# Ring Opening of a Formal Cyclopentylmethyl Radical in the Thermolysis of Di(*tert*-alkyl)(1-norbornyl)methanols

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In the thermolysis of di(1-adamantyl)(1-norbornyl)methanol, $Ad_2NorCOH$, **1a**, in toluene at 220–265 °C, C–C bond cleavage within the norbornyl group of the first-formed (1-adamantyl)(1-norbornyl)ketyl radical (by loss of Ad$^{\bullet}$) leads to ring-opened ketones and several ketonic cross-products. These are isomeric with the secondary alcohol, AdNorCHOH, and with the regular cross-product, AdNorSCOH (S = benzyl), respectively, also present in the product mixture. Formation of the ring-opened thermolysis products is particularly favoured by high temperature and the use of deuteriated solvent, which slows hydrogen transfer from the solvent to the intermediate ketyl radical. The new products are cyclopentane derivatives, formed by cleavage of the norbornyl C(1)–C(2) bond, in agreement with MM2 calculations on the transition states. Self-consistent values for the cage effect have been determined by measuring the extent of 1-[$^2$H] labelling of the adamantane formed in [$^2H_8$]toluene and by scavenging the ketyl radical with benzenethiol in [$^1H_8$]toluene. The product composition of the scavenger-free reaction in [$^1H_8$] or [$^2H_8$]toluene has been interpreted by kinetic simulation based on the steady state approximation, a Simplex procedure being used to optimise several rate constants, in particular those for hydrogen transfer from toluene to the ketyl radical and ring opening of the latter. The Arrhenius pre-exponential factor and activation energy are both much greater for ring opening than for hydrogen transfer.

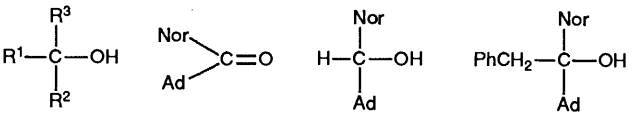
Radical additions to alkenes and, in particular, those leading to cyclic products are of great importance in both physical and synthetic organic chemistry.[1,2]

In the reverse reaction, a ring system, usually strained, adjacent to a radical centre, opens to give an acyclic species or one with fewer rings. The exothermic opening of the cyclopropyl group in a cyclopropylmethyl radical ($k = 1 \times 10^9$ s$^{-1}$ at 25 °C) constitutes a very fast radical clock widely used for the detection of radical intermediates.[3–5] Cyclobutyl opens several orders of magnitude slower than cyclopropyl (*ca.* $5 \times 10^3$ s$^{-1}$ at 25 °C).[6] Nevertheless, in the β-pinene system, radical addition frequently leads to rearranged products resulting from the opening of the four-memberd ring.[7] The β-scission of cyclopentylmethyl and higher cycloalkylmethyl radicals is endothermic and occurs too slowly to compete with intermolecular reactions.[8] The activation energy for ring opening of the cyclopentylmethyl radical is estimated to be about 23 kcal mol$^{-1}$ † which, taken with the usual pre-exponential factor for ring opening [log ($A$/s$^{-1}$) = 13],[9] suggests a rate constant in the $10^{-4}$ s$^{-1}$ range, *i.e.* some $10^9$ slower than that for the cyclisation of the hex-5-enyl radical.[10]

A few years ago, however, we reported that the di(1-norbornyl)ketyl radical, $Nor_2\dot{C}OH$, formed by the thermolysis of a (*tert*-alkyl)di(1-norbornyl)methanol, ring-opened to give (3-ethylcyclopentyl)(1-norbornyl)ketones.[11] Formally this amounts to opening of both cyclopentyl and cyclohexyl rings. Ring opening of the di(1-norbornyl)ketyl radical competes with hydrogen atom transfer to or from the ketyl radical, as well as with other termination reactions. In previous work[12,13] we have shown that kinetic simulation of product data can be used to obtain semi-quantitative information about the various reactions of ketyl radicals. Insofar as the introduction of a new reaction process, *i.e.* ring opening, gives rise to new products it should be possible to extend this procedure to calculate the relative rates of hydrogen transfer from solvent to ketyl radical and opening of this latter.

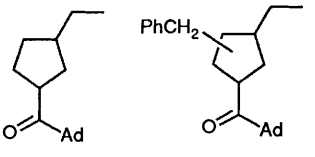
† 1 cal = 4.184 J.

Di(1-adamantyl)(1-norbornyl)methanol, **1a**, was chosen for this study, to take advantage of the fact that hydrogen transfer from the bridgehead 'leaving radical' is prohibited, thus reducing somewhat the number of possible reaction processes. The presence of a *tert*-butyl radical in the thermolysis of (1-adamantyl)(*tert*-butyl)(1-norbornyl)methanol, **1b**, also examined but in less detail, makes for a rather more complicated reaction scheme.




**1** **2** **3** **4**

**1a**; $R^1 = R^2 = Ad$; $R^3 = Nor$
**1b**; $R^1 = Ad$; $R^2 = Bu^t$; $R^3 = Nor$
**1c**; $R^1 = R^2 = R^3 = Ad$
**1d**; $R^1 = Oc$; $R^2 = R^3 = Nor$




**5** **6**

## Results

*Thermolysis of Di(1-adamantyl)(1-norbornyl)methanol*, **1a**.—*Product identification.* Previous work[11–13] on the thermolysis of tri(*tert*-alkyl)methanols, such as **1c**, **1d** and others where the leaving radical is *tert*-butyl, has shown that in toluene the major products are bibenzyl (from self-reaction of the solvent-derived radical), di(*tert*-alkyl)ketone, di(*tert*-alkyl)methanol and a cross-product from reaction of the benzyl and di(*tert*-alkyl)ketyl radicals.

Inspection of the gas chromatogram of the 220–265 °C thermolysis products of **1a** in toluene reveals important novel features. There are peaks just before those corresponding to the

**Table 1** Temperature and solvent isotope effects on product composition (%) from the thermolysis of di(1-adamantyl)(1-norbornyl)methanol, **1a**, in toluene (relative molar yields; absolute values in parentheses).

| Temp./ °C | Bibenzyl | Ring-open. ket.[a] | | Unsat. ring-op. ket. | | Normal ketone | Sec. alc.[a] | | Ring-open. cross-prod. | Normal cross-prod. | Cage effect |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5-h | 5-d | 7a | 7b | | 3-h | 3-d | | | |
| In [$^1H_8$]toluene | | | | | | | | | | | |
| 220 | 61.3 (58) | 4.8 | | | 0.2 | 33.7 (32) | 56.4 (53) | | 3.9 | 1.0 (0.8) | 30[c] |
| 232 | 58.4 (56) | 6.1 | | 0.1 | 0.5 | 33.2 (31) | 53.5 (51) | | 5.4 | 1.2 (1.2) | 28[c] |
| 245 | 57.0 (54) | 8.0 | | 0.2 | 0.6 | 32.6 (32) | 48.9 (46) | | 8.0 | 1.6 (1.5) | 27[c] |
| 255 | 56.0 (53) | 9.4 | | 0.3 | 0.9 | 32.0 (30) | 45.0 (42) | | 10.5 | 1.9 (1.7) | 26[c] |
| 265 | 51.8 (49) | 10.6 | | 0.4 | 1.2 | 32.0 (31) | 40.5 (39) | | 12.8 | 2.5 (2.3) | 25[c] |
| In [$^2H_8$]toluene | | | | | | | | | | | |
| 220 | 42.4 | 3.8 | 3.9 | 0.1 | 0.4 | 44.0 | 3.1 | 31.4 | 10.6 | 2.3 | 29[d] |
| 232 | 39.8 | 4.6 | 4.2 | 0.2 | 0.8 | 43.8 | 31.0[b] | | 13.0 | 2.5 | |
| 245 | 37.4 | 5.2 | 4.4 | 0.4 | 1.3 | 42.4 | 2.5 | 25.1 | 15.7 | 2.9 | 27[d] |
| 255 | 35.5 | 6.1 | 4.4 | 0.9 | 1.9 | 41.2 | 24.3[b] | | 18.1 | 3.0 | |
| 265 | 34.4 | 6.9 | 4.6 | 1.0 | 2.4 | 41.3 | 2.5 | 18.6 | 19.4 | 3.3 | 26[d] |

[a] **3**-d and **5**-d refer to the deuteriated components of **3** and **5**, **3**-h and **5**-h to the normal components. [b] Total yield; deuterium content not determined. [c] By scavenging. [d] By isotopic labelling.

