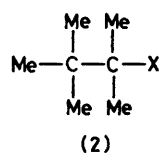
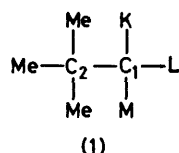


## Effect of $sp^2$ and $sp$ Hybridised Atoms on Barriers to Rotation in Highly Substituted Ethanes. Steric Acceleration of Conformational Processes

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Barriers to rotation about the central bond of the 1,2,2-trimethylbutyl (triptyl) group, *i.e.* barriers to rotation of the *t*-butyl group, are reported for a series of triptyl compounds  $\text{Bu}^t\text{-C}(\text{CH}_3)_2\text{X}$ , where the atom in X bonded to the triptyl group is an  $sp^2$  or  $sp$  hybridised carbon. Barriers in some similar compounds are also reported. Results are discussed in terms of the interactions arising during rotation, and of steric acceleration of conformational processes.

DYNAMIC n.m.r. spectroscopy has proved a particularly useful technique for measuring barriers to rotation in



- |                          |  |
|--------------------------|--|
| a; X = CN                | e; X = <i>m</i> -ClC <sub>6</sub> H <sub>4</sub> |
| b; X = CHO               | f; X = <i>m</i> -PhC <sub>6</sub> H <sub>4</sub> |
| c; X = CO <sub>2</sub> H | g; X = CMe=CH <sub>2</sub>                       |
| d; X = C(Me)=O           | h; X = C(CH <sub>2</sub> Br)=O                   |

highly substituted ethanes, most particularly barriers to rotation of a *t*-butyl group in (1) where none,<sup>1-3</sup> one,<sup>4,5</sup> or two<sup>6</sup> of K, L, and M are hydrogen atoms.

<sup>1</sup> B. L. Hawkins, W. Bremser, S. Borcic, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1971, **93**, 4472.

<sup>2</sup> J. E. Anderson, C. W. Doecke, and H. Pearson, *J.C.S. Perkin II*, 1976, 336 and earlier work cited therein.

<sup>3</sup> S. Hoogasian, C. H. Bushweller, W. G. Anderson, and G. Kingsley, *J. Phys. Chem.*, 1976, **80**, 643 and earlier work cited therein.

1,2,2-Trimethylbutyl (triptyl) compounds of type (2) which is a more specific example of (1) have been much used to study the effect of individual groups X on rotation.<sup>2,3</sup> A series of such compounds (2) has been reported, with barriers ranging from 6.97 when X = H<sup>7</sup> to 11.14 kcal mol<sup>-1</sup> when X = I,<sup>2</sup> but there are no examples as yet of compounds with substituents wherein the point of attachment to the triptyl group is an  $sp^2$  or  $sp$  hybridised carbon atom.

We now report and discuss barriers to rotation in the compounds (2a—h) and (3a—e).

### RESULTS

In the <sup>1</sup>H n.m.r. spectrum of compounds (2a—f) the *t*-butyl signal appears as a singlet at ambient temperature, and as a 2 : 1 doublet at a suitably low temperature, usually *ca.* -120° (see Table 1), indicating that rotation of the *t*-butyl group is slow on the n.m.r. timescale at the low temperature. Barriers to rotation of the *t*-butyl group were calculated from these spectral changes in the usual way.<sup>8</sup> Table 2 lists typical values for barriers in these

<sup>4</sup> F. A. L. Anet, M. St. Jacques, and G. N. Chmurny, *J. Amer. Chem. Soc.*, 1968, **90**, 5243.

<sup>5</sup> P. E. Stevenson, G. Bhat, C. H. Bushweller, and W. G. Anderson, *J. Amer. Chem. Soc.*, 1974, **96**, 1067.

<sup>6</sup> C. H. Bushweller, S. Hoogasian, W. G. Anderson, and L. J. Letendre, *J.C.S. Chem. Comm.*, 1975, 152.

<sup>7</sup> J. E. Anderson and H. Pearson, *J. Amer. Chem. Soc.*, 1975, **97**, 764.

<sup>8</sup> J. E. Anderson and H. Pearson, *J. Chem. Soc. (B)*, 1971, 1209.

compounds, the full list of barriers determined over a range of temperatures for each compound being given in the Experimental section.

