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Rate of Cyclization of Perfluoro-4-Oxa-5-hexenyl Radical. Use of Tributylgermanium Hydride as an Effective H-Transfer Agent for Perfluoro-*n*-alkenyl Radicals†

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In carrying out competition experiments which are designed to provide absolute rate constants for very fast radical processes, one wishes to generate the radical in question in an environment where it can undergo two (or more) competitive processes, one of known rate, with the other(s) to be assessed by simple determination of product ratios as a function of substrate concentrations.

Such quantitative competition studies of radical reactions usually involve chain processes where there is competition between a hydrogen transfer reaction and some addition process, either bimolecular or intramolecular (cyclization). As such, it is necessary to have available a selection of chain-carrying hydrogen transfer agents with a wide range of reactivities. For studies of perfluoro-*n*-alkyl radicals we have therefore developed a small but kinetically diverse group of efficient H-transfer agents which ordinarily might be expected to meet virtually every kinetic need within the range covered.[1−3]

The efficacy of such competition experiments is vitally dependent on the premise that these observed processes are efficient to the virtual exclusion of deviant competitive reactions of the radical or of the primary products of radical reaction. Generally, excellent yields of the products in question are required for one to be confident about the quantitative validity of the determined rate constants.

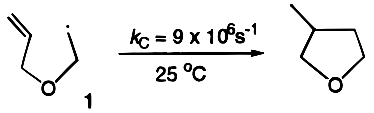
In the course of our studies of the influence of fluorine-substitution on the rates and regiochemistry of radical cyclization processes,[1] we wished to determine the influence of an ether linkage on the rates of perfluoro-5-hexenyl radical cyclization. The only ether systems quantitatively examined within the hydrocarbon 5-hexenyl radical system have been 3-oxa-species, such as **1**.[4] The rate of apparently exclusive 5-*exo*-cyclization of **1** was determined to be *39 times faster* than that of the parent, non-oxa radical.

Such rate enhancement was attributed by Beckwith to reflect the favorable effect of the relatively short C−O bond and the small C−O−C bond angle on the bending and torsional strain of the 5-*exo* transition state structure.[5]

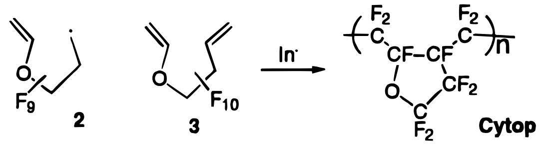
Table 1. Rate Constants of Hydrogen Transfer to Perfluoro-*n*-alkyl Radicals[2]

H-transfer agent	*n*-Bu_3SnH	$(TMS)_3SiH$	$(TMS)_2MeSiH$	Et_3SiH
k_H (10^6 M^{-1} s^{-1})	203	51	16.3	0.75

Scheme 1



Scheme 2



The initial perfluoro-5-hexenyl ether radical system which we have examined is the vinyl ether radical, **2**. This cyclization is of particular interest because it provides a kinetic model for the cyclopolymerization process of diene **3**, to form Cytop (Asahi Glass), which is a commercial, amorphous resin that exhibits outstanding chemical, thermal, and electrical properties.[6−8]

Preliminary studies of the cyclization of **2** indicated that its rate, like that of **1**, was enhanced relative to that of its non-oxa, perfluoro-5-hexenyl radical parent, such that $(TMS)_3SiH$ should have been an appropriate reducing agent for the quantitative competitive study.

However, attempted use of $(TMS)_3SiH$ led to a complex product mixture in which the yields of the desired products, **5** and **6**, were unsatisfactorily low. We considered that a likely reason for these unsatisfactory results was the intervention of competitive processes involving addition of the propagating $(TMS)_3Si^\bullet$ radical to the vinyl ether function of both the radical precursor **4** and the vinyl ether product **5**. (Attempted use of *n*-Bu_3SnH in the study led to similar results, further aggravated by the smaller ratio of cyclization to reduction caused by the 3.9-fold greater k_H of the tin reagent.) It was observed, via control experiments, that these two H-transfer agents (and possibly also their R_3MBr products of chain transfer) underwent facile addition to product **5** during and after the consumption of starting bromide **4**. The implication of this destructive process in these studies, of course, placed in question the efficacy of the measured **6**:**5** product ratios which were required for determination of the value of k_C.

Such problems with *n*-Bu_3SnH and $(TMS)_3SiH$ were not new to us. Experimentally, we had observed that both reagents gave similar problems in our earlier study of the perfluoro-5-hexenyl radical.[1] Fortunately, in that case we found that Et_3SiH was sufficiently reactive to give good ratios of cyclization and H-transfer products, while not giving significant products from olefin addition. Perhaps the success with Et_3SiH was due to its much greater rate of bromine atom abstraction (20 times faster

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† Contribution no. 7360.