ketone, **2**, and the cross-product, **4**. The lower retention time component (which appears as a doublet of approximately equal peaks on capillary GLC) can, on the basis of its mass (MS) or ion trap detector (ITD) spectrum, $^1H$ and $^{13}C$ NMR spectra and comparison with the product isolated from the thermolysis of (1-bicyclo[2.2.2]octyl)di(1-norbornyl)methanol, **1d**,[11] be identified as *cis* and *trans* ring-opened ketones, **5a** and **b**, containing a cyclopentyl group and isomeric with the secondary alcohol, **3**.*

The new higher retention time peak comprises several benzyl-substituted ring-opened ketones, **6a–g**, geometric and/or positional isomers of each other, which are also isomeric with the regular cross-product, **4**, which, however, is a tertiary alcohol. Attempts to determine the structures of **6** by ITD and MS studies, using both electron impact and chemical ionisation, were unsuccessful, nor was it possible to isolate any one component for NMR study. The IR spectrum of a five-component fraction showed a carbonyl absorption at 1694 $cm^{-1}$, indicating, in agreement with the ITD and MS work, that the predominant cyclopentanes are not benzylated at the 1-position adjacent to the carbonyl group. The carbonyl frequencies of **5** and of 1-adamantyl cyclopentyl ketone are at 1696 and 1694 $cm^{-1}$, respectively, whereas that of 1-adamantyl 1-benzylcyclopentyl ketone is at 1683 $cm^{-1}$, typical of di(*tert*-alkyl) ketones.[14] Benzylation of **5** resulted in a mixture of two ketones whose retention times were similar to those of **6b** and **6c**, but which had quite different ITD spectra. The main peaks (but not the relative intensities) were displaced to *m/z* 28 daltons higher than those of 1-adamantyl 1-benzylcyclopentyl ketone. Nevertheless, the peaks corresponding to **6b** and **6c** are sufficiently broad to accommodate small amounts of 1-benzylated isomers; it can be seen from the ITD spectra† that only at the retention times corresponding to these isomers does **6** show significant fragments at *m/z* 157 and 186, characteristic of the 1-benzyl derivatives.

Capillary GLC also revealed the presence of two minor products with retention times between those of the ring-opened ketones and the regular ketone. ITD analysis of these suggests that they are unsaturated ring-opened ketones (denoted **7a** and **b**) formed by hydrogen abstraction from the ring-opened radical. The overall yields of these, and all other ring-opened products, increase with the thermolysis temperature (Table 1), indicating that the activation enthalpy is higher and/or the activation entropy for ring opening is less negative than that for hydrogen transfer from the solvent to the ketyl radical, as was previously inferred from more qualitative data on the thermolysis of **1d**.[11]

*Isotope effects on product composition and deuterium labelling.* When the reaction is run in [$^2H_8$]toluene the ring-opened ketones are partially deuteriated, there being comparable CI–ITD peaks at both *m/z* 261 and 262 whereas in the non-labelled ketones the M + 2 peak is only about 20% of M + 1. The amount of non-labelled ring-opened ketone (expressed as a percentage of the total yield of **5**, without any distinction of the two isomers) ranged from *ca.* 54% at 220 °C to 61% at 265 °C; results are given in Table 1. The extent of deuteriation of the secondary alcohol, AdNorCLOH, **3**, (L = H or D) is much greater, being close to 90% according to CI–ITD measurements. This is somewhat higher than that found in the thermolysis of tri(1-adamantyl)methanol, **1c**, about 70–80% depending on the temperature.[12]

*Radical scavenging by a hydrogen atom acceptor.* The progressive addition of benzophenone (BP) causes approximately linear changes in the product composition (Table 2). At 245 °C the ratios of **3** to **5** and of **4** to **6** are practically constant at 6.0 ± 0.3 and 0.23 ± 0.02, respectively, regardless of the BP concentration up to [BP]/[**1a**] = 0.4. The cut-off points and the ceiling are somewhat less well defined than in the case of **1c**, previously studied,[12] but, taking the linear initial and final sections for each component, we find the average intersection at a [BP]/[**1a**] ratio of 0.45 ± 0.06. This agrees well with the sum of the limiting values of the yields of the cross-product, BPSH, and bibenzyl, namely, 0.38 + 0.08 = 0.46.[12]

*The cage effect and scavenging by a hydrogen atom donor.* The cage effect, determined by measuring the AdH content of the adamantane formed when the reaction was run in [$^2H_8$]toluene, was 0.29, 0.27 and 0.26 at 220, 245 and 265 °C, respectively. As we have shown in a previous paper,[13] a second approach to the cage effect consists in scavenging, by means of a powerful hydrogen atom donor, all ketyl radicals which escape from the cage. Above a certain scavenger concentration the ketone yield is reduced to that which is formed within the cage, further amounts of scavenger having no effect. This was confirmed by

* Note added in proof: We have now prepared **5a** and **b** by a five-step synthesis from ethyl 3-ethyl-2-oxocyclopentanecarboxylate (*i*, $NaBH_4$/EtOH; *ii*, $Ac_2O/H_2SO_4/Et_2O$; *iii*, Bu$^t$OK/Bu$^t$OH; iv, $H_2$/Ni; *v*, 1-AdBr/Li/THF). The product, obtained as two isomers in approximately equal amounts, was identical in all respects to that obtained by the thermolysis of **1b**.

† ITD spectra are available as a supplementary publication. [Supp. pub. no. 56864 (21 pp.)].

**Table 2** Effect of benzophenone on the thermolysis of di(1-adamantyl)(1-norbornyl)methanol, **1a**, in [$^2H_8$]toluene at 245 °C (relative molar yields in percent; absolute yields in parentheses).

| [BP]/[**1a**] | Bibenzyl | Ring-open. ketones[a] | Normal ketone[b] | Sec. alc. | BPSH | Ring-open. cross-prod. | Normal cross-prod. | AdH | **3/5** | **4/6** |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.0 | 57.0 (54) | 8.2 | 33.2 (32) | 48.9 (46) | | 8.0 | 1.6 | | 6.0 | 0.20 |
| 0.1 | 44.7 | 6.8 | 48.0 | 39.1 | 8.5 | 5.0 | 1.2 | (102) | 5.8 | 0.24 |
| 0.2 | 34.5 | 5.2 | 61.9 | 29.2 | 17.2 | 3.0 | 0.7 | (100) | 5.6 | 0.23 |
| 0.3 | 22.4 | 2.9 | 77.3 | 18.1 | 26.1 | 1.3 | 0.3 | (100) | 6.2 | 0.23 |
| 0.4 | 15.3 | 1.6 | 88.4 | 10.0 | 32.8 | | | (100) | 6.3 | |
| 0.5 | 12.0 (13) | 0.9 | 92.5 (93) | 6.6 (7) | 35.0 (36) | | | (98) | | |
| 0.6 | 10.1 | 0.7 | 94.6 | 4.7 | 36.4 | | | (96) | | |
| 0.8 | 9.1 | 0.3 | 97.1 | 2.6 | 38.1 | | | (98) | | |
| 1.0 | 9.0 (9) | | 97.6 (99) | 2.4 | 36.8 (36) | | | (97) | | |
| 2.0 | 8.2 (8) | | 99.4 (100) | 0.6 | 37.7 (39) | | | (102) | | |

[a] Includes **7a**. [b] Includes **7b**.

**Table 3** Effect of benzenethiol (TH) on the thermolysis of di(1-adamantyl)(1-norbornyl)methanol, **1a**, in [$^1H_8$]toluene at 245 °C (relative molar yields in percent; absolute yields in parentheses).

| [TH]/[**1a**] | Bibenzyl | Benzyl arylsulph. | Diaryl disulph. | Ring-opened ketones | Normal ketone | Sec. alc. | AdH |
|---|---|---|---|---|---|---|---|
| 0.0 | 57.0 (54) | | | 8.2[c] | 33.2[d] | 48.9 (46) | (99) |
| 0.2 | 35.0 | 14.8 | 0.5 | 2.3 | 31.9 | 65.8 | |
| 0.5 | 17.4 | 26.8 | 4.9 | 0.4 | 29.6 | 70.0 | |
| 1.0 | 6.9 (7) | 28.9 | 16.0 (16) | | 28.1 (28) | 71.9 (70) | (104) |
| 2.0 | 1.8 (2) | 21.3 | 36.0 (36) | | 27.5 (26) | 72.5 (70) | (101) |
| 4.0 | | 11.2 | 50.9 (52) | | 27.3 (26) | 72.7 (70) | (98) |
| 2.0[a] | 0.6 (1) | 17.1 | 39.2 (39) | | 30.3 (29) | 69.7 (67) | (101) |
| 2.0[b] | 3.6 (4) | 25.1 | 30.0 (30) | | 25.8 (25) | 74.2 (72) | (102) |

[a] 220 °C. [b] 265 °C. [c] Includes **7a**. [d] Includes **7b**.

