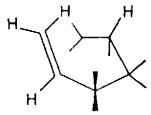
The Effect of Non-bonded Interactions on the Regioselectivity of Cyclization of the Hex-5-enyl Radical

By **Athelstan L. J. Beckwith** * and **Tony Lawrence**, Organic Chemistry Department, University of Adelaide Adelaide, South Australia, Australia 5000

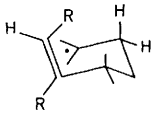
Treatment of 1-bromo-2,2,5-trimethylhex-5-ene (9a) with tributylstannane affords 2,5,5-trimethylhex-1-ene (13a), 1,1,3,3-tetramethylcyclopentane (12a), and 1,1,4-trimethylcyclohexane (15a). Accurate determination of the yields allows the rate constants for the *endo*- and *exo*-modes of cyclization of the 2,2,5-trimethylhex-5-enyl radical (10a) to be determined. Comparison of the kinetic parameters with those for the 2,2-dimethylhex-5-enyl radical (10b) and related species indicates that interaction of the pseudo-axial 2-methyl substituent with the *syn*-proton at C-6 disfavours the formation from (10b) of the chair-like six-membered transition state (5). The effect is, however, too small to account for the high regioselectivity of ring closure of the parent hex-5-enyl radical.

STEREOELECTRONIC effects play a major role in determining the direction of intramolecular addition in alkenyl radicals.[1,2] The suggestion [1,3,4] that the hex-5-enyl radical undergoes predominantly 1,5-*exo*-cyclization because of the necessity for maximum overlap to be attained in the transition state between the semi-occupied 2*p* orbital and the vacant π^* orbital has been widely accepted, and has been formalised in Baldwin's rules.[5] Nevertheless, it is clear that other factors also contribute to the observed regioselectivity of this and related ring closures. As expected,[6] the value of $\Delta S^{\ddagger}$ for 1,5-cyclization is more favourable than that for 1,6.[7] However, $\Delta H^{\ddagger}$ is also more favourable for formation of the smaller ring, and at ordinary temperatures it is the difference in this parameter rather than $\Delta\Delta S^{\ddagger}$ which mainly controls the 1,5/1,6 cyclization ratio.[7]

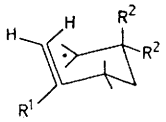
Another factor possibly contributing to the regioselectivity of ring closure of the hex-5-enyl radical has been investigated by Julia and his co-workers [8] who developed Le Bel's hypothesis † that a non-bonded interaction between the pseudo-axial proton at C-2 and the *syn*-proton at C-6 may destabilise the chair-like transition state (2) by comparison with that (1) on the pathway for



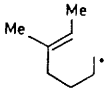
(1)



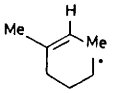
(2) R = H
(3) R = Me



(4) R^1 = H, R^2 = Me
(5) R^1 = R^2 = Me



(6)



(7)

1,5-cyclization. In accord with this hypothesis the *E*-isomer (6) of 5,6-dimethylhex-5-enyl radical affords both five- and six-membered cyclic products with the latter predominating, whereas the *Z*-isomer (7), for which 2,6-non-bonded interaction in a chair-like transition state (3) should be much more severe, undergoes exclusively 1,5-cyclization.

† Suggested by Professor N. Le Bel in a discussion with Professor Julia (see ref. 8).

Unfortunately the yield of cyclic products was relatively low ($\leqslant$20%) under the experimental conditions employed by Julia [8] and consequently it is not possible to obtain from his data a quantitative estimate of the severity of the non-bonded interaction. We have chosen, therefore, to examine the behaviour of the radical (10a) which was expected to give good yields of cyclic products under appropriate conditions. Also, comparison of the behaviour of (10a) with (7) might reveal the extent of any interaction between the 6-methyl substituent and the pseudo-axial proton at C-4. Treatment of the bromo-compound (9a) with tributylstannane in benzene gave a mixture of (12a), (13a), and (15a) which was accurately analysed by gas chromatography. In most experiments the material balance was excellent, and the relative yields (Table 1) varied with stannane concentration as expected on the basis of the accepted reaction mechanism.[9] For comparison, the behaviour of the 2,2-dimethylhex-5-enyl radical (10b) was also examined. The yields of cyclic (12b) and acyclic (13b) products obtained when (9b) was treated with tributylstannane are given in Table 2. Relative rate constants calculated by substitution of the data into the appropriate integrated rate equation [7] are also presented. The usual treatment of rate constants at various temperatures afforded activation parameters which are given in Table 3 together with data available from previous work in these laboratories [10] for the radicals (8a) and (8b), and rate constants for the cyclization of (6) and (7) calculated from Julia's data.[8]

