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Substituent Effects on the Solvolysis Rates and Gas Phase Stabilities of 1,2,2-Trimethyl-1-phenylpropyl and 1,2,2-Trimethyl-1-(2-methylphenyl)propyl Systems

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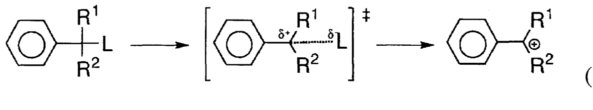
Substituent effects on the solvolysis rates of 1,2,2-trimethyl-1-phenylpropyl chlorides in 80% (v/v) aq acetone at 45 °C and 1,2,2-trimethyl-1-(2-methylphenyl)propyl *p*-nitrobenzoates in 50% (v/v) aq ethanol at 75 °C were correlated with the Yukawa–Tsuno equation to give $\rho = -4.28$ and $r = 0.91$, and $\rho = -2.78$ and $r = 0.70$, respectively. The reduction in r values from $r = 1.00$ for full conjugation is ascribed to deviation from coplanarity of the carbocationic center and the benzylic π-system in the transition state. Substituent effects on the gas phase stabilities of 1,2,2-trimethyl-1-phenylpropyl cations and 1,2,2-trimethyl-1-(2-methylphenyl)propyl cations were correlated to give $\rho = -9.1$ and $r = 0.89$, and $\rho = -6.6$ and $r = 0.70$, respectively. The identical r values were obtained for the transition states and for the intermediates. The experimentally obtained torsion angles for twisting estimated from the relationship $r/r_{\max} = \cos^2\theta$ are in good agreement with theoretically calculated dihedral angles of the corresponding Becke3LYP/6-31G* optimized carbenium ions. This identity provides convincing evidence for occurrence of steric inhibition of resonance through loss of coplanarity and provides strong support for our characterization of the r value as a resonance demand parameter.

The Yukawa–Tsuno (Y–T) equation (Eq. 1)[1] is a useful tool to relate the reactivity to the structure of the transition state or the intermediate in the conjugative aryl-substituted systems;

$$\log(k/k_0) \text{ or } \log(K/K_0) = \rho(\sigma^0 + r\Delta\bar{\sigma}_R^+), \qquad (1)$$

where k (or K) is the rate (or equilibrium) constant for a given reaction of a ring-substituted derivative and k_0 (or K_0) is the corresponding value for the unsubstituted one. σ^0 is the normal substituent constant which involves no additional π-electronic interaction between the substituent and the reaction center, and $\Delta\bar{\sigma}_R^+$ is the resonance substituent constant measuring the capability for π-delocalization of *p*–π-electron donor substituent, defined by $\sigma^+ - \sigma^0$. In this equation, the r value is the parameter measuring the degree of resonance interaction between the carbocationic center and the benzene π-system. We have successfully applied Y–T Eq. 1 to an ionization process (Eq. 2) of various benzylic solvolyses.[1—3)]



(2)

The r value changes widely with the reaction; it is not limited only to values lower than unity ($0 < r < 1$) but in many cases it is significantly higher than unity ($r > 1$).

This resonance demand r parameter should be closely related to the degree of π-overlap between the aryl-π-orbital and incipient vacant p-orbital of the benzylic carbenium ion. Hence, examination of the dependence of the r-value upon dihedral angle between the two p-orbitals should provide convincing evidence as to the origin of the empirical resonance demand parameter.

