It is of interest to note that Hepler[15] has demonstrated that only for a reaction series entailing a linear $\Delta G-\Delta H$ relationship can a Hammett type correlation be followed precisely at more than one temperature, although this is difficult to check experimentally.[13] Table X shows the ρ values obtained for plots of the form of Figure 3, using the results at temperatures 25, 40, 60, 80, and 90°, and omitting in the determinations of 4,4′,4″-trimethoxy-, 4,4′-dimethoxy-, 4,4′,4″-trimethyl-, 4,4′,4″-trichloro-, and 4,4′,4″-tris(trimethylammonium perchlorate)triphenylmethanols.

The existence of correlations between pK_a values derived from the acidity function approach, and other physicochemical parameters not depending on acidity function theory for their definition, is of vital importance in establishing the thermodynamic validity of such pK_a values. Such correlations have been reported for the H_0 scale;[3,16] the σ^+ correlations and the linear free energy–enthalpy relationship discussed above in the present study testify to the authenticity of the pK_{R^+} and hence H_R values obtained. These pK_{R^+} values (eq 5) are thus thermodynamic quantities accurately

$$pK_{R^+} = 0.00034\Delta H_{25} + 0.86919 \qquad (5)$$

related to the standard state of pure water. The H_R values may be utilized with some confidence for the correlation of rates for appropriate acid catalyzed reactions at elevated temperatures; in this context work is currently in hand[17] to utilize these data in the interpretation of nitration studies[7] as detailed initially.

Acknowledgment. The authors thank Professor E. M. Arnett for his helpful correspondence during the course of this work.

Supplementary Material Available. Data supplementary to this article will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, refering to code number JACS-75-760.

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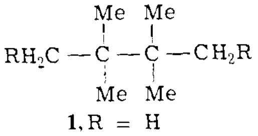
A Secondary Effect on Barriers to Rotation in Substituted Ethanes

J. E. Anderson* and H. Pearson

Contribution from the Ralph Forster Laboratory of Organic Chemistry, University College, London WC1E 6BT, United Kingdom. *Received March 19, 1974*

Abstract: The temperature-dependent nmr spectra for a number of closely related substituted ethanes have been studied by full line shape analysis to give barriers to rotation. These range from 10.4 to 13.8 kcal mol^{-1}. The variation in barriers cannot be explained satisfactorily by primary steric effects alone. The data are best rationalized on the basis of a compression effect operating in the eclipsed transition state.[1]

When rotation of a *tert*-butyl group attached to an sp^3 hybridized carbon atom is slow on the nmr time scale, it is usually possible to obtain activation parameters for the rotation by examining the temperature dependence of the nmr spectrum.[2] Bulky substituents, such as alkyl groups[3] or halogen atoms[4] raise the barrier to rotation due to increased steric interactions along the t-Bu–C(sp^3) bond in an eclipsed transition state. However, substituent effects on barrier heights cannot always be explained by such primary steric effects along the ethane bond and more subtle secondary effects need to be considered. We now describe one of these, that of bulky groups not directly attached to the ethane bond, but separated from it by one atom, *i.e.*, β-substituents, which give rise to unusually high barriers to rotation. For example, while the barrier in hexamethylethane (**1**) may be reasonably estimated to be between 9.6[5] and 10.0[6] kcal mol^{-1}, we have found that introduction of two *tert*-butyl substituents in a β position giving 2,2,4,4,5,5,7,7-octamethyloctane (**2**) leads to a barrier of 13.8 kcal mol^{-1}. An interpretation of this and other observations is presented in this paper.



$$RH_2C-\underset{Me}{\overset{Me}{C}}-\underset{Me}{\overset{Me}{C}}-CH_2R$$

1, R = H
2, R = *t*-Bu

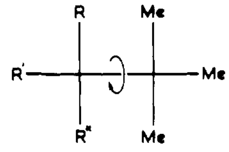
Table I. *tert*-Butyl Chemical Shift Data for **3–12**[a]

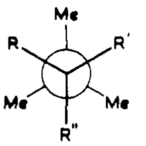
Compound	Room temp[b]	Low temp			Low temp, °C
3	1.10	1.12 (67%)		0.98 (33%)	−112
4[c]	1.09	1.17	1.10	0.98	−100
5	1.20	1.13	1.21	1.24	−112.4
6	1.09	1.13	1.09	0.99	−99
7	1.07	1.31 (33%)		0.93 (67%)	−74.8
8	1.14	1.13 (67%)		0.94 (33%)	−113
9	1.25	1.30	1.30	1.17	−138
10[d]	0.86	0.91 (67%)		0.72 (33%)	−148
11	0.99	0.89	0.96	1.16	−138
12	1.24	1.29	1.16	1.16	−94.9

[a] Solvent is CF_2Cl_2, except for **7** where $CHFCl_2$ was used. [c] Ambient probe temperature of about 33°. [b] Data refer to the ethyl-d_5 compound. [d] Data refer to the deuterated (d_7) compound.