The results obtained show that cyclization of the 2,2-dimethylhex-5-enyl radical (10b) is both more rapid and

TABLE 1

Reduction of 6-bromo-2,5,5-trimethylhex-1-ene (9a) with Bu_3SnH

/°C	$[Bu_3SnH]_0$ [a]/ mol l^{-1}	Relative yields/% (13a)	(12a)	(15a)	$k_{1,5}k_H^{-1}$/ l mol^{-1}	$k_{1,6}k_H^{-1}$/ T mol^{-1} l
45	0.038	33	47	20	0.043	0.018
	0.151	68	22	10	0.040	0.018
80	0.038	25	51	24	0.063	0.029
	0.151	57	30	14	0.064	0.030
100	0.038	20	55	25	0.086	0.040
	0.151	50	34	16	0.083	0.039

[a] Initial concentration; final concentration = 0.622 × $[Bu_3SnH]_0$.

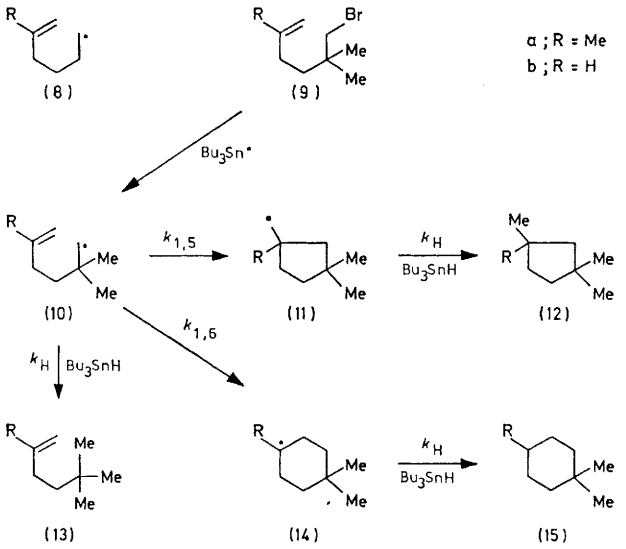
TABLE 2

Reduction of 6-bromo-5,5-dimethylhex-1-ene (9b) with Bu_3SnH

T/°C	$[Bu_3SnH]_0$ [a] mol l^{-1}	Relative yields (%) (12b)	(13b)	$k_{1,5}k_H^{-1}$/l mol^{-1}
30	0.20 [b]	94	6	1.57
	1.00 [b]	77	23	1.55
	1.39 [b]	70	30	1.45
40	1.24 [b]	75.5	24.5	1.74
	1.39 [b]	73	27	1.72
55	1.86 [c]	62	38	1.98
80	0.50	90	10	2.28
	1.00	83	17	2.31

[a] Initial concentration. [b] Final concentration = 0. [c] Final concentration = 0.61 mol l^{-1}.

more regiospecific than cyclization of the parent radical (8b). About 2% of the cyclic products obtained from the latter arise by 1,6-ring closure, but we were unable to detect any of the analogous product (15b) arising from



reactions involving (10b). Having regard to the sensitivity of the analytical methods used, we believe this indicates the ratio of *exo*-/*endo*- cyclization in (10b) to be >100 : 1. Such high regiospecificity supports the view that non-bonded interactions in the transition state (4) will be more severe than in the unsubstituted case (2).

Since all the acyclic radicals examined in the course of this work are primary, it is reasonable to assume that values of k_H, the rate constant for hydrogen atom transfer from stannane, are approximately the same.[9] Consequently, comparison of values of k_c/k_H for the various radicals provides a measure of their relative rates of cyclization. Similarly, the activation parameter differences given in Table 3 are all related to $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reaction of a primary radical with tributylstannane. Approximate absolute values of the parameters for cyclization can be obtained by adding the appropriate values for the stannane reaction ($\Delta H^{\ddagger} = 3.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = -18$ cal mol^{-1} K^{-1}) obtained from a comparison of the data for hex-5-enyl radical by direct [11] and indirect [7] methods.

