were also present. However, no attempts were made to assign these minor signals. The stereo- and regiochemistry was established by examining 2-methyl-6-(3-oxobutyl)cyclohexanone, as described below.

***trans*-2-Methyl-6-(3-oxobutyl)cyclohexanone:**[8] IR (neat) 1710 (s), 1360 (s), 1160 (s), 1125 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.00 (d, J = 7 Hz, 3 H), 1.1–2.9 (m with a singlet at 2.14, 15 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 14.51, 23.79, 25.61, 29.84, 35.63, 37.53, 41.51, 45.77, 49.92, 209.03, 213.98. In addition to the above set of signals for the trans 2,6-isomer, those assignable to the cis 2,6-isomer and the 2,2-isomer were also present. Those assignable to the cis 2,6-isomer appear at 15.56, 20.51, 24.83, 30.02, 33.01, 35.09, 41.44, 42.77, 48.26, 208.25, 216.47 ppm. ^{1}H NMR signal for the 2-Me group of the cis 2,6-isomer appears at 1.06 ppm. The ratio of the 2,6-isomers to the 2,2-isomer was 95:5 and that of the trans 2,6-isomer to its cis isomer was 60:40.

2-Methyl-2-(3-chloro-2-butenyl)cyclohexanone:[8] IR (neat) 1705 (s), 1665 (m), 1450 (m), 1375 (m), 1125 (m), 1065 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.00 (s, 3 H), 1.0–2.5 (m with peaks at 1.67, 2.00, and 2.23, 13 H), 5.40 (t, J = 7 Hz, 1 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 21.26, 22.61, 26.08, 27.44, 36.82, 38.38, 38.76, 48.44, 121.73, 131.82, 213.79.

2-Methyl-2-(3-oxobutyl)cyclohexanone:[8] IR (neat) 1710 (s), 1450 (m), 1370 (m), 1170 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.07 (s, 3 H), 1.1–3.0 (m with a singlet at 2.17, 15 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 21.01, 22.64, 27.44, 31.17, 38.44, 38.81, 39.50, 48.26, 209.86, 215.90.

2-(3-Chloro-2-butenyl)cyclohexanone:[3-5] IR (neat) 1710 (s), 1670 (m), 1450 (s), 1130 (m), 1060 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.0–2.8 (m with a singlet at 2.06, 14 H), 5.50 (t, J = 7 Hz, 1 H).

2-(3-Oxobutyl)cyclohexanone:[3-5] IR (neat) 1710 (s), 1450 (m), 1355 (m), 1165 (m), 1130 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.1–2.6 (m with a singlet at 2.12).

2-(3-Chloro-2-butenyl)cyclopentanone:[15] IR (neat) 1730 (s), 1640 (m), 1150 (m), cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.0–2.8 (m with a peak at 1.90, 12 H), 5.44 (t, J = 7 Hz, 1 H).

2-(3-Oxobutyl)cyclopentanone:[16] IR (neat) 1730 (s), 1450 (m), 1410 (m), 1360 (m), 1175 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.0–3.0 (m with a singlet at 2.15).

4-Methyl-7-chloro-6-octen-3-one: IR (neat) 1710 (s), 1455 (m), 1380 (m), 1100 (m), 1020 (m), 975 (m), 800 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.8–1.4 (m with peaks at 0.93, 1.13, and 1.16, 6 H), 1.6–3.0 (m with a singlet at 2.10, 8 H), 5.47 (t, J = 7 Hz, 1 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 7.66, 16.09, 26.06, 31.80, 33.99, 45.29, 122.80, 131.77, 213.75.

5-Methyl-2,6-octanedione: IR (neat) 1710 (s), 1460 (m), 1410 (m), 1360 (m), 1165 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.05 (t, J = 7 Hz, 3 H), 1.10 (d, J = 7 Hz, 3 H), 1.5–2.1 (m, 2 H), 2.15 (s, 3 H), 2.2–2.8 (m, 5 H).

Acknowledgments are made to the National Science Foundation and the National Institutes of Health for support of this research. Some experimental data provided by Drs. H. Matsushita and R. A. John were useful in carrying out this study.

