radical **19** (0.233 g) in THF (90 mL), and the resulting mixture was left (4 days) under argon and in the dark. Evaporation of the solvent gave a solid, which by TLC (silica gel, pentane) afforded starting radical **19** (0.104 g, 45%) and the corresponding αH compound **23** (0.092 g, 39%).

(b) This reaction was also attempted as in the reduction of methoxy radical **14**. Starting material was recovered (93%).

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Registry No. **1**, 4070-01-3; **2**, 30482-37-2; **3**, 29972-98-3; **4**, 65638-91-7; **5**, 82902-20-3; **6**, 82891-69-8; **7**, 82902-21-4; **8**, 544-25-2; **9**, 82916-74-3; **10**, 1499-10-1; **11**, 34568-78-0; **13**, 67173-39-1; **14**, 71947-01-8; **15**, 71947-02-9; **16**, 82891-71-2; **17**, 67173-40-4; **19**, 64269-29-0; **20**, 82891-72-3; **21**, 82891-73-4; **23**, 82891-74-5; **24**, 79839-44-4; **25**, 82891-75-6.

Thermolysis of Highly Congested *tert*-Butyldialkylcarbinols with Bridgehead Substituents: Molecular Mechanics Treatment of Radical-Forming Processes

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The thermolysis rate constants of eight tertiary alcohols, $R^1R^2R^3COH$, bearing a *tert*-butyl group (R^3) with various combinations of *tert*-butyl, *tert*-amyl, 1-adamantyl, 1-bicyclo[2.2.2]octyl, and 1-norbornyl substituents at the tertiary carbon have been measured in dodecane. The effects of these groups on the rate of *tert*-butyl cleavage are roughly additive and in quantitative agreement with their known steric requirements, except for *tert*-amyl which appears to be smaller than E_s' would suggest. Activation energies can be interpreted in terms of strain energy changes, calculated by molecular mechanics; several different models are used to describe the reaction and, where possible, three different force fields. The most satisfactory description of the reaction is based upon Allinger's MM2 force field, with the assumption that the radical intermediate, $R^1R^2C{\cdot}OH$, can be represented by the corresponding dialkylcarbinol. Product analysis shows that the *tert*-butyl radical is formed in preference to any other, except *tert*-amyl, but small amounts of products arising from C–Ad fission are detected in certain cases. This result, in accordance with previous molecular mechanics calculations on thermolysis rates, indicates that the radical strain energies in bridgehead systems must be slightly greater than those of the corresponding alkanes but substantially less than those of the related carbocations.

Before ESR spectroscopy was able to provide detailed structural information about alkyl radicals,[1] attempts were made to investigate the geometric requirements of the radical center by measuring the rate of formation of bridgehead radicals by the thermolysis of peresters[2,3] and azoalkanes[3] or by determining the selectivity of radicals in certain reactions, such as decarbonylation,[4] or by other means.[5,6] While there was fairly good agreement on the order of radical stability, i.e., 1-adamantyl > 1-bicyclo[2.2.2]octyl > 1-norbornyl, there was some doubt about the position of the *tert*-butyl radical, B·, on this scale. According to different criteria, it was reckoned to be less stable, as stable, or much more stable than 1-Ad·.[7,8]

In recent years there have been important developments in this area of free-radical chemistry. The idea that radical formation rates express their stability has given way to the understanding that rates refer only to transition states.[9] There has also been considerable reinvestigation of the azoalkane and perester thermolysis reactions upon which stabilities were based. Perester decomposition for a long time known has to be subject to polar effects[10] and is believed to have an early transition state, rather remote from the intermediate radical.[11] Recent studies have, moreover, shown that the mechanism of decomposition is not necessarily the same for all structures, the extent of R–C and O–O bond breaking varying considerably.[12]

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Table I. Rate Constants and Thermodynamic Parameters for Thermolysis of Tertiary Alcohols in Dodecane

no.	R^1	R^2	R^3	10^5k, s^{-1} (T_1, °C)	10^5k, s^{-1} (T_2, °C)	10^5k, s^{-1} (T_3, °C)	10^5k, s^{-1} (T_4, °C)	$\Delta H^\ddagger$, kcal·mol^{-1}	$\Delta S^\ddagger$, cal·mol^{-1}·K^{-1}	$\Delta G^\ddagger$ (200 °C) kcal·mol^{-1}
1[a]	B	B	B	4.46 (165.0)	25.0 (180.0)	123 (195.0)	467 (209.5)	43.0 ± 0.5	16.7 ± 1.0	35.0
2[a,b]	A	B	B	11.1 (150.0)	53.8 (165.0)	255 (180.5)	1170 (195.5)	40.2 ± 0.7	13.9 ± 1.6	33.7
3[a]	Ad	B	B	6.60 (150.0)	35.2 (165.0)	171 (180.0)	709 (195.0)	40.2 ± 0.2	15.3 ± 0.5	33.0
4[a]	Oc	B	B	13.0 (165.0)	66.0 (180.2)	263 (194.2)	1260 (210.5)	41.5 ± 0.3	16.3 ± 0.6	33.8
5[a]	N	B	B	3.37 (200.0)	16.7 (215.5)	71.7 (230.0)	281 (245.0)	47.1 ± 0.2	18.3 ± 0.4	38.5
6	Ad	Ad	B	10.3 (135.0)	56.9 (150.0)	266 (165.0)	1190 (180.5)	37.5 ± 0.2	14.4 ± 0.4	30.7
7	Ad	Oc	B	2.95 (135.0)	16.7 (150.0)	84.6 (165.0)	422 (180.5)	39.3 ± 0.2	16.3 ± 0.4	31.6
8	Ad	N	B	15.0 (201.0)	63.3 (215.5)	254 (230.0)	899 (244.5)	45.3 ± 0.2	18.5 ± 0.4	36.5

