J. Org. Chem. 1988, 53, 1632–1641

reactions of the *n*-nonyl and *tert*-butyl radicals with Tempo would suggest a value for k_1 of ca. 8–9 × 10^8 M^{-1} s^{-1} for the reaction of the cyclopentyl radical with Tempo in hydrocarbon solvents.

Experimental Section

All reagents and solvents used in this work were of the highest purity available commercially (>98%). They were either used as received or were further purified by standard procedures.

The lasers that were used are described in footnote a of Table I. The laser flash photolysis apparatus has been adequately described in earlier publications from this laboratory.[40,41] In a typical experiment, 2 mL of a solution of Tempo [(1 × 10^{-5})–(5 × 10^{-3}) M] in isooctane containing the precursor of the radical of interest was placed in a 7 × 7 mm^2 Suprasil quartz tube and was deoxygenated by purging for ca. 2–5 min with oxygen-free nitrogen. Up to 8 pulses from the laser were employed per sample, the results being signal-averaged. In all cases examined, identical results were obtained in these "static" systems as in systems in which fresh reagents flowed continuously through the cell.

Acknowledgment. We thank Dr. J. C. Scaiano for a generous allotment of time on his laser flash photolysis system and Professor A. L. J. Beckwith for a sample of **2** and for making his own results[13] available to use prior to publication.

Registry No. 1, 2564-83-2; 2, 80037-90-7; $CH_3(CH_2)_7CH_2\bullet$, 32757-65-6; $(CH_3)_3CCH_2\bullet$, 3744-21-6; $(CH_3)_3C\bullet$, 1605-73-8; $PhCH_2\bullet$, 2154-56-5; $PhMeCH\bullet$, 2348-51-8; $PhMe_2C\bullet$, 4794-07-4; $Ph_2CH\bullet$, 4471-17-4; $Ph_2MeC\bullet$, 51314-23-9; $Ph_3C\bullet$, 2216-49-1; 1-$C_{10}H_7CH_2\bullet$, 7419-60-5; 2-$C_{10}H_7CH_2\bullet$, 7419-61-6.

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[40] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753.

[41] Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396–4403.

Kinetics of the Coupling Reactions of the Nitroxyl Radical 1,1,3,3-Tetramethylisoindoline-2-oxyl with Carbon-Centered Radicals

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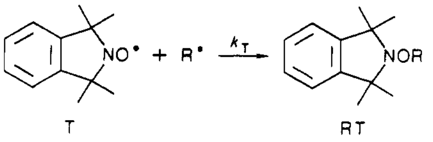
Radical clocks have been used to study the kinetics of the coupling of the nitroxyl radical 1,1,3,3-tetramethylisoindoline-2-oxyl (T) in cyclohexane or benzene with a variety of carbon-centered radicals including simple unhindered primary, secondary, and tertiary radicals (**1**, **2**, **3**, **4**, **5**, **8**, and **9**), neopentyl radicals (**6** and **7**), an alkoxyalkyl radical (**10**), an acyl radical (**11**), and alkoxycarbonyl radicals (**12** and **13**). The reaction rates are slower than expected for diffusion control. Within the limits of experimental error the coupling rate constant, k_T, for each radical is ca. 1 × 10^9 M^{-1} s^{-1} and is given by $\log k_T = 9.7 - 0.9/\theta$. Tempo couples with carbon-centered radicals at similar rates. The coupling reaction can be used as a kinetic probe. By this means discrepancies in existing data for some clocks have been resolved and the cyclopropylmethyl–butenyl radical rearrangement has been recalibrated ($\log k_r = 13.3 - 7.4/\theta$).

Introduction

Stable nitroxides are very efficient radical scavengers or traps and as such have been used to investigate the mechanisms of reactions involving putative free radical intermediates. This paper describes a reaction and analysis technique designed to extend the use of nitroxide radical coupling from a qualitative mechanistic probe to a reliable method for evaluating the kinetic parameters and stereochemistry of radical reactions.

1,1,3,3-Tetramethylisoindoline-2-oxyl (T)[1] and similar species[2] couple with carbon-centered radicals (R•), but not with oxygen-centered radicals, to give stable alkoxyamine products (RT).[3-8] Solomon and his co-workers[4] have used this selective coupling reaction to trap and identify reactive intermediates in the initial stages of free radical polymerizations of commercial and theoretical importance.



By analogy with other radical–radical termination processes, the rate constant, k_T, for nitroxide coupling has been assumed to be at or near the diffusion-limited value.[5] For example, Robbins and Eastman[6] used an estimated value of 10^{10} M^{-1} s^{-1} for the rate constant for coupling of the phenylacetyl radical with Tempo (2,2,6,6-tetramethylpiperidineoxyl) in their determination of the rate of decarbonylation (**11** → **11′**) of the former. More recent literature data suggest a lower value. Schmid and Ingold[7] found the rate constants for coupling of *n*-hexyl radical with various nitroxides in benzene to be 3–5 × 10^8 M^{-1} s^{-1} at 40 °C and these values agree well with the results of pulse radiolysis studies on reactions in water.[8] A laser flash photolysis study[9] of the coupling of cyclopropyl radical

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[1] Griffiths, P. G.; Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 397–402.

[2] Rizzardo, E.; Serelis, A. K.; Solomon, D. H. *Aust. J. Chem.* **1982**, *35*, 2013–2025, and references cited therein.

[3] Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1985**, *36*, 1573–1588.

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[5] (a) Griffiths, P. G.; Rizzardo, E.; Solomon, D. H. *J. Macromol. Sci., Chem.* **1982**, *17*, 45–53. (b) Grant; R. D.; Griffiths, P. G.; Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 2447–2459.

[6] Robbins, W. K.; Eastman, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 6077–6079.

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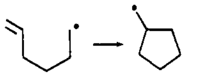
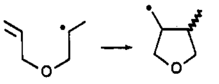
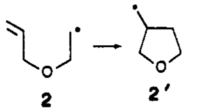
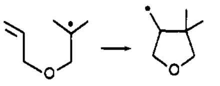
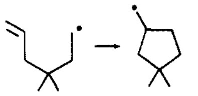
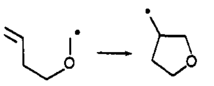
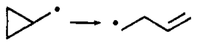
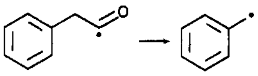
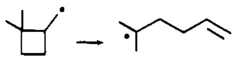
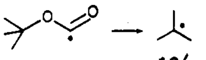
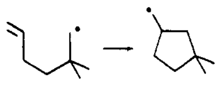
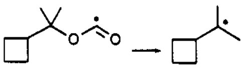
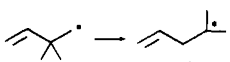
0022-3263/88/1953-1632$01.50/0

Table I. Clock Reactions

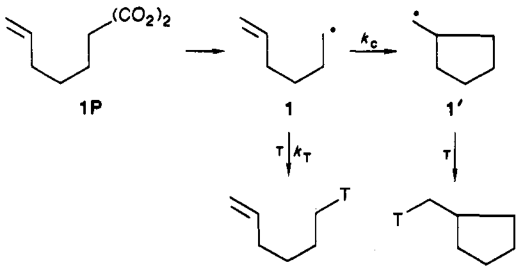
reaction	precursor[a,b]	reaction	precursor[a,b]
 1 1′	DAP (60–125 °C)	 8 8′	BPE (60–122 °C)
 2 2′	DAP (60–125 °C)	 9 9′	BPE (60–122 °C)
 3 3′	DAP (60–125 °C)	 10 10′ (= 2′)	BPE (60–122 °C)
 4 4′	DAP (40–80 °C) BPE (60–125 °C)	 11 11′	PhCH$_2$CHO with DBPO (40–80 °C), TBHN (100 °C)
 5 5′	DAP (80 °C)	 12 12′	see text
 6 6′ (= 3′)	DAP (60–125 °C)	 13 13′	see text
 7 7′	DAP (60–125 °C)		

[a] Radical precursors were diacyl peroxides (DAP), *tert*-butyl peresters (BPE), di-*tert*-butyl peroxyoxalate (DBPO), and *tert*-butyl hyponitrite (TBHN). [b] Temperature ranges over which the clock reactions were studied are given in brackets.

with Tempo gave $k_T = 1.2 \times 10^9$ M^{-1} s^{-1} at 25 °C. However, ESR measurements using nitroxides in polymerizing mixtures and nitroxide/oxygen competition experiments[10] gave values more than an order of magnitude lower.

The use of the nitroxide coupling reaction as an accurate kinetic probe requires the determination of reliable values of k_T for a variety of radical types. In the present work k_T has been measured by the use of suitable free radical rearrangements as radical "clocks".[11] The direct determination of k_T for various radicals and Tempo by laser flash photolysis is described in the accompanying paper by Chateuneuf, Lustyk, and Ingold.[12]

Scheme I



1P 1 1′ 1T 1′T

One of the best known and most accurately calibrated of radical clocks is the irreversible ring closure of the 5-hexenyl radical (1) to the cyclopentylmethyl radical (1′).[13] When this reaction is conducted in such a way that ring closure competes with trapping of the initial radical by T (Scheme I) the relative yields of uncyclized (1T) and cyclized (1′T) products are related to [T].

Under pseudo-first-order conditions (i.e. when the initial trap concentration $[T]_i$ is much greater than that of the precursor $[\mathbf{1P}]_i$)[14] the steady-state kinetic equations give

$$k_T/k_c = [1T]/\{[1'T][T]_i\} \qquad (1)$$

where [1T]/[1′T] is the ratio of the final molar concentrations of the alkoxyamine products. Since k_c is known for this reaction,[13] k_T can be calculated.

The literature provides a wealth of radical rearrangements which can be used as clocks.[11,15] However, the clock reactions preferred for the present purpose were those which (a) have been reliably calibrated in the experimental temperature range, (b) give stable coupled products which can be readily resolved by liquid chromatography and identified by their spectral/analytical data, and (c) have accessible rate constants (i.e. 10^5 s^{-1} < k_r < 10^9 s^{-1}). The clocks employed are listed in Table I. For convenience each radical has been assigned a number N, the corresponding radical arising from the clock reaction is designated N′, the respective products from coupling with the nitroxide T are NT and N′T, and the radical precursor is NP.

Results

Radical Trapping Method. Accurately determined mixtures of the nitroxide, T, and the radical precursor in

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[9] Johnston, L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 4877–4881.