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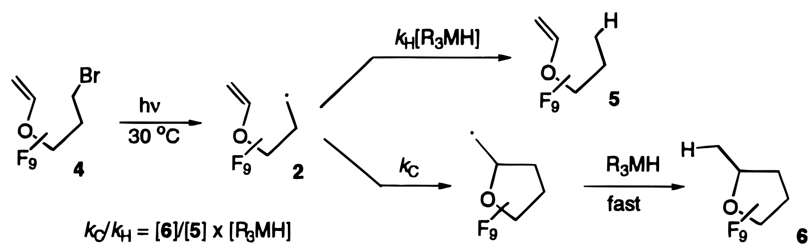
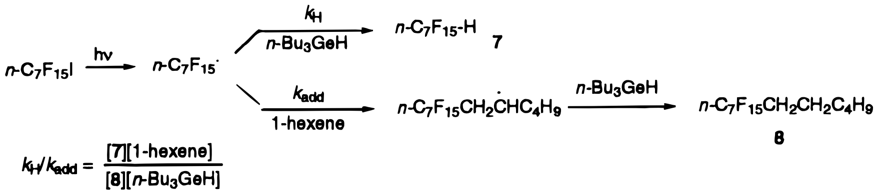
Scheme 3



Scheme 4



than $(TMS)_3SiH$ in reaction with RCH_2Br).[9–12] (We have also found that Et_3SiH reduces *perfluoro-n*-alkyl iodides 10 times faster than hydrocarbon *n*-alkyl iodides.)[13]

Unfortunately, because its rate of H-transfer to perfluoro-*n*-alkyl radicals is 70 times slower than that of $(TMS)_3SiH$,[14] Et_3SiH could not readily be used as the hydrogen atom transfer agent for our study of **4**. It was therefore decided to have a look at *n*-Bu_3GeH, which is a slightly less reactive H-transfer agent than $(TMS)_3SiH$ in hydrocarbon radical systems,[14,15] as a possible H-transfer agent for perfluoroalkenyl radical systems.

The value of k_H for hydrogen atom transfer from *n*-Bu_3GeH to perfluoro-*n*-alkyl radicals was determined by the competition study which is shown in Scheme 4. Since k_{add} for 1-hexene has been determined to be $7.9\ (\pm 0.7) \times 10^6\ M^{-1}\ s^{-1}$ at 298 K,[16] it was therefore possible to convert the experimental values of k_H/k_{add}, determined from the data in Table 2, into a value for k_H of $1.5\ (\pm 0.2) \times 10^7\ M^{-1}\ s^{-1}$.[17]

In terms of relative H-transfer ability, *n*-Bu_3GeH turns out to have virtually the same reactivity as $(TMS)_2SiMeH$, and it is a factor of 3.4 times slower than $(TMS)_3SiH$.[3] Consistent with the expected impact of its more favorable polar transition state for hydrogen transfer, it is 150 times more reactive with *n*-$R_F^•$ than it is with *n*-$R^•$.

When *n*-Bu_3GeH was used as the chain-transfer agent in the competitive cyclization study of radical **2**, as the results in Table 3 indicate, minimal addition of the propagating germanyl radical to either **4** or **5** was observed, excellent yields of reaction products **5** and **6** were obtained, and a plot of the data provided a value of $k_C = 3.5\ (\pm 0.3) \times 10^6\ s^{-1}$.[17] Since there are no available rate data for the addition of the various Sn, Si, and Ge radicals to fluorinated alkenes,[18] much less to trifluorovinyl ethers, one cannot unambiguously assess those factors which make Et_3SiH and *n*-Bu_3GeH "cleaner" reagents in our photoinduced cyclization studies of perfluoroalkenyl and alkenyl ether radical systems.

Our measured rate of cyclization of perfluorovinyl ether radical **2** is ~7 times faster than that of the perfluoro-5-hexenyl radical ($4.9 \times 10^5\ s^{-1}$)[1] and ~14 times faster than that of the parent, hydrocarbon 5-hexenyl radical.[15] Although the ether function in **2** should be expected to give rise to a beneficial effect on transition state strain as it did in the hydrocarbon system, **1**,[4,5] also important in the case of **2** will be the electronic impact of the oxygen being bound directly to the vinyl group which is undergoing addition. Since we have already demonstrated that the rates of addition of perfluoro-*n*-alkyl radicals to olefins are directly correlated to the ionization potentials of the olefins,[16] it would be interesting to know how perfluorination affects the IP's of alkyl vinyl ethers. Certainly one would expect the ionization potential of **3** to be *substantially* higher (thus lower reactivity) than that of an analogous hydrocarbon alkyl vinyl ether because of the diminished basicity (i.e., donor ability) of its lone-pair, but it may be lower than that of a terminal perfluoroalkene π system, as is present in the perfluoro-5-hexenyl radical. Unfortunately, there are no experimental IP data on perfluorovinyl ethers available to substantiate this. However, to give some idea of the effect of proximate fluorine substitution on the ionization potential of a related system, $CF_3CH_2OCH_3$ has an IP 0.8 eV greater than $CH_3CH_2OCH_3$ (10.53 vs 9.72 eV).[19]