[a] $\Delta S^\ddagger$ and $\Delta G^\ddagger$ are statistically corrected. [b] For loss of *tert*-amyl radical: $\Delta H^\ddagger = 39.0 \pm 0.7$; $\Delta S^\ddagger = 14.1 \pm 1.6$; $\Delta G^\ddagger = 32.4$.

Azoalkane decomposition, which was thought to be free of the first shortcomings, is now held to proceed by both concerted and nonconcerted mechanisms.[8,13,14]

Studies on hydrocarbon thermolysis[15-18] have now shifted the emphasis from the stability of the radicals formed to that of the precursor, expressed by its "strain enthalpy". We felt that it would be interesting to combine this new approach with the more traditional approach to the study of bridgehead radical-forming thermolyses. The opportunity was presented by recent advances in the Barbier-type one-pot organolithium condensation by which 1-adamantyl can be introduced into congested alcohols.[19,20] Earlier work had shown that tri-*tert*-butylcarbinol[21] is thermolyzed in the same way as tri-*tert*-butylmethane[22] and that ring-substituent effects on *o*-tolyldi-*tert*-butylcarbinol thermolysis rates were very small, with a reaction constant of only about 0.1 (240 °C).[23] This would therefore appear to be a reaction where polar effects are negligible and where the transition state involves the homolysis of a single C–C bond.

We have now studied several tertiary carbinols containing various combinations of *tert*-butyl (B) with 1-adamantyl (Ad), 1-bicyclo[2.2.2]octyl (Oc), 1-norbornyl (N), and *tert*-amyl (A) groups. The results are interpreted in terms of strain-energy changes, calculated by molecular mechanics on the basis of various hydrocarbon force fields, frequently used to represent alcohols, and Allinger's MM2 force field, which includes alcohols explicitly.[24]

Results and Discussion

Correlation of Alcohol Thermolysis Rates: Formation of the *tert*-Butyl Radical. Alcohol decomposition rates in dodecane (Table I) were measured by GLC, a saturated linear hydrocarbon being used as an internal reference. This method, however, broke down for the most reactive and least volatile compound, **6**, which was largely decomposed on the column under the mildest GLC conditions that could be empoloyed. In this case, the rates are based on measurement of the IR carbonyl absorption of the product ketone.

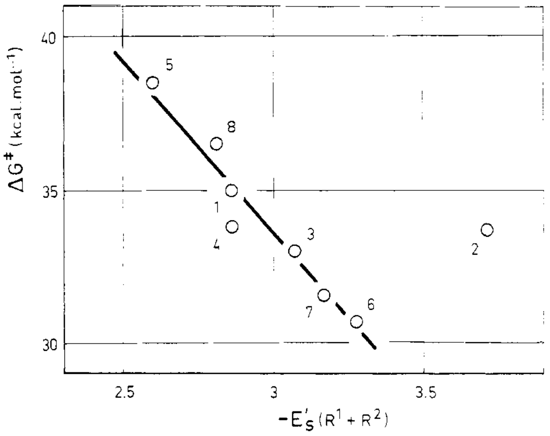

Figure 1. Correlation of $\Delta G^\ddagger$ for alcohol thermolysis against revised Taft–Ingold steric parameters, E_s'.

Since the *tert*-amyl and the 1-adamantyl derivatives do not react exclusively with loss of B·, the rates have been corrected accordingly. Alcohols **2** and **6** were studied over 50 °C ranges; for the other alcohols, it was assumed that the Ad·/B· (and Oc·/B·) ratios do not vary with temperature. The correction is so small that any variation can be safely disregarded. In the case of alcohol **2**, it is possible to calculate $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the formation of the other radical, *tert*-amyl, but the Ad·/B· ratio is so low, even for **6**, that the rate constants for the formation of Ad· lack the necessary precision. All compounds show large positive $\Delta S^\ddagger$ values (13.9–18.5 cal·mol^{-1}·K^{-1}) consistent with the radical mechanism of the reaction and with related data on hydrocarbons.[16,18,22]

Though all the bridgehead structures investigated are formally analogues of *tert*-butyl, there are, as expected, important variations in reactivity, the most reactive compound being diadamant-1-yl-*tert*-butylcarbinol (**6**), which is some 50 times as reactive as tri-*tert*-butylcarbinol (**1**) and about 2000 times as reactive as the norbornyl derivative **5**.

