(126 °C) and/or by exposure to aqueous methanol. For example, the TMIO–CCl_3 adduct (from alkyl radical/CCl_4 reactions) was partially solvolized during analysis by the HPLC eluent.

Laser Flash Photolysis. The laser flash photolysis apparatus and k_T calibration methods have been adequately described in earlier publications from this laboratory;[6,20] experimental conditions are given in the table footnotes. Quenching rate constants were calculated by least-squares fitting of k_{exptl} vs [$T^\bullet$] data for at least six evenly incremented [$T^\bullet$] over an appropriate range of [$T^\bullet$] (viz., such that the decay or grow-in rate constant, k_{exptl}, was in the range $(2–30) \times 10^5$ s^{-1}). Digitally averaged decay curves from three to six laser flashes were used to determine each k_{exptl} value. The effect of photolytic consumption of nitroxide on the k_{exptl} values was assessed in each solvent by comparing data from repeated sets of laser flashes; no appreciable corrections were required. However, for ABNO (where the nitroxide increments were of necessity very small) and in CH_2Cl_2 as solvent[32] the number of flashes needed to be kept to a practical minimum (viz., three or four) to avoid underestimating k_T.

Acknowledgment. We thank Dr. J. Daroszewski for his help with the statistical calculations and preparation of the figures and the Association for International Cancer Research and the National Foundation for Cancer Research for partial support of this work. K.U.I. also wishes to thank the Alexander von Humboldt Foundation and the organic chemists at the Universities of Freiburg and Essen, Germany, for their generous hospitality during the time that this work was written up.

Registry No. 1, 87110-24-5; **2**, 87110-25-6; TMIO, 80037-90-7; TEMPO, 2564-83-2; ABNO, 31785-68-9; benzyl, 2154-56-5; nonyl, 32757-65-6; neopentyl, 3744-21-6.

Kinetics of Nitroxide Radical Trapping. 2. Structural Effects[1]

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Contribution from the Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. *Received September 16, 1991*

Abstract: Laser flash photolysis and kinetic competition product studies have demonstrated that in isooctane at ambient temperatures the rate constant for coupling of carbon-centered radicals with persistent nitroxides, k_T, depends upon the degree of steric hindrance to coupling and upon the extent of resonance stabilization of the carbon radical. Sterically induced reductions in the magnitude of k_T are observed for changes in both the structure of the nitroxide and the structure of the carbon radical. Thus, for any particular carbon radical k_T is largest for the Bredt's rule protected nitroxides, 9-azabicyclo[3.3.1]nonane-*N*-oxyl (ABNO) and nortropane-*N*-oxyl, while for the "usual" di-*tert*-alkyl nitroxides k_T decreases along the series, 1,1,3,3-tetramethylisoindoline-2-oxyl ≥ 2,2,5,5-tetramethylpiperidin-1-oxyl (Tempo) > di-*tert*-butyl nitroxide, i.e., k_T decreases on going from a five-membered ring to a six-membered ring to a noncyclic structure. Cyclopropyl and triphenylmethyl are trapped at the fastest and slowest rates, respectively, the corresponding k_T values being 3.0×10^9 and 1.2×10^8 M^{-1} s^{-1} for ABNO and 2.1×10^9 and $<1 \times 10^6$ M^{-1} s^{-1} for Tempo. Steric effects in the carbon radicals are more pronounced for Tempo than for ABNO. For example, the ratio of k_T's for the trapping of nonyl and *tert*-butyl is 1.7 for Tempo but 1.3 for ABNO, while for the trapping of benzyl and cumyl the ratio of k_T's is 4.1 for Tempo and 0.9 for ABNO. The effect of resonance stabilization can be illustrated by the k_T values for three sterically unhindered primary radicals, *n*-nonyl, benzyl, and 2-naphthylmethyl, viz., 1.2×10^9, 4.8×10^8, and 5.7×10^7 M^{-1} s^{-1}, respectively, for Tempo and 2.2×10^9, 1.2×10^9, and 8.1×10^8 M^{-1} s^{-1}, respectively, for ABNO.

The trapping of transient carbon-centered radicals, $U^\bullet$, by persistent nitroxides, $T^\bullet$, to afford stable trialkylhydroxylamines, UT (reaction 1) has proven to be a valuable kinetic and mecha-

$$U^\bullet + R_2NO^\bullet \xrightarrow{k_T} UONR_2$$

$$U^\bullet + T^\bullet \xrightarrow{k_T} UT \qquad (1)$$

nistic probe for radical-induced polymerizations,[3-5] radical rearrangements,[6-9] and homolytic dissociations.[10-12] Detailed kinetic analysis of systems in which the nitroxide radical trapping (NRT) reaction occurs in competition with unimolecular and/or other bimolecular reactions of $U^\bullet$ [3-14] obviously requires reliable trapping rate constants, k_T. Furthermore, these need to be measured under a variety of conditions and with a variety of $U^\bullet/T^\bullet$ combinations.

