Photolysis of a β-Azo Perester, a Bifunctional Initiator. The Fragmentation Rate of a β-Peroxy Ester Radical Determined by the Cyclopropylcarbinyl Clock Method

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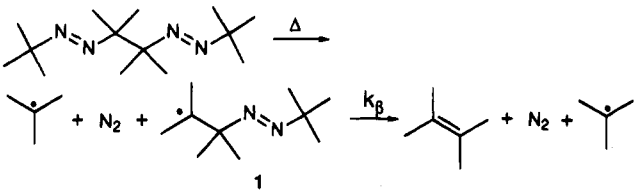
Received March 21, 1994®

Two free radical initiators containing an azo group and a perester moiety on adjacent carbons have been prepared. On long wavelength UV irradiation, these compounds lose nitrogen to afford β-perester radicals. The cyclopropylcarbinyl radical clock technique has been used to determine that the lifetime of these radicals at 25 °C toward β-scission and decarboxylation is 480 ns. The potential utility of β-azo peresters as bifunctional free radical initiators is briefly discussed.

We reported recently that generation of a radical center β to the azo group induces fragmentation to nitrogen, an olefin, and another radical.[1] β-Azo radical **1** is of short but finite lifetime; $k_\beta = 3.8 \times 10^9\ s^{-1}$ at 153.5 °C. This result invited comparison with another class of free



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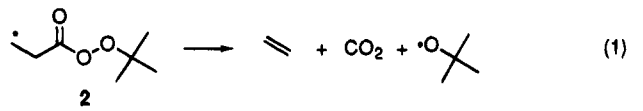
radical initiators, the peresters.[2] We became interested in the rate at which a carbon-centered radical such as **2** fragments to an oxygen-centered *tert*-butoxy radical (eq 1), a process that we calculate to be exothermic by 41 kcal/mol.[3] Although β-perester radicals have been invoked in the induced decomposition of acetylenic diacyl



(1)

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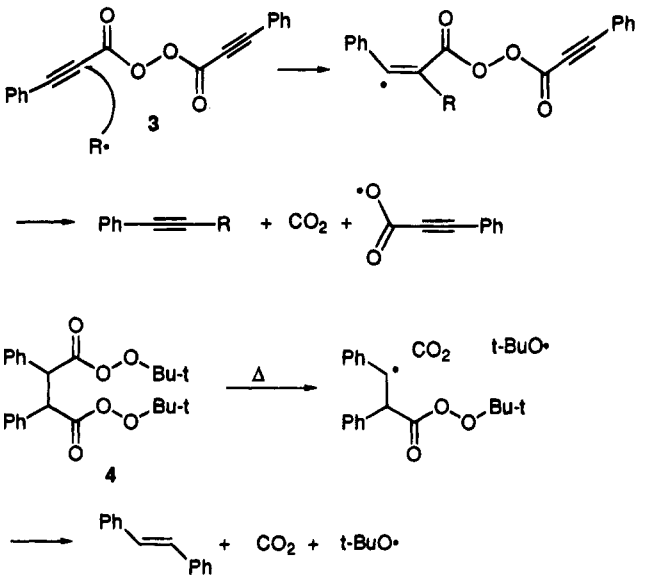
peroxide **3**[4] and in the thermolysis of bisperester **4**,[5] nothing is known about their lifetime. More generally, β-scission of free radicals is a common reaction,[6-8] yet few absolute rates have been reported.[9,10]



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In the present study, we chose to generate a tertiary β-perester radical by long wavelength UV photolysis of a bifunctional initiator[11,12] containing both an azo group and a β-perester moiety. Irradiation of **5** at 366 nm produces β-perester radical **6**, which can react with some scavenger (SH) if decarboxylation is not too rapid (cf. Scheme 1). If the trapping rate is known, the ratio of CO_2 to scavenging product **7** yields the desired k_β. Unfortunately, none of the scavengers tried was successful: thiophenol induced the decomposition of **5** and 2,2,6,6-tetramethylpiperidine-*N*-oxyl (Tempo)[13] gave a trapping product that was too labile for GC analysis. Since bimolecular trapping of **6** did not lead to a value of k_β, it was necessary to employ an intramolecular competition, for which purpose we selected the cyclopropylcarbinyl (CPC) clock.[14] As shown in Scheme 2, photolysis of **8** affords **9**, which either rearranges or decarboxylates. Knowledge of k_r and determination of the amount of product arising via each pathway allows calculation of k_β. A noteworthy characteristic of **5** and **8** is that long wavelength irradiation selectively cleaves the azo moiety while thermolysis breaks the O–O bond to generate a β-azo radical. Since the latter radicals are already

® Abstract published in *Advance ACS Abstracts,* June 1, 1994.