Inspection of the $\Delta G^\ddagger$ values shows that the substituent effects are roughly additive; i.e., the replacement of a given group by another has approximately the same effect, whatever the unchanged groups. Thus, 1-adamantyl, 1-bicyclooctyl, and 1-norbornyl are associated with increments of about 2.1, 1.3, and −3.5 kcal·mol^{-1}, respectively, relative to *tert*-butyl. This suggests that the rate data

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could be expressed in terms of a conventional linear free energy relationship by means of the modified Taft–Ingold steric parameters,[25] E_s', for example (Figure 1). This approach works quite well for seven data points (correlation coefficient = 0.970; $\delta = -5.3$). The large deviation of the last point indicates that E_s' seriously overestimates the steric requirements of the *tert*-amyl group in these congested alcohols. The more recently proposed parameter scale,[26] ζ_f, based on front-strain effects calculated by molecular mechanics, performs rather poorly (correlation coefficient 0.897), though no one point deviates markedly.

A more interesting approach to the interpretation of steric effects on this decomposition is suggested by the work of Rüchardt,[16–18] who correlated $\Delta G^\ddagger$ for the thermolysis of hydrocarbons against their "strain enthalpies", H_{sp}, again obtained by molecular mechanics calculations.[27,28] The possibility that the radical intermediate was also strained was generally ignored.[29] In the present case, certain substituents are intrinsically strained due to their polycyclic nature. Since this contribution to the overall strain energy will be largely conserved in the reaction transition state, it is necessary to make allowance for it in the calculations.

In MM treatments of solvolysis it is common practice to base the calculation of the initial state on the alkane, RH[30–32] or RMe,[20,32,33] corresponding to the reactant, RX, and to assume that the effect of the leaving group will be constant or proportional to the strain energy within a series of compounds. The transition state is assumed to resemble the carbocationic intermediate, for which Schleyer's force field is parameterized,[30] and correlation of rate in terms of strain energy change is sought.[34] Radical-forming transition states have also been attributed carbocation character for the needs of MM calculations,[5,31,35] this approach being justified by the correlation between rates of solvolysis and of azoalkane and perester thermolysis.[14,36,37] Therefore, following previous authors, we could represent the reaction

$$R^1R^2BCOH \rightarrow R^1R^2C{\cdot}OH + B{\cdot}$$

by

$$R^1R^2BCH \rightarrow R^1R^2C^+H \qquad \text{(model I)}$$

neglecting the contribution of B·, which should be a constant.

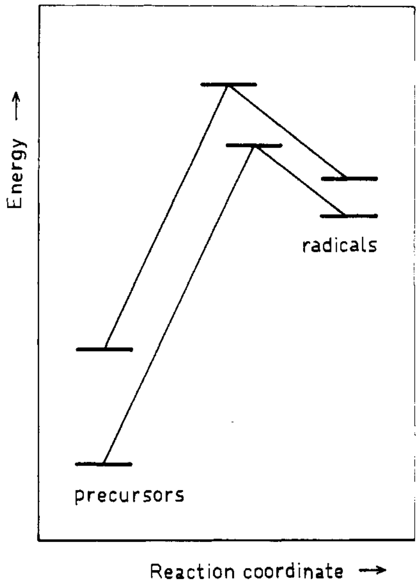

Figure 2. Schematic energy profiles for alcohol thermolysis.

In fact, for this particular set of compounds there are only minimal differences between the strain energies of the carbocations and the corresponding dialkylmethanes. Consequently, the reaction can equally well be expressed as model II,

$$R^1R^2BCH \rightarrow R^1R^2CH_2 \qquad \text{(model II)}$$

which means that we can adopt other hydrocarbon force fields for the interpretation of the data. All calculations have therefore been repeated with Allinger's 1971[38] and MM2[24,39] force fields. The former has been extended by Mislow[40] to benzenoid systems (which will be the subject of a forthcoming study) and the latter is, as regards both energy and structure, competitive with or superior to any previously reported force field.

According to calculations based on Schleyer's force field,[27] replacing a *tert*-butyl group by 1-Ad, Oc, or N increases the strain energy of the disubstituted methanes by constant increments of 6.8, 12.8, and 13.8 kcal·mol^{-1}, respectively, slightly less than the differences between isobutane and the parent hydrocarbons, adamantane, bicyclo[2.2.2]octane, and norbornane: 7.8, 13.8, and 17.9 kcal·mol^{-1}, respectively. Corresponding increments for the trialkylmethanes are 9.1, 14.5, and 8.2 kcal·mol^{-1}, which show that, though highly strained, the 1-norbornyl group is easier to incorporate into a congested system than the other substituents, including *tert*-butyl (since the overall strain energy increase is always less than its intrinsic contribution). Analogous results are obtained with Allinger's force fields, though the differences in the ways in which the force fields are defined and in the bond and group energy increments lead to significant variations in the numerical values.

We now make the usual assumption that the relative rates are proportional to the strain energy change associated with the shift from the initial state to the transition state, and attempt to correlate $\Delta G^\ddagger$ against Δ strain. At this point it is useful to consider what can be expected from this treatment.

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(34) Since strain energies are more correctly described as "strain enthalpies", it would seem more reasonable to plot $\Delta H^\ddagger$ against Δ strain, but, in practice, all authors assume, explicitly or implicitly, the existence of isokinetic or isoentropic relationships and use either the more precisely determined $\Delta G^\ddagger$ or its equivalent, log k, at a suitable temperature. The isokinetic temperature for the data in Table I is 1400 ± 400 °C.

