Tetrahedron Vol. 34, pp. 1597–1604
© Pergamon Press Ltd., 1978. Printed in Great Britain

0040–4020/78/0501–1597/$02.00/0

LEAVING GROUP, STERIC AND SUBSTITUENT EFFECTS IN HIGHLY CONGESTED SYSTEMS

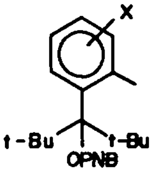
THE ACID-CATALYSED DEHYDRATION OF ARYLDI-TERT-BUTYLCARBINOLS AND THE SOLVOLYSIS OF THEIR *p*-NITROBENZOATES

John S. Lomas and Jacques-Emile Dubois*
Laboratoire de Chimie Organique Physique de l'Université Paris VII, associé au C.N.R.S., 1 rue Guy-de-la-Brosse, 75005 Paris, France

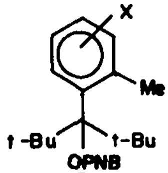
(*Received in UK 2 December 1977; Accepted for publication 22 December 1977*)

Abstract—*Ortho*-tolyldi-t-butylcarbinols exist in two well-defined, stable forms: *anti*-periplanar, 3 and *syn*-periplanar, 5. The rate constant for the acid-catalysed dehydration of the ap isomer in anhydrous acetic acid at 25°C is about 10^4 times greater than that of the sp isomer. Generally speaking, the high reactivity of the ap alcohols is due to ground state steric strain, but secondary steric effects upon resonance stabilisation of the intermediate carbonium ion and entropy effects lower the rate ratio in the case of the 4-methoxy and prehnityl derivatives, respectively. The activity of phenyldi-t-butylcarbinols, 4 lies halfway between that of 3 and 5. When *p*-nitrobenzoyl chloride is added to the 3 and 5 alkoxides, only the ap alcohol gives a *p*-nitrobenzoate, 2. This PNB solvolyses at 25° about 10^3 times faster than phenyldi-t-butylcarbinyl PNB, 1. Comparison of the rate ratios for alcohol dehydration (3/4) and PNB solvolysis (2/1) shows that the leaving group has only a small effect upon the *ortho*-tolyl/phenyl rate ratio. Reaction constants, ρ for alcohol dehydration are very similar for the three series (−4.19, −3.90 and −4.12 for 3, 4 and 5, respectively) showing thus little variation of substituent-sensitivity with reactivity. In contrast, that of the more reactive PNB, 2 is −1.93, amongst the lowest ever found for S_N1 solvolysis, while that of 1 is very different, −2.96. Since neighbouring group effects are absent in these systems, these latter variations can only be attributed to differences in the extent of charge separation in the solvolysis transition state, both being earlier than that of t-cumyl PNB ($\rho = -4.60$).

In tertiary carbinyl systems, when an aryl group is attached to a C atom bearing other bulky substituents, the solvolysis reactivities of the *p*-nitrobenzoate esters (PNB) are affected by secondary steric effects upon resonance stabilisation of the incipient carbonium ion. Predictions based on the anticipated effects of strain relief then fail: thus, against all expectation, phenyldi-t-butylcarbinyl PNB, 1 is less reactive than t-cumyl PNB.[1,2] A Me substituent in the *ortho*-position of 1, however, enhances the rate[3] by a factor of 10^2 at 85°, clearly a primary steric effect.



1

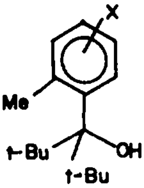


2

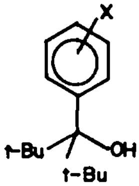
a: X = 4-OMe
b: X = 4-Me
c: X = 5-Me
d: X = H
e: X = 4-Cl
f: X = 5-Cl
g: X = 3,4,5-Me_3

In studies on the solvolysis of such systems it has been the custom to use the *p*-nitrobenzoates since they are very often the only stable derivatives available. However, in recent years, it has been realised that the choice of the leaving group has an important bearing upon the relative rates of solvolysis. The abnormally high reactivities of compounds such as tri-t-butylcarbinyl PNB,[4] 2-t-butyl-2-adamantyl PNB[5] and *trans, trans, trans*-perhydro-9b-phenyalyl PNB[6] owe a great deal to leaving group steric effects. We have therefore adopted a small leaving group, water, to investigate substituent effects upon solvolysis rates in sterically congested systems.[1] Alcohol dehydration can be considered as acid-catalysed solvolysis and, since in anhydrous media the rate determining step is formation of the carbonium ion,[7] this reaction is directly comparable with the solvolysis of *p*-nitrobenzoates.

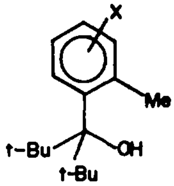
The recent synthesis of rotameric ap (3) and sp (5) *ortho*-tolyldi-t-butylcarbinols[8] gave us a unique opportunity of examining, by comparison with phenyldi-t-butylcarbinols, 4, steric effects upon reactivity and substituent effects in ***highly congested systems of well-defined geometry***. The structure of 2 has not been previously considered, but in order to discuss leaving group effects upon reactivity by comparing PNB solvolysis and alcohol dehydration, we have determined its conformation on the basis of circumstantial evidence.