Solvent effects on the kinetics of NRT were analyzed in the preceding paper.[15] Earlier work[6,16] has afforded accurate Arrhenius expressions for the effect of temperature on the rates of trapping of certain alkyl and benzylic radicals by Tempo and the isoindolinoxyl radical TMIO. In the present paper we report k_T measurements which were designed to probe the effects on the kinetics of NRT of (i) resonance stabilization of $U^\bullet$, (ii) steric protection of the radical center in $U^\bullet$, and (iii) steric protection

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(2) NRCC Research Associate 1988–1990.

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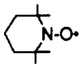
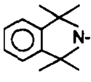
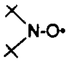
of the NO moiety in T$^•$. Some remarkable differences have been discovered between the reactivities of the "common", persistent di-*tert*-alkyl nitroxides, Tempo, TMIO, and di-*tert*-butyl nitroxide (DBNO), and the "uncommon", Bredt's rule protected, persistent bicyclic nitroxides, ABNO and NTNO.



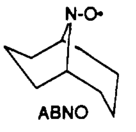
Tempo



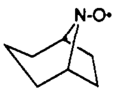
TMIO



DBNO



ABNO



NTNO

Experimental Section

Nitroxides. Tempo and DBNO were commercial products (Aldrich, Milwaukee, WI) which were purified by sublimation and reduced pressure distillation, respectively. 1,1,3,3-Tetramethylisoindoline-2-oxyl (TMIO) was prepared by the method of Solomon and co-workers[17] and purified as described previously.[15] 9-Azabicyclo[3.3.1]nonane-*N*-oxyl (ABNO) and nortropane-*N*-oxyl (NTNO) were prepared as described previously.[15,18] Thermal decomposition of ABNO and NTNO was minimized by storage in the solid state at -28 °C. Freshly prepared solutions of these two nitroxides were always employed. The more labile of these two compounds, NTNO,[18] was used within 8 h of its preparation and was used to measure solely the kinetics of trapping of the benzyl and cumyl radicals. Since the rate constants for the trapping of these two resonance stabilized radicals by ABNO and by NTNO were equal within our experimental error (vide infra) no further work was done with the more unstable bicyclic nitroxide, NTNO.

Carbon-Centered Radicals. For the time-resolved kinetic measurements the U$^•$ radicals were generated in the presence of T$^•$ by 308 or 337 nm laser flash photolysis (LFP) of appropriate precursors. For radicals **1**$^•$, **2**$^•$ and **4**$^•$–**7**$^•$ (for structures, see Table I) these precursors were 0.1 M solutions of the parent diacyl peroxides, reaction 2. For radicals **8**$^•$

$$(UCO_2)_2 \xrightarrow[308\ \text{nm}]{h\nu} 2U^• + 2CO_2 \qquad (2)$$

and **10**$^•$ the precursors were the parent ketones at 0.04 M and 0.005 M concentrations, respectively, reaction 3. For radicals **3**$^•$, **13**$^•$–**18**$^•$, and

$$U_2CO \xrightarrow[308\ \text{nm}]{h\nu} 2U^• + CO \qquad (3)$$

20$^•$ the LFP was carried out with 308-nm radiation while for **11**$^•$ and **12**$^•$ it was carried out with 337-nm radiation, the precursors being 0.15 M solutions of the parent hydrocarbon[19] and 0.5 M di-*tert*-butyl peroxide, reactions 4 and 5. For radical **19**$^•$ the 308 nm LFP on di-*tert*-butyl

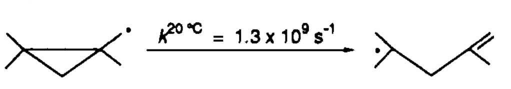
$$(CH_3)_3COOC(CH_3)_3 \xrightarrow[308\ \text{or}\ 337\ \text{nm}]{h\nu} 2(CH_3)_3CO^• \qquad (4)$$

$$(CH_3)_3CO^• + UH \rightarrow (CH_3)_3COH + U^• \qquad (5)$$

peroxide was followed by *tert*-butoxyl addition to 0.1 M 1,1-diphenylethylene, reaction 6. Radical **9**$^•$ was made by the very rapid ring opening

$$(CH_3)_3CO^• + H_2C{=}C(C_6H_5)_2 \rightarrow (CH_3)_3COCH_2\dot{C}(C_6H_5)_2 \qquad (6)$$

of **3**$^•$, reaction 7.

