Thermal [1,3] Sigmatropic Rearrangements of 2,2-Difluoro-1-vinylcyclopropanes

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Abstract: The thermal rearrangements of 2,2-difluoro-1-vinylcyclopropane, **1**, and *trans*- and *cis*-2,2-difluoro-1-(1-propenyl)cyclopropanes, **2** and **3**, give rise largely to formal [1,3] sigmatropic processes to form 3,3-difluoro-substituted cyclopentenes. Such results and kinetics for the rearrangements are consistent with preferential initial homolytic cleavage of the C_1–C_3 bond of each molecule.

In general, substitution of a hydrocarbon system with increasing numbers of fluorine substituents leads to increased stabilization of the carbon skeleton as reflected by the enhancement of such a systems's thermal stability. This incremental stabilization is reflected dramatically by the isodesmic eq 1 and 2.[1]

$$2CH_3CH_2F \rightarrow CH_3CHF_2 + CH_3CH_3 \qquad (1)$$
$$\Delta H = -13.1 \text{ kcal/mol}$$
$$3CH_3CHF_2 \rightarrow 2CH_3CF_3 + CH_3CH_3 \qquad (2)$$
$$\Delta H = -19.1 \text{ kcal/mol}$$

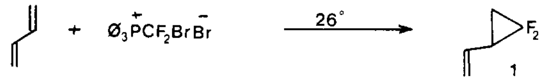
Such *stabilization* by fluorine substituents is contrasted by the effect of fluorine substituents on the kinetic stability of cyclopropane. O'Neal and Benson were the first to comment on the unusual kinetic effects of fluorine substitution on cyclopropane.[2] Fragmentary early studies supported the idea that fluorine substitution gives rise to an increase in strain and hence kinetic reactivity of cyclopropane systems.[3]

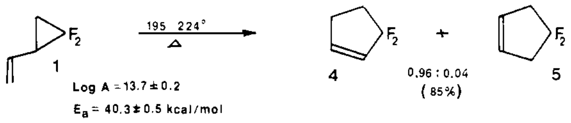
More recently much quantitative data on *gem*-difluorocyclopropane systems has become available which indicates clearly that the enhanced reactivity cannot be visualized simply as a strain effect. Geminal fluorine substitution specifically weakens that bond *opposite* to the CF_2 group by 8–10 kcal/mol,[4] while it has only a much less significant weakening effect upon the bond adjacent to it, weakening it by O–2 kcal/mol.[5]

The effect of geminal fluorine substitution on the thermal rearrangement of vinylcyclopropanes provides a prime example of this specific kinetic effect. We wish to report in this paper details of the thermal rearrangement of 2,2-difluoro-1-vinylcyclopropane, **1**, as well as the syntheses and thermal isomerizations of *trans*- and *cis*-2,2-difluoro-1-(1-propenyl)cyclopropanes, **2** and **3**. All three undergo formal [1,3] sigmatropic shifts as their major rearrangement pathway. The results reported in this paper for **1** derive in part from a reexamination of this system and constitute a *correction* of the recent original report.[6]

Results

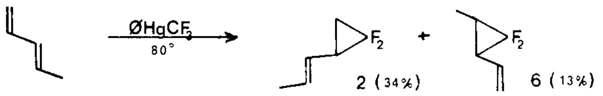
2,2-Difluoro-1-vinylcyclopropane, **1**, was prepared via Burton's method[7] of CF_2: addition to 1,3-butadiene. **1** was characterized unambiguously by its spectral properties, most notably its ^{1}H and ^{19}F NMR spectra (see Experimental Section). The thermal isomerization of **3** was carried out, in the gas phase, in a well-conditioned Pyrex vessel with the results shown below. Yields were determined by direct analysis of the gaseous product mixture by GLPC using an internal standard, while the efficacy of this analysis was verified by a low-temperature ^{19}F NMR analysis of the product mixture condensed directly into an NMR tube. In our original presentation of this work,[6] **5** was reported to be the *only* product, while in fact it is only a minor (4%) product.[8] Both the major product **4** and the minor product **5** were unambiguously characterized from their spectra.

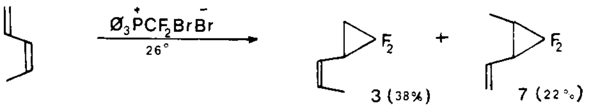




The rates of isomerization of **1** to **4** and **5** (with **4** and **5** not resolved) were measured for six temperatures (see Table I), and an Arrhenius plot of the rate data gave a good straight line, with the frequency factor and energy of activation being calculated by the method of least squares. Rate constants obtained by comparing product to starting material ratios were, within experimental error, the same as those obtained noting loss of starting material vs. an internal standard.

trans- and *cis*-2,2-difluoro-1-(1-propenyl)cyclopropanes, **2** and **3**, were readily prepared along with the isomers *trans*- and *cis*-2,2-difluoro-3-methyl-1-vinylcyclopropanes, **6** and **7** via CF_2: addition to *trans*- and *cis*-piperylene using Seyferth's[9] and Burton's[7] methods, respectively.





