Reaction of 2-NFL and 3-NFL with N_2O_5 in CCl_4. These reactions were carried out at 25 °C as described above with the following amounts of reagents used: 2-NFL, 5 mg (0.02 mmol) in 10 mL of CCl_4 and 2.2 mg of N_2O_5 (0.02 mmol) in 1 mL of CCl_4; 3-NFL, 10 mg (0.04 mmol) in 20 mL of CCl_4 and 4.4 mg of N_2O_5 (0.04 mmol) in 2 mL of CCl_4. Products from both reactions were separated by chromatgraphy on silica gel 60 with CCl_4/CH_2Cl_2 (9:1 v/v) elution. From the reaction of 2-NFL with N_2O_5 the following products were isolated (unreacted 2-NFL, 20%).

2,5-Dinitrofluoranthene (**4**, 1.5 mg, 25% yield); ^1H NMR ($CDCl_3$) δ 8.99 (d, 2, $J_{(4,6)} = 1.7$ Hz, C_1H and C_6H), 8.81 (d, 2, $J_{(1,3)} = 1.7$ Hz, C_3H and C_4H), 8.04–7.99 (m, 2, C_7H and $C_{10}H$), 7.58–7.53 (m, 2, C_8H and C_9H); MS, *m/z* (relative intensity) 292 (M^+, 100%), 246 ($[M - NO_2]^+$, 40%), 200 ($[M - 2NO_2]^+$, 88%).

1,2,5-Trinitrofluoranthene (**5**, 1 mg, 15% yield); ^1H NMR ($CDCl_3$) δ 8.88 (d, 1 , $J_{(4,6)} = 2$ Hz, C_6H), 8.79 (d, 1, C_4H), 8.52 (s, 1, C_3H), 8.05–7.97 (m, 2, C_7H and $C_{10}H$), 7.66–7.52 (m, 2, C_8H and C_9H); MS, *m/z* (relative intensity) 337 (M^+, 100%), 307 ($[M - NO]^+$, 7%), 245 ($[M - 2NO_2]^+$, 17%), 199 ($[M - 3NO_2]^+$, 43%), 187 ($[M - 2NO_2 - NO - CO]^+$, 61%).

5-Nitrofluoranthene oxide (presumably 2,3-oxide) was isolated from the reaction mixture by semipreparative HPLC on an Ultrasphere Si column (55% *n*-hexane, 45% CH_2Cl_2): MS, *m/z* (relative intensity) 263 (M^+, 62%), 247 ($[M - O]^+$, 98%), 217 ($[M - NO_2]^+$, 33%), 201 $[M - O - NO_2]^+$, 100%), 200 ($[M - O - HNO_2]^+$, 70%), 189 ($[M - NO_2 - CO]^+$, 20%).

From the reaction of 3-NFL with N_2O_5 the following compounds were isolated (unreacted 3-NFL, 20%).

2,4-Dinitrofluoranthene (**7**, 3 mg, 30% yield); ^1H NMR ($CDCl_3$) δ 9.68 (d, 1, $J_{(1,3)} = 2$ Hz, C_3H), 8.72 (d, 1, $J_{(5,6)} = 8.5$ Hz, C_5H), 8.69 (d, 1, C_1H), 8.09 (d, 1, C_6H), 7.99–7.91 (m, 2, C_7H and $C_{10}H$), 7.58–7.48 (m, 2, C_8H and C_9H); MS, *m/z* (relative intensity) 292 (M^+, 100%), 262 ($[M - NO]^+$, 30%), 246 ($[M - NO_2]^+$, 15%), 200 ($[M - 2NO_2]$, 60%), 188 ($[M - NO_2 - NO - CO]^+$, 40%).