Results

In the ambient-temperature nmr spectra of compounds **3–12**, the *tert*-butyl resonance appears as a singlet which, on lowering the sample temperature, broadens and eventually splits into two lines of relative intensity 2:1 (compounds **3**, **7**, **8**, **9**, and **10**) or into three lines of equal intensity (compounds **4**, **5**, **6**, and **11**). Compound **9** at low temperature shows only two of relative intensities 2:1, presumably due to two of the peaks being accidentally isochronous. Table I lists the chemical shift data for the *tert*-butyl signals in **3–12** at the high and low temperature limits.





3, R = R′ = CH_3; R″ = Cl
4, R = CH_3; R′ = CH_2CH_3; R″ = Cl
5, R = CH_3; R′ = CH_2Ph; R″ = Cl
6, R = CH_3; R′ = CH_2-*t*-Bu; R″ = Cl
7, R = R′ = CH_2Ph; R″ = Cl
8, R = R′ = CH_3; R″ = Br
9, R = CH_3; R′ = CH_2Ph; R″ = Br
10, R = R′ = CH_3; R″ = H
11, R = CH_3; R′ = CH_2Ph; R″ = H
12, R = CH_3; R′ = *t*-Bu; R″ = Cl

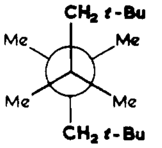
The ambient-temperature nmr spectrum of **2** comprises the expected three singlets of relative intensities 2:6:9. As the temperature is lowered, the signal of the methylene group broadens and splits below about −20° to an unsymmetrical doublet of relative shift 9.2 Hz (0.092 ppm) at −45° and of intensity ratio 0.356:0.644 obtained by measurement of areas under absorption peaks.[7] The signals for the *tert*-butyl groups and the geminal methyl groups of **2** do not split into multiplets in the low-temperature spectrum recorded at 100 MHz operating frequency, although the latter signal shows signs of broadening. In the spectrum of **2** recorded at 220-MHz operating frequency at −80°, the geminal dimethyl group appears as a narrowly spaced triplet (δ 0.914, 0.920, and 0.927), the three peaks being of approximately equal intensities. The *tert*-butyl signal is still a singlet under these conditions.

These spectral changes should not be due to rotation about the CH_2–C bonds in **2**, which should be fast at all temperature considered here; rather, these separate signals are considered to represent the *trans*-**2a** and *gauche*-**2b** and -**2c** conformations, respectively, which are interconverting slowly on the nmr time scale at low temperatures. Since the geminal-dimethyl signal appears as an approximately 1:1:1 triplet when rotation is slow, there must be about twice as much of the gauche isomer (which has two kinds of environment for a methyl group) as of the trans isomer (which has only one such environment). As far as the methylene signals are concerned, each isomer is expected to give one singlet[8] so the more intense of the two observed methylene signals is assigned to the gauche conformation. On the basis of relative intensity, the trans conformation is more stable than a gauche conformation by 44 cal mol^{-1} at about −59°.

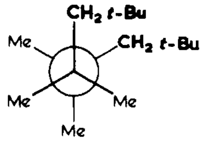
Table II. Rotation in the Series **2–12**

Compound	ΔG*, kcal mole^{-1}	$k_{rotation}$, sec	*T*, °K
2	13.80	7.0	254.5
3	10.43	134.0	216.6
4[a]	10.68	18.0	205.2
5	10.85	19.7	209.0
6	11.80	9.0	220.1
7	11.41	152.0	237.4
8	10.73	50.0	214.2
9	11.30	10.0	212.0
10[b]	6.97	72.0	143.4
11	7.10	174.0	151.2
12	11.42	8.3	212.9

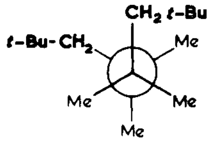
[a] Data refer to the ethyl-d_5 compound. [b] Data refer to the $(CD_3)_2$-CD–$C(CH_3)_3$ compound.



2a



2b

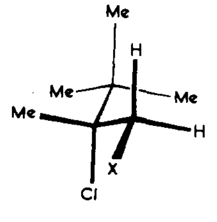


2c

Rate constants for rotation about the central carbon-carbon bond were obtained by a visual fitting of computer simulated to experimental spectra using the temperature-dependent *tert*-butyl resonance.[2c] Table II shows rate constants determined at typical temperatures and the free energy of activation for the rotational process derived from these data using the Eyring equation.[9] Tables in the experimental section give rate constant and other data at several temperatures for each compound.