Adduct **7** undergoes predominant thermal [1,5] hydrogen shift while the *trans*-isomer **6** undergoes competitive [1,3] alkyl and [1,5] hydrogen shifts. These reactions have been described in detail elsewhere.[10]

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(1) The equations are derived from published heats of formation of the relevant components: Pedley, J. B.; Rylance, J. "Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds"; University of Sussex: United Kingdom 1977.

(2) O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1968**, *72*, 1866.

(3) (a) Jefford, C. W.; Mareda, J.; Gheret, J. C. E.; Karbengele, T.; Graham, W. D.; Gruger, U. *J. Am. Chem. Soc.* **1976**, *98*, 2585. (b) Sargeant, P. B. *Ibid.* **1969**, *91*, 3061.

(4) (a) Dolbier, W. R., Jr.; Enoch, H. O. *J. Am. Chem. Soc.* **1977**, *99*, 4532. (b) Dolbier, W. R., Jr. *Acc. Chem. Res.* **1981**, *14*, 195.

(5) (a) Dolbier, W. R., Jr.; Fielder, T. H., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 5577. (b) Dolbier, W. R., Jr.; Al-Sader, B. H.; Sellers, S. F.; Elsheimer, S. *Ibid*, **1981**; *103*, 715.

(6) Dolbier, W. R., Jr.; Al-Sader, B. H.; Sellers, S. F.; Koroniak, H. *J. Am. Chem. Soc.* **1981**, *103*, 2138.

(7) Burton, D. J.; Naae, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 8467.

(8) In the original examination of the system, the isolation of the product mixture for NMR analysis unfortunately involved condensation and storage on the vacuum line prior to sample preparation. It is now known that **4** as well as all allylic gem-difluoro systems is very prone to decomposition in a condensed state at temperatures >0 °C **4** apparently decomposed *after* yield determination but prior to NMR sample preparation. Also in the earlier study **5** was not GLPC resolved from **4**.

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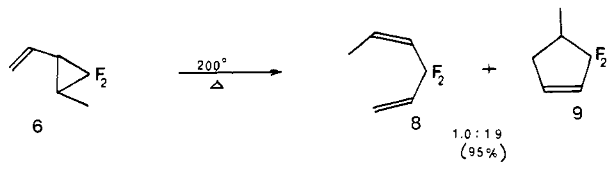
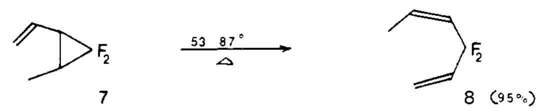
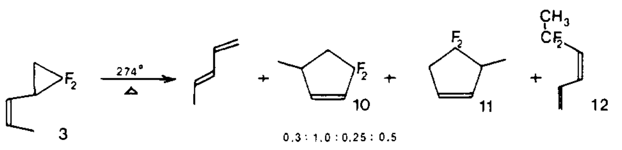
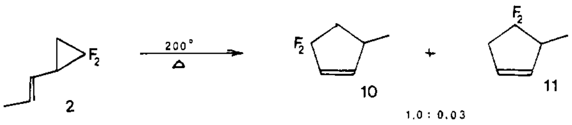




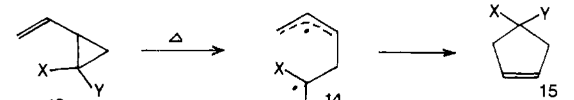
In contrast, the *trans*- and *cis*-2,2-difluoro-1-(1-propenyl)-cyclopropanes undergo thermal rearrangements largely via [1,3] sigmatropic processes, with the mass balances in each case being >90%. The products were unambiguously characterized by their spectral properties with the ^{13}C NMR spectra proving particularly definitive. The rates of rearrangement of **2** and **3** were found to be 3.2 × 10^{-5} s^{-1} and 2.50 × 10^{-5} at 200.65 and 273.65 °C, respectively. The ratio of products in each product mixture was unambiguously ascertained. GLPC analyses with internal standard provided yields which were verified by direct ^{19}F NMR analyses of the product mixtures as described.