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Table II. Strain Energy Changes Associated with Various Models for Alcohol Thermolysis

	Δ strain energy, kcal·mol^{-1}							
no.	model I[a]	model II[b]	model II[a]	model II[c]	model III[b]	model III[a]	model III[c]	model IV[b]
1	34.2	31.2	34.2	30.1	37.0	42.3	37.9	34.5
2	34.6	31.5	34.8	30.9	38.4	44.3	39.6	35.7
3	36.2	32.9	36.2	32.5	37.9	43.8	39.2	35.7
4	35.4	32.3	35.6	31.9	37.4	43.3	38.7	34.8
5	29.0	26.6	28.9	25.3	34.1	38.6	34.3	30.5
6	38.6	34.9	38.8	35.5	39.1	45.8	41.1	37.2
7	37.9	34.3	38.2	34.8	38.0	44.5	38.8	36.1
8	30.8	28.0	30.6	27.3	35.3	40.4	36.2	31.8
intercept[d]	60.5 ± 1.7	61.6 ± 2.1	59.4 ± 1.7	56.8 ± 1.2	87.6 ± 7.5	79.3 ± 4.0	77.8 ± 6.4	71.6 ± 4.2
gradient	0.76 ± 0.05	0.87 ± 0.07	0.73 ± 0.05	0.74 ± 0.04	1.44 ± 0.20	1.06 ± 0.09	1.34 ± 0.17	1.09 ± 0.12
corr coeff	0.988	0.983	0.987	0.992	0.945	0.978	0.941	0.965

[a] Schleyer. [b] Allinger MM2. [c] Allinger, 1971. [d] $\Delta G^{\ddagger}$ extrapolated to Δ strain energy = 0.

Figure 2 illustrates the energy profiles for the thermolysis of two compounds, where one is rather more strained than the other and where the difference between the strain energies of the radical intermediates arising from the two precursors is less than that between the precursors. Provided that the energy profiles of the reactions of different compounds are roughly parallel on both sides of the transition states, we can see that a certain fraction, less than the totality of Δ strain, will be relieved in the transition state. Consequently, for the strain energy calculation to be a valid description of the reaction, the gradient of $\Delta G^{\ddagger}$ vs. Δ strain should not be greater than unity. Secondly, if the plot is extrapolated to the point where Δ strain is zero, we should obtain $\Delta G^{\ddagger}$ for an unstrained precursor going to an unstrained transition state, which is related to the C–C bond dissociation energy, $D_{\text{C–C}}$, by the equation: $D_{\text{C–C}} = \Delta G^{\ddagger} + T\Delta S^{\ddagger} + \text{RT}$. Values of $D_{\text{C–C}}$ vary from about 69 to 88 kcal·mol^{-1} for hexamethylethane and ethane,[41] respectively. Only about half of this range is attributable to the strain energy difference, some 9 kcal·mol^{-1} according to MM2 force field calculations; the remainder has not been satisfactorily explained, though it has been suggested that there is special stabilization of the ground state of the less strained hydrocarbons.[16,17,42] The other view, that the radicals are stabilized by alkyl substituents, has been criticized.[36] In view of the structural similarities between our system and the cleavage of hexamethylethane, we might expect to find a $D_{\text{C–C}}$ value nearer the lower end of the range, in the neighborhood of 78 (i.e., 69 + 9) kcal·mol^{-1}.

Correlations (models I and II) of the statistically corrected activation energies (at 200 °C) against Δ strain give slightly unsatisfactory results (Table II). Although the correlation coefficients are quite good, the intercept on the $\Delta G^{\ddagger}$ axis is 56.8–61.6 kcal·mol^{-1}, depending on the force field. For thermolysis at 300 °C of hydrocarbons giving rise to analogous radicals, $R^1R^2CH\cdot$, $\Delta G^{\ddagger}$ ($\Delta H_{\text{sp}} = 0$) is 66.5 kcal·mol^{-1}. The corresponding bond dissociation energies are 70.2 (for the highest value of the $\Delta G^{\ddagger}$ intercept) and 76.2 kcal·mol^{-1} for alcohols and hydrocarbons, respectively. This suggests that the OH group stabilizes a radical by at least 6 kcal·mol^{-1}, which is greater than any previous estimate.[41]

Clearly, a hydrogen atom underestimates the steric requirements of an OH group, and this error will be most noticeable in the congested compounds, with the result that the Δ strain values are too small. The customary alternative is to replace OH by Me, since in certain cases the steric effect of an OH group is better represented by methyl than by hydrogen:[43]

$$R^1R^2BCMe \rightarrow R^1R^2CHMe \quad \text{(model III)}$$

This approach, however, generally disimproves the quality of the correlation and gives unreasonably high estimates of the $\Delta G^{\ddagger}$ intercept (77.8–87.6 kcal·mol^{-1}) and of the slope (1.06–1.44), probably because the methyl group now exaggerates the steric requirements of OH. Finally, therefore, Allinger's MM2 force field and program[24] were used to calculate the strain energies of the trialkylcarbinols and the corresponding dialkylcarbinols. Insofar as there is little difference between the strain energies of dialkylmethanes or dialkylethanes and the related carbocations and if, as we shall show later, the strain energy of a radical lies close to that of the molecule obtained by adding a hydrogen atom, this model (model IV)

$$R^1R^2BCOH \rightarrow R^1R^2CHOH \quad \text{(model IV)}$$

should give the most realistic account of the strain energy changes involved in the reaction. This proves to be the case; though the resulting correlation (Figure 3) is not the best from a statistical point of view, the parameters are now close to the expected values: slope 1.09 ± 0.12 and $\Delta G^{\ddagger}$ intercept = 71.6 ± 4.2 kcal·mol^{-1}, which is equivalent to a bond dissociation energy of 80.1 kcal·mol^{-1}.

