Tetrahedron Vol 43, No. 1, pp. 39 to 44, 1987
Printed in Great Britain.

0040-4020/87 $5.00 + .00

THE THERMAL DEAZETATIONS OF FLUORINATED 2,3-DIAZABICYCLO[3.2.0]HEPT-2-ENES

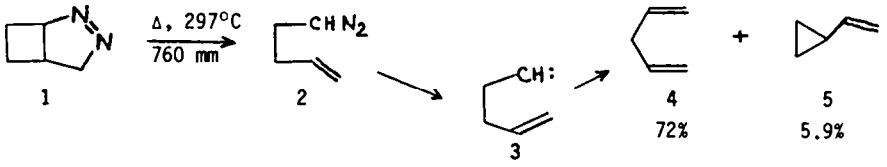
WILLIAM R. DOLBIER, JR.* and DHEYA M. AL-FEKRI[1,2]

Department of Chemistry, University of Florida
Gainesville, FL 32611

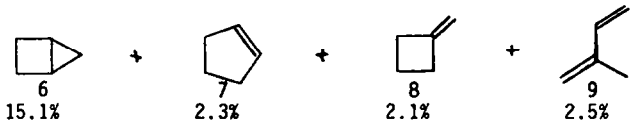
(*Received in USA* 30 *September* 1986)

Abstract - Thermal deazetation of difluoro- and tetrafluoro-2,3-diazabicyclo[3.2.0]hept-2-enes proceed via two parallel mechanistic pathways, one involving formation of a diradical via simple N_2 loss, and the other proceeding via a retro-dipolar cycloaddition process. A key finding was the absence of isolation of a bicyclopentane product in the difluoro case.

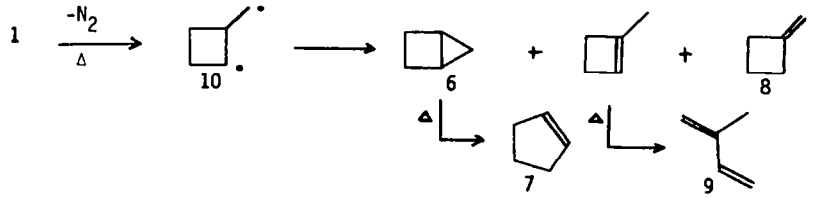
The thermal deazetation of 2,3-diazabicyclo[3.2.0]hept-2-ene has been shown to take place largely via a retro-1,3-dipolar cycloaddition process followed by N_2 loss and subsequent rearrange-



ment or insertion of the intermediate carbene **3**.[3] The bicyclopentane product **6** can also easily be

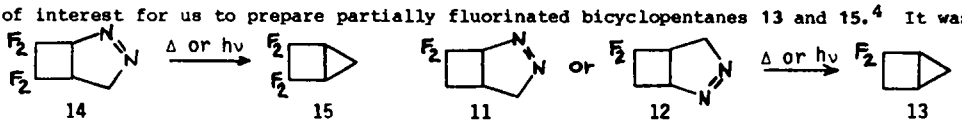


construed as deriving from carbene precursor **3**, and even minor products cyclopentene **7** and methylenecyclobutane **8** can logically derive from **3**, via vinylic C-H insertion. Only the minor isoprene product **9** can not easily have been derived therefrom. Of course, it is recognized that it



is likely that much of the minor products **6-9** actually derive from the intermediate diradical, **10**, which is not related to the retro-cycloaddition process.

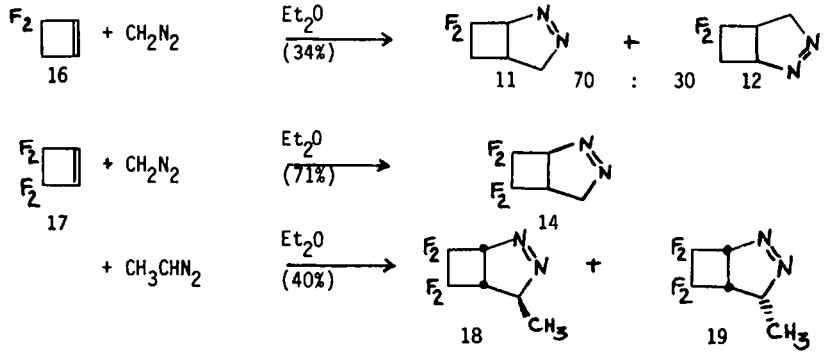
In our general studies of the effect of fluorine substituents on thermal homolytic processes, it was of interest for us to prepare partially fluorinated bicyclopentanes **13** and **15**.[4] It was



naturally assumed that they could be prepared via the deazetation of the azobicyclics **11** and **13** which are analogous to **1**. Indeed **15** could be prepared via thermolysis of **14**, but the pyrolysis of **11** quite unexpectedly did not produce any of the desired **13**. This paper presents and discusses the results of thermal deazetation of **11** and **14**, as well as **18**, a methyl-substituted analogue of **14**.