Discussion

The vinylcyclopropane → cyclopentene thermal interconversion is a reaction which has been studied in great mechanistic detail, with a great accumulation of evidence in favor of a diradical mechanism.[11] In general, radical-stabilizing substituents in the 2-position lower the activation energy for the rearrangement and lead to the product **15**, which would derive from cleavage of the C_1–C_2 bond to form the diradical intermediate **14**.[12]



13 a X=Me Y=H
b X=Ph Y=H
c X=OMe Y=H
d X=Y=Cl

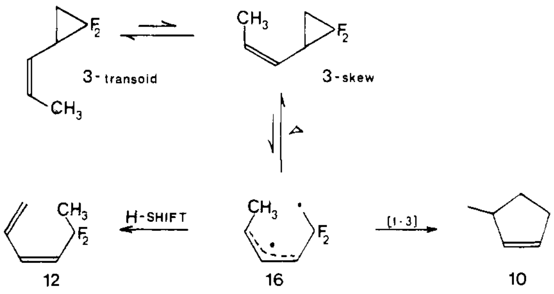
Flowers and Frey examined the kinetics of the thermal isomerization of the parent hydrocarbon (**13**, X = Y = H) and obtained the activation parameters[13] log A = 13.6 and E_a = 49.7 kcal/mol, while **13a,b,c** were found to have activation energies for rearrangement, via C_1–C_2 cleavage, of 48.6, 44.7, and 41.0 kcal/mol, respectively.[12] 2,2-Dichloro-1-vinylcyclopropane (**13d**) also rearranged regiospecifically and with a significant rate enhancement.[12d]

Remarkably unique then are the results of **1**, **2**, and **3** wherein highly regioselective cleavage of the C_1–C_3 bond occurs. These results are consistent, however, with the fact that fluorine substituents do not seem to provide stabilization to a carbon radical site, as well as with those earlier-mentioned results which indicate a selective incremental energy advantage to cleavage of the bond opposite to the CF_2 group.

The preexponential factor for the rearrangement of **1** was very similar to that for the parent hydrocarbon system while, as would be expected for a mechanism involving homolytic cleavage of the bond *opposite* to the CF_2 group, an incremental decrease in activation energy of 9.4 kcal/mol was observed for the rearrangement of **1**.

The products and rates of rearrangement of **2** and **3** are consistent with this mechanistic picture and may be compared with rearrangements of the similar hydrocarbon systems (2-methyl-1-propenyl)cyclopropane[14] and (*trans*-1-butenyl)cyclopropane.[15]

The rearrangement of *trans*-2,2-difluoro-1-(1-propenyl)cyclopropane, **2**, closely paralleled that of **1**, leading to a similar ratio of C_1–C_3 vs. C_1–C_2 cleavage. The *trans*-methyl group of **2** exerted almost no effect upont its *rate* of rearrangement with k_2/k_1 = 2.5 at 200.65 °C. On the other hand the *cis*-isomer rearranged much slower (k_2/k_3 = 343 at 273.65 °C). The diminished reactivity of **3** toward the [1,3] rearrangment can be understood in terms of the increased difficulty for **3** to attain the cisoid or skewed conformation required for the [1,3] shift process to be operative. An interesting H-shift product, **12**, is also observed in the thermolysis of **3**. It could logically arise either via diradical **16** or from a direct, concerted process of **3**.



Because of the >6 kcal/mol increase of E_a of **3** relative to **2**, even the difluorocarbene extrusion process, which leads to the observation of piperylene as a product, begins to be energetically competitive. Such extrusion processes are common place in *gem*-difluorocyclopropane pyrolyses[16] but had not been observed as being competitive with the rearrangements of **1** and **2**.

The observation of a minor but significant amount of product seemingly derived from C_1–C_2 cleavage is worth further discussion. Homolytic cleavage of this bond should not have been competitive with C_1–C_3 cleavage. Cleavage of analogous bonds adjacent to the CF_2 groups of 2,2-difluoro-1-methylenecyclopropane, **17**,[5a] and 1,1-difluorospiropentane, **18**,[5b] exhibited incremental lowerings of activation energy equal to 1 or 2 kcal/mol, while cleavage of the C_1C_2 bonds of **1**, **2**, and **3** *clearly* were enhanced more than this. With the noted amounts of products **5** and **11** being formed from **1** and **2** respectively, an approximate E_a lowering for C_1–C_2 cleavage of **1** and **2** would be *6.3 kcal/mol*,[17] as compared to the 9.4 kcal/mol for C_1–C_3 bond cleavage. This C_1–C_2 incremental lowering is very much larger than any other such enhancement of adjacent bond cleavage we have observed. Such a large enhancement seems inconsistent with a homolytic cleavage process being involved, and it may be possible that a pericyclic process

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(9) Seyferth, D.; Hopper, S. P. *J. Org. Chem.* **1972**, *37*, 4070.

(10) Dolbier, W. R., Jr.; Sellers, S. F. *J. Org. Chem.* **1982**, *47*, 1.

(11) (a) Willcott, R. M., III; Cargle, V. H. *J. Am. Chem. Soc.* **1967**, *89*, 723. (b) *Ibid.* **1969**, *91*, 4310. (c) Mazzocchi, P. H.; Tamburin, H. J. *Ibid.* **1970**, *92*, 7220. (d) Doering, W., von E.; Sachdev, K. *Ibid.* **1975**, *97*, 5512. (e) Andrews, G. D.; Baldwin, J. E. *Ibid.* **1976**, *98*, 6705.

