[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}; ^{1}H 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}; ^{1}H 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}; ^{1}H 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}; ^{1}H 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}; ^{1}H 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}; ^{1}H 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): ^{1}H 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): ^{1}H 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): ^{1}H 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. ^{1}H 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. ^{1}H NMR spectrum ($CDCl_3$) of the oil showed only very broad, unassignable peaks.

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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.

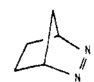
Communications

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

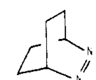
Summary: Addition of triazolinedione to bicyclobutane followed by hydrolysis–oxidation gives the title compound, which decomposes thermally to give bicyclobutane.

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.

1

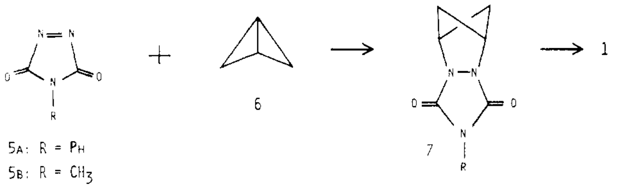


2

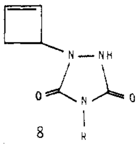


3

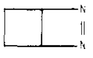
4



5A: R = Ph
5B: R = CH_3



8



9

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

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† Contribution No. 6412.

[1] (a) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99–150. (b) Adam, W.; De-lucchi, O. *Angew Chem., Int. Ed. Engl.* **1980**, *19*, 762–79.

[2] Mirbach, M. J.; Liu, K-C.; Mirbach, M. F.; Cherry, W. R.; Turro, N. J.; Engel, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 5122–9.

0022-3263/81/1946-4092$01.25/0

Table I. Decomposition Data for Bicyclic Azoalkanes

compd	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel}[a]
1	33.7 ± 0.2	10.0 ± 0.3	1.0
2	36.2[b]	6.1[b]	0.0057
3	44.3[b]	9.5[b]	10^{-6}
9	32.9 ± 0.5[c]	4.1 ± 1.4[c]	0.14

[a] Relative rates (s^{-1}) at 120 °C calculated from data of the previous two columns. [b] Average of values in ref 1a. [c] Reference 10.

of bicyclo[2.1.0]pentane in acetone to give an adduct analogous to **7** in quantitative yield.[3] Electron-deficient olefins react with **6** to give bicyclo[2.1.1]hexane derivatives and cyclobutenes ("ene" products).[4] A stepwise, biradical mechanism is implicated.[4] We have found that reaction of **5a** or **5b** with **6** in CH_2Cl_2, $CHCl_3$, THF, or acetone is rapid at room temperature (as monitored by the disappearance of the color of **5**) but gives a complex mixture of products which contains <5% of the desired adduct **7** (vide infra). However, addition of **5** in a small amount of ether to a solution of **6** in a large volume of *n*-hexane at 63 °C results in a much slower reaction, and the ^1H NMR of the crude product shows **7** as the only adduct. Flash chromatography[5] on silica gel (3:1 CH_2Cl_2/Et_2O) gives a 40% isolated yield of **7**.[6] The decreased polarity of the reaction medium is the major factor responsible for the improved yield. We have not characterized the remaining material, but we suspect that some form of polymerization has occurred. The total absence of "ene" adduct **8** in the crude product mixture, and the marked solvent effect on the rate and product composition could signal a change in mechanism from that discussed above.

Hydrolysis–oxidation of **7b** by a slight modification of Gassman's procedure[7] produced **1** as an extremely volatile white solid in 65% yield.[8] The UV spectrum of **1** (*n*-hexane) is highly structured, relative to related compounds,[2] with an intense 0,0 band [λ_{max} 331 nm (ϵ 1360), $w_{1/2}$ = 2.4 nm] and three smaller peaks (325 (143), 320 (186), 316 (124)]. This result is consistent with the rigid structure of **1**.[2]

Thermal decomposition of **1** in C_6D_6 was studied over four temperatures in the range 85–115 °C, and the kinetics proved to be cleanly first order.[9] The sole detectable product (≥99.8% by 500-MHz ^1H NMR) was bicyclobutane (**6**). Table I lists activation parameters and relative rates for **1**–**3** and 2,3-diazabicyclo[2.2.0]hex-2-ene (**9**), an isomer of **1** prepared recently by Carpenter.[10] Although the strain energy of **1** is calculated to be 31 kcal/mol greater than that of **2**,[11] the two structures show only a modest difference in ΔH^{*}. This is no doubt due to the fact that much of the strain in **1** is retained in the transition state in the form of a four-membered ring. Empirical force field calculations[12] indicate that **9** is approximately 7 kcal/mol more strained than **1**, but this difference is not reflected in the activation parameters or relative rates for decomposition (Table I). If the force field method can be considered reliable for such highly strained structures, then this result is consistent with an orbital symmetry factor[10] which raises the barrier to decomposition in **9** or leads to different mechanisms for **9** and **1**.