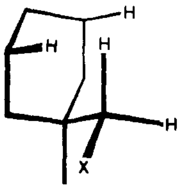
Discussion

In the series **2–12** the barrier measures the difference in the energy between the staggered ground state and an eclipsed transition state. Replacement of a methyl group substituent in **3** by CH_2X leads to an increase in the barrier of between 0.25 (**3** *vs.* **4**) and 1.37 (**3** *vs.* **6**) kcal mol^{-1}. Insofar as the ground state conformation of such molecules is expected to be as in **13**,[10] with the group X remote from interaction along the ethane bond, the effect of X on the barrier is surprising. The contrast with another well-known



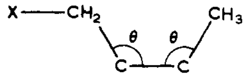
13

conformational situation emphasizes this. Thus, the free energy difference between axial and equatorial ethylcyclohexane (the A value),[12,13] 1.75 kcal mol^{-1}, is very similar to that of methylcyclohexane, 1.70 kcal mol^{-1},[12,13] and this is explained in terms of a conformation, **14**, in which the group X (X = methyl in ethylcyclohexane) is remote from the destabilizing 1,3-diaxial interactions.[14] Now **13** resembles **14** to the extent that X in **13** is remote from interactions along the ethane bond, yet it has a marked effect on the barrier to rotation about that bond. An explanation of the effect of changing X in molecules does not in fact suggest itself, from an examination of the likely ground state conformation.



14

In a presumably eclipsed transition state, direct opposition of groups along the ethane bond may be expected to have the effect of increasing bond angles θ in **15**, causing a compression of the three substituents at either end of the ethane bond. Thus, for compounds of type **3**, replacement of a methyl group by CH_2X leads to a transition state, **16**, where the X group interacts with the chlorine atom and the methyl group, and we suggest that it is this unfavorable interaction that produces the high barrier to rotation. It would be an oversimplification to suggest that the group X is involved in no steric interactions[15] in the ground state of **13** but the above explanation is based on there being *enhanced* interactions due to compression in the transition state, **16**.



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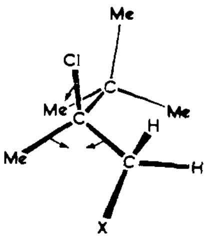


16

A particularly clear demonstration of the compression effect is given by **6** where X is a *tert*-butyl group. The barrier to rotation is 11.8 kcal mol^{-1}, an enhancement of 1.4 kcal mol^{-1}, and is in fact greater than in **12**,[3] 11.4 kcal mol^{-1}. Replacement of the *tert*-butyl substituent in **12** by a neopentyl group leads to a higher barrier. The contrast with the A values of the two groups is striking.[16] The estimated A value of the *tert*-butyl group is 5.6 kcal mol^{-1}, while for the neopentyl group it is about 2.0 kcal mol^{-1}. The postulated secondary steric effect obviates the unlikely conclusion suggested by consideration of eclipsing interactions alone.

Replacement of two methyl groups in hexamethylethane, **1**, by two neopentyl groups, *i.e.*, **2**, has no less striking effect. The hindrance to compression at both ends of the ethane bond produces a barrier of 13.8 kcal mol^{-1}. This barrier is, in fact, that for interconversion of gauche and trans isomers; the gauche-gauche barrier may be different and probably higher. To our knowledge, this is the largest barrier reported for a simple acyclic alkane.

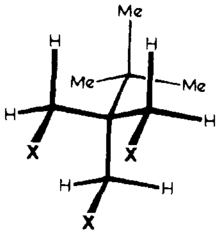
The effect of compression during rotation is reminiscent of B strain.[17,18] Enhanced reactivity of certain *tert*-alkyl compounds in reactions involving carbonium ions is attributed to relief of steric interactions, B strain, in a planar ion compared with the tetrahedral starting compound. It may be that the compression we envisage is adequately described as increased B strain in the eclipsed conformation. This suggested compression effect has analogy in earlier work of Sederholm and Newmark[19] who showed that the barrier to rotation (trans-gauche) in $CCl_2Br\text{-}CF_2Br$, **17**, is 10.8 kcal mol^{-1}, while the barrier (trans-gauche), in $CClBrF\text{-}CFClBr$, **18**, is only 10.1 kcal mol^{-1}, although each transition state has the same pairs of eclipsing atoms. Although the barrier differences may reflect differing ground state energies, the authors suggested that **17** has the higher barrier because one of the carbons has three bulky halogen atoms attached, rendering "distortion" of the tetrahedron in the transition state more difficult. The results reported here suggest that this distortion is a compression.

It is interesting at this juncture to compare the pairs of compounds **10** and **11**, **3** and **5**, and **8** and **9**. In each case the barrier rises on substitution of a benzyl group for a methyl group, *i.e.*, on the introduction of a β-phenyl substituent.