3 (ap)



4



5 (sp)

RESULTS AND DISCUSSION

Steric effects upon alcohol dehydration rates. *Ortho*-tolyldi-t-butylcarbinol exist in two atropisomeric forms, *syn*-periplanar (sp), 5 and *anti*-periplanar (ap), 3. In the former the OH group is very close to the *ortho*-Me group, whereas in the second the OH group is close to the 6-hydrogen, the 2-Me being in the vicinity of the t-Bu groups.[8]

Preliminary measurements on the parent compound (X = H) showed that the ap isomer was about 10^4 times more reactive than the sp isomer in acid-catalysed dehydration.[8] From the most reactive ap alcohol to the least reactive sp alcohol in our series, the reactivity range is about 10^7 since a factor of 10^3 is introduced by the high sensitivity of the reaction, passing as it does through an intermediate carbonium ion, to substituent variation. As far as possible all rates were determined in anhydrous acetic acid containing 3% v/v of sulphuric acid, but in a number of cases where the half-life would be inconveniently short (less than 30 s) or long (greater than 1 month) it was necessary to resort to lower or higher acidities. Data sets for 3 and 5 in 3% acid are therefore incomplete. Rather than calculate the missing data by extrapolation we prefer to consider the behaviour of alcohols 3, 4 and 5 in 1%, 3% and 10% acid, respectively. Data at different acidities correlate well, with slopes near unity, for all three sets of alcohols:

$$\log k_3\,(3\%) = 0.97 \log k_3\,(1\%) + \text{const.}$$

(5 points, coeff. corr. = 0.999)

$$\log k_4\,(10\%) = 1.00 \log k_4\,(3\%) + \text{const.}$$

(7 points, coeff. corr. = 0.999)

$$\log k_5\,(10\%) = 0.95 \log k_5\,(3\%) + \text{const.}$$

(5 points, coeff. corr. = 0.997).

Consequently, the errors incurred in comparing reaction constants and relative rates at different acidities should in general be no greater than 5%.

The relative rates (Table 1) for the isomeric alcohols are in good agreement with our previous indirect estimate for the parent compounds. For the five least reactive alcohols the ap/sp ratio has a mean value of $10^{4.1}$, but it is significantly smaller for 4-OMe and prehnityl.

Two reasons were previously advanced for this large reactivity difference:[8] slow protonation of the OH group in the sp isomer, 5, and enhancement of the reactivity of 3 by relief of steric strain between the *ortho*-Me group and the t-Bu groups. Subsequent work shows however that the second factor is sufficient in itself, without the

Table 1. Rate constants for the acid-catalysed dehydration of aryldi-t-butylcarbinols in anhydrous acetic acid at 25°C (k in s^{-1}). Reaction constants and resonance parameters

		$[H_2SO_4]$			
Cpd	X	1%(0.182M)	3%(0.554M)	10%(1.82M)	$10^{-4}k_3/k_5$
3a	4-OMe	4.62×10^{-3}			0.31
4a		5.89×10^{-5}	7.12×10^{-4}	1.58×10^{-2}	
5a		1.48×10^{-6}	1.48×10^{-5}	2.95×10^{-4}	
3b	4-Me	1.80×10^{-3}	2.15×10^{-2}		0.98
4b			1.70×10^{-4}	4.31×10^{-3}	
5b			2.19×10^{-6}	6.62×10^{-5}	
3c	5-Me	9.97×10^{-4}	1.29×10^{-2}		1.31
4c			8.91×10^{-5}	2.10×10^{-3}	
5c			9.87×10^{-7}	2.82×10^{-5}	
3d	H	6.00×10^{-4}	7.17×10^{-3}		1.19
4d			5.14×10^{-5}	1.20×10^{-3}	
5d			6.02×10^{-7}	1.53×10^{-5}	
3e	4-Cl	7.93×10^{-5}	8.81×10^{-4}	1.78×10^{-2}	1.06
4e			6.02×10^{-6}	1.36×10^{-4}	
5e				1.68×10^{-6}	
3f	5-Cl	1.50×10^{-5}	2.23×10^{-4}	5.79×10^{-3}	1.33
4f			1.73×10^{-6}	4.08×10^{-5}	
5f				4.35×10^{-7}	
3g	$3,4,5\text{-}Me_3$	7.24×10^{-3}			0.28
5g		2.60×10^{-6}	3.33×10^{-5}	8.08×10^{-4}	
3	ρ^a	-4.19 ± 0.14	-4.00 ± 0.05		
	r^a	0.16 ± 0.08			
4	ρ		-3.90 ± 0.06	-3.90 ± 0.06	
	r		0.30 ± 0.05	0.31 ± 0.04	
5	ρ			-4.12 ± 0.04	
	r			0.30 ± 0.03	

[a] standard deviation follows values.

introduction of any supplementary hypothesis. The steric energy of 3 is calculated by molecular mechanics[9] to be greater than that of 5 by 5.9 or 6.6 kcal/mol, depending on the hydrocarbon model used.[10] If we assume that the activation entropy is the same for the dehydration of both isomers, a relative rate of $10^{4.1}$ at 25° corresponds to an activation enthalpy difference of 5.6 kcal/mol. This figure is so close to the difference in the steric energies, ΔSE, that we can reasonably affirm that the relative reactivity is a reflection of the relative ground state stability of the isomers, ΔG°, and that no further explanation is required[11] (Fig. 1).

The prehnityl derivatives, 3g and 5g, are exceptional, rates being higher by factors of 1.5 and 3.7, respectively, than expected on the basis of simple additivity of substituent effects. The buttressing effect of the neighbouring Me groups increases the steric energy of both prehnityl derivatives, but molecular mechanics calculations fail to reveal that the difference in the ground state energies is smaller for prehnityl than for *ortho*-tolyl, as required by the smaller rate ratio. On the contrary, when the prehnityldi-t-butylethanes (i.e. a Me group is taken as an approximation to the OH group of the alcohol) are compared, ΔSE rises to 7.2 kcal/mol, suggesting that the reactivity difference between ap and sp isomers should be greater than usual. However, this argument does not take into account possible entropy effects which may be important in such crowded structures where there is little rotational freedom. Thermodynamic data on the solvolysis of *ortho*-tolydi-t-butylcarbinyl *p*-nitrobenzoates, given below, illustrate this point.

