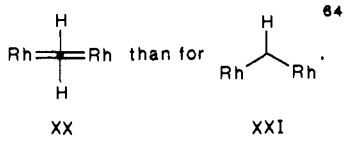
exhibited by a particular bimetallic tungsten hydride then permits the assessment of the static or fluxional nature of the complex if the appearance of its ^1H NMR spectrum does not unambiguously establish its nature (e.g., by the intensities of the ^{183}W satellites associated with each signal). If the complex is indeed fluxional with respect to hydride ligand exchange, the $J_{^1H-^{183}W}$ evident in its ^1H NMR spectrum may be analyzed in terms of the expected $^nJ_{^1H-^{183}W}$ values in static isomers to gain some insight into the types of fluxional processes operative. Inferences concerning fluxionality drawn in this manner are usually consistent with the exchange mechanisms indicated by variable temperature ^1H NMR studies. Although it is true that bridging hydride ligands show chemical shifts in areas upfield of those due to terminal ones, the fact that these regions always overlap even in any one particular family means that a particular resonance cannot be used diagnostically to determine the terminal or bridging nature of a particular hydride ligand in a bimetallic organotungsten complex.

The magnitudes of $^1H-^{183}W$ couplings appear to be influenced primarily by the magnitudes of the valence s-electron densities at the tungsten centers. Within a given family of bimetallic tungsten hydrides, these couplings decrease in the order I > II > III ≃ IV ≃ W – H. This fact suggests that the four groupings in the above series which contain bridging hydride ligands are best viewed as single units held together by delocalized bonding which extends over all atoms involved in the bridging system. To convey this view, we advocate the use of the "fused" representations of the tungsten–hydrogen bonding in these bridging systems as shown. Finally, we note that similar trends appear to exist for the coupling of hydrides to other transition-metal centers e.g., $^1J_{^1H-^{103}Rh}$ is greater for



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and hence analyses of the ^1H NMR spectra of other bimetallic hydrides in a manner identical with that outlined in this paper may well prove to be quite fruitful.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and F.W.B.E. and to the University of British Columbia for the award of a graduate fellowship to J.T.M. We also thank Professor M. B. Hall for valuable discussions.