**Table 4** Product composition for the thermolysis of (1-adamantyl)(*tert*-butyl)(1-norbornyl)methanol, **1b**, in toluene (relative molar yields in percent; absolute yields in parentheses).

| Temp./°C | Bibenzyl | Ring-open. ketones | **7a** | **7b** | Normal ketone | Sec. alc. | Ring-open. cross-prod. | Normal cross-prod. | Cage effects | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Ketone | Sec. alc. |
| 205 | 69.4 (66) | 3.3 | | 0.1 | 14.0 (13)[a] | 77.5 (74) | 3.3 | 1.8 (2) | 8.5 | 8.7 |
| 230 | 66.3 (64) | 5.8 | 0.1 | 0.5 | 15.1 (14)[a] | 68.9 (66) | 6.6 | 3.0 (3) | 7.0 | 7.0 |
| 255 | 58.1 (56) | 9.0 | 0.5 | 1.0 | 15.8 (15)[a] | 56.3 (54) | 12.9 | 4.4 (4) | 6.3 | 6.0 |

[a] Includes **7b**.

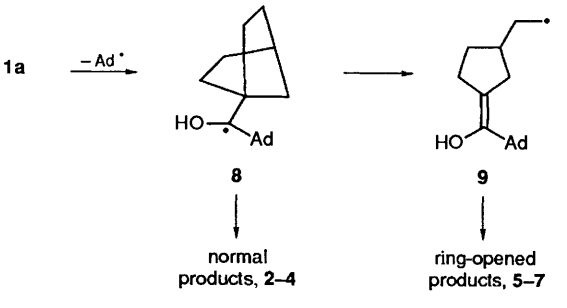
adding benzenethiol (TH) in molar ratios, with respect to starting alcohol, of 0.2 to 4.

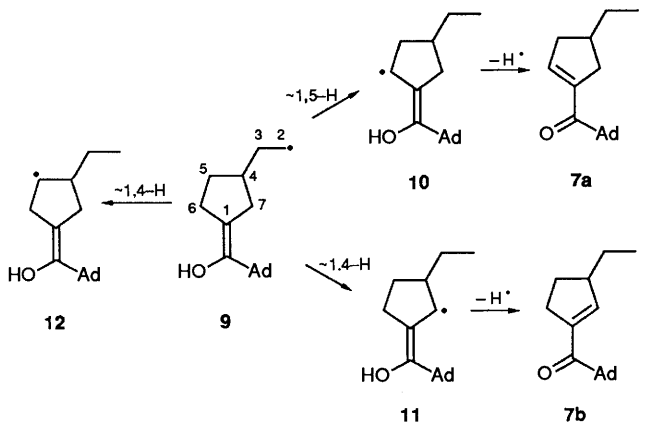
As can be seen from Table 3, at 245 °C the ketone yield is smaller than in the absence of thiol and changes very little when [TH]/[**1a**] is increased beyond 0.5, the lowest yield being very close to the cage effect determined by isotopic analysis of the adamantane. At all temperatures there is good agreement between the cage effects found by scavenging ([TH]/[**1a**] = 2) and by deuterium labelling of the adamantane. Cage effects at 232 and 255 °C were measured solely by scavenging. The Arrhenius activation energy calculated from the temperature dependence of the cage effect {by plotting log [(1 − *Y*)/*Y*] against 1/*T*, where *Y* is the cage effect}, is 2.6 kcal mol$^{-1}$, *i.e.* of the same order of magnitude as previous determinations on this and other reactions.[13]

*Thermolysis of* (1-*Adamantyl*)(tert-*butyl*)(1-*norbornyl*)*methanol*, **1b**.—Alcohol **1b** was examined less extensively (Table 4). The same ring-opened products are formed but at the same temperature their yields tend to be higher than for **1a**. This is explained, at least in part, by the much smaller cage effects for **1b** thermolysis, *i.e.* a greater fraction of the ketyl radical escapes from the cage. The distribution of the ring-opened cross-products, **6a–g**, is the same as in the thermolysis of **1a** (see Supplementary Material). Because of its easier accessibility and greater solubility, this alcohol was used in preference to **1a** in the semi-preparative thermolysis experiment (see Experimental Section).

## Discussion

*Formation of Ring-opened Products*.—The ring opening of the ketyl radical, **8**, is the reverse of radical addition to an alkene and, as such, should give rise to an ω-radical-enol, **9**, which would then abstract a hydrogen atom from solvent or another ketyl radical to give an enol.[15] Reaction of the initial ring-opened radical with benzyl radical would give only two isomers of **6**, while the capillary GLC results require at least 7 or 8






structures. This multiplicity of ring-opened cross-products can only be explained in terms of 1,4- and 1,5-hydrogen migrations. The preferred 1,5-migration[1b] from C(6) to C(2) will convert the primary radical, **9**, into a secondary radical, **10**; reaction of this latter with benzyl radical, followed by ketonisation, will lead to four enantiomeric pairs of 1,2,4-trisubstituted cyclopentanes. Less favoured, but conceivable,[16] 1,4-hydrogen migrations from C(7) or C(5) to give **11** and **12**, followed by combination with benzyl, will provide eight more enantiomer pairs. If the C–C double bond is still in place, **10** and **11** are allylic radicals and would therefore be thermodynamically preferred to **9** and **12**. Since there is no significant variation in the relative intensities of the components of the **6a–g** multiplet with change of solvent or temperature (Supplementary Material), it seems reasonable to assume that combination is slow compared to 1,4- or 1,5-migration.

It is not clear how or when, in the absence of acid or base, enol–ketone tautomerisation occurs.[17] Although the intramolecular 1,3-hydrogen shift from oxygen to carbon is predicted on theoretical grounds to be prohibitively slow,[18] vinyl alcohol rearranges fairly readily to acetaldehyde,[19] and ketone-derived enols are known to be even less stable than those derived from aldehydes.[20] This kinetic instability of enols has been attributed to 'complicating intermolecular or ionic reactions',[18a] including presumably those involving catalytic sites on the walls of the reaction vessel.[21] However, experiments on the radical opening of 1-cyclopropylethan[$^2H_1$]ol show that 60% of the resulting pentan-2-one is labelled in the 3-position,[15d,22] suggesting that ketonisation does, nevertheless, involve a 1,3-hydrogen shift or intermolecular hydrogen transfer. Curiously, more attention has been paid to the 1,5-hydrogen shift (10% labelling in the 5-position) which leads from the *cis*-enol to the enoxyl radical.[22,23] In norbornyl ring opening, while successive migrations [1,5 from C(6) to C(2), then 1,4 from O to C(6)] would give an analogous radical, this would be expected to react with benzyl radical at C-(1); though not completely excluded, this process seems to be of minor importance.

*Scheme for the Reaction of* **1a** *in Toluene.*—The scheme (Scheme 1) which can be assumed on the basis of the observed products and previous knowledge of this type of reaction includes several features which did not arise in the case of **1c**: formation of a set of rapidly interconverting ring-opened radicals, **8–12** (A•); hydrogen-transfer from the solvent, SL (where L = H or D), or ketyl radical, **8**, to A• to give ring-opened ketones, **5a** and **b** (AH); hydrogen abstraction from A• to give unsaturated ring-opened ketones, **7a** and **b** [A(−H)], and, finally, cross-reactions of the various ring-opened radicals with benzyl radical leading to ring-opened cross-products, **6a–g** (AS).

The conventional book-keeping procedure for the radicals S•, AdNorĊOH and A• gives eqns. (1)–(3) from which eqn. (4) may

$$\text{for S}^\bullet: \quad 1 - a + b + h = d + e + 2f + l + m \tag{1}$$

$$\text{for AdNorĊOH}: \quad 1 - a = b + 2c + d + e + g + i + j \tag{2}$$

$$\text{for A}^\bullet: \quad g = h + i + j + 2k + l + m \tag{3}$$

$$f = b + c + h + i + j + k \tag{4}$$

be derived. In other words, the bibenzyl yield should be equal to the sum of the secondary alcohol and ring-opened ketone yields. It can be seen from Table 1 that this equation is satisfied at all temperatures in both normal and deuteriated toluene, the bibenzyl yield in fact exceeding the sum by an average of 0.3 ± 0.9%.