The deviation of the 4-OMe derivatives, 3a and 5a, cannot be explained in this way, and is attributable to differences in resonance stabilisation of the two systems, as is shown by the following analysis. The constancy of the rate ratio for the *meta*-substituted derivatives indicates that the reaction constants, ρ, are virtually identical for the two isomers, despite the difference in their reactivities. They have values of −4.19 (3 in 1% acid) and −4.12 (5 in 10% acid) which are typical of alcohol dehydration[12] and of carbonium ion reactions in general. The value for phenyldi-t-butylcarbinols is very similar, −3.90 (in 3% or 10% acid).

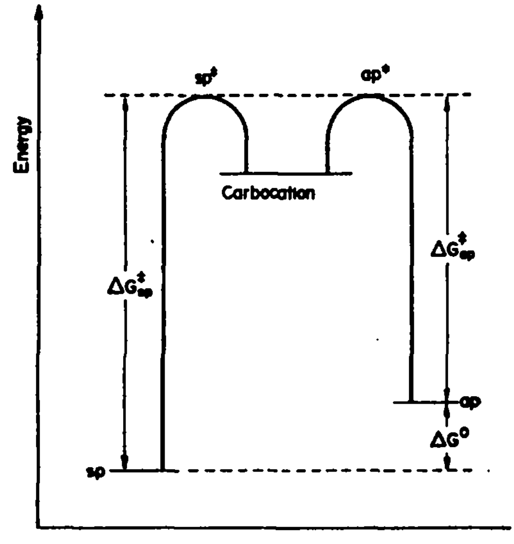


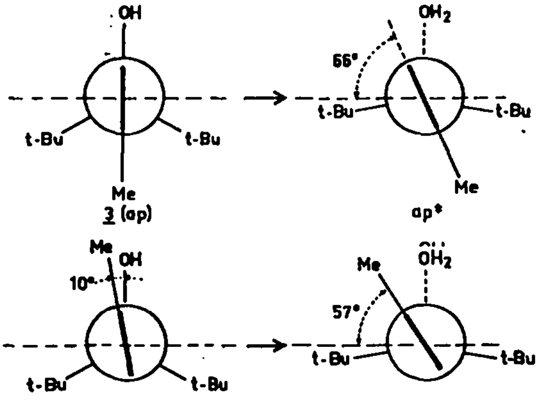
Fig. 1. Energy diagram for the dehydration of ortho-tolyldi-t-butylcarbinols.

Now, the coefficient r in the Yukawa–Tsuno equation:[13]

$$\log k/k_0 = \rho(\sigma^{\circ} + r\Delta\sigma^{+})$$

is defined so as to indicate the magnitude of resonance stabilisation of the incipient carbonium ion by electron-donating substituents. Since $\Delta\sigma^{+}$ is much greater for 4-OMe than for the other *para*-substituents in our series, the rates of 3a, 4a and 5a tend to dominate in our estimation of r. Nevertheless, although the r values, 0.16 ± 0.08 (3), 0.30 ± 0.05 (4) and 0.30 ± 0.03 (5), may depend a little on the acidity,[16] the resonance effect of a *para*-substituent is clearly greater in 5 than in 3.

The resonance energy may be considered to follow an equation of the form: $E_{\theta} = E_0 \cos^2 \theta$, where E_0 is the resonance energy corresponding to a situation in which the aryl group is in the plane of the carbonium ion, and E_{θ} when there is an angle θ between these planes.[17] It has frequently been assumed that r of the Yukawa–Tsuno equation is equivalent to E_{θ}/E_0 and that θ can thus be calculated.[18] Values of 0.16 and 0.30 correspond to angles of 66° and 57° for ap and sp, respectively. This difference can be understood if we assume that in the transition state the two t-Bu groups have not attained coplanarity with the charge-bearing atom. Rotation of the aryl ring to increase the overlap between its orbitals and the empty sp^2 orbital would be impeded in isomer 3 by interactions between the *ortho*-Me group and one of the t-Bu groups. In the transition state for the dehydration of the other isomer, no comparable interaction would arise. Thus, although the dehydration of these two alcohols must go through a common carbonium ion intermediate, the structures of the transition states leading to this intermediate could reflect the geometries of the starting alcohols.[19] In the phenyl derivative, 4 the r value is very similar to that of the sp isomer 5, probably because there is no *ortho*-Me group which can interact with a t-Bu group.



It must be emphasised that, however qualitative our values of r and θ may be, we do not accept the assumption that the transition state or the intermediate carbonium ion has the orthogonal structure,[1,2] in which $\theta = 90°$ and resonance stabilisation is negligible. The geometry of the transition state depends on the balance of steric and resonance energies; it is dangerous to place too much faith in molecular models which, of course, completely overlook the potential importance of the second factor.[22,23]

Apart from two exceptions, therefore, the reactivity difference between the ap and sp alcohols is a reflection of ground state strain. In the case of the prehnityl derivatives, entropy effects are important and the anomalous ap/sp ratio of the 4-OMe derivatives can be attributed to secondary steric effects upon resonance stabilisation of the transition states ap$^{\neq}$ and sp$^{\neq}$. It is less easy to understand why the reactivity of the phenyldi-t-butylcarbinol series, 4, falls about halfway between those of the *ortho*-tolyldi-t-butylcarbinols. The calculated difference in the steric energies depends markedly on the hydrocarbon model and, more seriously, we have no way of estimating the energies of the two carbocations. We shall see below that the polar contribution of the *ortho*-Me group can enhance the rate by only a small factor, and that conjugative effects are similar in all three systems. It seems likely, therefore, that the reactivity of 4 is also to be understood in terms of the changes in steric strain associated with the passage from the ground state to the transition state.