In the first pair **10** and **11**, the third substituent is a hydrogen atom, in the second pair it is a chlorine atom, and in the third pair it is a bromine atom. In line with this increasing size of the third substituent, the difference in barrier between the two members of the pair increases.

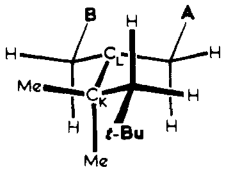
X	H	Cl	Br
Compounds involved	**10, 11**	**3, 5**	**8, 9**
$\Delta\Delta G^*$ (kcal mol^{-1})	0.2	0.4	0.6

The substitution of two or three $-CH_2X$ groups will not necessarily lead to even higher barriers, since at some point a ground state, such as **19**, with X-X parallel (1,3) interactions will become unbearably crowded, but in **7**, which has two CH_2X groups (X = Ph), the secondary effect is self-reinforcing, as shown by the barrier of 11.4 kcal mol^{-1}, compared with 10.85 kcal mol^{-1} for **5** (one CH_2Ph group), and 10.43 kcal mol^{-1} for **3** (no CH_2Ph group).



19

The result for the gauche-trans equilibrium in **2b** deserves some further comment. The trans and one of the gauche isomers are represented in extended form in **20**, the isomerism being about the central $C_K\text{-}C_L$ bond and the *tert*-butyl groups presumably being located trans-antiparallel to this bond. Only these *tert*-butyl groups make the molecule different from hexamethylethane, and, as they are re-



20

trans: A = H, B = *t*-butyl
gauche: A = *t*-butyl, B = H

mote from the C_K–C_L bond, it is to be expected that the energies of the two conformations should be almost the same. In the Results Section we have shown that the gauche conformation is less stable than the trans by 44 cal/mol^{-1} at −59°.

This may be taken to mean that even though remote from each other, the two *tert*-butyl groups are aware of each other (otherwise the conformers would be of equal energy) or, perhaps more likely, it may indicate some external influence. The trans isomer is more elongated than the gauche, the maximum separation of hydrogens appearing from models to be 10.5 Å compared with 9.4 Å, and it may be that the elongated molecule better fits spaces in the solvent. The molecule **2b** would make a suitable model for studying the effect of solvents and, perhaps, solution pressure[20] on molecular conformation. Separate signals for isomers are readily observed at reasonably accessible temperatures, at which a wide range of solvents is available. Further, **2b** is a saturated, unsubstituted alkane which should have no specific interactions with a solvent.

Where measurements of rate constants over a wide range of temperatures has been possible, *i.e.*, for **3**, **4**, **5**, **7**, **8**, and **9**, an Eyring plot leads to values of ΔH^* and ΔS^* for the rotation. These are reported in the Experimental Section. We expect that entropies of activation be small but not necessarily zero, for rotation in the compounds studied here. Since it is notoriously difficult to separate ΔG^* values obtained by the dynamic nmr method into enthalpy and entropy contributions, we shall make no comment on these values other than to note that they are all close to zero.

It is convenient in discussions of substituent effects, as in this paper, to consider that in all other respects the molecule is ideal. This clearly is not so, but for lack of better knowledge, we assume, for example, that the dihedral angles in the ground and transition states are 60 and 0°, respectively. For similar reasons we ignore the possibility that strain arising during rotation about the carbon–carbon bond under consideration may be relieved to some extent by other smaller rotations within the molecule or by distortions other than the compression which is the subject of this paper. It is by choosing systems which concentrate on one possible distortion that the complex overall picture may eventually be completed.

Experimental Section

Variable-temperature nmr spectra were measured and rate constants were obtained as described previously.[2c,3] The 220-MHz spectrum of **2** at −80° was recorded by PCMU, Harwell, United Kingdom, using fluorodichloromethane as solvent.

The resonance for the unique methyl group in **4**, **5**, **6**, and **9** is a doublet which collapses in each case to a singlet on irradiation of one of the diastereotopic methylene protons.[2c] The unique methyl in **11** is a doublet of doublets which collapses to a single doublet (J = 6.7 Hz) on irradiation of one of the diastereotopic methylene protons.