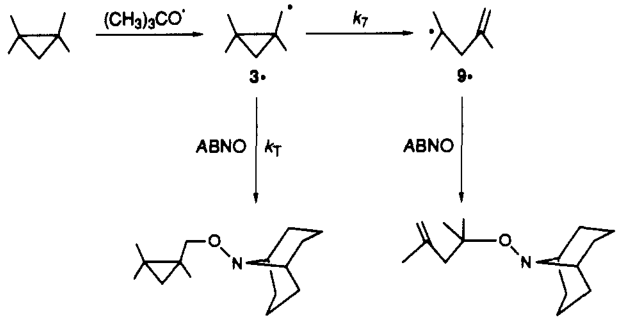


(7)

3• **9•**

Kinetics of NRT. The laser flash photolysis equipment and our general methods have been adequately described in earlier communications from this laboratory.[8,9,14,16,20] The time evolution in the concentration of U$^•$ was optically monitored, directly or indirectly (vide infra), at seven evenly spaced concentrations of nitroxide. For radicals **1**$^•$–**10**$^•$ all of the nitroxides were added to the other reactants in increments of 5.0 × 10^{-4} M. For radicals **11**$^•$–**20**$^•$ the increments were 1.2 × 10^{-3} M for Tempo, TMIO, and DBNO but the increments were only 6.0 × 10^{-4} M for ABNO and NTNO. The pseudo-first-order rate constants, k_{exptl}, for decay of the α-arylcarbinyl radicals, **10**$^•$–**20**$^•$, were monitored via the radical's own UV absorption at $\lambda_{\max}$. A plot of k_{exptl} vs [T$^•$] affords k_T, viz.

Scheme I



$$k_{\text{exptl}} = k_0 + k_T[T^•] \qquad (8)$$

The *tert*-alkyl radicals **8**$^•$ and **9**$^•$ were similarly monitored via their (weak) absorptions near 317 nm. The other alkyl radicals were monitored at 327 or 329 nm following their addition to the *probe*: 1,1-diphenylethylene, reaction 9. This probe was purified as described previously.[15] Occasionally β-methylstyrene was used as a *probe.*

$$U^• + H_2C{=}C(C_6H_5)_2 \rightarrow UCH_2\dot{C}(C_6H_5)_2 \qquad (9)$$

Ideally, on the time scale of our radical quenching experiments (viz., 0.5–5 μs) the UV absorption of the probe adduct radical, $UCH_2\dot{C}(C_6H_5)_2$, should grow into a *plateau* value before decaying more slowly by bimolecular self-reactions and by NRT. Under such conditions, measurement of the pseudo-first-order grow-in rate constant, k_{exptl}, at a fixed probe concentration affords k_T according to eq 10.[21]

$$k_{\text{exptl}} = k_0 + k_9[H_2C{=}C(C_6H_5)_2] + k_T[T^•] = k'_0 + k_T[T^•] \qquad (10)$$

In practice, 1,1-diphenylethylene was an effective probe *only* for the sterically encumbered nitroxides, Tempo, TMIO, and DBNO. This is because the resonance stabilized and sterically hindered adduct radicals, $UCH_2\dot{C}(C_6H_5)_2$, are very much less reactive toward these three nitroxides than are the precursor alkyl radicals, U$^•$. Unfortunately, this is not the case for the unhindered bicyclic nitroxides, ABNO and NTNO. In order to determine $k_{T(\text{ABNO})}$ for the nonbenzylic carbon-centered radicals, **1**$^•$, **2**$^•$, **4**$^•$, and **7**$^•$ and for the two naphthylmethyl radicals, **11**$^•$ and **12**$^•$, we therefore combined LFP data for reaction of U$^•$ with a hindered nitroxide, generally Tempo, with data from a direct, competitive experiment. Such competitive experiments involved the *thermal* generation of U$^•$ in the presence of two nitroxides at known relative concentrations and measurement of the relative yields of the two trialkylhydroxylamine products.[22] The ratio of the trapping rate constants by, for example, ABNO and Tempo is then given by

$$k_{T(\text{ABNO})}/k_{T(\text{Tempo})} = ([\text{U-ABNO}]/[\text{U-Tempo}])/([\text{ABNO}]/[\text{Tempo}]) \qquad (11)$$

As an example, a degassed mixture containing 5.0 × 10^{-2} M [ABNO], 0.10 M [Tempo], and 5.0 × 10^{-3} M didecanoyl peroxide in isooctane was maintained at 40 °C in the dark for 18 h, following which the trapped nonyl radical products were analyzed by HPLC–mass spectrometry (LC–MS).[8,9,22] The product ratio, [C_9H_{19}-ABNO]/[C_9H_{19}-Tempo] was 0.88 ± 0.05. From eq 11 this yields $k_{T(\text{ABNO})} = 1.76k_{T(\text{Tempo})}$ at 40 °C. Similar experiments at 20, 60, and 80 °C gave [C_9H_{19}-ABNO]/[C_9H_{19}-Tempo] = 0.85, 0.90, and 0.82, respectively, demonstrating that there is no significant difference between the temperature dependencies for nonyl radical NRT by these two nitroxides.[23] We estimate, therefore, that at 18 °C $k_{T(\text{ABNO})} \approx 2.2 \times 10^9\ M^{-1}\ s^{-1}$ for the nonyl radical.