The solvolysis of aryldi-t-butylcarbinyl p-*nitrobenzoates.* Solvolysis rates were determined in acetic acid containing 0.01 M sodium acetate by the spectroscopic method of Bartlett and Tidwell,[24] at temperatures ranging from 30° to 130°. Rate constants at 25° are given in Table 2. The reaction constant for PNB, 1, calculated from the three reliable *meta*-substituents, Me, H and Cl, is −2.96. From the deviations of the *para*-substituents, OMe, Me and Cl, a value of 0.41 is obtained for the coefficient r of the Yukawa–Tsuno equation.[25]

There is a slight difficulty in determining the reaction constant for the solvolysis of 2, since the 5-Cl derivative, 2f behaved anomalously (Experimental). Nevertheless, a good linear correlation (Fig. 2) exists between the six *ortho*-tolyl derivatives and the corresponding phenyl derivatives, with a slope of 0.65 ± 0.02, which corresponds to a ρ value of −1.93 if r is unchanged. If r were significantly different in 2, the points for 2a, 2b and 2e would deviate systematically to one side or other of the regression line through the other points. Since no such deviation is found we presume that r is similar in 1 and 2. At present there are no structural data which would allow us to interpret this result in terms of the geometries of the ground state and the transition state,[22] as we did for the alcohols above.

Both ρ values are substantially smaller than those observed for less congested tertiary carbinyl derivatives, such as t-cumyl PNB where ρ is −4.72[26] or −4.60[27] at 25°. Frequently S_N1 solvolyses have small ρ values when the electron demand of the charged carbon is largely satisfied by some electron donor other than the aryl group, such as a cyclopropyl group, a C=C double bond or another phenyl group.[28] The exceptionally low values found in this work cannot be attributed to assistance by any other group, nor even to migrating Me since tertiary systems have no requirement for neighbouring group assistance. In fact, solvent effect studies[3] show clearly that these small ρ values are consistent with the occurrence of an early transition state; at 85° the m values of 2 are 30% smaller than those of 1, and all are substantially smaller than expected for an S_N1 solvolysis under these conditions.[29] The transition state occurs progressively earlier as ground state strain increases from t-cumyl PNB to 1 to 2.

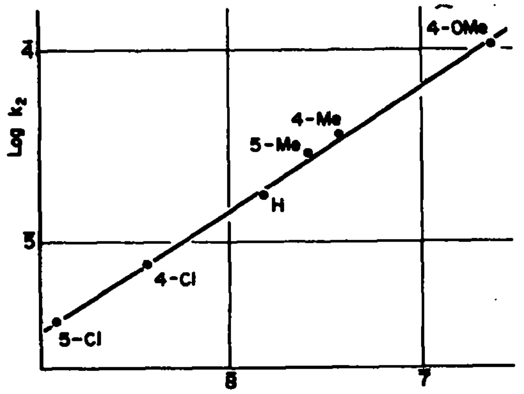


Fig. 2. Correlation of *ortho*-tolyl- and phenyl-di-t-butyl-carbinyl *p*-nitrobenzoate solvolysis rate constants (25°C; acetic acid, 0.01 M NaOAc).

Leaving group effect on the reactivity of aryldi-t-butylcarbinyl derivatives. As stated at the beginning of this paper, before the leaving group effect can be discussed it is necessary to determine the conformation of 2. There exist two *ortho*-tolyldi-t-butylcarbinols, but there is no evidence for the existence of more than one *p*-nitrobenzoate.

In the ap alcohols 3 and in phenyldi-t-butylcarbinols 4, the OH group has been shown by spectroscopic studies to behave similarly, as regards its accessibility, whereas the sp alcohols 5 are dissimilar in this respect, the OH group being less accessible.[10] It seemed likely then that 3 should behave like 4 in forming *p*-nitrobenzoates and that 5 should not. The *ortho*-tolyldi-t-butylcarbinyl *p*-nitrobenzoate would therefore have the ap conformation. In the absence of X-ray crystallographic or other unambiguous structural data, this prediction was confirmed as follows.

The PNB, 2, is most easily obtained by addition of *p*-nitrobenzoyl chloride to the product of adding di-t-butylketone to *ortho*-tolyl-lithium without isolation of the alcohol. Direct introduction of suitably treated samples of the entire reaction mixture into the low temperature GLC system[10] shows that the PNB, revealed by its olefinic decomposition products,[30] is formed at the expense of the ap isomer, 3. This result was confirmed in attempts to obtain 2 from the purified alcohols by the regeneration of the alkoxide in ether. No PNB was obtained from the sp alcohol, modest yields from the ap isomer. We conclude, therefore, that the PNB, 2, has the ap conformation.

The introduction of an *ortho*-Me group causes a rate increase of about 10^3 in the solvolysis of 1. Since 2 has the ap conformation, this factor is to be compared with that between the ap alcohol 3 and the phenyl derivative 4, approximately $10^{2.1}$. The polar effect of the *ortho*-Me group ($\rho\sigma$, where $\sigma_{o\text{-Me}}$ is −0.15) will be about twice as great in dehydration as in solvolysis, i.e. in the ratio of the reaction constants. The residual, purely steric, effect of the Me group is therefore about a factor of 500 in solvolysis and 40 in dehydration.