The proportion of gauche and trans isomers for **2b** was determined from several spectra of the methylene hydrogens recorded between −45 and −70°, by measuring the area under almost completely resolved peaks using a planimeter. The temperature range is limited by the onset of exchange broadening at high temperatures and of other broadening at lower temperatures. The reproducibility of area measurements is not good enough for temperature dependence of proportions of isomers to be detected. In fact, the measure of fractional population of the less common isomer varied between 0.336 and 0.384, the mean value being 0.356. The less intense signal was assigned to the trans isomer from the appearance of the *gem*-dimethyl signal in a 220-MHz spectrum, as described in the Results Section. After allowing for the twofold degeneracy of the gauche isomer, these figures give a range of 5–89 cal mol^{-1} for the free-energy difference between a gauche and the trans confirmation. The mean value is 44 cal mol^{-1}, the trans being more stable than the gauche. The ratio of peak areas is always less than 2:1. For the calculation of rate constants in **2** the methylene region was treated as a 2:1 doublet since the full treatment for gauche–trans isomerization in such a case is complex.[21] On the basis of this approximate treatment, the mean rate of rotation is 7 and 15 sec^{-1} at −18.7 and −10.8°, where ΔG^* is 13.82 and 13.86 kcal mol^{-1} at these temperatures.

The following sections give all rate data for the compounds studied. Each list gives a series of temperatures (K°), rate constants at that temperature (sec^{-1}), and the corresponding ΔG^* value (kcal mol^{-1}). Results previously reported[2c] for **3** and **5** gave temperatures at the bottom of the tube. Results presently reported for these compounds show the temperature in the region of the sample within the rf coils and are more accurate because of this. It is considered that rate constants are accurate to ±10%, temperatures to better than ±2°, where values of ΔG^* calculated from a given rate constant at a given temperature are accurate to better than ±0.2 kcal mol^{-1}.

2-Chloro-2,3,3-trimethylbutane (3): 216.6, 134, 10.43; 215.5, 114, 10.45; 213.9, 88, 10.48; 212.8, 87, 10.43; 211.3, 60, 10.50; 208.0, 48, 10.43; 205.9, 38, 10.41; 203.4, 31, 10.36; 201.2, 24, 10.35; 198.9, 18.5, 10.33; 196.6, 12.0, 10.37; 194.2, 10.1, 10.31; 192.3, 8.1, 10.29; 189.3, 5.4, 10.28. ΔH^* = 8.9 kcal mol^{-1} and ΔS^* = −7.1 eu.

3-Chloro-2,2,3-trimethylpentane-*4,4,5,5,5-d$_5$* (4): 198.0, 6.7, 10.68; 201.2, 12.0, 10.62; 203.2, 15.0, 10.64; 205.2, 18.0, 10.68; 207.6, 28.0, 10.63; 210.2, 40.0, 10.62; 212.2, 54.0, 10.59; 215.9, 72.0, 10.66; 218.3, 89.0, 10.69. ΔH^* = 11.0 kcal mol^{-1} and ΔS^* = 1.8 eu.

2-Chloro-1-phenyl-2,3,3-trimethylbutane (5): 189.6, 1.45, 10.79; 91.7, 2.05, 10.78; 194.1, 3.3, 10.74; 196.8, 4.8, 10.74; 199.4, 7.6, 10.71; 200.8, 9.1, 10.71; 202.0, 9.8, 10.75; 203.3, 10.0, 10.82; 204.3, 13.8, 10.74; 206.7, 15.5, 10.82; 209.0, 19.7, 10.85; 211.4, 24.5, 10.89; 214.6, 34.6, 10.91; 217.8, 53, 10.89; 220.1, 64, 10.93. ΔH^* = 9.53 kcal mol^{-1} and ΔS^* = −6.2 eu.

3-Chloro-2,2,3,5,5-pentamethylhexane (6): 212.2, 3.4, 11.76; 218.6, 7.5, 11.79; 220.1, 9.0, 11.80; 222.3, 10.5, 11.85; 237.9, 52, 11.95; 240.7, 71, 11.95; 243.5, 104, 11.91. As these results were obtained with the *tert*-butyl signal of the neopentyl group overlapping the temperature dependent *tert*-butyl signal, there is a greater error involved.

2-Benzyl-2-chloro-3,3-dimethyl-1-phenylbutane (7): 210.6, 7.0, 11.37; 223.2, 26.0, 11.49; 229.7, 45.0, 11.59; 233.3, 112.0, 11.36; 237.4, 152.0, 11.41; 239.5, 215.0, 11.36; 244.6, 360.0, 11.36; 248.2, 490.0, 11.40. ΔH^* = 11.93 kcal mol^{-1} and ΔS^* = 2.1 eu.

2-Bromo-2,3,3-trimethylbutane (8): 195.0, 4.2, 10.70; 198.0, 6.4, 10.70; 201.0, 9.0, 10.73; 203.9, 10.5, 10.83; 206.8, 17.0, 10.79; 208.1, 19.0, 10.81; 211.2, 46.0, 10.61; 214.2, 50.0, 10.73; 218.0, 78.0, 10.69; 220.6, 112.0, 10.71; 222.8, 135.0, 10.74. ΔH^* = 10.84 kcal mol^{-1} and ΔS^* = −0.5 eu.

