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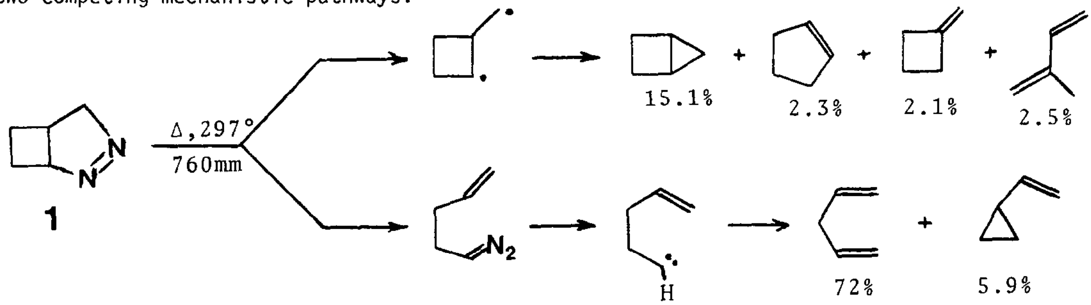
THE THERMAL DEAZETATION OF 6,6,7,7-TETRAFLUORO-2,3-DIAZABICYCLO[3.2.0]HEPT-2-ENE

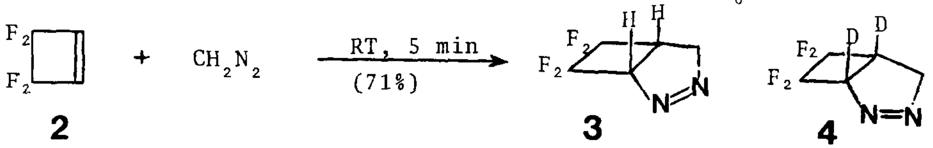
William R. Dolbier, Jr.* and Dheya M. Al-Fekri
Department of Chemistry, University of Florida
Gainesville, Florida 32611

Summary: The mechanisms of formation of five products from the deazetation of the title compound and a remarkable thermodynamic methyl substituent effect are presented and discussed.

In 1972 Bergman reported that the bicyclopyrazoline 1 underwent thermal deazetation *via* two competing mechanistic pathways.[1]

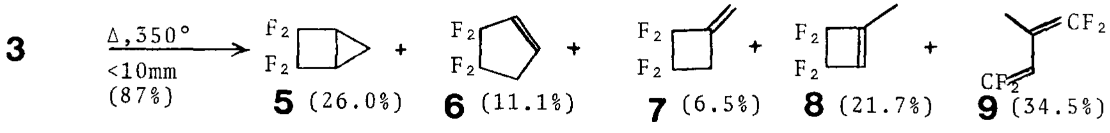


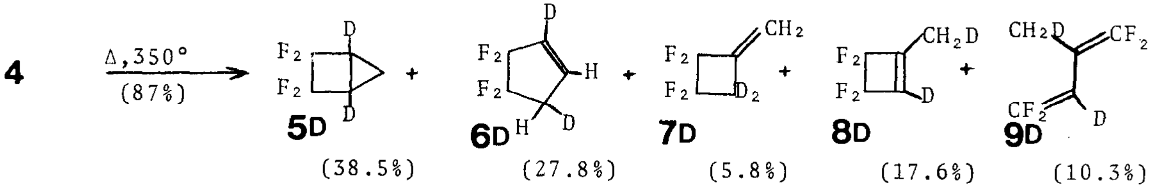
Within the context of our general interest in the effect of fluorine substituents on the thermal behavior of molecules, we desired to prepare 2,2,3,3-tetrafluorobicyclo[2.1.0]pentane. To this end 6,6,7,7-tetrafluoro-2,3-diazabicyclo[3.2.0]hept-2-ene, 3, was prepared *via* the