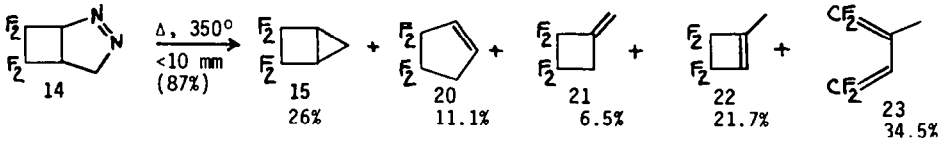
RESULTS AND DISCUSSION

The desired difluoro and tetrafluoro diazabicyclo[3.2.0]heptenes, **11** (and **12**) and **14** were prepared by the addition of diazomethane to 3,3-difluorocyclobutene, **16**,[5] and 3,3,4,4-tetrafluorocyclobutene, **17**,[6] respectively. The difluoro adduct was a 2.4:1 ratio of isomers **11** and **12** with **11** being the major product. A methyl-substituted analogue of **14** was synthesized by the addition of diazoethane to **17** to form 4-methyl-6,6,7,7-tetrafluoro-2,3-diazabicyclo[3.2.0]hept-2-ene, **18**. This adduct, which appeared to be contaminated by a small amount of isomer **19**, was not fully characterized due to its instability to proton rearrangement, but was utilized in the crude state for the



pyrolysis work. For the same reason, difluoroazobicyclics **11** and **12** were not separated but were used in the pyrolyses as a mixture.

The results of deazetation of the fluorinated 2,3-diazabicyclo[3.2.0]hept-2-enes, as in the case of the parent **1** seem generally consistent with a process consisting of two independent, parallel mechanisms: (a) a retro-1,3-dipolar cycloaddition to form a diazoalkene such as **2** with subsequent loss of N_2 to form a carbene (i.e. **3**), and (b) direct loss of N_2 to form a diradical such as **10**. For the tetrafluoro system, **14**, results comparable to those for the parent system were

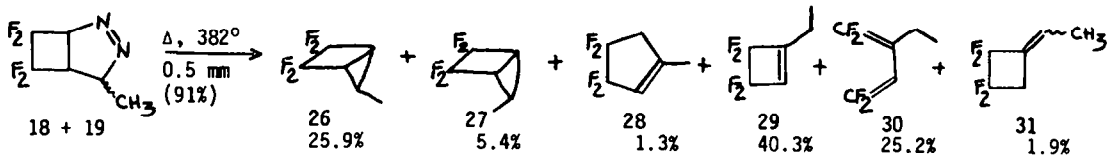


obtained, except that 1,4-pentadiene or vinylcyclopropane products which could be unambiguously, directly-attributable to the intermediacy of the analogous carbene **24** were not observed, nor could they have been because of the presence of the fluorine substituents. More importantly products **22**

24 25

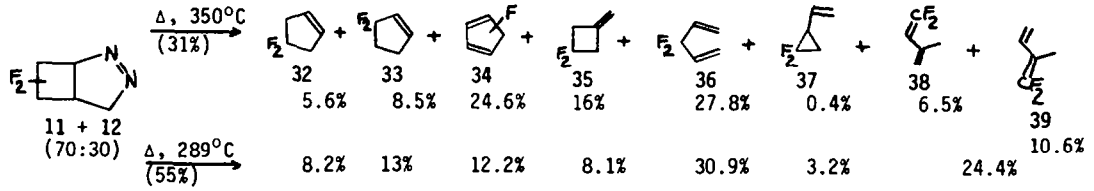
and **23**, which could only have derived from the alternative pathway involving diradical **25**, are major products in this pyrolysis while they were very minor in the hydrocarbon system. Hence, it is reasonable to surmise that the retro-cycloaddition pathway, which dominated in the hydrocarbon system, plays a significantly diminished role in the deazetation of the tetrafluoro system. One recognizes that products **15**, **20**, and **21**, as in the hydrocarbon system, could have derived via either the carbene or the diradical pathway.