Registry No. **2**, 17392-07-3; **3**, 939-60-6; *cis*-**6**, 60450-46-6; *trans*-**6**, 60416-04-8; *cis*-**7**, 85893-55-6; *trans*-**7**, 85893-56-7; Pd(PPh$_3$)$_4$, 14221-01-3; BEt$_3$, 97-94-9; 2-methylcyclohexanone, 583-60-8; 2,3-dichloropropene, 78-88-6; 2-methyl-2-(2-chloro-2-propenyl)cyclohexanone, 72009-03-1; *cis*-2-methyl-6-(2-chloro-2-propenyl)cyclohexanone, 85893-57-8; *trans*-2-methyl-6-(2-chloro-2-propenyl)cyclohexanone, 85893-58-9; 2-methyl-2-(2-oxopropyl)cyclohexanone, 27943-50-6; 2-(2-oxopropyl)cyclohexanone, 6126-53-0; 2-(2-chloro-2-propenyl)cyclopentanone, 41100-30-5; 2-(2-oxopropyl)cyclopentanone, 60415-94-3; *cis*-2-methyl-6-(3-chloro-2-butenyl)cyclohexanone, 85893-59-0; *trans*-2-methyl-6-(3-chloro-2-butenyl)cyclohexanone, 85893-60-3; 2-methyl-2-(3-chloro-2-butenyl)cyclohexanone, 4071-75-4; 2-methyl-2-(3-oxobutyl)cyclohexanone, 4071-58-3; 2-(3-oxobutyl)cyclohexanone, 26942-62-1; 2-(3-chloro-2-butenyl)cyclopentanone, 57428-31-6; 2-(3-oxobutyl)cyclopentanone, 1489-27-6; 4-methyl-7-chloro-6-octen-3-one, 85908-77-6; 5-methyl-2,6-octanedione, 30466-33-2; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; 3-pentanone, 96-22-0; 1,3-dichloro-2-butene, 926-57-8.

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Evidence for Viscosity Effects on Disproportionation–Combination Ratios of *tert*-Butyl Radicals in Solution[1]

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Received December 20, 1982

Photolysis of di-*tert*-butyl ketone (2,2,4,4-tetramethyl-3-pentanone) in solution ultimately gives solvent-separated *tert*-butyl radicals (Scheme I).[2] In the absence of a scavenger these radicals form encounter pairs that quantitatively collapse to the disproportionation products 2-methylpropane (R(+H)) and 2-methylpropene (R(−H)), or the combination product 2,2,3,3-tetramethylbutane (R–R; Scheme I).[2,3] It has been shown that even in media of high viscosity, the *tert*-butyl radicals can be fully scavenged, indicating that loss of CO from the first-formed Me$_3$CC(O)· radical does not occur in the initial cage.[4] Cage disproportionation (k'_{-1}) yielding Me$_3$CCHO does compete with separative diffusion (k_D), but it is not a major process even at high viscosity.[2a]

Schuh and Fischer showed in *n*-alkane solvents that the encounter of two *tert*-butyl radicals (k_t) is governed by translational diffusion and that every such encounter leads to termination either by disproportionation (k_d) or combination (k_c).[3] Additionally, they documented both a temperature and solvent dependence for the k_d/k_c ratio.[2,3] They concluded that these dependences most likely were related to viscosity variation; however, they were unable to eliminate solvent internal pressure as the important variable.[2a,5]

For example, they varied solvent over a homologous series of *n*-alkanes from C$_8$ to C$_{16}$ and found an increase in the k_d/k_c ratio. The same ratio decreased with increasing temperature. While this suggests that k_d/k_c depends directly on viscosity because η increases from C$_8$ to C$_{16}$ and decreases with increasing temperature, internal pressure (P_i) also varies in the same way with solvent and temperature.[5]

We now report the effects of externally applied pressure on the k_d/k_c ratio. These data both support the proposed dependence on viscosity and provide evidence against an internal pressure dependence.

Results and Discussion

Degassed samples of 0.17 M di-*tert*-butyl ketone in *n*-octane were photolyzed at various pressures with use of a specially designed optical cell. The time of the photolyses were adjusted to provide less than 5% conversion of the ketone. The reaction products 2-methylpropane, 2-methylpropene, and 2,2,3,3-tetramethylbutane were immediately analyzed by GLC. The resulting concentrations are reported in Table I.

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(1) High Pressures Studies. 27. Part 26: Neuman, R. C., Jr.; Sylwester, A. P. *J. Org. Chem.*, in press.

(2) (a) Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2463. (b) Schuh, H.; Fischer, H. *Int. J. Chem. Kinet.* **1976**, *8*, 341.

(3) Schuh, H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130.

(4) Tanner, D. D.; Rahimi, P. M. *J. Am. Chem. Soc.* **1982**, *104*, 225.