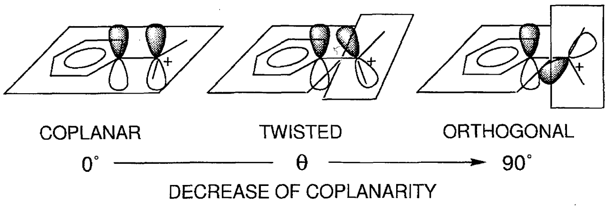
The carbenium transition state of a benzylic system carrying two bulky alkyl groups may be released from steric congestion most effectively by twisting the aryl group out of coplanarity. Tanida and Matsumura[4] carried out the study of aryl substituent effects in the solvolyses of several tertiary benzylic systems having bulky substituents and pointed out that the results give significantly reduced r values compared with $r \cong 1.00$ for solvolysis of the uncongested coplanar *t*-benzyl sytems due to the loss of coplanarity between the aryl and the carbenium center. We have also carried out further investigations on the precise dependence of resonance demand r upon the steric bulk of alkyl groups in a series of benzylic solvolysis systems.[5—10] The solvolysis of 1-*t*-butyl-3,3-dimethyl-1-phenylbutyl *p*-nitrobenzoate (**2**), 1-isopropyl-2,2-dimethyl-1-phenylpropyl *p*-nitrobenzoate (**3**), and 1-*t*-butyl-2,2-dimethyl-1-phenylpropyl *p*-nitrobenzoate (**4**) afforded Y–T correlations with $r = 0.78$, 0.68, and $r = 0.27$, respectively.[6,10] Furthermore, in the solvolysis of 1,2,3,4-tetrahydro-4-methyl-1,4-ethanonaphthalen-1-yl triflate (**5**), where the carbocation 2pπ AO located at the bridgehead of the bicyclic skeleton is set orthogonal to the benzo-π-orbital, the r value was found to be 0.0.[7]

The efficiency of resonance interaction is expressed as a function of $\cos^2\theta$, where θ is the dihedral angle between the two overlapping p-orbitals (Scheme 1),[3,11,12] and the resonance energy is considered to follow Eq. 3:

$$RE_\theta/RE_{\max} = r/r_{\max} = \cos^2\theta. \tag{3}$$

where $RE_{\max}$ is the resonance energy corresponding to a situation in which the aryl group lies in the plane of the carbenium ion, and RE_θ is that when there is an angle θ between these planes. It may be assumed that $r_\theta/r_{\max}$ of the Y–T equation is equivalent to $RE_\theta/RE_{\max}$ and then θ can be calculated by Eq. 3.

The ρ value is an important parameter in the analysis of the substituent effect, but it has not been interpreted sufficiently due to the complexities arising from the solvent and temperature effects. In our solvolysis studies, not only the r values but also the $|\rho|$ values were found to decrease for resonance-hindered systems.[10] The absolute value of ρ decreases from −4.6 of 1-methyl-1-phenylethyl system (**1**) to −3.4 of 1-*t*-butyl-3,3-dimethyl-1-phenylbutyl (**2**) and −3.1 of 1-isopropyl-2,2-dimethyl-1-phenylpropyl systems (**3**). In case of 1-*t*-butyl-2,2-dimethyl-1-phenylpropyl system (**4**), the ρ value is −2.2, which is a half of that of **1**. The $|\rho|$ value seems to decrease systematically as the bulkiness of benzyl substituents increases. This fact is expected to be a clue which suggests the origin of the ρ value. The reduction of $|\rho|$ value in the hindered systems is generally explained by the shift of transition state toward an earlier position along the reaction coordinate due to increased steric strain of the ground state reactant.[4,13,14] The comparisons of ρ and r values in solvolyses with those obtained in the corresponding gas phase cations should provide the definitive answer to such a problem concerning the position of transition state in the reaction coordinate. Thermodynamic stabilities of cations in the gas phase correspond to those of cationic intermediate in S_N1 solvolyses, so that the correlation results for cations can be interpreted directly as characteristic of intermediates.



Scheme 1. Decrease of resonance interaction.

Thus, it is expected that the ρ value in the gas phase will provide important information to interpret the ρ value in solvolysis.

We have successfully analyzed the substituent effects of the gas phase stability of benzylic carbocations in terms of Eq. 1.[3,15] The r values for the gas-phase stabilities of the cations have values identical to those of the corresponding benzylic S_N1 solvolyses. From this identity, the varying resonance demand r in solvolysis should be an essential feature of the incipient carbocation intermediate as well as of the solvolysis transition state.

We carried out ab initio calculations to optimize the structures of parent cations for sterically congested system.[12,16] It was found that the theoretical dihedral angles θ_{calc} optimized at the RHF/6-31G* level agreed well with corresponding θ_{sol} values estimated from the solvolyses.[3,10,12] This fact provides theoretical support for the claim that the r value is a good parameter to indicate the degree of resonance interaction between benzylic pπ-orbital and benzene π-system.