In an analogous experiment the methyl-substituted azobicyclic **18** was pyrolyzed at 382°C to give a 91% yield of six products, in relative amounts very much comparable to those from the pyrolysis of **14**. Isomers **26** and **27** were distinguished unambiguously by homonuclear decoupling experiments. The major products from the pyrolysis of **18** are cyclobutene **29** and diene **30**, which comprised a total of 65.5% compared to a total of 56.2% for the analogous pair (**22** and **23**) from the pyrolysis of **14**. As for **14**, a diminished role for the retro-cycloaddition pathway is indicated for

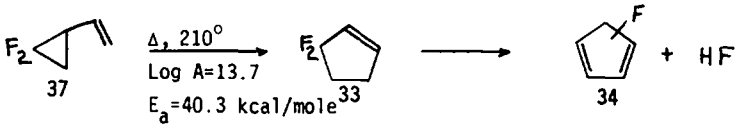


the thermal deazetation of **18**.

The results from the pyrolysis of the mixture of 7,7- and 6,6-difluoro-2,3-diazabicyclo-[3.2.0]hept-2-enes, **11** and **12**, are, as might be expected, intermediary between those of the nonfluorinated and tetrafluoro sytems. Significant amounts of products **36** and **37**, which most

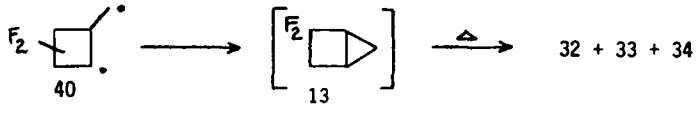


likely derive from the retro-cycloaddition pathway, are observed. Interestingly, the major product (28-30%) of this pyrolysis, 3,3-difluoro-1,4-pentadiene, **36**, can derive only from the retro-cycloaddition pathway of the minor (30%) component, **12**, of the starting mixture. In contrast the only product which unambiguously derives from the retro-cycloaddition of major component (**11**) of the starting mixture is 1,1-difluoro-2-vinylcyclopropane, **37**, which is isolated in very small yield. Of course it is known that **37** should rearrange easily under the conditions of the pyrolysis:[7]

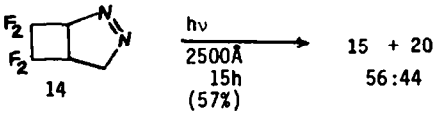


Hence the rather substantial amounts of **33** and **34** (8.5 and 24.6%) formed in the pyrolysis could well be an indication of a significant formation of **37** as an intermediate. The differences in product ratios for the two temperatures undoubtedly derives from the thermal lability of products such as **32**, **33** and **37**.

A key aspect of the pyrolyses of **11** and **12** was the lack of ability to isolate 2,2-difluorobicyclopentane **13** as a product. Both the parent **6** and the tetrafluorobicyclopentanes **15**, **26** and **27** were found in substantial amounts from similar pyrolyses. There is no reason to believe that the difluoro analog **13** should be inhibited from forming via the expected intermediate diradical **40**.



Therefore one must assume that **13** was formed, but did not survive the conditions of the pyrolyses. This means that **13** must be much more reactive than the tetrafluoro or parent species, which rearrange with activation energies of 54 and 47 kcal/mole respectively.[4,8] In contrast, the rearrangement of **37**, which survives the pyrolysis at least in part, has an E_a of 40 kcal/mole. This would seem to indicate that the unobservable **13** must rearrange with an E_a of even less than 40 kcal/mole. This implies a substantial diminishment in stability of **13** relative to its symmetric analogs, **6** and **15**. It is hoped that an eventual alternate synthesis of **13** will substantiate the above hypothesis. In this regard it is worth mentioning that while photolysis of **14** resulted in



the formation of bicyclopentane **15** in moderate yield,[4] to our surprise a similar photolysis of the **11** and **12** mixture led only to tars with no **13** being detectable.

In conclusion, while no retro-cycloaddition pathway is required to rationalize the products

derived from deazetations of tetrafluoro azo species **14** and **18**, the deazetation of the analogous difluoro azo compound mixture **11** and **12** must proceed via a substantial retro-cycloaddition mechanistic component. Without an alternate synthesis of difluorobicyclopentane **13**, one can only speculate about the reason for its absence as a product in this reaction.