Registry No. Cp_2WH_2, 1271-33-6; $[Cp_2WH_3]^+$, 51263-09-3; $Cp_2W(H)Ph$, 11077-71-7; $Cp_2W(CH_3)_2$, 39333-53-4; $Cp_2WH_2{\cdot}W(CO)_5$, 104780-32-7; $Cp_2WH_2{\cdot}Mo(CO)_5$, 104780-33-8; $Cp_2MoH_2{\cdot}W(CO)_5$, 104780-34-9; $[(CpWH)_2(\mu\text{-}H)\{\mu(\eta^2\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)\}]^+$, 76857-70-0; $[Cp_2W(\mu\text{-}H)_2Pt(PEt_3)(Ph)]^+$, 85762-71-6; $[Cp_2HW(\mu\text{-}H)Pt(PEt_3)_2(Ph)]^+$, 85762-69-2; $[Cp_2W(\mu\text{-}H)_2Rh(PPh_3)_2]^+$, 73413-09-9; $[CpW(\mu,\sigma\text{:}1\text{-}5\text{-}\eta\text{-}C_5H_4)(\mu\text{-}H)IrH(dppe)(PPh_3)]^+$, 83221-85-6; $[CpW(\mu,\sigma\text{:}1\text{-}5\text{-}\eta\text{-}C_5H_4)(\mu\text{-}H)_2IrH(PPh_3)_2]^+$, 83214-92-0; $Cp_2WH_2{\cdot}AlEt_3$, 11084-59-6; $Cp_2WH_2{\cdot}ZnCl_2$, 79736-32-6; $CpW(CO)_3H$, 12128-26-6; *cis*-$CpW(CO)_2(PMe_3)H$, 31811-36-6; *trans*-$CpW(CO)_2(PMe_3)H$, 31852-08-1; $CpW(PMe_3)H_5$, 95029-85-9; $CpW(PMe_3)_2(\eta^2\text{-}C_5H_8)H$, 95029-87-1; $[\{CpW(CO)_3\}_2(\mu\text{-}H)]^+$, 68868-71-3; $[\{CpW(CO)_3\}(\mu\text{-}H)\{CpMo(CO)_3\}]^+$, 68893-52-7; $[CpW(CO)_2]_2(\mu\text{-}H)(\mu\text{-}OMe)$, 81628-79-7; $[\{CpW(CO)_2\}_2(\mu\text{-}H)(\mu\text{-}MeCCMe)]^+$, 89199-40-6; $[CpW(CO)_2](\mu\text{-}H)(\mu\text{-}CHMe)[Pt(PMe_3)_2]$ (isomer 1), 104870-90-8; $[CpW(CO)_2](\mu\text{-}H)(\mu\text{-}CHMe)[Pt(PMe_3)_2]$ (isomer 2), 104870-91-9; $Cp(CO)_2\overline{WCH(PMe_3)CHCOMe}$, 92416-46-1; $[(Ph_3PC_5H_4)W(CO)_3H]^+$, 47663-26-3; $[CpW(CO)_2]_2(\mu\text{-}H)_2$, 86307-87-1; $[(\eta^5\text{-}C_5Me_5)W(CO)_2]_2(\mu\text{-}H)_2$, 86307-89-3; $CpW(CO)_3(SnMe_3)$, 12093-29-7; $[HW(CO)_5]^-$, 77227-36-2; $[HW(CO)_4\{P(OMe)_3\}]^-$, 91839-87-1; $[HW(CO)_4(PMe_3)]^-$, 82963-31-3; $[\{W(CO)_5\}_2(\mu\text{-}H)]^-$, 73740-64-4; $[\{W(CO)_5\}(\mu\text{-}H)\{Mo(CO)_5\}]^-$, 103310-31-2; $[\{W(CO)_5\}(\mu\text{-}H)\{Cr(CO)_5\}]^-$, 77110-95-3; $[\{W(CO)_4P(OMe)_3\}_2(\mu\text{-}H)]^-$, 84850-83-9; $[\{W(CO)_4P(OMe)_3\}(\mu\text{-}H)\{Cr(CO)_5\}]^-$, 82963-40-4; $[\{W(CO)_4P(OMe)_3\}(\mu\text{-}H)\{W(CO)_5\}]^-$, 82963-42-6; $[W(CO)_3(NO)\{P(OMe)_3\}](\mu\text{-}H)[W(CO)_5]$, 60219-55-8; $[W(CO)_5](\mu\text{-}H)[AuPPh_3]$, 83601-25-6; $[W(CO)_5](\mu\text{-}H)[Cp_2Ta(CO)]$, 85601-17-8; $[\{W(CO)_5\}\{Fe(CO)_4H\}]^-$, 101032-82-0; $[W(CO)_3](\mu\text{-}Co)(\mu\text{-}C^2\text{-}CH_2C_6H_4Me\text{-}4)(\mu\text{-}dppm)[Re(CO)_3]$, 91864-59-4; $[\{W(CO)_4\}_2(\mu\text{-}H)_2]^{2-}$, 52032-33-4; $W(CO)_5[PMePh_2]$, 18534-36-6; $CpW(NO)_2H$, 69532-01-0; $[\{CpW(NO)_2\}_2(\mu\text{-}H)]^+$, 79329-49-0; $[\{CpW(NO)_2\}(\mu\text{-}H)\{CpMo(NO)_2\}]^+$, 79329-52-5; *trans*-$CpW(NO)H_2\{P(OPh)_3\}$, 96429-81-1; $[CpW(NO)I]_2(\mu\text{-}H)_2$, 104780-35-0; $[CpW(NO)H]_2(\mu\text{-}H)_2$ (isomer 1), 104870-92-0; $[CpW(NO)H]_2(\mu\text{-}H)_2$ (isomer 2), 104870-93-1; $[CpW(NO)\{P(OPh)_3\}]_2(\mu\text{-}H)_2$, 96444-57-4; $Cp(NO)(Cl)\overline{W\{CHCHC(O)Me\}}$, 92184-47-9; $CpW(NO)IH\{P(OPh)_3\}$, 73199-23-2; W, 7440-33-7.

Supplementary Material Available: Tabulations of the atomic coordinates of the hydrogen atoms, the thermal parameters, and the weighted least-squares plane of a cyclopentadienyl ligand (3 pages); observed and calculated structure factors for $[CpW(NO)H]_2(\mu\text{-}H)_2$ (6 pages). Ordering information is given on any current masthead page.