Di-*tert*-butyl hyponitrite was used as a thermal source of *tert*-butoxyl radicals, reaction 12, for hydrogen abstraction from parent UH hydro-

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(19) Only low concentrations of the alkyl aromatic hydrogen atom donors **11**H–**18**H and **20**H were used in order to avoid undesirable solvent effects due to UH on k_T[8,9] and unwanted UV absorptions. This is possible in alkane solvents (SH) such as isooctane and cyclohexane because the solvent-derived radicals, S$^•$, are transparent at the monitoring wavelength. Furthermore, the signal due to U$^•$ grows in very rapidly because it is determined by the *total* hydrogen atom donating ability of the reactant solution, i.e., $k_{\text{grow-in}} = k_5^{\text{UH}}[\text{UH}] + k_5^{\text{SH}}[\text{SH}]$. Under our conditions $k_5^{\text{SH}}[\text{SH}]$ has a value of ca. 5 × $10^6\ s^{-1}$. All the alkyl aromatic hydrocarbons were purified by percolation through active alumina and distillations (Kugelrohr) immediately prior to use.

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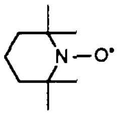
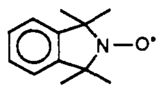
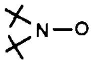
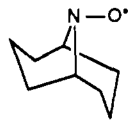
(21) For more details and typical LFP traces, see ref 16.

(22) All "kinetic products" were stable under the reaction conditions and were stable in the HPLC solvent.

(23) The activation energies for NRT must therefore be essentially equal.

Table I. Rate Constants, $10^{-7}k_T/(M^{-1}\ s^{-1})$, for Nitroxide Radical Trapping at 18 ± 2 °C[a]

	radical, U•					
no.	structure	λ_{max}/nm	Tempo	TMIO	DBNO	ABNO
1•	$CH_3(CH_2)_7\dot{C}H_2$		123 ± 26 P[b]	128 ± 31 P	108 ± 28 P 113 ± 29 C	216 ± 41 C
2•	$(CH_3)_3C\dot{C}H_2$		106 ± 35 P 96 ± 22 P[b]	112 ± 32 P	89 ± 36 C	202 ± 39 C
3•	$(CH_3)_2\overline{CCH_2C}(CH_3)\dot{C}H_2$		106 ± 35[c]	121 ± 40 O[d]		191 ± 32 O[d]
4•	$H_2\overline{CCH_2C}^{\bullet}H$		210 ± 26 P[e]			296 ± 34 C
5•	$H_2\overline{C(CH_2)_2C}^{\bullet}H$		141 ± 28 P			
6•	$H_2\overline{C(CH_2)_3C}^{\bullet}H$		102 ± 21 P	121 ± 31 C		178 ± 40 C
7•	$H_2\overline{C(CH_2)_4C}^{\bullet}H$		95 ± 22 P	103 ± 28 C	76 ± 29 C	172 ± 42 C
8•	$(CH_3)_3C^{\bullet}$	317	68 ± 17 P 76 ± 16 D[b]	91 ± 21 C[f] 88 ± 12 D[b]	68 ± 18 C[f]	165 ± 39 C[f]
9•	$H_2C{=}C(CH_3)CH_2\dot{C}(CH_3)_2$	317	52 ± 12 D		46 ± 13 D	160 ± 51 C
10•	$C_6H_5\dot{C}H_2$	317	48 ± 8 P[e] 49 ± 8 D[b]	55 ± 5 D[b]	46 ± 4 D	118 ± 9 D[g]
11•	1-naphthyl-$\dot{C}H_2$	366	8.2 ± 0.2 D[b]	9.1 ± 1.8 C		76 ± 5 C
12•	2-naphthyl-$\dot{C}H_2$	380	5.7 ± 1.8 D[b]	8.2 ± 1.9 C		81 ± 30 C
13•	$C_6H_5\dot{C}HCH_3$	321	16 ± 4 D[b] 19 ± 2 D	30 ± 11 C		86 ± 18 C
14•	$C_6H_5\dot{C}HCH{=}C(CH_3)_2$[h]	317	1.9 ± 0.4 D			90 ± 12 D
15•	$C_6H_5\dot{C}H\overline{CHCH_2CH_2}$	325	10 ± 1 D			78 ± 12 D
16•	$C_6H_5\dot{C}(CH_3)_2$	322	11.8 ± 0.1 D[b] 12 ± 1 D	17 ± 3 C	6.2 ± 0.3 D	133 ± 8 D[i]
17•	$(C_6H_5)_2\dot{C}H$	320	$4.6_3 \pm 0.0_2$ D[b]	7.7 ± 0.9 C		82 ± 4 D
18•	$(C_6H_5)_2\dot{C}CH_3$	320	$4.5_8 \pm 0.4_7$ D[b]			
19•	$(C_6H_5)_2\dot{C}CH_2OC(CH_3)_3$	329	4.2 ± 0.7 D	5.6 ± 0.5 C	3.0 ± 0.4 D	59 ± 5 D
20•	$(C_6H_5)_3\dot{C}$	332	<0.1 D[b]	<0.1 D		12 ± 3 D