Further studies concerning the mechanisms of the reactions described herein and the photochemical decomposition of **1** are underway.

Note Added in Proof. We have learned that Dr. Amey from Du Pont has also been studying the reactions of triazolinediones with bicyclobutanes with some very interesting results. See accompanying Note in this issue.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the Camille and Henry Dreyfus Foundation for support of this work, and the use of the Southern California Regional NMR Facility located at Caltech and supported by the National Science Foundation.

Registry No. 1, 72192-13-3; **5b**, 13274-43-6; **6**, 157-33-5; **7b**, 78715-55-6.

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[3] Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 4695–8.

[4] Gassman, P. G. *Acc. Chem. Res.* **1971**, *4*, 128–36.

[5] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–5.

[6] We have found it to be more convenient to work with **7b**: ^1H NMR ($CDCl_3$) δ 1.75 (dd, 2 H, H_a), 2.30 (m, 2 H, H_b), 3.08 (s, 3 H), 4.70 (t, 2 H, H_c); complete spectral simulation gives: $J_{aa'}$ = 6.5, J_{ab} = 8.4, J_{bc} = 2.0 Hz; ^{13}C NMR ($CDCl_3$) δ 25.74 (CH_3), 40.55 (CH_2), 62.32 (CH), 161.30 (C=O); IR ($CHCl_3$) 1720 cm^{-1}; mp 134–134.5 °C. Anal. Calcd for ($C_7H_9N_3O_2$) C, H, N.

[7] Gassman, P. G.; Mansfield, K. T. *Org. Synth.* **1969**, *49*, 1–6. We have obtained better yields using cupric bromide instead of cupric chloride.

[8] ^1H NMR (C_6D_6) δ 1.22 (m, 2 H), 1.60 (dd, 2 H) 4.40 (t, 2 H); preliminary spectral simulation gives coupling constants essentially identical with those for **7b**; ^{13}C NMR (CCl_4) δ 59.01 (CH_2), 76.36 (CH); mp (sealed tube) 63–4 °C; IR (CCl_4): 3020, 2960, 2870, 1475, 1430, 1260, 1210, 1100, 1015, 960 cm^{-1}; mass spectrum (degassed sample, 15 eV), *m/e* 54 (98), 39 (100), 28 (55).

[9] Thermolyses were performed in C_6D_6 in sealed NMR tubes and were monitored by multiple ^1H NMR integrations. All rate plots and the Arrhenius and Eyring plots gave linear correlation coefficients of 0.9998 or better. Rate constant × 10^5 s^{-1} (T, °C): 0.321 ± 0.006 (84.98), 1.20 ± 0.03 (95.04), 4.20 ± 0.08 (104.97), 13.5 ± 0.4 (115.06), E_a = 34.4 ± 0.2 kcal/mol, log A = 15.50 ± 0.09.

[10] Wildi, E. A.; Van Engen, D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1980**, 102, 7994–6.

[11] Kao, J.; Huang, T-N. *J. Am. Chem. Soc.* **1979**, *101*, 5546–57.

[12] Calculations performed in the present work using the force field of ref 11.

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A Versatile and Selective Route to Difunctional Trisubstituted (*E*)-Alkene Synthons via Zirconium-Catalyzed Carboalumination of Alkynes[1]

Summary: The Zr-catalyzed carboalumination of propargyl and homopropargyl derivatives containing OH, $OSiMe_2Bu$-*t*, SPh, or I provides, in a highly stereo- and regioselective manner, the corresponding (*E*)-(2-methylalkenyl)dimethylalkanes, which are convertible to various difunctional trisubstituted (*E*)-alkene synthons.

Sir: Trisubstituted olefins with two proximal functional groups such as **1**–**4** are potentially useful synthons for the synthesis of a variety of natural products of terpenoid origin. In principle, the syn methylmetalation of propargyl or homopropargyl derivatives followed by replacement of the carbon–metal bond with heterofunctional groups Z or CH_2Z would provide a versatile route to **1**–**4**. In practice, however, all previously reported controlled carbometalation reactions of propargyl and homopropargyl derivatives,[2]

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[1] Selective Carbon–Carbon Bond Formation via Transition Metal Catalysis, 19. Controlled Carbometalation 9. Part 8. T. Yoshida and E. Negishi, *J. Am. Chem. Soc.*, **103**, 1276 (1981).