[10] Aleksandrov, A. L.; Pliss, E. M.; Shivelov, V. F. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1979**, *28*, 2262–2266. Pliss, E. M.; Aleksandrov, A. L. *Izv. Akad Nauk SSSR, Ser. Khim.* **1974**, 2197–2201.

[11] Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317–323.

[12] Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.*, previous paper in this issue.

[13] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742.

[14] Where this is not true eq 1 can be replaced by a numerically integrated expression.

[15] Beckwith, A. L. J. In *Radical Reaction Rates in Liquids*, Landoldt-Bornstein, New Series; Fischer, H., Ed.; Springer: West Berlin, 1984; Vol. 13a.

cyclohexane or benzene were degassed by 4 freeze/thaw cycles and sealed in vacuo in ampules which were then immersed in constant temperature (±0.2 °C) oil baths for about 10 to 20 reaction half-lifes.[16] Where the reaction was very rapid (e.g. reactions involving *tert*-butyl peroxyoxalates above 80 °C) the precursor was injected through a septum into a small vial containing a purged preheated solution of T.

Product mixtures were analyzed by reversed-phase high performance liquid chromatography (RP-HPLC)[17] with isocratic or gradient elution (methanol/water). Since T contains an aromatic chromophore isolated from the coupling site, UV detection at 270 nm was uniformly sensitive to the trap and trapped products (except **11T**, see product spectral data). Hence, the ratios of HPLC peak areas were equal to the ratios of molar concentrations of trapped products. Small samples of the substituted hydroxylamines produced by trapping were obtained by preparative reverse or normal phase HPLC or by MPLC (medium pressure liquid chromatography) and were identified by their spectral and analytical data.

Product Stability. The thermal stabilities of the product mixtures were tested by prolonged heating. Radical product ratios were unaffected below 120 °C except for **10T** and for those containing trapped tertiary alkyl radicals (**5′T**, **7′T**, **9T**, **12′T**, and **13′T**). However, in the range 115–130 °C the rate of change was slow (e.g. $k \sim 2.5 \times 10^{-5}$ s^{-1} for **7T**/**7′T** in cyclohexane at 125 °C) compared with the peroxide decomposition rates ($k \sim 2 \times 10^{-3}$ s^{-1} for **7P** at 125 °C).[16] Consequently, accurate kinetic data were available up to about 130 °C for all of the rearrangements studied here.

The stabilities of the products under the conditions used for analysis were tested by the analysis of solutions of product mixtures in the HPLC mobile phase (80–95% methanol) at intervals of time. Only **10T** was significantly labile, presumably by solvolysis of this acetal-like product; this problem was overcome by buffering the mobile phase with 0.5% sodium acetate.

Generation of Radicals. Alkyl radicals were generated by thermolysis of appropriate diacyl peroxides (eq 2) or *tert*-butyl peresters (eq 3) as indicated in Table I. The latter, which were used when the correspondwing diacyl peroxides could not be prepared or decomposed too rapidly to give accurate kinetic data, gave more complex product mixtures because of the production of *tert*-butoxyl radicals (eq 3). When the solvent (S–H) was a good hydrogen

$$(RCO_2)_2 \rightarrow 2R^{\bullet} + 2CO_2 \qquad (2)$$

$$RCO_2OBu\text{-}t \rightarrow R^{\bullet} + CO_2 + {}^{\bullet}OBu\text{-}t \qquad (3)$$

donor (e.g. cyclohexane), it underwent hydrogen atom abstraction by *tert*-butoxyl radicals to afford S. Hence in such solvents the peresters gave S–T together with the expected products R–T and R′–T. With benzene as solvent a complex mixture of products arose via β-scission, by reactions of the solvent, and by hydrogen atom abstraction from the precursor, products, and trap.[18]

Table II. Relative Yields of Hydroxylamines from Hex-5-enyl Radical in Cyclohexane at 80.8 °C

$[T]_1$[a] (mM)	$[\bar{T}]$[b] (mM)	%(1T + 1′T)[c]	1T(%)/1′T(%)[d]
0.465	0.437	9.3	0.451 (22)
0.931	0.875	10.4	0.874 (39)
1.86	1.75	11.5	1.84 (8)
4.19	3.94	10.2	4.09 (12)

[a] Stock solutions were 0.500, 1.00, 2.00, and 4.50 mM in T; these figures were corrected for thermal expansion based on a coefficient of 0.00124/°C. [b] Mean concentrations during the reactions were calculated from $[\bar{T}] = [T]_i(100 + \%T)/200$, where %T is the %HPLC area assigned to T in the product mixture. [c] Percentages of total integrated area using UV detection at 270 nm; actual yields based on **1P** were in the range 60–80%. [d] Product ratios were averaged from three runs; the standard deviation is in units of the last significant figure.

Table III. Temperature Variation of k_T/k_c for Hex-5-enyl Radical 1

temp, °C	$[\bar{T}]$[b] (mM)	yield 1T (%)	yield 1T′ (%)	k_T/k_c (M^{-1})
60.4	0.91	3.84	2.53	1670
	1.83	0.34	1.46	1620
80.8	0.87	4.87	5.57	1010
	1.75	6.81	3.70	1050
100.0	0.84	6.91	3.74	645
	1.69	6.23	5.76	640
123.5	0.83	3.47	10.87	385
	1.53	6.74	11.84	372

[a] Temperatures are ± 0.3 °C. [b] Stock solutions were 1.00 and 2.00 mM in T at 22 °C; the concentrations were corrected for thermal expansion.

The yields of trapped products were usually in the range 50–90%, with diacyl peroxides generally being less productive than peresters. Low yields reflect the tendency of peroxides to (a) decompose by polar routes,[19] (b) give solvent cage radical recombination products, and (c) undergo nitroxide-induced decomposition.[20]

Determination of Kinetic Parameters. For all of the irreversible rearrangements studied here the expected rate expression (eq 1) was followed to within experimental error. Illustrative data obtained for the 5-hexenyl ring closure (**1** → **1′**) are given in Table II. Linear regression analysis gives

$$[1T]/[1'T] = -0.011 + 1043[\bar{T}](M), \ \langle r \rangle = 0.9999$$

thus, $k_T/k_c(1) = 1043$ M^{-1} at 80 °C. Substitution of the literature value[13] of k_c of 1.38×10^6 s^{-1} gives $k_T = 1.4 \times 10^9$ M^{-1} s^{-1} at 80 °C in cyclohexane.

Arrhenius expressions for the rate ratios k_T/k_c were obtained by thermolysis of sets of identical reaction mixtures at various temperatures. To optimize analytical precision over the temperature range, the trap concentrations were chosen to give approximately equal concentrations of trapped initial and rearranged radicals ([1T] ≃ [1′T]) at an intermediate temperature.

The usual Arrhenius treatment of the data obtained in this way for **1** → **1′** (Table III) gives eq 4 ($\theta = 2.3RT$)

$$\log (k_T/k_c) = -0.65 + 5.93/\theta, \ \langle r \rangle = 0.9985 \qquad (4)$$

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[16] At low trap concentrations the decomposition rates of the peroxide precursors could be estimated from of these or similar species available in *Organic Peroxides*; Swern, D., Ed; Wiley-Interscience: New York, 1970.

[17] GC analysis was unsuitable because the alkoxyamine products, especially those of tertiary alkyl and stabilized radicals, were unstable at the required injector/column temperatures; see, for example: Bolsman, T. A. B. M.; Blok, A. P.; Frijns, J. H. G. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 313–319. Cuthbertson, M. J.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 1957–1970. Beckwith, A. L. J.; O'Leary, M., unpublished results.

[18] Recent investigations have shown that the unwanted abstraction products can be reduced or eliminated in some cases by the addition of 1,4-cyclohexadiene. The cyclohexadienyl radical generated by hydrogen atom abstraction undergoes disproportionation rather than coupling with T.

[19] Taylor, K. G.; Govindan, G. C. K.; Kaelin, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2091–2099.

[20] Moad, G.; Rizzardo, E.; Solomon, D. H. *Tetrahedron Lett.* **1981**, *22*, 1165–1168.

Table IV. Kinetic Parameters for Radical Clocks and Nitroxide Coupling Reactions

	clock reactions[a]				experimental data[b]			trapping kinetics		
reactn	$10^{-6}k_r$ (80 °C) (s^{-1})	log (A_r/s^{-1})	E_r (kcal/mol)	ref	k_T/k_r (80 °C) (M^{-1})	log ($A_Tt\cdot A_r^{-1}/M^{-1}$)	$E_r - E_T$ (kcal/mol)	$10^{-8}k_T$ (80 °C) ($M^{-1}\ s^{-1}$)	log ($A_T/M^{-1}\ s^{-1}$)	E_t (kcal/mol)
1 → **1′**	1.35	10.37 (32)	6.85 (42)	13	930	−0.6	5.9	14	9.7	0.9
2 → **2′**	26.5	9.9	4.0	23	82	−0.3	3.5	19	9.6	0.5
3 → **3′**	19.1	10.5 (2)	5.2 (6)	21	68	−0.5	4.2	13	10.0	1.0
4 → **4′**	44.1	11.3 (17)[c]	5.9 (11)[c]	25, 33	2.41	−3.9	7.0	1.0	7.4	−1.1
	157.0	13.9 (4)	7.7 (2)	33, 34				43	10.0	0.6
5 → **5′**	7.41	13.03 (36)	9.95 (58)	24	242 (60)			18 (8)		
6 → **6′**	9.46	9.7 (2)	4.4 (6)	21	118	−0.8	4.5	11	8.9	−0.1
7 → **7′**	19.7	10.49	5.16	54	28	−2.0	5.7	5.5	8.5	−0.5
	24.0[d]	11.33[d]	6.38[d]	*d*				6.6	9.3	0.7
8 → **8′**	11.5	9.6 (6)	4.1 (10)	27	74	−0.45	3.8	10	9.2	0.3
9 → **9′**	34	9.7 (4)	3.5 (8)	this work	57	−0.6	3.8	19	9.1	−0.3
10 → **10′**	0.42	10.7 (5)	8.2 (5)	23	2010 (400)			8		
11 → **11′**	25.6	11.0 (4)	5.8 (6)	38	27[e]	−0.9[e,f]	3.8[e,f]	7	10.1	2.0
12 → **12′**	3.6	13.8 (4)	11.7 (8)	47	630	−4.3[f]	11.4[f]	23	9.5	0.3
	4.1[g]	14.0[g]	12.1[g]					48	10.9	1.9
13 → **13′**	12	13.4 (10)	10.2 (14)	25	149	−3.7[i]	9.6	18	9.7	0.6
	60[g]	14.0[g]	10.2[g]		169[f,g]			72	10.3	0.6

[a] $\log k_r = \log A_r - \Delta E_r/2.3RT$; errors, where available, have been corrected to 95% confidence limits; figures derived from stannane experiments are based on the most recent values for k_H, ref 26. [b] The solvent was cyclohexane and the relative Arrhenius parameters are for the temperature range 60–125 °C except where otherwise indicated. [d] Arrhenius expression derived from the published data. [e] Derived by use of k_H for neopentyl radicals, ref 13. [g] In benzene. [g] Figures obtained by use of the higher estimate for $2k_T$ (*tert*-butyl), see text, ref 47. [h] Temperature range 40–90 °C. [i] Temperature range 20–80 °C.