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(2) (a) Rüchardt, Ch. *Fortschr. Chem. Forschung* **1966**, *6*, 251. (b) Singer, L. A. In *Organic Peroxides*; Swern, D., Ed.; Wiley: New York, 1970; Vol. 1. (c) Sawaki, Y. In *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1993.
(3) For the heat of formation of peresters, see Swain, H. A.; Silbert, L. S.; Miller, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 2562.
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(14) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

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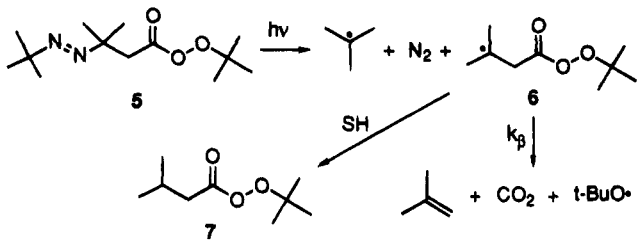
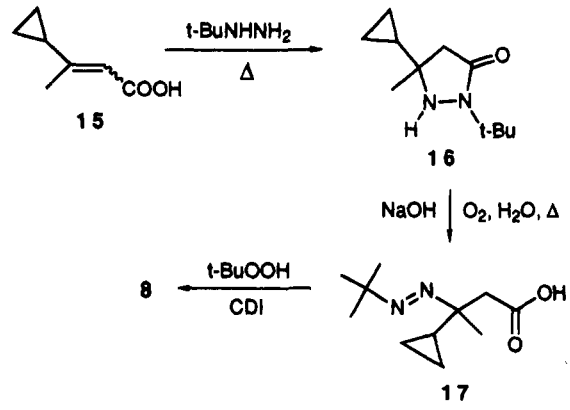
Scheme 1. Decarboxylation versus Scavenging of 6



known,[1] we shall discuss only the photochemical loss of nitrogen from **5** and **8**. It is interesting that these compounds can decompose to as many as 6 fragments: *tert*-butyl radical, N_2, an olefin, CO_2, acetone, and methyl radical.

Syntheses

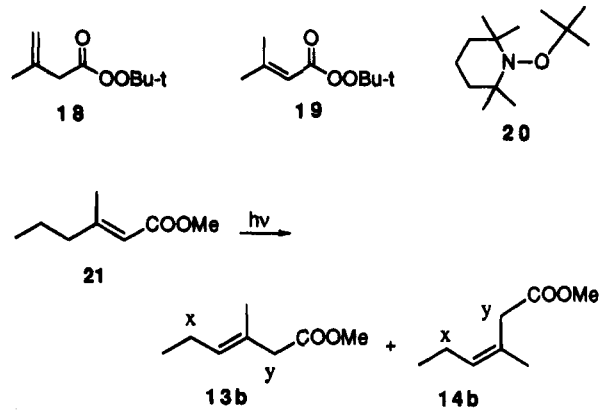
The preparation of **8** was accomplished in three steps starting from 3-cyclopropyl-2-butenoic acid (**15**).[15] On heating with *tert*-butylhydrazine, **15** led to pyrazolidinone **16**[16] which was hydrolyzed and oxidized with sodium hydroxide and O_2 to azo acid **17**. Finally, this acid was converted to **8** using *tert*-butyl hydroperoxide and carbonyldiimidazole (CDI).[17] A similar route starting from β,β-dimethylacrylic acid led to **5**.



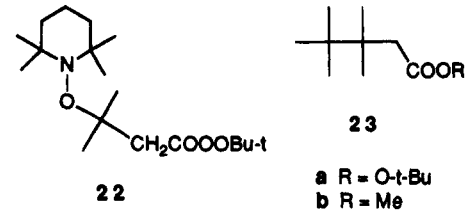
Several potential photolysis products were also synthesized independently, namely, peresters **7**, **18**, and **19**, hydroxylamine **20**,[18] methyl esters **13b**, **14b** (by photodeconjugation of **21**), and **24b**, **25b**, and **26b** (see Scheme 3 and Experimental Section). Throughout this paper, the suffix a will refer to *tert*-butyl peresters while b will signify methyl esters.

Results

Hydrogen-donating scavengers such as 1,4-cyclohexadiene are not suitable for kinetic studies of **6** because the trapping product **7** is indistinguishable from the cage disproportionation product. The 366-nm photolysis of **5** in benzene[19] in the presence of Tempo (cf. Table 1) yielded



disproportionation products **7**, **18**, and **19**, recombination product **23a**, hydroxylamine **20** from scavenging of *tert*-butyl radicals, and presumably **22**, which was too labile for GC analysis.[21] Since **23a** was also too unstable for



GC assay, the reaction mixture was transesterified[22,23] with NaOMe/MeOH to produce the methyl ester **23b**, which was then quantified by GC; however, no transesterification product attributable to **22** could be detected. A control transesterification of authentic **24a** gave **24b** in 91% yield. Even though we were unable to demonstrate formation of **22**, the presence of disproportionation products and the lower yield of **7**, isobutene, and CO_2 with Tempo present (cf. Scheme 1) imply that β-perester radical **6** has a finite existence.

A successful approach to determining the lifetime of β-perester radicals employed azo perester **8** which, on 366-nm photolysis in C_6H_5F solvent at 25 °C, led to 11 products that were quantified by GC. With no added radical scavenger, **9** underwent disproportionation to **24a**–**26a**, recombination to **27a**, and β-scission to **12** (cf. Scheme 3). Since most of these products are peresters that are too unstable for GC assay, they were quantified as their methyl esters (**24b**–**26b**, **27b**), as described above. Authentic samples of compounds **12**, **24b**, and **26b** were used for GC peak identification but the structure of **27b** rests only on the similarity of its NMR spectrum to that of **23b** and on CI-GC-MS.