In order to discuss the dependence of the ρ and r values upon the steric bulk of benzylic alkyl groups, it is necessary to gather substituent effect data both for the solvolysis and the carbocation for a series of tertiary benzylic cations of varying extents of twisting of the aryl group out of coplanarity with the benzyl carbenium center. In the present study, we have chosen as congested systems; 1,2,2-trimethyl-1-phenylpropyl chloride (**6**)[17] and its *o*-Me derivative, 1,2,2-trimethyl-1-(2-methylphenyl)propyl *p*-nitrobenzoate (**7**) (Chart 1). In this paper, we report the substituent effects on the solvolysis rates for **6** and **7** systems and gas phase stabilities for the corresponding benzylic cations **6C**$^+$ and **7C**$^+$.

Results and Discussion

Substituent Effects on Solvolysis Rates. *Meta* and *para* substituted derivatives of 3,3-dimethyl-2-phenyl-2-butanols and 3,3-dimethyl-2-(2-methyl- and 4- and 5-substituted phenyl)-2-butanols were prepared by reaction of the corresponding aryllithium with 3,3-dimethyl-2-butanone, and converted into their chlorides and *p*-nitrobenzoates, respectively. Solvolysis rates of the chlorides **6** in 80% (v/v) aq acetone (80A) and *p*-nitrobenzoates **7** in 50% (v/v) aq ethanol (50E) were measured conductimetrically. Data are listed in Table 1.

The substituent effects on these systems were analyzed on the basis of Y–T equation (Eq. 1) and the results were compared with those of the Brown $\rho^+\sigma^+$ equation[19] in Table 2.

The r value generally remains the same for a tertiary dialkylbenzyl system irrespective of different leaving groups and varying solvents.[4,13,19] The less congested 1-methyl-1-phen-

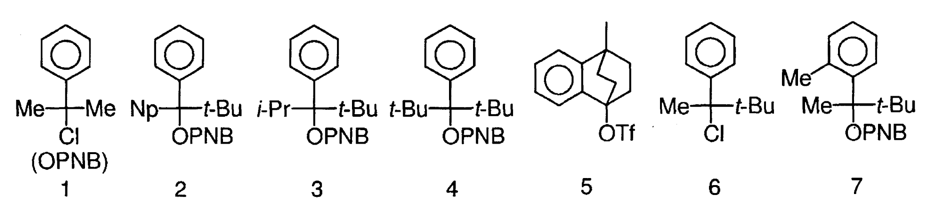


Chart 1.

Table 1. Solvolysis Rates of 1,2,2-Trimethyl-1-phenylpropyl Chlorides **6** and 1,2,2-Trimethyl-1-(2-methylphenyl)propyl *p*-Nitrobenzoates **7**

Subst.	**6**[a)] $10^5\ k_t/s^{-1}$ in 80A at 45 °C	**7**[b)] $10^5\ k_t/s^{-1}$ in 50E at 75 °C
p-MeO-*m*-Me	7232[c)]	
p-MeO	2927[c)]	105.6
p-MeS	224.2	
p-PhO	134.0	
3,4,5-Me_3	65.87	
p-MeO-*m*-Cl	59.42	11.78
m,*p*-Me_2	37.87	18.88
p-Me	19.69	9.890
p-*t*-Bu	13.21	
p-MeS-*m*-Cl	9.385	
p-Ph	5.760	
3,5-Me_2	4.117	
2-Naph	4.016	
m-Me	2.332	4.343
p-F	1.859	
H	1.323	1.920
p-Cl	0.3053	0.7819
p-Br	0.2859	
m-F	0.06016[c)]	
m-Cl	0.03931[c)]	0.1863
m-CF_3	0.009720[d)]	
p-CF_3	0.008376[d)]	

a) Chlorides in 80% aq acetone (80A) at 45 °C; Ref. 9. b) *p*-Nitrobenzoates in 50% aq ethanol at 75 °C. c) Extrapolated from other temperatures. d) Estimated from rate data in 50% aq acetone (50A) based on the linear logarithmic rates relation between 80A and 50A.