2-Bromo-1-phenyl-2,3,3-trimethylbutane (9): 205.2, 3.6, 11.34; 207.7, 4.8, 11.36; 210.5, 7.2, 11.35; 212.0, 10.0, 11.30; 215.0, 15.0, 11.29; 215.6, 19.0, 11.22; 219.0, 22.0, 11.34; 220.6, 23.0, 11.41; 222.7, 33.0, 11.36. ΔH^* = 8.76 kcal mol^{-1} and ΔS^* = 5.9 eu.

2,2-Dimethyl-3-(methyl-d_3)-butane-*3,4,4,4-d$_4$* (10): 136.6, 14.0, 7.07; 143.4, 72.0, 6.97; 144.8, 91.0, 6.97.

1-Phenyl-2,3,3-trimethylbutane (11): 140.4, 24.0, 7.12; 143.7, 51.0, 7.08; 147.9, 98.0, 7.11; 151.2, 174.0, 7.10. ΔH^* = 7.04 kcal mol^{-1} and ΔS^* = 0.4 eu.

3-Chloro-2,2,3,4,4-pentamethylpentane (12): 212.9, 8.3, 11.42; 214.7, 9.4, 11.47; 215.0, 10.1, 11.46; 217.0, 14.0, 11.43; 218.3, 18.0, 11.39; 218.7, 26.0, 11.25; 219.7, 25.5, 11.31; 221.6, 33.0, 11.31; 226.7, 39.4, 11.49; 229.0, 66.0, 11.38; 232.4, 98, 11.37. ΔH^* = 11.84 kcal mol^{-1} and ΔS^* = 2.1 eu.

Table III

Compound		Nmr[a,b]
2	n^{20}D 1.4516 (lit.[26] nD 1.4470)	0.99 (12 H, s), 1.04 (18 H, s), 1.39 (2 H, 2)
3	Mp 134–135° (lit.[22] mp 133°)	1.10 (9 H, s), 1.57 (6 H, s)
4	Bp 62–66° at 25 mm (lit.[23] 87° at 62 mm)	1.07 (9 H, s), 1.43 (3 H, d, J = 0.6 Hz), 0.8–1.2 (3 H, m), 1.4–2.17 (2 H, m)[c]
5	Mp 59.5° (see ref 2c)	1.20 (9 H, s), 1.33 (3 H, d, J = 0.8 Hz) 3.08 (2 H, q, J = 13.8 Hz), *ca.* 7.3 (5 H, b, s)
6	Bp 51–55° at 2 mm (lit.[24] 72.5–74° at 8 mm)	1.09 (9 H, s), 1.12 (9 H, s), 1.65 (3 H, d, J = 0.9 Hz), *ca.* 1.87 (2 H, m)
7	Mp 130–131°	1.07 (9 H, s), 3.12 (4 H, q, J = 14.7 Hz), *ca.* 7.2 (10 H, m)
8	Mp 151–153° (lit.[25] mp 150–152°)	1.14 (9 H, s), 1.78 (6 H, s)
9	Mp 45°	1.25 (9 H, s), 1.55 (3 H, d, J = 0.7 Hz) 3.18 (2 H, q, J = 13.9 Hz), 7.17 (5 H, bs)
10	Bp 75–77° (lit.[25] bp 80.75°)	0.86 (9 H, s), 0.87 (6 H, d, J = 6.7 Hz), *ca.* 1.32 (1 H, m)
11	Bp 63° at 3 mm	0.76 (3 H, dd, ^3J = 6.7 Hz, ^4J = 0.65 Hz), 0.99 (9 H, s), *ca.* 1.5 (1 H, m), 2.52 (2 H, m), 7.11 (5 H, m)
12	Mp 86° (lit.[27] mp 86.5–87°)	1.24 (18 H, s), 1.61 (3 H, s)

[a] Values are ppm downfield from TMS (δ) and are measured in CF_2Cl_2 solution. [b] Key: s = singlet, d = doublet, dd = double doublet, m = multiplet, bs = broad singlet, q = quartet. [c] Measured in CCl_4 solvent.

Compounds **3**, **4**, **5**, **6**, **8** and **10** were prepared by standard methods.[2c,22-25] The deuterated (d_7) form of **10** was used. The corresponding deuterated (d_5) chloride of **4** was prepared using ethyl-d_5 bromide in the Grignard reaction to form the alcohol. The chloride was finally purified by using a 20 ft × 0.8 in. Carbowax 20M column, an oven temperature of 75°, and a flow rate of 220 ml/min; the retention time was 43 min.