1,2,4-Trinitrofluoranthene (**8**, 2 mg, 15% yield); ^1H NMR ($CDCl_3$) δ 9.58 (s, 1, C_3H), 8.81 (d, 1, $J_{(5,6)} = 8$ Hz, C_5H), 8.15 (d, 1, C_6H), 7.98 (d, 1, $J_{(9,10)} = 7$ Hz, $C_{10}H$), 7.82 (d, 1, $J_{(7,8)} = 7$ Hz, C_7H), 7.62–7.51 (m, 2, C_8H and C_9H); MS, *m/z* (relative intensity) 337 (M^+, 100%), 307 ($[M - NO]^+$, 14%), 245 ($[M - 2NO_2]^+$, 5%), 199 ($[M - 3NO_2]^+$, 36%), 198 ($[M - 3NO_2 - H]^+$, 42%), 187 ($[M - 2NO_2 - NO - CO]^+$, 86%).

Reactions of FL with Benzoyl Nitrate ($BzONO_2$) in CH_3CN and CCl_4 Solutions. The reactions were carried out according to methods described in the literature.[39] For the reaction in CH_3CN, 2 g of FL (0.01 mol), 1.9 g of $AgNO_3$ (0.01 mol), and 1.5 g of benzoyl chloride (BzOCl, 0.01 mol) were used. BzOCl, dissolved in 10 mL of CH_3CN, was added dropwise to a stirred solution of FL and $AgNO_3$ in 80 mL of CH_3CN at 0 °C.

For the reaction in CCl_4 solution, $BzONO_2$ was generated from 4.8 g of BzOCl (0.034 mol), in 10 mL of CCl_4 and 7.3 g of $AgNO_3$ (0.043 mol) at −15 °C. Immediately after filtration, 50% of the reaction product was added to a solution of FL (2 g, 0.01 mol) in 40 mL of CCl_4 at 0 °C. The $BzONO_2$ was assumed to be in excess of FL, but the $BzONO_2$ solution was not analyzed.

After 2.5 h of stirring at 0 °C, the reaction mixtures were poured onto crushed ice, and diluted sodium hydroxide was added. Thirty milliliters of benzene was also added to the CH_3CN solution. The organic layers were separated and the solvents distilled under reduced pressure. The remaining material was dissolved in CH_2Cl_2 and analyzed by GC/MS.

It was also checked in a separate reaction that the NFL isomer distribution from the reaction of FL with $BzONO_2$ in CCl_4 solution was identical when the reaction mixture was analyzed by GC/MS after 1.5 and 2.5 h of reaction, without $BzONO_2$ hydrolysis. It was concluded from HPLC quantification, which was carried out after every 30 min of reaction, that the maximum yield of FL conversion ($\sim$10%) was reached after 1.5 h and did not change after an additional 1 h of stirring.

Reaction of Gaseous N_2O_5 with FL in Gaseous and Adsorbed States. Teflon-impregnated glass fiber (TIGF) filters coated with FL were exposed in the dark for 45 min in a collapsible 6400-L all-Teflon chamber, as described elsewhere.[11-13] Three 45-min exposures were conducted with initial concentrations of 5 ppm N_2O_5, 5 ppm N_2O_5 + 10 ppm NO_2, and 10 ppm NO_2 + 1 ppm HNO_3 (control exposure). At the end of each exposure, approximately 75% of the chamber volume was sampled through a polyurethane foam (PUF) plug to collect the gas-phase products of FL reactions, and the FL-coated filters were removed. The exposed filters were Soxhlet extracted with CH_2Cl_2, and the NFL isomers were quantified by HPLC[11,14] and identified by GC/MS analysis with multiple ion detection (MID). The PUF plugs were Soxhlet extracted with CCl_4 and, after semipreparative HPLC purification,[11,12] were analyzed by GC/MS.

Acknowledgment. We thank Dr. Robert Lee of the University of California, Riverside, Department of Chemistry for conducting the ^1H NMR experiments. Dr. Joseph E. Rice is thanked for the generous gift of the hydroxyfluoranthene isomers. We also thank Tricia McElroy for able technical assistance. The financial support of the US Department of Energy through Contract DE-AM03-76SF00034, Project DE-AT03-79EV10048-A007 (project officers, Drs. D. A. Ballantine and G. Stapleton), is gratefully acknowledged.