Table 2. Results of Correlation Analysis for 1,2,2-Trimethyl-1-phenylpropyl Solvolyses

Solvolysis systems	Correlation	ρ	r	R[a)]	SD[b)]	n[c)]
6[d)]	Y–T Eq.	−4.28±0.08	0.91±0.03	0.9986	0.088	22
	Brown Eq.	−4.06±0.06	(1.00)	0.9978	0.108	22
	meta-corr.	−4.19±0.09		0.9988	0.062	7
7[e)]	Y–T Eq.	−2.78±0.11	0.70±0.06	0.9980	0.064	8
	Brown Eq.	−2.25±0.16	(1.00)	0.9845	0.163	8
	meta-corr.	−2.78±0.32		0.9933	0.116	3

a) Correlation coefficients. b) Standard deviations. c) Numbers of substituents involved. d) Chlorides in 80% aq acetone at 45 °C. e) *p*-Nitrobenzoates in 50% aq ethanol at 75 °C.

ylpropyl and 1-isopropyl-2-methyl-1-phenylpropyl solvolyses both gave linear Y–T correlations with $r = 1.0$ independent of the polar effect of varying alkyl group.[8)]

The substituents effect in the solvolysis of less congested **6** in 80A at 45 °C is illustrated by the so-called Y–T plots in Fig. 1. Because of only small decrease in r in the solvolysis of **6**, it does not appear statistically significant enough to bring about a clear failure of the Brown σ^+ correlation. However, the σ^+ plots are neither randomly scattered nor smoothly curved; the discontinuously split pattern of the σ^+ plot in principle should be incompatible with any mechanistic interpretation other than inadequacy of σ^+. In fact a slightly better Y–T correlation with the lower r value of 0.91 was statistically observed, compared to $\rho^+\sigma^+$ analysis (Table 2).

The behavior of varying resonance demand is very clear in the solvolysis of **7** in Fig. 2, compared to that of **6**. While the *m*-substituents are correlated linearly with σ^0 to give a reference ρ_m line, the σ^+ points (open circles) of *p*-π-donor substituents deviate significantly and consistently downward from the *m*-line, suggesting an r value for this system lower than unity. The line-segments between σ^+ and σ^0 values for *p*-π-donor substituents measure the resonance capabilities of these substituents, i.e., the $\Delta\overline{\sigma}_R^+$ values. The ρ_m line divides all these line-segments at a constant internal ratio of 0.70, which represents the r value for this system. Thus, the Y–T correlation (ρ_{YT}) line can be defined as a line intersecting all line-segments for p-π-donors at such a constant ratio of r. In the application of Eq. 1 to the present data of **7**, we have obtained an excellent correlation ($\rho = -2.78$ and $r = 0.70$), as shown in Table 2.

Figure 3 shows the dependence of the standard deviations

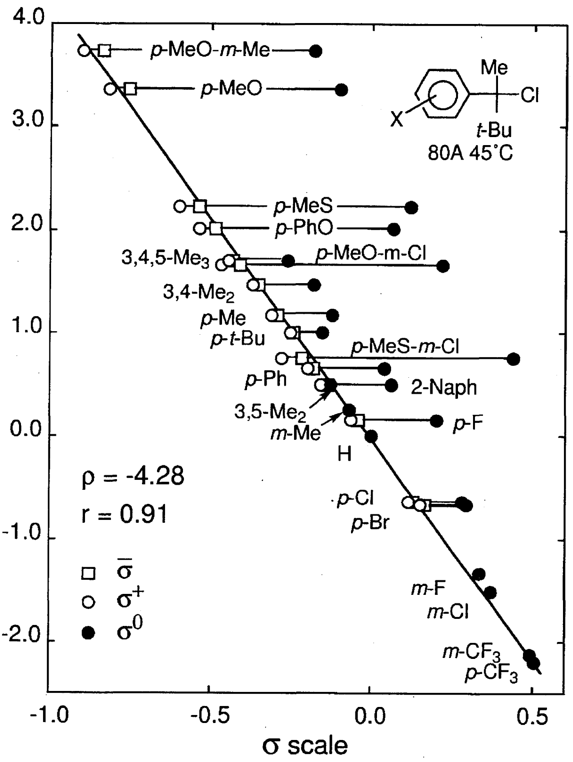


Fig. 1. The Y–T plots of substituent effect on the solvolysis of 1,2,2-trimethyl-1-phenylpropyl chlorides in 80% aq acetone at 45 °C: Open circles, σ^+, closed, σ^0, and squares, $\bar{\sigma}$ for $r = 0.91$.

