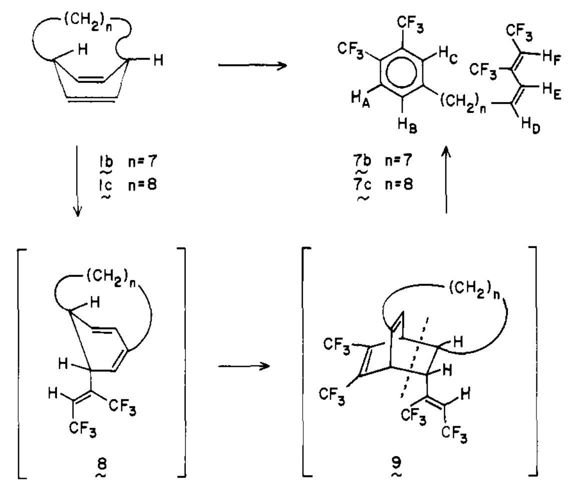
Scheme III



purification. Its exact M_r (calcd for $C_{22}H_{27}N_3O_2$ 365.208; found: 365.209) confirmed the 1:1 nature of the adduct. The ^{13}C NMR and mass spectral fragmentation patterns were very similar to those of **3c**, while the ^1H NMR differed considerably from **3c**, both in the positions and splitting patterns of H_2, H_3, H_5, and H_6. In view of this data, the minor adduct has been *tentatively* assigned structure **6**.

Addition of perfluoro-2-butyne to **1b** and **1c** appeared to occur in a more precedented fashion. As shown in Scheme III, heating of **1b** with perfluoro-2-butyne for 58 h at 140 °C gave 70% of **7b**, while **7c** was formed from **1c** in 66% yield after 6 days under the same conditions. The structures were readily determined from their NMR spectra. Mechanistically, we believe **1** underwent an initial ene reaction to give **8** which then added a second equivalent of perfluoro-2-butyne to produce **9**. A reverse Diels-Alder reaction of **9** would give **7**.[15]

In summary, distortion of a 1,4-cyclohexadiene through "trans" bridging as in **1** results in a complete change in the reactions with potent dienophiles. The unique products which resulted from these cycloaddition reactions required that our distortion of the 1,4-cyclohexadiene moiety provide the impetus for mechanistically new reaction paths.

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE78-10231, which supported this investigation, and Grant CHE77-28505 which aided in the purchase of an Enraf-Nonius X-ray diffractometer. We thank Mr. M. McGuiggan and Professors L. Pignolet and J. Z. Gougoutas for their help in the X-ray study.

Supplementary Material Available: Tables of bond distances, bond angles, thermal parameters, and atom coordinates (4 pages). Ordering information is given on any current masthead page.

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[15] Surprisingly, **1b** and **1c** failed to react with either dicyanoacetylene or dimethyl acetylenedicarboxylate on heating at 140–170 °C for 6 days.

Synthesis, Structure, and Reactivity of the (i,o)-Diazabicyclo[*n*.2.2]alkene Skeleton. Extremely Facile Cleavage of a C–N Bond

Paul G. Gassman* and Rebecca C. Hoye

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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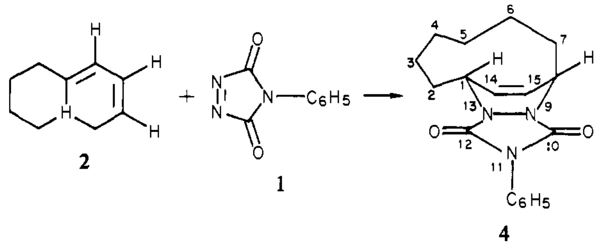
Our interest in the synthesis and reactivity of bicyclic molecules with inverted bridgeheads[1] has prompted us to explore the addition of the very reactive dienophile, *N*-phenyl-1,2,4-triazoline-3,5-dione (**1**) to relatively small, cyclic, *cis,trans*-1,3-dienes. Recently, we demonstrated that maleic anhydride can be added to *cis,trans*-cyclodeca-1,3-diene (**2**) to give the (i,o)-bicyclo[6.2.2]dodecene system, albeit in very low yield.[1d] We now wish to report that **1** adds to **2** in excellent yield and *cis,trans*-cyclonona-1,3-diene (**3**) in acceptable yield to produce (1i,8o)-11-phenyl-9,11,13-triazatricyclo[6.5.2.0^{9,13}]pentadec-14-ene-10,12-dione (**4**) and (1i,7o)-4-phenyl-2,4,6-triazatricyclo[5.5.2.0^{2,6}]tetradec-13-ene-3,5-dione (**5**), respectively.[2] Single-crystal X-ray structure determination for both **4** and **5** indicated large distortions from normal bonding parameters. These distortions were reflected in the thermal rearrangement of **5** at 50 °C.

