,5-dione (4b): mp 67–69 °C; IR (Nujol) 3375, 1750, 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (s, 3, CH_3), 1.77 (d, 3, CH_3, $J \approx 1.5$ Hz), 2.14, 2.46 (AB m, 2, CH_2, $J_{AB} \approx 14$ Hz), 3.12 (s, 3, NCH_3), 4.90 (br s, 1, NH), 5.93 (m, 1, CH); mass spectrum (high resolution) calcd 195.1015, found 195.1007. Isolated yield = 67%.

2-(1-Methyl-3-carboxamidocyclobuten-3-yl)-4-phenyl-1*H*,2*H*-1,2,4-triazole-3,5-dione (4c): ^1H NMR (acetone-d_6) δ 1.81 (br s, 3, CH_3), 2.12, 2.46 (AB m, 2, CH_2, $J_{AB} \approx 14$ Hz), 3.90 (br s, 3, NH, NH_2), 6.00 (m, 1, CH), 7.55 (m, 5, ArH). Not isolated.

2-(1-Methyl-3-carboxamidocyclobuten-3-yl)-4-methyl-1*H*,2*H*-1,2,4-triazole-3,5-dione (4d): ^1H NMR (acetone-d_6) δ 1.75 br s, 3, CH_3), 2.18, 2.50 (AB m, 2, CH_2, $J_{AB} \approx 14$ Hz), 3.05 (s, 3, NCH_3), 3.96 (br s, NH, NH_2), 5.87 (m, 1, CH). Not isolated.

2-(1-Methyl-3-(carbomethoxy)cyclobuten-3-yl)-4-phenyl-1*H*,2*H*-1,2,4-triazole-3,5-dione (4e): ^1H NMR ($CDCl_3$) δ 1.78 (br s, 3, CH_3), 2.20, 2.52 (AB m, 2, CH_2, $J_{AB} \approx 14$ Hz), 3.71 (s, 3, CH_3), 4.91 (br s, 1, NH), 6.05 (m, 1, CH), 7.48 (m, 5, ArH). Not isolated.

Reactions of 9. Thermal Reaction. A solution of **1d** (0.26 g, 2.8 mmol) and **9** (0.49 g, 2.8 mmol) in 25 mL of toluene was heated at reflux for 5 days. ^1H NMR spectrum of the mixture showed only unreacted starting materials.

Photochemical Reaction. A cyclohexane solution (10 mL) of **1d** (0.43 g, 4.6 mmol) and **9** (0.81 g, 4.6 mmol) was placed in a stoppered quartz tube and irradiated at 254 nm for 4 days in a Rayonet photochemical reactor. Removal of solvent at reduced pressure gave a viscous yellow oil. ^1H NMR spectrum ($CDCl_3$) of the oil showed only very broad, unassignable peaks.

Acknowledgment. We gratefully acknowledge the many helpful discussions and unique insight provided by Dr. Tadamichi Fukunaga.

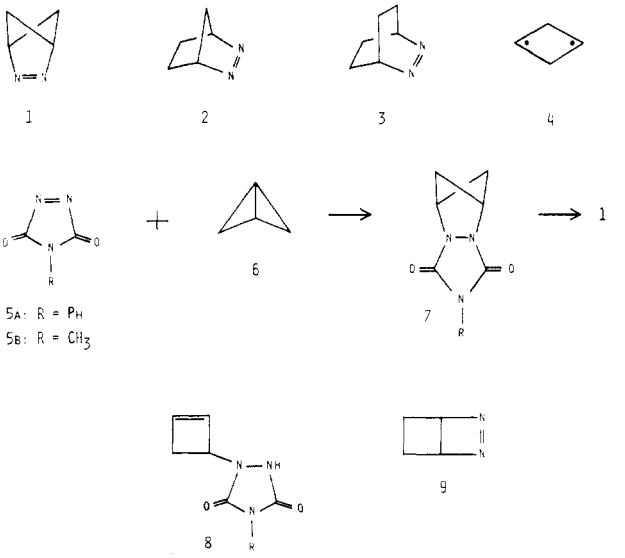
Registry No. 1a, 930-25-6; **1b**, 822-76-4; **1c**, 30493-92-6; **1d**, 694-25-7; **2a**, 4233-33-4; **2b**, 13274-43-6; **3a**, 78698-28-9; **3b**, 78698-29-0; **3c**, 78698-30-3; **3d**, 78698-31-4; **3e**, 78698-32-5; **4a**, 78698-33-6; **4b**, 78698-34-7; **4c**, 78698-35-8; **4d**, 78698-36-9; **4e**, 78698-37-0; **9**, 1972-28-7.

Communications

2,3-Diazabicyclo[2.1.1]hex-2-ene. Synthesis and Thermal Decomposition†

Summary: Addition of triazolinedione to bicyclobutane followed by hydrolysis–oxidation gives the title compound, which decomposes thermally to give bicyclobutane.

Sir: Cyclic and bicyclic 1,2-diazenes have been the subject of numerous investigations concerning their spectroscopic properties and their chemistry as potential sources of novel biradicals and strained hydrocarbons.[1,2] Remarkably, one of the simplest such structures, 2,3-diazabicyclo[2.1.1]-hex-2-ene (**1**), has not been prepared previously. This structure is of considerable interest, both in relation to the much studied higher homologues diazabicyclo[2.2.1]-heptene (**2**) and diazabicyclo[2.2.2]octene (**3**) and as a potential precursor to the interesting biradical 1,3-cyclobutanediyl (**4**). We report herein the synthesis and spectroscopic characterization of 1 and a study of its thermal decomposition.



The synthesis of **1** depended upon the thermal addition of triazolinedione (**5**) across the strained central C–C bond in bicyclo[1.1.0]butane (**6**) to give **7**. Roth has reported that **5a** adds across the strained C–C bond of a derivative

† Contribution No. 6412.

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