The Cyclopropylmethyl Free Radical Clock. Calibration for the Range 30–89 °C

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Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada. *Received March 25, 1986*

Abstract: The Arrhenius equation for the ring-opening isomerization of cyclopropylmethyl radicals (R•) to 3-buten-1-yl radicals (R′•) for the 303–362 K temperature range was determined by thermolysis of (cyclopropylmethyl)(1-hydroxy-1-methylethyl)diazene in the presence of excess 1,1,3,3-tetramethylisoindolin-2-yloxy (Y•). Rate constants for coupling of R• with Y• were assumed to be proportional to diffusion-controlled rate constants (k_d) and rate constants (k_i) for the isomerization were calculated from k_d (corrected) and product ratios (RY/R′Y). The temperature dependence of k_i, given by log $(k_i/s^{-1}) = (13.9 \pm 0.4) - (7.6 \pm 0.2)/\theta$, is significantly different from that determined by kinetic EPR spectroscopy in the temperature range 128–153 K; log $(k_i/s^{-1}) = (11.34 \pm 0.85) - (5.94 \pm 0.57)/\theta$, where $\theta = 2.3RT$ kcal mol^{-1}.

Rate constants for radical–molecule reactions, eq 1, can be estimated conveniently by means of competition kinetics, provided that R• undergoes a competitive reaction, often a unimolecular isomerization, eq 2, for which the rate constant is known.[1] Radical processes for which the absolute rate constants have been de-

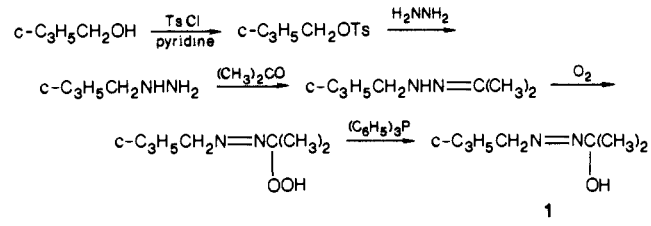
$$R^\bullet + Z \xrightarrow{k_Z} \text{products} \quad (1)$$

$$R^\bullet \xrightarrow{k_i} R'^\bullet \quad (2)$$

(1) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

0002-7863/86/1508-7981$01.50/0

Scheme I



termined are known as free radical clocks.[1] More than a dozen primary alkyl radical clocks, with rate constants spanning more than 7 orders of magnitude, are now available as kinetic standards.[1]

The accuracy of rate constants for radical-molecule reactions (eq 1), acquired by the competition method, is necessarily limited by the accuracy of calibration of the clock. Many rate constants for free radical rearrangements are based on kinetic EPR spectroscopy, and a built-in limitation of that method[2] is that the data must be acquired in a range of temperatures such that $k_i \simeq 10^3$ s^{-1}. Consequently, fast radical clocks, with $k_i(298\ K) \simeq 10^{7-8}$, have been calibrated at temperatures below −100 °C, very far away from the range of temperatures in which many reactions of interest (eq 1) occur at convenient rates. The use of such radical clocks at ambient or higher temperatures therefore involves not only considerable extrapolation by means of Arrhenius parameters but also the implicit assumption that the Arrhenius relationship is linear over a range of temperatures very much larger than that over which those parameters were determined.

The cyclopropylmethyl-to-3-buten-1-yl radical isomerization is one of the fastest primary alkyl radical rearrangements that have been followed.[1,3] Rate constants for that rearrangement, determined by kinetic EPR spectroscopy for the temperature range 128–153 K, gave $\log (k/s^{-1}) = (11.34 \pm 0.85) - (5.94 \pm 0.57)/\theta$, where $\theta = 2.3RT$ kcal mol^{-1}.[3] We wished to use the cyclopropylmethyl free radical clock to study some fast atom abstraction reactions at ca. 325 K, and we therefore set out to calibrate that clock over a range of temperatures near that value.

Method

The system chosen involves competition kinetics between a bimolecular radical–radical reaction (near to the diffusion-controlled limit) and the unimolecular ring opening of interest. The source of cyclopropylmethyl radicals was hydroxydiazene **I**, prepared according to Scheme I. It was chosen for its convenient thermolysis rate at 303–362 K and for its very clean chemistry in the presence of **2** (Scheme II).