When a chloroform solution of molar equivalents of **1**[3] and **2**[4] was stirred at 25 °C for 30 min, an 80% yield of **4**[5] was obtained as a white solid, mp 177–179 °C; ^1H NMR ($CDCl_3$) δ 7.60–7.04



(5 H, m), 6.52–6.20 (2 H, m), 5.07 (1 H, d of t, J = 4 and 5 Hz), 4.63 (1 H, m), and 3.08–0.87 (12 H, br m). The structural assignment was rigorously established through single-crystal X-ray analysis.[6,7] Figure 1 shows an ORTEP stereoview of **4** and Table I lists the bond lengths and bond angles. The structural characteristics of **4** and **6**[1d] were very similar. The C_1–C_2–C_3 angle of **4** was contracted to 105.5° (vs. 107.8° for **6**) as it is "pulled" back. The C_6–C_7–C_8 angle of **4** was expanded to 123.2° (vs. 123.9° for **6**) as it was bent to minimize the nonbonded interaction with the hydrogen at C_1. The other four C–C–C bond angles in

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(1) (a) Gassman, P. G.; Korn, S. R.; Thummel, R. P. *J. Am. Chem. Soc.* **1974**, *96*, 6948. (b) Gassman, P. G.; Korn, S. R.; Bailey, T. F.; Johnson, T. H.; Finer, J.; Clardy, J. *Tetrahedron Lett.* **1979**, 3401. (c) Gassman, P. G.; Bailey, T. F.; Hoye, R. C. *J. Org. Chem.* **1980**, *45*, 2923. (d) Gassman, P. G.; Hoye, R. C. *J. Am. Chem. Soc.* **1981**, preceding paper in this issue. (e) Gassman, P. G.; Hoye, R. C., submitted for publication.

(2) For a discussion of nomenclature in these systems, see ref 1a. Also see: Simmons, H. E.; Park, C. H.; Uyeda, R. T.; Habib, M. F. *Trans. N.Y. Acad. Sci.* **1970**, *32*, 521. The i term has been assigned to that bridgehead carbon having a hydrogen or other nonbridging substituent which resides inside the bicyclic (polycyclic) cavity. The o term has been allocated to that bridgehead carbon having a hydrogen or nonbridging substituent which resides outside the bicyclic (polycyclic) cavity. The i bridgehead has been assigned numbering position 1. Standard IUPAC numbering for the remainder of the bicyclic (or polycyclic) system has then been used. A detailed discussion of nomenclature in these systems and of the problems which occur will be presented in a full paper on this subject.

(3) For the preparation of **1**, see: Cookson, R. C.; Gupta, S. S.; Stevens, I. D. R.; Watts, C. T. *Org. Synth.* **1971**, *51*, 121. See also: Stickler, J. C.; Pirkle, W. H. *J. Org. Chem.* **1966**, *31*, 3444.

(4) For the preparation of **3**, see: Blomquist, A. T.; Goldstein, A. *J. Am. Chem. Soc.* **1955**, *77*, 1001.

(5) Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds except **10**, which was analyzed as its acetylated derivative.

(6) The white crystals of $C_{18}H_{21}N_3O_2$ belonged to the triclinic space group $P\bar{1}$. The measured cell constants a = 8.101 (2), b = 9.921 (2), c = 10.304 (2) Å; α = 93.00 (2), β = 100.02 (2), and γ = 104.80 (1)° gave a calculated density of 1.33 g/cc for four molecules in the unit cell at ambient temperature. Data were collected on a fully automated Enraf-Nonius CAD4 diffractometer by using a variable rate ω–2θ scan technique and graphite monochromatized Cu Kα radiation (λ = 1.54184 Å). After Lorentz-polarization corrections, 2267 of 2993 unique reflections (76%) with 2θ = 0–140° were observed for $[F_o > 2\sigma(F_o)^2]$. A combination of direct methods and difference Fourier synthesis was used to locate all nonhydrogen atoms.[7] The positions for all hydrogen atoms were calculated and refined by full-matrix least-squares analysis. The R factor for the structure was 0.049.