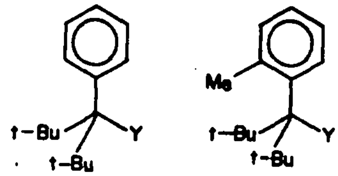
In systems previously studied, PNB solvolysis is much more sensitive to changes in the level of steric congestion than is alcohol dehydration. Thus, the t-Bu/Me ratio for the alkyldi-t-butylcarbinyl system increases by a factor of 750 on going from the alcohols to the PNB's,[4] while for 2-alkyl-2-adamantyl the increase is somewhat smaller,[5] by a factor of 120. These increases in the t-Bu/Me ratio depend to a large extent on leaving group steric interactions (F-strain). The relatively small change

Table 2. Rate constants for the solvolysis of aryldi-t-butylcarbinyl *p*-nitrobenzoates in anhydrous acetic acid (0.01 M NaOAc) (k in s^{-1})

Cpd	130.1°	115.0°	99.8°	84.6°[a]	69.8°	25°[b]	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
	Temperature (°C)							
1a			3.19×10^{-3}	6.18×10^{-4}	1.16×10^{-4}	2.33×10^{-7}	27.4	2.6
1b		4.83×10^{-3}	9.65×10^{-4}	1.74×10^{-4}	2.90×10^{-5}	3.85×10^{-8}	29.3	5.7
1c		3.59×10^{-3}	7.44×10^{-4}	1.26×10^{-4}	2.12×10^{-5}	2.68×10^{-8}	29.5	5.7
1d		2.18×10^{-3}	4.29×10^{-4}	8.05×10^{-5}	1.24×10^{-5}	1.59×10^{-8}	29.5	4.8
1e	2.71×10^{-3}	6.60×10^{-4}	1.24×10^{-4}	2.20×10^{-5}		3.86×10^{-9}	30.0	3.6
1f	1.43×10^{-3}	3.43×10^{-4}	6.04×10^{-5}	1.00×10^{-5}		1.35×10^{-9}	31.0	4.8

Cpd	69.8°	60.1°	50.5°	40.0°	30.2°	25°[b]	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
	Temperature (°C)							
2a			2.56×10^{-3}	7.46×10^{-4}	2.06×10^{-4}	1.04×10^{-4}	23.6	2.3
2b		2.92×10^{-3}	9.97×10^{-4}	2.71×10^{-4}	7.43×10^{-5}	3.66×10^{-5}	24.0	1.8
2c		2.44×10^{-3}	7.80×10^{-4}	2.15×10^{-4}	5.96×10^{-5}	2.89×10^{-5}	24.3	2.1
2d		1.54×10^{-3}	4.93×10^{-4}	1.33×10^{-4}	3.53×10^{-5}	1.72×10^{-5}	24.7	2.4
2e	2.11×10^{-3}	7.07×10^{-4}	2.13×10^{-4}	5.94×10^{-5}		7.36×10^{-6}	25.0	1.8
2f		3.63×10^{-4c}	1.36×10^{-4c}	2.88×10^{-5c}		3.77×10^{-6}	25.6	2.3
2g			3.86×10^{-3}	1.08×10^{-3}	2.86×10^{-4}	1.41×10^{-4}	24.4	5.6

[a] given as 85° in ref. 4,14 [b] extrapolated [c] extrapolated from data in aqueous acetic acid.



1, 4 **2, 3**

		1, 4	**2, 3**
rel. rate	Y = OPNB	1	1080
	Y = OH	1	140

in the *ortho*-tolyl/phenyl ratio, a factor of about 10 only, on going from the alcohols to the PNB's, shows therefore that leaving group steric interactions are not greatly increased by the introduction of a 2-Me group in the aryldi-t-butylcarbinyl system. In the PNB there are repulsive interactions involving the CO oxygen, the CO carbon and/or the *p*-nitrophenyl moiety, but these do not vary greatly on going from **1** to **2**, except insofar as the interactions between 2-Me and t-Bu group distort the bond angles and, thus, slightly increase interactions between the *p*-nitrobenzoyl group and the aryl group or the t-Bu groups, depending on the position of the *p*-nitrobenzoyl group.

Thermodynamic parameters of the solvolysis reaction; the prehnityl anomaly. Activation entropies for the solvolysis of these highly congested *p*-nitrobenzoates fall in the range 2–6 eu and may be taken as indicative that ion-pair return is not an important process in the solvolysis of these systems.[31] The value of $\Delta S^{\neq}$ for series **1** is practically constant and slightly higher than that for series **2**, with one exception, the prehnityl derivative **2g** which has an anomalously high value.

The instability of the ap derivatives and, consequently, their high reactivity arise essentially from non-bonding interactions between the *ortho*-Me group and the two t-Bu groups. The prehnityl derivative, **2g**, in view of the four adjacent Me groups should be the most congested of all the PNB's in this study and would, therefore, be expected to be the most reactive. It might also be expected to have the lowest $\Delta H^{\neq}$ since ground state strain increases from **1** to **2a–f** to **2g** and $\Delta H^{\neq}$ drops by 4–5 kcal/mol on going from **1** to **2a–f**. In fact, **2g** reacts 40% faster than predicted from the rates of **2b–d**, but this enhancement is due essentially to the favourable entropy term, about 3 eu higher than for **2a–f**. The activation enthalpy, on the other hand, is as high as for **2c** or **2d**.

The first result supports our remarks concerning the possible importance of entropy effects upon the ratio **3g**/**5g** in the dehydration of the alcohols. Secondly, the unexpectedly high $\Delta H^{\neq}$ value suggests that the transition state for solvolysis of **2g** is also strained and that the overall strain energy change on going from the ground state to the transition state is not particularly favourable.[32] Other factors, however, such as solvation and resonance stabilisation, may also be involved.