2,2,4,4,5,5,7,7-Octamethyloctane (**2**) was prepared by treatment of 2-halo-2,4,4-trimethylpentane with magnesium in tetrahydrofuran. Best yields (20%) were obtained from the chloro compound; the halo compound was prepared by addition of hydrogen halide to 2,4,4-trimethylpentene. **2** was obtained as a colorless oily residue after distilling off all that boils below 60-100 mm and was vacuum distilled at 0.01 mm at room temperature (20°).

2-Bromo-1-phenyl-2,3,3-trimethylbutane (**9**) was prepared by addition of phosphorus tribromide (19.8 g, 73 mmol) to the vigorously stirred alcohol 1-phenyl-2,3,3-trimethylbutan-2-ol (6.6 g, 34 mmol) in methylene chloride (20 ml) at −78°. After stirring for 3 hr, the mixture was allowed to attain room temperature and was poured onto about 30 g of cracked ice. The methylene chloride layer was washed with water (two 20-ml portions) and 20% sodium bicarbonate (one 30-ml portion) and dried over $MgSO_4$. The solvent was removed under vacuum at room temperature to leave the crude bromide as a brown solid (7.8 g, 83%). The bromide was recrystallized from pentane to yield the pure bromide, mp 45°. The instability of this compound at room temperature made a fully satisfactory elementary analysis difficult.

Anal. Calcd for $C_{13}H_{19}Br$: C, 61.21; H, 7.46. Found: C, 59.51; H, 7.98.

2-Benzyl-3,3-dimethyl-1-phenylbutan-2-ol (**22**) was prepared by addition of *tert*-butyllithium in pentane (70 ml, 0.16 *M*) to a stirred solution of dibenzyl ketone (27 g, 0.13 *M*) in toluene (150 ml) at −40°. After addition, stirring was continued for 8 hr at −78°. After warming to 0° the red-colored mixture was hydrolyzed carefully with water. The organic layer was separated, washed with water (100 ml) and dried over $MgSO_4$. Removal of the solvent yielded a pale yellow liquid. Distillation yielded a fraction, bp 136-140° at 0.3 mm, which solidified at room temperature. Recrystallization from 80% ethanol yielded **22** (6.75 g, 20%), mp 63°.

Anal. Calcd for $C_{19}H_{24}O$: C, 85.02; H, 9.02. Found: C, 85.34; H, 9.22. ν_{max} 3550 cm^{-1} (OH).

Dehydration of **22** (4.44 g, 16.6 mmol) was achieved by refluxing with *N,N*-dimethyl-*p*-toluidine (3.38 g, 25 mmol) and acetyl chloride (2.02 g, 25.7 mmol). After cooling to room temperature, ether (40 ml) and dilute (10%) sulfuric acid (40 ml) were added to the mixture. The ether layer was separated and washed thoroughly with 10% sulfuric acid and water, and dried over $MgSO_4$. Removal of the solvent yielded 4.7 g of a pale yellow liquid which was taken up in a little 96% ethanol; scratching caused a white solid (3 g) to crystallize. The white solid was shown by nmr to be a mixture of *cis*- and *trans*-2-benzyl-3,3-dimethyl-1-phenylbut-1-ene (**23**).

2-Benzyl-2-chloro-3,3-dimethyl-1-phenylbutane (**7**) was obtained by bubbling dry hydrogen chloride gas through the olefin mixture **23** (3 g in 50 ml of methylene chloride) at −40° for 5 hr. After warming to room temperature the mixture was poured onto about 50 g of cracked ice. The methylene chloride layer was washed with 10% sodium bicarbonate (two 100-ml portions) and saturated sodium chloride (two 30-ml portions) and dried over $MgSO_4$. Removal of the solvent at water pump pressure left a yellow oil (3.1 g) which solidified on scratching. Recrystallization from pentane (twice) and 95% ethanol (twice) yielded **7**, mp 130-131°.

Anal. Calcd for $C_{19}H_{23}Cl$: C, 79.54; H, 8.10. Found: C, 79.54; H, 8.05.

1-Phenyl-2,3,3-trimethylbutane (**11**) was prepared by shaking the olefin mixture, **23** (2.5 g, 143 mmol), in an atmosphere of hydrogen in the presence of 10% palladium on charcoal catalyst (50 mg), resulting in the rapid uptake of 349 ml (theoretical uptake by a compound = 348 ml) of hydrogen. After filtration, fractional distillation yielded the alkane, **11**, bp 63° at 3 mm. The alkane was further purified by glpc using a 20 ft × 4 in. Carbowax column; the retention time of the alkane was 58 min at an oven temperature of 170° and a flow rate of 86 ml/min.

Anal. Calcd for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.23; H, 11.18.

Table III lists physical constants and ambient temperature nmr data for the compounds studied.

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(8) The gauche isomers **2b** and **2c** should give an AB quartet, but the relative shift of the A and B parts should be very small, since all substituents are magnetically very similar.

