Tetrahedron Vol. 48, No. 22, pp. 4641-4648, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

Ring Closure of 2,2-Dimethyloct-7-en-3-yl Radical: A System Exhibiting Unusual Solvent Dependence

Athelstan L.J. Beckwith,* Matthew D. Cliff and Carl H. Schiesser*

Department of Chemical Sciences, Deakin University, Geelong, Victoria, Australia, 3217

*Research School of Chemistry, Australian National University, GPO Box 4, Canberra, A.C.T., Australia, 2601

(*Received in UK* 13 *April* 1992)

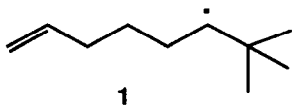
Key Words: Radical Ring Closure; Tributyltin Hydride; Solvent Effect; Arrhenius Parameters; Stereoselectivity

Abstract: *The ring closure of the 2,2-dimethyloct-7-en-3-yl radical (1) has been studied. In hexane at 25°C, reaction of the radical precursor, O-(2,2-dimethyloct-7-en-3-yl)-O-phenylthionocarbonate (8) with tri-n-butyltin hydride (AIBN initiator) proceeds to give trans-1-tert-butyl-2-methylcyclopentane (10) as the major ring closed product (trans/cis = 3.1). The rate constant for the trans-mode of ring closure was found to be 8.7 x 10^4 s^{-1} at 25°C with an activation energy of 5.5 kcal.mol^{-1}, while the corresponding values for the cis-mode of cyclization are 2.8 x 10^4 s^{-1} and 8.7 kcal.mol^{-1}. The stereoselectivity displays the usual temperature dependence. Surprisingly, stereoselectivity is also improved when solvent polarity is increased (trans/cis = 5.9 in 1-propanol at 25°C), a phenomenon not previously identified.*

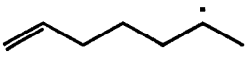
In recent years, ring closures of substituted alkenyl radicals have received widespread attention[1-4], especially by synthetic chemists who have provided many elegant examples of the utility of radical cyclization as a key step in the overall strategy for the preparation of a wide range of complex molecules.[5-10]

Work in our laboratories[11-14] and elsewhere[15-17] has played an important role in the understanding of the factors affecting radical ring closure. The regiochemistry can be rationalized in terms of the *stereo-electronic hypothesis*, as shown in the force-field treatment of the ground and transition states involved in these reactions[12,18]. This treatment has also been largely effective in predicting the stereochemical outcome of these reactions. The transition states bear marked resemblance to the chair and boat forms of cyclohexane, with clearly distinguishable pseudo-axial and pseudo-equatorial positions. The observed stereochemical preferences can be explained by consideration of whether the substituent is in a pseudo-axial-chair, pseudo-equatorial-boat or in the preferred pseudo-equatorial-chair position[11,12,14,18]. A useful guideline based on these observations is that 2- and 4- substituted hexenyl systems prefer to cyclize mainly trans while the 3-substituted cases cyclize mainly cis.

When the hexenyl radical is substituted at position 1, the distinction between pseudo-axial and pseudo-equatorial is less clear. While the force-field approach correctly predicts the preferred mode of ring closure of the hept-6-en-2-yl radical (**2**)[12,18] and the title radical[12] (**1**) (see later), the calculated differences in strain energies between the appropriate transition structures (0.5 or 0.9 kcal.mol^{-1} for **1** and 0.2[12] kcal.mol^{-1} for **2**) are well within the limits of error usually associated with molecular mechanics[19] and do not provide a convincing demonstration of the validity of the force-field method for this system.



1



2

In order to further establish the effects operating in these systems, we chose to investigate the chemistry of the 2,2-dimethyloct-7-en-3-yl radical (**1**). To our surprise this system exhibited a much larger stereoselectivity

than expected on the basis of force-field calculations, with significant dependence on both temperature and solvent, which we now report.