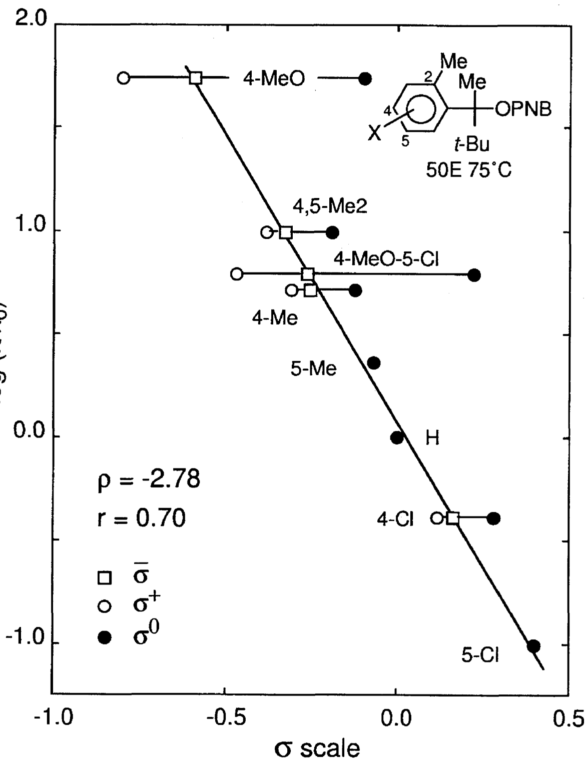


Fig. 2. The Y–T plots of substituent effect on the solvolysis of 1,2,2-trimethyl-1-(2-methylphenyl)propyl p-nitrobenzoates in 50% aq ethanol at 75 °C: Open circles, σ^+, closed, σ^0, and squares, $\bar{\sigma}$ for $r = 0.70$.

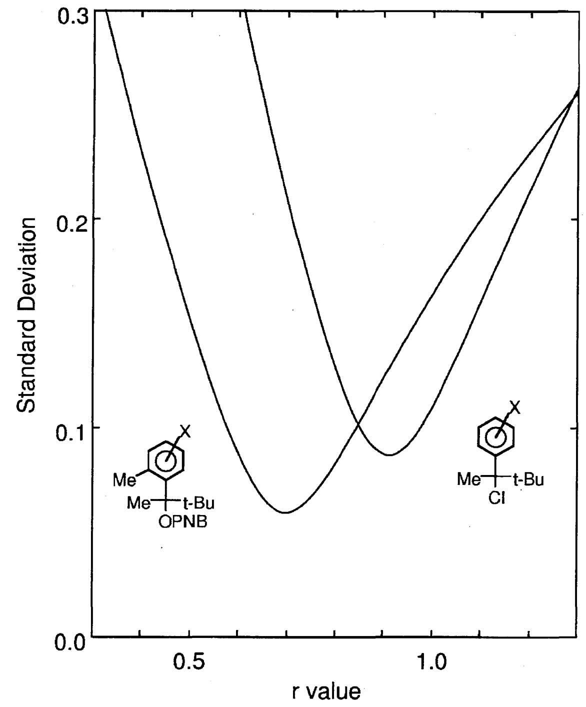


Fig. 3. The plots of standard deviations as a function of r values for the solvolyses of 1,2,2-trimethyl-1-phenylpropyl chlorides and 1,2,2-trimethyl-1-(2-methylphenyl)propyl p-nitrobenzoates.

(SD) upon r in the least-squares fitting to Eq. 1 without constraining the ρ value. The SD changes sensitively with varying r, giving a sharp wedge-shaped plot; any deviation from the best-fit r causes a sharp increase in the SD value. The steepness rather than the depth of the wedge plot is a more direct measure of the validity of the r value and therefore will be important for discussing varying resonance demand. The r values of 0.91 for **6** and 0.70 for **7** are statistically distinguished from $r = 1.00$ for **1**. Even if a large possible uncertainty in the r value may be allowed, the r value of 0.70 assigned for **7** is well outside the range of applicability of the σ^+ scale ($r = 1.00$).