The data in Table 3 indicate that at 80 °C the rate constant $k_{1,5}$ for ring closure of the 2,2-dimethylhex-5-enyl radical (10b) is almost ten times larger than that for the analogous reaction of the unsubstituted radical (8b). This type of rate enhancement, which has been noted previously both for this [12] and other radical reactions,[13] is attributable to the Thorpe–Ingold or '*gem*-dialkyl' effect.[14–16] In terms of the explanation advanced by Allinger and Zalkow [15] the introduction of the two methyl substituents into hex-5-enyl radical causes extra *gauche* interactions in the ground state which are partly relieved when the cyclic transition state is attained. The net result is that the free energy of the reactant ground state is raised relative to that of the cyclic transition state and the rate of ring-closure is enhanced accordingly. In this case the activation data reveal that the introduction of the two methyl substituents has little effect on the entropy term. The change in $\Delta\Delta H^{\ddagger}$, however, of *ca.* 1.3 kcal mol^{-1} is about what would be expected for two additional gauche interactions in the reactant radical (10b) as compared with the parent; [17] it is this change in the enthalpy term which is mainly responsible for the observed rate enhancement. The conclusion that alkyl substituents affect predominantly the enthalpy of the reactant is consistent with the results of a recent investigation of carbonium ion cyclizations.[16]

Introduction of an alkyl group at the 5-position in hex-5-enyl radical completely changes the regioselectivity of ring closure. The value of $k_{1,5}/k_{1,6}$ at 80 °C for 5-methylhex-5-enyl radical (8a) reported here is different from those previously recorded (0.40 [8] and *ca.* 25 [18]). However, our results have been independently confirmed in three separate sets of experiments and are considered to be reliable.[19] Examination of the individual rate constants for (8a) and the parent radical (8b) shows that the change in regioselectivity is due partly to a small

TABLE 3

Relative rate constants at 80 °C and parameters [a] for radical cyclization

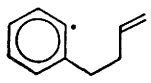
Radical	$k_{1,5}/k_{1,6}$	1,5-Cyclization $k_{1,5}k_H^{-1}$/l mol^{-1}	$\Delta\Delta H^{\ddagger}$	$\Delta\Delta S^{\ddagger}$	1,6-Cyclization $k_{1,6}k_H^{-1}$/l mol^{-1}	$\Delta\Delta H^{\ddagger}$	$\Delta\Delta S^{\ddagger}$	Ref.
(8b)	50	0.24	3.0 ± 0.1	5.8 ± 0.4	0.005	4.7 ± 0.3	3.0 ± 0.4	7
(8a)	0.73	0.008	4.8 ± 0.2	5.7 ± 0.6	0.012	4.3 ± 0.2	3.3 ± 0.4	10, 19
(10b)	>100	2.32	1.7 ± 0.1	6.6 ± 0.4				This work
(10a)	0.47	0.065	3.0 ± 0.1	3.0 ± 0.3	0.030	3.3 ± 0.1	2.4 ± 0.2	This work
(6)	0.57	0.012			0.021			8
(7)	Large	0.18						8

[a] $\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}_c - \Delta H^{\ddagger}_H$ (kcal mol^{-1}); $\Delta\Delta S^{\ddagger} = \Delta S^{\ddagger}_c - \Delta S^{\ddagger}_H$ (cal mol^{-1} K^{-1}).

enhancement in the rate of 1,6-ring closure but mainly to a dramatic decrease in the rate of the 1,5-reaction. The former rate enhancement may reasonably be attributed to the stabilizing effect of the methyl substituent on the product radical. The origins of the strong retardation of the rate of 1,5-ring closure brought about by the methyl substituent are less clear. Possibly ' B-strain ' [20] becomes more severe as C-5 moves towards tetrahedral co-ordination at the transition state. Transannular non-bonded interactions probably have little effect, for the rate retardation observed in this work is very similar to that recently determined in an intermolecular system.[21]

Ring closure of the trisubstituted radical (10a) affords similar quantities of five- and six-membered cyclic products. Comparison of the kinetic data (Table 3) with those for 5-methylhex-5-enyl radical (8a) shows that the *gem*-dimethyl substituents, as expected, enhance the rates of both modes of cyclization. However, the enhancement factor for 1,6-ring closure (2.5) is much less than that (8.1) for 1,5-; *i.e.* ' *gem*-dialkyl ' acceleration of the latter cyclization is three times more effective than it is for the former. This difference represents an unfavourable contribution to the free-energy of formation of the six-membered transition state (5) relative to the analogous five-membered transition state of *ca.* 0.8 kcal mol^{-1}.

We conclude that the type of non-bonded interaction envisaged by Julia [8] and Le Bel between the pseudo-axial methyl substituent at C-2 and the *syn*-proton at C-6 does destabilise the six-membered transition state (5). However, the magnitude of the effect is small and will be much less when, as in the parent radical (8b), there is no alkyl substituent at C-2. It appears, therefore, that purely steric effects play little part in determining the regioselectivity of cyclization of hex-5-enyl radical, a conclusion supported by the observation that alkenylaryl radicals [*e.g.* (16)] in which there is no pseudo-axial substituent at C-2 in the six-membered transition state undergo exclusive 1,5-ring closure.[4] The hypothesis that cyclization of alkenyl radicals is mainly controlled by stereoelectronic effects [1] remains valid.