Results and Discussion

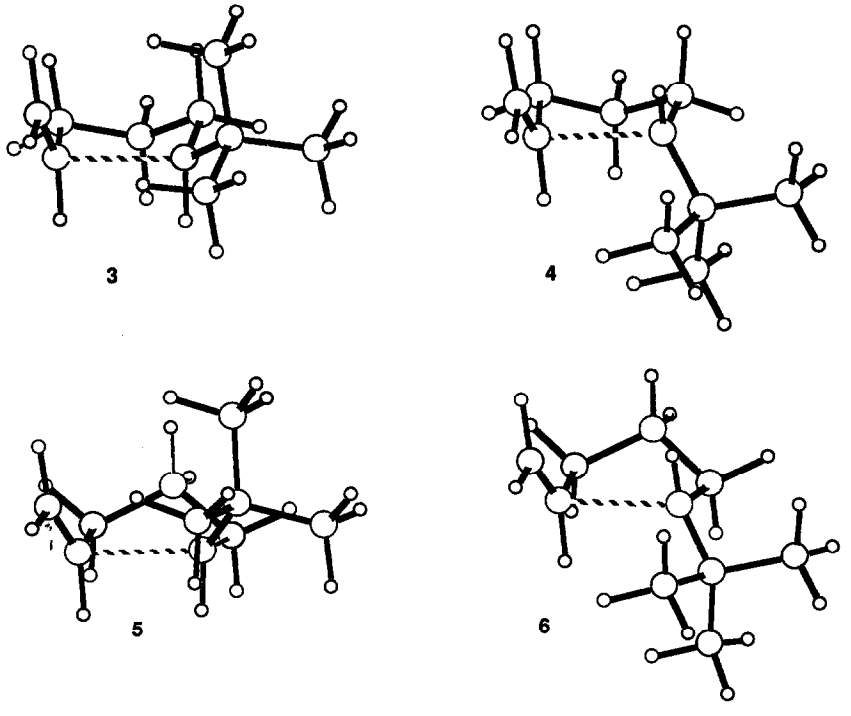
Force-field calculations were performed on the transition states involved in the ring-closure of **1** by the Spellmeyer-Houk model[18] as well as that developed in our laboratories[12] (Beckwith-Schiesser model). These calculations indicate the possible existence of four transition structures for the *exo* mode of cyclization; namely a chair-like and a boat-like structure for each of the cis and trans modes of cyclization. The calculated activation energies[12,18] corresponding to the transition structures depicted in Figure 1 are listed in Table 1.

Table 1 Calculated Activation Energies (ΔE_s)[a] for the Different Modes of Cyclization of the 2,2-Dimethyloct-7-en-1-yl Radical (**1**).

Method	Transition Structure			
	3 (*cis-chair*)	**4** (*trans-chair*)	**5** (*cis-boat*)	**6** (*trans-boat*)
B.S.[b]	8.5	8.1	11.1	8.0
S.H.[c]	9.6	8.7	10.6	9.1

[a] Energies in kcal.mol^{-1}. For definitions see reference 12 and 18. [b] Beckwith-Schiesser. [c] Spellmeyer-Houk.

Figure 1. Calculated Transition Structures for the Ring-Closure of the 2,2-Dimethyloct-7-en-3-yl Radical (**1**).



