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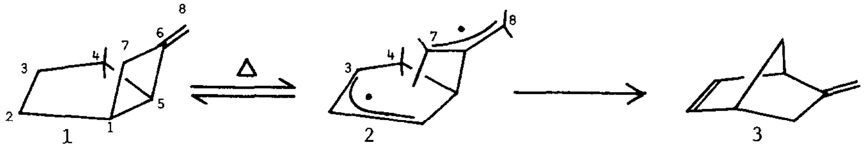
THE THERMAL ISOMERIZATION OF 6-DIFLUOROMETHYLENEBICYCLO[3.2.0]HEPT-2-ENE

William R. Dolbier, Jr., Carlos A. Piedrahita[1] and Basil H. Al-Sader[2]
Department of Chemistry, University of Florida
Gainesville, Florida 32611

Summary. The thermal isomerization of 6-difluoromethylenebicyclo[3.2.0]hept-2-ene procee via two competing 1,3-sigmatropic processes, with an E_a nearly identical to that of the hydrocarbon.

Sigmatropic isomerizations of the 6-methylenebicyclo[3.2.0]hept-2-ene system have been examined extensively by Hasselmann.[3,4,5] A relatively slow automerization process of 1 was

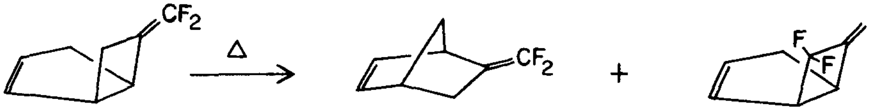


1 2 3

shown to compete with its isomerization to 3, both processes proceeding ostensibly via the bis-allyl diradical 2. Hasselmann moreover demonstrated that the 1,3-sigmatropic process, wherein C-7 migrated to C-3, was somewhat preferred over the 3,3-process. He attributed this result to the reluctance, due to steric repulsions, of the allyl radical to rotate through the methylene group at C-4. This argument was subsequently enhanced by his elegant study of the methylated 6-methylenebicyclo[3.2.0]hept-2-enes.[4]

We would like to report, at this time, results from our investigation of the thermal izomerization of 6-difluoromethylenebicyclo[3.2.0]hept-2-ene, 4, a rearrangement which takes place exclusively via two competing 1,3-sigmatropic processes.

4 was prepared in 29% yield from bicyclo[3.2.0]hept-2-ene-6-one[6] by the difluoro-Wittig process of Burton and Naae.[7] It showed a characteristic intense IR absorption at 1740cm^{-1}, and gave the following NMR spectra: ^{1}H(CCl_4) δ 5.72 (S,2H), 3.72-3.16 (m,2H), 3.10-2.72 (m,1H), 2.53 (d,2H) and 2.45-2.15 (m,1H); ^{19}F(CCl_4) δ-16.6(TFA,ext) (AB quartet, J_{AB} = 69Hz).[8]



4 5 6

84% 16%

The major observed product was 5-difluoromethylenebicyclo[2.2.1]hept-2-ene, 5,[9] which can be formed formally via a 1,3-sigmatropic shift of C-7 to C-3, while the minor product, 7,7-difluoro-6-methylenebicyclo[3.2.0]hept-2-ene, 6,[12] can be formed via the 1,3-sigmatropic shift of C-1 to C-8.

The products were formed under kinetic control as demonstrated by the consistency of the ratio of 5:6 through many half lives of the reaction. Wtih a strain energy of 30.6 kcal/mole for the bicyclo[3.2.0]heptane system versus 17.0 kcal/mole for the bicyclo[2.2.1]heptane system,[13] it can be seen why 5 is formed irreversibly from 4. The fact that 6 is also formed irreversibly can be understood in terms of the generally accepted, but not generally well-verified, thermodynamic affinity of fluorine substituents for sp^3 hybridized carbon.