(12) (a) Ellis, R. J.; Frey, H. M. *J. Chem. Soc.* **1964**, 5578. (b) Roth, W. R.; Konig, J. *J. Liebigs Ann. Chem.* **1965**, *688* 28. (c) Simpson, J. M.; Richey, H. G., Jr. *Tetrahedron Lett.* **1973**, 2545. (d) Ketley, A. D.; Berlin, A. J.; Gorman, E.; Fisher, L. P. *J. Org. Chem.* **1969**, *31*, 305.

(13) Flowers, F. C.; Frey, H. M. *J. Chem. Soc.* **1961**, 3547.

(14) Elliot, C. S.; Frey, H. M. *J. Chem. Soc.* **1965**, 345.

(15) Ellis, R. J.; Frey, H. M. *J. Chem. Soc.* **1964**, 4188.

(16) (a) Mitsch, R. A.; Neuvar, E. W. *J. Phys. Chem.* **1966**, *70*, 546. (b) Herbert, F. P.; Kerr, J. A.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1965**, 5710 (c) Atkinson, B.; McKeagan, D. *J. Chem. Soc., Chem. Commun.* **1966**, 189. (d) Quero, E. D.; Ferrero, J. C.; Staricco, E. H. *Int. J. Chem. Kinet.* **1977**, *9*, 339.

(17) This is calculated assuming identical preexponential factors for C_1–C_2 and C_1–C_3 bond cleavage. The kinetic data obtained for the rearrangements of **1** did not allow for discrimination of C_1–C_2 and C_1–C_3 components.

is indeed involved in the formation of **5** and **11**. Fluorines at the migrating carbon may indeed *enhance* the possibility of a [1,3] sigmatropic rearrangement.[18]

In any event, while the mechanism for formation of *minor* products **5** and **11** must still be considered in question, it is clear that the *major* products formed in the [1,3] sigmatropic rearrangement processes of **1**, **2**, and **3** are completely consistent with a diradical mechanism being involved.

Experimental Section

All GLPC separations were accomplished on a Varian Aerograph 90-P with helium as the carrier gas and fitted with one of the following columns: column *A*, 18 ft × $^1/_4$ in. 20% SE30 on Chrom P 60/80; column B, 10 ft × $^1/_4$ in. 10% DNP on Chrom P 60/,0; column C, 20 ft × $^1/_4$ in. 20% ODPN on Chrom P 60/80. All product ratios and kinetic data were obtained by GLPC using a Hewlett-Packard 5710A fitted with a flame ionization detector and a gas injection system and coupled to a Hewlett-Packard 3380 integrator. In this case a $^1/_8$ in. × 20 ft 5% ODPN column was used at 30 °C. All IR spectra, unless otherwise stated, were obtained as liquid films between KBr disks using a Perkin-Elmer 283B. NMR spectra were obtained in $CDCl_3$ at ambient temperature by using a Varian XL-100 instrument at 100.1 MHz for ^1H and 94.06 MHz for ^{19}F or a FX 90 instrument at 25.2 MHz for ^{13}C, proton decoupled. The internal standard for ^1H and ^{13}C was Me_4Si and for ^{19}F was $CFCl_3$. Mass spectra were obtained on an AEI-MS 30 instrument.

2,2-Difluoro-1-vinylcyclopropane, 1. A three-necked flask charged with 21.8 g of triphenylphosphine (0.083 mol) and 150 mL of triglyme (distilled from $LiAlH_4$) and fitted with a solid addition tube containing 19.3 g of KF (4 × 0.083 mol), a rubber septum, and a dry-ice-cooled condenser was attached to a Schlenk line and the system maintained in a dry, oxygen-free atmosphere of N_2. A 17.5-g sample of dibromodifluoromethane (0.083 mol) was added to the magnetically stirred solution using a cooled syringe. A white precipitate formed immediately and was stirred for 30 min prior to addition of 4.5 g (0.083 mol) of 1,3-butadiene by distillation of the diene from a bulb through a syringe needle into the system. Finally the KF was added and the mixture stirred for 24 h. All volatile materials were then flash distilled to a liquid N_2-cooled trap. The contents of this trap were then fractionally distilled at 760 mm. The fraction boiling at 20–50 °C was further purified by GLPC, column A, ambient, 65 mL/min, to give 4.75 g (55%) of **1**: IR (gas) 1640, 1475, 1367, 1295, 1226 cm^{-1}; NMR ($CDCl_3$) δ 5.0–5.8 (vinylic, complex m, 3 H), 2.0–2.6 (CH, complex m, 1 H), 0.9–2.0 (CH_2, complex m, 2 H); ϕ 135.0 (midpoint) (AB with further splitting, J_{AB} = 156.5 Hz, $\Delta\nu_{AB}$ = 1235.6 Hz, $J_{F\text{-}cis\text{-}H}$ = 12.5 Hz, $J_{F\text{-}trans\text{-}H}$ = 4 Hz); mass spectrum gave M^+ 104.043 17 ± 0.0022 (21.6 ppm), calcd for $C_5H_6F_2$ 104.043 76, dev 0.000 54 (5.6ppm).

