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THE THERMAL REARRANGEMENTS OF 1,1,2,2,4,4-HEXAFLUOROSPIROPENTANE AND PERFLUOROSPIROPENTANE

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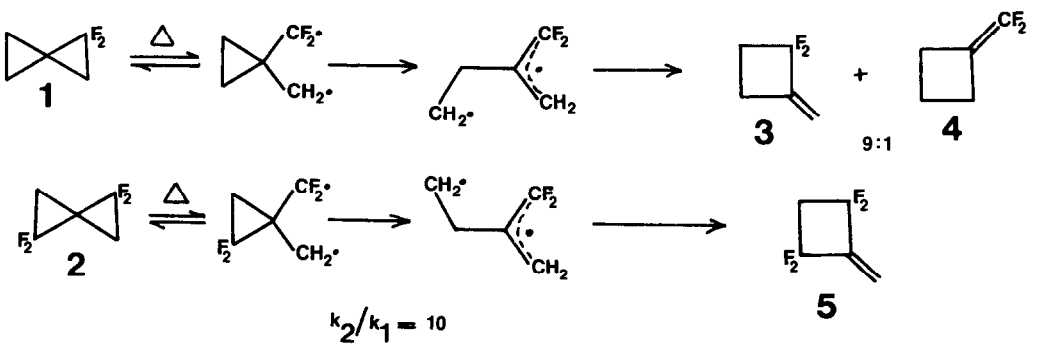
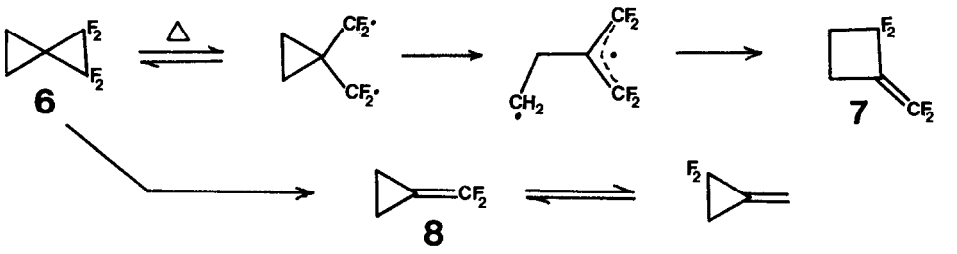
Summary: The title compounds were synthesized via CF_2: addition to the respective methylenecyclopropanes. The hexafluorospiropentane thermally rearranges to 2,2,4,4-tetrafluoro-1-(difluoromethyiene)cyclobutane in competition with CF_2: extrusion, whereas perfluorospiropentane decomposes exclusively by CF_2: extrusion.

Upon thermolysis, gem-difluorocyclopropanes decompose by two competitive pathways: bond homolysis, usually leading to rearrangement, and difluorocarbene extrusion.[1,2] In no group of compounds are the factors which determine the relative facility with which these two processes compete so well demonstrated as in the fluorinated spiropentanes.

From the exclusive rearrangement observed for 1,1-difluorospiropentane, 1,[3] and 1,1,4,4-tetrafluorospiropentane, 2,[4] it is apparent that extrusion does not compete with rearrangement when one or both of the cyclopropane units bears but two geminal fluorine substituents. However, since 1,1,2,2-tetrafluorospiropentane, 6,[4] decomposes principally by CF_2: extrusion, the addition of a second CF_2 group to one of the cyclopropane units apparently enhances the extrusion process substantially, relative to rearrangement.





Indeed, the activation parameters for these processes, when compared with those for CF_2: extrusions from 1,1-difluoro- and 1,1,2,2-tetrafluorocyclopropane,[2a] indicate that the second CF_2 group enhances extrusion by ~ 8 kcal/mole, whereas it enhances rearrangement by only ~ 6 kcal/mole.

It was also of interest to determine the effect of adding a third and fourth CF_2 group to the spiropentane system. We wish to report now the syntheses of these compounds and to discuss their behavior upon thermolysis.

1,1,2,2,4,4-Hexafluorospiropentane 9, prepared readily in 63% yield by the addition of CF_2: (from thermolysis of HFPO) to 2,2-difluoro-(difluoromethylene)cyclopropane,[5] was easily characterized by its ^1H and ^{19}F NMR spectra and its mass spectrum: δ2.32 (t of p, J = 6.8, 3.1 Hz), ϕ131.5 (t of p, J = 6.8, 7.2 Hz), ϕ144.9 (t of t, J = 7.2, 3.2 Hz); Exact mass: 176.00786 (dev. 10.2 ppm).

Perfluorospiropentane, 10, prepared similarly by the addition of CF_2: to perfluoromethylenecyclopropane,[6] was characterized by its ^{19}F NMR and mass spectrum: δ142.0 (singlet); Exact mass: 211.98745 (dev. 1.1 ppm).

Upon thermolysis in the gas phase, 9 underwent competitive rearrangement and CF_2: extrusion, comparable to the behavior of 6. Rate constants were obtained for six temperatures and are given in Table 1. Activation parameters for the two pathways are given in Table 3. Product 11 was characterized by its NMR, ir and mass spectrum: δ3.26 (t of p, J = 1.4, 8.0 Hz), ϕ69.63 (t of p, J = 1.4, 4.4), ϕ97.49 (t of t, J = 8.4); IR, 1775cm^{-1}; Exact mass: 176.00638 (dev. 1.8 ppm).