TABLE 1  
Chemical shift data <sup>a</sup> for hydrogens in compounds of series (2)

	Bu <sup>t</sup> <sup>b</sup>	C(CH <sub>3</sub> ) <sub>2</sub>	Other signals
(2a)	1.07 (1.17, 0.95; -118.9)	1.29	
(2b)	0.98 (1.03, 0.94; -135.9)	1.03	CHO 9.72
(2c)	1.02 (1.04, 0.95; -136.7)	1.19	
(2d)	1.15 (1.18, 1.11; -137.1)	1.12	CH <sub>3</sub> C=O 2.06
(2e)	0.84 (0.73, 0.99; -109.0)	1.33	Ar 7.0-7.4
(2f)	0.90 (0.81, 1.04; -111.0)	1.41	Ar 7.0-7.4
(2g)	0.93	1.07	CH <sub>3</sub> C= 1.82 olefinic 4.74, 4.93
(2h)	0.95	1.23	CH <sub>2</sub> 4.30

<sup>a</sup> Downfield from internal Me<sub>4</sub>Si. <sup>b</sup> The first two figures in parentheses are the chemical shifts of the two signals of the 2:1 doublet observed at low temperature, the shift of the more intense of the signals being given first. The third figure is the temperature (°C).

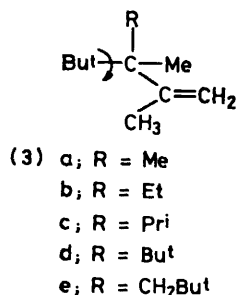
The spectra of compounds (2g and h) were expected to show similar behaviour at low temperature, but although there is broadening analogous to that observed in the cases

TABLE 2  
Barriers to rotation of the t-butyl group in compounds (2a-h) <sup>a</sup>

Compound	Substituent	T/K	k/s <sup>-1</sup>	Barrier (kcal mol <sup>-1</sup> )
(2a)	C≡N	170.0	25	8.7
(2b)	CHO	154.5	34	7.8
(2c)	COOH	152.1	21.5	7.8
(2d)	C(Me)=O	143.2	15	7.5
(2e)	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	177.3	52	8.8
(2f)	<i>m</i> -C <sub>6</sub> H <sub>4</sub> Ph	178.3	40	8.9
(2g)	C(Me)=CH <sub>2</sub>	Not observed, see text		
(2h)	C(CH <sub>2</sub> Br)=O	Not observed, see text		

<sup>a</sup> Rate constants and barriers at other temperatures are reported in the Experimental section.

of (2b-d), at no temperature down to -158° are two distinct signals observed for the t-butyl group. Since for (2b-d) the relative shift of the distinct signals at low

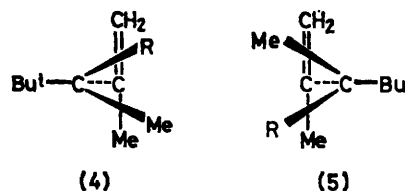


temperature are 9, 9, and 7 Hz (at 100 MHz) and these signals are poorly resolved due to line-broadening at low temperatures, we think that the barrier in (2g and h) is similar to that in (2b-d), but the relative shift is too small

<sup>a</sup> J. E. Anderson, C. W. Doecke, and D. I. Rawson, *Tetrahedron Letters*, 1975, 3531.

to resolve. Another explanation, that the barrier in (2g and h) is much smaller than in (2b-d) seems less likely.

The conformational situation in compounds of type (3) is more complex. The barrier to rotation of the olefinic group, C(CH<sub>3</sub>)=CH<sub>2</sub>, is greater than that of the t-butyl group.<sup>9</sup> As a result, for (3b-e), at moderately low temperatures at which rotation of the t-butyl group is still fast on the n.m.r. timescale, separate sets of signals are seen for two different conformations of these molecules, probably close to (4) and (5). The populations of these conformations are not the same.<sup>9</sup>



Of particular relevance to this work however, there are further changes in the n.m.r. spectra of the t-butyl signals in these compounds at even lower temperatures, changes which can be associated with rotation of the t-butyl group becoming slow on the n.m.r. timescale. Surprisingly

TABLE 3  
Rotation of the t-butyl group in compounds (3a-e)

