intermediate which is formed allows rearrangement of the allyl group. Apparently, the predominance of the *trans*-crotyl isomer is a result of preferential formation and collapse of certain σ-crotyl isomers.[19]

These systems are among the few chiral organometallic compounds for which the absolute configuration at the metal has been determined.[20-23] Since these complexes are quite stable to racemization, they provide a ready route to asymmetric synthesis by using previously developed chemistry.[24,1] Stereospecificity in replacement of the X group in the (NMCp)Mo(η^3-C_3H_5)(NO)(X) systems appears to be general. The specific rotations of the iodide complexes recovered from the cycles shown in eq 3 were identical within experimental error to that of the starting iodide.

$$(+)\text{-}[(\text{NMCp})\text{Mo}(\eta^3\text{-}C_3H_5)(\text{NO})(O_3SC_6H_5)] \underset{C_6H_5SO_3Ag}{\overset{\text{NaI}}{\rightleftharpoons}} (-)\text{-}[(\text{NMCp})\text{Mo}(\eta^3\text{-}C_3H_5)(\text{NO})(\text{I})] \underset{\text{NaI}}{\overset{AgPF_6/CH_3CN}{\rightleftharpoons}} (-)\text{-}[(\text{NMCp})\text{Mo}(\eta^3\text{-}C_3H_5)(\text{NO})(CH_3CN)]PF_6 \quad (3)$$

Acknowledgments. We thank Professor Richard D. Adams for helpful discussions. This research was supported by a grant from the National Science Foundation (CHE79-11201).

Supplementary Material Available: A listing of structure factor tables (34 pages). Ordering information is given on any current masthead page.

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[24] On sabbatical leave from Tel-Aviv University.

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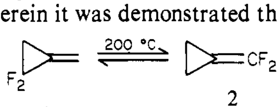
Synthesis and Thermal Isomerization of 2,2,3,3-Tetrafluoromethylenecyclopropane

Sir:

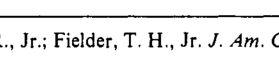
In an earlier communication, we reported a kinetic and thermodynamic investigation of the difluoromethylenecyclopropane system **1** ⇌ **2**, wherein it was demonstrated that the *gem*-difluoro



1 2
log A = 13.2 E_a = 38.3 ± 0.4 kcal/mol

substituents of **1** modestly enhance its rate of rearrangement relative to the parent hydrocarbon.[1] Furthermore, the equilibrium thermodynamics ($\Delta H^\circ = -1.9$ kcal/mol) indicated that cyclopropyl *gem*-difluoro substituents are more destabilizing than vinylic *gem*-difluoro substituents on a methylenecyclopropane.

We now report the synthesis of the two tetrafluoromethylenecyclopropane isomers **3** and **4** and the remarkable effect of the second pair of fluorine substituents on their thermal interconversion.



3 4

Scheme I

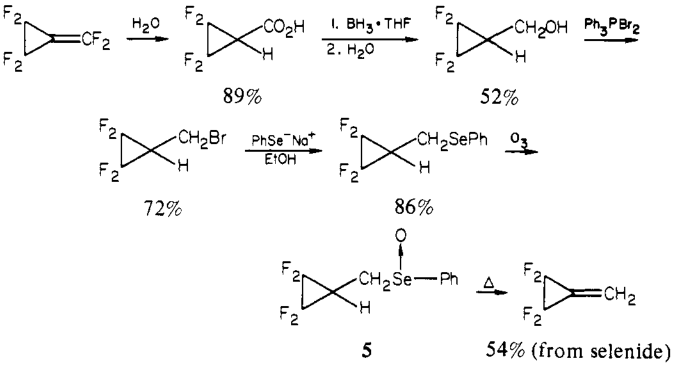
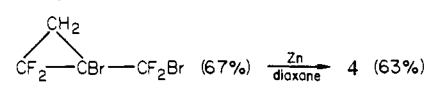


Table I. Rate Constants for 3 → 4

temp, °C	150.50	151.75	153.33	155.25	156.75	159.25
10^5k, s^{-1}	234	254	284	350	383	469

1-(Difluoromethylene)-2,2-difluorocyclopropane (**4**) was synthesized relatively easily from 2,3-dibromo-3,3-difluoropropene[2] by the two-step sequence shown below.[3] Unfortunately, **4** did not isomerize to **3** when heated to temperatures as high as 350 °C. At temperatures above 360 °C, **4** extruded :CF_2 to form 1,1-difluoroallene. It is concluded from these results that **3** must be *significantly* more destabilized than we had anticipated.