(16)

Finally, there arises the question of why the radical (7) gives no six-membered cyclic product; why does the presence of a *syn*-methyl substituent at C-6 disfavour the formation of six-membered state more than a pseudo-axial methyl at C-2? One possible explanation is that there are non-bonded interactions of the 6-methyl substituent in (3) with the pseudo-axial protons at both C-2 and C-4, and that the latter may be more severe than the former. The validity of this hypothesis will be tested by further investigation of the behaviour of appropriately substituted hex-5-enyl radicals.

EXPERIMENTAL

General experimental details have been given previously.[13b] The following columns were used for g.l.c.: (*a*) 4.6 m × 2.1 mm 5% Apiezon on Varaport 30 metal column, (*b*) 3.1 m × 6.4 mm 20% FFAP on Chromosorb W glass column, (*c*) 6.2 m × 3.2 mm 2.5% FFAP on Varaport 30 metal column, (*d*) 6 m × 8 mm 14% Carbowax 20M on Chromosorb A glass column, (*e*) 6.1 m × 3.2 mm 20% Carbowax 20M on Varaport 30 metal column, and (*f*) 4.6 m × 2.1 mm 5% Carbowax 20M on Varaport 30 metal column.

Reactions of bromo-compounds with tributylstannane were carried out as previously described [13b] in benzene, purified by fractional freezing. G.l.c. analysis was conducted on columns (*f*) and (*e*) in series at 90 °C for 6-bromo-5,5-dimethylhex-1-ene, and on column (*e*) at 120 °C for 6-bromo-2,5,5-trimethylhex-1-ene. The results are given in Tables 1 and 2.

Ethyl 2,2-Dimethylhex-5-enoate.—Lithium di-isopropylamide [22] (0.1 mol) in tetrahydrofuran (100 ml) was stirred at −78 °C while ethyl isobutyrate (11.5 g) was added dropwise. Stirring was continued, and after 30 min 4-bromobut-1-ene (13.5 g) in hexamethylphosphoric triamide (20 ml) was slowly added. After the addition the mixture was allowed to warm up during 12 h to 20 °C, when it was diluted with water and extracted with light petroleum (b.p. 30—40 °C). After being washed with dilute hydrochloric acid and with sodium hydrogen carbonate solution, the organic layer was distilled to afford the required *ester* (14 g, 82%), b.p. 28 °C at 0.02 mmHg, n_D^{20} 1.448 6 (Found: C, 70.2; H, 10.3. $C_{10}H_{18}O_2$ requires C, 70.5; H, 10.6%), *m/e* 170 (M^+), δ 1.25 (3 H, t, *J* 7 Hz, OCH_2CH_3), 1.18 (6 H, s, 2 × CH_3), 1.3—2.0 (4 H, m, CH_2CH_2), 4.1 (2 H, q, *J* 8 Hz, OCH_2), 4.7—5.2 (2 H, m, $=CH_2$), and 5.2—6.1 (1 H, m, =CH); $\nu_{max.}$ 1 640 and 1 720 cm^{-1}, homogeneous by g.l.c. [column (*a*), 120 °C].

6-Bromo-5,5-dimethylhex-1-ene (9b).—The foregoing ester (4.25 g) was stirred with lithium aluminium hydride (1.0 g) in diethyl ether (25 ml) at ambient temperature for 14 h. After dropwise addition of sodium hydroxide solution to the mixture, the supernatant liquid was decanted and distilled to afford 2,2-dimethylhex-5-en-1-ol, b.p. 41 °C at 0.5 mmHg (2.6 g, 80%), n_D^{24} 1.441 2 (lit.,[12] 1.442 5), δ 0.85 (6 H, s, 2 × CH_3), 1.1—1.5 (2 H, m, CH_2), 1.7—2.3 (2 H, m, CH_2), 3.2 (1 H, s, OH), 3.3 (2 H, s, OCH_2), 4.7—5.2 (2 H, m, $=CH_2$), and 5.4—6.2 (1 H, m, =CH); $\nu_{max.}$ 1 600 and 3 100 cm^{-1}, homogeneous by g.l.c. [column (*a*), 120 °C]. Treatment of this alcohol (2.6 g) with triphenylphosphine and carbon tetrabromide in dichloromethane as previously described [12] gave crude 6-bromo-5,5-dimethylhex-1-ene (2.1 g, 54%). Preparative g.l.c. [column (*d*), 110 °C] afforded the pure bromide [12] (1.2 g, 30%), b.p. 59 °C at 0.5 mmHg, *m/e* 190/192 (M^+), δ 1.0 (6 H, s, 2 × CH_3), 1.3—1.7 (2 H, m, CH_2), 1.8—2.3 (2 H, m, CH_2), 3.3 (2 H, s, CH_2Br), 4.8—5.3 (2 H, m, $=CH_2$), and 5.4—6.1 (1 H, m, =CH); $\nu_{max.}$ 3 100 and 1 640 cm^{-1}, homogeneous by g.l.c. [column (*c*), 90 °C].