Compound	Chemical shift <sup>a</sup> of Bu <sup>t</sup>		ΔG <sup>‡</sup> / kcal mol <sup>-1</sup>
	At high temperature	At low temperature	
(3a) <sup>b</sup>	0.93	No change	Not observed
(3b) <sup>c</sup>	0.93	0.87, 0.90, 0.90	8.5 (-115.0 °C)
(3c) <sup>d</sup>	0.99	0.74, 0.98, 1.16	9.6 (-82.0 °C)
(3d) <sup>e</sup>	1.03	1.19, 1.02, 0.86	9.9 (-70.0 °C)
(3e) <sup>d</sup>	1.04	1.24, 1.02, 0.84	10.6 (-70.0 °C)
	0.90	0.88, 0.88, 0.76	10.3 (-75.0 °C)

<sup>a</sup> Downfield from internal Me<sub>4</sub>Si. <sup>b</sup> This is also compound (2g) of Tables 1 and 2. The results are repeated here. <sup>c</sup> Changes due to rotation of the t-butyl group in this compound were not unequivocally observed. See text. <sup>d</sup> Only the t-butyl signal of the major isomer about the sp<sup>3</sup>-sp<sup>2</sup> bond was observed clearly. <sup>e</sup> The association of the six lines at low temperature with the two lines at high temperature is equivocal.

however, at the lowest temperatures at which spectral measurements could be made, not all t-butyl rotations were demonstrably slow on the n.m.r. timescale.

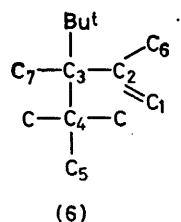
TABLE 4  
Carbon-13 chemical shifts <sup>a</sup> in (3d)

Carbon atom <sup>b</sup>	Temperature	
	74 °C Rotation fast	Temperature 0 °C Rotation slow <sup>c</sup>
C <sub>1</sub>	115.70	115.38, 115.89 *
C <sub>2</sub>	170.30	Not observed
C <sub>3</sub>	40.04	38.7, 40.49 *
C <sub>4</sub>	31.03	Not observed
C <sub>5</sub>	31.04	30.40 * 31.14
C <sub>6</sub>	20.29	19.61, * 20.64
C <sub>7</sub>	27.77	26.82, * 26.90

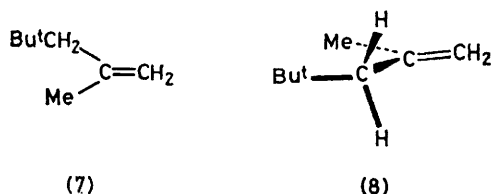
<sup>a</sup> Downfield from internal Me<sub>4</sub>Si. <sup>b</sup> The numbering is shown in diagram (6). <sup>c</sup> More intense of the two signals is asterisked.

Table 3 lists typical values of barriers to t-butyl rotation in compounds (3b-e) and significant spectral data.

The chemical shifts of the carbon atoms in the natural abundance carbon-13 spectra of (3d), recorded when t-butyl rotation is fast and when it is slow on the n.m.r. timescale are shown in Table 4, the atom numbering being as shown in (6).



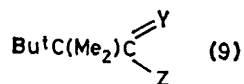
The spectrum of 2,4,4-trimethylpent-1-ene (7) was also temperature independent down to  $-165^\circ$ . The coupling



constants of the olefinic hydrogens to the two allylic groups, *viz.* the 2-methyl and the methylene groups, are very different. Decoupling experiments show that the 2-methyl group has couplings of *ca.* 0.9 and 1.6 Hz to the olefinic hydrogens, the larger presumably being a *cis*-coupling,<sup>10</sup> while the  $\text{CH}_2$  group has a *cis*-coupling of *ca.* 0.9 Hz and a *trans*-one of *ca.* 0 Hz, which agrees well with a conformation close to type (8) being preferred. The observed couplings in such circumstances should be very different, for the 2-methyl group is averaged by rotation through at least three equivalent conformations.

#### DISCUSSION

The barrier in (2a), 8.7 kcal mol<sup>-1</sup>, is intermediate as might be expected, between that already determined<sup>2</sup> for analogues with X = F, 8.04, and X = Cl, 10.43 kcal mol<sup>-1</sup>, and similar in size to that for X = OMe,<sup>11</sup> 8.3 kcal mol<sup>-1</sup>.