A direct synthesis of 2,2,3,3-tetrafluoromethylenecyclopropane, therefore, was required. After several unsuccessful approaches, **3** was prepared from perfluoromethylenecyclopropane[4] (Scheme I).[5,6]

It was found that **3** rearranged to **4** cleanly, with good first-order kinetics in the gas phase at 150 °C. Rates were obtained at six temperatures,[8] and an Arrhenius plot of these data gave a good straight line with the frequency factor and energy of activation being calculated by the least-squares method: log $A = 12.6 \pm 0.5$, $E_a = 29.6 \pm 1$ kcal/mol.

The relative rate of rearrangement of **3** vs. **1** at 150 °C is calculated to be 7850—a remarkable indication of the *nonadditivity* of the two CF_2 group effects on the stability of the methylenecyclopropane system. (At 150 °C, the relative rate of rearrangement of **1** vs. methylenecyclopropane itself is calculated to be only 4.4.) The seemingly small effect, if any, of fluorine substituents on radical stability[9-11] suggests that this is truly a

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[1] Dolbier, W. R., Jr.; Fielder, T. H., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 5577.

[2] Blomquist, A. T.; Longone, D. T. *J. Am. Chem. Soc.* **1957**, *79*, 4981.

[3] Satisfactory analytical data were obtained for all new compounds. The structure of **4** was unambiguously established by its physical and spectral properties: bp 18–19 °C; IR (gas) 1810 cm^{-1} (C=CF_2); NMR (neat) δ 1.72 (t of t, J = 6.5, 1.8 Hz); ϕ 71.5 (d of p, 1, J = 32.5, 6.5 Hz), 85.3 (d of p, 1, J = 32.5, 6.5 Hz), 131.3 (complex m, 2).

[4] (a) Smart, B. E. *J. Am. Chem. Soc.* **1974**, *96*, 927. (b) Smart, B. E. U.S. Patent 3 816 553, 1974.

[5] Spectral properties of **3**: IR (gas) 1740 cm^{-1} (C=CH_2); NMR ($CDCl_3$) δ 6.5 (s); ϕ 141.33 (complex m). Mass spectroscopy gave (M^+) 126.00951 [standard deviation = 0.00078 (6.2 ppm)]. Calculated (M^+) 126.00926 [deviation = 0.00025 (2.0 ppm)].

[6] Although most alkyl selenoxides eliminate under very mild conditions and generally cannot be isolated, selenoxide **5** was isolated as a white crystalline compound, and it needed to be heated to temperatures >100 °C before elimination was observed.[7]

[7] Cyclopropyl selenoxides recently have been used to synthesize alkylidenecyclopropanes, with a similar high temperature being required for their elimination: Halazy, S.; Krief, A. *Tetrahedron Lett.* **1979**, 4233.

[8] The relatively small range of temperatures used in this study was dictated by the melting point of the eutectic mixture used in our salt-bath thermostat (150 °C).

[9] O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1968**, *72*, 1866.

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ground-state effect and does not reflect the relative stabilities of the intermediate fluorinated trimethylenemethane diradicals. In fact, it appears that as the number of fluorine substituents on an allyl radical increases, its delocalization energy decreases.[12,13]

If one makes the reasonable assumption that the cyclopropane ring strains of **1** and **4** should be approximately the same, then their rates of fragmentation should be about the same, and an equilibrium constant for **3** $\rightleftharpoons$ **4** ($K = 7850$) and a $\Delta G° \approx -7.5$ kcal/mol can be estimated. This compares with the $\Delta G° = -1.7$ kcal/mol for **1** $\rightleftharpoons$ **2**. The experimental $\Delta G^{\ddagger}$ values for **3** and **1** are 30.3 and 37.7 kcal/mol, respectively. These numbers reflect a tremendous "extra" destabilization by the second CF_2 group of **3**. This perhaps should not be totally surprising since cyclopropanes are generally considered to have significant "olefinic" character, and it is well-known that adding a second pair of fluorines to vinylidene fluoride to create tetrafluoroethylene also gives rise to further substantial, nonadditive destabilization of the olefinic system.[14-16] (Vinylidene fluoride and tetrafluoroethylene are estimated to be more strained than ethylene by 4 and 16 kcal/mol, respectively.) Indeed, the disparate equilibria for the two systems perhaps can be best understood by viewing **3** as a tetrafluoroethylene-type species that, consequently, is significantly more destabilized than **1**, **2**, or **4**.