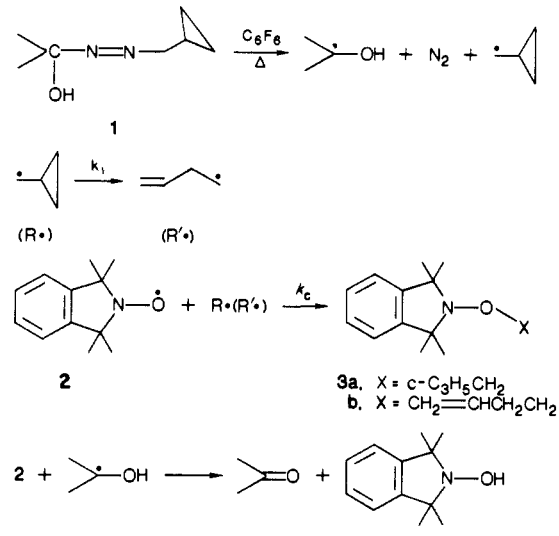
Experimental Section

Cyclopropylmethyl Tosylate. To 14.5 g (0.20 mol) of cyclopropylmethanol was added 42 g (0.22 mol) of p-toluenesulfonyl chloride, with ice cooling and in an atmosphere of dry N_2. To the cold and well-stirred solution was added dry pyridine (48 g, 0.6 mol) over a period of 1 h, and the resulting solution was kept at 0–5 °C for 2 h. After overnight storage in the freezer at about −10 °C, the reaction mixture was acidified with ice-cold, 10% aqueous HCl and extracted three times with ether (50 mL). The ether extract was dried over magnesium sulfate, and the solvent was evaporated to yield crude cyclopropylmethyl tosylate (31 g, 68.5%).

Cyclopropylmethyl Hydrazine. Cyclopropylmethyl tosylate (11.3 g, 0.050 mol) was added gradually during 1 h to a stirring, ice-cooled solution of hydrazine hydrate (50 g, 1 mol) in ethanol (25 mL). The temperature was then allowed to rise to 20 °C where it was kept for 2 h before it was raised to 40 °C and kept at that temperature for 2 h. The solution was allowed to stand overnight at room temperature before the bulk of the ethanol was taken off with a rotary evaporator. Continuous extraction of the residual liquid with ether, for 3 days, drying of the ether with $MgSO_4$, and evaporation of the ether yielded crude cyclopropylmethyl hydrazine (4.0 g, 92%) as a syrupy liquid which was used directly for the next step.

Cyclopropylmethyl Hydrazone of Acetone. To crude cyclopropylmethyl hydrazine (4.0 g, 0.046 mol) in anhydrous benzene (20 g) was

Scheme II



added, dropwise and with stirring, 10 g of acetone in 15 min. The resulting mixture was shaken at room temperature in an atmosphere of N_2 for 1 h before the temperature was raised for 1 h to the reflux temperature. The mixture was cooled and dried over $MgSO_4$. It was filtered, the drying agent was washed with benzene, and the combined benzene filtrate was dried again over $MgSO_4$. Further filtration, followed by evaporation of the solvent, left crude hydrazone (2.2 g) as a viscous liquid which was fractionally distilled. Acetone (cyclopropylmethyl)hydrazone (1.6 g, 28%) boiled at 42–43 °C (0.5 Torr); ^1H NMR ($CDCl_3$) δ 0.08–0.63 (m, 4 H), 0.77–1.27 (m, 1 H), 1.75 (s, 3 H), 1.93 (s, 3 H), 3.01 (d, 2 H), 3.80–4.70 (s, br, 1 H); ^{13}C NMR ($CDCl_3$) δ 2.80, 10.26, 15.21, 24.81, 55.88, 145.36; UV(hexane) λ_{max} (ε) 290 (16.1), 358 (2.7); IR (neat) 3420, 3240, 3080, 2992, 2904, 2842, 1660 (weak), 1140 cm^{-1}; MS (high resolution), m/z 126.1167, calcd for $C_7H_{14}N_2$ 126.1158.