In (2b–h) we are concerned with rotation about the  $\text{Bu}^t\text{-CMe}_2\text{X}$  bond, and presumably with a staggered ground state and an eclipsed transition state. However, the conformation or mixture of conformations about the triptyl-X bond may not be the same in these two states, and so the energy contributions from the interactions of Y and Z in (9) with the methyls of the t-butyl group may differ. This is important since in each of (2b–h) the  $sp^2$  hybridised atom is a carbon atom and thus the direct interactions along the  $\text{Bu}^t\text{-CXMe}_2$  bond are superficially the same. It seems reasonable to consider that the barrier is made up of a basic contri-

bution, much the same for each of (2b–h), due to direct eclipsing interactions, and a secondary contribution due to changing long range interactions of Y and Z with the t-butyl methyl groups.

For determining these long range effects, a suitable reference compound may well be (2a) where X =  $\text{C}\equiv\text{N}$ . Since the  $\text{C}\equiv\text{N}$  group is linear, long range interactions between the group attached to the carbon (*i.e.* the nitrogen atom) and the t-butyl group are likely to be small, and there is no possible change in conformation about the triptyl-CN bond during rotation of the t-butyl group. The barrier to t-butyl group rotation in this compound (2a) is 8.7 kcal mol<sup>-1</sup>, which is greater than that in almost every other member of series (2). This brings up the question of steric acceleration.

*Steric Acceleration of Conformational Processes.*—It is intriguing to consider why *long-range* steric interactions may lead to reduced barriers to conformational processes such as rotation in highly substituted ethanes. The principal cause of such barriers in ethanes is direct eclipsing interactions in the transition state. Consider a reference ethane and its derivative which bears a substituent not directly at the C–C bond [for example at K in structure (1) rather than at C-1], but such that the substituent is close to the groups on the other carbon [*i.e.* C-2 in (1)] of the bond.

In the ground state for the ethane rotation in the reference compound, the molecule is at the foot of a potential energy well, as far as the conformation along the ethane bond is concerned. Insofar as the remote substitution to give the derivative can be considered as a perturbation of the reference compound, it is likely to lead to an increase in energy of the ground state. In the transition state for rotation in the reference compound, the potential energy is at a maximum. To the extent that remote substitution can be considered to be a perturbation, the substitution may be accommodated with a reduction of the transition state energy. Considered this way, the effect of substitution would be to produce a lower barrier.

The whole philosophy of looking for and rationalising substituent effects on any chemical process is that changing substituents merely perturbs the course of the process, so such an approach to internal rotation is consistent with other approaches to substituent effects.

There are many other barriers which may be discussed in terms of steric acceleration, for example the barrier to rotation about the  $\text{C}_\alpha\text{-C}_\beta$  bond in (10) drops from 9.4 to 7.7 kcal mol<sup>-1</sup> when R is changed from hydrogen to methyl,<sup>12</sup> reflecting interactions between the group R and the methyls on the  $\beta$ -carbon atom, which are better accommodated in the transition state for rotation. In contrast, R is *directly* involved in rotation about the phenyl- $\text{C}_\alpha$  bond. The barrier to rotation about that bond *increases* from <10 for R = H<sup>12</sup> to 14.2 kcal mol<sup>-1</sup> for R = Me.<sup>13</sup>

The barrier to rotation in (11; R = Pr<sup>i</sup>) is 6.0 kcal

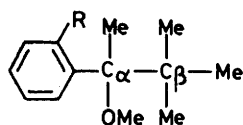
<sup>10</sup> M. Barfield and B. Chakrabarti, *Chem. Rev.*, 1969, **69**, 757.

<sup>11</sup> J. E. Anderson and D. I. Rawson, unpublished results.

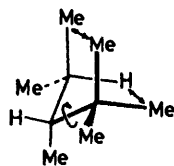
<sup>12</sup> J. E. Anderson and H. Pearson, *J.C.S. Perkin II*, 1974, 1779.

<sup>13</sup> J. E. Anderson and H. Pearson, *J.C.S. Perkin II*, 1977, 699.