When photolysis of **8** was conducted with added 1,4-cyclohexadiene (CHD) as radical scavenger, new products **13a** and **14a** appeared (cf. Scheme 2). These compounds were again analyzed as their methyl esters, which were identified by comparison with authentic samples. As shown in Table 2, the recovery of nitrogen and of perester groups ($\Sigma CO_2 = CO_2 + \mathbf{13} + \mathbf{14} + \mathbf{24} + \mathbf{25} + \mathbf{26} + \mathbf{27}$) was generally over 90%.

Discussion

Irradiation of **8** led cleanly to the products listed in Table 2. The presence of **13** and **14** indicates that both

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(19) The nitrogen quantum yield of this photolysis without scavenger was 0.44, indicating that like 2,2′-dimethyl-2,2′-azopropane, **5** undergoes photoisomerization to the labile cis isomer.[20]
(20) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99
(21) Tetramethylisoindole-*N*-oxyl[13] would presumably afford a scavenging product amenable to HPLC assay, but this compound was not tried.
(22) Milas, N. A.; Surgenor, D. M. *J. Am. Chem. Soc.* **1946**, *68*, 642.
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Scheme 2. Photolysis Mechanism of 8

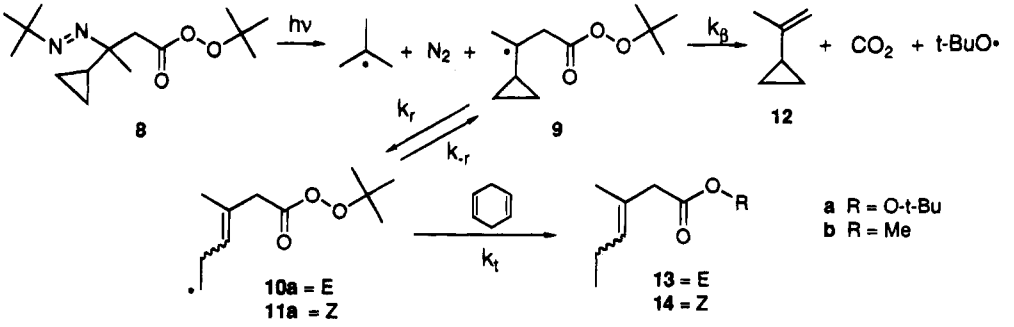


Table 1. Yield (%) of Photolysis Products of 5 in Benzene

[Tempo], M	N_2	CO_2	C_4H_{10}[a]	C_4H_8[b]	CH_4	t-BuOH	7	18	19	23a	20
0	101	39	36	75	3	35	31	6	3	13	0
0.09	103	27	33	52	0	53	15	3	18	12	32

[a] Isobutane. [b] Isobutene.

Scheme 3. Reactions of 9 in the Absence of Scavenger

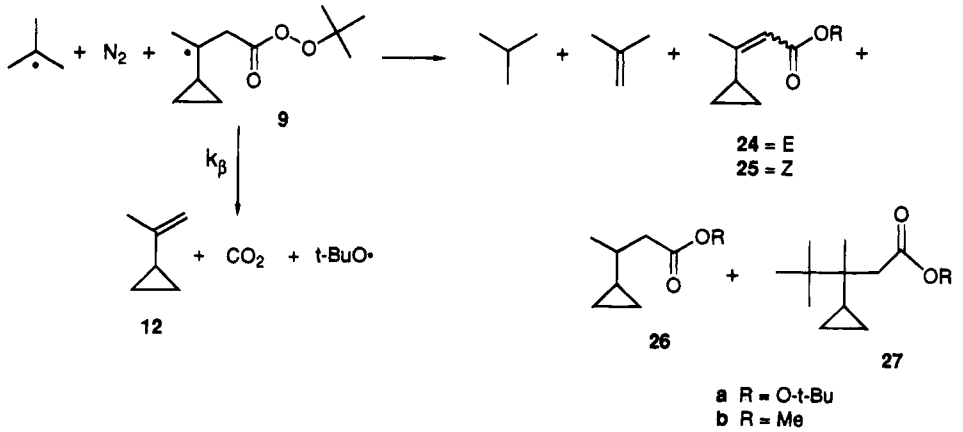


Table 2. Product Yields (%) from 336-nm Photolysis of 8 in C_6H_5F with 1,4-Cyclohexadiene

[CHD], M	N_2	CO_2	C_4H_{10}[a]	C_4H_8[b]	12	13b	14b	24b	25b	26b	27b	ΣCO_2
0	92	27	29	46	26	0	0	17	5	34	13	96
0.91	91	13	59	27	17	12	5	16	3	30	10	89
1.75	88	11	52	28	8	17	7	15	4	31	10	95
3.0	90	9	48	22	8	19	7	15	2	28	11	91

[a] Isobutane. [b] Isobutene.

Table 3. GC Conditions for Product Study

column	DB-5[a]	DBwax[b]	OV-17[c]	XE-60[d]
head pressure (psi)	13	13.5		
He flow at detector (mL/min)			30	30
injector temperature (°C)	120	180	150	180
detector temperature (°C)	150	250	180	200
oven initial temperature (°C)	30	30	50	180
initial time (min)	10	5	0	30
temperature program rate (°C/min)	10	4	10	0
oven final temperature (°C)	120	150	120	180
final time (min)	15	0	5	0

[a] Capillary DB5, 30 m × 0.25 mm. [b] Capillary DBWAX, 30 m × 0.53 mm. [c] Preparative OV-17, 15% on Chromosorb W, 60–80 Mesh, 8 ft × 1/4 in. [d] Preparative XE-60, 15% on Chromosorb P, 40–60 mesh, 15 ft × 1/4 in.