[a] Solvent was isooctane for radicals **1•**–**10•** and isooctane/UH mixtures for radicals **11•**–**20•** except as noted for **8•**. For precursors of U• see Experimental Section. The methods used to measured k_T are indicated as follows: P, probe with monitoring of the $UCH_2\dot{C}(C_6H_5)_2$ radical's growth at 327 or 329 nm unless otherwise noted; D, direct monitoring of the decay of U• via its own absorption using the wavelength indicated under λ_{max}/nm; C, competitive kinetics with Tempo and another nitroxide with analyses of the trialkylhydroxylamine products; O, other. Errors represent 95% confidence levels (±2σ) but include random errors only. Estimated cumulative errors are given for C data. [b] Reference 16, $T = 20 \pm 2$ °C. [c] Assumed to be the same as for the structurally "analogous" radical, **2** (see ref 9). [d] Rate constant is based on relative clocking data for reaction 7 (**3•** → **9•**) with Tempo, with TMIO, and with ABNO, viz., $(k_{T(TMIO)}/k_7)/(k_{T(Tempo)}/k_7)$ and $(k_{T(ABNO)}/k_7)/(k_{T(Tempo)}/k_7)$ with $k_{T(Tempo)}$ having an assumed value (see footnote *c*). [e] The probe was 0.04 M β-methylstyrene, $\lambda_{max} = 321$ nm. A fresh solution was used for each concentration of Tempo (see ref 26). A value for $k_T = (1.2 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$ has been reported for this reaction in benzene at 25 ± 2 °C; see ref 26. [f] In cyclohexane, the value given for $k^{8\bullet}_T$ is based on $k^{8\bullet}_{T(Tempo)} = (7.6 \pm 1.6) \times 10^8\ M^{-1}\ s^{-1}$, i.e., on the D value for NRT of **8•** by Tempo. [g] For the benzyl radical NRT by NTNO, $k_T = (120 \pm 8) \times 10^7\ M^{-1}\ s^{-1}$, D. [h] Note that this is actually an allylic radical with two sites for trapping by the nitroxide. [i] For the cumyl radical NRT by NTNO, $k_T = (127 \pm 11) \times 10^7\ M^{-1}\ s^{-1}$, D.

carbons in some competitions involving trapping of the cyclohexyl radical,[24] **7•**, trapping of the *tert*-butyl radical, **8•**, and trapping of the naphthylmethyl radicals, **11•** and **12•**.

$$(CH_3)_3CONNOC(CH_3)_3 \xrightarrow{\Delta} 2(CH_3)_3CO^{\bullet} + N_2 \qquad (12)$$

Results

Values of k_T measured at 18 ± 2 °C using the techniques outlined in the Experimental Section are given in Table I. For radicals **1•**–**10•** the solvent was 2,2,4-trimethylpentane (isooctane) except for the competitive experiments with the *tert*-butyl radical, **8•**, for which it was cyclohexane. For radicals **11•**–**20•** the solvent was an isooctane/UH mixture. For comparative purposes some of our earlier LFP measurements of k_T in isooctane[16] are included in Table I.

Solvent effects on the kinetics of NRT can be quite pronounced.[15] In particular, they manifest themselves as a decrease in k_T at high nitroxide concentrations.[8,9] To explore this phenomenon further we made use of reaction 7, the ring opening of radical **3•** to form **9•**, and radical trapping with ABNO; see Scheme I.[25] This ring opening, which we have calibrated by NRT,[9] is extremely rapid ($k_7 = 2.0 \times 10^9\ s^{-1}$ at 37 °C)[9] and is therefore well suited for measuring k_T at high nitroxide concentrations. Di-*tert*-butyl hyponitrite was thermally decomposed at 37 °C in 1,1,2,2-tetramethylcyclopropane (**3H**) as solvent in the presence of various concentrations of ABNO. At [ABNO] = 5.2 × 10^{-2}, 0.21, 0.48, and 0.82 M (saturated) values of $k_7/k_{T(ABNO)}$ = [ABNO]([**9**-ABNO]/[**3**-ABNO]) = 0.84, 1.06, 1.33, and 1.61 M, respectively. These data yield

$$k_7/k_{T(ABNO)} = 0.82\ M + 0.99[ABNO];\ \langle r \rangle = 0.995 \qquad (13)$$

The corresponding data for Tempo[9] yield

$$k_7/k_{T(Tempo)} = 1.46\ M + 0.5[Tempo];\ \langle r \rangle = 0.975 \qquad (14)$$

Hence, $(k_{T(ABNO)}/k_{T(Tempo)})_{T\to 0} = 1.46/0.82 = 1.8$, a value which has been employed to calculate $k_{T(ABNO)}$ for **3•**; see Table I.

Discussion

The following conclusions can be drawn from an examination of the kinetic data from Table I.

(1) NRT of a wide variety of carbon-centered radicals occurs for each radical at a decreasing rate along the series ABNO (≈NTNO)[26] ≫ TMIO ≳ Tempo > DBNO. This order of reactivity is clearly a consequence of steric factors in the nitroxides.

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[24] As in previous studies,[6,8,15] the kinetic data were not affected by the U• precursor, e.g., $k_{T(ABNO)}/k_{T(Tempo)}$ values for cyclohexyl radicals generated by thermolysis of dicyclohexylcarbonyl peroxide and by thermolysis of di-*tert*-butyl hyponitrite in the presence of cyclohexane were identical.