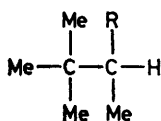
mol<sup>-1</sup> compared with 6.9 kcal mol<sup>-1</sup> (11; R = Me).<sup>14</sup> The long range interaction which causes the *reduction*



(10)



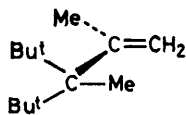
(12)



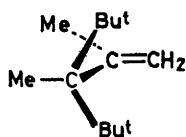
(11)

of the barrier in (11a) is indicated in (12), the likely ground state conformation.

The situation here postulated parallels the steric acceleration of chemical reactions, and should be considered where introduction of bulky substituents leads to lower barriers to conformational processes. Nor need the conformational process be rotation about a single



(13)



(14)

bond. It is well known that large alkyl groups lower barriers to nitrogen inversion,<sup>15</sup> and that simple substitution almost invariably leads to slightly lower barriers to ring inversion in cyclohexane.<sup>16</sup>

The barrier to *t*-butyl group rotation in (3b-d) increases slightly with the size of the group R, in a way that parallels exactly the compounds of type Bu<sup>t</sup>-CMe-(R)Cl.<sup>17</sup> The unusually high barrier in (3e) may reflect the role of a secondary steric effect of the type that has been demonstrated previously<sup>7</sup> for the neopentyl group.

It is worth making some comment on the different barriers in (3d). The less populated isomer has the higher barrier to *t*-butyl rotation, and from the carbon-13 chemical shift information this appears to be like (13) while the more populated isomer is close to (14). We can see no obvious rationalisation of these two results, for

<sup>14</sup> C. H. Bushweller and W. G. Anderson, *Tetrahedron Letters*, 1972, 1811.

<sup>15</sup> See p. 325 of J. M. Lehn, *Fortsch. Chem. Forsch.*, 1970, **15**, 311.

<sup>16</sup> See Table 4 in J. E. Anderson, *Fortsch. Chem. Forsch.*, 1974, **45**, 139.

<sup>17</sup> J. E. Anderson and H. Pearson, *Chem. Comm.*, 1971, 871.

<sup>18</sup> J. Byers and W. C. Hickinbottom, *J. Chem. Soc.*, 1948, 1334.

there are clearly many factors involved, not least the problem of the conformation about the *sp*<sup>3</sup>-*sp*<sup>2</sup> bond.

#### EXPERIMENTAL

Spectra were recorded on a Varian HA100 spectrometer at 100 MHz operating frequency, or on a Varian CFT20 spectrometer at 20 MHz operating frequency for carbon-13 spectra. Calculated exchange-modified spectra were computer-generated using methods described previously.<sup>8</sup>

Solutions were normally *ca.* 0.1M in CF<sub>2</sub>Cl<sub>2</sub> solvent, but (2d) was recorded in 2 : 1 CF<sub>2</sub>Cl<sub>2</sub>-CD<sub>3</sub>C<sub>6</sub>D<sub>5</sub>, since the *t*-butyl peak separation at low temperature in CF<sub>2</sub>Cl<sub>2</sub> solvent is too small to be resolved. Compound (2h) was of poor solubility, and no solvent could be found in which evidence of slow rotation of even the *t*-butyl group was seen at low temperature. There was much broadening and overlap with the *gem*-dimethyl signal such as might obscure such evidence, so that there is no good reason for concluding that the barrier to *t*-butyl rotation in this case is significantly different from that for similar compounds (2a-e).

The following are rate constants and barriers to rotation Δ*G*<sup>‡</sup> for various compounds studied (*T*/°C, *k*/s<sup>-1</sup>, Δ*G*<sup>‡</sup>/kcal mol<sup>-1</sup>): (2a) -85.9, 255, 8.72; -89.7, 160, 8.72; -93.0, 110, 8.69; -95.2, 85, 8.67; -97.1, 75, 8.62; -98.2, 66, 8.60; -100.7, 27, 8.78; -103.2, 25, 8.67; -106.1, 13, 8.74; -110.1, 10, 8.61; -115.1, 5.5, 8.60; (2b) -118.7, 34, 7.76; -122.3, 12.5, 7.87; -127.8, 3.6, 7.93; (2c) -121.1, 21.5, 7.77; -126.9, 7.5, 7.76; (3c) -90.0, 12, 9.64; -86.0, 21, 9.65; -82.0, 40, 9.62; -75.0, 50, 9.90; -65.0, 170, 9.91; -60.0, 360, 9.84. Values for other compounds are given in Table 2.