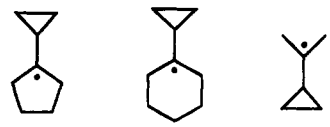
geometrically isomeric radicals **10a** and **11a** were formed, as is usual in CPC rearrangements.[24] As the concentration of CHD was increased from 0 to 3 M, the yield of CO_2 and **12** fell in parallel while the yield of **13** and **14** increased correspondingly. In contrast, the yield of **24–26** and **27** showed little change, suggesting that these products arise mainly in the solvent cage. Since **24–26** are disproportionation (k_{dis}) products while **27** is a recombination (k_{rec}) product, the data show that k_{dis}/k_{rec} is 4.1–5.0, which is exactly in the range expected for tertiary radicals.[25,26]

The product yield data were analyzed by a simple kinetic scheme where β-scission of **9** competes with reversible ring opening (cf. Scheme 2). A plot of (yield of CO_2)/(yield of **13a** + **14a**) versus 1/[CHD] should be linear and give an intercept equal to k_β/k_r. The three CHD concentrations in Table 2 indeed produced a straight line whose intercept was 0.16 ± 0.03. To calculate k_β from the intercept, we shall take k_r as (1.3 ± 0.3) × 10^7 s^{-1}, the average of the rearrangement rate constants that we determined for **28** and **29**.[27] Both higher and lower values of k_r have been reported for

(24) Beckwith, A. L. J.; Ingold, K. U. In *Free Radical Rearrangements in Ground and Excited States*; De Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, p 162.

(25) Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441.
(26) Burshtein, A. I.; Khudyakov, I. V.; Yakobson, B. I. *Prog. React. Kinet.* **1984**, *13*, 221.
(27) Engel, P. S.; Culotta, A. M. *J. Am. Chem. Soc.* **1991**, *113*, 2686.

30[28,29] but preliminary results on **30** from this laboratory[30] support our earlier figure. Thus we obtain k_β =

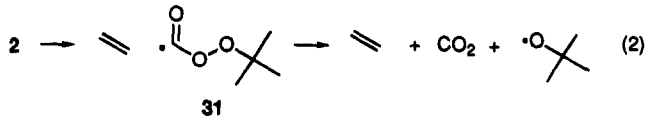


28 **29** **30**

$(2.1 \pm 0.6) \times 10^6$ s^{-1} and a lifetime for β-scission of **9** at 25 °C equal to 480 ± 140 ns.

The plot of (yield of CO_2)/(yield of **13a** + **14a**) versus 1/[CHD] gives a slope of 0.54 ± 0.05, which equals $k_\beta k_{-r}/k_t k_r$. Although more external data are required, an independent value of k_β can be derived from this slope. The known value of $k_t = 1.0 \times 10^5$ M^{-1} s^{-1} [27] and the assumption that k_r/k_{-r} for **9** is the same as for **28** (273)[27] leads to $k_\beta = 1.5 \times 10^7$ s^{-1}, which is 7 times higher than the value obtained from the intercept. However, this approach is surely less reliable than the one involving only one external parameter.

Although we have depicted scission of β-perester radicals as a one-step reaction (cf. eq 1), it is possible that an acyl radical (**31**) intervenes (cf. eq 2). If this radical decarboxylated relatively slowly, it might be



31 (2)

scavenged by CHD and turn up as *tert*-butyl performate.[32] The CO_2 balance would then be lowered and transesterification would give methyl formate as a product. A GC search for methyl formate was negative and the CO_2 balance was generally over 90% (cf. Table 2), consistent with cleavage of **2** directly to three fragments or with rapid β-scission of **31**. However, there is a distinct possibility that CHD is a poor scavenger for **31**.[33] A more compelling argument is based on a comparison of **31** with t-BuOCO•, whose decarboxylation is about 40 kcal/mol less exothermic than that of **31**. Decarboxylation of t-BuOCO• proceeds with a rate constant of 1.4×10^5 s^{-1} at 25 °C;[35] hence, if **31** is an intermediate in the fragmentation of β-perester radicals, its lifetime is likely to be short indeed.

In view of the two sets of weak bonds in **5** and **8**, the question arises whether these compounds might serve as a bifunctional initiators of polymerization.[11,12] Addition of *tert*-butyl radicals to styrene occurs with a rate constant of 1.3×10^5 M^{-1} s^{-1}.[36] If **6** is of similar reactivity, it will attack neat styrene (8.7 M) at a rate of 1.1×10^6 s^{-1} and will decarboxylate at a rate of 2.1×10^6 s^{-1}. Thus only 34% of the perester groups will be incorporated into the polymer for use as a second initiator. In contrast to **6**, radical **9** rearranges 6 times faster than it decarboxylates. The resulting primary radicals **10a** and **11a** should undergo ring closure (k_{-r}) 44 times slower than the β-scission that dominated the chemistry of **6**. Thus the majority (86%) of **9** that escapes the solvent cage will become an end group of the polymer in the form of **10a** and **11a**, suggesting that **8** is a better bifunctional initiator than **5**. Azo perester **8** is of further interest because one stage of polymerization could be initiated photochemically and a second stage by heating the perester-containing polymer. The reverse sequence of initiation events would fail on account of the short lifetime of β-azo radicals at elevated temperature,[1] but this problem could be surmounted by increasing the number of carbons separating the two functional groups.