EXPERIMENTAL SECTION

NMR Spectra are in CCL_4 at 60, 100 or 300 MHz for ^1H, 56.5, 94.1 or 282.3 MHz for ^{19}F and 75.5 or 226.4 MHz for ^{13}C. ^1H and ^{13}C chemical shifts are reported in ppm downfield from TMS, while ^{19}F chemical shifts are reported in ppm upfield from $CFCl_3$ internal standard.

1,2,3,3,4,4-Hexafluorocyclobutene.

Based on a published procedure,[6] 27.6g (0.169 mole) 81% of product was obtained: IR, gas phase 1790, 1400, 1150, 960 cm^{-1}. ^{19}F NMR ($CDCl_3$, 56.5 MHz) ϕ 120.5 (d of d J=20 Hz, 10.6 Hz), 129.89 ppm (d of t, virtual pentet, J=21 Hz, 10.5 Hz).

3,3,4,4-Tetrafluorocyclobutene, **17**.

Identical procedure to the published[6] one was followed to obtain 4g (0.031 mole, 23%) of a colorless liq bp 54-55°C of **17**: ^1H NMR ($CDCl_3$, 60 MHz) δ 6.74 ppm (m); ^{19}F NMR (282.3 MHz) ϕ 111.10 ppm (S); ^{13}C NMR (226.4 MHz) δ 123.45 (t, J_{CF}=287 Hz), 143.27 ppm (p).

6,6,7,7-Tetrafluoro-2,3-diazabicyclo[3.2.0]hept-2-ene, **14**.

An ether soln of diazomethane (35 ml) was prepared from 3.5 g (17.5 mmoles) N-methyl-N-nitroso-P-toluenesulfonamide.[9] The soln was vac transferred to a 160 mL glass tube with a rotoflow teflon stopcock and 2.2 g (17.5 mmoles) **17** were condensed into the tube, which was sealed under vacuum. After five minutes at RT, the clear, colorless soln was concentrated by rotary evapn at 200 Torr and the ether was removed completely under 3 Torr. The residue was a white solid 2.06 g (0.0122 mol, 71%) and was stored on dry ice under nitrogen: mp 25.5°C; IR (neat film) 1545, 1425, 990, 910, 800, 730, 680 cm^{-1}; ^1H NMR (100 MHz) δ 3.07 (br. m, 1H), 4.83 (d of d, J_{AB}=19 Hz, J=8 Hz, 1H), 5.08 (d of t, J_{AB}=18 Hz, J=3 Hz, 1H), 5.73 ppm (br. m, 1H); ^{19}F NMR (94.1 MHz) ϕ 113 (J_{FF}=223 Hz), 115 (J_{FF}=218 Hz), 121 (J_{FF}=223 Hz), 124 ppm (J_{FF}=218 Hz); ms gave M^+ 168.0317±0.0021 (13 ppm), calcd for $C_5H_4F_4N_2$ 168.0310 dev=0.0006 (4.1 ppm).

Thermolysis of **14**.

Through a 22 cm by 2.5 cm Vigreux column heated at 350°C was vac transferred 0.87 g (5.2 mmol) **14** over a period of 4 h at a pressure of 0.25-0.4 Torr. A total of 500 mg (69%) crude liq pyrolyzate was collected in a vacuum trap at liq-N_2 temp. The products were isolated by prep GC (20 ft. by 1/4 in. in 10% DNP at 55°C, 33 mL/min.) to give: 39 mg (5.34%) of **15**: IR (gas), 3100, 3015, 1370, 1330, 1150, 1065, 970, 875, 780, 580, 465 cm^{-1}; ^1H NMR (60 MHz) δ 1.43 (m, 2H), 2.55 ppm (m, 2H); ^{19}F NMR (94.1 MHz), ϕ 116.6 (mid point, AB, J_{AB}=209.5 Hz, $\Delta\nu$=1447.1 Hz); ^{13}C NMR (226.4 MHz) δ 7.39 (C_5), 21.8 (C_1), 115.7 ppm (CF_2, complex t, J_{CF}=285.8 Hz); ms gave M^+ 140.0239±0.0016 (11.8 ppm), calcd for $C_5H_4F_4$ 140.0249 dev=0.0013, (9.8 ppm).