Lastly, the relatively fast rate of cyclization of **2** is consistent with the fact that $C_3F_7OCF{=}CF_2$ is about 8 times more reactive than $CF_3CF{=}CF_2$ toward addition of perfluoroalkyl radicals at 60 °C.[20] Moreover, these two independent indications that perfluoroalkyl radicals add more readily to perfluorovinyl ethers than to perfluoroalkenes mitigate against cyclization of **2** being a good model for homocyclopolymerization of diene monomer **3**.[6–8] Because perfluoroalkyl radical addition to **3** should be preferentially to the perfluorovinyl ether linkage, it

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(9) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 3292–3296.

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(17) All errors are calculated as propagated errors.

(18) In its addition to *trans*-1,3-pentadiene, *n*-$Bu_3Ge^•$ adds slower than either *n*-$Bu_3Sn^•$ or $Et_3Si^•$ (4.6, 6.8, and $14 \times 10^7 M^{-1}\ s^{-1}$, respectively.)[10]

(19) NIST Standard Reference Database 25. *NIST Structures and Properties Database and Estimation Program 1991*; U.S. Department of Commerce, Gaithersburg, MD.

(20) Carlson, D. P. (DuPont), private communication.

Scheme 5

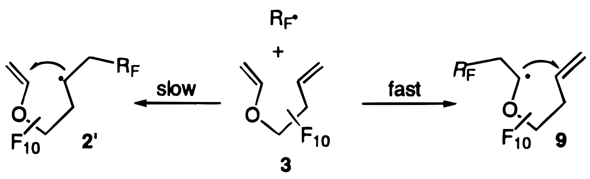

Table 2. Competition Data for the Reaction of Perfluoro-*n*-heptyl Radical with 1-Hexene and Tributylgermanium Hydride at 303 K[a]

[1-hexene]	[Bu_3GeH]/[1-hexene]	**8/9**	yield, %
1.76	0.31	0.74	94
1.51	0.44	0.97	96
1.26	0.63	1.31	99
1.01	0.90	1.79	99
0.75	1.37	2.66	100
0.58	1.97	3.94	97

[a] Computed slope = $k_H/k_{add} = 2.42 \pm 0.05$.

would appear that a better model system to examine from that respect would be radical **9**. The generation and cyclizations of radicals such as **9** are currently under investigation.

Experimental Section

Materials. Perfluoro-*n*-heptyl iodide was obtained commercially (PCR, Inc.) and used as received. Tributylgermanium hydride was prepared by the reaction of *n*-Bu_3GeCl with $LiAlH_4$.[21] 1,1,2,2,3,3-Hexafluoro-3-bromopropyl trifluorovinyl ether (**4**) was provided by the CR & D Department of DuPont, and no further purification of the sample was needed. Both 1-H-perfluoro-*n*-heptane, **7**, and 1-*n*-hexylperfluoro-*n*-heptane, **8**, had been prepared and characterized in earlier work.[2] All compounds used in this work were >96% pure, as determined by ^{1}H NMR and analytical gas chromatography (SE-30), and all products were purified by preparative gas chromatography using a $^1/_4$ × 10 ft SE-30 column.

Procedure for Determination of the Rate Constant for H-atom Transfer (k_H) to the Perfluoro-*n*-heptyl Radical from Tri-*n*-butylgermanium Hydride. Reaction samples were prepared by adding 8 μL of radical precursor (perfluoro-*n*-heptyl iodide) to benzene-d_6 in a Pyrex NMR tube into which appropriate amounts of Bu_3GeH[21] and 1-hexene were charged. Six such samples, varied in the amounts of Bu_3GeH and 1-hexene (Table 2), were needed to carry out the rate determination. Each reaction mixture was degassed (freeze and thaw) three times and sealed with rubber septa under argon in a Pyrex NMR tube and then photolyzed using a Rayonet reactor for 4 h to complete its reactions (monitored by ^{19}F NMR). The amounts of products (reduction **7** and addition **8**) were quantitatively determined by ^{19}F NMR. $PhCF_3$ was used as the internal standard to calculate the NMR yield of each reaction. The ratios of reduced product **7** to addition product **8** were obtained by measuring the integral of the corresponding peaks in the ^{19}F NMR (CF_2-H, δ −138.1 for **7**; CF_2-CH_2, δ −114.4 for **8**).[2] These ratios of **7**/**8**, obtained for varied concentrations and ratios of 1-hexene and tri-*n*-butylgermanium hydride, permitted the determination of the ratio, k_H/k_{add}, using the equation given in the discussion section.