The isomerization followed good first-order kinetics throughout, with rate constants given in Table I. Arrhenius plots of the rate data gave the activation parameters in Table II

Table I. Rate Constants for 4 → 5 + 6

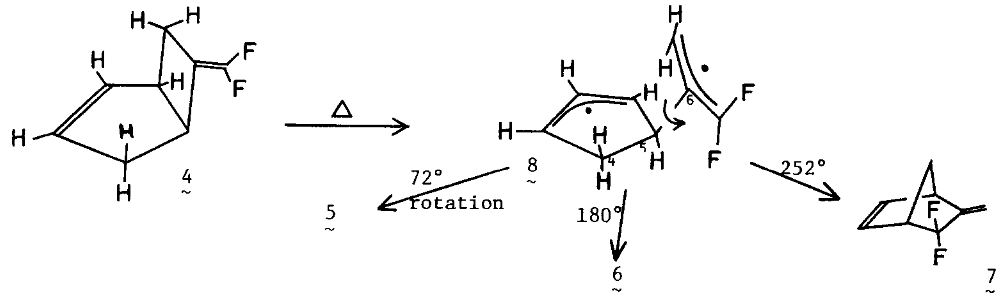
Temp. °C	208.0	213.8	219.6	235.8	239.3
$10^6\ k_5(S^{-1})$	23.7	39.0	63.7	232.	291.
$10^6\ k_6(S^{-1})$	4.08	7.00	11.3	46.7	61.2

Table II. Activation Parameters for 4 → 5 + 6

Rearrangement	LogA	Ea(kcal/mole)
4 → 5 + 6	13.6	39.9
4 → 5	13.2	39.3
4 → 6	13.9	42.4
1 → 3	13.8	39.9

Comparison of our kinetic results with those of Hasselmann[3] indicates that gem-difluoro substitution at the 8-position has not had appreciable effect on the activation parameters for isomerization of the 6-methylenebicyclo[3.2.0]hept-2-ene system. A reasonable corrollary conclusion can also be reached, that the allylic radical stabilization energy is not significantly affected by fluorine substitution. While O'Neal and Benson alluded to such a lack of effect of fluorine on radical stability in 1968,[14] this comprises, to our knowledge, the first corroborative experimental probe of this effect within the context of a pericyclic process.

The fact that *no* 3,3-sigmatropic component is observed in this isomerization, in spite of the fact that such a product, 6,6-difluoro-5-methylenebicyclo[2.2.1]hept-2-ene, 7, should be thermodynamically more stable than 4, 5 or 6, seems to be predicated by steric effects on conformational processes of the initially formed diradical 8. The *exclusivity* of 1,3-processes for conversion of 8, as compared to Hasselmann's less selective partitioning of 2, can be attributed to the significantly greater barrier for passage of the CF_2 end of the allyl radical in 8 through the CH_2 group at C-4 than for the comparable rotation of 2.



Rather, the rotation of the C-5, C-6 bond preferentially proceeds across the face of the cyclopentenyl radical, having the opportunity to form the major product, 5, after only a 72° rotation (requiring no passage through the C-4 CH_2 group) and being able to form the minor product 6 after a rotation of 180° requiring a passage of the allylic C-7 CH_2 group through the C-4 CH_2 group, a process which appears to have an incremental barrier of ~1.9 kcal/mole[3]). Formation of 7 would, precluding the passage of the allylic CF_2 group through the C-4 CH_2 group, require a rotation of 252°. Thus its absence can be readily understood.

The investigation of the rearrangement of **4** thus enhances our understanding of the effect of fluorine as a substituent on the energetics and ultimate outcome of thermal sigmatropic processes.

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References and Footnotes

1. Taken in part from the Ph.D. Dissertation of CAP, University of Florida, 1978.
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8. Exact mass of **4** - calcd for $C_8H_8F_2$: 142.0593, found: 142.0599.
9. Product **5** is identical in all ways to the previously reported product from the cycloaddition of 1,1-difluoroallene to cyclopentadiene.[10,11] It had the intense IR absorption characteristic of a $=CF_2$ group at 1775 cm^{-1}, and an ^{19}F NMR spectrum (CCl_4) at δ-15.5(ABquartet, J_{AB} = 71 Hz) and exact mass - calcd for $C_8H_8F_2$: 142.0593, found: 142.0585.
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12. Product **6** is characterized by its IR, mass and NMR spectra: ^1H NMR (CCl_4), δ 5.97-5.77 (m,1H), 5.74-5.55(m,1H), 5.53-5.36 (m,1H), 5.31-5.15 (m,1H), 3.93-3.61 (m,1H), 3.30-3.09 (m,1H) and 2.83-2.23 (m,2H); ^{19}F NMR, δ-19.7 (TFA,ext)(AB quartet, J_{AB} = 215 Hz); exact mass - calcd for $C_8H_8F_2$: 142.0593, found: 142.0585.
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