[25] For simplicity, only the major (1,2) ring-scission of **3•** is shown in this scheme.

[26] NRT rate measurements were made for NTNO only on the benzyl and cumyl radicals; see Table I, footnotes *g* and *i*, respectively.

That is, the NO moiety is fully "exposed" in the two Bredt's rule protected nitroxides, ABNO and NTNO, but it is sterically encumbered in the other three nitroxides. The extent of this steric shielding is somewhat greater for di-*tert*-butyl nitroxide than for the cyclic nitroxides, Tempo and TMIO, because the encumbering methyl groups on the carbon atoms adjacent to the NO group are "tied back" by the formation of a ring. The smaller ring size in TMIO compared with Tempo reduces the extent of steric protection in the former radical. As a consequence TMIO is a somewhat more reactive trap than Tempo but the difference in their reactivity is not large.

(2) NRT by the sterically encumbered nitroxides is very much more sensitive to the steric demands of the attacking carbon-centered radical than are the unencumbered nitroxides. As an example, compare the relative rates of trapping of nonyl and *tert*-butyl radicals with Tempo for which $k_T^{1\bullet}/k_T^{8\bullet} \sim 1.7$, whereas for the Bredt's rule protected nitroxide, ABNO, this ratio has a value of 1.3. An even more dramatic example of the importance of steric effects in both the carbon-centered radical and nitroxide is provided by a comparison of the relative rates of trapping of the resonance stabilized benzyl and cumyl radicals with Tempo, for which $k_T^{10\bullet}/k_T^{16\bullet} \sim 4$, and with the two unencumbered bicyclic nitroxides, ABNO and NTNO,[26] for which this ratio has a value of only ca. 0.9.

(3) The rate of NRT by the "common" sterically encumbered nitroxides of sterically undemanding radicals decreases dramatically when their resonance stabilization surpasses some critical value. Thus, for nonane, toluene, and methylnaphthalene the relevant RCH_2–H bond strengths, D[U–H], are ca. 100, 88, and 85 kcal/mol, respectively,[27] while for NRT by Tempo the relative k_T values for nonyl, **1•**, benzyl, **10•**, and 2-naphthylmethyl, **12•**, radicals are, respectively, 1.0:0.39$_4$:0.046. By way of contrast, for the unencumbered nitroxide, ABNO, any such "break" in NRT rates must occur only with radicals having greater resonance stabilization than naphthylmethyl since the relative k_T values for **1•**, **10•**, and **12•** are 1.0:0.54$_6$:0.375, respectively.

(4) There is an even more dramatic difference in NRT trapping rates between Tempo and ABNO for sterically crowded, resonance-stabilized carbon-centered radicals. Thus, for NRT of nonyl, **1•**, *tert*-butyl, **8•**, benzyl, **10•**, cumyl, **16•**, 2-*tert*-butoxy-1,1-diphenylethyl, **19•**, and triphenylmethyl, **20•**, radicals the $k_{T(ABNO)}/k_{T(Tempo)}$ ratios are 1.76, 2.29, 2.47, 11.2, 14.0, and >120, respectively.[28] ABNO is therefore the nitroxide trap of choice for calibrating fast clock reactions (rearrangements) of resonance stabilized radicals.[30]

(5) For the sterically undemanding but highly reactive[31] cyclopropyl radical, **4•**, NRT by Tempo is almost as rapid as NRT by ABNO, viz., $k^{4\bullet}_{T(ABNO)}/k^{4\bullet}_{T(Tempo)} = 1.4$.

(6) For the very sterically demanding and highly resonance stabilized trityl radical, **20•**, there is no measurable trapping by Tempo or TMIO ($k_T < 1 \times 10^6$ M^{-1} s^{-1}). These results are consistent with a report[32] that the reaction of the trityl radical with analogous, sterically encumbered nitroxides is reversible at room temperature (in which connection, it might be noted that the reaction of the trityl radical with oxygen is also reversible at ambient temperatures).[33-35] By way of contrast to its apparent lack of reaction with Tempo and TMIO, the trityl radical is rather rapidly trapped by ABNO, $k_T = 1.2 \times 10^8$ M^{-1} s^{-1}. This result serves further to emphasize the potential utility of ABNO and related nitroxides for trapping sterically crowded, resonance stabilized carbon-centered radicals.