CONCLUDING REMARKS

The foregoing discussion shows that the reactivity of aryldi-t-butylcarbinyl systems is a complex function of primary and secondary steric effects whose quantitative interpretation is as yet incomplete. Provided that the modification of the crowding in the hydrocarbon part of the molecule is small and remote from the leaving group, the identity of the latter has only a small effect upon the *relative rates*. On the other hand, an interesting feature of this study is that the *reaction constant*, *ρ*, varies very little,[13] if at all, in the case of the alcohols, **3**, **4** and **5** despite a reactivity increase by a factor of 10^4 whereas, in the solvolysis of the *p*-nitrobenzoates, **1** and **2**, it drops substantially as the reactivity increases by 10^3.

Diametrically opposed opinions regarding the validity of the reactivity-selectivity principle have been expressed,[33] but to our knowledge this is the first system which appears to provide evidence both for and against this relationship, depending on the leaving group. Insofar as any secondary steric effect upon transmission of the resonance effects of electron-donating *para*-substituents is taken care of by the parameter r in the Yukawa–Tsuno equation, the *ρ* values should reflect the extent of bond breaking in the transition state.[34] Therefore, the high *ρ* values for alcohol dehydration suggest that the rate-determining transition state, wherein the C–O bond is broken, is uniformly close to the carbonium ion intermediate, regardless of the ground state energy of the molecule. In solvolysis, on the other hand, the extent of charge separation, as evidenced by the *ρ* values of **1** and **2**, is sensitive to the degree of steric congestion in the molecule. Nevertheless, it is clear that there is no general cause-and-effect relationship between reactivity and *ρ* even in PNB solvolysis; although it has the greater *ρ* value, t-cumyl PNB solvolyses 10 times faster than **1**, the rates of **1** and **2** being anomalously low because of secondary steric effects upon stabilisation of the transition state by the aryl group. An additional possibility is that an unfavourable strain energy change is associated with the formation of the carbonium ion in the solvolysis of the t-Bu derivatives[32] due to the fact that the $C–C^+$ bonds are normally shorter than C–C bonds.

The difficulties involved in the quantitative interpretation of large structural effects upon reactivity are further illustrated by the following example. Whereas the Ph/Me ratio for the solvolysis of R-di-t-butylcarbinyl *p*-nitrobenzoates is already unexpectedly small (0.19 in 70% aqueous acetone at 100°),[1] that for the dehydration of the corresponding alcohols[36] is 10^5 times less than predicted[37] by the Peters–McManus–Harris equation:[27,35] $\log k_{Me}/k_{Ph} = \gamma^+\rho^+$. Although the PNB deviation could conceivably be attributed to steric hindrance to resonance stabilisation, that of the alcohols certainly cannot be. The fact that the reactivity ratio, both for Ph/Me and t-Bu/Me,[3,4] increases with the size of the leaving group suggests that strain energy changes are important in both cases. Unfavourable strain energy changes would reduce the dehydration rates of the most congested alcohols; in PNB solvolysis leaving group steric interactions would increase the energy of congested ground states the most and, therefore, raise the Ph/Me and t-Bu/Me ratios.

Strain energy calculations may eventually provide a quantitative interpretation of abnormal Ph/Me and t-Bu/Me ratios and, optimistically, of steric effects upon solvolysis in general. It would then be possible in examining the effect of a structural modification to discern whether the relative rate changes because one compound is more reactive or because the other is less reactive than usual.[38] With this approach in its present state of development, alcohol dehydration seems better fitted to theoretical treatment than *p*-nitrobenzoate solvolysis.

EXPERIMENTAL

Analytical data for all new alcohols and *p*-nitrobenzoates are given in Table 3. M.ps are uncorrected. Series **2** *p*-nitrobenzoates

Table 3. Microanalytical data for new alcohols and *p*-nitrobenzoates

Cpd	mp, bp/mm	Calculated				Found			
		C	H	N	Cl	C	H	N	Cl
1c	158-9°	72.03	7.62	3.65		71.92	7.99	4.02	
1f	144-5°	65.42	6.49	3.49	8.78	65.38	6.30	3.85	9.24
2a	dec.	69.71	7.56	3.39		69.24	7.99	3.62	
2b	dec.	72.51	7.86	3.52		72.36	7.92	3.92	
2c	dec.	72.51	7.86	3.52		72.45	8.08	3.80	
2d	dec.	72.03	7.62	3.65		72.10	7.34	3.58	
2e	dec.	66.09	6.75	3.65	8.48	65.96	7.07	3.47	8.81
2f	dec.	66.09	6.75	3.35	8.48	65.80	7.03	3.80	8.13
2g	dec.	73.38	8.29	3.29		73.36	7.91	3.60	
3e	38-39°,-	71.49	9.38		13.19	71.64	9.58		13.38
4b	34°,119°/2	81.99	11.18			81.85	11.43		
4c	- ,107°/1.5	81.99	11.18			82.09	11.19		
4e	33°,133°/3	70.71	9.10		13.91	70.49	9.08		14.15
4f	- ,120°/2	70.71	9.10		13.91	70.65	9.46		14.00
5e	-,-	71.49	9.38		13.19	71.66	9.60		13.42

decomposed before melting when slowly heated to about 120°. No liquid phase is observed until the product, *p*-nitrobenzoic acid, starts to melt at about 230°.