(7) All calculations were carried out on a PDP 11/34 computer by using the Enraf-Nonius SDP programs. This crystallographic computing package is described by Frentz, B. A. In "Computing in Crystallography"; Schenck, H., Olthof-Hazekamp, R., van Konigweld, H., Bassie, G. S., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

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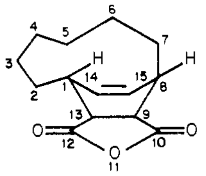
Table I. Selected Bond Distances and Bond Angles for (1i,8o)-11-Phenyl-9,11,13-triazatricyclo[6.5.2.0^{9,13}]pentadec-14-ene-10,12-dione (**4**)

atoms	angle, deg	atoms	angle, deg
C8–C15–C14	119.31 (14)	N11–C10–O	127.42 (13)
C15–C14–C1	113.84 (14)	N13–C12–N11	104.32 (11)
C14–C1–C2	118.24 (13)	N13–C12–O	128.74 (12)
C1–C2–C3	105.54 (13)	N11–C12–O	126.83 (13)
C2–C3–C4	116.25 (14)	C8–N9–C10	121.47 (11)
C3–C4–C5	119.15 (15)	C8–N9–N13	117.43 (10)
C4–C5–C6	117.11 (16)	C10–N9–N13	107.81 (11)
C5–C6–C7	118.21 (15)	C1–N13–C12	131.95 (12)
C6–C7–C8	123.15 (13)	C1–N13–N9	111.37 (11)
N9–C10–N11	105.62 (11)	C12–N13–N9	110.21 (10)
N9–C10–O	126.95 (14)	C10–N11–C12	111.30 (11)
atoms	**distance, Å**	**atoms**	**distance, Å**
C8–C15	1.518 (2)	C8–N9	1.496 (2)
C14–C15	1.310 (2)	C1–N13	1.454 (2)
C1–C14	1.510 (2)	N9–N13	1.426 (1)
C1–C2	1.516 (2)	N9–C10	1.366 (2)
C2–C3	1.524 (2)	C10–O	1.218 (2)
C3–C4	1.534 (3)	C10–N11	1.395 (2)
C4–C5	1.552 (3)	N11–C12	1.431 (2)
C5–C6	1.561 (2)	C12–O	1.215 (2)
C6–C7	1.547 (2)	C12–N13	1.356 (2)
C7–C8	1.547 (2)		

Table II. Selected Bond Distances and Bond Angles for (1i,7o)-4-Phenyl-2,4,6-triazatricyclo[5.5.2.0^{2,6}]tetradec-13-ene-3,5-dione (**5**)

atoms	angle, deg	atoms	angle, deg
C7–C14–C13	115.82 (18)	N6–N2–C3	110.18 (13)
C14–C13–C1	112.30 (18)	N6–N2–C1	107.00 (13)
C13–C1–C12	119.76 (17)	C3–N4–C5	111.19 (14)
C1–C12–C11	103.05 (18)	N4–C5–N6	106.44 (14)
C10–C11–C12	115.49 (20)	N6–C5–O	125.88 (17)
C9–C10–C11	119.65 (20)	N4–C5–O	127.66 (17)
C8–C9–C10	122.20 (19)	N4–C3–O	126.84 (18)
C7–C8–C9	122.57 (19)	N2–C3–N4	104.14 (15)
C5–N6–N2	106.35 (13)	N2–C3–O	128.78 (17)
N2–N6–C7	115.56 (13)		
atoms	**distance, Å**	**atoms**	**distance, Å**
C7–C14	1.493 (3)	C7–N6	1.522 (2)
C13–C14	1.318 (3)	C1–N2	1.483 (2)
C1–C13	1.500 (3)	N2–N6	1.434 (2)
C1–C12	1.505 (2)	C5–N6	1.396 (2)
C11–C12	1.534 (3)	C5–O	1.214 (2)
C10–C11	1.538 (4)	C5–N4	1.379 (2)
C9–C10	1.563 (3)	C3–N4	1.411 (2)
C8–C9	1.561 (3)	C3–N2	1.369 (2)
C7–C8	1.567 (3)	C3–O	1.194 (2)