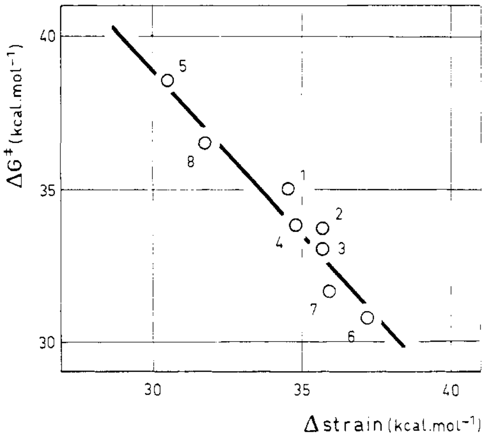

Figure 3. Correlation of $\Delta G^{\ddagger}$ for alcohol thermolysis against strain energy change (model IV; Allinger MM2 force field).

The validity of this approach to the description of alcohol thermolysis rates can be confirmed by running analogous calculations on alkanes, for which it should

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Table III. Strain Energy Changes Associated with RB_2CH Alkane Thermolysis

R	$\Delta G^{\ddagger}$	Δ strain energy,[a] kcal·mol^{-1}	Δ strain energy,[b] kcal·mol^{-1}	Δ strain energy,[c] kcal·mol^{-1}
H	65.4	7.4	9.2	6.1
Me	58.7	14.7	14.1	11.3
Et	55.5	20.3	19.5	16.9
i-Pr	51.2	24.6	23.4	21.4
B	40.7	34.2	31.2	30.1
intercept[d]		72.6 ± 1.2	75.3 ± 1.7	71.3 ± 1.3
gradient		0.90 ± 0.06	1.08 ± 0.08	0.99 ± 0.07
corr coeff		0.994	0.992	0.993

[a] Schleyer. [b] Allinger MM2. [c] Allinger, 1971. [d] $\Delta G^{\ddagger}$ extrapolated to Δ strain energy = 0.

perform even better, since present-day force fields have been optimized for such compounds. One series of alkanes studied by Rüchardt,[22,49] RB_2CH, lends itself particularly well to this treatment, since their thermolysis leads also to the formation of B·. For the sake of comparison with the alcohol data, the ΔG^{*} values were adjusted to 200 °C, and strain energies, as defined by Allinger, were used rather than H_{sp}. We then obtain a ΔG^{*} intercept of approximately 75.3 kcal·mol^{-1}, corresponding to a C–C bond dissociation energy of 84.8 kcal·mol^{-1} (average ΔS^{*} = 18.1 cal·mol^{-1}·K^{-1}). The slope of the plot, 1.08 ± 0.08 (Table III), is virtually identical with that for alcohols.

These results show that for both alcohols and alkanes the totality of the strain energy difference between reactant and radical intermediate is reflected in the variation of the activation energy for radical formation and, therefore, that the transition state is very close energetically to the radicals themselves. This implies, by the principle of microscopic reversibility, that the barrier to radical recombination is negligibly small. This conclusion is consistent with the finding that recombination of isopropyl[44] and of *tert*-butyl[45] radicals involves an activation energy close to zero. The recombination of aryl-*tert*-butyl-carbinyl radicals is, however, diastereoselective,[46] while highly substituted tertiary radicals are well-known to be persistent.[47]

Our calculations on very strained alkanes indicate that MM2 tends to give high gradients (see Table II). In the present case, the other two force fields do indeed give lower values than MM2, but both are, nevertheless, close to unity.[48] In both respects, therefore, D_{C-C} and the gradient, the hydrocarbon data are in reasonable agreement with expectation, whatever the force field used. This result would appear then to justify our two assumptions (1) that the effect of the "leaving group" (B·) is constant and (2) that the strain energy of the intermediate radical $R^1R^2C·OH$ is close to that of the alcohol R^1R^2CHOH.

The stabilization of the radical intermediate by an OH group can be estimated by comparing our data for tri-*tert*-butylcarbinol with that for tri-*tert*-butylmethane:[49] Δ strain values are 34.5 and 31.1 kcal·mol^{-1}, respectively, while the corresponding ΔG^{*} values are 35.0 and 40.7 kcal·mol^{-1}. Consequently, the OH group must stabilize the $B_2C·OH$ radical by 2.3 kcal·mol^{-1} compared to $B_2C·H$. A more general, though possibly less precise, value can be deduced from Figure 4 where the alcohol and hydrocarbon data are compared; the gap between the two data sets indicates that the intermediate is stabilized by the OH group to the extent of about 4.7 kcal·mol^{-1}.