The results for thermolysis of **1b** are analogous with those for **1a**. There are, however, differences which can be attributed to the reactions, both inside and outside the cage, of the *tert*-butyl radical. Because the *tert*-butyl radical reacts more slowly with the solvent than 1-Ad• and can act as a hydrogen atom donor,[13] it is involved in a variety of additional reactions which do not concern the adamantyl radical (Scheme 2). In particular, because of the self- and cross-reactions of the *tert*-butyl radical, the bibenzyl yield falls below the sum of the ring-opened ketone and secondary alcohol yields,[13] this latter being much higher than in the case of **1a**.

*Isotope Effects.*—There are two points in Scheme 1 where solvent isotope effects can obviously arise, namely, hydrogen transfer from the solvent to the ketyl and ring-opened radicals.

| Process | Fraction | Rate const. |
|---|---|---|
| $Ad_2NorCOH \longrightarrow AdNorĊOH + Ad^\bullet$ | 1 | $k_1$ |
| $AdNorĊOH + Ad^\bullet \longrightarrow AdNorCO + AdH$ | $a$ | $k_2$ |
| $Ad^\bullet + SL \longrightarrow AdL + S^\bullet$ | $1 - a$ | $k_3$ |
| $AdNorĊOH + SL \longrightarrow AdNorCLOH + S^\bullet$ | $b$ | $k_4$ |
| $2\,AdNorĊOH \longrightarrow AdNorCO + AdNorCHOH$ | $c$ | $k_5$ |
| $AdNorĊOH + S^\bullet \longrightarrow AdNorSCOH$ | $d$ | $k_6$ |
| $AdNorĊOH + S^\bullet \longrightarrow AdNorCO + SH$ | $e$ | $k_7$ |
| $2\,S^\bullet \longrightarrow S_2$ | $f$ | $k_8$ |
| $AdNorĊOH \longrightarrow A^\bullet$ | $g$ | $k_9$ |
| $A^\bullet + SL \longrightarrow AL + S^\bullet$ | $h$ | $k_{10}$ |
| $A^\bullet + AdNorĊOH \longrightarrow AH + AdNorCO$ | $i$ | $k_{11}$ |
| $A^\bullet + AdNorĊOH \longrightarrow A(-H) + AdNorCHOH$ | $j$ | $k_{12}$ |
| $2A^\bullet \longrightarrow AH + A(-H)$ | $k$ | $k_{13}$ |
| $A^\bullet + S^\bullet \longrightarrow AS$ | $l$ | $k_{14}$ |
| $A^\bullet + S^\bullet \longrightarrow A(-H) + SH$ | $m$ | $k_{15}$ |

**Scheme 1**

| Process | Rate constant |
|---|---|
| $AdNorC\dot{O}H + Bu^t{}^{\bullet} \longrightarrow AdNorCO + C_4H_{10}$ | in cage |
| $AdNorC\dot{O}H + Bu^t{}^{\bullet} \longrightarrow AdNorCHOH + C_4H_8$ | in cage |
| $AdNorC\dot{O}H + Bu^t{}^{\bullet} \longrightarrow AdNorCO + C_4H_{10}$ | $k_{16}$ |
| $AdNorC\dot{O}H + Bu^t{}^{\bullet} \longrightarrow AdNorCHOH + C_4H_8$ | $k_{16}$ |
| $SH + Bu^t{}^{\bullet} \longrightarrow S^{\bullet} + C_4H_{10}$ | $k_{17}$ |
| $S^{\bullet} + Bu^t{}^{\bullet} \longrightarrow SH + C_4H_8$ | $k_{18}$ |
| $S^{\bullet} + Bu^t{}^{\bullet} \longrightarrow Bu^tS$ | $k_{18}$ |
| $2\,Bu^t{}^{\bullet} \longrightarrow C_8H_{18}, C_4H_8 + C_4H_{10}$ | $k_{19}$ |
| $A^{\bullet} + Bu^t{}^{\bullet} \longrightarrow AH + C_4H_8$ | $k_{20}$ |
| $A^{\bullet} + Bu^t{}^{\bullet} \longrightarrow A(-H) + C_4H_{10}$ | $k_{20}$ |

**Scheme 2**

The former is manifested by a drop in the secondary alcohol yield and an overall increase in the yield of ring-opened products of all types when thermolysis is conducted in [$^2H_8$]toluene (Table 1). The second concerns the distribution of these latter, the proportion of ring-opened ketones, **5**, being smaller in [$^2H_8$]toluene than in [$^1H_8$]toluene. As shown above, in [$^2H_8$]toluene the greater part of **5** is formed not by reaction with the solvent but by radical–radical reactions. In this respect the behaviour of the ring-opened radical, **9**, is in marked contrast to that of the normal ketyl radical, **8**, which reacts primarily with the solvent to form secondary alcohol. For the di(1-adamantyl)ketyl radical also, even in [$^2H_8$]toluene, most of the secondary alcohol is formed by hydrogen abstraction from the solvent, little being formed by self-disproportion of the ketyl radicals.[12]

*Hydrogen Acceptor Scavenger Effects.*—The essential reactions involving BP and the hydroxybenzhydryl radical, BPH$^{\bullet}$, are presented in Scheme 3. The reason the BP effect is less clear-

$$AdNorC\dot{O}H + BP \longrightarrow AdNorCO + BPH^{\bullet}$$
$$2\,BPH^{\bullet} \longrightarrow BP + BPH_2$$
$$BPH^{\bullet} + S^{\bullet} \longrightarrow BPSH$$
$$BPH^{\bullet} + S^{\bullet} \longrightarrow BP + SH$$

**Scheme 3**

cut than for **1c**, and that a trace of secondary alcohol remains even when there is an excess of acceptor, could lie in the relative rates of hydrogen transfer from the ketyl radical to BP and from the solvent to the radical. In the case of **1c**, at lower temperatures (145–185 °C), hydrogen transfer from the ketyl radical to BP was clearly much faster than any other reaction of this radical.[13] However, if increasing the temperature accelerates the second process (hydrogen transfer from solvent) more than the first, we could reach a situation where the two processes are of comparable importance.

The constancy of the **3**/**5** and **4**/**6** ratios is a simple consequence of the fact that when BP is available the ketyl radical is converted to ketone whereas, when the BP is exhausted, further ketyl radical gives the normal product distribution, but with reduced overall yields of all the components except, of course, the regular ketone. Since all ring-opened products are ultimately quenched at high BP concentrations, it is clear that they and the secondary alcohol are formed from the ketyl radical outside the cage. This, however, does not imply that ring opening requires a solvent molecule, merely that it is slower than diffusion of the ketyl radical from the cage.

*Hydrogen Donor Scavenger Effects.*—The essential reactions involving benzenethiol and the thiyl radical are presented in Scheme 4. In the presence of increasing concentrations of benzenethiol the bibenzyl, normally formed in the same yield as the secondary alcohol, **3** and the ring-opened ketones, **5**, is progressively replaced by benzylphenylsulfide (TS) and diphenylsulfide ($T_2$), with the disulfide almost negligible at the lowest thiol/**1a** ratio but predominating at high thiol concentration. The benzylphenylsulfide yield therefore rises to a maximum as thiol/**1a** increases and then falls off.

$$Ad^{\bullet} + TH \longrightarrow AdH + T^{\bullet}$$
$$AdNorC\dot{O}H + TH \longrightarrow AdNorCHOH + T^{\bullet}$$
$$S^{\bullet} + TH \longrightarrow SH + T^{\bullet}$$
$$T^{\bullet} \longrightarrow T_2$$
$$S^{\bullet} + T^{\bullet} \longrightarrow TS$$