When combined with the literature expression for log k_c,[13] this gives the temperature dependence of k_T

$$\log k_T = 9.7 - 0.9/\theta \qquad (5)$$

Hence at 25 °C in cyclohexane, $k_T = 1.1 \times 10^9\ M^{-1}\ s^{-1}$.

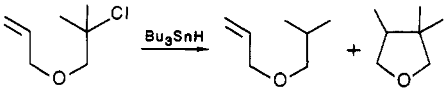
Alkyl Radicals. Values of k_T and of the associated Arrhenius parameters obtained as described above for the simple alkyl radicals **1**–**3** and **5**–**9** are listed in Table IV. Also included are data for the cyclopropylmethyl radical ring opening (**4** → **4′**), discussion of which is presented separately below. As the rate constants for the clock reactions for primary alkyl radicals **1** to **6** span a large range of values,[11,21-23] the required trap concentrations vary from about 10^{-4} M for **1** to concentrated solutions in benzene (~1 M) for **4**.[22] The clocks used also cover a range of radical size from C4 to C8 and of structure from unhindered to neopentyl.

The secondary and tertiary alkyl "horlogerie"[11] is much less well-stocked than the primary. The ring opening of **13′** was too slow[24,25] to be useful, while experimental difficulties[26] precluded the use of the calibrated 1-methylhex-5-enyl and 1,1-dimethylhex-5-enyl radical ring closures. However, the ether analogues **8** and **9** provided clocks with convenient rates and separable products. Ring closure of radical **8** has been previously reported to favor formation of the cis product [k_c(cis)/k_c(trans) = 2.3 at 65 °C].[27b] In accord with this observation formation of the cis stereoisomer of the trapped product **8′T** was found to be preferred over the temperature range 60–120 °C. The observed ratios of products fit the expression

$$\log k_c(\text{cis})/k_c(\text{trans}) = -0.7 + 1.8/\theta,\ \langle r \rangle = 0.96$$

which gives k_c(cis)/k_c(trans) = 2.9 at 65 °C.

The rearrangement **9** → **9′** had not been previously studied. It was calibrated for this work by the reaction of tributylstannane with the tertiary alkyl chloride **14**. For example, neat stannane with 10% (molar) of **14** and a trace of AIBN gave a 31:69 ratio of the uncyclized (**15**) and cyclized ether (**16**) products, respectively, at 80 °C. The relative cyclization rate obtained in the usual way[21] over the range 40–90 °C is given by



14 **15** **16**

$$\log k_c/k_H = 1.25(\pm\ 0.70) - 0.45(\pm\ 0.50)/\theta$$

The most recent value of k_H[28] (for *tert*-butyl radicals) then gave the value presented in Table IV. The rate constant at 65 °C ($2.6 \times 10^7\ s^{-1}$) for ring closure of **9** is slightly greater than those for the primary radical **2** ($1.7 \times 10^7\ s^{-1}$) and the secondary radical **8** ($8.2 \times 10^6\ s^{-1}$). These results conform to the trend in the analogous all-carbon series[27] but run counter to thermodynamic and steric expectations and counter to the trend observed for α-substituted cyclopropylmethyl[29] and cyclobutylmethyl radical[24] ring openings. They can perhaps be rationalized on the basis of Pross'[30] radical reactivity observations (i.e. tertiary > secondary > primary for nucleophilic radical additions) combined with steric considerations.

Cyclopropylmethyl Radical. Radical **4** was generated from bis(cyclopropylacetyl) peroxide (40–80 °C) and from *tert*-butyl cyclopropylperacetate (60–125 °C). The diacyl peroxide gave low radical yields; for example, at 60 °C the yield of **4T** plus **4′T** was only 15% (HPLC). Other studies have shown that this peroxide decomposes primarily by polar routes.[31,32] The perester gave much better yields

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(21) Beckwith, A. L. J.; Easton, C. J.; Lawrence, T.; Serelis, A. K. *Aust. J. Chem.* **1982**, *36*, 545–560.

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

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(25) Ingold, K. U.; Maillard, B.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 970–974.

(26) The open-chain and cyclized trapped species had nearly identical HPLC retention.

(27) (a) Burkhard, P.; Roduner, E.; Hochmann, J.; Fischer, H. *J. Phys. Chem.* **1984**, *88*, 773–777. (b) Beckwith, A. L. J.; Blair, I. A.; Phillipou, G. *Tetrahedron Lett.* **1974**, 2251–2254.

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(29) Beckwith, A. L. J.; Moad, G. *J. Chem. soc., Perkin Trans. 2* **1980**, 1473–1482.

(30) Pross, A. *Isr. J. Chem.* **1985**, *26*, 390–394.

(31) Taylor, K. G.; Govindan, C. K.; Kaelin, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2091–2099.

Table V. Yields of Hydroxylamines Formed from Cyclopropylmethyl Radical 4 in Cyclohexane

temp, °C	reactn time (h)	$10^{-3}[\bar{T}]^b$ (M^{-1})	**4T**(%)/ **4′T**(%)	k_T/k_r (M^{-1})	yield (%)
40.2	172^c	94.9	0.85	9.01	22
	172^c	191	1.7	8.67	19
59.4	102	46.5	0.24	5.22	21
		93.1	0.46	4.96	26
		181	0.86	4.76	19
80.0	19	22.1	0.057	2.53 (15)	52
		44.6	0.11	2.49	58
		89.8	0.22	2.43	61
		178	0.46	2.38	44
		260	0.63	2.43	38
100.0	5	82.9	0.13	1.59	81
		168	0.26	1.57	64
122.0	0.6	83.0	0.07	0.876	82
		160	0.14	0.881	76

[a] Temperatures are ±0.3 °C. [b] Corrected for trap decrement and thermal expansion of the solvent; stock solutions were 25.0, 50.1, 100, 200, and 300 mM in T at 22 °C; in each experiment $[T]_i = 13.3[\mathbf{4P}]_i$. [c] Bis(cyclopropylacetyl)peroxide precusor.

especially at higher temperatures (80–90% at 100 °C), although the product mixture was contaminated with compounds formed via hydrogen atom abstraction as outlined above. However, product ratios **4T**/**4′T** did not depend on the choice of precursor.

Possible changes in the activity coefficient of T at the relatively high concentrations required to study this rearrangement were shown to be negligible by the excellent fit of data obtained from 0.02 to 0.3 M (saturated in T) to eq 1: $\mathbf{4T}/\mathbf{4'T} = 0.003 + 2.48[\bar{T}]$ with $\langle r \rangle = 0.9991$ (5 concentrations) at 80 °C in cyclohexane. The Arrhenius expression for k_T/k_r obtained from data at 40 °C, 59 °C, 80 °C, 100 °C, and 122 °C with at least two $[T]_i$ (0.20 M and 0.10 M) at each temperature is given in Table IV.

The cyclopropylmethyl radical ring opening was studied with a view to testing the trapping technique on a very fast radical clock and one in which the rapid quenching rate of T would provide a great experimental advantage over the conventional reductive techniques. However, its status as a radical clock at near ambient temperatures is open to question because (a) ESR data[22] obtained over the range 128–153 K show a large amount of scatter, (b) as pointed out by Mathew and Warkentin[33] the previous data give the corrected Arrhenius expression $\log k_r = 11.3 - 5.9/\theta$, $\langle r \rangle = 0.851$, from which the calculated rate constant (9.6×10^6 s^{-1} at 25 °C) is much lower than those indicated by product studies, i.e. $4\text{–}8 \times 10^7$ s^{-1} (triphenylstannane),[29] and 1.5×10^8 s^{-1} (tributylstannane),[35] and (c) on theoretical grounds the preexponential term is too low; a value of at least 10^{13} s^{-1} is to be expected.[22,36]

The data presented in Tables IV and V support this conclusion. Both the corrected Arrhenius coefficients for k_r obtained from Ingold's ESR measurements[22,34] and those suggested by Warkentin[34] give results for k_T which are out of step with those obtained by the use of other clocks. It appears, therefore, that neither of the available calibrations for the cyclopropylmethyl radical rearrangement is correct; in the Discussion section below we suggest an alternative approach.

Table VI. Hydroxylamines Obtained from Phenylacetyl Radical at 80 °C in Benzene[a]

$[T]_i$ (mM)	yield **11T** (%)	yield **11′T** (%)	yield Me-T[b] (%)	**11T**(%)/ **11′T**(%)[c,d]
151 (+5% **11P**)	10.10	2.52	0.30	4.0
92 (+10%)	8.17	2.91	0.21	2.8
55 (+10%)	5.81	4.21	0.17	1.4

[a] $[T]_i = 20[\text{DBPO}]_i$. [b] Trapped methyl. [c] HPLC areas corrected for absorptivity difference. [d] Linear regression give $\mathbf{11T}(\%)/\mathbf{11'T}(\%) = 0.08 + 26.7[T]_i$, $\langle r \rangle = 0.983$; thus $k_T/k_D = 26.7$ M^{-1} at 80 °C.

Alkoxymethyl Radicals. The ring-closure of (3-butenyloxy)methyl radical, **10**, has previously been investigated in these laboratories by steady-state ESR[23] and by tributylstannane reduction.[37] Thermolysis of *tert*-butyl (3-butenyloxy)peroxyacetate (**10P**) in the presence of low concentrations of T (0.05–0.5 mM) afforded both of the expected products, **10′T** and **10T**. The former was shown to be identical with **2′T** by NMR and by HPLC peak enhancement. The uncyclized hydroxylamine, **10T**, was labile above 90 °C and was acid-sensitive (see above).