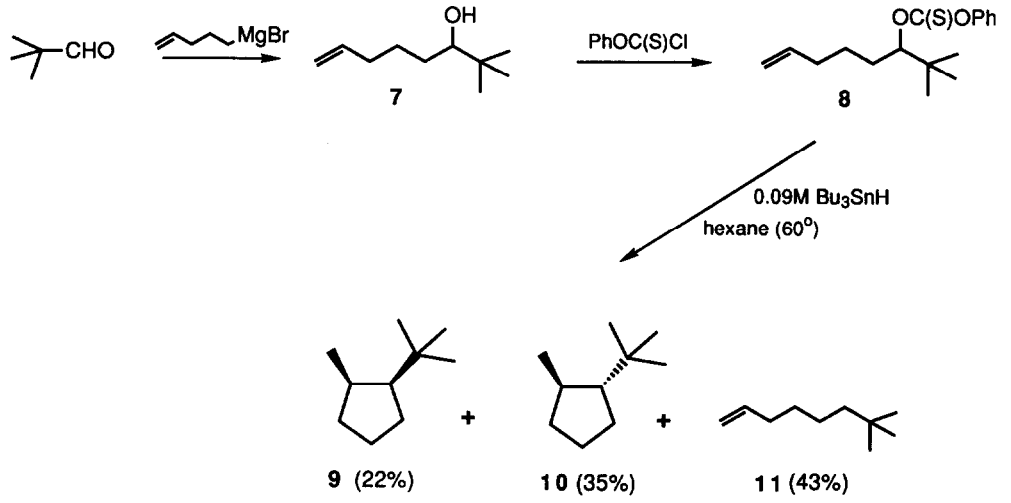
Clearly, the Spellmeyer-Houk method predicts that the ring closure of **1** should proceed via a chair-like transition structure for both the cis and trans modes of cyclization, while our method suggests that the cis mode of cyclization proceeds via a chair while the trans product can arise via either a chair or boat-like structure. Furthermore, both models predict that the trans product should dominate, with the Spellmeyer-Houk method indicating a 0.9 kcal.mol^{-1} energy difference while our method puts this separation at 0.5 kcal.mol^{-1}. These values are substantially smaller than the experimentally determined difference in activation energies of 3.2 kcal.mol^{-1} (see later) suggesting that factors other than steric are important in the cyclization of **1**.

In previous experimental studies we have employed halides[11,20,21], dithio-[13] and thiono- carbonates[22,23] as free radical precursors. In this study we were unable to prepare the halide from the readily available alcohol (**7**), presumably because **7** is a secondary neopentyl system. However, when **7**, prepared by the addition of 4-pentenylmagnesium bromide to trimethylacetaldehyde, was treated with phenyl chlorothionoformate and pyridine in dichlormethane, the required thionocarbonate (**8**) was obtained in good yield (Scheme 1).

Gas chromatography (GC) of the mixture obtained when the thionocarbonate (**8**) was treated with ten equivalents of tri-n-butyltin hydride (0.09M) in hexane at 60°C (AIBN initiator) detected three hydrocarbon products, namely cis-1-*tert*-butyl-2-methylcyclopentane (**9**, 22%), the corresponding trans isomer (**10**, 35%) and the olefin, 7,7-dimethyloct-1-ene (**11**, 43%). The olefin (**11**) was identified by NMR spectroscopy after the above reaction was repeated using 3M tri-n-butyltin hydride in *tert*-butylbenzene at 80° and was the sole hydrocarbon product isolated by preparative GC.

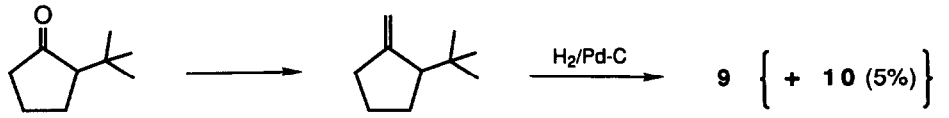
The assignment of the other two products proved to be less straight forward. They were isolated by preparative GC after the above reaction was repeated with 0.06M tri-n-butyltin hydride in hexane. The ^{1}H NMR spectrum of the major isomer (of higher GC retention time) revealed a doublet (δ 0.85, J = 7.1 Hz) assigned to the methyl group and a singlet (δ 0.93) assigned to the *tert*-butyl group. The minor isomer had a doublet (δ 0.97, J = 6.8 Hz) and a singlet (δ 0.84) for the equivalent groups in its ^{1}H NMR spectrum.

Scheme 1



An authentic sample of **9** was eventually prepared from 2-*tert*-butylcyclopentanone (**12**)[24] as depicted in Scheme 2. Methylenation of **12** by the method of Lombardo[25] gave the alkene (**13**) in quantitative yield. Hydrogenation of **13** gave the required hydrocarbon (**9**) contaminated with about 5% of the isomer (**10**). This hydrocarbon corresponded to the minor component in the cyclization reaction.

Scheme 2



12 **13**

Inspection of models of the olefin (**13**) suggests that hydrogenation should occur with a high degree of diastereoselectivity. Reaction at the metal surface should occur such that the bulky *tert*-butyl group is orientated away from the region of reaction, resulting in cis arrangements of substituents in the product.