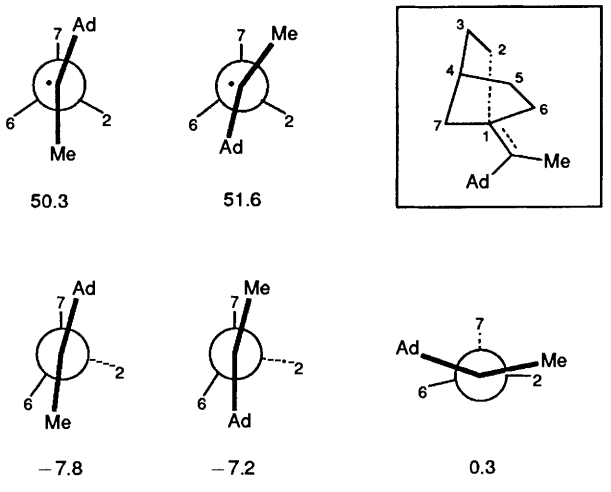
**Scheme 4**

For a given thiol concentration, the distribution of the coupling products varies significantly with the temperature. The higher the temperature, the greater the yields of bibenzyl and benzylphenylsulfide, the overall 'benzyl' yield increasing at the expense of the 'thiyl' yield. This is qualitatively consistent with the difference in the activation barriers for hydrogen transfer from thiol and from toluene [TH + Bu$^t{}^{\bullet}$: log ($A$/dm$^3$ mol$^{-1}$ s$^{-1}$) = 9.26; $E_a$ = 1.50 kcal mol$^{-1}$; $PhCH_3$ + Bu$^t{}^{\bullet}$ log $A$ = 5.91; $E_a$ = 6.93 kcal mol$^{-1}$].[24,25] Given that benzenethiol reacts with different alkyl radicals with very similar rate constants,[24] we can attempt to estimate the relative rates of reaction of thiol and toluene with Ad$^{\bullet}$ and $AdNorC\dot{O}H$ from the appropriate Arrhenius functions, neglecting transfer from thiol to benzyl radical.[26] This calculation predicts, however, rate ratios ([toluene]/[thiol] = 750) of 750, 590 and 480 at 220, 245 and 265 °C, respectively, in favour of thiol; consequently, no 'benzyl' products should be seen. In fact, the crude rate ratios, based on the relative yields of 'thiyl' and 'benzyl' products, are 5.2, 3.7 and 2.6 at the same temperatures. If nothing else, this result serves to underline the dangers of long-range extrapolation of Arrhenius functions.

In the thermolysis of **1c** at 145–185 °C the thiyl/benzyl ratio is noticeably higher[13] and, when [$^2H_8$]toluene is used, benzyl products do disappear, except at the highest temperature. Comparison of these two donors by kinetic simulation, which would enable us to distinguish the adamantyl and ketyl radicals, is only possible when the reaction is quantitative or near-quantitative, with complete accountability of all the products. By analogy with eqn. (4), mass balance requires that the sum of the yields of **3** and **5** be equal to the sum of the bibenzyl, TS and $T_2$ yields, but this condition is not satisfied, probably due to desulfurisation of the thiol or the thiyl radical.[27] Further, at high thiol concentration one would expect the combined radical yield to increase with temperature, as more radicals escape from the cage, but the experimental data are not altogether consistent with this expectation. Again, there is an apparent shortfall of sulfur-containing products, rather greater than that found at lower temperatures for the thermolysis of **1c**.[13]

*Regioselectivity in the Ring Opening of the* 1-*Norbornyl Group.*—In this and other work[11] we find that (*tert*-alkyl)(1-norbornyl)ketyl radicals formed in the thermolysis of di(*tert*-alkyl)(1-norbornyl)methanols undergo ring opening, particularly at high temperatures, substituted cyclopentanes being the only products. The selectivity of this reaction is readily explained by means of molecular mechanics (MM) calculations[28] on suitable models of the radicals[29] and of the transition states[1h,30] for their ring opening, this process being considered as the reverse of intramolecular radical addition to an alkene.

As neither Houk's parameters[30] for radical cyclisation nor Allinger's for radicals[29] accommodates heteroatoms, the OH group was replaced by the isoelectronic methyl group; this is common practice in MM calculations on reactivity and should lead to no important errors in the relative energies of the radicals and the transition states.[31] According to Allinger's force field the radical has two conformations of fairly similar energies, the more stable (steric energy 50.3 kcal mol$^{-1}$) being that which places the C(1)–C(2) bond very roughly orthogonal to the plane of the radical (in fact, the radical is distinctly




pyramidal), the adamantyl group being almost eclipsed with C(7) and the methyl group antiparallel to C(7). In the less stable conformation (steric energy 51.6 kcal $mol^{-1}$) the positions of the adamantyl and methyl groups are reversed. Both these conformers will open to give the observed cyclopentane derivatives, the transition state for the opening of the former having the lowest steric energy (−7.8 as against −7.2 kcal $mol^{-1}$). However, owing to the Curtin–Hammett principle,[32] if the transition state for opening of a conceivable but apparently unstable conformer* with C(7) roughly orthogonal to the radical plane were lower than those for the other two, cyclohexanes would be formed. In fact, the opening of such a conformer has a transition state 8 kcal $mol^{-1}$ higher than the minimum value, thus excluding this eventuality.

*Kinetic Simulation.*—(a) *Thermolysis of* **1a**. Mathematical simulation of the product data follows the SSAIKS procedure used previously.[12,13] Rate constant $k_1$ is experimentally determined.[11] In our study of **1c**, rate constants $k_2$ and $k_3$ were ignored, it being assumed that reaction within the cage, diffusion from the cage, and reaction of Ad$^{\bullet}$ with the solvent are so fast that ketyl and benzyl radicals enter the bulk solution at a rate determined solely by $k_1$ and the cage effect. This assumption is supported by the fact that reactions of the 1-adamantyl radical with species other than the solvent are of very minor importance, as is shown by the quasi-identity of the bibenzyl and secondary alcohol yields.[12] In the present case, it is justified by obedience to eqn. (4). Benzyl radicals are produced also, though more slowly, by reaction of the ketyl or ring-opened radicals with the solvent, with rate constants $k_4$ and $k_{10}$, respectively (Scheme 1). We again extrapolated $k_8$ (benzyl self-termination) from Fischer's data.[33]

In preliminary calculations on the [$^2H_8$]toluene data we used seven constraints, these being the yields of normal and deuteriated ring-opened ketones, unsaturated ring-opened ketones, normal and deuteriated secondary alcohol, ring-opened cross-products and bibenzyl. Optimisation of $k_4$, $k_9$, $k_{10}$, $k_{11}$, $k_{12}$, $k_{14}$ and $k_{15}$ at any temperature for various combinations of $k_5$, $k_{11} + k_{12}$ and $k_{13}$, with $k_6 + k_7 = k_8$ as usual,[12,13] indicated that large volumes of the three-dimensional space thus defined gave exactly the same fit. In order to reduce the number of possible combinations we therefore applied what Fischer calls the 'cross-termination Ansatz' (CTA), *i.e.* the rate constant for a cross-reaction is twice the square root of the product of the rate constants for the two appropriate self-reactions.[34] In the Scheme we have three such cross-reactions, which give rise to eqns. (5)–(7).

$$k_6 + k_7 = 2(k_5k_8)^{\frac{1}{2}} \quad (5)$$

$$k_{11} + k_{12} = 2(k_5k_{13})^{\frac{1}{2}} \quad (6)$$

$$k_{14} + k_{15} = 2(k_8k_{13})^{\frac{1}{2}} \quad (7)$$

With the arbitrary assumption that $k_{13} = k_8$,† it follows that $k_5 = k_8/4$, $k_{11} + k_{12} = k_8$ and $k_{14} + k_{15} = 2k_8$. Rate constants $k_4$, $k_9$, $k_{10}$, $k_{11}$ and $k_{14}$ were then optimised for [$^2H_8$]-toluene.‡ The contributions of $k_{12}$ and $k_{15}$ were found to be small and virtually temperature-independent, representing *ca.* 1.6 and 0.7% of $k_{11} + k_{12}$ and $k_{14} + k_{15}$, respectively. Using these values, rate constants $k_4$, $k_9$ and $k_{10}$ were then determined for [$^1H_8$]toluene with five constraints (**3**, **5**–**7** and bibenzyl). Details are given in Table 5.

The isotope effects on each rate constant show no well defined temperature dependence, average values in the range 220–265 °C being 5.2 ± 0.9, 1.6 ± 0.2 and 3.6 ± 0.5 for $k_4$, $k_9$ and $k_{10}$, respectively, The small kinetic isotope effect upon ring opening is surprising; it is hard to affirm that this value is real and is not an artefact resulting from the various approximations. Nevertheless, other scenarios gave a similar result and attempts to impose a unique $k_9$ value for both solvents greatly reduced the quality of the simulations. Calculated values of the disproportionation/combination ratio for the reaction of benzyl and ketyl radicals are slightly higher than usual,[13] averaging 3.0 ± 1.0 and 3.8 ± 0.8 for normal and deuteriated solvent, respectively. The Arrhenius plots for $k_4$ and $k_{10}$ are roughly parallel; in contrast, $k_9/k_4$ nearly doubles with every 20–25 °C increase in temperature.