Registry No. 1, 206-44-0; **2**, 13177-29-2; **3**, 33611-88-0; **4**, 102493-21-0; **5**, 102493-22-1; **7**, 102493-19-6; **8**, 102493-20-9; **9**, 102493-17-4; **10**, 102493-16-3; **11**, 102493-15-2; **12**, 85923-82-6; HNFL, 32516-82-8; N_2O_5, 10102-03-1; fluoranthenequinone, 39407-42-6; 5-nitrofluoranthene 2,3-oxide, 102493-18-5.

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(39) Halvarson, K.; Melander, L. *Ark. Kemi*, **1957**, *11*, 77–88.

N-Hydroxypyridine-2-thione Esters as Radical Precursors in Kinetic Studies. Measurements of Rate Constants for Hydrogen Atom Abstraction Reactions

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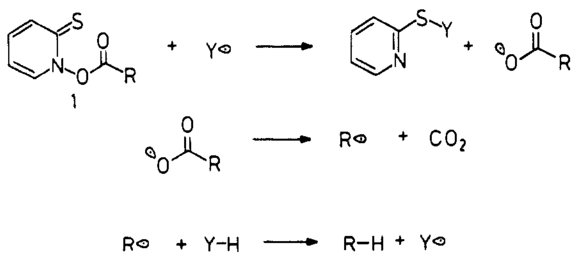
Abstract: *N*-Hydroxypyridine-2-thione esters were employed as radical precursors in kinetic studies. Radical chain reactions of the precursor esters gave 2,2-dimethyl-3-butenyl and 5-hexenyl. These radicals either were trapped by H-atom donors or rearranged, and the rate constants for trapping were determined from the known rate constants for rearrangement and measured product yields. For hydrogen atom donors that reacted too slowly to trap radicals before rearrangement, an estimate of the rate constants for hydrogen atom transfer was made from the yields of rearranged hydrocarbon and alkyl pyridyl sulfide (formed by scavenging of the alkyl radical by the precursor ester). The methods work for a variety of H-atom donors, including thiols, stannanes, phosphines, silanes, and reactive hydrocarbons. The rate constants determined for reduction of alkyl radicals by dicyclohexylphosphine, 1,4-cyclohexadiene, and THF are important for mechanistic studies of potential electron-transfer processes in reactions of nucleophiles with alkyl halides.

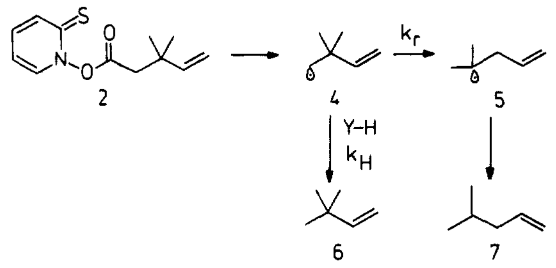
The rate constants for reactions of radicals can be measured directly by the use of a spectrophotometric or spectroscopic technique or indirectly by the use of competition reactions which are often based on a radical clock reaction. The limitations of

Scheme I



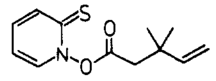
Y = R'S, R'$_3$Sn, R'$_3$C, R'$_3$Si

Scheme II

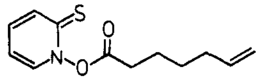


the latter approach are that the radical reaction used for comparison must have a well-measured rate constant and, for practicality, a relatively clean source of radicals must be available.[1a] Barton's recently developed radical precursors, *N*-hydroxypyridine-2-thione esters (**1**),[2] promised to provide convenient sources of radicals for kinetic studies since these compounds can be used to produce radicals in chain reactions in which tin-, carbon-, or sulfur- (and apparently silicon-) centered radicals propagate the chain (Scheme I). In this paper we report the use of Barton's precursors in measurements of the rate constants for hydrogen atom transfer to carbon-centered radicals. The 2,2-dimethyl-3-butenyl rearrangement[3] and the 5-hexenyl cyclization[7] were used as radical clocks.[8]

The precursor esters **2** and **3** were prepared by reaction of the appropriate acid chloride with the sodium salt of *N*-hydroxypyridine-2-thione.[2] Previously, compounds **1** have been used without purification,[2] but we were able to purify the esters by column chromatography on silica gel in columns wrapped in aluminum foil to protect the reagents from light.