Thermal Isomerizations and Kinetics—General Remarks. All thermal isomerizations are carried out in highly conditioned, spherical, Pyrex vessels of 100–200-mL capacity. These vessels are submerged in a stirred, thermostated, molten-salt bath (eutectic mixture, 50–50 by weight of $NaNO_2$ and KNO_3, mp ~150 °C). Temperature is measured via a Chromel–Alumel thermcouple in coordination with a Tinsley Type 3387 E potentiometer. The thermocouple is immersed in a well which is placed midway between the center of the two pyrolysis vessels. The temperature is controlled by using a Hallikainen (Now TOTCO) Instrument, Thermotrol proportional controller with a Model 1256 A platinum resistance probe. The temperature is constant to ±0.1 °C. Thermocouple-derived temperatures were calibrated with thermometers (Brooklyn Thermometer Co.). The thermocouple and thermometer temperatures were found to be close enough that any possible systematic error in the precision of T was found to contribute a smaller error than the standard deviations of the activation parameters. The vinylcyclopropanes were initiated into the pyrolysis vessels by expansion from a contiguous vacuum line. Initial pressures of kinetic runs varied between 2 and 20 mm of vinylcyclopropane plus any internal standards and/or inert gases. Where internal standards were utilized, mixtures of vinylcyclopropane and internal standard are mixed and *stirred* for many hours in a section of the vacuum line and checked by GLPC for homogenity before the mixture is allowed to expand into the pyrolysis vessel. Where nonisomeric products are formed (i.e., in CF_2: extrusion process) and where internal standards are used, GLPC sensitivities are first calibrated by using standard mixtures.

Each kinetic pyrolysis run is sampled 6–8 times by removing a small fraction of the pyrolysis mixture by expansion into a small section of the vacuum line into a vessel, diluting with Argon, and removing to make multiple GLPC injections via a gas sampling valve. A Hewlett-Packard 5710A gas chromatograph in conjunction with an HP-3380S Integrator is used for all analyses. Base-line resolution of peaks is observed under all GLPC quantitative analyses. Each point in a rate constant is an average of at least three GLPC runs. Each rate constant plot contains at least six points, while all reported rate constants and activation parameters are derived by a linear least-squares analysis of the experimental data, with each such analysis yielding a correlation coefficient of at least 0.999.

Table I. Rate of Thermal Isomerization of 2,2-Difluoro-1-vinylcyclopropane

T, °C	194.91	203.38	208.32	213.38	218.55	224.25
10^5k	0.751	1.62	2.46	4.01	6.24	9.45

The gas sampling technique utilized in all of the vinylcyclopropane kinetic runs introduced multiple pressure variations per run. The fact that good unimolecular behavior was nevertheless always observed for >5 half-lives indicates clearly the lack of significant surface effect problems. The kinetic apparatus, as well as the technique utilized in determining rate constants, is modeled after the apparatus and technique of Dr. H. M. Frey, University of Reading, England.

Thermal Isomerization of 2,2-Difluoro-1-vinylcyclopropane. **1** was pyrolyzed in the gas phase at 258 °C for 45 min, condensed into a liquid N_2-cooled trap, analyzed, and separated by GLPC, column B, ambient, 85 mL/min, to give a 3,3-difluorocyclopentene, **4**, as the major product (96% of product): IR (gas) ν_{max} 1069 cm^{-1}, also 959, 1167, 1370 cm^{-1}; NMR ($CDCl_3$, – 10 °C) δ 2.53 and 2.66 (overlapping complex m, 4H), 6.23 (vinyl, d of t, J = 5.8, 2.2 Hz, 1H), 6.75 (vinyl, d of t, J = 5.8, 2.3 Hz, 1 H); ϕ 83.85 (complex t of t, J = 14.3 and 7.9 Hz);^{13}C δ 142.0 (C_1, t, $^3J_{C-F}$ = 10.1 Hz), 134.1 (C_3, t, $^1J_{C-F}$ = 236.2 Hz), 127.2 (C_2, t, $^2J_{C-F}$ = 27.8 Hz), 33.1 (C_4, t, $^2J_{C-F}$ = 25.6 Hz), 29.2 (C_5, t, $^3J_{C-F}$ = 2.4 Hz); mass spectrum gave M^+ (base peak) 104.0432 ± 0.0004 (3.8 ppm), calcd for $C_5H_6F_2$: 104.0437, dev 0.0005 (4.9 ppm); other major peaks *m/e* 103, 85, 84, 83 77, 65, 57, 54, 53, 51, 40, 39.