31 mg (4.25%) of **20**: IR (gas), 3095, 1610, 1500, 1440, 1370, 1345, 1015, 915, 770, 730, 585, 470 cm^{-1}; ^1H NMR (60 MHz) δ 2.92 (t of t, J=12 Hz, J=3 Hz, 2H), 6.03 (d of t, J=4 Hz, J=2 Hz, 1H), 6.42 ppm (m, 1H); ^{19}F NMR (94.1 MHz) ϕ 113 (br. s, 2F), 118 (5, J=11.2 Hz, 2F); ^{13}C NMR (226.4 MHz) 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 gave M^+ 140.0246±0.0011 (8 ppm), calcd for $C_5H_4F_4$ 140.0249 dev=0.0002 (1.9 ppm).

24 mg (3.3%) of **21**:[10] IR (gas) 3055, 1600, 1500, 1225, 845 and 575 cm^{-1}; ^1H NMR (60 MHz) δ 3.15 (t of t, J_{HF}=11 Hz, J=3 Hz, 2H), 5.54 (m, 1H), 5.87 (m, 1H); ^{19}F NMR (94.1 MHz) ϕ 115.5 (br. s), 116.7 (t, J_{FH}=11 Hz).

85 mg (11.67%) of **22**: IR (gas) 1630, 1445, 1320, 890, 735, 480 and 415 cm^{-1}; ^1H NMR (60 MHz) δ 6.45 (t, J_{HF}=11 Hz, 1H), 1.92 ppm (br. s, 3H); ^{19}F NMR (94.1 MHz) ϕ 111.97 (m, 2F), 117.6 ppm (m, 2F); ^{13}C NMR (226.4 MHz) δ 9.6 (s, CH_3), 120 (complex t's, J_{CF}=290 Hz, CF_2's), 136 (m, C_2), 154 ppm (m, C_1).

73 mg (10.02%) of **23**: λmax 254 nm; IR (gas) 1715, 1230, 1300, 1100, 910, 810 and 575 cm^{-1}; ^1H NMR (60 MHz) δ 4.88 (d of m, J_{HF}=26 Hz, 1H), 1.8 ppm (quart. J=3 Hz, 3H); ^{19}F NMR (94.1 MHz) ϕ 84, 85.7, 91.5, 94.5 ppm (all complex octets, J_{F-F}=210 Hz, $^3J_{F-H}$=10 Hz, $^3J_{F-H}$=6 Hz, downfield F's d of sextet. J_{F-F}=210 Hz, J_{F-H}=10 Hz). The relative ratios of products were determined by an analytical gc run (FID detector), assuming that all isomers had equal sensitivity.

4-Methyl-6,6,7,7-tetrafluoro-2,3-diazabicyclo[3.2.0]hept-2-ene, **18**.

An ether soln of diazomethane (prepared from 9 g (0.0396 mole) N-ethyl-N-nitroso-p-toluenesulfonamide)[11] was added to 2.5 g (0.0198 mole) **17**, in an identical procedure to the synthesis of **14** to give, after 3 minutes at 5°C, 1.44 g (40%) of colorless liq: mp ~ 15°C; IR (neat) 2990, 1550, 1460, 1350, 1210, 1150, 910, 880, 780, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 1.45 (d, J=6 Hz, 3H), 2.8 (m, 1H), 5.28 (9, 1H), 5.8 ppm (br. d of t, J=8 Hz, 4Hz, 1H).

Thermolysis of **18**.

An identical procedure was employed as described for thermolysis of **14** but at 382°C. Starting with 0.97 g (0.0053 mole) of **18**, a total of 0.75 g (0.0048 mole, 91%) crude liq pyrolyzate was collected. The products were isolated by prep GC (20 ft. by 1/4 in. in 20% DNP at 55°C, 40 mL/min.) to give: 150 mg (19.6%) of **26**: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.1 (d of t, $J_{CH_3-H(gem)}$=6.15 Hz, $J_{CH_3-H(vic)}$=1.13 Hz, J_{CH_3-F}=1.15 Hz, 3H), 1.559-1.787 (q, J_{H-CH_3}=6.26 Hz, $J_{H-H(vic)}$=1.47 Hz, J_{H-F}=0.8 Hz, 1H), 2.28-2.36 ppm (d of t of d, $J_{H-F(cis)}$=11.8 Hz, $J_{H-H(vic)}$=1.5 Hz, $J_{H-F(trans)}$=3.75 Hz, 2H); ^{19}F NMR (282.3 MHz) ϕ 116.3 (midpoint, AB, J_{AB}=210.07 Hz, Δν=443.85 Hz, 4F, downfield F's virtual d J_{FH}=11.9 Hz, upfield F's br. s); ^{13}C NMR (226.4 MHz) δ 13.86 (s, CH_3), 15.49 (t, J_{C-F_2}=2.7 Hz, C_5), 29.5 (q of m, J_{C-F_2}=31.4 Hz, C_1, C_4), 115.17 ppm (t, J_{C-F_2}=274.9 Hz, C_2, C_3); ms gave M^+ $-CH_3$, 139.0173±0.0016 calcd for $C_5H_3F_4$ 139.0170 dev. 0.0002 (1.6 ppm).