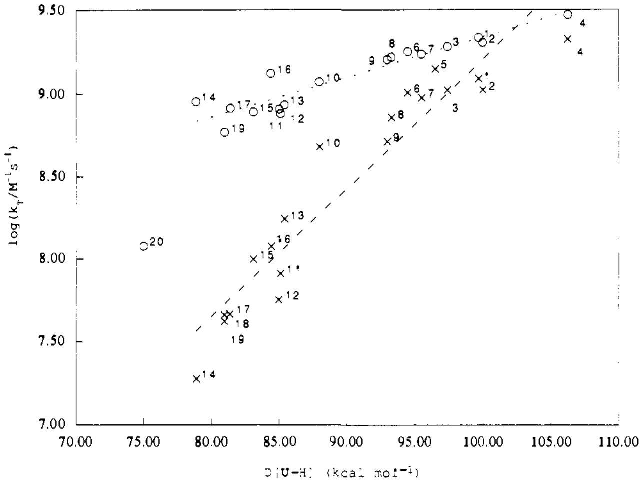

Figure 1. Plot of log (k_T/(M^{-1} s^{-1})) against the U–H bond dissociation energy for Tempo, × (log (k_T/(M^{-1} s^{-1})) = 1.429 + 0.0778 (D[U–H]/(kcal mol^{-1})), $\langle r \rangle$ = 0.950), and for ABNO, ○ (log (k_T/(M^{-1} s^{-1})) = 6.959 + 0.0238 (D[U–H]/(kcal mol^{-1})), $\langle r \rangle$ = 0.937, which ignores point 20 and is the line shown; or, log (k_T/M^{-1} s^{-1}) = 6.235 + 0.0315 (D[U–H]/kcal mol^{-1}), $\langle r \rangle$ = 0.862, if point 20 were to be included in the correlation). See also footnote 36.

In addition, we might note that the relative rates of nonyl radical trapping by Tempo and ABNO are essentially unchanged over a temperature range from 20 to 80 °C (see Experimental Section). Therefore, at least over this temperature range rate constants for NRT by ABNO can be calculated using the Arrhenius activation energy of 1.7 kcal/mol measured previously[16] for the nonyl radical + Tempo reaction.

As might be expected from the six itemized points made above, plots of log ($k_T^{U\bullet}$/M^{-1} s^{-1}) versus the U–H bond dissociation energy[27] for Tempo and ABNO show moderate correlations, $\langle r \rangle$ = 0.950 and 0.862 (or 0.937 if $k_{T(ABNO)}$ (triphenylmethyl) is ignored), respectively (see Figure 1).[36] The slope of the free energy plot[36] is greater for NRT by Tempo than for NRT by ABNO because of the greater sensitivity of Tempo to the resonance stabilization and steric demands of the carbon-centered radicals. Presumably, bond formation at the NRT transition state is more advanced for Tempo than for ABNO.

Although ABNO is an excellent trap for carbon-centered radicals it must be admitted that oxygen is an even better trap, at least in terms of the rate constants for the two reactions (though not of course in terms of the ease with which a high concentration of the trap may be obtained nor in terms of the ease of product identification). For example, the rate constants for trapping by oxygen of the *tert*-butyl[37] and benzyl[37,38] radicals in low viscosity, alkane solvents are ca. 5×10^9 and ca. 2.7×10^9 M^{-1} s^{-1}, respectively,[39] whereas the rate constants for the trapping of these two radicals by ABNO under similar conditions are ca. 1.7×10^9

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(27) *CRC Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990–1991; pp 9-95, 9-96.

(28) In this connection we note a report[29] that norpseudopelletirine-*N*-oxyl (a close analogue of ABNO) is from 1.4 to 5.8 times as reactive as Tempol (4-hydroxy-Tempo) in trapping some radicals of undefined structure obtained by the pulse radiolysis of certain purines in water.

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(36) This figure is given solely for illustrative purposes. We recognize that plots of the kind shown in this figure cannot be linear but must curve over to a limiting k_T value at high D[U–H] because, for the more reactive radicals, k_T approaches the diffusion-controlled limit.[15] Mathematical manipulation to linearize these plots did not appear worthwhile, particularly in view of the "scatter" of the experimental data.

(37) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095–5099.

(38) Tokumura, K.; Ozaki, T.; Nosaka, H.; Saigusa (Ejiri), Y.; Itoh, M. *J. Am. Chem. Soc.* **1991**, *113*, 4974–4980.

(39) A rate constant of 2.77×10^9 M^{-1} s^{-1} has also been reported for the benzyl radical + O_2 reaction at 25 °C in water.[40] It is clear that solvent effects on the rates of trapping of carbon-centered radicals are far less important for their reactions with oxygen than for their reactions with nitroxides.[15]

(40) Marchaj, A.; Kelley, D. G.; Bakac, A.; Espenson, J. H. *J. Phys. Chem.* **1991**, *95*, 4440–4441.

and 1.2×10^9 M^{-1} s^{-1}, respectively. Thus, for these two carbon-centered radicals, oxygen is about twice as reactive as ABNO, a result which might be rationalized by noting that oxygen has two sites for reaction compared with one site for ABNO, or by noting the spin-statistical factors for the two reactions, viz., $^1/_2$ for oxygen and $^1/_4$ for ABNO.