2-(2,2-Dimethylhex-5-enyloxy)tetrahydropyran.— 2,2-Dimethylhex-5-en-1-ol (14.2 g) was added dropwise with stirring to dihydropyran (25 g) containing concentrated hydrochloric acid (0.2 ml) while the temperature of the mixture was maintained at 50—60 °C. After addition the mixture was stirred for 2 h, then shaken with sodium carbonate solution and distilled to afford the required *tetrahydropyranyl ether* (18.8 g, 79%), b.p. 72 °C at 0.1 mmHg (Found: C, 73.5; H, 11.3. $C_{13}H_{24}O_2$ requires C, 73.5; H, 11.4%), *m/e* 212 (M^+) δ 0.9 (6 H, s, 2 × CH_3), 1.1—2.4

(10 H, m, methylene), 3.0 and 3.5 (2 H, ABq, J_{AB} 9 Hz, OCH_2CMe_2), 3.3—4.1 (2 H, m, OCH_2CH_2), 4.6 (1 H, br s, OCHO), 4.8—5.3 (2 H, m, $=CH_2$), and 5.5—6.2 (1 H, m, =CH), homogeneous by g.l.c. [column (*c*), 126 °C].

Tetrahydro-2-(2,2-dimethyl-5-hydroxyhexyloxy)pyran.—The foregoing tetrahydropyranyl ether (15 g) was added dropwise to a stirred solution of mercuric acetate (22.5 g) in water (70 ml) and tetrahydrofuran (70 ml) at ambient temperature. After the addition the mixture was stirred for a further 15 min, then worked up in the usual way [23] to afford the required *alcohol* (14.5 g, 89%), b.p. 109 °C at 0.2 mmHg (Found: C, 68.2; H, 11.7. $C_{13}H_{26}O_3$ requires C, 67.8; H, 11.4%), *m/e* 230 (M^+), δ 0.9 (6 H, s, 2 × CH_3), 1.2 (3 H, d, *J* 7 Hz, CH_3), 1.0—2.0 (10 H, m, methylene), 2.2 (1 H, s, OH), 3.0 and 3.5 (2 H, ABq, J_{AB}, 9 Hz, OCH_2CMe_2), 3.3—4.1 (2 H, m, OCH_2CH_2), and 4.6 (1 H, br, s, OCHO); $\nu_{max.}$ 3 300 cm^{-1}.

Tetrahydro-2-(2,2-dimethyl-5-oxohexyloxy)pyran.—Oxidation of the foregoing alcohol (19.8 g) with pyridinium chlorochromate by the usual procedure [24] afforded the required *ketone* (15.7 g, 80%), b.p. 106 °C at 0.2 mmHg (Found: C, 68.6; H, 10.6. $C_{13}H_{24}O_3$ requires C, 68.4; H, 10.6%); *m/e* 228 (M^+), δ 0.9 (6 H, s, 2 × CH_3), 1.4—1.9 (8 H, m, methylene), 2.2 (3 H, s, CH_3CO), 2.2—2.7 (2 H, m, CH_2CO), 3.0 and 3.5 (2 H, ABq, J_{AB} 9 Hz, OCH_2CMe_2), 3.3—4.1 (2 H, m, OCH_2CH_2), and 4.6 (1 H, br s, OCHO); $\nu_{max.}$ 1 720 cm^{-1}.