(Cyclopropylmethyl)(1-hydroperoxy-1-methylethyl)diazene. Acetone (cyclopropylmethyl)hydrazone (0.50 g, 0.004 mol) in dry petroleum ether (20 mL, bp 40–60 °C), cooled with ice and stirred, was exposed to O_2 in a gas system fitted with a gas burette and a manometer. When absorption of O_2 ceased and an aliquot freed from solvent no longer had the two methyl singlets of the hydrazone, the entire solution was stored in the freezer. ^1H NMR ($CDCl_3$) δ 0.17–0.77 (m, 4 H), 1.03–1.40 (m, 1 H), 1.47 (s, 6 H), 3.67 (d, 2 H), 9.47 (s, br, 1 H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 3.51, 9.20, 21.84, 73.60, 102.89; UV (hexane) λ_{max} (ε) 292 (10.2), 358 (21.9); IR (neat) 3320, 3080, 2988, 2936, 1680, 1179, 847 cm^{-1}; iodometric titration, 99.9 and 99.9%.

(Cyclopropylmethyl)(1-hydroxy-1-methylethyl)diazene (1). The above hydroperoxide (2.4 mmol) in petroleum ether was added slowly to a solution of triphenylphosphine (0.70 g, 2.7 mmol) in 12 mL of petroleum ether, cooled to 0–5 °C. The flask was then kept at ca −5 °C overnight when the precipitated Ph_3PO was filtered off, and the filtrate was evaporated at 10–15 °C with a rotary evaporator. The crude residue was subjected to bulb-to-bulb distillation under high vacuum, from a bulb at room temperature to a receiver in liquid N_2. Colorless **1** (0.23 g, 67%) was an oil at room temperature: ^1H NMR ($CDCl_3$) δ 0.07–0.63 (m, 4 H), 0.97–1.33 (m, 1 H), 1.34 (s, 6 H), 3.68 (d, 2 H), 4.73 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 3.30, 9.01, 26.90, 71.39, 93.60; UV (hexane) λ_{max} (ε) 290 (9.8), 338 (19.2); IR (neat) 3410, 3080, 2982, 2933, 1685, 1215 cm^{-1}; MS (high resolution), m/z 125.1082, calcd for $C_7H_{13}N_2$ (M^+ − OH) 125.1080.

1,1,3,3-Tetramethylisoindolin-2-yloxyl (2). Synthesis and purification of **2** by the published procedure gave material with properties matching those described.[4]

Thermolysis of 1. Stock solutions of each of **1** and **2** in C_6F_6 were prepared in volumetric flasks at room temperature. Aliquots of these stock solutions were taken with calibrated syringes to prepare reaction solutions (Table I) which were sealed into short tubes, to minimize the free space, after several freeze–pump–thaw cycles under vacuum. Thermolyses were carried out by immersing the tubes in oil baths controlled to ±0.2 °C, and the temperatures were measured with calibrated thermometers. At 30 °C, complete decomposition of **1** took about 30 days. Tubes kept at 89 °C were left for 3 days. These reaction times, determined by running parallel reactions with much lower concentrations

(2) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 193.
(3) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024.
(4) Griffiths, P. G.; Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 397.

Table I. Product Ratios, Viscosities, and Rate Constants[a]

T (K)[b]	$[2]_{av}$[c] (M)	$[1]_{init.}$[d] (M)	**3b**/**3a**[e]	mean[f]	$\eta(C_6F_6)$, cP	k_d,[g] M^{-1} s^{-1}	k_i, s^{-1}
303	0.153	0.0113	0.940		0.839	9.00×10^9	2.70×10^8
			0.990	0.980 ± 0.036			
			1.01				
323	0.149	0.0113	1.69		0.648	1.24×10^{10}	6.43×10^8
			1.77	1.74 ± 0.04			
			1.76				
343	0.148	0.00915	2.75		0.516	1.66×10^{10}	1.42×10^9
			2.97	2.88 ± 0.11			
			2.91				
362	0.145	0.00915	4.37		0.426	2.12×10^{10}	2.75×10^9
			4.59	4.48 ± 0.11			
			4.47				

[a] The only additional products were acetone (quantitative), N_2 (not determined), and 2-hydroxy-1,1,3,3-tetramethylisoindoline, not fully separated from **2**. [b] ±0.2°. [c] Calculated from the initial concentration, assuming that 1 mol of **1** leads to consumption of 2 mol of **2**. Corrected for solvent expansion. [d] Reactions were carried to completion; $[1]_{final} \simeq 0$. [e] Ratio determined by gas chromatography. Each number represents a separate run and is the average value for at least three injections. The detector responses for the isomers were assumed to be equal. [f] Errors are standard deviations. [g] Calculated from $k_d = 1/4(2 + d_1/d_2 + d_2/d_1)8RT/30\eta$,[5] where η is in cP and d_1/d_2 was estimated, from molecular models, to be about $^1/_2$.

of **2** in NMR tubes, with periodic monitoring, were more than sufficient for total decomposition of **1**.