In summary, compounds **5** and **8** are clean photochemical precursors of β-perester radicals, but **8** has more potential as a bifunctional initiator. Driven by entropy and formation of the stable CO_2 fragment, β-scission of **6** and **9** converts a carbon-centered radical to a more reactive *tert*-butoxyl one with a rate constant of $(2.1 \pm 0.6) \times 10^6$ s^{-1} at 25 °C.

Experimental Section

General Methods. The instruments employed here are the same as in a previous publication[27] except that all ^1H NMR spectra are recorded at 250 MHz and all ^{13}C spectra at 65 MHz. The CI-GC-MS work on **23b** and **27b** employed a 60-m Carbowax column in a Hewlett-Packard 5989A instrument.

Thiophenol, fluorobenzene, and 1,4-cyclohexadiene were distilled and the latter was then passed over alumina immediately before use. To purify *tert*-butyl hydroperoxide, a 100-g portion was dissolved in 1200 mL of pentane and ~5 g of solid KCl was added. The mixture was shaken and then allowed to stand for 3 h at room temperature. The separated aqueous phase was removed and the pentane solution was dried at 5 °C over $MgSO_4$. After removal of the $MgSO_4$ by filtration, the pentane was rotary-evaporated and the residue was distilled at 15 mm. The purity of this *tert*-butyl hydroperoxide was found to be 93.5% by iodometric titration.[37] The NMR solvents $CDCl_3$ and C_6D_6 from Cambridge Isotope Laboratory was used without further purification. The purity of all new compounds was established by ^1H NMR spectroscopy (see supplementary material).

All samples for photolysis were freeze-thaw degassed three times and sealed on a vacuum line, using dry ice-2-propanol (−78 °C) as a cooling bath. Photolyses were conducted using an Oriel 500-W high pressure mercury lamp and a 366-nm filter consisting of a 5 cm length of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (10 mg/100 mL water) and a Corning 7−54 glass filter.

1-*tert*-Butyl-3-cyclopropyl-3-methyl-5-pyrazolidinone (16) was made by Prentice's procedure[16] starting with *tert*-butylhydrazine and 3-cyclopropyl-2-butenoic acid (**15**).[15] The crude product was purified by distilling at 5 mmHg and collecting the material: bp 137−142 °C; yield 51%; ^1H NMR ($CDCl_3$) δ 0.15−0.51 (4H, m), 0.89 (1H, m) 1.18 (3H, s), 1.39 (9H, s), 2.10 (2H, m); ^{13}C NMR ($CDCl_3$) δ 0.70, 1.16, 17.85,

(28) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687.
(29) Burkhard, P.; Roduner, E.; Hochmann, J.; Fischer, H. *J. Phys. Chem.* **1984**, *88*, 773.
(30) Unpublished results obtained by Dr. Shu-Lin He in this laboratory by applying our previous method[27] to 2,2'-dicyclopropyl-2,2'-azopropane.[31] **Note Added in Proof.** A value of 4.1×10^7 s^{-1} was reported: Beckwith, A. L. J.; Bowry, V. W. *J. Am. Chem. Soc.* **1994**, *116*, 2710. A larger k_r increases the calculated β-scission rate of **9**. In collaboration with Drs. K. V. Ingold and J. Lusztyk, we are attempting to resolve the discrepancy between k_r determined by thiophenol trapping and nitroxyl radical trapping.
(31) Timberlake, J. W.; Martin J. C. *J. Org. Chem.* **1968**, *33*, 4054.
(32) Rüchardt, Ch.; Hecht, R. *Chem. Ber.* **1964**, *97*, 2716.
(33) The pivaloyl radical reacts at least 10 times more slowly with n-Bu_3SnH than does simple R• while CHD reacts about 20 times more slowly with R• than does n-Bu_3SnH. Since n-Bu_3SnH cannot efficiently intercept t-BuCO• [34] before decarbonylation ($k = 1 \times 10^5$ s^{-1}), it is most unlikely that CHD would be able to do so. One would not expect **31** to abstract hydrogen faster than t-BuCO•; hence, CHD should be a poor hydrogen donor to **31**.
(34) Lusztyk, J.; Lusztyk, E.; Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 292.
(35) Ruegge, D.; Fischer, H. *Int. J. Chem. Kinet.* **1986**, *18*, 146. We thank a referee for calling this work to our attention.
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24.69, 27.50, 43.58, 56.78, 58.13, 172.24; MS 57 (34), 81 (80), 99 (30), 109 (100), 125 (83), 140 (59), 181 (26), 196 ($M^{+\cdot}$, 53); HRMS calcd for $C_{11}H_{20}N_2O$ *m/e* 196.1576, found *m/e* 196.1577.