These systems constitute a continuous spectrum of resonance demand parameters reflecting the bulk of α-alkyl substituents in the tertiary benzylic solvolysis series, which covers from the Brown σ^+ reference system **1** of entire benzylic π-delocalization to the σ^0 system for **5** as the lowest extreme of exalted π-delocalization, as summarized in Table 3. The decrease in the r parameter can be understood if we assume that in the transition state the aryl group has not attained complete coplanarity with the sp^2 reaction site. The correlations of substituent effects in **6**, **2**, **3**, and **7**, bearing moderately bulky alkyl groups, should therefore be of particular importance for exploring the continuity of variation in resonance effect with varying steric effects. Rotation of the aryl ring to increase the overlap between its orbital and the empty p orbital would be impeded in **4** and also somewhat in **2**, **3**, **6**, and **7** by steric interactions between aryl and benzylic alkyl groups.

The ρ values for the Y–T correlations, i.e., ρ_{YT} values, for

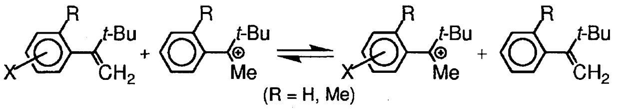
Table 3. Tertiary Benzylic Systems

Systems	**1**	**6**	**2**	**7**	**3**	**4**	**5**
Solvolysis							
ρ_{sol} value	$-3.96^{a,b)}$ $-4.54^{g)}$	$-4.28^{c)}$	$-3.37^{a,d)}$	$-2.78^{a)}$	$-3.09^{a,d)}$	$-2.2^{a,e)}$	$-2.2^{f)}$
r_{sol} value	1.0	0.91	0.78	0.70	0.68	0.27	0.0
$\theta_{sol}/^{\circ}$ h)	0	17	28	33	34	59	90
Gas Phase							
ρ_{gas} value	$-9.5^{i)}$	−9.1	$-6.7^{b)}$	−6.6			
r_{gas} value	1.0	0.89	$0.81^{b)}$	0.70			
$\theta_{gas}/^{\circ}$ h)	0	19	25	33			
MO Calculation							
$\theta_{calc}/^{\circ}$							
B3LYP/6-31G*	3	23	29	34	33	67	90
MP2/6-31G*	8	27	36	36	36	69	90
RHF/6-31G* j)	5	24	26	36	33	76	90

a) *p*-Nitrobenzoates in 50% aq ethanol at 75 °C. b) Unpublished data in this laboratory. c) Chlorides in 80% aq acetone at 45 °C, Ref. 9. d) Ref. 10. e) Ref. 6. f) Triflates in 80% aq ethanol at 75 °C, Ref. 7. g) Chlorides in 90% aq acetone at 25 °C, Ref. 19. h) Based on $\cos^2\theta = r/r_{max}$ where $r_{max} = 1.00$. i) Ref. 15a. j) Refs. 12 and 16 except for **7C**$^+$.

6 and **7** are also substantially smaller than those observed for uncongested tertiary benzyl substrates **1** (Table 3). It is concluded simply that the decrease in ρ value is consistent with the occurrence of an early transition state, as the ground state strain is progressively increased.[4,13,14] However, the diminution of ρ_{YT} as well as ρ_m occurs independently of the progressive change in resonance demand (r) caused by the steric loss of resonance.

Substituent Effects on Gas Phase Basicities. Substituent effects on gas phase basicities for 2-phenyl-3,3-dimethyl-1-butenes (**8**) and 2-(2-methylphenyl)-3,3-dimethyl-1-butenes (**9**), whose conjugate acids correspond to the cationic intermediate **6C**$^+$ and **7C**$^+$ in solvolyses of **6** and **7**, were measured at 343 K by the standard free energy changes of the proton-transfer equilibria (Eq. 4).