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Table I. Yields of 2-Methylpropane, 2-Methylpropene, and 2,2,3,3-Tetramethylbutane from Photolysis of Di-*tert*-Butyl Ketone in *n*-Octane at Several Pressures (25 °C)

P, atm	P, MPa	η, cp[a]	M × 10^3 R(+H)[b]	R(−H)[c]	RR[d]	R(+H)/RR	R(−H)/RR
34	3.4	0.530	4.871	5.688	1.114	4.28 ± 0.09	5.13 ± 0.02
			1.534	1.893	0.3674		
680	68.9	0.915	1.495	1.778	0.3562	4.34 ± 0.14	5.22 ± 0.23
			1.858	2.259	0.4146		
1020	103.4	1.133	3.425	3.950	0.7617	4.81 ± 0.31	5.38 ± 0.19
			3.778	4.102	0.7372		
1837	186.1	2.160	2.887	3.267	0.5025	6.00 ± 0.25	6.37 ± 0.14
			2.272	2.267	0.3638		

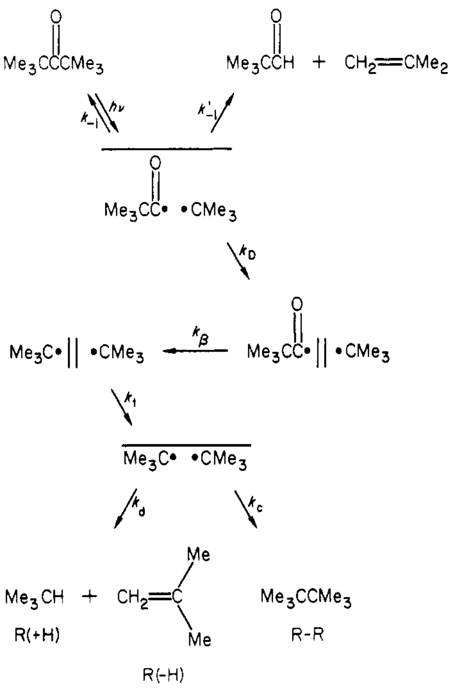
[a] Calculated from data compiled by Bridgeman, P. W. "Collected Experimental Papers"; Harvard University Press: Cambridge, MA, 1964; Vol. 4, p 2043. [b] 2-Methylpropane. [c] 2-Methylpropene. [d] 2,2,3,3-Tetramethylbutane.

Table II. Yields of 2-Methylpropane, 2-Methylpropene, and 2,2,3,3-Tetramethylbutane from Photolysis of Di-*tert*-Butyl Ketone in Several *n*-Alkane Solvents at Atmospheric Pressure (25 °C)[a]

solvent	η, cp[b]	P_i[c,d]	ΔP_i[c,e]	R(+H)/RR	R(−H)/RR
n-C_8H_{18}	0.514	2626 (266.1)	0 (0)	5.40	5.26
n-$C_{10}H_{22}$	0.859	2766 (280.3)	140 (14.2)	5.71	5.71
n-$C_{12}H_{26}$	1.37	2870 (290.8)	244 (24.7)	5.92	6.08
n-$C_{14}H_{30}$	2.10	3014 (305.4)	388 (39.3)	6.38	6.30
n-$C_{16}H_{34}$	3.09			6.95	6.70

[a] Data from ref 2a. [b] Rossini, F. D. "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds"; American Petroleum Institute Research Project 44, Carnegie Press, 1953. [c] Values not in parentheses in units of atmospheres; values in parentheses in units of megapascals. [d] Internal pressure (P_i) values at 20 °C taken from Allen, G.; Gee, G.; Wilson, G. J. *Polymer* 1960, 1, 456. [e] $\Delta P_i = P_i(n\text{-alkane}) - P_i(n\text{-octane})$.

Scheme I



For comparison, we have compiled the data collected by Schuh and Fischer at 25 °C in several *n*-alkanes (Table II) that span a viscosity range comparable to that obtained in *n*-octane over the pressure range studied by us.[6] A comparison of our data at 34 atm in *n*-octane with those of Schuh and Fischer in *n*-octane at atmospheric pressure indicates that our ratios are lower than theirs. Although we took care to avoid loss of R(+H) and R(−H) from our reaction samples, it is likely that there was more opportunity for loss of these volatile products in our studies. Additionally, there is a bigger difference between the ratios R(+H)/RR and R(−H)/RR in our results (Table I) than in those reported by them (Table II).