This cis arrangement was confirmed when the product of hydrogenation was subjected to an ^1H NMR NOE experiment. Selective irradiation of the methyl doublet resulted in a 10% enhancement of the *tert*-butyl singlet, thus confirming the cis arrangements of substituents in the product of hydrogenation (**9**).

Kinetic experiments were performed in hexane under pseudo-first-order conditions employing ten equivalents of tri-n-butyltin hydride. Product distributions were determined by GC. Relative rates of cyclization were determined by use of the integrated rate equation:

$$\frac{k_c}{k_H} = \frac{[\mathbf{9} \text{ or } \mathbf{10}][Bu_3SnH]}{[\mathbf{11}]}$$

where k_c is the rate constant for the cis or trans mode of ring closure and k_H is the rate constant for hydrogen abstraction of **1** from tri-n-butyltin hydride. Substitution of appropriate values[16] of k_H yielded values for the cis and trans cyclization rate constants (k_{cis}, k_{trans}) which are listed in Table 2 with other relevant data.

Table 2 Relevant Kinetic Data for the Ring Closure of the 2,2-Dimethyloct-7-en-2-yl Radical (**1**) in Hexane.

Temp[a]	$[Bu_3SnH]$[b]	%			k^c_{cis}	k^c_{trans}	trans/cis
		9	**10**	**11**			
-33	0.036	-	-	-	-		15.6
7	0.036	11	47	42	0.91	3.9	4.2
25	0.088	11	36	53	2.8	8.7	3.1
45	0.051	20	43	37	5.7	13.0	2.2
60	0.088	22	35	43	12.0	19.0	1.6
80	0.088	29	35	36	26.0	32.0	1.3
92	0.088	31	37	32	35.0	42.0	1.2

[a]Temperature in °C. [b]Average concentration (M). [c]x 10^{-4} s^{-1}.

Inspection of Table 2 reveals that **1** ring closes more slowly than the parent hexenyl system, which cyclizes with a rate constant[26] of 2.3 x 10^5 s^{-1} at 25°, or the hept-6-en-2-yl radical (**2**), which has a combined rate constant[20] for the similar process of 1.5 x 10^5 s^{-1} at 25°. The combined rates constant for the cyclization of **1** of 1.2 x 10^5 s^{-1} at 25°, comprising mainly the trans rate constant of 8.7 x 10^4 s^{-1}, is higher than expected on the basis of steric bulk in the associated transition states.

Linear regressional analysis of the data in Table 2 provides the following Arrhenius equations:

$$\log k_{cis} = 10.8 \pm 0.4 - (8.7 \pm 0.5)/\theta$$

$$\log k_{trans} = 8.9 \pm 0.4 - (5.5 \pm 0.5)/\theta$$

where $\theta = 2.3RT$ kcal.mol^{-1}. Clearly, the trans mode of cyclization is preferred over that for the cis by 3.2 kcal.mol^{-1}. It is also apparent that the force-field treatment, as discussed earlier, has significantly underestimated this energy difference which is responsible for the pronounced temperature dependence observed for the stereoselectivities, with trans/cis ranging from 15.6 at -33°, to 1.2 at 92°.

The linear free-energy relationships put the energy barrier ($E^{\neq}$) for the cis mode of cyclization at 8.7 kcal.mol^{-1} and the value for the pre-exponential term (log A) at 10.8. These values are consistent with intuition. Most hexenyl radical ring closures have associated log A values of between 10 and 11[22,26]. The energy barrier of 8.7 kcal.mol^{-1} is as expected given the steric requirements for cyclization of **1** in the cis mode. Less bulky systems, like hexenyl itself and **2** have energy barriers of 6.8[28] and 6.9[27] kcal.mol^{-1} respectively.

The data for the trans mode of cyclization reveal some interesting features. The value for log A of 8.9 is lower than expected for hexenyl ring closures. This indicates that the transition state leading to **10** (trans) is more ordered than that leading to **9** (cis). The energy barrier of only 5.5 kcal.mol^{-1} is lower than that for the hexenyl radical itself, suggesting that the transition state for the formation of **10** is somehow stabilized or that the ground state energy is raised by a Thorpe-Ingold effect[28] as has been postulated for the cyclization of the 3-*tert*-butylhex-5-enyl radical[14].