35 mg (4.6%) of **27**: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.38 (d, $J_{CH_3-H(gem)}$=6.9 Hz, 3H), 1.76 (sextet of triplet, $J_{H-CH_3(gem)}$=6.9 Hz, $J_{H-H(vic)}$=7.0 Hz, $^4J_{H-F}$=2.3 Hz, 1H), 2.52 ppm (m, $^3J_{H-F}$=9.7 Hz, $^3J_{H-H}$=7.0 Hz, $^3J_{H-F}$=3.6 Hz, 2H); ^{19}F NMR (282.3 MHz) ϕ 111.54 (midpoint, AB, J_{AB}=216.1 Hz, Δν=4726.0 Hz); ^{13}C NMR (226.4 MHz) δ 11.49 (s, CH_3), 19.34 (t, $^3J_{C-F}$=3.8 Hz), 28.18 (d of d with fine splitting, $^2J_{C-F}$=32.5 Hz), 114.95 (t, $^1J_{C-F}$=264.2 Hz); ms gave M^+ $-CH_3$, 139.0160±0.0006 calcd for $C_5H_3F_4$ 139.0170, dev=0.0013 (-7.5 ppm).

5 mg (0.66%) of **28**: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.91 (t of m, $^5J_{CH_3-F}$=4.2 Hz, $^4J_{CH_3-H}$=1.48 Hz, $^4J_{CH_3-H_2}$=1 Hz), 2.84 (t of m, $^3J_{CH_2-F}$=11.6 Hz, $J_{CH_2-CH_3}$=1.2 Hz), 5.64 ppm (br. s with fine splitting J_{H-F}=1.8 Hz, $^4J_{H-CH_3}$=1.5 Hz); homonuclear proton decoupling of compd **28**: irrad of H_2 changes CH_3 to a simple triplet J-4.2 Hz; irrad of H_5 changes CH_3 to a simple triplet J=4.2 Hz and H_2 to a br. s with fine splitting J=1-1.5 Hz; irrad of CH_3 changes H_5 into triplet (J=11.6 Hz) of doublet (J=1.2 Hz); ^{19}F NMR (282.3 MHz) ϕ 110.22 (br. s with fine splitting, $^3J_{F-H(vinylic)}$=1 Hz); 116.32 ppm (t of m, $^3J_{F-H_2}$=11.6 Hz, $^4J_{F-H}$=1.3 Hz); ^{13}C NMR (226.4 MHz) δ 17.84 (s, CH_3), 43.17 (t, CH_2, $^2J_{CH_2-F_2}$=25.7 Hz), 120.22 (t, 26.0 Hz), 121.48 (t, $^2J_{C-F}$=252.6 Hz), 149.9 ppm (complex mult, quaternary C).

200 mg (26.9%) of **29**: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.18 (t, $^3J_{H-H}$=7.5 Hz, 3H), 2.31 complex m, $^3J_{H-H}$=7.5 Hz, 2H), 6.43 ppm (t of p, $^4J_{H-F}$=11.5 Hz, $^3J_{H-F}$=1.8 Hz, $^4J_{H-H}$=1.8 Hz, 1H); ^{19}F NMR (282.3 MHz) ϕ 111.68 (br. s with fine splitting), 116.09 ppm (d with fine splitting $^4J_{F-H}$=11.4 Hz); ^{13}C NMR (226.4 MHz) δ 9.85 (s, CH_3), 18.27 (s, CH_2), 134.01-135.08 (m, $^2J_{C-F}$=14.2 Hz, $^3J_{C-F}$=10.4 Hz), 160.47 ppm (t, J= not obvious, quaternary carbon, weak). The combined yield of isolated products was 70%. Order of elution was **29**, **26**, **27**, **28**, and (**30** + **31**). The identifications of **30** and **31** were based upon the similarity of their spectra, as a mixture, to those of **23** and **21** from the pyrolysis of **14**. The reported ratios of products were determined by analytical gc (FID) assuming identical sensitivities for each isomer.