Synthesis of aryldi-t-butylcarbinols. Tertiary alcohols were prepared by addition of di-t-butylketone to the appropriate aryllithium in ether at room temp. as described previously.[1,8,10]

Synthesis of aryldi-t-butylcarbinyl p-*nitrobenzoates.* Phenyldi-t-butyl-carbinyl PNB's, 1 were synthesised by the method of Tanida and Matsumura.[1] *ortho*-Tolyldi-t-butylcarbinyl PNB's, 2b, 2c and 2d were prepared by direct addition of *p*-nitrobenzoyl chloride in ether to the crude alcohol mixture containing the Li salts of 3 and 5. In the case of 2d this reaction was followed by "low temperature" GLC analysis.[10] A mixture of 3d and 5d was prepared by the addition of di-t-butylketone (0.9 g, 6.2 mmol) in ether to a solution of *ortho*-tolyl-lithium (0.2 M, 6.3 mmol) in the same solvent. Octadecane (0.4 g) was then added and a small sample of the mixture taken for analysis. *p*-Nitrobenzoyl chloride (1.17 g, 6.3 mmol) in ether (25 ml) was added dropwisely to the cooled (−20°) mixture, which was then allowed to attain room temp. before being washed with aqueous K_2CO_3 and dried. GLC analysis revealed peaks corresponding to the olefins formed by pyrolysis of the PNB in the injector,[1,39] and residual alcohols. Whereas the ratio 5d/octadecane was unchanged, 3d/octadecane decreased to 6% of its value prior to the addition of *p*-nitrobenzoyl chloride.

Compounds 2a, 2e and 2f were prepared by a small modification of the method of Kaiser and Woodruff[39] in which ether replaced THF as solvent. Treatment of the pure ap alcohols, 3 with an equimolar amount of n-BuLi[40] regenerates the alkoxide which reacts with *p*-nitrobenzoyl chloride to give the PNB in yields of 27–47%. Attempts to prepare PNB's from 5 were fruitless.

Dehydration and solvolysis rates. Rate constants were measured conventionally.[7,10,24] Only in 10% H_2SO_4/AcOH was it necessary to use an external standard[10] for GLC determination of the alcohol concentrations. At lower acidities the hydrocarbons were sufficiently soluble to be used directly in the mixture.[7] Solvolysis rates are the mean of duplicate determinations agreeing to within 1–4%. Dehydration rates are the mean of 2–5 runs agreeing to within 1–7%, the poorest reproducibility being for the very slow runs where it was necessary to store samples for several days or weeks before GLC analysis.

Difficulty was experienced in determining the solvolysis rates of 2f: in anhydrous AcOH the UV absorption (257 nm) of the "infinity" samples was very high and the kinetic plots were non-linear. When the reaction was run in aqueous AcOH (2–16 M water) this phenomenon disappeared and the rate constants could be determined over 3 half-lives as usual. The data given in Table 2 for 2f are therefore values extrapolated by means of the Grunwald–Winstein equation[41] ($\log k/k_0 = mY$) to pure AcOH ($Y = -1.64$).

Reaction products. According to Tanida and Matsumura,[1] solvolysis of 1 gives only an olefin and a cyclopropyl derivative: this we confirmed. The dehydration products are time-dependent: initially the same products are formed as in solvolysis but they are subsequently rearranged, fragmented and polymerized. No further study of these secondary products was carried out.

REFERENCES

[1] H. Tanida and H. Matsumura, *J. Am. Chem. Soc.* 95, 1586 (1973).

[2] W. Duismann and C. Rüchardt, *Chem. Ber.* 106, 1083 (1973).

[3] J. S. Lomas and J. E. Dubois, *J. Org. Chem.* 40, 3303 (1975).

[4] J. E. Dubois and J. S. Lomas, *Tetrahedron Letters* 1791 (1973).

[5] J. S. Lomas, P. K. Luong and J. E. Dubois, *J. Am. Chem. Soc.* 99, 5478 (1977).

[6] J. Slutsky, R. C. Bingham, P. v. R. Schleyer, W. C. Dickason and H. C. Brown, *Ibid.* 96, 1969 (1974). This paper is a valuable source of refs to the earlier literature on leaving group effects.

[7] J. S. Lomas, D. S. Sagatys and J. E. Dubois, *Tetrahedron* 29, 2157 (1973).

[8] J. S. Lomas and J. E. Dubois, *J. Org. Chem.* 41, 3033 (1976).

[9] For leading references to this approach, see: N. L. Allinger, *Adv. Phys. Org. Chem.* 13, 1 (1976); O. Ermer, *Struct. Bonding* 27, 161 (1976); E. M. Engler, J. D. Andose and P. v. R. Schleyer, *J. Am. Chem. Soc.* 95, 8005 (1973).

[10] J. S. Lomas, P. K. Luong and J. E. Dubois, *J. Org. Chem.* 42 3394 (1977).

[11] Resonance stabilisation of the transition state by the aryl group may, however, be slightly greater in 5 than in 3 (*vide infra*).

[12] D. S. Noyce, D. R. Harrter and R. M. Pollack, *J. Am. Chem. Soc.* 90, 3791 (1968).

[13] Y. Yukawa and Y. Tsuno, *J. Chem. Soc. Japan, Pure Chem. Sect.* 86, 873 (1965); Y. Yukawa, Y. Tsuno and M. Sawada, *Bull. Chem. Soc. Japan* 39, 2274 (1966). Our use of the Yukawa–Tsuno equation[14] has been criticised by Johnson[15] who considers that a regular Hammett treatment is just as good. The choice depends on the importance one attaches to the badly-correlated 3-CF_3 derivative. This group is anomalous in that σ^+ is greater than σ and does not feature in Yukawa's work. For this reason and in view of the anticipated difficulty in synthesising the 2-Me derivatives we have abandoned this

substituent. Johnson also claims that the use of Hammett σ values obviates "the need for special explanations for conformation in these molecules", as though this were an advantage. Although interpretation of r is not easy, the possibility of investigating transition state geometry by this means is not to be neglected. Furthermore, differences in resonance stabilisation are likely to modify the ρ values if the rate data are assumed to fit the Hammett equation. Hammett ρ values are -3.82, -3.97 and -4.31 for **3**, **4** and **5**, respectively.