2



3

Rate constants for hydrogen abstraction reactions from various reducing agents (Y–H) could be measured by the type of competition reaction shown in Scheme II for ester **2**. Since the rate of rearrangement of radical **4** to radical **5** is known, the second-order rate constant for reduction of **4** (k_H) is approximated by eq 1 where k_r is the first-order rate constant for rearrangement, **6**/**7** is the observed product ratio, and $[Y\text{-}H]_m$ is the mean concentration of the reducing agent.[9a]

Table I. Rate Constants for Hydrogen Atom Abstraction by Carbon-Centered Radicals

H-atom donor	radical	solvent	temp[a] (°C)	k_H[b] ($M^{-1}\ s^{-1}$)
$(CH_3)_3CSH$	**4**	THF	32	$(1.07 \pm 0.04) \times 10^7$
	4	THF	50	1.0×10^7
Ph_2PH[c]	**8**	benzene	50	1.5×10^7
n-Bu_3SnH	**4**	THF	50	4.9×10^6
$(c\text{-}C_6H_{11})_2PH$	**4**	THF	27	$(1.0 \pm 0.5) \times 10^6$
	4	THF	50	1.1×10^6
	8	benzene	50	$(7.0 \pm 0.3) \times 10^5$
1,4-cyclohexadiene	**4**	THF	50	$(4.8 \pm 0.2) \times 10^5$
	8	benzene	50	$(2.3 \pm 0.3) \times 10^5$
Ph_3SiH[d]	**5**	THF	50	0.9×10^4
	9	benzene	50	3×10^4
Et_3SiH[d]	**5**	THF	50	3×10^3
	9	benzene	50	7×10^3
THF[d]	**5**	THF	50	$2 \times 10^3\ (s^{-1})$[e]
	9	THF	50	$6 \times 10^3\ (s^{-1})$[e]

[a] ±2 °C. [b] Second-order rate constants with error limits (1σ) are for studies with multiple runs; those without error limits are single run results. [c] The total yield of hydrocarbons was ca. 50%; see text. [d] These reagents trap only rearranged radicals **5** and **9**; approximate rate constants were determined by eq 2 by using the value $k_T = 2 \times 10^6\ M^{-1}\ s^{-1}$. [e] Pseudo-first-order rate constants measured in THF.

$$k_H = k_r\,(1/[Y\text{-}H]_m)(\mathbf{6}/\mathbf{7}) \qquad (1)$$

In practice, there is a limitation to the kinetic approach in Scheme II. If the reductions of the radicals **4** and **5**, or, in the case of ester **3**, 5-hexenyl (**8**) and cyclopentylmethyl (**9**), by Y–H are slow, then these radicals can react with their precursors to give alkyl pyridyl sulfides. However, for the slow reductions we studied, approximate rate constants could be determined. By measuring the amounts of rearranged and unrearranged alkyl pyridyl sulfides from reactions of **2** and **3** in the absence of good reducing agents, we determined the second-order rate constants for reactions of **4** with **2** ($k_T = 3.4 \times 10^6\ M^{-1}\ s^{-1}$ at 50 °C) and of **8** with **3** ($k_T = 1.2 \times 10^6\ M^{-1}\ s^{-1}$ at 50 °C). With the assumption that the rate constant $k_T = 2 \times 10^6\ M^{-1}\ s^{-1}\ s^{-1}$ at 50 °C is a reasonable approximation for the rate constant for reaction of any radical with an *N*-hydroxypyridine-2-thione ester,[10] we could estimate the rate constants for reductions by poor reducing agents by measuring the amounts of hydrocarbon product and alkyl pyridyl sulfide and using eq 2 where k_T is the second-order rate constant for radical trapping by **2** or **3**, H is the hydrocarbon product yield, S is the sulfide product yield, and $([T]/[Y\text{-}H])_{eff}$ is the effective ratio of the reagents throughout the reaction.[9b]