2,2,5-*Trimethylhex-5-en-1-ol.*—The foregoing ketotetrahydropyranyl ether (16.0 g) was added to the Wittig reagent prepared from methyltriphenylphosphonium iodide (30 g) and potassium t-butoxide (10 g) in benzene (200 ml) and tetrahydrofuran (200 ml). The mixture was stirred at ambient temperature for 12 h, then heated under reflux for 48 h. After being cooled, and diluted with ether (300 ml), the mixture was filtered, and the filtrate was washed with sodium carbonate solution and with brine. Removal of the solvent gave crude product, extraction of which with light petroleum afforded, after fraction distillation, *tetrahydro-2-(2,2,5-trimethylhex-5-enyloxy)pyran* (12.4 g, 78%), b.p. 95 °C at 0.4 mmHg (Found: C, 74.6; H, 11.4. $C_{14}H_{26}O_2$ requires C, 74.3; H, 11.6%), *m/e* 226 (M^+); δ 0.9 (6 H, s, 2 × CH_3), 1.3—2.4 (10 H, m, methylene), 1.75 (3 H, s, CH_3), 3.0 and 3.5 (2 H, ABq, J_{AB} 9 Hz, OCH_2CMe_2), 3.3—4.1 (2 H, m, OCH_2CH_2), 4.6 (1 H, br, s, OCHO), and 4.7 (2 H, s, $=CH_2$); $\nu_{max.}$ 1 640 cm^{-1}.

A sample (11.5 g) of this ether was added to methanol (100 ml) containing toluene-*p*-sulphonic acid (0.2 g), and the mixture was stirred at 20 °C for 2 h. Brine and ethyl acetate were then added to the mixture, and the organic layer was washed with sodium carbonate and distilled to afford 2,2,5-*trimethylhex-5-en-1-ol* (5.2 g, 72%), b.p. 42 °C at 1 mmHg (Found: C, 75.8; H, 12.4. $C_9H_{18}O$ requires C, 76.0; H, 12.8%); δ 0.9 (6 H, s, 2 × CH_3), 1.1—2.3 (4 H, m, CH_2CH_2), 1.8 (4 H, 2 overlapping s, CH_3 and OH), 3.4 (2 H, s, CH_2OH), and 4.7 (2 H, s, $=CH_2$); $\nu_{max.}$ 3 300 and 1 640 cm^{-1}.

6-*Bromo*-2,5,5-*trimethylhex*-1-*ene* (9a).—Carbon tetrabromide (4.0 g) was added slowly in small portions to a stirred mixture of 2,2,5-trimethylhex-5-en-1-ol (1.5 g), triphenylphosphine (3.4 g), and dichloromethane (10 ml) at ambient temperature. After being stirred for a further 12 h the mixture was worked up in the usual way [12] to afford a mixture (0.97 g, 45%), b.p. 55 °C at 0.7 mmHg, of isomeric olefinic bromides. Preparative g.l.c. [column (*d*), 120°], was employed to isolate a pure sample of 6-*bromo*-2,5,5-*trimethylhex*-1-*ene* (Found: C, 53.0; H, 8.3; Br, 38.6. $C_9H_{17}Br$ requires C, 52.7; H, 8.3; Br, 39.0%), δ 1.05 (6 H, s, 2 × CH_3), 1.3—2.1 (4 H, m, CH_2CH_2), 1.7 (3 H, s, CH_3), 3.3 (2 H, s, CH_2Br), and 4.7 (2 H, s, $=CH_2$); $\nu_{max.}$ 1 640 cm^{-1}. The second component of the mixture was isolated by preparative g.l.c. and tentatively identified as 6-bromo-2,5,5-trimethylhex-2-ene on the basis of its n.m.r. spectrum: δ 1.0 (6 H, s, 2 × CH_3), 1.6 and 1.7 (6 H, 2s, allylic CH_3), 2.1 (2 H, d, *J* 8 Hz, CH_2), 3.3 (2 H, s, CH_2Br), and 5.2 (1 H, br, t, *J* 8 Hz, =CH).

5,5-*Dimethylhex*-1-*ene* (13b).—Neopentylmagnesium bromide, prepared from neopentyl bromide [25] (3.02 g) and magnesium (0.5 g) in tetrahydrofuran (15 ml), was added dropwise to a boiling solution of allyl bromide (3.03 g) in tetrahydrofuran under reflux. After the addition the mixture was heated for a further 20 min, then cooled, diluted with water, and extracted with pure pentane. Distillation of the extract gave 5,5-dimethylhex-1-ene (1.6 g, 70%), b.p. 100 °C (lit.,[12] 99—101 °C), δ 1.0 (6 H, s, 3 × CH_3), 1.1—1.7 (2 H, m, CH_2), 1.8—2.2 (2 H, m, CH_2), 4.7—5.2 (2 H, m, $=CH_2$), and 5.4—6.2 (1 H, m, =CH); $\nu_{max.}$ 1 640 and 900 cm^{-1}, homogeneous by g.l.c. [column (*e*), 100 °C].