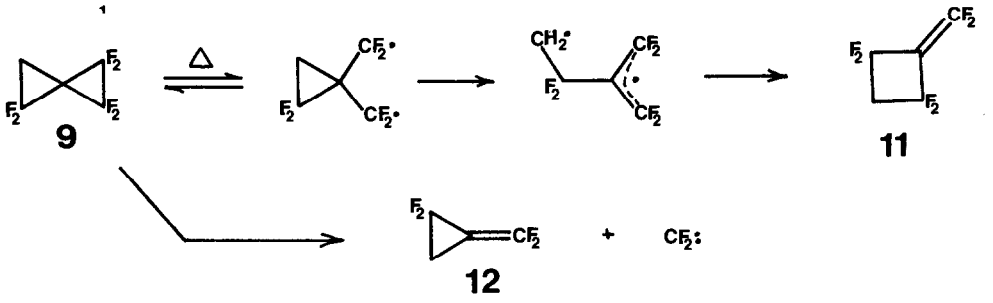


Table 1	1,1,2,2,4,4-Hexafluorospiropentane Rates: 9 → 11 + 12					
k x $10^5 sec^{-1}$	1.42	2.085	3.48	5.47	8.41	13.03
T	248.75	253.0	259.3	264.8	270.0	275.6
12/11	0.88	0.92	0.97	0.99	1.03	1.09

Just as the addition of geminal fluorines in the 4-position enhanced the rearrangement of 2 in comparison to 1 (k_2/k_1 = 9.4 at 320°), rearrangement of 9 is also enhanced relative to 6 (k_9/k_6 = 1.3 at 260°). These rate enhancements reflect the weakening of the C_3-C_5 bond in both 2 and 9 by the geminal fluorines at C_4. Interestingly, the extrusion process of 8 was somewhat slowed relative to that of 6 (k_9/k_6 = 0.92), with the net result that extrusion plays a smaller role in the decomposition of 9 than for 6 (k_{ext}/k_{rearr} = 1.03 for 9 vs 1.38 for 6 at 270°).

Unexpectedly, the thermolysis of perfluorospiropentane, 10, led only to CF_2: extrusion. No rearrangement product could be detected. Rate constants were obtained for six temperatures (see Table 2), with the activation parameters listed in Table 3.

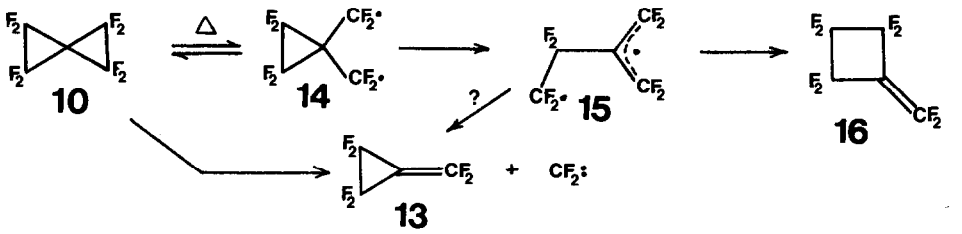
Table 2	Perfluorospiropentane Rates: 10 → 13					
k x $10^5 sec^{-1}$	3.41	5.05	6.89	14.3	19.7	33.9
T	246.4	249.8	254.5	262.75	267.4	274.0

Table 3 Activation Parameters for Fluorinated Spiropentane Thermolyses

Reaction	Log A	E_a	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$	Mean Temperatures
1 → 3 and 4	16.1	58.0	56.8	11.7	49.6	339.1°
2 → 5	14.75	51.7	50.5	5.6	47.2	322.0°
6 → 7	13.75	45.35	44.2	1.2	43.6	286.3°
6 → 8	14.95	47.4	46.3	6.7	42.5	286.3°
9 → 11	13.6	44.7	43.6	0.51	43.35	261.8°
9 → 12	15.35	49.0	48.0	8.6	43.4	261.8°
10 → 13	15.0	46.2	45.2	6.9	41.5	259.0°

Since the process of extrusion for 10 is not so much enhanced (k_{10}/k_9 = 6.3 at 260°) that it should swamp out the rearrangement, the question exists as to why rearrangement is not observed. Certainly the initial cleavage of 10 to diradical 14 is not expected to be

adversely affected by the additional CF_2 group. Either cleavage to 15 is slowed with a resultant increase in return to 10 and hence a greater fraction of extrusion, or the stabilized diradical 15 preferentially loses CF_2: to give 13 instead of closing to 16. At present, there is no evidence to distinguish between these possibilities. The thermal behavior of the would-be arrangement product, perfluoromethylenecyclobutane, 16, could shed some light on this question and its synthesis is currently in progress.



Thus with the investigations of 9 and 10, we have completed our systematic study of the effect of increasing gem-difluorosubstitution on the thermal chemistry of spiropentane. The results are completely consistent with our current understanding concerning the effect of fluorine substituents on the thermodynamic and kinetic stability of a cyclopropane ring.

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