$$k_H = k_T\,([T]/[Y\text{-}H])_{eff}(H/S) \qquad (2)$$

Table I contains second-order rate constants for radical reductions by various donors. The reactions were run in Pyrex vessels in a thermostated bath with visible irradiation (150-W tungsten lamp) for initiation. Reactions were typically complete within

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[1] Kaplan, L. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; John Wiley & Sons, Inc.: (a) Vol. 1, 1978, pp 170–176, (b) Vol. 3, 1985, p 248 and ref 83.

[2] Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901–3924 and references therein.

[3] The temperature-dependent function for rearrangement of 2,2-dimethyl-3-butenyl is $\log k/s^{-1} = (10.64 \pm 0.28) - (5.26 \pm 0.28)/\theta$ ($\theta = 2.3RT$ kcal/mol, errors are 2σ). This function has been recalculated from our original report[4] by using the recently reported rate constant for trapping of 2,2-dimethylpropyl by Bu_3SnH[5] for the rate constant of the competition reaction. The function has been confirmed in another laboratory.[6]

[4] Newcomb, M.; Williams, W. G. *Tetrahedron Lett.* **1985**, *26*, 1179–1182.

[5] Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594–4596.

[6] Beckwith, A. L. J., private communication. We thank Professor Beckwith for informing us of this result prior to publication.

[7] The temperature-dependent function for cyclization of 5-hexenyl is $\log k/s^{-1} = (10.37 \pm 0.32) - (6.85 \pm 0.42)/\theta$ ($\theta = 2.3RT$ kcal/mol, errors are 2σ). Cf.: Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742.

[8] For a discussion of radical clocks see: Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317–323.

[9] (a) The use of the mean concentration in eq 1 is a reasonable approximation for our experimental design wherein excess Y–H was used; the largest error introduced by employing eq 1 rather than an integrated form of the equation was <1% when [Y–H] = 0.2 M. (b) The integrated form was used in eq 2 since the use of mean concentrations would introduce a 10–15% error.

[10] (a) The assumption that the tertiary radical **5** will react with **2** with a rate constant of $2 \times 10^6\ M^{-1}\ s^{-1}$ is poor; this will lead to estimates of rate constants for H-atom transfer to **5** which are greater than the actual value for these reactions. (b) The values for k_T are important for those attempting to use esters **1** in synthesis. With these rate constants and rate constants for additions of radicals to various alkenes (cf.: Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753–764), one could predict whether or not scavenging of the radical by ester **1** would interfere with a desired radical addition reaction. Accurate measurement of k_T values is currently a subject of interest in our group.

1 h, and yields of hydrocarbons were typically 90–100% in cases where eq 1 applied except for the reaction with diphenylphosphine. In the reaction with Ph_2PH, the yield of hydrocarbon products was only ca. 50% and no pyridyl sulfide products were detected; this suggests that alkyl radicals add to the aryl groups in part.[11] In multiple run experiments, five measurements were made, and the concentration of hydrogen atom donor was varied by a factor of 6 to 9. The method permits study with S–H, Sn–H, C–H, and Si–H donors, the radicals from which appeared to carry the chain reaction in Scheme I successfully. It was also possible to study P–H donors, but it appeared that the chain reaction was not carried well with the phosphorus-centered radicals; the reactions could be run to nearly complete consumption of the precursor esters by extended (several hour) visible irradiation. Extended reaction times in the reactions of dicyclohexylphosphine in THF apparently led to problems in precision; in this case the yields of volatile hydrocarbons were lower than typically observed.