The experimental rate ratio $k_T/k_r = 3805$ M^{-1} (±300 M^{-1}) at 60 °C when combined with the extrapolated ESR cyclization rate constant ($k_r = 2.4 \times 10^5$ s^{-1})[23] gave a trapping rate constant $k_T = 9.1 \times 10^8$ M^{-1} s^{-1} at 60 °C. This is consistent with values derived for alkyl radicals in view of the uncertainty in the ESR rate expression and its extrapolation.

Acyl Radicals. Decarbonylation of the phenylacetyl radical **11** has been studied by ESR[11,38] ($k_D = 9 \times 10^2$ s^{-1} at 156 K), CIDNP[39] ($k_D = 5\text{–}10 \times 10^6$ s^{-1} at 31 °C), ESR spin trapping[40] ($k_D > 7 \times 10^6$ s^{-1} at 40 °C), and more recently by laser flash photolysis[41] ($k_D = 5.6 \times 10^6$ s^{-1} at 25 °C, $\log k_D = 11.0 - 5.8/\theta$). As the data obtained by laser flash photolysis were expected to be the most accurate they were used to calibrate k_T (Table IV).

The radical **11** was produced by hydrogen atom abstraction from phenylacetaldehyde by the *tert*-butoxyl radicals generated by thermolysis of di-*tert*-butyl peroxyoxalate (DBPO). The major products, **11T** and **11′T**, were isolated in 60–80% yield (based on DBPO). However, at low concentrations of aldehyde (<5%) significant quantities of Me-T were also detected. Presumably Me-T arises from trapping of the methyl radicals formed by β-scission of *tert*-butoxyl radicals. The product formed via hydrogen atom abstraction from the benzylic position of phenylacetaldehyde (i.e. trapped α-formylbenzyl) was suspected among the minor products but was too labile to be isolated by HPLC.

The results obtained at 80 °C are summarized in Table VI. If $k_D = 2.65 \times 10^7$ s^{-1} at 80 °C,[41] the trapping rate constant has a value in benzene at 80 °C of 8.3×10^8 M^{-1} s^{-1}. Similar experiments performed over the temperature range 40–100 °C gave the rate coefficients presented in Table IV.

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(32) Walling, C.; Waits, H. P.; Milovanonic, J.; Pappiaonnov, C. G. *J. Am. Chem. Soc.* **1970**, *92*, 4927–4932.

(33) Mathew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981–7984.

(34) Mathew and Warkentin[33] have used the radical trapping method (with GC analysis[16]) to calibrate this rearrangement. k_T was assumed to be one-fifth of the diffusion-limited rate calculated theoretically, i.e. $\log k_T = 11.5 - 3.2/\theta$; this rate constant is still about three times higher than that calculated in this work from **1** → **1′**. However, their expression $\log (k_T/k_i) = -3.1 + 5.45/\theta$ over the range 30–90 °C is not in serious conflict with that given in Table IV considering the different solvents used (hexafluorobenzene versus cyclohexane).

(35) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902–7015.

(36) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1968.

(37) Pigou, P. E., unpublished results.

(38) Brunton, G.; McBay, H. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 4447–4450.

(39) Lehr, G. F.; Turro, N. J. *Tetrahedron* **1981**, *37*, 3411–3434.

(40) Perkins, M. J., Roberts, B. P. *J. Chem. Soc., Perkins Trans. 2* **1974**, 297–303.

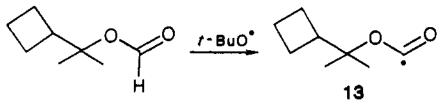
(41) Gould, I. R.; Baretz, B. H.; Turro, N. J. *J. Phys. Chem.* **1987**, *91*, 925–929.

Alkoxycarbonyl Radicals. The rate of decarboxylation of the *tert*-butoxycarbonyl radical ($\mathbf{12} \rightarrow \mathbf{12'}$) has been measured over a wide temperature range by steady-state ESR.[42] However, the absolute rate constant for this clock (and for $\mathbf{13} \rightarrow \mathbf{13'}$) may be about five times faster than that originally reported due to uncertainty in the rate of bimolecular termination of *tert*-butyl radicals.[43] The higher estimates of the decarboxylation rate agree well with Rüegge and Fischer's recent calibration by time-resolved ESR[47] (used in Table IV). Decarboxylation $\mathbf{13} \rightarrow \mathbf{13'}$ has also been calibrated by steady-state ESR;[48] the rate is significantly faster than $\mathbf{12} \rightarrow \mathbf{12'}$ and consequently is more convenient for competition with the trapping reaction.

The radicals **12** and **13** were generated from the appropriate *OO-tert*-butyl monoperoxyoxalate esters *17* (R = *t*-Bu or c-$C_4H_7CMe_2$). Since nitroxides are known to

$$\underset{\mathbf{17}}{\mathrm{ROCOCO_2OBu}\text{-}t} \rightarrow \mathrm{RO\dot{C}O} + \mathrm{CO_2} + t\text{-}\mathrm{BuO^{\bullet}}$$

induce decomposition of diacyl peroxides,[20] it is conceivable that T may produce one or both of the products (e.g. **13T**, **13′T**) by a pathway not involving dissociated free radicals. Evidence against this hypothesis includes the observations that (a) the rate of decomposition of the precursor was independent of [T] throughout the range 1 mM to 10 mM, (b) there was excellent adherence to eq 1, and (c) **13** generated from the formate ester **18** by abstraction with *tert*-butoxyl radicals at 60 °C and 80 °C gave data identical with those obtained when **13** was generated from the peroxide **13P**.



13

18

T versus Tempo. Most other measurements[7,8] of coupling rates of radicals with nitroxides have been conducted with Tempo or with 4-substituted Tempo. In order to correlate these measurements with k_T we have performed direct competition experiments between Tempo and T for ethyl radicals.

Equimolar mixtures of Tempo and T with 0.2 equiv of dipropionyl peroxide were heated in cyclohexane and then analyzed by GC.[49] The rate ratio k_T/k_{Tempo} over a wide range of concentrations was very close to unity, i.e. $k_T = 1.05(\pm\ 0.08)k_{\mathrm{Tempo}}$. Although the difference in rates may be amplified for more stable and/or sterically hindered[50] radicals, this result indicates that rates obtained for Tempo and for T should be more or less interchangeable for coupling with "normal" alkyl radicals.[12,51]

Discussion

The data presented in Table IV reveal no clearcut correlation between the magnitude of k_T and the stability or geometry of the carbon-centered radicals undergoing nitroxide coupling. For example, k_T appears to have much the same value at 80 °C for the primary alkyl radicals, **1**, **2**, **3**, **5**, and **6**, the secondary radical **8**, the tertiary radical **9**, the alkoxyalkyl radical **10**, and the acyl radical **11**. This does not necessarily mean that there is no such relationship; indeed, the results of concurrent laser flash photolysis studies[12] indicate that highly stabilized and/or sterically hindered radicals certainly do show lower values of k_T. However, in our case the variations in k_T are most likely to reflect uncertainties both in the present set of experiments and in those used to determine the kinetics of clock reactions. The most reliable data should be those obtained by the use of the well-studied hexenyl system ($\mathbf{1} \rightarrow \mathbf{1'}$). It is noteworthy that the value of $k_T(\mathbf{1})$ is very close to that derived from the earlier set of experiments described in our preliminary communication[52] and to that reported for the reaction of the nonyl radical with Tempo.[12]

The variations in the Arrhenius parameters presented in Table IV are more pronounced. Once again, they probably reflect, at least in part, the experimental uncertainties in the determination of the kinetics of both the clock and the nitroxide coupling reactions. As before, the data obtained by use of the hexenyl cyclization ($\mathbf{1} \rightarrow \mathbf{1'}$) are likely to be the most reliable. Therefore, until more accurate data become available we suggest that eq 6 be

$$\log k_T = 9.7 - 0.9/\theta \qquad (6)$$

used to calculate rate constants for the coupling reaction of the nitroxide T in nonpolar solvents with all simple primary, secondary, and tertiary alkyl radicals and with acyl or alkoxycarbonyl radicals. We also suggest that within the temperature range 0–80 °C no substantial error will be introduced if the value of k_T for the coupling reactions of T with all sterically unhindered carbon-centered radicals in nonpolar solvents is assumed to be 1×10^9 s^{-1}. Since we have shown that T and Tempo are of approximately equal reactivity, the same assumption applies to coupling of the latter.

On the basis of these assumptions it is possible to resolve previous discrepancies in the calibration of some important radical clocks. For example, we have noted above that neither the earlier kinetic data[22,23] nor those recently presented[33,34] for ring-opening of cyclopropylmethyl radical (**4**) give plausible values of k_T. More acceptable data can be obtained by assuming that k_T for **4** is the same as that for the hexenyl radical **1**. The experimental rate ratios k_T/k_i (Table V, where k_i is the rate constant for the reaction $\mathbf{4} \rightarrow \mathbf{4'}$) were combined with values of k_T calculated from eq 6 to give $\mathbf{k}_i$ from 40 °C to 123 °C. These data (14 points) were combined with the ESR data (14 points)[22] by a least-squares fit to the transition-state equation, $k_i/T = A \exp(-E/RT)$. At around 140 K this gave $\log k_i = 12.9$

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[42] Griller, D.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1972**, 747–756.

[43] (a) In their estimation of k_D Griller and Roberts[42,46] initially used the following kinetic data for the termination of *tert*-butyl radicals: $2k_t = 5.7 \times 10^{10} \exp(-1000/T)$, $= 2.10^9$ M^{-1} s^{-1} at 298 K in di-*tert*-butyl peroxide. However, they later suggested that the rate constant should be increased approximately fivefold.[44] Subsequent measurements have supported the higher value, e.g. $2k_t = 1.2.10^{11} \exp(-1000/T)$ in methylpentane,[45] and $2k_t = 8.1 \times 10^9$ at 298 K in di-*tert*-butyl peroxide.[46]

[44] Perkins, M. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2*, **1975**, 77–82; footnote.

[45] Schuh, H.; Hamilton, E. J.; Paul, H.; Fischer, H. *Helv. Chim. Acta* **1974**, *57*, 2011–2024.

[46] Watts, G. B.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 851–854.

[47] Rüegge, R.; Fischer, H. *Int. J. Chem. Kinet.* **1986**, *18*, 145–158.