When this reaction is carried out in different solvents, an unexpected general increase in diastereoselectivity is observed as the dipole moment of the solvent is increased. This effect is listed in Table 3.

Table 3 Solvent Dependences of the trans/cis Ratio and Approximate Differences in the Activation Energies ($\Delta E^{\neq}$) and log A (Δlog A) in the Ring Closure of the 2,2-Dimethyloct-7-en-3-yl Radical (**1**).

Temp[a]	Hexane	Ether	Ethanol	1-Propanol
25	3.1	2.7	4.4	5.9
45	2.2	2.4	3.2	4.0
80	1.3	1.7	1.8	2.0
95	1.2	1.3	1.6	1.7
$\Delta E^{\neq}$ (cis-trans)[b]	3.2	2.2	3.2	4.0
Δlog A (cis-trans)	1.9	1.2	1.7	2.2

[a]Temperatures in °C. [b]Approximate energies in kcal.mol^{-1}.

Inspection of Table 3 reveals an almost 2-fold increase in stereoselectivity in progressing from hexane to 1-propanol. We are not aware of any previous recognition of this phenomenon, in which the stereochemical outcome of the ring closure of an alkenyl radical is affected by solvent. Corey, however, notes that the ratios of endo-endo and exo-exo-4,5-disubstituted 1,2-dioxabicyclo[2.2.1]heptanes formed in the ring closure of a 1,2-dioxolane are solvent dependent[29], while more recently Snider has reported that the regiochemistry of manganese (III)-based oxidative free-radical ring closures is solvent dependent[30].

Linear regressional analysis of the trans/cis ratios given in Table 3 yield approximate values for the differences in activation energy ($\Delta E^{\neq}$) and log A (Δlog A) for the cis and trans modes of cyclization of **1** in the various solvents in this study. While it is apparent that the differences in Arrhenius parameters for the cis and

trans-modes of cyclization are solvent dependent, the experimentally-determined changes are neither sufficiently accurate nor sufficiently consistent to allow any firm conclusions to be drawn. What is clear is that the trans/cis ratio increases as solvent dipole moment is increased and that changes in activation energy and entropy are possible both involved.

Solvent effects are often associated with polar intermediates or transition states in chemical reactions. A good example is the S_N2 reaction, which proceeds via a polar transition state. Increasing solvent polarity has a large accelerating effect on reaction rate[31]. Is it possible that **1** cyclizes via polar transition states? If this were the case, then small differences in the polarity of the cis and trans transition states might be expected to lead to significant differences in the rates of ring closure in different solvents.

Having discovered what is clearly an unusual phenomenon, we were interested in whether or not other systems also display such a solvent dependence. In similar experiments to those outlined in the study of **1**, we have found that the hept-6-en-2-yl radical (**2**), generated from the corresponding bromide[27] and the 1,1,1-trifluorohept-6-en-2-yl radical (**14**), generated from the corresponding thionocarbonate, exhibited similar solvent effects, although not nearly as pronounced as that observed for **1**. For example, the cis/trans ratio for **2** shifts from a value of 3.3 in hexane at 25° to 3.6 in 1-propanol, while the similar ratio for **14** shifts from 1.2 to 1.7 under the same conditions. Four other systems studied exhibited no such effect.

Experimental

Trimethylacetaldehyde and phenyl chlorothionoformate were purchased from Aldrich and were used without further purification. Tri-n-butyltin hydride was prepared as previously described[32] and distilled before use.

Medium performance liquid chromatography (MPLC) was performed using a Merck LiChroprep Si 60 (40-63 μm) column with a Waters R-403 differential refractometer detector. Analytical GC was performed using a dimethyl siloxane 25QC2/BP1 capillary column purchased from Scientific Glass Equipment (SGE) in a Varian 6000 or Hewlett-Packard 3390A gas chromatograph equipped with a Hewlett-Packard 3390A integrator. Preparative GC was performed using either a 20% SE-30 on Chromosorb W (80-100 mesh) or 20% Carbowax on Chromosorb W column.