3-(*tert*-Butylazo)-3-cyclopropylbutanoic Acid (17). To 300 mg of **16** in 25 mL of water was added 2 g of NaOH. The reaction mixture was stirred under reflux while oxygen was bubbled through the solution. After 7 h, the reaction mixture was cooled to 25 °C and washed with ether, and the aqueous layer was acidified with 3 M HCl to pH 1; then, the water layer was extracted three times with ether. The combined ether extracts were dried over $MgSO_4$. After removal of the ether under reduced pressure, the residue (which contained **15** as byproduct) was purified by column chromatography on silica gel, eluting with 40% ethyl acetate in hexane: yield 57%; ^1H NMR ($CDCl_3$) δ 0.41–0.50 (5H, m), 1.18 (9H, s), 1.22 (3H, s), 2.65 (2H, AB pattern, J = 14.5 Hz); ^{13}C NMR ($CDCl_3$) δ 0.15, 0.59, 19.85, 21.73, 26.60, 44.19, 67.88, 67.94, 174.82; MS *m/e* 29 (55), 41 (59), 57 (100), 85 (71), 127 (13), 212 ($M^{+\cdot}$, 0.2), 213 ($M^{+\cdot}$ + 1, 2); HRMS calcd for $C_{11}H_{20}N_2O_2$ *m/e* 212.1525, found *m/e* 212.1521.

***tert*-Butyl 3-(*tert*-butylazo)-3-cyclopropylperbutanoate (8).** Into a 25-mL three-neck flask was placed a solution of 1,1-carbonyldiimidazole (0.27 g) in 3 mL of THF under N_2. A 0.19-g portion of **17** in 5 mL of THF was added. After stirring for 30 min, *tert*-butyl hydroperoxide (0.15 mL) was added dropwise at room temperature. The reaction mixture was stirred at room temperature for 24 h and was extracted with ether. The ether extracts were washed three times with 0.1 M NaOH and were dried over $MgSO_4$. After removal of the solvent, the residual yellow oil was purified by column chromatography on florsil using 20% EtOAc in hexane as eluent: yield 59%; ^1H NMR ($CDCl_3$) δ 0.36–0.46 (5H, m), 1.14 (9H, s), 1.23 (3H, s), 1.33 (9H, s), 2.58 (2H, AB pattern, J = 14.4 Hz); ^{13}C NMR ($CDCl_3$) δ 0.29, 0.36, 19.44, 21.45, 26.21, 26.72, 40.12, 67.13, 67.22, 82.93, 168.83; UV (C_6H_6) λ_{max} = 370 nm, ϵ = 23.7.

***tert*-Butyl 3-cyclopropyl-2-perbutenoate (24a)** was made from **15** by the *tert*-BuOOH/CDI method.[17] The product was mainly the *E* isomer: ^1H NMR ($CDCl_3$) δ 0.27–0.60 (4H, m), 0.98–1.05 (1H, m), 1.21 (9H, s), 1.84 (3H, s), 5.60 (1H, s).

***tert*-Butyl 3-(*tert*-butylazo)-3-methylperbutanoate (5)** was made by the same general route as **8**. First, 1-*tert*-butyl-3,3-dimethyl-5-pyrazolidinone was synthesized by Prentice's procedure[16] from *tert*-butylhydrazine. The crude product was purified by distilling at 10 mmHg and collecting the material: bp 103–105 °C; yield 62%; GC on DB-5 (Table 3) showed only one peak; ^1H NMR ($CDCl_3$) δ 1.22 (6H, s), 1.40 (9H, s), 2.03 (1H, s), 2.35 (2H, s); ^{13}C NMR ($CDCl_3$) δ 25.76, 27.55, 48.52, 55.68, 56.74, 173.04; MS *m/e* 27 (78), 39 (100), 41 (87), 57 (36), 114 (68), 170 ($M^{+\cdot}$, 8), 171 ($M^{+\cdot}$ + 1, 30); HRMS calcd for $C_9H_{18}N_2O$ *m/e* 170.1419, found *m/e* 170.1422. This pyrazolidinone was converted to 3-(*tert*-butylazo)-3-methylbutanoic acid similarly to the preparation of **17**. The azo acid was purified by column chromatography on silica gel with 30% ethyl acetate in hexane as eluent. The product, a yellow liquid that solidified in the freezer, was obtained in 30% yield: ^1H NMR (C_6D_6) δ 1.15 (9H, s), 1.22 (6H, s), 2.45 (2H, s); ^{13}C NMR ($CDCl_3$) δ 26.14, 27.37, 45.37, 67.91, 68.46, 176.94; MS *m/e* 27 (100), 29 (58), 41 (76), 57 (74), 59 (78) 101 (21), 187 ($M^{+\cdot}$ + 1, 1); HRMS calcd for $C_9H_{18}N_2O_2$ *m/e* 186.1368, found *m/e* 186.1370. The azo acid was converted to **5**, a light yellow liquid, in 62% yield using t-BuOOH/CDI:[17] ^1H NMR (C_6D_6) δ 1.16 (9H, s), 1.17 (9H, s), 1.29 (6H, s), 2.42 (2H, s); ^{13}C NMR ($CDCl_3$) δ 24.9, 26.2, 26.6, 40.6, 66.9, 67.1, 83.0, 168.8; UV (hexane) λ_{max} = 366 nm, ϵ = 20.