[48] Ingold, K. U.; Maillard, B.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* 1981, 970–974.

[49] These products were volatile and stable enough for accurate GC analysis.[17]

[50] There are indications that adducts of T with hindered stabilized radicals are more thermostable than those with Tempo; see: Bizilj, S.; Kelly, D. P.; Serelis, A. K.; Solomon, D. H.; White, K. E. *Aust. J. Chem.* **1985**, *38*, 1657–1671.

[51] We have recently developed a technique for measuring the scavenging efficiency of any radical trap by using a radical clock *and* T in competition reaction mixtures. Results confirm that Tempo and T have about equal efficiencies for alkyl radicals (primary, secondary, and tertiary).

[52] Beckwith, A. L. J.; Bowry, V. W.; O'Leary, M.; Moad, G.; Rizzardo, E.; Solomon, D. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1003–1004. The rate ratios reported in this communication were substantially correct but the Arrhenius parameters for k_T have now been significantly amended because of the use of more precise analytical techniques and the more scrupulous removal of oxygen which competes directly with the nitroxide for coupling with carbon-centered radicals.

$- 7.0/\theta$ while at ordinary temperatures

$$\log k_i = 13.3 - 7.4/\theta \qquad (7)$$

The overall correlation coefficient was 0.989. This Arrhenius equation is consistent with theoretical predictions and with the experimental preexponential for the related cyclobutylmethyl ring opening[24] (e.g. **5** → **5′**). The rate constant, $k_i = 8 \times 10^7$ s^{-1} at 25 °C, agrees well with other estimates for this radical[29,35] and (comparatively) with estimated rates for substituted cyclopropylmethyl radicals.[25,53] We suggest, therefore, that eq 7 be adopted for the calculation of k_i for the cyclopropylmethyl radical clock (**4** → **4′**) within the temperature range 40–130 °C.

Discrepancies in the values of the rate constants for decarbonylation of the phenylacetyl radical **11** can be similarly reconciled. In earlier work Robbins and Eastman[6] assumed a diffusion-controlled coupling rate constant for acyl radicals with Tempo of 10^{10} M^{-1} s^{-1} to derive a rate of about 10^8 s^{-1}, for k_D(**11**). Substitution of a more reasonable estimate, about 1×10^9 M^{-1} s^{-1}, gives $k_D \simeq 10^7$ s^{-1} at 25 °C; this brings all of the above estimates for k_D to agreement to within experimental uncertainties. Extrapolation of the rate expression from flash photolysis to 156 K gives $k_D \simeq 750$ s^{-1} or by the more exact procedure (for large temperature differences) of extrapolating the implied transition-state rate expression to 156 K gives $k_D \simeq 980$ s^{-1} in good agreement with the ESR figure.[38]

The Arrhenius parameters for coupling of T with the alkoxycarbonyl radical **12** are similar to those determined for alkyl radicals, but the derived trapping rate constant at 80 °C (2.2×10^9 M^{-1} s^{-1}) is a little larger than most of the others in Table IV; possibly the reaction is aided by the polar nature of **12**. However, the results tend to confirm the accuracy of the recently published[47] rate expression for **12** → **12′**.

The rate of decarboxylation of the alkoxycarbonyl radical **13** → **13′** is less well-defined. If we accept that k_D(**13**) has the same values as k_D(**12**), it is possible to deduce the Arrhenius expression (eq 8) for the rate constant k_D(**13**).

$$\log k_D(\mathbf{13}) = 13.0 - 10.0/\theta \qquad (8)$$

This is close to the original ESR data.[48] The marked lowering of E_A and log A relative to those for **12** → **12′**[47] (Table IV) suggests participation of the cyclobutyl ring bonds in the transition structure for C–O bond fission.

The only other radicals for which the kinetic data deviate significantly from eq 6 are the two neopentyl species **6** and **7**. Although in these cases it is possible that the trapping rates are affected by steric hindrance, it seems more likely that the deviations reflect experimental errors in both the calibration[21,54] and trapping experiments.

Finally, it is noteworthy that all of the values of k_T determined here are about 1 order of magnitude less than would be expected for a reaction under diffusion control. Since the observed activation energies are *less* than those expected for diffusion-controlled processes, the low values of k_T are associated with low values of log A (9.7 as compared with ca. 11.5 for bimolecular termination of simple alkyl radicals in nonpolar solvents).[55] Although the basis of this entropic barrier to coupling cannot be identified at present, we believe that it is associated with the dipolar character of nitroxide radicals and with the electronic and solvent reorganization which must occur when coupling takes place. It seems significant that the kinetics of nitroxide coupling are highly solvent-dependent.[56]

Conclusion

The kinetic data discussed above indicate that a wide range of alkyl, substituted-alkyl, acyl, and alkoxyacyl radicals couple with the nitroxide radical T or with Tempo at less than the diffusion-controlled rates in nonpolar solvents. For many practical purposes the rate constant k_T can be assumed to be ca. 1×10^9 M^{-1} s^{-1} within the temperature range 0–80 °C. More accurate values can be obtained from the Arrhenius expression (eq 6). The data is in satisfactory agreement with the results of concurrent laser flash photolysis experiments.[12]

These values of k_T constitute an important data base for the utilization of nitroxide coupling as a kinetic probe for a wide variety of radical reactions. The method lacks many of the drawbacks of the tin hydride method, i.e., reagent reactivity (with air, activated double bonds and carbonyl groups, halocarbons, with nitro, sulfoxy, disulfide and peroxide groups), and the stannyl byproducts which can be very difficult to remove. The nitroxide also carries the advantage of having a much greater radical quenching rate (~10^9 M^{-1} s^{-1} versus ~10^6 M^{-1} s^{-1}) and less selectivity than tin hydrides.

The potential of the method has been exemplified by the calibration of the cyclopropylmethyl rearrangement **4** → **4′**. Our new data (eq 7) now allow this rearrangement to be employed as a reliable kinetic standard for fast radical reactions.[57] The nitroxide coupling reaction is clearly capable of providing quantitative data on ring-substituted cyclopropylmethyl radicals for which rearrangement rates were previously inaccessible.

Other valuable kinetic data obtained or confirmed in the course of this work include Arrhenius expressions for the decarbonylation of phenylacetyl radical **11** and for decarboxylation of the alkoxycarbonyl radicals **12** and **13**.

In future communications k_T will be further defined in a wide range of solvents and calibration data for a number of alkyl, cyclopropyl, and aryl radical rearrangements will be presented.

Experimental Section

Melting points were determined on a Reichert hot stage microscope. Spectra were recorded on the following instruments: JEOL FX-200, MH-100, and PMX-60 (^{1}H NMR), JEOL FX-200 (^{13}C NMR at 50.1 MHz), Perkin-Elmer 683 (IR), and Varian DMS90 (UV–vis). IR spectra were taken on CCl_4 solutions in 0.5-mm NaCl cells and UV–vis spectra on methanol solutions in 10-mm silica cells. Gas chromatography was performed on a Varian 6000 instrument with a vitreous silica capillary column (25 m) (25QC2/BP5 1.0) with helium carrier gas. Elemental analyses were performed by the ANU Analytical Service unit.

High pressure liquid chromatography (HPLC) was performed with a Spectra Physics SP-8000B ternary proportionating pump, digital integrator, and UV–vis detector (analytical cell). Columns used were 1, Alltech ODS (5 μm) 4.6 mm × 250 mm; 2, Altex ODS (5 μm) 10 mm × 250 mm; and 3, Dupont C-8 (10 μm) 10 mm × 300 mm.

Reaction/Analysis Technique. For kinetic studies reaction mixtures were made up volumetrically from common stock solutions and then degassed by the freeze/thaw method (4 cycles at 0.1 mm, liquid N_2 coolant) and sealed in 1-mL Pyrex ampules.

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Whenever possible, a series of reaction mixtures (e.g. for Table II) were heated simultaneously and analyzed under identical HPLC conditions. Solvent loss during degassing was found to be less than 3%, and peroxide decay up to the heating stage was insignificant (by HPLC). After completion of the reaction the solvent was evaporated in vacuo and the residue dissolved in MeOH before analysis; product ratios were not affected by this process.

All analyses were carried out on column 1 with isocratic H_2O/MeOH elution (1.3 mL/min) and with UV detection at 270 nm (analytical UV cell). Under these conditions and with base-line component separation the analytical precision was better than 5% for yields and 3% for product ratios. The hydroxylamines **5T** and **5′T** which had identical HPLC retention times were isolated by HPLC and the product ratios determined by NMR by integrating CH_2O on **5T** and $=CH_2$ on **5′T**; the precision obtained (~15%) did not warrant a full kinetic study. Other product isolations were readily performed on a small scale with columns 2 or 3. For difficult separations the different polar selectivities of silica and ODS were used in two-step separations, i.e. flash chromatography (2% → 10% ether in pentane) followed by reverse-phase HPLC of the fractions.

Materials. The nitroxyl radical T was made in three steps from *N*-benzylphthalimide in 25% overall yield by the procedure of Griffiths et al.,[1] mp 128 °C (lit.[1] mp 128–129 °C). *tert*-Butyl hydroperoxide (70% aqueous) was dried by standing over successive small amounts of 3 Å sieve in the cold (4 °C). Phenylacetaldehyde was distilled twice before use to remove polymers. Other reagents were used without purification. Di-*tert*-butyl peroxyoxalate[60] (DPBO), di-*tert*-butyl hyponitrite[61] (TBHN), di-*tert*-butyl monoperoxyoxalate6[0] (**12P**), bis(6-heptenoyl) peroxide[7] (**1P**), bis(cyclopropylacetyl) peroxide[62] (**4P**), and 1-methyl-1-cyclobutylethyl formate[42] were prepared by literature procedures. Allyl isobutyl ether (**16**) which was required as a GC standard was prepared by the literature method[58] while 3,3,4-trimethyltetrahydrofuran (**17**, 74%), bp 105–107 °C, was made by distillation from *p*-toluenesulfonic acid of the diol obtained by $LiAlH_4$ reduction of trimethylsuccinic acid.[59]

General Procedures. (1) Hydrolysis. Esters were hydrolyzed by stirring in a solution of KOH (1.5 molar equiv in a little water) in the appropriate alcohol (e.g. allyl ester in aqueous allyl alcohol) until the starting material was consumed (GC). The usual workup followed by Kügelrohr distillation afforded the carboxylic acid, the purity of which was checked by a small-scale diazomethane esterification and GC analysis.