The minor product (4% of product) was identified to be 3,3-difluorocyclopentene, **5**: IR (gas) 657, 896, 1056, 1150, 1250, 1336, 1428, and 1626 cm^{-1}; NMR ($CDCl_3$, ambient) δ 5.97 (vinyl, complex m, 2 H), δ 3.00 (CH_2, t with further splitting, J = 16 Hz, 4 H); ϕ 70.42 (t of p; J_t = 2.5 Hz, J_P = 16 Hz); mass spectrum gave M^+ 104.04303 ± 0.001 03 (9.9ppm), calcd M^+ 104.043 76, dev 0.0096 (7.0 ppm).

The kinetics for the thermal rearrangement of **1** were carried out as described above. The rates were determined on the basis of product to starting material ratio in all but one case where the rate was determined by the decrease of starting material relative to internal standard (pentane). The latter rate constant ($k_{212.4}$ = 3.54 × 10^{-5} s^{-1}) was consistent with those obtained by the former method. This run also allowed determination of the yield for the reaction which was >85%. The rates are given in Table I.

Addition of Difluorocarbene to *trans*-Piperylene. In a 50-mL Carius tube were placed 5.0 g of (trifluoromethyl)phenylmercury[9] (0.0142 mol), 6.4 g of sodium iodide (0.0142 × 3 mol), 25 mg of tetra-*n*-butylammonium iodide, and 25 mg of 18-crown-6 ether, from a drybox, all materials scrupulously dried. The Carius tube was then attached to a vacuum line and evacuated and 2.0 g of piperylene (Aldrich, mostly trans, 0.029 mol) transferred from calcium hydride into the tube. The tube was then sealed *in vacuo* and heated at 82 °C for 12 h in an oil bath. The tube was then cooled and opened, and all volatile materials were vacuum transferred and separated by GLPC column C, 50 °C, 50 mL min^{-1}, to give unreacted starting material plus two products. The major product was *trans*-2,2-difluoro-1-(1-propenyl)cyclopropane, **2**: 0.57 g (34.2%); IR (gas) 965, 1015, 1029, 1110, 1205 (s), 1272, 1320, 1477 (s), 2935 cm^{-1}; NMR δ 5.03–5.78 (vinyl, complex m, 2 H), 1.75–2.27 (allylic, complex m, 1 H), 1.70 (CH_3, d, J = 6.3 Hz, 3 H), 1.04–1.7 (cyclopropyl, complex m, 2 H); ϕ 135.39 (midpoint) (AB, J_{AB} = 155.2 Hz, $\Delta\nu_{AB}$ = 1259.9 Hz, downfield F is complex t, $J_{F\text{-}cis\text{-}H}$ = 12.5 Hz, upfield F is complex d of d, $J_{F\text{-}cis\text{-}H}$ = 13 Hz, $J_{F\text{-}trans\text{-}H}$ = 4.9 Hz); mass spectrum gave M^+ 118.0597 ± 0.0004 (3.2 ppm), calcd for $C_6H_8F_2$ 118.0594, dev 0.0003 (2.4 ppm); other major fragments *m/e* 103 (base), 97, 90, 83, 77, 67, 53, 51, 41, 39; bp 79.5–81 °C.

The minor product (0.22 g, 12.9%) proved to be *trans*-2,2-difluoro-3-methyl-1-vinylcyclopropane, 6: IR (film) 733, 842, 910, 964, 1000, 1038, 1149, 1203 (s), 1257 (s), 1420, 1480 (s), 1648, 2988 cm^{-1}. NMR δ 5.0–5.73 (vinyl, complex m, 3 H), 1.2–1.9 (CH, overlapping complex m, 2 H), 1.23 (CH_3, complex m, 3 H); ϕ 138.95 (midpoint), (AB, J_{AB} = 155.5 Hz, $\Delta\nu_{AB}$ = 305.05 Hz, downfield F is complex d; J = 14.0 Hz, upfield F is a complex d, J = 13.0 Hz); mass spectrum gave M^+ 118.0593 ± 0.000 48 (4.0 ppm), calcd for $C_6H_8F_2$ 118.0594, dev = –0.0001 (1.2 ppm); other major fragments *m/e* 103 (base), 97, 90, 83, 78, 77, 67, 64, 53, 51, 41, and 39; bp 78.5–79.5 °C.

Addition of Difluorocarbene to *cis*-Piperylene. Difluorocarbene was added to *cis*-piperylene (Tridon-Fluka) in the manner of Burton et al.[7]

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(18) Carpenter, B. K., private communication.

as described above to give the products separated by GLPC, column C, ambient, 150 mL min^{-1}.