(4)

The relative basicities ($-\delta\Delta G^0$) obtained are summarized in Table 4. The relative stabilities of 1,2,2-trimethyl-1-phenylpropyl cations (**6C**$^+$) are plotted against the corresponding values of 1-methyl-1-phenylethyl cations (**1C**$^+$) in Fig. 4, the plot being regarded as a gas-phase σ^+-plot.[15a] There seems to be an excellent linear relationship ($R = 0.999$, SD = ±0.20) with a slope of unity for *meta* substituents and *p*-π-acceptor group, $(-\delta\Delta G^0_{6c^+})/2.303RT = 0.98\times(-\delta\Delta G^0_{1C^+})/2.303RT - 0.17$, and all *p*-π-donor substituents deviate slightly but systematically downward from this correlation line. Downward deviations of *p*-π-donors which are proportional to their $\Delta\overline{\sigma}^+_R$ are observed; the stronger π-donor substituents show the larger deviations. An application of Eq. 1 to **6C**$^+$ provides an r value of 0.89 lower than the unity for 1-methyl-1-phenylethyl cation with a comparable ρ of −9.1 (Fig. 5).

Table 4. Relative Gas Phase Stabilities $(-\delta\Delta G^{\circ})^{a)}$ of 1-Methyl-1-phenylethyl **1C**$^+$, 1,2,2-Trimethyl-1-phenylpropyl **6C**$^+$, and 1,2,2-Trimethyl-1-(2-methylphenyl)-propyl **7C**$^+$ Cations

Subst.	$-\delta\Delta G^{\circ}/\mathrm{kcal\,mol^{-1}}$		
	1C$^+$	**6C**$^+$	**7C**$^+$
p-MeO	10.5	8.6	5.1
p-MeS	10.0	8.1	
m,*p*-Me_2	6.1		3.5
p-MeO-*m*-Cl	6.7	5.5	2.9
p-Me	4.1	3.6	2.4
3,5-Me_2	3.5	3.6	
m-Me	1.8	2.0	1.4
H	$0.0\ (199.1)^{b)}$	$0.0\ (198.0)^{b)}$	$0.0\ (197.2)^{b)}$
p-F	−0.1	−0.7	
p-Cl	−0.4		−0.8
m-Cl	−4.7	−4.3	−3.5
m-F	−5.1	−4.7	
m-CF_3	−6.3	−6.0	
p-CF_3		−7.2	

a) In kcal mol^{-1}, a positive sign denotes greater basicity. b) Absolute GB values in kcal mol^{-1}.

$$\log(K/K_0) = (-\delta\Delta G^{\circ}_{6C^+})/2.303RT = -9.1(\sigma^0 + 0.89\Delta\overline{\sigma}^+_R)$$
$$(R = 0.999,\ SD = \pm 0.23). \qquad (5)$$

As the r value of 1.01 for 1-methyl-1-phenylpropyl and 1.02 for 1-ethyl-1-phenylpropyl cations are practically the same r value for **1C**$^+$,[20] it seems reasonable to assume the r value of unity for coplanar and tertiary benzylic cations, regardless of varying α-alkyl groups in the same way as in the solvolyses described above. Thus the reduced $r = 0.89$ obtained for 1,2,2-trimethyl-1-phenylpropyl cation (**6C**$^+$) seems to be significant, though not distinctly small, and can be attributed to the decreased resonance interaction between benzylic p-orbital and benzene π-system caused by the twisted structure.

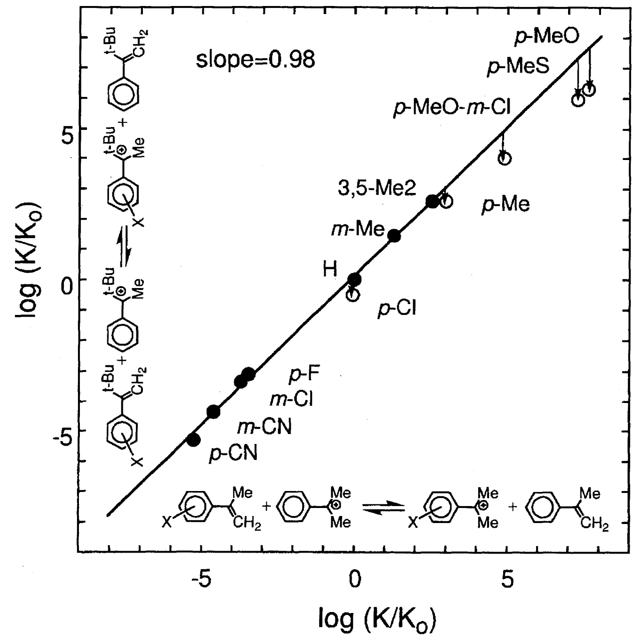


Fig. 4. Plots of gas phase stabilities of 1,2,2-trimethyl-1-phenylpropyl cations against those of 1-methyl-1-phenylethyl cations.