(2) Acid Chlorides. To a solution of the acid in benzene (5 volumes) was added oxalyl chloride (2 molar equiv) and then a few microliters of DMF. The vigorous reaction was complete after about 15 min at room temperature. The excess of reagent was removed by careful evaporation and by displacement with a further quantity of benzene. Since some of the acid chlorides (e.g. for 4) had low bp's vigorous evaporation was avoided.

(3) Diacyl Peroxides. The acid chloride and finely powdered Na_2O_2 (1.2 molar equiv) in dry ether (~5 volumes) was treated with small aliquots (~5 μL) of water until the initially vigorous reaction subsided. The mixture was washed successively with water, saturated aqueous $NaHCO_3$, and brine, then dried ($MgSO_4$), and evaporated to give diacyl peroxides in 60–90% yields and >90% iodometric[63] purity. The carbonyl bands in the IR and the α-protons in the NMR spectra were very useful guides to purity.

(4) *tert*-Butyl Peresters. The acid chloride in pentane was slowly added to a mixture of anhydrous *tert*-butyl hydroperoxide (0.95 molar equiv) and pyridine (1.8 molar equiv) in pentane (10–20 volumes) at <10 °C and then the resulting solution was stirred for 1 h longer at room temperature. The mixture was washed successively with water, cold 15% H_2SO_4, water, saturated aqueous $NaHCO_3$, and brine and then evaporated to give the peresters in 50–80% yields. Purity was checked by NMR, IR, and iodometric titration.[63]

Bis(3-(allyloxy)propanoyl) Peroxide (2P). Allyl 3-(allyloxy)propanoate[64] was converted by procedures 1, 2, and 3 into the required peroxide (53%) of 98% purity (iodometric): ^{1}H NMR δ ($CDCl_3$, 100 MHz) 2.60 (t, 2 H), 3.61 (t, 2 H), 3.96 (d, 2 H), 5.10 (m, 2 H), 5.80 (m, 1 H); IR ν_{max} 1785, 1805 (C=O, Fermi split) cm^{-1}.

Bis(4,4-dimethyl-6-heptenoyl) Peroxide (3P). Diethyl isopropylidenemalonate[65] (20.0 g) was added to a cooled (−30 °C) mixture of allylmagnesium bromide (formed at 0 °C from 16.4 g of allyl bromide) and CuCl (0.5 g) in ether (200 mL) and then allowed to warm slowly to room temperature. The usual workup gave diethyl (1,1-dimethylbut-3-enyl)malonate (20.3 g, 85%), bp 101–104 °C at 2.0 mm: ^{1}H NMR δ (CCl_4, 100 MHz) 1.05 (s, 6 H), 1.25 (t, 6 H), 2.15 (d, 2 H), 3.12 (s, 1 H), 4.12 (q, 4 H), 5.00 (m, 2 H), 5.65 (m, 1 H); IR ν_{max} 1741 cm^{-1}. The malonate was decarbethoxylated by Krapcho's method[66] to give ethyl 3,3-dimethylhex-5-enoate (6.61 g, 82%), bp 70–72 °C at 6.0 mm (91% GC): ^{1}H NMR δ (CCl_4, 100 MHz), 1.00 (s, 6 H), 1.22 (t, 3 H), 2.04 (d, 2 H), 2.10 (s, 2 H), 4.03 (q, 2 H), 5.01 (m, 2 H), 5.70 (m, 1 H). The ester was converted via procedures 1 and 2 into the acid chloride (4.0 g), which was added to excess diazomethane in ether (from 23 g of Diazald, ≃3 molar equiv) at 0 °C. After 3 h at 0 °C, evaporation of the mixture yielded 1-diazo-4,4-dimethylhept-6-en-2-one (4.1 g, 98%) which was dissolved in methanol (50 mL) and treated (at 50 °C) with 0.5-mL portions of a solution of silver benzoate (0.3 g) in triethylamine (3 mL) as previously described.[67] Filtration and distillation gave methyl 4,4-dimethylhept-6-enoate (3.61 g, 81%), bp 80–81 °C at 12 mm (91% GC). A sample (1.0 g) was purified by flash chromatography on silica gel with 2% → 5% ether in pentane and converted by procedures 2 and 3 to the required peroxide (91% from acid chloride) of >97% purity by ^{1}H NMR and iodometric titration: ^{1}H NMR δ (CCl_4, 100 MHz) 0.94 (s, 6 H), 1.60 (t, 2 H), 2.02 (d, 2 H), 2.15 (t, 2 H), 5.01 (m, 2 H), 5.70 (m, 1 H); IR ν_{max} 1775, 1800 cm^{-1}.

Bis[(2,2-dimethylcyclobutyl)acetyl] Peroxide (5P). Methyl (2,2-dimethyl-3-oxocyclobutyl)acetate (3.4 g), prepared from α-pinene in five steps,[68] was treated with BF_3 etherate (10 mL) and ethanedithiol (8 mL). After 8 h the reaction mixture was diluted with pentane and washed successively with water, 5% aqueous NaOH (twice), and brine, and then dried and evaporated to give the thioketal (3.8 g) which was desulfurized with Raney nickel W2 (20 g) in boiling methanol (200 mL) to give, on workup, methyl (2,2-dimethylcyclobutyl)acetate (1.66 g, 56%). This ester was purified to 97% (GC) by flash chromatography on silica gel with 3% ether in pentane: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.00 (s, 3 H), 1.07 (s, 3 H), 1.60 (m, 4 H), 1.98 (m, 1 H), 2.32 (m, 3 H), 3.13 (s, 3 H); IR ν_{max} 1738 (C=O) cm^{-1}. The purified ester was converted by procedures 1, 2, and 3 into the required peroxide (62%): IR ν_{max} 1778, 1805 cm^{-1}.

Bis(3,3-dimethylhept-6-enoyl) Peroxide (6P). 3-Butenylmagnesium bromide was conjugatively added to diethyl isopropylidenemalonate[65] at −10 °C and the resulting malonate ester decarbethoxylated as for **3P** to give ethyl 3,3-dimethylhept-6-enoate (55% overall), bp 68–72 °C at 0.5 mm: ^{1}H NMR (CCl_4, 100 MHz) δ 1.00 (s, 6 H), 1.3 (m, 4 H), 2.1 (m, 5 H), 4.01 (q, 2 H), 5.00 (m, 2 H), 5.81 (m, 1 H); IR ν_{max} 1735 (C=O) cm^{-1}. This was converted by procedures 1, 2, and 3 into the title peroxide (48%) of 94% purity (iodometric): ^{1}H NMR (CCl_4, 100 MHz) δ 1.05 (s, 6 H), 1.50 (t, 2 H), 2.10 (m, 2 H), 2.35 (s, 2 H), 5.00 (m, 2 H), 5.78 (m, 1 H); IR ν_{max} 1778, 1790 (C=O) cm^{-1}.

Bis(3,3-dimethylpent-4-enoyl) Peroxide (7P). 3,3-Dimethylpent-4-enoic acid[69] was converted by procedures 2 and 3 into the title peroxide (85%) of 95% purity (iodometric): ^{1}H NMR ($CDCl_3$, 60 MHz) δ 1.18 (s, 6 H), 2.36 (s, 2 H), 4.93, (m, 2 H), 5.87

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(q, 1 H); IR ν_{max} 1770, 1790 (C═O) cm^{-1}.

***tert*-Butyl 3-(Allyloxy)-2-methylperoxypropanoate (8P).** α-Alkylation of propanoic acid with allyl chloromethyl ether[70] using the method of Pffefer et al.[71] (*with* HMPA) gave 3-(allyloxy)-2-methylpropanoic acid (76%), bp 80–87 °C at 0.3 mm, 95% purity (GC of Me ester): ^{1}H NMR (CCl$_4$, 60 MHz) δ 1.11 (d, 3 H), 2.52 (m, 1 H), 3.35 (m, 2 H), 3.75 (d, 2 H), 5.05 (m, 2 H), 5.65 (m, 1 H), 10.35 (s, 1 H); IR ν_{max} 1752 (C═O) cm^{-1}. It was converted by procedures 2 and 4 into the title perester (80%) with 95% purity (iodometric): ^{1}H NMR (CCl$_4$, 60 MHz) δ 0.99 (s, 2 H), 1.04 (f, 3 H), 2.56 (m, 1 H), 3.36 (m, 2 H), 3.77 (d, 2 H), 5.03 (m, 2 H), 5.65 (m, 1 H); IR ν_{max} 1776 (C═O) cm^{-1}.

***tert*-Butyl 3-(Allyloxy)-2,2-dimethylperoxypropanoate (9P).** Isobutyric acid was α-alkylated as above (*without* HMPA)[71] to give 3-(allyloxy)-2,2-dimethylpropanoic acid (70%), bp 84–87 °C at 0.3 mm, 96% pure (GC of methyl ester): ^{1}H NMR (CCl$_4$, 60 MHz) δ 1.18 (d, 6 H), 3.35 (m, 2 H), 3.85 (d, 2 H), 5.05 (m, 2 H), 5.45 (m, 1 H), 11.35 (s, 1 H); IR ν_{max} 1750 (C═O) cm^{-1}. It was converted by procedures 2 and 4 into the title perester (65%), 98% pure (iodometric): ^{1}H NMR (CCl$_4$, 60 MHz) δ 1.13 (s, 9 H), 1.21 (s, 6 H), 3.38 (s, 2 H), 3.87 (d, 2 H, 6 Hz), 5.15 (m, 2 H), 5.30 (m, 1 H); IR ν_{max} 1774 cm^{-1}.

***tert*-Butyl (3-Butenyloxy)peracetate (10P).** 3-Butenol (1.86 g, 30 mmol) was added to a slurry of NaH (1.50 g, 60 mmol) in DMF (15 mL). After 1 h bromoacetic acid (4.17 g, 30 mmol) in DMF (15 mL plus 1 mL decane to control frothing) was added slowly, andd the mixture was then stirred for a further 2 h. Dilution with water and extraction with CH$_2$Cl$_2$ followed by the usual procedure for isolation of the acidic component gave (3-butenyloxy)acetic acid (2.10 g, 63%), bp 70–80 °C at 0.3 mm: ^{1}H NMR (CCl$_4$, 100 MHz) δ 2.42 (q, 2 H), 3.61, (t, 2 H), 3.97 (s, 2 H), 5.00 (m, 2 H), 5.75 (m, 1 H), 11.2 (br s, 1 H); IR ν_{max} 1760 (C═O) cm^{-1}. It was converted via the imidazolide[7] into the required perester (0.90 g, 75%), 92% pure (iodometric): ^{1}H NMR (CCl$_4$, 100 MHz) δ 1.15 (s, 9 H), 2.40 (q, 2 H), 3.63 (t, 2 H), 4.00 (s, 2 H), 5.00 (m, 2 H), 5.75 (m, 1 H); IR ν_{max} 1773 (C═O) cm^{-1}.