The major product (37% yield) proved to be *cis*-2,2-difluoro-1-(1-propenyl)cyclopropane, **3**: IR 740, 937, 1013, 1098, 1225 (s), 1300, 1370, 1470 (s), 1670 (w), 3050 cm^{-1}; NMR δ 5.5–6.1 and 4.65–5.5 (vinyl, complex m, 1 H each), 2.0–2.8 (allylic, complex m, 1 H), 1.7 (CH_3, d, $J = 6$ Hz, 3 H), 1.6–2.2 and 0.75–1.6 (cyclopropyl CH_2, complex m, 1 H each), ϕ 135.06 (midpoint) (AB, $J_{AB} = 155$ Hz, $\Delta\nu_{AB} =$ 1237.3 Hz, downfield F is a complex t, $J = 13.5$ Hz to each cis-H, upfield F is a d of d of d, $J_{F\text{–cis-H}}$ 13.5 Hz, other $J = 2, 5$ Hz); mass spectrum gave M^+ 118.060 27 ± 0.0022 (18.7 ppm), calcd for $C_6H_8F_2$ 118.0594, dev 0.000 86 (7.3 ppm); other major fragments *m/e* 103 (base), 97, 83, 78, 77, 67, 53, 51, 41, 39; bp 71.5–73 °C.

The minor product (21.9%) was *cis*-2,2-difluoro-3-methyl-1-vinylcyclopropane, **7**: IR 937, 1100, 1130, 1205, 1280 (s), 1477 (s), 1642, 3000 cm^{-1}; NMR (0 °C) δ 5.14–5.59 (vinyl, complex m, 3 H), 2.0–2.4 and 1.59–2.0 (CH, complex multiplets, 1 H each), 1.12 (CH_3, complex m, 3 H); ϕ 138.46 (midpoint) (AB, $J_{AB} = 154.55$ Hz, $\Delta\nu_{AB} = 2463.71$ Hz, downfield F, complex t, $J_{F\text{–cis-H}} = 14$ Hz, upfield F is a br s); mass spectrum gave M^+ 118.0595 ± (4.9 ppm), calcd for $C_6H_8F_2$ 118.0594, dev 0.000 08 (0.7 ppm); other major fragments *m/e* 103 (base), 97, 90, 83, 77, 67, 64, 53, 51, 41, 39

Pyrolysis of *trans*-2,2-Difluoro-1-(1-propenyl)cyclopropane, 2. **2** was pyrolyzed kinetically at 200.65 °C and for preparative purposes at 275 °C for 1 h. The products were separated by GLPC, preparatively on column C at 50 °C to give two products.

The major product (~97% of product) proved to be 3,3-difluoro-5-methylcyclopentene, **10**: IR (gas) ν_{max} 1370 cm^{-1}, also 1627, 1163, 983 cm^{-1}; NMR ($CDCl_3$, 0 °C) δ 6.23 (vinyl, d of d, $J = 5.8, 1.5$ Hz, 1), 5.81 (vinyl, d of d, $J = 5.7, 2$ Hz, 1), 2.96 (CH, complex m, 1), 2.83–2.7 (CH_2, complex m, 1), 1.59–2.08 (CH_2, complex d of d, $J = 14.2$ Hz, 1), 1.35 (CH_3, d, $J = 7$ Hz, 3); ϕ 83.72 (midpoint) (AB, $J_{AB} = 250.82$ Hz, $\Delta\nu_{AB} = 331.6$ Hz, downfield F is a d of t, $J_{F\text{–cis-H}} = 17.1$ Hz, $J_{F\text{–trans-H}} \simeq J_{F\text{–vinyl}} = 5$ Hz, upfield F is a (C_5, of d of d, $J_{F\text{–cis-H}} = 19.5$ hZ, $J_{F\text{–trans-H}} = 13.8$ Hz, $J_{F\text{–vinyl}} = 4.5$ Hz); δ 147.6 (C_1, t, ${}^3J_{C-F} = 10.1$ Hz), 126.2 (C_2, d of d, ${}^2J_{C-F} = 27.2, 28.4,$ Hz), 133.6 (C_3, t, ${}^1J_{C-F} = 240.5$ Hz), 41.8 (C_4, d of d, ${}^2J_{C-F} = 22.9, 25.3$ Hz), 36.9 (C_5, t, ${}^3J_{C-F} = 2.5$ Hz) 20.4 (C_6, d of d, ${}^4J_{C-F} = 1.5, 5.1$ Hz), mass spectrum gave 118.0595 ± 0.0002 (2.3 ppm), calcd for $C_6H_8F_2$ 118.0594, dev +0.0001 (1.0 ppm).

The minor product (~3% of the product mixture) was 4,4-difluoro-3-methylcyclopentene, **11**: IR (gas) ν_{max} 1160 cm^1; NMR ($CDCl_3$, 0 °C) δ 5.66 (vinyl, complex m, 2), 3.0 (CH, bm, 1), 2.81 (CH_2, t, $J_{H-F} = 15$ Hz, 2), 1.06 (CH_3, d of d, $J = 2.5, 7.3$ Hz); ϕ 101.19 (midpoint), (AB, $J_{AB} = 223.8$ Hz, $\Delta\nu_{AB} = 1159.6$ Hz, downfield F is a d of t of t, $J = 17, 15, 2.4$ Hz, upfield F is a d of t of t, $J = 3.5, 15, 2.4$ Hz); ^{13}C NMR δ 134.0 (C_2, d of d, ${}^3J_{C-F} = 2.75, 5.2$ Hz), 125.5 (C_1, t, ${}^3J_{C-F} = 4.88$ Hz), 41.31 (C_5, t, ${}^2J_{C-F_3} = 27.8$ Hz), 46.44 (C_3, d of d, ${}^2J_{C-F} = 24.1$ and 27.1 Hz), 12.78 (C_6, d of d, $J_{C-F} = 2.75, 10.3$ Hz); mass spectrum gave M^+ 118.0593 ± 0.0008 (7.2 ppm), calcd for $C_6H_8F_2$ 118.0594, dev −0.0001 (0.8 ppm).