Arrhenius parameters for the hydrogen transfer reactions are as follows [rate constant, log ($A$/$dm^3$ $mol^{-1}$ $s^{-1}$), $E_a$ in kcal $mol^{-1}$]. In [$^2H_8$]toluene: $k_4$, 10.3 ± 0.1, 20.3 ± 0.3; $k_{10}$, 8.6 ± 0.5, 17.6 ± 1.4; in [$^1H_8$]toluene: $k_4$, 9.5 ± 0.8, 16.8 ± 2.1; $k_{10}$, 10.1 ± 0.4, 19.9 ± 0.8. The $k_4$ data for AdNorĊOH in [$^1H_8$]toluene are significantly different from those which can be calculated from the rate constants for other ketyl radicals of the same type:[13] log $A$ = 7.6–8.3 and $E_a$ = 12.6–13.7 kcal $mol^{-1}$ at generally lower temperatures (145–220 °C). Since, however, the changes are compensatory the reactivity of AdNorĊOH is compatible with that of the other ketyl radicals in the range 200–300 °C.

Activation parameters for $k_9$ are as follows (solvent, log $A$, $E_a$): [$^2H_8$]toluene, 16.0 ± 0.2, 31.8 ± 0.4; [$^1H_8$]toluene, 16.2 ± 1.2, 31.9 ± 2.6. These values can be compared with those for the ring opening of cycloalkylmethyl radicals found by kinetic EPR spectroscopy:[6,9a] pre-exponential factors for cyclopropylmethyl, cyclobutylmethyl and 1-cyclobutyl-1-methylethyl radicals are 12.5, 13.1 and 13.6, respectively, all substantially lower than for $k_9$, even after correction (−0.3) of this latter for the fact that the norbornyl group contains two equivalent C–C bonds which may cleave. Even if we consider that the only truly comparable value is that for the 1-cyclobutyl-1-methylethyl radical, where ring opening converts a tertiary to a primary radical, our log $A$

* When minimisation of the radical was started in this conformation it invariably flipped to the most stable.

† In this type of simulation it is impossible to know simultaneously the concentration and the rate constant of a radical unless the radical has been investigated independently. Consequently, one reaction of each new radical must be assigned an arbitrary rate constant. The other rate constants concerning this radical will be linearly or quadratically related to the arbitrary value.

‡ Values of [$^1$H]**3** and [$^1$H]**5**, considered to be less reliable than the overall yields of **3** and **5**, were only half-weighted in the optimisation; no rate constant changed by more than 10% when either or both were ignored altogether.

**Table 5** Kinetic simulation of product data for thermolysis of **1a** in toluene. [Arbitrary: $k_6 + k_7 = k_8 = k_{13}$. CTA: $k_{11} + k_{12} = k_8$; $k_5 = k_8/2$; $k_{14} + k_{15} = 2k_8$. Optimised: $k_{12} = 0.016\,(k_{11} + k_{12})$; $k_{15} = 0.007\,(k_{14} + k_{15})$].

| Temp./ °C | $[\mathbf{1a}]_{corr}/10^{-2}$ mol dm$^{-3}$ | $[tol]_{corr}$/ mol dm$^{-3}$ | $k_1/s^{-1}$ | $k_8/10^{11}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_4[tol]/10^3$ s$^{-1}$ | $k_9/s^{-1}$ | $k_{10}[tol]/10^2$ s$^{-1}$ | rms[a] % | disp./ comb.[b] |
|---|---|---|---|---|---|---|---|---|---|
| In [$^2H_8$]toluene | | | | | | | | | |
| 220 | 0.468 | 7.05 | $0.199 \times 10^{-3}$ | 0.192 | 0.140 | $0.807 \times 10^2$ | 0.477 | 0.2 | 4.7 |
| 232 | 0.456 | 6.87 | $0.672 \times 10^{-3}$ | 0.207 | 0.215 | $0.168 \times 10^3$ | 0.697 | 0.1 | 4.5 |
| 245 | 0.441 | 6.66 | $0.228 \times 10^{-2}$ | 0.222 | 0.357 | $0.371 \times 10^3$ | 0.990 | 0.1 | 3.6 |
| 255 | 0.432 | 6.50 | $0.577 \times 10^{-2}$ | 0.235 | 0.511 | $0.697 \times 10^3$ | 1.29 | 0.2 | 3.3 |
| 265 | 0.421 | 6.33 | $0.137 \times 10^{-1}$ | 0.248 | 0.697 | $0.119 \times 10^4$ | 2.04 | 0.5 | 2.9 |
| In [$^1H_8$]toluene | | | | | | | | | |
| 220 | 0.468 | 7.05 | $0.199 \times 10^{-3}$ | 0.192 | 0.921 | $0.144 \times 10^3$ | 1.50 | 0.5 | 3.2 |
| 232 | 0.456 | 6.87 | $0.672 \times 10^{-3}$ | 0.207 | 1.01 | $0.217 \times 10^3$ | 2.21 | 0.4 | 4.5 |
| 245 | 0.441 | 6.66 | $0.228 \times 10^{-2}$ | 0.222 | 1.76 | $0.593 \times 10^3$ | 3.81 | 0.2 | 3.1 |
| 255 | 0.432 | 6.50 | $0.577 \times 10^{-2}$ | 0.235 | 2.70 | $0.126 \times 10^4$ | 5.55 | 0.5 | 2.3 |
| 265 | 0.421 | 6.33 | $0.137 \times 10^{-1}$ | 0.248 | 2.99 | $0.183 \times 10^4$ | 6.91 | 0.3 | 2.0 |

[a] Root mean square value for the differences between calculated and experimental yields. [b] Disproportionation/combination ratio for reaction of benzyl and ketyl radicals.

**Table 6** Kinetic simulation of product data for thermolysis of **1b** in toluene [Arbitrary: $k_6 + k_7 = k_8 = k_{13}$. CTA: $k_{11} + k_{12} = k_8$; $k_5 = k_8/2$; $k_{14} + k_{15} = 2k_8$; $k_{18} = 2(k_8k_{19})^{\frac{1}{2}}$; $k_{20} = 2(k_{13}k_{19})^{\frac{1}{2}} = k_{18}$].

| Temp./ °C | $[\mathbf{1a}]_{corr}/10^{-2}$ mol dm$^{-3}$ | $[tol]_{corr}$/ mol dm$^{-3}$ | $k_1/s^{-1}$ | $k_4[tol]/10^3$ s$^{-1}$ | $k_8/10^{11}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_9/s^{-1}$ | $k_{10}[tol]/10^2$ s$^{-1}$ | $k_{17}[tol]/10^5$ s$^{-1}$ | $k_{18}/10^{11}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_{19}/10^{11}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | rms[a] % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 205 | 0.483 | 7.27 | $0.224 \times 10^{-3}$ | 0.495 | 0.175 | $0.45 \times 10^2$ | 0.80 | 0.13 | 0.318 | 0.145 | 1.3 |
| 230 | 0.458 | 6.90 | $0.252 \times 10^{-2}$ | 1.13 | 0.204 | $0.24 \times 10^3$ | 2.2 | 0.26 | 0.366 | 0.164 | 2.1 |
| 255 | 0.432 | 6.50 | $0.223 \times 10^{-1}$ | 2.37 | 0.235 | $0.11 \times 10^4$ | 5.2 | 0.49 | 0.415 | 0.183 | 1.8 |

[a] Root mean square value for the differences between calculated and experimental yields.

value remains about 2 units too high. The combined rate constant $k_6 + k_7$ for reaction of ketyl and benzyl radicals.* would therefore have to be *ca.* $10^{-2}$ $k_8$ for our log $A$ to fall in line with the EPR measurements. The activation energy, on the other hand, should be independent of this scale factor and is to be compared with that for cyclopentylmethyl opening (23.3 kcal mol$^{-1}$) estimated from the computed $\Delta H^\circ$ and the known activation energy for hex-5-enyl cyclisation. Again, it is too great. This may be in part due to stabilisation of the ketyl radical by the OH and adamantyl groups, though strain relief associated with opening of the norbornyl system would be expected to favour this reaction.

In terms of the Eyring equation, the differences in log $A$ and $E_a$ for $k_4$ and $k_9$ correspond to greater activation enthalpies and higher entropies (in absolute magnitude, *i.e.* less negative or more positive) for ring opening as compared to hydrogen transfer from the solvent to the ketyl radical. The corresponding differences between the two hydrogen transfer reactions are smaller and apparently random.