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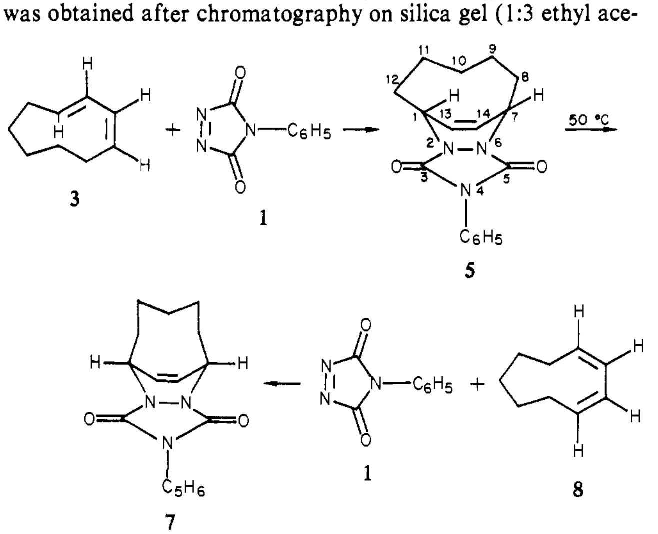
the hexamethylene chain were also widened to an average value of 117.7° (vs. 117.6° for **6**).

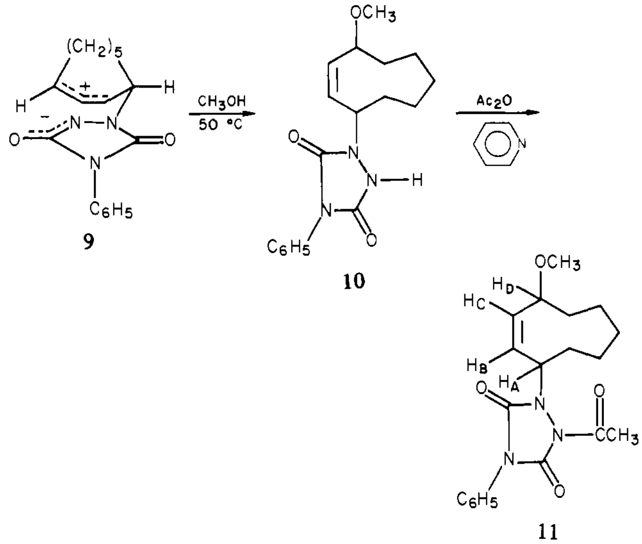
In a similar manner, when a chloroform solution of **1** and **3**[8] was stirred at 25 °C for 2 h, a 14% yield of **5**, mp 150–154 °C, was obtained after chromatography on silica gel (1:3 ethyl acetate–hexane eluant); ^{1}H NMR (CDCl$_3$) δ 7.62–7.10 (5 H, m), 6.43 (1 H, t, J = 8 Hz), 6.29 (1 H, d of d, J = 2 and 7 Hz), 5.15 (1 H, br q, J = 7 Hz), 4.57 (1 H, br q, J = 8 Hz) and 2.83–0.81 (10 H, br m); ^{13}C NMR (CDCl$_3$) δ 155.78, 151.94, 132.47, 132.29, 131.67, 128.81 (2 C), 127.85, 125.41 (2 C), 56.64, 55.55, 37.63, 30.79, 30.58, 28.45, and 27.47. Again, single-crystal X-ray analysis substantiated the structural assignment.[7,9] Figure 2 is an ORTEP stereoview of **5**, and Table II lists the bond angles and bond lengths. The effect of removing one methylene unit from the bridging chain of **5** (relative to **4** and **6**) showed up in several ways. The C_1–C_{12}–C_{11} angle in **5** was 103.0 vs. 105.5° for the related angle of **4**. The average C–C bond length for the methylene chain of **5** was 1.545 vs. 1.540 Å for **4**. Somewhat surprising was the C_7–C_8–C_9 angle of **5** which was smaller (122.6°) than the corresponding angle of **4** (123.9°). In part, this appeared to be compensated for by an enlargement of the other three C–C–C angles of the pentamethylene bridge which averaged 119° (vs. 117° for **4**).