[14] J. S. Lomas and J. E. Dubois, *Tetrahedron Letters* 407 (1976).

[15] I. Roberts, C. D. Johnson and P. G. Taylor, *Tetrahedron* 33, 2123 (1977).

[16] The rate constant for dehydration of **5a** increases unusually slowly when the acid concentration is raised from 1% to 10%; data for **4a** are unexceptional and no data for **3a** at high acidity are accessible.

[17] M. J. S. Dewar, *J. Am. Chem. Soc.* 74, 3345 (1952); L. Pauling and R. B. Corey, *Ibid.* 74, 3964 (1952); L. L. Ingraham, *Steric Effects in Organic Chemistry* (Edited by M. S. Newman), Chap. 11. Wiley, New York (1956).

[18] A. F. Hegarty and J. E. Dubois, *Tetrahedron Letters* 4839 (1968); J. E. Dubois and A. F. Hegarty, *J. Chem. Soc.* B, 638 (1969); J. E. Dubois, A. F. Hegarty and E. D. Bergmann, *J. Org. Chem.* 37, 2218 (1972); A. F. Hegarty, J. S. Lomas, W. V. Wright, E. D. Bergmann and J. E. Dubois, *Ibid.* 37, 2222 (1972); J. E. Dubois, M. F. Ruasse and A. Argile, *Tetrahedron* 31, 2921 (1975).

[19] Crystallographic studies on aryldi-t-butylcarbinols[20] or analogous compounds[21] show that in the solid state the plane of the aryl ring makes an angle of 10–12° with that containing the C–O bond and C_1. This value is approximately confirmed by molecular mechanics calculations on the sp isomer.[10] For the ap isomer molecular mechanics gives a value of 2°.

[20] E. Hough, *Acta. Cryst.* to be published.

[21] H. van Koningsveld, *Cryst. Struct. Comm.* 3, 491 (1973).

[22] Stuart–Briegleb models suggested[14] that the ring was turned through an angle of about 45° in **1** and **4**, whereas with CPK models there is no difficulty in constructing a model corresponding to the crystallographic structure of **4** (J. M. A. Baas, personal communication).

[23] Ultimately, molecular mechanics should be applicable to conjugated systems: N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.* 95, 3893 (1973); A. Warshel and M. Karplus, *Ibid.* 94, 5612 (1972).

[24] P. D. Bartlett and T. T. Tidwell, *Ibid.* 90, 4421 (1968).

[25] From data for para-substituted compounds in 70% aq. acetone at 100°, $\rho = -1.79$ and $r = 0.49$.[1] In acetic acid at this temp., $\rho = -2.1$.

[26] H. C. Brown, M. Ravindranathan and E. N. Peters, *J. Org. Chem.* 42, 1073 (1977).

[27] E. N. Peters, *Ibid.* 42, 1419 (1977).

[28a] H. C. Brown, *The Nonclassical Ion Problem*, Chap. 10. Plenum Press, New York (1977); [b] W. L. Jorgensen, *J. Am. Chem. Soc.* 99, 3840 (1977).

[29] This interpretation has been criticised by Johnson *et al.*[15] Though their statement that "The variation of the Hammett ρ values with solvent is . . . a sufficient condition to produce . . . a linear correlation between log k and m" is correct, it begs the question. Depending on the viewpoint chosen, one must either explain why the Hammett ρ values vary with solvent or why m varies with the reactivity. In choosing the second way of looking at the results, we concluded that the variation of m indicates (substituent-dependent) changes in the transition state separation. Alternatively, we could have concluded that the complementary variation of ρ with solvent (see Ref. 13 in our note[3]) indicates (solvent-dependent) changes in charge separation. The smoothing of our results and the calculation of rate data in 80% aq. ethanol[15] only obscure this point.

[30] G. J. Abruscato and T. T. Tidwell, *J. Am. Chem. Soc.* 92, 4125 (1970).

[31] D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry and P. v. R. Schleyer, *Ibid.* 92, 5977 (1970); D. N. Kevill, K. C. Kolwyck and F. L. Weitl, *Ibid.* 92, 7300 (1970).

[32] Molecular mechanics calculations suggest that the abnormally low dehydration rate of tri-t-butylcarbinol is not due to steric desolvation of the intermediate carbonium ion, but to an unfavourable strain energy change associated with the formation of this species (D. Khoury and P. v. R. Schleyer, personnal communication).

[33] The notion of selectivity has been extended to embrace the sensitivity of a reaction rate to substituent and solvent effects, i.e. ρ or m values: C. D. Johnson, *Chem. Rev.* 75, 755 (1975); B. Geise, *Angew. Chem.* (Int. Edn.) 16, 125 (1977); A. Pross, *Adv. Phys. Org. Chem.* 14, 69 (1977).

[34] This point does not seem to have been appreciated by recent authors.[27,35]

[35] S. M. McManus and J. M. Harris, *J. Org. Chem.* 42, 1422 (1977).

[36] Rates for methyl derivative extrapolated from the data in Ref. 7 to the 3–10% sulphuric acid range.

[37] The methyl group substituent constant, γ^+, lies probably in the range 0.6 to 0.8 for the acid-catalysed dehydration of well-behaved alcohols (J. S. Lomas and J. E. Dubois, unpublished results).

[38] Ref. 28*a*, Chap. 2.

[39] E. M. Kaiser and R. A. Woodruff, *J. Org. Chem.* 35, 1198 (1970).

[40] Organo-lithium catalysed rotation[10] is too slow in ether-containing media to convert a significant amount of **3**–**5** in the time required for this experiment.

[41] E. Grunwald and S. Winstein, *J. Am. Chem. Soc.* 70, 846 (1948).