Infra-red spectra were measured on a Perkin-Elmer 683 Infra-red spectrophotometer. NMR spectra were recorded on a JEOL PNM-FX200 or JNM-GX270 spectrometer using deuteriochloroform ($CDCl_3$) as solvent. Mass spectra were measured on either a VG Micromass 7070F or an AEI MS 902 mass spectrometer operating at 70 eV. Chemical ionization (CI) mass spectra were recorded using ammonia as reagent gas.

2,2-Dimethyloct-7-en-3-ol (7). Trimethylacetaldehyde (920 mg, 10.7 mmol) was added to an ice-cold solution of 4-pentenylmagnesium bromide (prepared from 5-bromopent-1-ene (2.0 g, 13.4 mmol) and magnesium (360 mg, 15.0 mmol) in ether (20 mL)). After heating at reflux for 30 min, the solution was poured into 10% hydrochloric acid (100 mL). After extracting with ether (2x), the combined extracts were dried and the solvent removed *in vacuo*. The residue was purified by flash chromatography with 10% ether in dichloromethane as eluent and subjected to bulb-bulb distillation (bp ca 50°/0.5 mm) to afforded the title alcohol as a colourless oil (680 mg, 41%). ^{1}H NMR δ 0.88 (s, 9H) 1,18-1.66 (m, 4H), 1.78 (s(br), 1H), 2.13-2.20 (m, 2H), 3.10-3.22 (m, 1H), 4.91-5.05 (m, 2H), 5.71-5.91 (m, 1H); IR (neat) 1640, 3380 (br) cm^{-1}. Anal. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.80; H, 12.63%.

O-(2,2-Dimethyloct-7-en-3-yl)-O-phenylthionocarbonate (**8**). 2,2-Dimethyloct-7-en-3-ol (**7**) (500 mg, 3.21 mmol), phenylchlorothionocarbonate (610 mg, 3.53 mmol) and pyridine (940 mg) were stirred in dichloromethane (15 mL) under nitrogen overnight. The yellow solution was poured into water (50 mL), extracted with ethyl acetate (2x), the combined extracts washed with 10% hydrochloric acid (4x), satd. $NaHCO_3$ and dried. Removal of the solvent *in vacuo* gave a yellow oil which was purified by flash chromatography with 8% ether in hexane as eluent to give the title thionocarbonate (**8**) as a colourless oil (720 mg, 77%). ^{1}H NMR δ

0.98 (s, 9H), 1.40-1.75 (m, 4H), 2.06-2.18 (m, 2H), 4.94-5.06 (m, 2H), 5.34 (t, J=6.4Hz, 1H), 5.69-5.88 (m, 1H), 7.05-7.42 (m, 5H); MS (CI), m/e 293 ($[M+H]^+$), calcd for $C_{17}H_{24}O_2S$: $[M+H]^+$ = 293.1575. Found: $[M+H]^+$ = 293.1571.

Cis and trans-1-*tert*-Butyl-2-methylcyclopentane (9, 10). O-(2,2-Dimethyloct-7-en-3-yl)-O-phenylthionocarbonate (**8**) (150 mg, 514 μmol), tri-n-butyltin hydride (165 mg, 565 μmol) and AIBN (ca 10 mg) were heated in hexane (10 mL) at reflux overnight. The solution was concentrated to ca 10 mL at reduced pressure. Analytical GC indicated three products. Bromine was added until the orange colour just persisted. Analytical GC revealed the absence of the minor of the three initial products. The sample was separated by preparative GC to give, as the product of lower retention time, cis-1-*tert*-butyl-2-methylcyclopentane (**9**) as a colourless oil. ^{1}H NMR δ 0.84 (s, 9H), 0.97 (d, J=6.8 Hz, 3H) 1.38-1.89 (m, 8H); ^{13}C NMR δ 23.8, 27.9 25.6, 29.4, 32.9, 34.4, 36.3, 57.6; MS, m/e 140 (M^+), calcd for $C_{10}H_{20}$: M^+ = 140.1565. Found: $M^{+\cdot}$ = 140.1569.