Many of the compounds (2) and (3) have been prepared previously. Compound (2b) was prepared from di-*iso*-butylene by the method of Byers and Hickinbottom.<sup>18</sup> Condensation of (2b) with hydroxylamine hydrochloride in formic acid solution in the presence of sodium formate led to (2a), m.p. 128-129° (lit.,<sup>19</sup> 131-132°). Oxidation of (2b) with potassium permanganate in sodium carbonate solution led to (2c), m.p. 193-194° (lit.,<sup>19</sup> 198.5-199°).

Compound (2d) was prepared from di-*t*-butyl ketone by treatment with concentrated sulphuric acid.<sup>20</sup> Compound (2h) was prepared from (2d) by treatment in carbon tetrachloride solution with bromine dissolved in the same solvent. Reaction was immediate, and a crystalline product melting at 41-44° was isolated, and characterised by its n.m.r. spectrum. Compound (2g) [≡ (3a)] was prepared by solvolysis of 3-chloro-2,2,3,4,4-pentamethylpentane<sup>7</sup> in aqueous dioxan which produces rearrangement and elimination, in a procedure analogous to that of Shiner and Meier<sup>21</sup> who treated the corresponding alcohol with sulphuric acid in the same solvent. Compound (2g), b.p. 99-105°, was separated from 1,1-di-*t*-butylethylene by distillation, and purified by g.l.c.

*m*-Chloro-*αα*-dimethylbenzyl alcohol (15) and 1-(*m*-biphenyl)-1-methylethanol (16) were prepared by a Grignard reaction in ether under argon of *m*-chloro- and *m*-phenyl-bromobenzene, respectively, with acetone. Conventional work-up led to the chloro-compound (15), b.p. 98.5-100° at 4 mmHg (lit.,<sup>22</sup> 88° at 2 mmHg) and to the

<sup>19</sup> L. Tsai, T. Miwa, and M. S. Newman, *J. Amer. Chem. Soc.*, 1957, **79**, 2530.

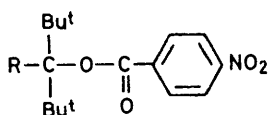
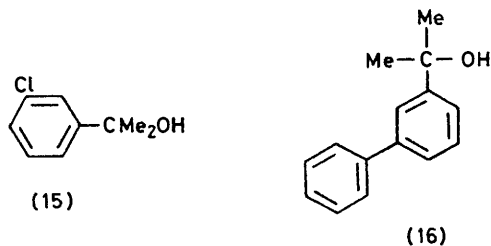
<sup>20</sup> P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, 1955, **77**, 2806.

<sup>21</sup> V. J. Shiner and G. F. Meier, *J. Org. Chem.*, 1966, **31**, 137.

<sup>22</sup> H. C. Brown, Y. Akamoto, and G. Ham, *J. Amer. Chem. Soc.*, 1957, **79**, 1907.

biphenyl derivative (16), b.p. 134—137° at 0.06 mmHg (Found: C, 85.15; H, 7.67.  $C_{15}H_{16}O$  requires C, 84.85; H, 7.6%).

The bromides corresponding to these alcohols were prepared therefrom by treatment in dichloromethane solution



- (17) a; R = Et  
 b; R = Pr<sup>i</sup>  
 c; R = Bu<sup>t</sup>

with dry hydrogen bromide gas. The bromides were obtained after conventional work-up as brown oils, readily eliminating hydrogen bromide. The crude bromides dissolved in dry n-hexane were treated with t-butyl-lithium in pentane solution, under argon. Work-up using ammonium chloride solution led to a complex mixture of compounds from which impure (2e and g) respectively could be isolated by chromatography on silica gel using light petroleum as eluant. For (2e) the parent  $M^+$  ion was not observed due to impurities but  $m/e$  153.047 2 ( $M^+ - C_4H_9$ ) was observed.  $C_9H_{10}^{35}Cl$  requires  $m/e$  153.047 1. For (2f),  $m/e$  252.187 8 ( $M^+$ ) was observed.  $C_{19}H_{24}$  requires  $M$ , 252.189 4.