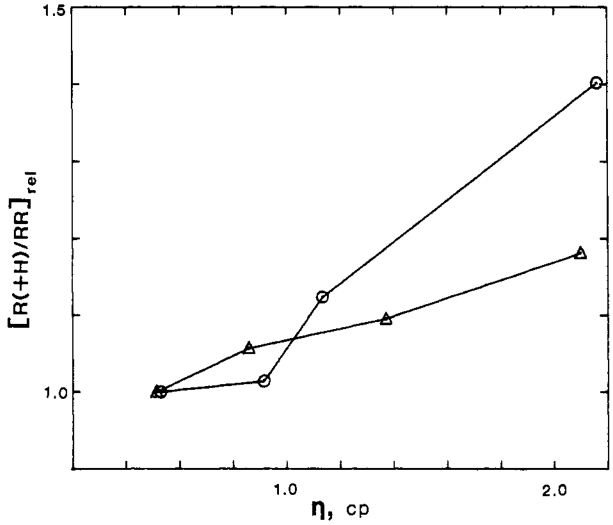


Figure 1. Viscosity dependence of $[R(+H)/RR]_{rel}$ (see ref 7) from the pressure studies (Table I) (○) and from the data of Schuh and Fischer (Table II) (△).

These two ratios should not be identical because (1) 2-methylpropene (but not 2-methylpropane) is formed from the disproportionation reaction (k'_{-1}) and (2) 2-methylpropene can react with *tert*-butyl radicals. However, neither of these reactions was found to be very significant by Schuh and Fischer and it is unlikely that these side reactions explain the differences in our studies. Most probably these arise from errors in calculating the absolute concentrations of R(+H) and R(−H), and in addition, such errors could contribute to the lower values in Table I. Schuh and Fischer noted that these ratios are difficult to measure and reported comparable differences between their early[2b] and most recent[2a] studies.

In spite of these differences, we believe that the results in Tables I and II clearly distinguish between a potential dependence of k_d/k_c on η or P_i. Normalized values of R(+H)/RR from Table I are plotted vs. solvent viscosity in Figure 1, along with normalized values of Schuh and

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(6) Externally applied pressure leads to dramatic increases in solvent viscosity; see data in Table I.

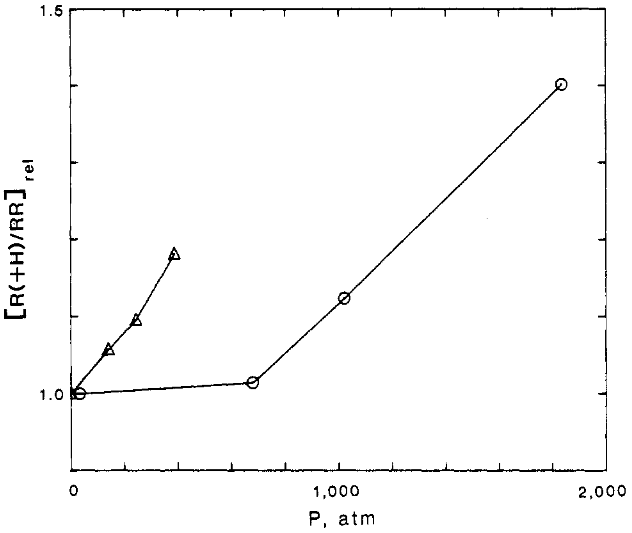

Figure 2. Pressure dependence of $[\mathrm{R(+H)/RR}]_{\mathrm{rel}}$ (see ref 7) from the pressure studies (Table I) (○) and from data of Schuh and Fischer (Table II) (△).

Fischer from Table II.[7] Similarly, these respective sets of normalized values of R(+H)/RR have been plotted as a function of pressure in Table II. In the first case (Figure 1), the viscosity values used for the pressure results are those shown in Table I. In the second case (Figure 2), the "pressure" values used for Schuh and Fischer's data in the *n*-alkane solvents are the values of ΔP_{i} given in Table II. In effect, we are normalizing all pressures to *n*-octane at 1-atm external pressure.[8]

We contend that the solvent variation data and pressure variation data correlate much better with viscosity (Figure 1) than with pressure (Figure 2). This provides support for the model developed to explain these results (Table II), which was based on the assumption that certain rotational motions of *tert*-butyl radicals would have significantly greater viscosity dependence than other rotational motions.[2a]

Experimental Section

Di-*tert*-Butyl Ketone (2,2,4,4-Tetramethyl-3-pentanone). This ketone was synthesized according to the procedures of Dubois and Bauer:[9] bp 83–84 °C (53 mm); NMR δ 1.27 (s); IR 1685 cm^{-1} (C=O) (lit.[9] bp 69.5 °C (48 mm); IR 1686.5 cm^{-1}). The IR spectrum of this ketone was identical with Sadtler IR spectrum no. 5681 of an authentic sample of this compound and with that of a commercial sample obtained from the Pfaltz and Bauer Co.