Reaction solutions were analyzed by gas chromatography on a glass column (8 ft × 1/8 in.) packed with OV-17 (3%) on Chromosorb P (AW, 100/120 mesh), in a Varian Vista 6000 instrument fitted with a flame ionization detector. The column temperature was held at 35 °C for 15 min before it was programmed at 5 °C min^{-1} to a maximum temperature of 220 °C, for analyses which included the assay for acetone (quantitative). Other assays, for **2**, **3a**, and **3b**, involved initial column temperatures of 100 °C and a similar program to 220 °C. Products were eluted in the following order: acetone, hexafluorobenzene, **2** and 2-hydroxy-1,1,3,3-tetramethylisoindoline (tailing peak), **3b**, **3a**. The co-elution of **2** and the hydroxy isoindoline was inferred from the fact that injection of **2** alone gave a sharp, symmetric peak. The mass spectrum of the material in the tailing peak was not significantly different from that of pure **2**.

Identification of 3a and 3b. Analysis by GC/MS gave, for both adducts, m/z 245 (M^+) 230 (100%), 190, 176, 160, 158, 145, 91, 55. The relative intensity of the signal at m/z 55 was greater in the spectrum of material assigned as **3a**. Incremental addition of Br_2 in CCl_4 to the reaction products, and GC analysis after each increment, showed that the component eluting second last was being destroyed and that component was therefore identified as **3b**. Excess **2**, contaminated by hydroxy isoindoline, had m/z 190 (M^+), 175, 160, 158, 145 (100%), 128, 115, 91. Adducts **3a** and **3b** were also separated from reactants and from other products, but not from each other, by preparative TLC; ^1H NMR of mixture ($CDCl_3$, 90 MHz) δ (**3a**) 0.15–0.76 (m, 4 H); ca. 0.9–1.3 (m, br, ca. 1 H), 1.49 (s), 3.79 (d, 2 H), 7.17 (m), (**3b**) 1.49 (s) 2.45 (dd, 2 H), 4.03 (t, 3 H), 5.14 (m, 2 H), 5.91 (m, 1 H), 7.17 (m). The signals shared by **3a** and **3b**, δ 1.49 and 7.17, integrated as expected on the basis of summation of other integrals. Furthermore, the ratio **3a**/**3b** inferred from the NMR spectrum was the same as that obtained by GC analysis of the same mixture. The high-resolution mass spectrum of the mixture had m/z 245.1792; calcd for $C_{16}H_{23}NO$, m/z 245.1781, m/z 230.1582; calcd for $C_{15}H_{20}NO$ ($M^+ - CH_3$), m/z 230.1546.

Viscosity Measurements. Viscosities of hexafluorobenzene (H) were measured at 298.5, 307, 318.8, 340.8, and 365 K with a viscometer calibrated with benzene (B) up to 340.8 K. The viscosities were calculated from the equation below, where η is the viscosity in cP, t is the flow

$$\eta_H/\eta_B = (t_H/t_B)(d_H/d_B)$$

and d is the density. The density values for benzene, as a function of temperature, were taken from the literature and those for hexafluorobenzene were calculated from the density at 20 °C (1.612) by assuming that the coefficient of cubical expansion (γ) is 1.237×10^{-3} deg^{-1}. Values of γ for other solvents are the following: CCl_4, $\gamma = 1.236 \times 10^{-3}$ deg^{-1}; C_6H_6, $\gamma = 1.237 \times 10^{-3}$ deg^{-1}.

Calculation of Diffusion-Controlled Rate Constants. Values of k_d were calculated from measured viscosities by means of the equation[5] below, where η is in cP, R is in erg deg^{-1}, T is in K, and k_d is in M^{-1} s^{-1}. The ratio of the diameters of the reacting radicals (d_1/d_2) was estimated from molecular models of R• and of **2** to be $^1/_2$.

$$k_d = 1/4(2 + d_1/d_2 + d_2/d_1)8RT/30\eta$$

(5) Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966; pp 625–629.