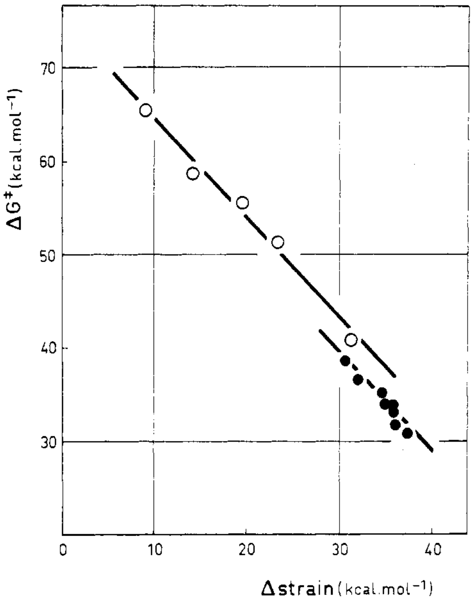


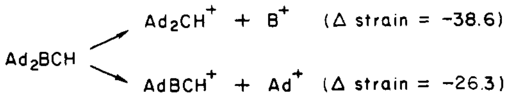
Figure 4. Comparison of alcohol and hydrocarbon thermolysis rates in terms of strain energy changes (Allinger MM2 force field).

These values bracket the reported differences in D_{C-C} for pairs of much smaller molecules: *tert*-butyl alcohol/isobutane (2.6 kcal·mol^{-1}) and *tert*-amyl alcohol/2-methylbutane (3.2 kcal·mol^{-1}), while the higher, more general value is not significantly different from that for ethanol/ethane (5.0 kcal·mol^{-1}).[41]

Formation of Radicals Other than *tert*-Butyl. Whereas the previous studies were generally concerned with the formation of a single radical from a single precursor, the present system is in all cases, except **1**, a "multiple choice question": which radical or radicals will be formed? For all but **2** where *tert*-amyl dominates, the almost exclusive answer is B·. However, careful product analysis revealed that the thermolysis of alcohols containing 1-adamantyl groups yields ketones and secondary alcohols arising from the formation of Ad·.

The result for alcohol **2** is fairly easy to understand. The strain energy of B_2CH_2 is 2.5 kcal·mol^{-1} less than that of $ABCH_2$ (Schleyer force field), which corresponds to a ΔG^{*} of 1.8 kcal·mol^{-1}, whereas the experimental value is 1.3 kcal·mol^{-1}. It only requires that the difference between the energies of the two radicals, *tert*-amyl and *tert*-butyl, be 0.5/0.73 kcal·mol^{-1} to explain completely the relative rates of their formation. This is, in fact, close to the difference between the strain energies of the parent hydrocarbons, AH and BH (1.0 kcal·mol^{-1}).

The formation of Ad· requires more careful consideration. For alcohol **6**, for example, the two decomposition paths can be represented in the hydrocarbon → carbocation approximation by



Corresponding data for the hydrocarbon → hydrocarbon approximation are

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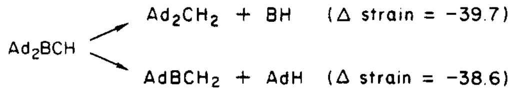
[49] Revised data for B_3CH and other RB_2CH alkanes: Hellmann, S. Ph.D. Thesis, University of Freiburg, 1982.



all data being based on Schleyer's force field.

It is clear therefore that the extent of reaction by the second path hinges on the magnitude of the steric energy of the 1-Ad radical. If it resembles the carbocation, formation of B· will be preferred by a very large factor, whereas if it is alkanelike, allowing for the statistical factor and assuming a gradient of 0.73 for the $\Delta G^{\ddagger}$ vs. Δ strain relationship (Table II, model II^a), we expect the Ad·/B· ratio to be 1:1.2 at 200 °C. The experimental value of about 1:20 indicates that the transition state for radical formation more closely resembles the latter situation. Applying the same reasoning to the other alcohols where Ad· is formed, we find that its abundance is 14-21 times less than is predicted by the second approximation given above.[50]

Since it matters little whether the other radicals, $Ad_2CH·$ or AdBCH·, are treated as carbocations or as alkanes, we can get an idea of the difference in strain energy between Ad· and B· from the Ad_2BCOH datum. Allowing for the factor of 0.73 for Schleyer's force field, we require that this be about 11.4 kcal·mol^{-1}, as compared to values of 7.8 and 19.2 kcal·mol^{-1} for the alkanes (AdH and BH) and the cations (Ad^+ and B^+), respectively. This result is consistent with molecular mechanics treatments of bridgehead perester and azoalkane thermolysis in terms of the alkane → cation model, for which slopes are typically low, 0.18–0.33, according to different studies.[5,31,35] Our datum is equivalent to a two-point plot with a slope of (11.4–7.8)/(19.2–7.8) = 0.29.