facile addition of diazomethane to 3,3,4,4-tetrafluorocyclobutene, 2, and its thermal and photochemical deazetation investigated. The structure of 3 was unambiguously demonstrated through spectral characterization of 3 [IR (neat film), 1545, 1425, 990, 910, 800, 730, 680 cm^{-1}; NMR's (CCl$_4$) ^{1}H, δ 3.07 (br.m, 1 H), 4.83 (d of d, J_{AB} = 19 Hz, J = 8 Hz, 1 H), 5.08 (d of t, J_{AB} = 18 Hz, J = 3 Hz, 1 H), 5.73 ppm (br.m, 1 H); ^{19}F, ϕ 113 (J_{FF} = 223 Hz), 115 (J_{FF} = 218 Hz), 121 (J_{FF} = 223 Hz), 124 ppm (J_{FF} = 218 Hz); ms, 168.0317 ± 0.0021 (M$^+$, 13 ppm), calcd for $C_5H_4F_4N_2$ 168.0310 (dev = 0.0006, 4.1 ppm)] and of 4 [^{1}H NMR (CDCl$_3$)[2], δ 4.74 (d, J_{AB} = 20 Hz, 1 H), 5.20 ppm (d, J_{AB} = 20 Hz, 1 H)].

The bicyclic pyrazolines **3** and **4** were pyrolyzed at 350° in a flow system in which **3** and **4** were allowed to evaporate, *in-vacuo*, and pass into a heated zone where partial deazetation occurred (~75% conversion). In each case, a mixture of five isomeric products was produced, in yields of 68 and 87%, respectively.





Spectroscopic data used to characterize products **5** - **9**:

5: IR (gas), 3100, 3015, 1370, 1330, 1150, 1065, 970, 875, 780, 580, 465 cm^{-1}; NMR's (CCl$_4$), ^{1}H, δ 1.43 (m, 2 H), 2.55 ppm (m, 2 H); ^{19}F, ϕ 116.6 (midpoint, AB, J_{AB} = 209.5 Hz, Δν = 1447.1 Hz); ^{13}C, δ 7.39 (C$_5$), 21.8 (C$_1$), 115.7 ppm (CF$_2$, complex t, J_{CF} = 285.8 Hz); ms, 140.0239 ± 0.0016 (M$^+$, 11.8 ppm), calcd for $C_5H_4F_4$ 140.0249 (dev = 0.0013, 9.8 ppm).

5-D: ^{1}H NMR (CCl$_4$)[2] (300 MHz), δ 1.36 (complex s, 1 H), 1.39 ppm (prob. t, J = 6.5 Hz, 1 H).

6: IR (gas), 3095, 1610, 1500, 1440, 1370, 1345, 1015, 915, 770, 730, 585 & 470 cm^{-1}; NMR's (CCl$_4$), ^{1}H δ 2.92 (t of t, J = 12 Hz and 3 Hz, 2 H), 6.03 (d of t, J = 4 Hz and 2 Hz, 1 H), 6.42 ppm (m, 1 H); ^{19}F, ϕ 113 (br.s, 2 F), 118 (t, J = 112 Hz, 2 F); ^{13}C, δ 39.2 (t, J_{CF} = 26.5 Hz), 120 (m), 126 (t, J_{CF} = 26.2 Hz), 137.8 ppm (m), no quat. C seen; ms, 140.0246 ± 0.0011 (M$^+$, 8 ppm), calcd for $C_5H_4F_4$ 140.0249 (dev = 0.0002, 1.9 ppm).

6-D: ^{1}H NMR (CDCl$_3$)[2], δ 3.0 (m, J = 12 Hz and 3 Hz, 1 H), 6.56 (br.s, 1 H).

7[3]: IR (gas), 3055, 1600, 1500, 1225, 845 and 575 cm^{-1}; NMR's (CCl$_4$) ^{1}H, δ 3.15 (t of t, J_{HF} = 11 Hz, J = 3 Hz, 2 H), 5.54 (m, 1 H), 5.87 (m, 1 H); ^{19}F, ϕ 115.5 (br.s), 116.7 (t, J_{HF} = 11 Hz).