The product of higher retention time proved to be trans-1-t-butyl-2-methylcyclopentane (**10**) which was isolated as a colorless oil. ^{1}H NMR δ 0.85 (d, J=7.1 Hz, 3H), 0.93 (s, 9H), 1.45-1.75 (m, 6H), 2.12 (m, 2H); ^{13}C NMR δ 16.8, 21.3 23.0, 29.8, 34.8, 35.5, 54.7; MS, m/e 140 ($M^{+\cdot}$), cald for $C_{10}H_{20}$: $M^{+\cdot}$ = 140.1565. Found: $M^{+\cdot}$ = 140.1570.

7,7-Dimethyloct-1-ene (11). O-(2,2-Dimethyloct-7-en-3-yl)-O-phenyl-thionocarbonate (**8**) (150 mg, 514 μmol), tri-n-butyltin hydride (165 mg, 565 μmol) and AIBN (ca 10 mg) were heated in *tert*-butylbenzene (50 μL) at 80° overnight. The sample was separated by preparative GC to give the title olefin (**11**) as a colorless oil. ^{1}H NMR δ 0.86 (s, 9H), 1.15-1.35 (m, 6H), 2.00-2.12 (m, 2H), 4.89-5.05 (m, 2H), 5.71-5.92 (m, 1H); MS, m/e 140 ($M^{+\cdot}$), cald for $C_{10}H_{20}$: $M^{+\cdot}$ = 140.1565. Found: $M^{+\cdot}$ = 140.1570.

1-*tert*-Butyl-2-methylenecyclopentane (13). Freshly prepared zinc/titanium tetrachloride/dibromemethane methylenating reagent[25] was added in portions to a solution of 2-*tert*-butylcyclopentanone[24] (**12**) (250 mg, 1.79 mmol) in dichloromethane (3 mL) until TLC indicated the absence of the starting ketone. The mixture was poured into sat sodium hydrogen carbonate (50 mL) and extracted with ether. The combined extracts were dried and the solvent removed to give the title olefin (**9**) as a pale oil, in quantitative yield. Analytical GC indicated purity in excess of 90%. ^{1}H NMR δ 0.89 (s, 9H), 1.15-1.87 (m, 4H), 2.10-2.32 (m, 3H), 4.80 (m, 1H), 4.97 (m, 1H); IR (neat): 1650 cm^{-1}. These data are consistent with literature reports[33].

Hydrogenation of 1-*tert*-butyl-2-methylcyclopentane (13).

1-*tert*-Butyl-2-methylenecyclopentane (**13**) (100 mg), 10% palladium on carbon (25 mg) and ethyl acetate (1 mL) were stirred at room temperature under hydrogen for 3 h. Analytical GC revealed the absence of starting olefin and the formation of two products corresponding to cis- (95%) and trans-1-*tert*-butyl-2-methylcyclopentane (5%) (**9, 10**) as previously prepared.

Kinetic experiments. An aliquot (100 μL) of a standard solution (0.036-2.0M) of tri-n-butyltin hydride in the required solvent was placed in a small pyrex tube, the required precursor (ca 0.001 mmol) and AIBN (ca 1 crystal) were added and the mixture degassed by the usual freeze-thaw technique, before being sealed under vacuum. After being thermolysed in an oil bath (T>50°) or irradiated with a 100W mercury lamp at a distance of 20 cm in a constant temperature water bath (T<50°) or liquid ammonia bath (T = -33°) for 4-6 h, the mixture was analysed by GC. Application of the appropriate integrated rate equation and published values for k_H (see text) produced the data displayed in Tables 2 and 3.