***OO*-*tert*-Butyl *O*-1-Cyclobutyl-1-methylethyl Monoperoxyoxalate (13P).** Treatment of 2-cyclobutylpropan-2-ol[46] with an excess of *tert*-butyl peroxalyl chloride[59] as described by Bartlett and Pincock[72] gave the title compound as a colorless oil (81%) which was pure by NMR and IR but gave erratic results (80–110%) on iodometric analysis:[63] ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.25 (s, 9 H), 1.44 (s, 6 H), 1.6–2.1 (m, 6 H), 2.70 (quin, 1 H); IR ν_{max} 1752, 1801 (C═O) cm^{-1}.

Trapped Products. The alkoxyamine products (TR) were identified by (a) HPLC relative retention times from which the size and polarity of the addend R could be assessed; (b) kinetic behavior, since the ratios of conjugate products (e.g. **1T/1′T**) varied with [T] as in eq 1; (c) NMR spectra which were readily dissected into trap (T) and addend (R) components and the identity of R could be established by comparison with spectra of authentic ROH, RBr, or RCl; (d) UV and IR (only given for C═O compounds) spectra and combustion analyses. UV spectra did not significantly vary and all products (except **11T**, **11′T**) in methanol had λ_{max} (log ϵ) 216 (3.45), 257 (2.71), 264 (2.06), 270 (3.00) nm. Unusual features of the ^{1}H and ^{13}C NMR spectra arising from near and nonequivalence of the trap's four methyl groups in the alkoxyamine have been previously reported[2–5] and studied.[73] The methyl protons (centered near δ 1.45) can appear as a broad singlet, a doublet, or as a triplet (6 H + 3 H + 3 H) of variable peak broadness depending on the steric bulk and symmetry of the carbon-centered group at the coupling site (e.g. the above features can be found with primary, tertiary, and some secondary alkyl groups). The splitting is temperature-dependent and has been ascribed[73] to slow inversion at the nitrogen center.

2-(5-Hexenyloxy)-1,1,3,3-tetramethylisoindoline (1T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.42 (br s, 12 H), 1.58 (m, 4 H), 2.12 (q, 2 H, 7.1 Hz), 3.94 (t, 2 H, 6.3 Hz), 5.00 (m, 2 H), 5.85 (m, 1 H), 7.05 (m, 2 H), 7.20 (m, 2 H). Anal. Calcd for C$_{18}$H$_{27}$NO: C, 79.07; H, 9.95. Found: C, 78.78; H, 9.71.

2-(Cyclopentylmethoxy)-1,1,3,3-tetramethylisoindoline (1′T): ^{1}H NMR, (CDCl$_3$, 200 MHz) δ 1.43 (br s, 12 H), 1.58 (m, 4 H), 1.85 (m, 4 H), 2.22 (tt, 1 H), 3.15 (d, 2 H, 7.1 Hz), 7.08 (m, 2 H), 7.11 (m, 2 H). Anal. Calcd for C$_{18}$H$_{27}$NO: C, 79.07; H, 9.95. Found: C, 79.45; H, 9.91.

2-(2-(Allyloxy)ethoxy)-1,1,3,3-tetramethylisoindoline (2T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.43 (br s, 12 H), 3.6, (m, 2 H), 4.0 (m, 4 H), 5.16 (m, 1 H), 5.80 (m, 2 H), 7.01 (m, 2 H), 7.21 (m, 2 H). Anal. Calcd for C$_{17}$H$_{25}$NO$_2$: C, 74.14; H, 9.15. Found: C, 74.04; H, 8.99.

2-((3-Tetrahydrofuranyl)methoxy)-1,1,3,3-tetramethylisoindoline (2′T ≡ 10′T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.43 (br s, 12 H), 2.00 (m, 2 H), 2.51 (m, 1 H), 3.67 (m, 2 H), 3.68–3.95 (m, 4 H), 7.01 (m, 2 H), 7.21 (m, 2 H). Anal. Calcd for C$_{17}$H$_{25}$NO$_2$: C, 74.14, H, 9.15. Found: C, 74.43; H, 8.96.

2-((3,3-Dimethylhex-5-enyl)oxy)-1,1,3,3-tetramethylisoindoline (3T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.91 (s, 6 H), 1.41 (t, 2 H, 7.3 Hz) overlaps with 1.44 (br s, 12 H), 1.95 (d, 2 H, 8.3 Hz), 3.91 (d, 2 H, 7.3 Hz), 4.94 (m, 1 H), 5.72 (m, 2 H), 6.98 (m, 2 H), 7.16 (m, 2 H). Anal. Calcd for C$_{20}$H$_{31}$NO: C, 79.68; H, 10.36. Found: C, 79.36; H, 10.25.

2-((3,3-Dimethylcyclopentyl)methoxy)-1,1,3,3-tetramethylisoindoline (3′T ≡ 6′T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.01 (s, 6 H), 1.43 (br s, 12 H), 1.53–1.90 (m, 6 H), 2.20 (m, 1 H), 3.14 (d, 2 H, 7.5 Hz), 7.02 (m, 2 H), 7.11 (m, 2 H). Anal. Calcd for C$_{20}$H$_{31}$NO: C, 79.68; H, 10.36. Found: C, 79.36; H, 10.25.

2-(Cyclopropylmethoxy)-1,1,3,3-tetramethylisoindoline (4T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ −0.10 to 0.91 (m, 4 H), 1.30–1.49 (m, 13 H), 3.71 (d, 2 H, 7.8 Hz), 6.97 (m, 2 H), 7.13 (m, 2 H). Anal. Calcd for C$_{16}$H$_{23}$NO: C, 78.32; H, 9.45. Found: C, 78.46; H, 9.44.

2-(3-Butenyloxy)-1,1,3,3-tetramethylisoindoline (4′T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.39 (br s, 12 H), 2.30 (m, 2 H), 3.75 (t, 2 H, 7 Hz), 4.90 (m, 2 H), 5.71 (m, 1 H), 6.97 (m, 2 H), 7.13 (m, 2 H). Anal. Calcd for C$_{16}$H$_{23}$NO: C, 78.32; H, 9.45. Found: C, 78.54; H, 9.75.

2-((2,2-Dimethylcyclobutyl)methoxy)-1,1,3,3-tetramethylisoindoline (5T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.92 (s, 3 H), 1.11 (d, 3 H, 3.4 Hz), 1.41 (br s, 12 H), 1.4–1.8 (m, 4 H), 1.95 (m, 1 H), 3.63–4.03 (m, 2 H), 7.05 (m, 2 H), 7.21 (m, 2 H); ^{13}C NMR (CDCl$_3$, 50.1 Hz) δ 22.5, 23.5, 25.3, 30.3, 30.6, 32.1, 34.9, 38.4, 42.8, 121.6, 127.0, 145.6. Anal. Calcd for C$_{19}$H$_{29}$NO: C, 79.44; H, 9.15. Found: C, 79.31; H, 9.26.

2-((1,1-Dimethylpent-4-enyl)oxy)-1,1,3,3-tetramethylisoindoline (5′T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.26 (2 s, 9 H), 1.31 (s, 3 H), 1.46 (s) overlaps 1.48 (t, 7 Hz, total 8 H), 2.20 (m, 2 H), 4.95 (m, 2 H), 5.72 (m, 1 H), 7.21 (m, 2 H). Anal. Calcd for C$_{19}$H$_{29}$NO: C, 79.44; H, 9.15. Found: C, 79.71; H, 8.98.

2-((2,2-Dimethylhex-5-enyl)oxy)-1,1,3,3-tetramethylisoindoline (6T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.95 (s, 6 H), 1.35–1.49 (m, 14 H), 2.01 (m, 2 H), 3.81 (s, 2 H), 4.95 (m, 2 H), 5.8 (m, 1 H), 7.01 (m, 2 H), 7.14 (m, 2 H). Anal. Calcd for C$_{20}$H$_{31}$NO: C, 79.68; H, 10.36. Found: C, 79.62; H, 10.08.

2-((2,2-Dimethylbut-3-enyl)oxy)-1,1,3,3-tetramethylisoindoline (7T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.05 (s, 6 H), 3.82 (s, 2 H), 4.8–5.1 (m, 2 H), 5.91 (dd, 1 H, 17 Hz/10 Hz), 6.98 (m, 2 H), 7.10 (m, 2 H). Anal. Calcd for C$_{18}$H$_{27}$NO: C, 79.07; H, 9.95. Found: C, 78.78; H, 9.71.

2-((1,1-Dimethylbut-3-enyl)oxy)-1,1,3,3-tetramethylisoindoline (7′T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.22 (s, 3 H), 1.31 (s, 3 H), 1.40 (s, 6 H), 1.51 (br s, 6 H), 2.36 (d, 2 H), 5.05 (m, 2 H), 5.9 (m, 1 H), 7.01 (m, 2 H), 7.20 (m, 2 H). Anal. Calcd for C$_{18}$H$_{27}$NO: C, 79.07; H, 9.95. Found: C, 79.45; H, 9.91.

2-(2-(Allyloxy)-1-methylethoxy)-1,1,3,3-tetramethylisoindoline (8T): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.26 (d, 3 H, 8.1 Hz), 1.33 and 1.53 (d + br s, 6 H + 6 H), 3.40 (m, 1 H), 3.60 (m, 1 H), 4.05 (m, 3 H), 5.2 (m, 2 H), 5.95 (m, 1 H), 7.00 (m, 2 H), 7.12 (m, 2 H). Anal. Calcd for C$_{18}$H$_{27}$NO$_2$: C, 74.70; H, 9.40. Found: C, 74.65; H, 9.38.