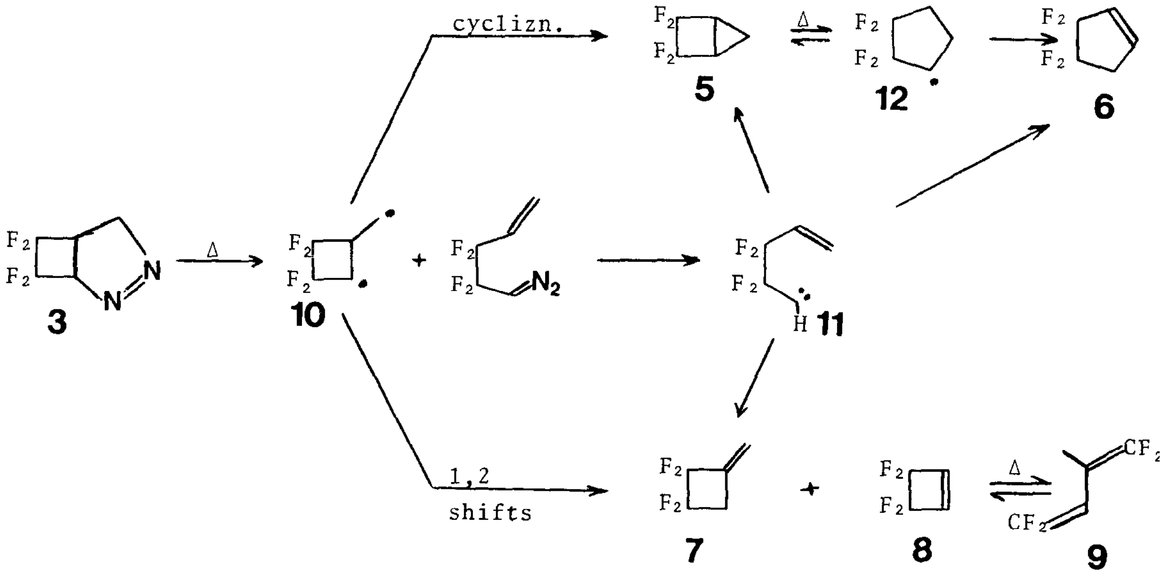
7-D: ^{1}H NMR (CDCl$_3$)[2], 5.68 (br.s), 5.98 ppm (br.s).

8: IR (gas), 1630, 1445, 1320, 890, 735, 480 & 415 cm^{-1}; NMR's (CCl$_4$) ^{1}H, δ 6.45 (t, J_{HF} = 11 Hz, 1 H), 1.92 ppm (br.s, 3 H); ^{19}F, ϕ 111.97 (m, 2 F), 117.6 ppm (m, 2 F); ^{13}C, δ 9.6 (CH$_3$, s), 120 (CF$_2$'s, complex t's, J_{CF} ≈ 290 Hz), 136 (C$_2$, m), 154 ppm (C$_1$, m).

8-D: ^{1}H NMR ($CDCl_3$)[2], δ 2.0 ppm (br.m).
9: λ_{max} 254 nm; IR (gas), 1715, 1230, 1300, 1100, 910, 810 and 575 cm^{-1}; NMR's (CCl_4) ^{1}H, δ 4.88 (d of m, J_{HF} = 26 Hz, 1 H), 1.8 ppm (quart., J = 3 Hz, 3 H); ^{19}F, φ 84, 85.7, 91.5, 94.5 ppm (all complex m's); ms, 140.0238 ± 0.0015 (M^+, 11.2 ppm), calcd for $C_5H_4F_4$ 140.0249 (dev = 0.0011, 7.4 ppm).
9-D: ^{1}H NMR ($CDCl_3$)[2], δ 1.80 ppm (br.m).