The rate constants we found appear to be reasonable when compared with other reported rate constants. The qualitative order of H-atom reactivity we found is consistent with that expected from studies with cyclopropyl radical[13] (RSH > 1,4-cyclohexadiene > THF) and with *tert*-butoxy radical[12] ($Bu_3SnH > Ph_3SiH > Et_3SiH \simeq$ THF). The phosphines reacted quite rapidly which is consistent with expectations based on the P–H bond strength.[1b] A qualitative conclusion that alkyl radicals react slowly with ethereal solvents was previously reported.[14a] An approximate rate constant for reaction of 1,4-cyclohexadiene with ethyl at 50 °C is 1×10^5 M^{-1} s^{-1}.[14b] The experimentally determined rate constant for reaction of **4** with Bu_3SnH shows that our kinetic approach via esters **1** works as expected; since the rate of rearrangement of **4** was based on the rate of trapping of 2,2-dimethylpropyl by Bu_3SnH,[3] the use of Bu_3SnH to trap **4** generated from ester **2** must provide a rate constant for trapping equal to that for 2,2-dimethylpropyl (calculated as 4.7×10^6 M^{-1} s^{-1} at 50 °C).[5]

Because of our interest in possible electron-transfer processes in reactions of nucleophiles with alkyl halides, processes which would lead to alkyl radicals, we have included in these studies three radical reduction reactions currently considered important in alkyl halide mechanistic probe studies; these are the reactions of dicyclohexylphosphine (DCPH), 1,4-cyclohexadiene, and tetrahydrofuran (THF). DCPH, introduced as a radical trap in Me_3SnNa reactions by Kuivila,[15] has been employed extensively in probe studies, but this trapping agent reacts too slowly to prevent most radical rearrangements; for example, the 5-hexenyl cyclization is typically the slowest radical probe rearrangement employed, and DCPH at 1 M will only trap 5-hexenyl with ca. 50% efficiency.[16,17] 1,4-Cyclohexadiene is even a poorer trapping agent; at 1 M concentration it will only trap 5-hexenyl with ca. 30% efficiency. THF, a solvent commonly employed, will trap 5-hexenyl with about 1% efficiency, and in most mechanistic probe studies it would be inappropriate to speculate that high yields of unrearranged hydrocarbon products arose from THF trapping.

Conclusion

The use of *N*-hydroxypyridine-2-thione esters (**1**) as radical precursors for kinetic studies should have widespread applications since in many cases these reagents are superior to the corresponding alkyl halides as radical sources. Reductions via radical chain reactions of esters **1** can be propagated with a variety of radicals whereas those of alkyl halides are mainly limited to tin-centered radicals. Visible irradiation of **1** permits radical chain initiation over a wide range of temperatures; we have run kinetic studies at 0 °C. When chain propagation fails, extended visible irradiation of **1** permits virtually quantitative radical generation. The esters **1** will be stable in some cases where alkyl halides will be labile (for example, in the case of alkyl-substituted cyclopropylcarbinyl halides). Finally, esters **1** are not subject to potentially undetectable radical chain isomerization reactions which, we have recently found,[20] can be a source of confusion in alkyl halide probe studies.[21]

Experimental Section

Preparations of radical precursors 2 and 3 followed the general procedures described by Barton et al.[2] The distilled acid chloride, 3,3-dimethyl-4-pentenoyl chloride or 6-heptenoyl chloride (ca. 20 mmol), was added over 0.5 h to a stirred slurry of 20 mmol of *N*-hydroxypyridine-2-thione sodium salt (Fluka) in 50 mL of benzene in a flask cooled in a −10 °C bath and shielded from light. The mixture was allowed to warm to room temperature, and stirring was continued for 12 h. The reaction mixture was filtered, and solvent was removed from the filtrant at reduced pressure. Silica gel chromatography (3:1 (v/v) hexane–ethyl acetate) in a column shielded from ligth gave the desired products. Ester **2**, recrystallized from hexane–ethyl acetate, was obtained as a yellow solid in 66% yield: mp 65–66 °C; ^1H NMR ($CDCl_3$) δ 6.5–7.7 (m, 4 H), 5.90 (dd, 1 H), 5.02 (d, 1 H), 4.99 (d, 1 H), 2.71 (s, 2 H), 1.26 (s, 6 H). Anal. C, H. Ester **3** was obtained as a yellow oil in 48% yield: ^1H NMR ($CDCl_3$) δ 6.5–7.8 (m, 4 H), 5.6–6.1 (m, 1 H), 4.85–5.15 (m, 2 H), 2.74 (t, 2 H), 1.9–2.2 (m, 2 H), 1.4–1.9 (m, 4 H).