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axial and equatorial position.
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Carbanions. XIV. 1,4 Migration of the *p*-Biphenylyl Group in Reactions of 4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane with Alkali Metals[1]

Erling Grovenstein, Jr.,* and Jung-Ung Rhee

Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332.
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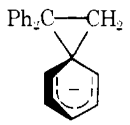
Abstract: 4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane reacts with potassium, cesium, and Cs-K-Na alloy in tetrahydrofuran (THF) to give 4-*p*-biphenylyl-1,1-diphenylbutyl anion as deduced from the nmr spectrum of the anion and products of carbonation and protonation. When the reaction with potassium is run in the presence of a small quantity of a sufficiently reactive proton donor such as *tert*-butyl alcohol, the product is 1-*p*-biphenylyl-1,1-diphenylbutane or products derived from the latter by subsequent reduction of the *p*-biphenylyl group. With sodium in refluxing dioxane the chloride gives 1-*p*-biphenylyl-1,1-diphenylbutane containing only some 7% of the rearranged hydrocarbon 4-*p*-biphenylyl-1,1-diphenylbutane; with potassium or cesium in the same solvent chiefly the rearranged hydrocarbon is obtained. From these results it is concluded that the chloride reacts with sodium, potassium, and cesium to give 4-*p*-biphenylyl-4,4-diphenylbutyl alkali metal compound which is either rapidly protonated or undergoes 1,4 migration of *p*-biphenylyl to give the more stable 4-*p*-biphenylyl-1,1-diphenylbutyl anion. Reaction of the chloride with excess lithium in THF at −75° gave 4-*p*-biphenylyl-4,4-diphenylbutyllithium (**4**) containing up to 47% of 4-*p*-biphenylyl-1,1-diphenylbutyllithium (**5**). Attempts to induce thermal rearrangement of the lithium compound **4** to **5** resulted primarily in protonation of **4**. Addition of the chloride to excess lithium biphenylide in THF at −75° gave **4** containing a little **5**; the percentage of **5** decreased as the concentration of lithium biphenylide increased. It is concluded that reaction of lithium biphenylide, and likely of lithium metal, with the chloride initially gives 4-*p*-biphenylyl-4,4-diphenylbutyl radical which either rearranges to 4-*p*-biphenylyl-1,1-diphenylbutyl radical or is reduced to the lithium compound **4**. The lithium compound **4** is readily rearranged to 4-*p*-biphenylyl-1,1-diphenylbutyl anion by potassium *tert*-butoxide in THF at −75°. The ease of 1,4 migration of *p*-biphenylyl in 4-*p*-biphenylyl-4,4-diphenylbutyl alkali metal compounds increases along the series: Li ≪ Na ≪ K or Cs: 1,4 migration is much less facile than analogous 1,2 migration of *p*-biphenylyl in carbanions.

Previous investigations[2] have shown that 1,2 migrations of aryl groups occur readily in organoalkali compounds in ethereal solvents. These rearrangements are believed[2d,3] to proceed by way of cyclic transition states or intermediates such as **1** from the 2,2,2-triphenylethyl anion. It might be expected that analogous 1,4 migrations of aryl would occur in carbanions, for example, by way of **2** from 4,4,4-triphenylbutyl anion. In fact, reaction of 4-chloro-1,1,1-triphenylbutane with alkali metals under a variety of conditions gave[4] only minor amounts of products of 1,4 migration of phenyl, and the reactions seemed too complex for study of the mechanism of the observed migration. In the present work reactions of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane with alkali metals have been studied in hope of avoiding the difficulties encountered in the simpler system, thanks to the expected superior migratory aptitude[5] of *p*-biphenylyl over phenyl in anionic rearrangements. In addition it was thought conceivable that the intermediate **3** might prove stable enough under mild conditions to be detectable by spectroscopic means or by "trapping" experiments.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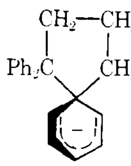
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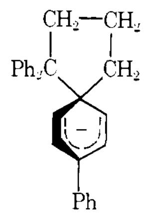
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Results and Discussion

4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane was allowed to react with alkali metals, and the products of reaction were identified after protonation or carbonation to give the corresponding hydrocarbons or carboxylic acids as shown in Scheme I. From reaction with molten potassium in tetrahydrofuran (THF) at 65°, carbonation gave in the acidic fraction only 5-*p*-biphenylyl-2,2-diphenylpentanoic acid (**7**), while methanolysis gave 4-*p*-biphenylyl-1,1-diphenylbutane (**9**) containing some 1.4% of 1-*p*-biphenylyl-1,1-diphenylbutane (**8**). Similar reaction with cesium metal at 65° gave **7** as the only acid from carbonation and a 98:2