Finally, the undoubted kinetic and presumed[41] thermodynamic superiority of ABNO as a carbon radical trap makes it a valuable alternative or adjunct to the usual di-*tert*-alkyl nitroxides for purposes such as "calibrating" radical clocks that are *ultrafast* or which involve resonance stabilized radicals.[30] However, ABNO's advantages will be offset to some extent by its thermal instability in solution[18] and, under the conditions we have frequently employed, by an apparent higher reactivity than Tempo toward *tert*-butoxyl radicals. In addition, the decrease in the magnitude of k_T which is seen with high concentrations of nitroxides is much more pronounced with ABNO than with Tempo (see eqs 13 and 14). We have previously attributed the reduction in k_T at high Tempo concentrations to an overall increase in the polarity of the solvent.[9] The same effect is expected to depress k_T at high concentrations of ABNO. However, in this case an additional factor comes into play since ABNO and other nonhindered nitroxides are known to dimerize reversibly in nonpolar solvents.[42-44] Thus, at high concentrations of ABNO the effective concentration of the trap, i.e., of the monomeric nitroxide, will be reduced because of dimerization with a consequent (apparent) reduction in k_T.

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Registry No. 1 diacyl peroxide, 762-12-9; **1**$^\bullet$, 32757-65-6; **2** diacyl peroxide, 1808-38-4; **2**$^\bullet$, 3744-21-6; **3**, 50876-33-0; **3**$^\bullet$, 139583-98-5; **4** diacyl peroxide, 54808-54-7; **4**$^\bullet$, 2417-82-5; **5** diacyl peroxide, 4904-55-6; **5**$^\bullet$, 4548-06-5; **6** diacyl peroxide, 101448-33-3; **6**$^\bullet$, 3889-74-5; **7** diacyl peroxide, 139584-01-3; **7**$^\bullet$, 3170-58-9; **8** ketone, 815-24-7; **8**$^\bullet$, 1605-73-8; **9**$^\bullet$, 50517-76-5; **10** ketone, 102-04-5; **10**$^\bullet$, 2154-56-5; **11**, 90-12-0; **11**$^\bullet$, 7419-60-5; **12**, 91-57-6; **12**$^\bullet$, 7419-61-6; **13**, 100-41-4; **13**$^\bullet$, 2348-51-8; **14**, 4489-84-3; **14**$^\bullet$, 139583-99-6; **15**, 4410-78-0; **15**$^\bullet$, 139584-00-2; **16**, 98-82-8; **16**$^\bullet$, 4794-07-4; **17**, 101-81-5; **17**$^\bullet$, 4471-17-4; **18**, 612-00-0; **18**$^\bullet$, 51314-23-9; **19**$^\bullet$, 139606-48-7; **20**, 519-73-3; **20**$^\bullet$, 2216-49-1; TMIO, 80037-90-7; DBNO, 6146-35-6; ABNO, 31785-68-9; $Ph_2C{=}CH_2$, 530-48-3; $(CH_3)_3C(O)_2C(CH_3)$, 110-05-4; Tempo, 2564-83-2; di-*tert*-butyl hyponitrite, 14976-54-6.

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The Surface Nature of Grignard Reagent Formation:[1] Cyclopropylmagnesium Bromide

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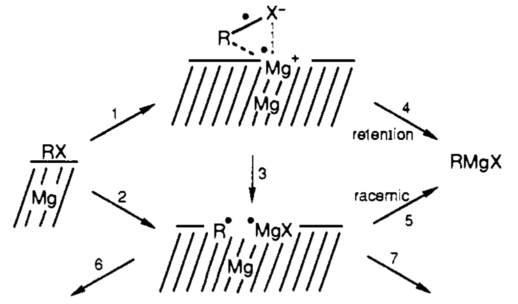
Abstract: The reaction of cyclopropyl bromide with magnesium in diethyl ether yielded directly, during formation of the Grignard reagent, ~25–30% cyclopropane. Also formed in the reaction was ~25% cyclopropylmagnesium bromide. The reaction, when conducted in perdeuterated diethyl ether and in diethyl ether in the presence of the radical trap deuterated dicyclohexylphosphine, showed that the cyclopropane is formed mainly by disproportionation of the cyclopropyl radicals on the magnesium surface (~85%) and only a small amount (~15%) by reaction of a "freely diffusing radical" with the solvent. The reaction in methanol-*O-d* yielded almost exclusively 1-deuteriocyclopropane. These results provide further experimental evidence that the basic assumption of the D-model "that all radicals leave the surface and diffuse freely in solution" is not valid.

Introduction

Although Grignard reagents are one of the most often used organometallic intermediates,[3] there is still disagreement on the mechanism of their formation. Currently two views are under consideration. One is represented by a mathematical model based on a kinetic analysis of the product distribution. In this model,[4] called the D-model, the alkyl halide accepts an electron from the magnesium surface to form a radical R$^\bullet$. In order for the existing kinetic data in the literature obtained under homogeneous solution conditions to be applicable, all the radicals must "leave the surface and diffuse freely in solution at all times". The radical can, while in solution, rearrange, disproportionate, dimerize, react with solvent, or, by diffusing back to the surface, react to form the

Scheme I. Proposed Mechanism for Grignard Reagent Formation



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[1] This work was supported by a grant from the National Science Foundation, to whom we are grateful.

[2] One of us (C.Z.) is grateful to the Alexander von Humboldt Stiftung for a Feodor Lynen Stipend.

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