(b) *Thermolysis of* **1b**. Kinetic simulation of the product composition for thermolysis of **1b** requires a rate constant for the self-termination of *tert*-butyl radicals, $k_{19}$, calculated from Fischer's work,[35] and for the cross-reaction of *tert*-butyl and benzyl radicals, $k_{18}$, estimated by the cross-termination Ansatz (Scheme 2). The rate constant for the cross-reaction of the ring-opened radicals and *tert*-butyl, $k_{20}$, can be estimated in the same way. That for hydrogen abstraction from toluene by *tert*-butyl, $k_{17}$, was calculated from our work[13] rather than from Fischer's;[25] values for $k_4$, $k_9$ and $k_{10}$ were calculated from the Arrhenius equations. In this way the product composition (**3**, **5**–**7** and bibenzyl) was reproduced with a root mean square deviation of 1–2% (Table 6), calculated yields of the secondary alcohol and bibenzyl being 2–4% less than those found. Inclusion of $k_{16}$ [$=2(k_5k_{19})^{\frac{1}{2}}$], for reaction of *tert*-butyl and ketyl radicals outside the cage, had no significant effect upon the fit. Given the uncertainties in the various extrapolations and perhaps excessive reliance upon the CTA, which is normally applicable to unhindered radicals reacting near the diffusion-controlled limit, this agreement is reasonably good.

* Constants $k_4$ and $k_9$ are linearly dependent on the 'arbitrary' constant sum, $k_6 + k_7$. Constant $k_{13}$, on the other hand, leaves $k_4$ and $k_9$ untouched but multiplies $k_{10}$ in proportion to the square root, *i.e.* if $k_{13} = fk_8$, then $k_{10}$ increases by a factor of $f^{\frac{1}{2}}$. Consequently, the relative values of $k_4$ and $k_9$ are not affected by the choice of $k_6 + k_7$ and $k_{13}$, while those of $k_4$ and $k_{10}$, for example, are.

## Conclusion

Thermolysis of congested tri(*tert*-alkyl)methanols, where one of the tertiary alkyl groups is 1-norbornyl, gives rise to (*tert*-alkyl)(1-norbornyl)ketyl radicals. At sufficiently high temperatures the norbornyl group ring-opens to give a disubstituted cyclopentane system, as 'predicted' *a posteriori* by MM calculations. Hydrogen transfer from or to the ring-opened radical gives rise to products isomeric with the regular ketone and the secondary alcohol, respectively, derived from the initial ketyl radical. Most important are a *cis*/*trans* pair of ring-opened ketones. In addition, fast 1,4- and 1,5-hydrogen migrations within the ring-opened radical, followed by reaction with benzyl radical, lead to several ketonic cross-products, isomeric with the normal cross-product formed by reaction of the ketyl radical with benzyl. Relative rates of hydrogen transfer to ketyl radical and ketyl ring opening have been estimated by kinetic simulation of the product composition found when **1a** is thermolysed in [$^2H_8$] and [$^1H_8$]toluene. The Arrhenius parameters, both the pre-exponential factor and the activation energy, for ring opening are greater than expected by comparison with literature data. The kinetic isotope effect for hydrogen transfer from the solvent to the ketyl radical is in the usual range,[13] and that

for the ring-opened radical slightly smaller. Unexpectedly, there appears to be a small kinetic isotope effect upon ring opening; though there is no literature on this topic, this result seems anomalous and may be an artefact of the simulation model. With this sytem we have unfortunately reached a point where the number of unknown rate constants exceeds the number of independent product data, unless the rate constants for radical–radical reactions are estimated by extrapolation of Arrhenius plots over 100 °C or more and/or application of the cross-termination Ansatz; neither procedure can be considered wholly satisfactory, but at present high temperature kinetic data on the radical reactions considered here are not available.

## Experimental

*Equipment.*—$^1$H and $^{13}$C NMR spectra were recorded on a Bruker AC 200 instrument; chemical shifts (in $CDCl_3$) are given in ppm with respect to tetramethylsilane. Preliminary MS studies were carried out at the University of Freiburg on a Finnigan MAT 44S; more extensive work, including the labelling studies, was performed on a Finnigan MAT ITD 800B (ITD = ion trap detector) with electron impact (EI) or chemical ionisation (isobutane) (CI). Details of the ITD results (bar graphs) are given in the Supplementary Material. The capillary gas chromatography retention times (CP-Sil 5) are used only to identify certain components and to give an indication of their relative positions in the chromatogram; total ion current chromatograms of **6a–g** are given in the Supplementary Material. IR spectra (in $CCl_4$) were recorded on a Perkin Elmer 780. Melting points are uncorrected.

*Thermolysis.*—General procedures for alcohol thermolysis and analysis of the products have been described elsewhere.[11–13] In several, but not all cases, internal standards were used in order to determine the absolute yields of certain of the products; these data are given in parentheses in the Tables. For kinetic simulation relative molar yields, based on the assumption that the ketones, secondary alcohol and the cross-products represent 100%, were used. Generally, the difference between the absolute and relative yields of bibenzyl, ketone and secondary alcohol is not more than 2–3%, while the yield of adamantane is virtually quantitative.

*ITD Spectra of Thermolysis Products of* **1a**.—All spectra show peaks corresponding to the fragmentation of $Ad^+$ (*m/z* 107, 93, 91, 79, 67).

[$^1H_8$]*Toluene*. The CI–ITD spectra of the ring-opened ketones, **5a** and **b** (retention times 397 and 402 s), are as follows; **5a**: *m/z* 135 (86%), 136 (13), 259 (6), 260 (13), 261 (100) and 262 (17); **5b**: *m/z* 135 (90%), 136 (12), 259 (9), 260 (6), 261 (100) and 262 (16). The EI spectra show a weak (3–6%) peak at *m/z* 260, the base peak being at *m/z* 135.

The ring-opened ketones are followed by two small components, **7a** and **b** (retention times 409 and 427 s), the former of which is particularly weak and is poorly separated from **5b**. The CI spectra have parent peaks at *m/z* 259 consistent with M + 1 for a ketone of molecular weight 258. This is confirmed by the parent peak at *m/z* 258 in the EI spectra. The component at 427 s shows, under EI conditions, a fragment at *m/z* 230 (7%) corresponding to M-28. These indications are consistent with ketones analogous to the ring-opened ketones but containing a C–C double bond. The large GLC separation of the two components and their different yields suggests that they are positional rather than geometrical isomers, with the ethyl group β to the double bond in **7b** but not in **7a**. Plausible structures are shown above.

Under CI conditions the normal ketone, **2** (443 s), has *m/z* 135 (70%), 136 (11), 257 (22), 258 (13), 259 (100, M + 1) and 260 (13) whereas, under EI conditions, the base peak is at *m/z* 135 and M is only 6%. The secondary alcohol, **3** (481 s) has, under CI, *m/z* 135 (100%), 242 (18), 243 (16) and 259 (11). Under EI the molecular ion cannot be detected, the strongest large fragment being at *m/z* 242 (M − 18, 16%).

The cross-products, **6a–g**, appear as a multiplet of at least seven components with retention times of 959, 979, 986, 1002, 1013, 1023 and 1033 s, respectively, followed by the regular cross-product, **4**, at 1253 s. Compounds **6a–g** appear to be isomers formed by reaction of a ring-opened radical with the benzyl radical. Under CI, **6a** has *m/z* 135 (47%), 333 (10), 334 (7), 349 (6), 350 (8), 351 (100) and 352 (22). **6b** and **6c** have very similar CI spectra; **6b**: *m/z* 135 (100%), 136 (11), 197 (16, M − 135 − 18), 215 (20, M − 135), 259 (10, M − 91), 333 (11, M − 17), 349 (5, M − 1), 350 (7, M), 351 (36, M + 1) and 352 (10, M + 2); **6c**: *m/z* 135 (100%), 136 (15), 197 (17), 215 (37), 259 (8), 333 (11), 349 (5), 350 (7), 351 (17) and 352 (5). The spectra of the other components are as follows; **6d**: *m/z* 135 (35%), 136 (5), 187 (7), 197 (4), 215 (4), 351 (100) and 352 (27); **6e**: *m/z* 135 (38%), 187 (7), 215 (9), 259 (6), 351 (100) and 352 (27); **6f**: *m/z* 135 (37%), 136 (8), 187 (12), 259 (4), 349 (4), 351 (100) and 352 (22); **6g**: *m/z* 135 (32%), 187 (8), 259 (5), 349 (8), 351 (100) and 352 (29).