Neither this figure nor the rate ratio upon which it depends can be easily compared with earlier data on rates of formation of Ad· and B·, from different precursors, which were considered to reflect the "stabilities" of these radicals. The old stability scales only measure the relative difference between the energy of the initial state and the transition state for radical formation. There are ample grounds for thinking that the mechanisms of the reactions chosen are by no means simple and not necessarily constant and that the thermodynamic stability of the intermediate, sometimes well removed from the transition state, is only one of the factors controlling the rate. It is not surprising then that different methods gave incompatible results.

Qualitatively, the relationship between the rates of formation of bridgehead radicals and the structure of the precursor can be understood as follows. If the bond angles about a bridgehead carbon are constrained to adopt regular tetrahedral values, as in 1-bicyclo[2.2.2]octyl and 1-adamantyl, or are substantially smaller, as in 1-norbornyl, and if the natural geometry of a carbon-centered radical is flatter than tetrahedral, the more the precursor hydrocarbon moiety is strained, the greater will be the increase in strain on going to the corresponding radical. However, the requirement for planarity in radicals is less stringent than in carbocations[7] (even the *tert*-butyl radical is distinctly pyramidal),[51] which means that the force constants imposing planarity are weaker. Consequently, even if the transition state is close to the radical itself, as we have established in alcohol and hydrocarbon thermolysis, the alkane → cation strain energy change seriously overestimates the importance of strain upon the rate. Nevertheless, the picture can be seriously modified if there are large "leaving group" steric effects. There are cases where substituent effects upon thermolysis are similar to[37,54] or greater than[54] those upon solvolysis.

Conclusion

Strain energy calculations give a generally satisfactory account of the relative reativities of highly strained alcohols in thermolysis. The most plausible approach, based on Allinger's alcohol force field, gives a correlation with gradient and $\Delta G^{\ddagger}$ intercept in fair agreement with expectation. Nevertheless, other, more approximate models based on trialkylmethanes and dialkylmethanes or carbocations give results that are sometimes statistically better, though the gradients and intercepts are not meaningful.

Calculations based on product analysis at 200 °C indicate that the strain energy difference between Ad· and B· radicals must be 3–4 kcal·mol^{-1} greater than that between the hydrocarbons. Comparison with data on alkane thermolysis shows that an OH group stabilizes a congested alkyl radical by 2.3–4.7 kcal·mol^{-1}.

The present situation in regards to bridgehead radicals, where data are, at best, qualitative and rather sparse, contrasts markedly with that for acyclic radicals, which have been the subject of numerous studies. The *tert*-butyl radical has received particular attention, and its heat of formation has been ascribed values ranging from 6.8 to 12.1 kcal·mol^{-1}, the most recent results[55] converging slightly to 8.3–10.5 kcal·mol^{-1}. There are two ways by which our knowledge of bridgehead radicals can be brought up to the same level as that on acyclic alkyl radicals. One is the calculational approach, which consists of parametrizing a force field so as to reproduce thermochemical data for acyclic and monocyclic alkyl radicals and then extending this to bicyclic and tricyclic systems. This procedure is, however, hazardous in the absence of ΔH_f data for bridgehead systems and must be completed by experimental studies. Apart from the method we have described here for comparing the strain energies of Ad· and B·, there is a wide variety of mainly gas-phase techniques that have yet to be applied to the study of the thermochemistry of these species.

Experimental Section

Alcohol Synthesis. Precursor ketones were synthesized by cuprous chloride catlayzed condensation of the appropriate acid chloride with *tert*-butylmagnesium chloride in ether.[56] Alchols **1**[57] and **3**[20] were prepared by published procedures; **2**, **4**, and **5**

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[50] The corresponding figure for the bicyclooctyl radical, based on compound **7**, is 18. We should therfore expect to find about 1% of products arising from the formation of Oc· in the thermolysis of **4**, but neither bicyclooctane nor di-*tert*-butyl ketone could be detected.

[51] The shape of the *tert*-butyl radical has been the subject of considerable debate. The latest ab initio calculations[52] support this statement, though other interpretations of the ESR studies[53] are possible.

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were prepared by reaction of *tert*-butyllithium with the appropriate ketone; **6**–**8** were prepared by the one-pot Barbier-type condensation of 1-bromoadamantane with the corresponding ketone by Li metal in ether.[19,20] Products were freed of residual ketone, secondary alcohols, and hydrocarbons by column chromatography on alumina (activity II–III) in ether/petroleum ether mixtures and crystallized from pentane. Yields of new alcohols ranged from 16 (**6**) to 45% (**4**). Alcohol **2** was an oil: IR (CCl_4) 3631 cm^{-1}. Anal. Calcd for $C_{14}H_{30}O$: C, 78.43; H, 14.10. Found: C, 78.20; H, 14.21. Alcohol **4**: mp 42 °C; IR (CCl_4) 3628 cm^{-1}. Anal. Calcd for $C_{17}H_{32}O$: C, 80.95; H, 12.70. Found: C, 81.02; H, 13.01. Alcohol **5** was an oil: IR (CCl_4) 3630 cm^{-1}. Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 81.07; H, 12.55. Alcohol **6**: mp 179.5 °C; IR (CCl_4) 3624 cm^{-1}. Anal. Calcd for $C_{25}H_{40}O$: C, 84.21; H, 11.31. Found: C, 83.99; H, 11.42. Alcohol **7**: mp 157 °C; IR (CCl_4) 3625 cm^{-1}. Anal. Calcd for $C_{23}H_{38}O$: C, 83.57; H, 11.59. Found: C, 83.64; H, 11.51. Alcohol **8**: mp 111 °C; IR (CCl_4) 3627 cm^{-1}. Anal. Calcd for $C_{22}H_{36}O$: C, 83.54; H, 11.39. Found: C, 83.30; H, 11.34.