2-((4-Methyl-3-tetrahydrofuranyl)methoxy)-1,1,3,3-tetramethylisoindoline (8′T). *cis*- and *trans*-**8′T** could not be preparatively separated (columns 2 or 3) but adequate analytical separation on column 1 was achieved at high retention times. By the use of the assignments for 4-methyltetrahydrofuran-3-

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methanol by Bogner et al.[74] as a guide, the NMR spectrum of the mixture could be analyzed: δ ($CDCl_3$, 200 MHz) cis 1.05 (d, CH_3, 6.8 Hz), 1.44 (br s, 4 CH_3), 2.53–2.65 (m, 2CH), 3.47 (m, 2 ring *cis*-CHH), 3.7–4.1 (m, 2 ring *trans*-CHH + CH_2OH), 7.10 (m, 2 Ar H), 7.23 (m, 2 Ar H); trans 1.12 (d, CH_3, 6.3 Hz), 1.44 (br s, 4 CH_3), 2.00–2.25 (m, 2 CH), 3.36 (m, ring *cis*-CHH), 3.61 (m, ring *trans*-CHH), 3.8–4.1 (m, 2 ring CHH + CH_2OH), 7.10 (m, 2 Ar H), 7.23 (m, 2 Ar H). NMR integration of the separable resonances was consistent with a cis to trans ratio of about 2.5. Anal. Calcd for $C_{18}H_{27}NO_2$: C, 74.70; H, 9.40. Found: C, 74.80; H, 9.51.

2-(2-(Allyloxy)-1,1-dimethylethoxy)-1,1,3,3-tetramethylisoindoline (9T): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.29 (s, 6 H), 1.23, 1.31, 1.46 (3 s, 12 H), 3.36 (s, 2 H), 3.99 (dt, 2 H), 5.08–5.28 (m, 2 H), 5.78–5.97 (m, 1 H), 7.10 (m, 2 H), 7.21 (m, 2 H). Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63. Found: C, 75.49; H, 9.31.

2-((4,4-Dimethyl-3-tetrahydrofuranyl)methoxy)-1,1,3,3-tetramethylisoindoline (9′T): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.03 (s, 3 H), 1.13 (s, 3 H), 1.21–1.55 (br m, 12 H), 2.27 (m, 1 H), 3.39–4.16 (m, 6 H), 7.08 (m, 2 H), 7.19 (m, 2 H). Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63. Found: C, 75.61; H, 9.72.

2-((3-Butenyloxy)methoxy)-1,1,3,3-tetramethylisoindoline (10T): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.43 (br s, 12 H), 2.15 (m, 2 H), 3.67 (t, 2 H, 7.8 Hz), 4.91–5.21 (m, 2 H), 5.75–6.00 (m, 1 H), 6.12 (s, 2 H), 7.11 (m, 2 H), 7.21 (m, 2 H). Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15. Found: C, 74.41; H, 9.27.

2-(Phenylacetoxy)-1,1,3,3-tetramethylisoindoline (11T), plates from hexane, mp 67–69 °C: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.35 (br s, 12 H), 3.77 (s, 2 H), 7.05–7.31 (m, 9 H); IR ν_{max} 1770, 1720 (C=O) cm^{-1}; UV λ_{max} (log ϵ) (MeOH), 224 (3.21), 257 (2.93), 264 (3.05), 270 (3.04) nm.

2-(Benzyloxy)-1,1,3,3-tetramethylisoindoline (11′T), plates from aqueous MeOH, mp 90–91 °C (lit.[5b] mp 89–91 °C), with all spectral data as previously reported.[5b] HPLC coinjection showed that **10T** and **10′T** had identical response factors at 270 nm (about 5% larger than "alkyl" products).

***tert*-Butyl 1,1,3,3-tetramethylisoindolin-2-yl carbonate (12T)**, plates from aqueous EtOH, mp 61–63 °C: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.41 (s, 6 H), 1.51 (s, 6 H), 1.53 (s, 9 H), 7.10 (m, 2 H), 7.21 (m, 2 H); IR ν_{max} 1778, 1750 (C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81. Found: C, 69.82; H, 8.46; N, 4.47.

2-*tert*-Butoxy-1,1,3,3-tetramethylisoindoline (12′T): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.30–1.52 (m, 21 H), 7.05 (m, 2 H), 7.23 (m, 2 H). Anal. Calcd for $C_{16}H_{25}NO$: C, 77.69; H, 10.19. Found: C, 77.50; H, 9.90.

1-Cyclobutyl-1-methylethyl 1,1,3,3-tetramethylisoindolin-2-yl carbonate (13T), plates from pentane, mp 71 °C: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.38 (s, 6 H), 1.43 (s, 6 H), 1.49 (2, 6 H), 1.60–2.10 (m, 6 H), 2.70 (quin, 1 H), 7.09 (m, 2 H), 7.24 (m, 2 H); IR ν_{max} 1773, 1748 (C=O) cm^{-1}. Anal. Calcd for $C_{20}H_{29}NO_3$: C, 71.44; H, 9.15; N, 4.38. Found: C, 71.11; H, 8.94; N, 4.05.

2-(1-Cyclobutyl-1-methylethoxy)-1,1,3,3-tetramethylisoindoline (13′T): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.25 (br s, 6 H), 1.36 (s, 6 H), 1.57 (br s, 6 H), 1.4–2.1 (m, 6 H), 2.50 (quin, 1 H, 7.3 Hz), 7.06 (m, 2 H); IR ν_{max} 2970, 2915, 2960, 1373, 1360, 910 cm^{-1}. Anal. Calcd for $C_{19}H_{29}NO$: C, 79.39; H, 10.17. Found: C, 79.17; H, 10.28.

Allyl 2-Chloro-2-methylpropyl Ether (14). Chloroacetic acid (11.7 g) in allyl alcohol (30 mL) was added to a solution of Na (7.5 g) in allyl alcohol (60 mL) at a rate which maintained reflux. Reflux (2 h), neutralization (CO_2), evaporation, acidification, ether isolation, and distillation afforded (allyloxy)acetic acid (10.5 g, 74%), bp 81–83 °C at 1.0 mm. The acid was converted to the methyl ester with BF_3 in methanol[75] and then converted with excess MeMgI to 1-(allyloxy)-2-methylpropan-2-ol (70% from the acid), bp 75–79 °C at 15 mm: NMR δ ($CDCl_3$, 200 MHz) 1.20 (s, 6 H), 2.42 (s, 1 H), 3.22 (s, 2 H), 3.99 (d t, 2 H), 5.15 (m, 2 H), 5.82 (m, 1 H). Attempts to make the bromide with concentrated HBr and PBr_3 at low temperature failed due to cleavage of the ether. However, treatment of the alcohol at 0 °C with concentrated $HCl/CaCl_2$ gave the title chloride (52%), bp 50–52 °C at 50 mm, GC purity 96%: NMR δ ($CDCl_3$, 200 MHz) 1.55 (s, 6 H), 3.44 (s, 2 H), 4.02 (d, 2 H), 5.19 (m, 2 H), 5.84 (m, 1 H).

Reaction of 14 with Tributylstannane. Mixtures of tributylstannane (10 molar equiv), **14**, and initiator in benzene were heated and analyzed (capillary GC) following procedures detailed elsewhere.[13] Reproducible kinetic data were difficult to obtain because of the high reactivity toward hydrostannylation of the double bond in **14** and **15**. However, slow initiation (di-*tert*-butyl peroxide above 80 °C), short reaction times, and high GC injection port temperature improved the precision.

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Registry No. **1**, 16183-00-9; **1T**, 113086-63-8; **1′T**, 113086-64-9; **2**, 3494-43-7; **2P**, 3395-63-9; **2T**, 113086-65-0; **2′T**, 113086-66-1; **3**, 86549-20-4; **3P**, 113086-67-2; **3T**, 113086-68-3; **3′T**, 113086-69-4; **4**, 2154-76-9; **4T**, 104877-20-5; **4′T**, 104877-21-6; **5**, 71880-26-7; **5P**, 113086-70-7; **5T**, 113086-71-8; **5′T**, 113086-72-9; **6**, 71880-21-2; **6P**, 113086-73-0; **6T**, 113086-74-1; **7**, 87110-24-5; **7P**, 87110-26-7; **7T**, 113086-75-2; **7′T**, 113086-76-3; **8**, 98041-04-4; **8P**, 113086-77-4; **8T**, 113086-78-5; **8′T** (isomer 1), 113086-79-6; **8′T** (isomer 2), 113086-80-9; **9**, 113086-81-0; **9P**, 113086-82-1; **9T**, 113086-83-2; **9′T**, 113086-84-3; **10**, 113086-85-4; **10P**, 113086-86-5; **10T**, 113086-87-6; **11**, 22673-58-1; **11T**, 113086-88-7; **11′T**, 89482-41-7; **12**, 34275-68-8; **12T**, 113086-89-8; **12′T**, 93524-81-3; **13**, 113086-90-1; **13P**, 113086-91-2; **13T**, 113086-92-3; **13′T**, 113086-93-4; **14**, 113086-94-5; **T**, 80037-90-7; Tempo, 2564-83-2; diethyl isopropylidenemalonate, 6802-75-1; diethyl (1,1-dimethylbut-3-enyl)malonate, 32119-46-3; ethyl 3,3-dimethylhex-5-enoate, 86549-23-7; 3,3-dimethylhex-5-enoyl chloride, 113086-95-6; 1-diazo-4,4-dimethylhept-6-en-2-one, 113086-96-7; methyl 4,4-dimethylhept-6-enoate, 113086-97-8; methyl (2,2-dimethyl-3-oxocyclobutyl)acetate, 27830-36-0; methyl 1,1-dimethyl-5,8-dithiaspiro[3,4]octane-2-acetate, 113108-99-9; methyl (2,2-dimethylcyclobutyl)acetate, 113086-98-9; ethyl 3,3-dimethyl-2-(ethoxycarbonyl)hept-6-enoate, 113086-99-0; ethyl 3,3-dimethylhept-6-enoate, 113087-00-6; 3,3-dimethylpent-4-enoic acid, 7796-73-8; 3-(allyloxy)-2-methylpropanoic acid, 113087-01-7; 3-(allyloxy)-2,2-dimethylpropanoic acid, 113087-02-8; (3-butenyloxy)acetic acid, 95123-53-8; 2-cyclobutylpropan-2-ol, 59383-67-4; *tert*-butylperoxalyl chloride, 7091-95-4.

Supplementary Material Available: Tables VII to XX give kinetic data, analytical conditions, and product retention times for clock reactions of radicals 1–13 (14 pages). Ordering information is given on any current masthead page.

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