[$^2H_8$]*Toluene*. The ring-opened ketones, **5a** and **b**, still have a base peak (CI–ITD) at *m/z* 261 (M + 1) but M + 2 and M + 3 are now 70–100% and 12–20%, respectively, indicating partial deuteriation. The spectra of the peaks at 409 and 427 s are not significantly different from those in [$^1H_8$]toluene, as is expected if they are olefinic ketones, **7a** and **b**, formed by hydrogen abstraction from the ring-opened radical. The spectrum of **2** is also unchanged. The secondary alcohol, **3**, is extensively deuteriated, as shown by the importance of the M − 1 peak at *m/z* 260 (12%). The CI spectra of the ring-opened cross-products formed in [$^2H_8$]toluene are generally analogous to those of the normal compounds except that the most significant peaks (except *m/z* 135 and 259) are 8 daltons higher.

*Deuterium Determinations.—Adamantane*. By ITD with electron ionisation, as previously described.[12] Samples at 220, 245 and 265 °C were found to contain 29, 27 and 26 ± 2% normal adamantane, the rest being 1-deuteriated.

*Ring-opened ketones,* **5a** *and* **b**. The deuterium content was calculated on the assumption that the distribution of intensities at *m/z* corresponding to M, M + 1 and M + 2 was reproduced one dalton higher for the deuterium-labelled ketones. Values for several [$^1H_8$]toluene samples were averaged to establish the intensity ratios; deuterium determinations are based on 2–4 [$^2H_8$]toluene samples. There being no systematic difference between the two isomers, values have been averaged. Results are listed in Table 1.

*Secondary alcohol,* **3**. Mixtures of normal and deuterium-labelled alcohols were used to calibrate the CI–ITD intensities at *m/z* 259 and 260. Values for AdNorCHOH as a percentage of total **3** in the 5–15% range are to within ±3%. Results are given in Table 1.

1-*Adamantyl Cyclopentyl Ketone.*—Synthesised by copper(I) chloride catalysed condensation[36] of 1-adamantylcarbonyl chloride with cyclopentyl magnesium bromide in diethyl ether at −10 °C: m.p. (from hexane) 57 °C (Found: C, 82.55; H, 10.5. $C_{14}H_{24}O$ requires C, 82.70; H, 10.41%); $\nu_{max}$/cm$^{-1}$ 1698; $\delta_C$ 26.4, 27.9, 31.3, 36.6, 37.9, 44.1, 46.5 and 219.2; CI–ITD: *m/z* 135 (100%), 136 (12), 231 (5) and 233 (17).

1-*Adamantyl* 1-*Benzylcyclopentyl Ketone.*—Synthesised by reaction of the above ketone with sodium amide and benzyl bromide in dimethoxyethane under reflux: m.p. (from hexane) 73–4 °C (Found: C, 85.4; H, 9.4. $C_{23}H_{30}O$ requires C, 85.66; H,

9.38%); $\nu_{max}/cm^{-1}$ 1683; $\delta_C$ 23.9, 28.2, 35.2, 36.6, 39.1, 43.0, 48.4, 62.1, 126.1, 127.9, 130.0 and 217.0; CI–ITD: *m/z* 135 (100%), 136 (10), 158 (35), 187 (18), 321 (7) and 323 (2).

1-(1-*Adamantyl*)-1-(1-*norbornyl*)-2-*phenylethanol*, **4**.—By the Barbier reaction of ketone **2** and benzyl bromide with lithium in diethyl ether at −20 °C. Isolated in 82% yield after chromatography on alumina; m.p. 103–4 °C (from hexane) (Found: C, 85.5; H, 9.9. $C_{25}H_{34}O$ requires C, 85.66; H, 9.78%); $\delta_H$ 1.1–2.1 (br m, 27 H), 2.97 (q, 2 H) and 7.1–7.4 (m, 5 H); $\delta_C$ 31.3, 31.4, 32.0, 32.7, 34.0, 37.2, 37.9, 38.1, 42.6, 43.9, 59.9, 78.6, 125.8, 127.8, 131.7 and 139.4; CI–ITD: *m/z* 135 (100%), 136 (10) and 259 (11).

*Semi-preparative Thermolysis of* **1b**.—Aliquots (1 $dm^3$) of a solution of **1b** (2.4 g, 7.6 mmol) in toluene (25 $dm^3$) were degassed and sealed under vacuum in medium thick-walled pyrex tubes (15 cm, 0.5 cm i.d., total volume *ca.* 3 $dm^3$). They were plunged one by one into an oil bath at 275 °C and were withdrawn after 100 s. (**DANGER**: Attempts to do this experiment on a larger scale or at higher temperatures occasionally resulted in explosions.) The tubes were cooled before opening, the aliquots combined and the solvent evaporated at reduced pressure. Chromatography on standard alumina (Merck, activity II–III) in light petroleum/diethyl ether mixtures gave, in order of elution: bibenzyl (0.323 g, 23%); ring-opened ketones, **5a** and **b** {0.075 g, 4%; $\nu_{max}/cm^{-1}$ 1696; $\delta_H$ 0.88 (t, $CH_3$ of ethyl), 1.34 (m, $CH_2$ of ethyl), 1.6–2.1 (br m, CH and $CH_2$ of Ad and cyclopentyl), 3.31 (m, CH of 1-cyclopentyl adjacent to carbonyl); $\delta_C$ 12.9 and 13.0 ($CH_3$ of ethyl), 28.0 (CH of Ad), 28.2 and 28.6 ($CH_2$ of ethyl), 30.2 and 31.1 [C(4) of cyclopentyl], 32.0 and 33.3 [C(5) of cyclopentyl], 36.6 ($CH_2$ of Ad), 36.7 and 38.0 [C(2) of cyclopentyl], 37.9 and 38.0 ($CH_2$ of Ad), 41.9 and 43.1 [C(3) of cyclopentyl], 43.1 and 44.3 [C(1) of cyclopentyl], 46.5 ($C_q$ of Ad), 218.8 and 219.0 (carbonyl carbon)}; a mixture of normal ketone, **2** ($\nu_{max}/cm^{-1}$ 1684; $\delta_C$ 28.2, 30.1, 33.6, 35.7, 36.7, 38.8, 42.1, 48.0, 60.3, 217.7) and **6a–g** (0.655 g); regular cross-product, **4** (0.238 g, 9%); secondary alcohol, **3** [0.740 g, 37%, m.p. 118–9 °C (from hexane); $\delta_H$ 1.1–1.8 (br m, 23 H), 1.96 (br s, 3 H), 2.07 (br s, 1 H), 3.22 (s, 1 H); $\delta_C$ 28.6, 29.6, 31.2, 31.5, 34.1, 34.6, 37.2, 39.0, 39.5, 44.5, 53.7 and 83.7]. Other materials (mixtures) amounted to 0.246 g. Column chromatography of the **2**/**6a–g** mixture on other grades of alumina reduced **6a–g** to a five-component mixture still asssociated with ketone **2**, from which it was separated with difficulty by thin layer chromatography on silica gel in 9:1 light petroleum/diethyl ether. The resulting fraction, an oil (0.041 g) had $\nu_{max}/cm^{-1}$ 1694. 1-Benzylation of **5a** and **b** ($NaNH_2$ and benzyl bromide in dimethoxyethane) gave a product with two GLC peaks corresponding approximately to **6b** and **6c**, but with quite different ITD spectra; 978 s: CI *m/z* 135 (100%), 136 (13), 186 (11), 197 (6), 215 (66), 216 (7) and 349 (7); EI *m/z* 135 (100%), 136 (20), 157 (15), 186 (19) and 187 (5); 985 s: CI *m/z* 135 (100%), 136 (13), 186 (16), 197 (4), 215 (57), 216 (11) and 349 (5); EI *m/z* 135 (100%), 136 (19), 157 (17) and 186 (22).

*Molecular Mechanics Calculations*.—Steric energies of the (1-(1-adamantyl)-1-(1-norbornyl)ethyl radical in both conformations are obtained with Allinger's MM2(85) force field.[29] The three possible transition states for ring opening are based on the same force field with the addition of Spellmeyer and Houk's parameter set.[30]

*Kinetic Simulation*.—The high reactivity of the 1-adamantyl radical with toluene and the fact that bridgehead species will not act as hydrogen atom donors make the scheme relatively simple. However, it is necessary to introduce terms for ring opening, reaction of the ring-opened radical with ketyl and benzyl radicals, with itself and with solvent. Hydrogen atom shifts which give rise to the ring-opened cross-product multiplet were considered to be fast as compared to other processes and, for this reason, do not enter into the rate equations for simulation. Unknowns were optimised by incorporating the SSAIKS procedure[12–13] into a Simplex program.[37] This converged much more rapidly than the single-factor procedure previously used.

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