3 **1** **5**

7 **1** **8**

The strain incorporated into **5** was apparent in its surprisingly facile thermal isomerization. On warming to 50–65 °C in certain solvents, **5** was cleanly converted into **7**, mp 183–184 °C. This material was identical with that prepared from the Diels–Alder addition of **1** to *cis*,*cis*-cyclonona-1,3-diene (**8**).[8] In contrast, **4** failed to undergo similar thermal isomerization even on heating at 150 °C for 3 days.[10]



9 **10** **11**

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[8] For the preparation of **3** and **8**, see: Fawcett, R. W.; Harris, J. D. *J. Chem. Soc.* **1954**, 2673.

[9] The white crystals of $C_{17}H_{19}N_3O_2$ belonged to the triclinic space group $P\bar{1}$. The measured cell constants a = 7.947 (1), b = 9.794 (1), c = 10.056 (1) Å; α = 89.97 (1), β = 99.83 (1), and γ = 105.10 (1)° gave a calculated density of 1.328 g/cc for the four molecules in the unit cell at ambient temperature. Data were collected on a fully automated Enraf–Nonius CAD4 diffractometer by using a variable rate ω–2θ scan technique and graphite monochromatized Cu Kα radiation (λ = 1.54184 Å). After Lorentz–polarization corrections, 1994 of 3139 unique reflections (64%) with 2θ = 0–156° were observed for $[F_o > 2\sigma(F_o)^2]$. A combination of direct methods and difference Fourier synthesis was used to locate all nonhydrogen atoms.[7] The positions of all hydrogen atoms were calculated and refined by full-matrix least-squares analysis. The R factor for the structure was 0.059.

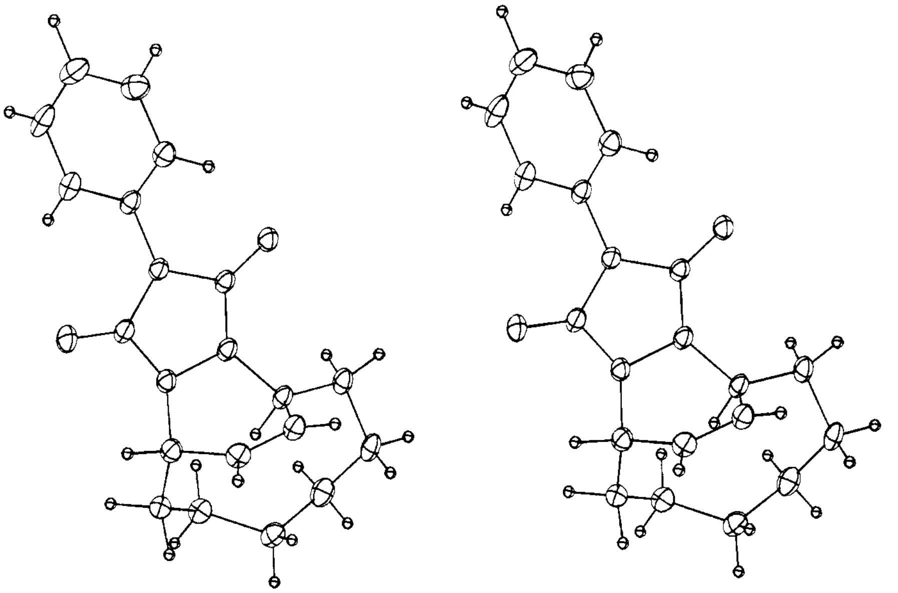

Figure 1. ORTEP stereoview of **4**.