Results and Discussion

Decomposition of **1** in hexafluorobenzene containing excess **2** was a very clean process, yielding only the products in Scheme II. 2-Hydroxy-1,1,3,3-tetramethylisoindoline was not isolated (Experimental Section), but it is the only reasonable coproduct to compete the overall stoichiometry.

Table I contains the rate constants (k_d) for diffusion-controlled capture of R• by **2**, calculated from measured viscosities (Experimental Section), as well as the analytical data and the values of k_i derived from eq 3. The value of [**2**] in eq 3 was taken as

$$k_i = k_c\frac{[\mathbf{3b}][\mathbf{2}]}{[\mathbf{3a}]} \qquad (3)$$

the average of the initial and final concentrations of **2**; usually $[2]_{av} = 0.92 - 0.94[2]_{init}$. That small correction for the change in concentration of **2** with time was applied in each case, and $[2]_{final}$ was estimated for each run to establish that **2** was indeed in ca. 10-fold stoichiometric excess throughout, with respect to $[1]_{initial}$. Rate constants (k_c, eq 3) for coupling of R• with **2** were obtained by dividing k_d values by five, i.e., $k_c = 0.2k_d$. The rationale for not using the k_d values themselves in eq 3, instead of k_c values, is discussed below.

Numerous estimates of rate constants for bimolecular radical–radical reactions, including coupling of 1°-alkyl radicals with stable nitroxyls, have been published.[6] Many of them came from pulse radiolysis studies of aqueous solutions, in which nitroxyls are undoubtedly H-bonded and, as a result, probably somewhat less reactive than they are in aprotic solvents. The rate constants range from values essentially at the diffusion-controlled limit to values about 10-fold smaller.[6] Other numbers have been obtained by the ESR or by the rotating sector techniques which gave, for example, $2k_t^{Cl_3C} = 5.8 \times 10^9$ M^{-1} s^{-1} at 300 K[7] (ESR) and $2k_t = 1.4–3.6 \times 10^9$ M^{-1} s^{-1} (sector) for coupling reactions of a variety of alkyl radicals and tin-centered radicals.[8] The latter rate constants are 2- to 6-fold below the theoretical maximum for diffusion-controlled reaction.[8] Recent measurements of k_c for coupling of **2** with alkyl radicals, based in part on the 5-hexenyl clock, suggest a value (60 °C) near 1.0×10^9 M^{-1} s^{-1}.[9] Finally, for coupling of benzyl radicals[10] and of cyclopropyl radicals[11] with

(6) Ingold, K. U. in Landolt-Börnstein *Numerical Data and Functional Relationships in Science and Technology*; Subvolume C, *Radical Reaction Rates in Liquids*; Fischer, H.; Ed.; Springer-Verlag: New York, 1983; vol. 13, p 181.
(7) Paul, H. *Int. J. Chem. Kinet.* **1979**, *11*, 495.
(8) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.
(9) In cyclohexane, which is about twice as viscous as hexafluorobenzene at 60 °C. Beckwith, A. L. J.; Bowry, V. W.; O'Leary, M.; Moad, G.; Rizzardo, E.; Solomon, D. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1003.
(10) Chateaneuf, J.; Lusztyk, J.; Ingold, K. U., personal communication. TEMPO is expected to react somewhat more slowly than **2** because of greater steric hindrance in TEMPO in which the alkyl groups at nitrogen are not tied back as tightly.

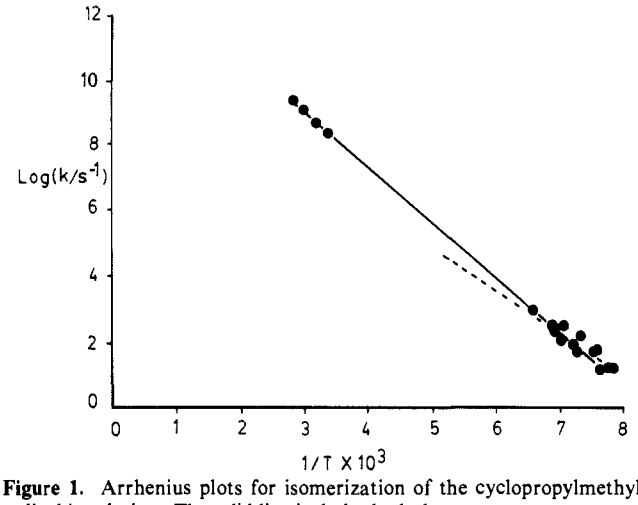


Figure 1. Arrhenius plots for isomerization of the cyclopropylmethyl radical in solution. The solid line includes both the present measurements and the earlier low-temperature data, corrected as indicated in the text. The dotted line represents the least-squares fit to the corrected low-temperature data alone.