Compounds (3b—d) were prepared by solvolysis of the *p*-nitrobenzoate esters (17a—c),<sup>13,20</sup> as previously described by Bartlett and Tidwell<sup>23</sup> for (3d). Compound (3b)

<sup>23</sup> P. D. Bartlett and T. T. Tidwell, *J. Amer. Chem. Soc.*, 1968, **90**, 4421.

<sup>24</sup> G. J. Abruscato and T. T. Tidwell, *J. Org. Chem.*, 1972, **37**, 4151.

emerged from a 10 ft  $\times$   $\frac{5}{8}$  in Apiezon L column at 108—110° in 47.5 mins when a helium carrier gas flow rate of 90 ml min<sup>-1</sup> was used (Found: C, 85.35; H, 14.3.  $C_{11}H_{22}$  requires C, 85.65; H, 14.35%). Compound (3c) emerged from a similar column at 160° in 49 min when other conditions were as for (3b) (Found:  $M^+$ , 168.190 8.  $C_{12}H_{24}$  requires  $M$ , 168.187 8). Compound (3d) emerged from a 6 ft  $\times$   $\frac{3}{8}$  in Apiezon L column at 115° in 21 min when a helium carrier gas flow rate of 90 ml min<sup>-1</sup> was used, and had a spectrum identical with that described previously.<sup>23</sup> Compound (3e), donated by Professor Tidwell, had been prepared by a previously reported procedure,<sup>24</sup> and was slightly contaminated with 1-*t*-butyl-1-neopentyl-2,2-dimethylcyclopropane.

The esters (17) were prepared from the corresponding alcohols<sup>25,26</sup> by a published method<sup>23</sup> using methyl-lithium instead of *n*-butyl-lithium. Ester (17a) has m.p. 100.5—101.5° (Found: C, 67.35; H, 8.55; N, 4.3.  $C_{18}H_{27}NO_4$  requires C, 67.25; H, 8.45; N, 4.35%); (17b) has m.p. 100—103° (decomp. 118°) [lit.,<sup>20</sup> 103—104° (decomp. 119°)]; (17c) has m.p. 102—103° (resolidifies 105°) [lit.,<sup>20</sup> 105—106°

TABLE 5

<sup>1</sup>H N.m.r. of compounds <sup>a</sup> not described elsewhere

Compound	<sup>1</sup> H N.m.r. data
(3b)	0.78 (3 H, t, <i>J</i> 7.2 Hz), 0.93 (9 H, s), 1.02 (3 H, d, <i>J</i> < 1 Hz), 1.78 (3 H, d, <i>J</i> 1.2 Hz), 1.36 (2 H, complex), 4.73 (1 H, complex), 5.04 (1 H, complex)
(3c)	0.95 (3 H, s), 0.99 (9 H, s), 0.76 (3 H, d, <i>J</i> 6.9 Hz), 1.06 (3 H, d, <i>J</i> 6.9 Hz), 1.80 (3 H, d, <i>J</i> 1.4 Hz), 2.29 (1 H, septet, <i>J</i> 6.9 Hz), 4.78 (1 H, complex), 4.84 (1 H, complex)
(17a)	1.16 (3 H, t, <i>J</i> 7.2 Hz), 1.25 (18 H, s), 2.61 (2 H, g, <i>J</i> 7.2 Hz), 8.21 (4 H, g <sup>1</sup> )
(17b)	1.22 (6 H, d, <i>J</i> 7.2 Hz), 1.38 (18 H, s), 3.98 (1 H, septet, <i>J</i> 7.2 Hz), 8.22 (4 H, g <sup>1</sup> )
(17c)	1.49 (27 H, s), 8.16 (4 H, g <sup>1</sup> )

<sup>a</sup> ca. 0.2M in CCl<sub>4</sub> solution except (3b and c) where the solvents are CF<sub>2</sub>Cl<sub>2</sub>-CBrF<sub>3</sub> (1 : 1) and CF<sub>2</sub>Cl<sub>2</sub> respectively

(resolidifies 108°)]. Table 5 shows n.m.r. data for compounds (3) and (17).

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<sup>25</sup> A. D. Petrov, E. B. Sokolova, and C. L. Kao, *Zhur. obshchei Khim.*, 1960, **30**, 1107.

<sup>26</sup> P. D. Bartlett and M. S. Swain, *J. Amer. Chem. Soc.*, 1955, **77**, 2801.