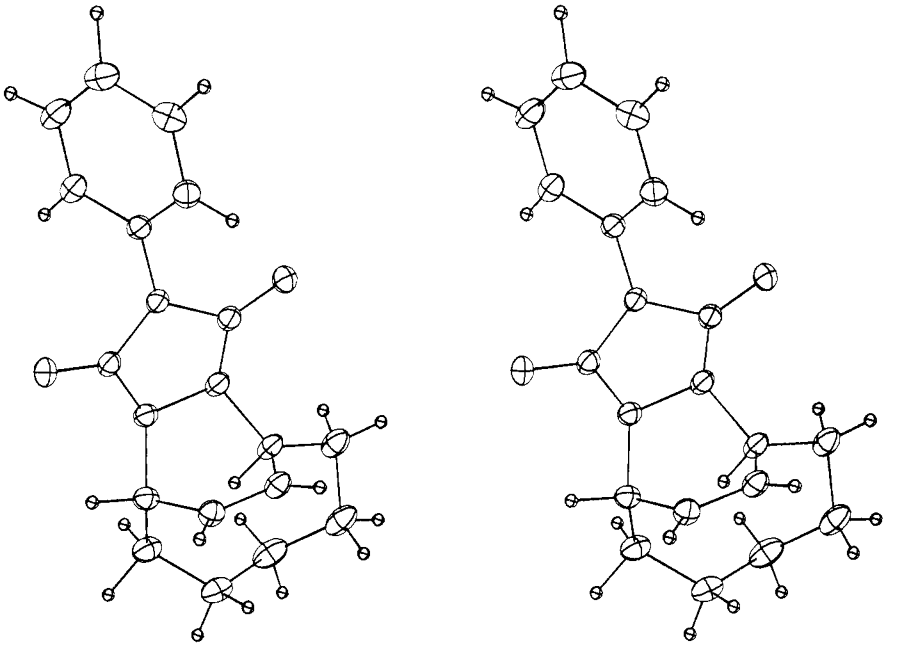

Figure 2. ORTEP stereoview of **5**.

Mechanistically, it would appear that the isomerization of **5** was most reasonably explained in terms of either a homolytic or heterolytic cleavage of the C_1–N_2 bond, followed by inversion of the bridgehead, and reclosure. The need for the allylic stabilization provided by the double bond was readily demonstrated. Catalytic hydrogenation of **5** over palladium on carbon resulted in the uptake of 1 equiv of hydrogen and produced the reduced analogue of **5** in 98% yield. This saturated compound could be recovered unchanged after 3 days at 80 °C. Evidence for the zwitterionic species, **9**, was obtained by warming of **5** in methanol to 50 °C for 1 h, which resulted in the formation of **10** in 73% yield. Acetylation of **10** with acetic anhydride in pyridine gave **11**. The *N*-acetyl and methoxy groups of **11** appeared as sharp singlets at δ 2.68 and 3.27, respectively. The two vinyl protons (H_B and H_C) occurred as a broad multiplet at δ 5.87. H_A and H_D occurred as multiplets at δ 4.11 and δ 5.22, respectively. Irradiation at δ 5.87 greatly simplified H_A and H_D, while irradiation of either H_A or H_D simplified the multiplet at δ 5.87. Thus, both of the substituents on the cyclononene ring were allylic. Clearly, the addition of methanol across the C–N bond of **5** at 50 °C is consistent with the intermediacy of **9**.

In summary, we have prepared the first example of an (i,o)-bicyclo[5.2.2]undecene derivative and unequivocally established its structure. The presence of two C–N bonds in this skeleton may have contributed significantly to its thermal instability. However, we would prefer to view this inherent instability as resulting from the strain incorporated in the skeleton being reflected in the extremely facile cleavage of the C–N bond of **5**. We are continuing our investigations in this area.

Acknowledgment. We are indebted to the National Science Foundation for Grant CHE78-10231, which supported this investigation, and for Grant CHE77-28505, which aided in the purchase of an Enraf-Nonius X-ray diffractometer. We thank M. McGuiggan and Professors L. Pignolet and J. Z. Gougoutas for their help in the X-ray study.

Supplementary Material Available: Tables of bond lengths, bond angles, thermal parameters, and atom coordinates (8 pages). Ordering information is given on any current masthead page.

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(10) It should be noted that under these conditions a portion of the starting material was converted into an insoluble, high molecular weight material. However, the majority of **4** was unchanged. Heating of **4** in methanol-d_4 for 14 h at 90 °C resulted in no change in **4**.