7,7- and 6,6-Difluoro-2,3-diazabicyclo[3.2.0]hept-2-ene, **11** and **12**.

An ether soln of diazomethane (70 mL) was prepared from 7.14 g (0.0285 mole) N,N'-dimethyl-N,N'-dinitrosoterephthalamide which was mixed with 0.828 g (0.0111 mole) **16** for 20 h at RT following same technique as described for synth of **14** to give 0.335 g (0.00372 mole) 33.5% of oily faint yellow liq: IR (film) 2945, 1545 cm^{-1} (main peaks); ^1H NMR ($CDCl_3$, 60 MHz) δ 5.8 (m, 1H), 5.2 (m, 1H, **12**) 4.6 (br. s with fine splitting, 2H), 1.5-2.9 (m, 3H): ^{19}F NMR ($CDCl_3$, 282.3 MHz) ϕ 95.55 ppm (midpoint AB, **11**, J_{AB}=207.7 Hz, Δν=1055.5 Hz, upfield F's d of d of d of d J_{F-F}=207.7 Hz, J_{F-H}=20 Hz, J_{F-H}=10.5 Hz, J_{F-H}=4.5 Hz, downfield F's, d of d of d of d of d, J_{F-F}=207.7 Hz, J_{F-H}=19.0 Hz, J_{F-H}=10.0 Hz, J_{F-H}=3.4 Hz, J_{F-H}=1.79 Hz), 94.0 ppm (midpoint AB, **12**, J_{AB}=197.4 Hz, Δν=2486.5 Hz, upfield F's d of d of d of d, J_{F-F}=197.4 Hz, $^3J_{F-H}$=21.3 Hz, $^3J_{F-H}$=11.1 Hz, $^4J_{F-H}$=4.3 Hz, downfield F's d of m, J_{F-F}=197.4 Hz, J_{F-H}=18.8 Hz, 14.9 Hz, 7.3 Hz and 4.9 Hz).

Thermolysis of **11** and **12**.

A mixt of **11** and **12** (0.4 g, 0.00303 mole) was pyrolyzed following an identical technique as described for thermolysis of **14** over a period of 80 min at 350°C. A crude product mixture in the amount of 0.15 g was obtained of which a total of 99.2 mg (31.7%) of purified products were obtained. The prods were isol by prep GC (12 ft. by 1/4 in. in 20% OV-210 at 55-60°C, 40 mL/min.) to give: 17.0 mg (17.1%) of **38** and **39**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.93 (d of d of d, virtual d of 9, J=4.2 Hz, 1.5 Hz and 0.86 Hz, CH_3 of **38**, 2.75 (virtual triplet, J=8 Hz, CH_3 of **39**), 4.82-4.91 (set of multiplets), 4.95-5.12 ppm (multiplet); ^{19}F NMR (282.3 MHz) ϕ 83.63 (d of d, J_{F-F}=34.2 Hz, $^3J_{F-H(trans)}$=28.9 Hz), 86.26 (d of d, J_{F-F}=34.8 Hz, $^3J_{F-H(cis)}$=4.1 Hz, of **38**, 89.1 (d, J_{F-F}=46.0 Hz), 91.85 (d of d of t, J_{F-F}=46.0 Hz, J_{F-H}=24.8 Hz, J_{F-H}=1.8 Hz, of **39**).

27.6 mg (27.8%) of **36**: ^{1}H NMR ($CDCl_3$, 100 MHz) δ 5.28 ppm (complex multiplet); ^{19}F NMR (282.3 MHz) ϕ 96.473 ppm (t of t of t, $^3J_{F-H}$=9.7 Hz, $^4J_{F-H}$=2.7 Hz, $^4J_{F-H}$=0.6 Hz); ^{13}C NMR (226.4 MHz) δ 117.83 (t, $^1J_{C-F}$=234.5 Hz), 120.01 (t, $^3J_{C-F}$=9.16 Hz), 132.46 ppm (t, $^2J_{C-F}$=29.19 Hz).