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(17) On sabbatical leave from the University of Baghdad, Baghdad, Iraq.

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Detection of Trialkylstannyl Radicals Using Laser Flash Photolysis

Sir:

The reactions of organotin compounds in photochemical and free-radical processes have received considerable attention.[1] Trialkylstannanes are widely used as reducing agents, reflecting the high reactivity of the tin–hydrogen bond toward free radicals and excited states.[2] Stannyl radicals are very reactive in halogen abstraction reactions[3] and have found wide application in ESR spectroscopy where they are frequently used to generate radicals from organic halides.[4] Trialkyltin radicals can be generated by a variety of methods, including hydrogen abstraction from the stannane,[2] attack of alkoxy radicals on hexalkylditin compounds,[4-6] and direct photolysis of the organotin substrates.[7] Despite the studies and applications mentioned above, few absolute rate constants involving the formation or reactions of tin radicals are known;[6] in addition, their ESR detection, while possible, remains difficult.[6-8] This communication reports preliminary results of a study of the formation and decay of tri-*n*-butylstannyl radicals by using laser flash photolysis.

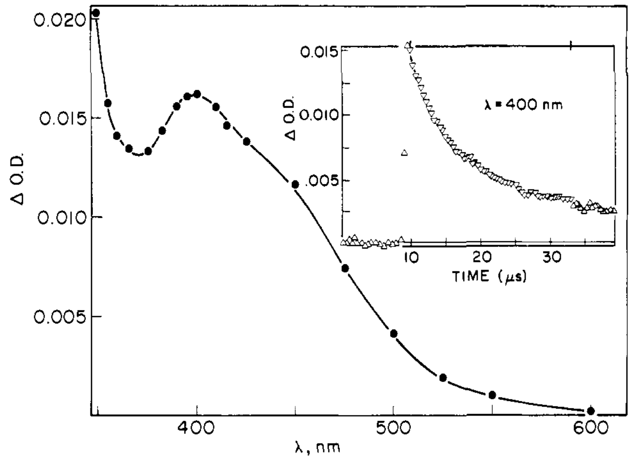

Figure 1. Transient spectrum obtained upon excitation of a 0.08 M solution of Bu_3SnH in di-*tert*-butyl peroxide. (Insert) Decay trace and second-order fit. The markers at the top indicate the region of the trace used to calculate the kinetics.

The experiments were carried out by monitoring the transient absorptions produced when the samples were excited with the pulses (337.1 nm, ~8 ns, ~10 mJ) from a nitrogen laser. For example, when a 0.08 M solution of Bu_3SnH in di-*tert*-butyl peroxide is irradiated, it leads to the formation of a transient species which exhibits the spectrum of Figure 1 and decays with second-order kinetics as illustrated in the insert in the same figure. Under these conditions, the laser pulses are absorbed almost exclusively (over 95%) by the peroxide which undergoes a fast and efficient decomposition to yield *tert*-butoxy radicals.[11] We propose that the transient spectrum shown in Figure 1 is due to the free radical $Bu_3Sn\cdot$ generated in reaction 2 which decays by recombination according to reaction 3.

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2\text{-}t\text{-BuO}\cdot \qquad (1)$$

$$t\text{-BuO}\cdot + Bu_3SnH \rightarrow Bu_3Sn\cdot + t\text{-BuOH} \qquad (2)$$

$$2Bu_3Sn\cdot \rightarrow Bu_6Sn_2 \qquad (3)$$

While it is rather surprising that $Bu_3Sn\cdot$ would absorb in this region, our assignment is also supported by the detection of the same species in the photolysis of azobis(isobutyronitrile) (AIBN) in the presence of Bu_3SnH. In this case, the spectrum was considerably weaker, reflecting the lower reactivity of carbon radical centers (compared with *tert*-butoxy) and, perhaps, a lower quantum yield of AIBN photodecomposition.

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(8) Lehnig, M. *Tetrahedron Lett.* **1977**, 3663–3667.

(9) The system is similar to that used before,[10] except that it employs a more powerful laser and it has been interphased to a PDP11/03-dedicated instrument.

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