Procedure for Determination of the Rate Constant (k_C) for the Intramolecular Cyclization of the Perfluoro-4-oxa-5-hexenyl Radical, 2. Reaction samples were made by adding 10 μL of radical precursor **4** to benzene-d_6 in a Pyrex NMR tube in which appropriate amounts of *n*-Bu_3GeH had been charged. Six of such samples, varied in the amounts of *n*-Bu_3GeH (Table 3), were needed to complete the rate determination. Samples were sealed in NMR tubes by rubber septa, degassed (freeze and thaw) three times under argon, and then photolyzed using a Rayonet reactor for 10 min (monitored by ^{19}F NMR) at room temperature. The products (reduced **5** and cyclized **6**) of the reactions were quantitatively analyzed by ^{19}F NMR. $PhCF_3$ was used as the internal standard to calculate the NMR yield of the reactions. The ratios of reduced **5** to cyclized **6** were obtained by measuring the integrals of the corresponding peaks in the ^{19}F NMR (CF_2H, δ −137.26 for **5**; CF_2H, δ −139.26 for **6**). The ratios of **5**:**6** were obtained for varied concentrations of *n*-Bu_3GeH, which were then combined with the respective concentrations of the reductant to allow the determination of the ratio k_H/k_C.

Table 3. Competition Data for the Reaction of Perfluoro-6-bromo-4-oxa-1-hexene, 4, with *n*-Bu_3GeH at 303 K[a]

[bromide]	[*n*-Bu_3GeH]	[**5**]/[**6**]	yield, %
0.052	0.41	2.71	98
0.052	0.52	3.07	98
0.052	0.62	3.57	96
0.052	0.69	3.88	97
0.052	0.74	4.10	97
0.052	0.82	4.49	99

[a] Computed slope = $k_H/k_C = 4.38 \pm 0.11$.

1,1,2,2,3,3-Hexafluoro-3-bromopropyl trifluorovinyl ether, 4: ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$), δ −64.28 (s, 2F), −83.77 (s 2F), −113.39 (d of d, J = 83 Hz, 65 Hz, 1F), −121.20 (s, 2F), −121.62 (d of d, J = 112 Hz, 83 Hz, 1F), −135.11 ppm (d of d, J = 112 Hz, 66 Hz, 1F); HRMS, calcd for C_5F_9OBr, 325.8989, found, 325.9018.

Preparation of 1,1,2,2,3,3-Hexafluoropropyl Trifluorovinyl Ether, 5, and 2-(difluoromethyl)perfluoro-1-oxacyclopentane, 6. The title compounds were prepared from the bromide **4**. To 0.55 mL of tributylgermanium hydride with 0.5 mL of degassed benzene in a Pyrex NMR tube was added 0.27 mL (1.59 mmol) of **4**. The mixture was photolyzed in a Rayonet reactor for 10 min. ^{19}F NMR analysis indicated that the reaction was finished. Through preparative GC (SE-30), the title compounds were isolated in a purity of >96%.

1,1,2,2,3,3-Hexafluoropropyl trifluorovinyl ether, **5**: ^{1}H NMR (300 M Hz, $CDCl_3$, TMS), δ 6.04 (t of t, J = 52 Hz, 5 Hz, 1H); ^{19}F NMR (282 M Hz, $CDCl_3$, $CFCl_3$), δ −86.56 (s, 2F), −113.08 (d of d, J = 83 Hz, 68 Hz, 1F), −121.45 (d of d, J = 110 Hz, 81 Hz, 1F), 132.44 (s, 2F), −134.71 (d of d, J = 112 Hz, 66 Hz, 1F), −137.26 ppm (m of d, J = 58 Hz, 2F); HRMS, calcd for C_5HF_9O, 247.9884, found, 247.9888.

2-(Difluoromethyl)perfluoro-1-oxacyclopentane, **6**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS), δ 6.03 (d of t, J = 52 Hz, 7 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$), δ −82.89 (d, J = 8 Hz, 1F), −82.99 (t, J = 7 Hz, 1F), −126.18 (d, J = 127 Hz, 1F), −129.16 (d of d, J = 262 Hz, 7 Hz, 1F), −131.63 (d, J = 262 Hz, 1F), −131.38 (s, 1F), −133.40 (m of d, J = 312 Hz, 1F), −135.43 (m of d, J = 250 Hz, 1F), −139.26 ppm (d of d, J = 312 Hz, 52 Hz, 1F); HRMS, calcd for C_5HF_9O, 247.9884, found, 247.9872.

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Supporting Information Available: ^{1}H and ^{19}F NMR of **5** and **6** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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