15.9 mg (16.0%) of **35**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.21 (t of t, $^3J_{H-F}$=11.9 Hz, $^4J_{H-H}$=2.5 Hz, 4H), 5.10 ppm (P, $^4J_{H-F}$=2.5 Hz, 2H); ^{19}F NMR (282.3 MHz) ϕ 95.62 (P, $^3J_{F-H}$=11.9 Hz); ^{13}C NMR (226.4 MHz) δ 44.79 (t, $^2J_{C-F}$=24.8 Hz, C_2), 110.48 (t, $^4J_{C-F}$=6.4 Hz), 117.45 ppm (t, $^1J_{C-F}$=176.8 Hz) quarternary C not seen. The spectrum contained also 0.36 mg (0.363%) of **37** whose spectra were identical with the published data.[7]

5.6 mg (5.6%) of **32** and 8.4 mg (8.5%) of **33**: ^{1}H, ^{19}F and ^{13}C NMR spectra were exactly identical and consistent with the published data.[7]

24.4 mg (24.6%) of 1-fluorocyclopentadiene, **34**: ^{1}H NMR ($CDCl_3$, 60 MHz) δ 2.81 (d, $^3J_{H-F}$=6 Hz, 2H), 5.6 (br. s with fine splitting, 1H), 6.45 ppm (br. s, 2H); ^{19}F NMR (282.3 MHz) ϕ 127.94 (t of d of d of d, J_t=6.0 Hz, $J_{d's}$=4.6 Hz, 2.5 Hz and 0.2 Hz). (A minor peak at ϕ 124 was assigned for 2-fluorocyclopentadiene); ^{13}C NMR (226.4 MHz) δ 36.60 (d, $^2J_{C-F}$=8.9 Hz), 103.37 (d, $^3J_{C-F}$=9.5 Hz), 126.78 (d, $^2J_{C-F}$=28.1 Hz), 134.66 (d, $^4J_{C-F}$=6.5 Hz), 163.01 ppm (d, $^1J_{C-F}$=268.3 Hz). (Contains also 2 peaks assigned for the minor component: δ 37.15 (d, $^3J_{C-F}$=20.2 Hz), 121.45 ppm ($^3J_{C-F}$=8.2 Hz)). The combined yield of isolated product was 31.7%. Order of elution was **39**, **38**, **36**, **35**, **37**, **34**, **32** and finally **33**, and the gc ratios of products reflected the isolated ratios. No FID analytical gc was run on this system.

Thermolysis of **11** and **12** at 205°C.

Same procedure was followed as described for the thermolysis at 350°C and resulted in recovery of both **11** and **12**.

Thermolysis of **11** and **12** at 288.7°C.

Identical procedure was followed as described for the thermolysis at 350°C using 0.15 g (0.00113 mole) of **11** and **12** mixt at 288.7°C. A total of 85 mg of pyrolyzate was obtained as a crude mixture of which 65.2 mg (55.2%) of pure products was collected. The prods were isol by prep GC to give: 15.9 mg (24.4%) of **38** and **39**, 20.1 mg (30.9%) of **36**, 5.3 mg (8.1%) of **35** and **37**, 5.3 mg (8.2%) of **32**, 8.5 mg (13.0%) of **33**, 8.0 mg (12.2%) of **34**.

Acknowledgement. The authors acknowledge with thanks the support of this research in part by the National Science Foundation.

REFERENCES

1. Taken in part form the Ph.D. dissertation of D. M. Al-Fekri, University of Florida, 1985.
2. Communicated in part: Dolbier, W. R. Jr.; Al-Fekri, D. M. Tetrahedron Lett. **1983**, 24, 4047.
3. White, D. H.; Condit, P. B.; Bergman, R. G. J. Am. Chem. Soc. **1972**, 94, 1348.
4. Dolbier, W. R. Jr.; Al-Fekri, D. M. J. Am. Chem. Soc. **1983**, 105, 6349.
5. Dolbier, W. R. Jr.; Al-Fekri, D. M. J. Org. Chem. Submitted for publication.
6. Fuller, G.; Tatlow, J. C. J. Chem. Soc. **1961**, 3198.
7. Dolbier, W. R. Jr.; Sellers, S. F. J. Am. Chem. Soc. **1982**, 104, 2494.
8. (a) Halberstadt, M. L.; Chesick, J. P. J. Am. Chem. Soc. **1962**, 84, 2688; (b) Steel, C.; Zand, C.; Hurwitz, P.; Cohen. S. G. ibid. **1964**, 86, 679.
9. De Boer, TH. J.; Backer, H. J. Org. Syn. IV, **1943**, 250 and 943.
10. Taylor, D. R. Tetrahedron Lett. **1967**, 3277.
11. Fieser, L.; Fieser, M. Reagents for Organic Synthesis **1967**, 1, 191.