Thermolysis Kinetics. Samples (25 μL) of a solution of the alcohol (0.1–0.01 M) and a suitable linear saturated hydrocarbon reference (at about half the alcohol concentration) in dodecane were sealed in Pyrex tubes and thermostated in an oil bath at 135–245 °C (45 °C ranges were used for each compound). Samples were withdrawn at convenient times, cooled, and analyzed by GLC on short, lightly loaded SE30 columns. Only compound **6** was too involatile and unstable to be analyzed in this way; its thermolysis could, however, be followed be measuring the IR absorption of the product ketone at 1678 cm^{-1}. For this purpose, rather larger samples (0.5 mL) were required. Measurements on compound **3** by both IR and GLC methods agreed within the experimental error (±3%). The addition of α-methylstyrene in concentrations up to 5 times that of **1** reduced its rate constant by no more than 2%, indicating that induced decomposition does not occur to any appreciable extent.

Product Analyses. One- to two-milligram samples of alcohols were sealed with 25 μL of *n*-dodecane in tubes with a total volume of about 250 μL and were thermostated at temperatures between 150 and 200 °C for times corresponding to 10–15 half-lives. After cooling, the contents were diluted with 0.5 mL of dichloromethane and analyzed by GLC on SE30 columns. Products were identified by comparing their retention times with those of authentic samples and/or by mass spectroscopy. Formation of radicals other than B· was revealed by the presence of anomalous ketones and secondary alcohols or by the appearance of adamantane, in the case of Ad·.

Alcohol **2** gave 69.5, 68.4, 67.5, and 66.7% of products derived from formation of the *tert*-amyl radical at 150, 165, 180 and 200 °C, respectively, while **6** gave 2.6, 3.5, 4.0, and 5.0% Ad· products at the same temperatures. Compounds **3**, **7**, and **8** gave, at 200° C, 1.4, 2.3 (plus 2.5% Oc·), and 2.0% Ad· products, respectively.

Molecular Mechanics Calculations. All calculations were performed on a Digital VAX 780/11 computer through the Iverson–Mislow program[58] BIGSTRN-2 (QCPE 410) and the Allinger-Yuh program[24] MM2 (QCPE 395).

In Allinger's 1971 and Schleyer's force fields the resulting steric energy is converted to ΔH_f (gas) by applying "general group increments", and from this latter quantity the strain energy is obtained by calculating an idealized enthalpy of formation from the "strainless increments".

In his later force field (QCPE 395), Allinger calculates ΔH_f slightly differently, allowing for translation/rotation and torsional contributions explicitly, while two quantities, "inherent strain" and "strain energy", are defined. Rüchardt uses another quantity, the "strain enthalpy", H_{sp}, defined as the difference between the calculated enthalpy of formation and the specific reference value, ΔH_f^N, calculated from group increments.[16] Normally this would be simply 2.4 kcal·mol^{-1} greater than Allinger's strain energy, but Rüchardt uses strainless increments taken from an earlier source,[59] although the currently proposed general increments, translation/rotation term, and torsional contributions are used to calculate ΔH_f. In order to maintain consistency between alkane and alcohol data, we have used Allinger's 1980 values throughout.

Acknowledgment. We are indebted to A. Adenier for invaluable technical assistance, to B. Galland and Drs. P. K. Luong and T. Couesnon for help in modifying and running the molecular mechanics programs, and to Professor Ch. Rüchardt and Dr. H.-D. Beckhaus for fruitful discussions and correspondance.

Registry No. 1, 41902-42-5; 2, 82902-97-4; 3, 66951-98-2; 4, 82902-98-5; 5, 82902-99-6; 6, 80514-85-8; 7, 82903-00-2; 8, 82903-01-3.

Supplementary Material Available: Tables IV to VII containing calculated steric energies, heats of formation, and strain energies of alkanes, carbocations and alcohols (4 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of Oxidation of Aromatic Aldehydes by Acid Bromate

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The kinetics of oxidation of benzaldehyde by potassium bromate in an acetic acid medium have been studied. The reaction is first order with respect to oxidant concentration whereas the order with respect to substrate is less than one. Hydrogen ion accelerates the rate of reaction. A mechanism involving the formation of an unstable bromate ester which decomposes to the reaction products has been suggested. The activation parameters associated with the rate-determining step and the thermodynamic values associated with the equilibrium stage have been computed. The effects of various functional groups on the ring at the ortho, meta, and para positions of benzaldehyde have also been examined.

It is well-known that potassium bromate is a strong oxidizing agent, having an oxidation potential of 1.44 V in an acidic medium.[1] This readily available reagent offers trouble-free workup of the reaction product compared to the other oxidizing agents.[2] The bromate ion oxidation of metal ions has been studied with different inorganic reductants. The reaction exhibits a remarkable variety of

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