TEMPO, $k_c^{23°C} \simeq 4.9 \times 10^8$ M^{-1} s^{-1} and $k_c^{25°C} = 1.2 \times 10^9$ M^{-1} s^{-1}, respectively.

The above evidence, taken together, indicates that coupling of R• (and R'•) with **2** is not quite diffusion-controlled. We have used $k_c = 0.2k_d$, not only because a factor of about 5 is indicted from the general trend outlined above but also because it aligns our k_i values ($k_i^{25°C} = 2.1 \times 10^8$ s^{-1}) with a rate constant for cyclopropylmethyl rearrangement ($k_i^{25°C} = 1.6 \times 10^8$ s^{-1}) based on H-abstraction from $HSnBu_3$[13,14] as the clock and with ring opening of the 3,5-cyclocholestan-6-yl radical ($k_i = 2.5 \times 10^8$ s^{-1} at 30 °C) clocked by means of H-abstraction from Ph_3SnH.[15-17] Rate constants for H-abstraction from $HSnBu_3$ by alkyl radicals are now quite well established by means of laser flash spectroscopy.[17]

The Arrhenius equation that fits the data of Table I and the kinetic EPR data[3] with correlation coefficient 0.9979 is given by

$$\log (k_i/s^{-1}) = (13.9 \pm 0.4) - (7.6 \pm 0.2)\theta$$

where $\theta = 2.3RT$ kcal mol^{-1}. The error in E is based on unweighted values of log k and on the assumption that errors in $1/T$ could be neglected. The error in log A represents the estimated range of attenuation factors (5 ± 2) for converting k_d to k_c. The Arrhenius equation does not change beyond its error limits if the factor for converting from k_d to k_c is allowed to change with temperature, from 5 at 89 °C to either 3 or 7 at 30 °C or from 5 at 30 °C to either 3 or 7 at 89 °C.

Values of k_i (Table I, Figure 1) are significantly larger than those extrapolated from low-temperature EPR data[3], which gives[18] $k_i^{25°C} = 9.7 \times 10^6$ s^{-1} vs. 2.1×10^8 s^{-1} from this work. The larger A factor from the present results ($10^{13.9}$ vs. $10^{11.3}$)[18] can be attributed to experimental difficulties inherent in the EPR method. An A factor as large as $10^{13.9}$ can be rationalized, at least qualitatively, in terms such as the fourfold degeneracy of the reaction path, the barrier to internal rotation of the exocyclic methylene group of cyclopropylmethyl,[19] and the increase in entropy of internal motion of the ring methylene groups at the transition state for ring opening.

In summary, a combination of the low-temperature kinetic EPR data, which gave rate constants more reliable than the Arrhenius parameters derived from them, with the present high-temperature data has led to substantial revision of the Arrhenius parameters for the fast radical clock that is used most frequently.

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Registry No. 1, 104877-17-0; **2**, 80037-90-7; **3a**, 104877-20-5; **3b**, 104877-21-6; cyclopropylmethanol, 2516-33-8; cyclopropylmethylhydrazine, 40487-93-2; cyclopropylmethyl radical, 2154-76-9; 3-buten-1-yl radical, 2154-62-3; cyclopropylmethyl tosylate, 1015-45-8; acetone cyclopropylmethylhydrazone, 104877-18-1; (cyclopropylmethyl)(1-hydroperoxy-1-methylethyl)diazene, 104877-19-2.

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(15) Calculated from the data of Cristol and Barbour[16] with 2.2×10^6 M^{-1} s^{-1} as the rate constant for H-abstraction from $HSnBu_3$ by radicals of the cyclohexyl type[17] and a factor of 5 for the estimated greater reactivity of $HSnPh_3$.[8]

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(18) Our least-squares treatment of the data in Table I of ref 3 leads to log $(k_i/2k_t/M) = -0.57 - 3.69/\theta$ whereas the authors[3] have +0.57 as the first term. Use of −0.57 leads to log $(k_i/s^{-1}) = 11.34 - 5.94/\theta$ and to $k_i^{298K} = 9.7 \times 10^6$ s^{-1}.

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