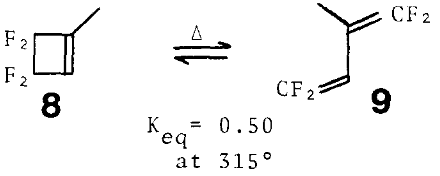
Photochemical deazetation of **3**, as a neat liquid, *in-vacuo,* and using 2500A° light for 15 h, led to the formation (57% yield) of only **5** and **6** in the relative yields of 56 and 44%, respectively.[4]

The results of thermal deazetation of **3** and **4** are perhaps best rationalized in terms of competitive formation of diradical and carbene intermediates **10** and **11** (the latter *via* retro-1,3-dipolar cycloaddition). While all observed products may be construed as having been formed from the single intermediate **10**, involvement of the carbene **11** cannot be ruled out as at least a partial source of **5**, **6**, & **7**. Products analogous to the 1,4-pentadiene and vinylcyclopropane observed by Bergman in the hydrocarbon system are not possible in our case because of the location of the fluorine substituents, but such a carbene as **11** could well cycloadd intramolecularly to form **5** or insert into vinylic C-H bonds to form **6** or **7**. While the deuterium-labelling experiment does not allow distinction of these two mechanistic pathways, it does exclude the possibility of direct formation of **6** from diradical **10** by a ring expansion. Cyclopentene **6** therefore is most likely formed from **5** *via* diradical **12** with perhaps some contribution from the carbene process. A control pyrolysis demonstrated that **5** will convert thermally to **6** at temperatures >350°.



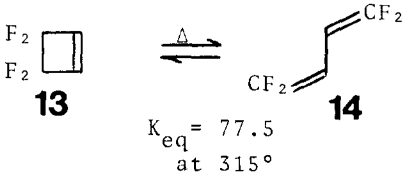
The lack of observation of an inhibitory isotope effect in formation of 6-D (the yield of 6-D is in fact more than double that of 6) rules out carbene insertion as the major pathway for formation of 6. As expected, one does observe isotope effects in the formation of methylcyclobutene, 8-D, and methylenecyclobutane 7-D.

Under the conditions of deazetation, methylcyclobutene product 8 was found to have partially equilibrated with its butadiene isomer 9. When allowed to fully equilibrate at 315° under static, gas-phase conditions, an equilibrium value for 9:8 of 0.50 was observed. The presence of so much cyclobutene isomer 8 at equilibrium was unexpected in view of the fact that Frey has observed a much greater thermodynamic preference for the butadiene isomer 14 in the system *sans* methyl group.[5] Indeed we observe only 1.3% of 13 in equilibrium at 315°. A comparison of the $8 \rightleftarrows 9$ and $13 \rightleftarrows 14$ equilibria indicates a rather dramatic thermodynamic effect ($\Delta\Delta G°$ = 5.9 kcal/mole) due to the presence (or absence) of the methyl substituent. We defer discussion of this unusual substituent effect until more related results can be accumulated. A reasonable preliminary assessment, however, would be that the interaction of vicinal methyl and fluorine substituents, as in 9, is destabilizing. Worth noting is the fact that substitution of an ethyl for the methyl substituent leads to an even greater shift in equilibrium (i.e. K = 0.24 at 315°).



8 **9**

K_{eq} = 0.50 at 315°



13 **14**

K_{eq} = 77.5 at 315°

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References & Footnotes

1. White, D. H.; Condit, P. B.; Bergman, R. G. *J. Am. Chem. Soc.*, 1972, *94*, 1348.
2. Only ^{1}H NMR's are provided for deuterium-labelled species since the ^{19}F and ^{13}C spectra are almost identical to those of the respective undeuterated species.
3. Taylor, D. R. *Tetrahedron Lett.* 1967, 3277.
4. In a control photolysis it was found that 5 did not convert significantly to 6 under the photolysis conditions.
5. Frey, H. M.; Hopkins, R. G.; Vinall, I. C. *J. Chem. Soc. Faraday I* 1972, 1874.

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