References

(1) Porter, N.A.; Magrin, D.R.; Wright, B.T. *J. Am. Chem. Soc.*, **1986**, *108*, 2787.
(2) Bischof, P. *Helv. Chim. Acta.*, **1980**, *63*, 1434.
(3) Curran, D.P.; Chen, M.-H.; Kim, D. *J. Am. Chem. Soc.*, **1986**, *108*, 2489.
(4) Fang, J.-M.; Chang, H.-T.; Lin, C.-C. *J. Chem. Soc. Chem. Commun.*, **1988**, 1385.
(5) Hart, D.J.; Huang, H.-C.; Krishnamurthy, R.; Schwartz, T. *J. Am. Chem. Soc.*, **1989**, *111*, 7507.
(6) Curran, D.P.; Chen, M.-H.; Kim, D. *J. Am. Chem. Soc.*, **1989**, *111*, 6265.
(7) Mehta, G.; Murthy, A.N.; Reddy, D.S.; Reddy, A.V. *J. Am. Chem. Soc.*, **1986**, *108*, 3443.
(8) Bachi, M.D.; Denenmark, D. *J. Org. Chem.*, **1990**, *55*, 3442.
(9) Curran, D.P.; Abraham, A.C.; Liu, H. *J. Org. Chem.*, **1991**, *56*, 4335.
(10) Curran, D.P.; Kim, D. *Tetrahedron*, **1991**, *47*, 6171.
(11) Beckwith, A.L.J. *Tetrahedron*, **1981**, *37*, 3073.
(12) Beckwith, A.L.J.; Schiesser, C.H. *Tetrahedron*, **1985**, *41*, 3925.
(13) Beckwith, A.L.J.; Bowry, V.W.; Schiesser, C.H. *Tetrahedron*, **1991**, *47*, 121.
(14) Beckwith, A.L.J.; Zimmermann, J. *J. Org. Chem.*, **1991**, *56*, 5791.
(15) Lamb, R.C.; Ayers, P.W.; Toney, M.K. *J. Am. Chem. Soc.*, **1963**, *85*, 3483.
(16) Chatgilialoglu, C.; Ingold, K.U.; Scaiano, J.C. *J. Am. Chem. Soc.*, **1981**, *103*, 7739.
(17) Julia, M.; Maumy, M. *Bull. Soc. Chim. Fr.*, **1968**, 1603.
(18) Spellmeyer, D.C.; Houk, K.N. *J. Org. Chem.*, **1987**, *52*, 959.
(19) Burkert, U.; Allinger, N.L. *Molecular Mechanics*, American Chemical Society, Washington D.C., 1982.
(20) Beckwith, A.L.J.; Blair, I.; Phillipou, G. *J. Am. Chem. Soc.*, **1974**, *96*, 1613.
(21) Beckwith, A.L.J.; Pigou, P.E. *Aust. J. Chem.*, **1986**, *39*, 77.
(22) Schiesser, C.H. Ph.D. Dissertation, Australian National University, **1986**.
(23) Robins, M.J.; Wilson, J.S.; Hansske, F. *J. Am. Chem. Soc.*, **1983**, *105*, 4059.
(24) Reetz, M.T.; Maier, W.F.; Chatziiosifidis, I. *Chem. Ber.*, **1980**, *113*, 3741.
(25) Lombardo, L. *Tetrahedron Lett.*, **1982**, *41*, 4293.
(26) Beckwith, A.L.J.; Easton, C.J.; Lawrence, T.; Serelis, A.K. *Aust. J. Chem.*, **1983**, *36*, 545.
(27) Beckwith, A.L.J.; Blair, I.A.; Phillipou, G. *Tetrahedron Lett.*, **1974**, 2251.
(28) Allinger, N.L.; Zalkow, V. *J. Org. Chem.*, **1960**, *25*, 701.
(29) Corey, E.J.; Shimoji, K.; Shih, C. *J. Am. Chem. Soc.*, **1984**, *106*, 6425.
(30) Snider, B.B.; Merritt, J.E.; Dombroski, M.A.; Buckman, B.O. *J. Org. Chem.*, **1991**, *56*, 5544.
(31) Ingold, C.K. *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N.Y., **1969**.
(32) Van der Kerk, G.J.M.; Noltes, J.G.; Luijten, J.G.A. *J. Appl. Chem.*, **1957**, 366.
(33) Senda, Y.; Kamiyama, S.; Imaizuma, S. *Tetrahedron*, **1977**, *33*, 2933.