***tert*-Butyl 3-Methyl-3-perbutenoate (18).** 3-Methyl-3-butenoic acid was prepared in 67% yield according to the literature:[38] ^1H NMR (C_6D_6) δ 1.61 (3H, s), 2.72 (2H, s), 4.72 (2H, d). In a three-neck flask was placed 318 mg of CDI in 15 mL of dry THF, and then 150 mg of the olefinic acid was added. After 1 h, all of the acid had disappeared, as determined by TLC. A 0.15-mL portion of 93.5% *tert*-butyl hydroperoxide was added dropwise at 0 °C. After raising the temperature to ambient, the mixture was stirred for another 8 h. Most of the THF was removed by rotary evaporation and 20 mL of 1 M NaOH solution was added. The mixture was extracted with 3 × 20 mL of ether and the combined ether layer was dried with K_2CO_3. After filtering off the drying agent, the ether was removed under reduced pressure. The final product **18** was purified by chromatography on florisil eluting with 20% ether in pentane: yield 33%; ^1H NMR (C_6D_6) δ 1.13 (9H, s), 1.61 (3H, s), 2.65 (2H, s), 4.75 (2H, br, s).

***tert*-Butyl 3-methylperbutanoate (7) and *tert*-Butyl 3,3-dimethylperacrylate (19).** The appropriate carboxylic acids were reacted with CDI and *tert*-butyl hydroperoxide as described above: yield of **7**, 42%; yield of **19**, 33%; ^1H NMR (C_6D_6) **7** δ 0.76 (6H, d), 1.16 (9H, s), 1.82 (2H, d), 2.00 (1H, m); **19** 1.26 (9H, s), 1.33 (3H, s), 1.99 (3H, s), 5.50 (1H, s).

***N*-*tert*-Butoxy-2,2,6,6-tetramethylpiperidine (20).**[18] Into a 1-cm UV cell was placed a solution of 46.6 mg of 2,2′-dimethyl-2,2′-azopropane and 42 mg of Tempo in 2.5 mL of pentane. The cell was freeze-thaw-degassed three times with liquid N_2 and then sealed under vacuum. Photolysis at 366 nm was carried out at room temperature for 2 h. The solvent was removed by rotary evaporation and the residue was purified by chromatography on silica gel with hexane as eluent. The product was a colorless liquid: ^1H NMR (C_6D_6) δ 1.18 (6H, s), 1.20 (6H, s), 1.40 (9H, s), 1.43 (6H, m).

Methyl 3-Methyl-3-hexenoate (13b, 14b). Ester **21** was prepared according to the literature[39] and the colorless product was collected at 87–88 °C/30 mm: ^1H NMR ($CDCl_3$) δ 0.90 (3H, t), 1.48 (2H, m), 2.11 (2H, t), 2.15 (3H, s), 3.68 (3H, s), 5.66 (1H, s). A 0.75-g portion of **21** was dissolved in 150 mL of pentane and the solution was irradiated at 254 nm with three low-pressure mercury lamps for 24 h.[40] After removal of the solvent, the residual mixture of **13b** and **14b** was separated by preparative GC on an OV-17 column (cf. Table 3). The *Z* isomer **14b**, which was the major one, had the shorter retention time: **13b** ^1H NMR ($CDCl_3$) δ 0.93 (3H, t), 1.67 (3H, s), 2.02 (2H, m), 2.98 (2H, s), 3.67 (3H, s), 5.35 (1H, t); **14b** ^1H NMR ($CDCl_3$) δ 0.93 (3H, t), 1.76 (3H, s), 2.02 (2H, m), 3.05 (2H, s), 3.67 (3H, s), 5.35 (1H, t); MS *m/e* 55 (84), 67 (55), 82 (100), 83 (64), 142 ($M^{+\cdot}$, 27). Assignment of configuration was made by NOESY on samples of **13b** and **14b** isolated by preparative GC. Compound **14b** showed a large signal enhancement corresponding to mutual relaxation of hydrogens x and y (see structures in text) but there was almost no enhancement for the same hydrogens in **13b**.

Methyl 3-Cyclopropyl-2-butenoate (24b, 25b). To a stirred solution of 0.25 g of **15**[15] in 20 mL of ether was added dropwise a solution of diazomethane in ether until the solution became slightly yellow. After all starting material had disappeared according to TLC, the solvent was removed to afford a mixture of **24b** and **25b**. The isomers were separated by preparative GC on an XE-60 column (cf. Table 3), with **24b** eluting first: ^1H NMR ($CDCl_3$) **24b** δ 0.75 (4H, m), 1.53 (1H, m), 1.98 (3H, s), 3.67 (3H, s), 5.69 (1H, s); **25b** 0.82 (4H, m), 1.53 (3H, s), 3.22 (1H, m), 3.669 (3H, s), 5.73 (1H, s); MS (mixture of **24b** and **25b**) *m/e* 79 (76), 81 (73), 97 (45), 112 (100), 125 (39), 140 ($M^{+\cdot}$, 2).