The rate (at 200.65 °C) was obtained from the ratio of total products with respect to starting material vs. time. The relative ratio of products did not vary over 5 half-lives. This coupled with the observation of good first-order kinetics over this period indicated that the products were stable under the conditions of the gas-phase pyrolyses. Moreover, to ensure that all products were accounted for, a direct NMR analysis of the product mixture which was condensed directly from pyrolysis vessel into NMR tube indicated that the ratio of products determined thusly was consistent with the GLPC ratio. The mass balance, as determined by this NMR experiment, also was excellent (~95%).

Pyrolysis of *cis*-2,2-Difluoro-1-(1-propenyl)cyclopropane, 3. **3** was pyrolyzed kinetically at 273.65 °C and preparatively at 293.5 °C for 220 min. GLPC separation, preparatively on column C at 30 °C, led to the isolation of four products. *cis*-Piperylene (15%) was identified by comparison of its IR (gas) spectrum with that of an authentic sample. **10** (49%) and **11** (12%) were also identified by comparison of their spectra to those reported above. *cis*-5,5-Difluoro-1,3-hexadiene, **12** (24%), identified as the final product: NMR ($CDCl_3$, 0 °C) δ 5.28–6.23 (vinylic, complex m, 5 H), 1.75 (CH_3, t, $J = 18.3$ Hz, 3), ϕ 83.7 (complex p, $J_{F\text{-Me}} \simeq J_{F\text{–vinyl H}} = 17$ Hz); mass spectrum gave M^+ 188 (56% of base peak $(M - CH_3)^+$.

The rate at 273.65 °C was measured as described above, and the integrity of the product mixture was verified by NMR as above, with the mass balance again being high (~93%).

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Registry No. 1, 694-34-8; **2**, 79517-52-5; **3**, 79517-51-4; **4**, 80997-33-7; **5**, 77613-68-4; **6**, 79517-50-3; **7**, 79517-49-0; **10**, 80997-34-8; **11**, 80997-35-9; **12**, 80997-36-0; 1,3-butadiene, 106-99-0; (*E*)-piperylene, 2004-70-8; (*Z*)-piperylene, 1574-41-0; (trifluoromethyl)phenylmercury, 24925-18-6; $Ph_3PCF_2Br{\cdot}Br$, 58201-66-4.

Intramolecular Oxidative Cyclization Reactions of Trivalent Phosphorus and Carbonyl Functions

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Abstract: Phosphonous diesters derived from the reaction of phenylphosphonous dichloride with 2-ketophenols readily undergo head-to-tail intramolecular cyclization in cases where the carbonyl function is an aldehyde, trifluoromethylacetophenone, or diaryl ketone. A methylimine function may also participate in such a reaction. Analogous intermolecular reactions proceed either sluggishly or not at all, indicating the important role of steric and entropy effects. The cyclization yields stable tricyclic phosphoranes; the pentavalent nature of the products was established using NMR techniques. Oxidative cyclization does not occur where the carbonyl group in the phosphonous diester is an ester or a sterically hindered diaryl ketone. A novel solvent and temperature-dependent equilibrium between the trivalent and pentavalent forms of the product derived from phenylphosphonous dichloride and 2-hydroxy-2′,4,4′-trimethoxybenzophenone is reported.

We have previously reported the synthesis of polycyclic phosphoranes by the reactions of salicylaldehyde and 2-hydroxybenzophenone with phenylphosphonous dichloride in the presence of an amine base.[1] Cragg and co-workers have also reported the formation of a tricyclic phosphorane from the base-catalyzed reaction of 2-hydroxyacetophenone and phenylphosphonous dichloride.[2] The structure of the polycyclic phosphoranes is well established in all these cases as a head-to-tail cyclization of a phosphonous diester, **1**. No experimental evidence for the intermediacy of **1** has been reported in any of these cases. Surprisingly, Gopinathan and co-workers[3] have reported that the

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(1) Harper, S. D.; Arduengo, A. J. *Tetrahedron Lett.* **1980**, 4331–4334.

(2) Cragg, G. M. L.; Davidowitz, B.; Fazakerley, G. V.; Nassimbeni, L. R.; Haines, R. J. *J. Chem. Soc., Chem. Commun.* **1978**, 510–511.

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