2,5,5-*Trimethylhex*-1-*ene* (13a).—Treatment of 3-chloro-2-methylpropene with neopentylmagnesium bromide as described above afforded the required *olefin* (60%), b.p. 108 °C (Found: C, 85.8; H, 14.1. C_9H_{18} requires C, 85.6; H, 14.4%); δ 1.0 (6 H, s, 2 × CH_3), 1.3—2.4 (4 H, m, methylene), 1.7 (3 H, s, CH_3), and 4.7 (2 H, s, $=CH_2$), homogeneous by g.l.c. [column (*e*), 120 °C].

1,1-*Dimethylcyclohexane* (15b).—4,4-Dimethylcyclohexan-1-ol (2.0 g), prepared by reduction of the ketone with lithium aluminium hydride, was heated with oxalic acid (2.9 g) at 150 °C, to afford 4,4-dimethylcyclohexane (1.3 g), b.p. 171 °C, which, on hydrogenation over platinum oxide in acetic acid gave 1,1-dimethylcyclohexane, b.p. 119 °C (lit.,[26] 119 °C), δ 0.9 (6 H, s, 2 × CH_3) and 1.0—1.5 (10 H, m, methylene), homogeneous by g.l.c. [column (*f*), 90 °C].

1,1,3-*Trimethylcyclopentane* (12b).—Treatment of 3,3-dimethylcyclopentanone [27] with methylmagnesium iodide and heating of the product with oxalic acid at 130 °C gave 1,4,4-trimethylcyclopentene [28] (82%), hydrogenation of which in acetic acid over platinum oxide afforded 1,1,3-trimethylcyclopentane, b.p. 106 °C (lit.,[29] 105—106 °C), δ 0.9 (3 H, d, *J* 6 Hz, CH_3), 1.0 (6 H, s, 2 × CH_3), and 1.2—1.8 (7 H, m, methylene and methine), homogeneous by g.l.c. [column (*f*), 90 °C].

1,1,3,3-*Tetramethylcyclopentane* (12a).—Treatment of cyclopentanone with potassium hydride and methyl iodide gave 2,2,5,5-tetramethylcyclopentanone, b.p. 47 °C at 23 mmHg, a sample (4.0 g) of which in diethyl ether (30 ml) was stirred for 15 h with lithium aluminium hydride at ambient temperature. The usual work-up afforded 2,2,5,5-*tetramethylcyclopentanol* (3.6 g, 90%), b.p. 53 °C at 15 mmHg (Found: C, 76.1; H, 12.7. $C_9H_{18}O$ requires C, 76.0; H, 12.8%), δ 0.9 (6 H, s, 2 × CH_3), 1.0 (6 H, s, 2 × CH_3), 1.6 (4 H, CH_2CH_2), 1.7 (1 H, s, OH), and 3.8 (1 H, s, CHO); $\nu_{max.}$ 3 300 cm^{-1}.

A sample (2.8 g) of this alcohol was stirred and refluxed with sodium hydride dispersion (50%, 1.0 g) and imidazole (0.4 g) in tetrahydrofuran (50 ml) for 3 h. Carbon disulphide (6 ml) was then added followed, after 0.5 h, by methyl iodide. After being refluxed for a further 0.5 h, the mixture was worked up in the usual way [30] to afford *O*-(2,2,5,5-tetramethylcyclopentyl) *S*-methyl dithiocarbonate, (3.1 g, 68%), b.p. 80 °C at 2 mmHg. Treatment of this

dithiocarbonate (3.0 g) with tributylstannane (4.6 g), in xylene (10 ml) in the usual way [30] gave 1,1,3,3-tetramethylcyclopentane (0.85 g, 52%), b.p. 118 °C (lit.,[31] 118.5 °C), n_D^{20} 1.412 6 (lit.,[31] 1.412 5), δ 0.9 (12 H, s, 4 × CH_3) and 1.0—1.8 (6 H, m, methylene), homogeneous by g.l.c. [column (*e*), 120 °C].

1,1,4-*Trimethylcyclohexane* (15a).—Treatment of 4,4-dimethylcyclohexanone [32] (2.5 g) with methylmagnesium iodide gave crude 1,4,4-trimethylcyclohexanol which was heated over anhydrous oxalic acid at 160 °C to give 1,4,4-trimethylcyclohex-1-ene (1.4 g, 57%), b.p. 138—140 °C (lit.,[33] 140 °C). Hydrogenation of this olefin in acetic acid over platinum oxide afforded 1,1,4-trimethylcyclohexane, b.p. 136 °C (lit.,[34] 135 °C), δ 0.9 (9 H, overlapping s and d, 3 × CH_3), and 1.1—1.7 (9 H, m, methylene and methine), homogeneous by g.l.c. [column (*e*), 120 °C].