Methyl 3-Cyclopropylbutanoate (26b). Attempted reduction of **24b** and **25b** with Mg in methanol[41] led to a mixture of **26b**, **13b**, and **14b**. Esters **26b** and **14b** could not be separated on five different preparative GC colums. The use of CuBr, Vitride, and s-BuOH[42] led to reduction of the ester group but excess $NaBH_4$ in MeOH at room temperature overnight[43] afforded a single product **26b** in 26% yield. The reaction was so slow that it was stopped when 73% of the starting material still remained. Pure **26b** was obtained by preparative GC on an OV-17 column (cf. Table 3): ^1H NMR ($CDCl_3$) δ 0.08–0.12 (2H, m), 0.40–0.44 (2H, m), 0.60 (1H, m),

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1.03 (3H, d, J = 6.5 Hz), 1.10 (1H, m), 2.30 (1H, dd, J_1 = 14.4 Hz, J_2 = 8 Hz), 2.42 (1H, dd, J_1 = 14.4 Hz, J_3 = 6.2 Hz), 3.67 (3H, s); MS (70 eV) m/e 59 (84), 69 (69), 74 (80), 82 (75), 127 (100), 142 ($M^{+\cdot}$, 2); ^{13}C NMR ($CDCl_3$) δ 3.56, 4.04, 17.68, 19.87, 36.27, 41.87, 51.36, 173.68.

2-Cyclopropylpropene (12) was prepared according to the literature.[44] In view of the low bp of the product, the reaction was stopped after 30 min to minimize loss by evaporation. After removal of the precipitate by filtration, the reaction mixture was washed with water and a GC-MS was run on the ethereal solution. **12**: MS m/e 27 (63), 29 (57), 65 (36), 67 (100), 82 (M, 39), which is similar to one of the photolysis products of **8**. By spiking the ethereal solution with the photolysis product mixture, it was confirmed by GC on a DB-5 column (temp 30 °C, retention time 3.85 min) that 2-cyclopropylpropene is a decomposition product of **8**.

Product Analysis. Gas yields were measured with a Töpler pump and gas buret. A series of three traps was used between the sample and the Töpler pump to fractionate the gases: liquid N_2 (−196 °C), a pentane slush bath (−120 °C), and a dry ice−acetone bath (−78 °C). The collected gases were analyzed on a Hewlett-Packard 5890 GC equipped with a molecular sieves 5A column at room temperature to separate N_2 and CH_4 and an n-octane/porisil column at 30 °C for 15 min and then programmed at 5 °C/min to 100 °C to separate CO_2, isobutane, and isobutene. The mole ratio of the gases was calculated using TC response factors from the literature.[45] After measuring the gas yield, the residue was dissolved in dry MeOH for transesterification.

Into a 25-mL three-neck flask under N_2 cooled to 0 °C, containing 1 mL of dry MeOH was added 60−70 mg of sodium (rinsed with pentane). After all the sodium had dissolved, the above MeOH solution of residue was added to the flask. The reaction mixture was stirred at 0 °C for 30 min, 5% HCl was added to bring the pH to ~7, and the mixture was extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried with K_2CO_3 and then injected into a GC-DB WAX column (cf. Table 3). Comparison with authentic samples showed that **8** afforded only **24b**−**26b** without added CHD but **20b**, **21b**, and **24b**−**26b** were produced in the presence of this radical scavenger. For quantitative analysis, the measured response factor for **21** was used for **13b**, **14b**, **26b**, and **27b**, and the response factor of **24b** and **25b** was determined separately. The response factors (area/mg) were as follows: N_2, 0.67; CO_2, 0.915; isobutene, 0.683; isobutane, 0.710; 2-cyclopropylpropene, 0.98; **13b**, **14b**, **26b**, **23**, 0.587; **24b**, **25b** 0.548. Because **23** differs from **26b** by only a *tert*-butyl group, we assumed that they have the same response factor.

Recombination product **23b** was isolated by transfesterification of **23a** from irradiated solutions of **5**, followed by preparative GC on OV-17, Table 3: ^1H NMR ($CDCl_3$) δ 0.89 (9H, s), 0.98 (6H, s), 2.3 (2H, s), 3.66 (3H, s); MS (EI) 57 (100), 73 (47), 83 (57), 101 (81), 116 (75), 141 (13), 157 (11); MS (CI, methane) 99 (16), 116 (13), 157 (23), 173 (M + 1, 100), 201 (M + 29, 11). Since no preparative GC peak was observed for the analogous compound **27b** on five different columns, the crude transesterification product was strongly evacuated to remove all volatiles. Spectral data were obtained on the residue, 80% of which was **27b**: ^1H NMR ($CDCl_3$) 0.94 (9H, s), 1.25 (3H, s), 0.6−1.0 (5H, m), 2.3 (2H, AB, J = 12.5 Hz), 3.63 (3H, s); MS (EI) 57 (45), 81 (82), 99 (91), 109 (100), 141 (98); MS (CI, methane) 111 (27), 141 (39), 143 (100), 183 (15), 199 (M + 1, 7), 227 (M + 29, 3). Photolysis of **8** followed by transesterfication, and photolysis of methyl 3-(*tert*-butylazo)-3-cyclopropyl butanoate, the methyl ester of **8**, both led to the same compound, **27b**, as confirmed by GC coinjection.

Acknowledgment. The authors gratefully acknowledge the National Science Foundation and the Robert A. Welch Foundation for financial support. We also thank Professor Martin Newcomb and Dr. Keith U. Ingold for helpful discussion concerning CPC rearrangement rates and we thank Dr. David Hatchey, Department of Pediatrics, Baylor College of Medicine, for the CI-GC-MS work.

Supplementary Material Available: 250-MHz ^1H NMR spectra of all new compounds (18 pages). This material is contained in libraries on microfiche, immmediately 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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