Kinetics of Hydrogen Atom Transfers. The following procedure is representative. Ester **2** (0.1 mmol) and *n*-nonane (20 mg, internal standard) were placed in a 1.0-mL volumetric flask. The flask was capped with a septum and flushed with Ar for 1 min. Tributylstannane (0.2 mmol) was added via syringe, and THF (freshly distilled from potassium–benzophenone) was added via syringe to the mark. The reaction flask was immersed in a thermostated bath for 1 min and then irradiated (150-W tungsten lamp). After 5 min, the reaction mixture was analyzed by capillary GC. Yields were calculated with use of predetermined response factors.

For multiple run experiments, five measurements were made with hydrogen atom donor concentrations varied from 0.2 to 1.2 M except for DCPH where the concentrations were varied from 0.2 to 1.9 M. For single run experiments, the hydrogen atom donor concentration was 0.2 M. For all experiments, the initial concentration of ester **2** or **3** was 0.1 M.

Acknowledgment. We thank the donors to the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation for financial support.

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(11) Aryl silyl radicals are known to add readily to their precursors.[12a]

(12) (a) Chatgilialoglu, C.; Ingold, K. U.; Lusztyk, J.; Nazran, A. S.; Scaiano, J. C. *Organometallics* **1983**, *2*, 1332–1335. (b) Baignée, A.; Howard, J. A.; Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 6120–6123.

(13) Johnston, L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 4877–4881.

(14) (a) Garst, J. F.; Ayers, P. W.; Lamb, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 4260–4261. (b) Hawari, J. A.; Engel, P. S.; Griller, D. *Int. J. Chem. Kinet.* **1985**, *17*, 1215–1219.

(15) Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833–839.

(16) Ashby has recently noted that DCPH trapping of 2,2-dimethyl-5-hexenyl was slower than the radical rearrangment. Cf.: Ashby, E. C.; Argyropoulos, J. N. *J. Org. Chem.* **1985**, *50*, 3274–3283.

(17) The value for H-atom donation from DCPH will permit the results of many qualitative studies to be reconsidered in quantitative terms. Some conclusions based on the fact that DCPH did not prevent a rearrangement should be reevaluated. For example, the conclusion reached by our group[18a] that cyclopropylcarbinyl radicals ($k_r = 1.3 \times 10^8$ s^{-1} at 25 °C)[19] were not the sole source of ring-opened products in reactions of R_3SnNa with cyclopropylcarbinyl bromide, based on the observation that DCPH did not prevent formation of 4-(trialkylstannyl)-1-butene is now shown not to be justified.

(18) (a) Newcomb, M.; Smith, M. G. *J. Organomet. Chem.* **1982**, *228*, 61–70. (b) Alnajjar, M. S.; Smith, G. F.; Kuivila, H. G. *J. Org. Chem.* **1984**, *49*, 1271–1276.

(19) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024–7026.

(20) Newcomb, M.; Sanchez, R. M.; Kaplan, J., submitted for publication.

(21) **Note Added in Proof**: The rate constants for reactions of biradicals formed in the Norrish type II reaction with octanethiol at 22 °C are ca. 1×10^7 M^{-1} s^{-1}. Cf.: Encinas, M. V.; Wagner, P. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 1357–1360.