Product Studies. A 0.17 M solution of 2,2,4,4-tetramethyl-3-pentanone was prepared in *n*-octane (Aldrich Gold label; H_2SO_4 washed and distilled) containing a small amount of benzene (0.014 M) as an internal standard. The solution was vacuum degassed via several freeze–pump–thaw cycles and brought to atmospheric pressure with pure dinitrogen. The solution was stored in a sealed container at 5 °C between experiments. Samples were withdrawn from the storage vessel and placed in the high-pressure optical cell in a nitrogen purged glovebag. The cell was pressurized and irradiated with a medium-pressure Hanovia mercury lamp at room temperature. Details of the optical cell and the photolysis apparatus have been described by Berge.[10] Under our conditions the solutions were irradiated for slightly less than 1 h to achieve conversion of ca. 5%.

Immediately after photolysis, the cell was depressurized and refrigerated at −5 °C for ca. 15 min to minimize loss of the volatile reaction products when the cell was opened. After opening, 1-μL injections of the reaction mixture were analyzed with a Varian Aerograph Series 1400 flame-ionization GLC in conjunction with a 30 ft × $^1/_8$ in. column containing 20% SF-96 on 60/80 firebrick at 90 °C. Solutions of authentic samples of 2-methylpropane, 2-methylpropene, and 2,2,3,3-tetramethylbutane were used to calibrate the column and peak areas were measured with a disc integrator.

Acknowledgment. Support by the National Science Foundation and the award of a University of California, Riverside, minigrant to M.E.F. are gratefully acknowledged. We also thank Dr. H. Schuh for helpful discussions and Dr. C. Berge for experimental assistance.

Registry No. Di-*tert*-butyl ketone, 815-24-7; *tert*-butyl radical, 1605-73-8.

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(7) From Table I we have calculated and plot $[\mathrm{R(+H)/RR}]_{\mathrm{P}}/[\mathrm{R(+H)/RR}]_{34\,\mathrm{atm}}$; from Table II we have calculated and plot $[\mathrm{R(+H)/RR}]_{n\text{-alkane}}/[\mathrm{R(+H)/RR}]_{n\text{-octane}}$.

(8) While the internal pressure of *n*-octane at atmospheric pressure is substantially greater than 1 atm, this solvent system is our reference point, and, thus, values of ΔP_{i} (Table II) are correctly plotted along with values of external pressure (Table I).

(9) Dubois, J. E.; Bauer, P. *J. Am. Chem. Soc.* **1976**, *98*, 6993.

(10) Berge, C. T. Ph.D. Dissertation, University of California, Riverside, CA, 1979.

Photochemical Retro-Diels–Alder Reaction. Vinylketene Formation by Stereospecific Triazole Elimination

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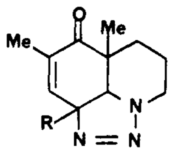
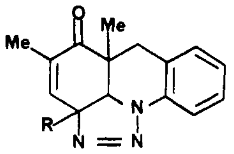
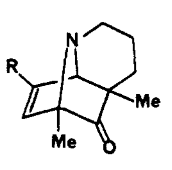
We have described the preparation of triazolines of type **1** and **2** by intramolecular azide–olefin cycloaddition from the appropriate 6-(3-azidopropyl)-2,4-cyclohexadien-1-one or 6-[*o*-azidobenzyl]-2,4-cyclohexadien-1-one. Triazolines **1a**, **1b**, and **2b** are excellent substrates for a new photochemical elimination–rearrangement to 2-azatricyclo$[4.4.0.0^{2,8}]$decenones **3a**, **3b**, and **4b**, respectively. This two-step sequence provides a method for accomplishing the synthetic equivalence of an intramolecular cycloaddition between a diene and a nitrene.[1]



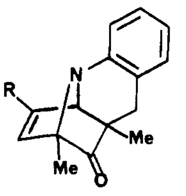
1a, R = Me
b, R = *t*-Bu



2a, R = Me
b, R = *t*-Bu



3a, R = Me
b, R = *t*-Bu



4a, R = Me
b, R = *t*-Bu

In marked contrast to **1a**, triazoline **2a** undergoes a different photorearrangement to give dienone **5** as the major reaction product.[1] Apparently diradical **6**, generated

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(1) Schultz, A. G.; Dittami, J. P.; Myong, S. O.; Sha, C.-K. *J. Am. Chem. Soc.* **1983**, *105*, 3273.

0022-3263/83/1948-2432$01.50/0 © 1983 American Chemical Society