We thank Dr. K. U. Ingold (N.R.C. Ottawa) for helpful discussions, and the Commonwealth of Australia for a Postgraduate Award (to T. L.). This work was supported by the Australian Research Grants Committee.

[9/349 *Received*, 5*th March*, 1979]

REFERENCES

[1] A. L. J. Beckwith, in ' Essays on Free-radical Chemistry,' *Chem. Soc. Special Publ.* **24**, 1970, p. 239.
[2] M. Julia, *Accounts Chem. Res.*, 1971, **4**, 386; *Pure Appl. Chem.*, 1974, **40**, 553; J. W. Wilt, in ' Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, New York, 1973, vol., 1 p. 333.
[3] A. L. J. Beckwith, G. E. Gream, and D. L. Struble, *Austral. J. Chem.*, 1972, **25**, 1081.
[4] A. L. J. Beckwith and W. B. Gara, *J.C.S. Perkin II*, 1975, 795.
[5] J. E. Baldwin, *J.C.S. Chem. Comm.*, 1976, 734.
[6] D. Capon and C. W. Rees, *J. Chem. Soc., Annual Reports*, 1964, **51**, 221; R. D. Rieke and N. A. Moore, *Tetrahedron Letters*, 1969, 2035; *J. Org. Chem.*, 1972, **37**, 413.
[7] A. L. J. Beckwith and G. Moad, *J.C.S. Chem. Comm.*, 1974, 472.
[8] M. Julia, C. Descoins, M. Baillarge, B. Jacquet, D. Uguen, and F. A. Groeger, *Tetrahedron*, 1975, **31**, 1737.
[9] D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, 1968, **90**, 7047.
[10] A. L. J. Beckwith, I. A. Blair, and G. Phillipou, *Tetrahedron Letters*, 1974, 2251.
[11] D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 6355.
[12] H. O. House and P. D. Weeks, *J. Amer. Chem. Soc.*, 1975, **97**, 2778.
[13] (*a*) A. J. Bloodworth, A. G. Davies, I. M. Griffin, B. Muggleton, and B. P. Roberts, *J. Amer. Chem. Soc.*, 1974, **96**, 7599; (*b*) A. L. J. Beckwith and G. Moad, *J.C.S. Perkin II*, 1975, 1726.
[14] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, ' Conformational Analysis,' Wiley, New York, 1965, p. 191.
[15] N. L. Allinger and V. Zalkow, *J. Org. Chem.*, 1960, **25**, 701.
[16] G. E. Gream and A. K. Seralis, *Austral. J. Chem.*, 1978, **31**, 863; and references cited therein.
[17] S. W. Benson, ' Thermochemical Kinetics,' Wiley, New York, 1968.
[18] C. Walling and A. Cioffari, *J. Amer. Chem. Soc.*, 1972, **94**, 6059.
[19] A. L. J. Beckwith, I. A. Blair, and R. B. Holloway, unpublished observations.
[20] H. C. Brown, H. Bartholomay, and M. D. Taylor, *J. Amer. Chem. Soc.*, 1944, **66**, 435.
[21] B. Giese and J. Meixner, *Tetrahedron Letters*, 1977, 2779.
[22] R. J. Cregge, J. L. Herrmann, C. S. Lee, J. E. Richman, and R. H. Schlessinger, *Tetrahedron Letters*, 1973, 2425.
[23] H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Amer. Chem. Soc.*, 1967, **89**, 1525.
[24] E. J. Corey and J. W. Suggs, *Tetrahedron Letters*, 1975, 2647.
[25] G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, 1964, **86**, 964.
[26] R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, 1948, **70**, 946.
[27] G. E. Hiegel and P. Burk, *J. Org. Chem.*, 1973, **38**, 3637.
[28] C. Magnusson and S. Thoren, *Tetrahedron*, 1974, **30**, 1431.
[29] J. B. McKinley, D. R. Stevens, and W. E. Baldwin, *J. Amer. Chem. Soc.*, 1945, **67**, 1455.
[30] D. H. R. Barton and S. W. McCombie, *J.C.S. Perkin I*, 1975, 1574.
[31] F. G. Gault and J. E. Germain, *Bull. Soc. chim. France*, 1959, 1365.
[32] F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, 1963, **28**, 1347.
[33] K. von Auwers and E. Lange, *Annalen*, 1915, **409**, 149.
[34] G. Mann, M. Mühlstädt, and J. Braband, *Tetrahedron*, 1968, **24**, 3607.