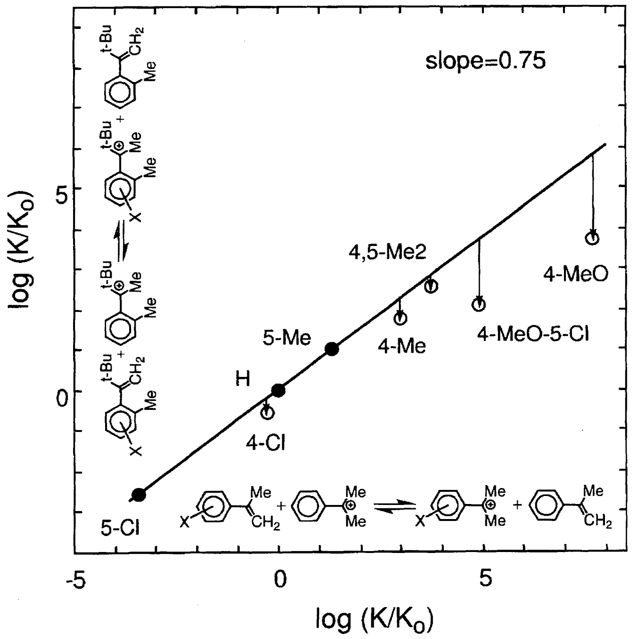


Fig. 6. Plots of gas phase stabilities of 1,2,2-trimethyl-1-(2-methylphenyl)propyl cations against those of 1-methyl-1-phenylethyl cations.

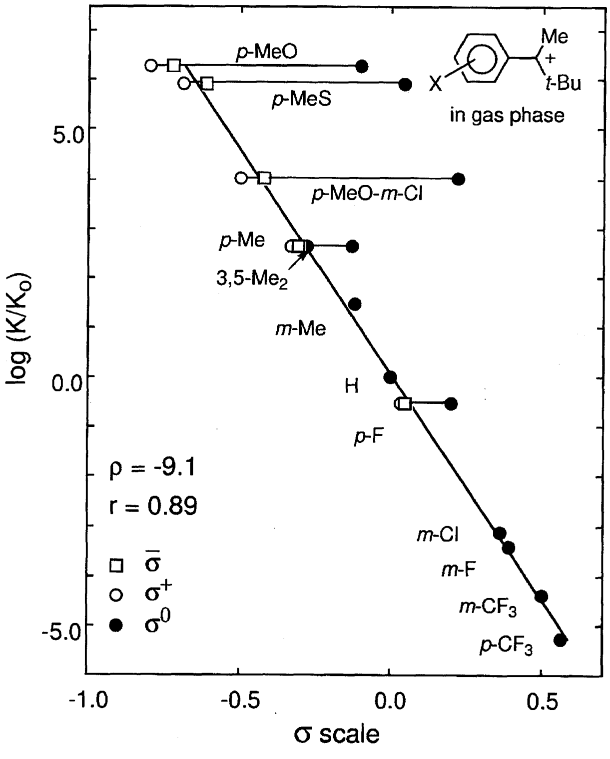


Fig. 5. The Y–T plots of substituent effect on the gas phase stabilities of 1,2,2-trimethyl-1-phenylpropyl cations: Open circles, σ^+, closed, σ^0, and squares, $\bar{\sigma}$ for $r = 0.89$.

A similar nonlinearity between the relative stabilities of 1,2,2-trimethyl-1-(2-methylphenyl)propyl cations (**7C**$^+$) and the corresponding values of **1C**$^+$ is shown in Fig. 6. Whereas the overall non-linearity is more significant for **7C**$^+$ ($R = 0.975$, SD = ±0.32) than for **6C**$^+$, there seems to be an excellent linear relationship with a slope of 0.75 for *m*-substituents, $(-\delta\Delta G^\circ{}_{7\mathrm{C}^+})/2.303RT = 0.75\times(-\delta\Delta G^\circ{}_{1\mathrm{C}^+})/2.303RT + 0.03$ ($R = 0.999$, SD = ±0.03), and all *p*-π-donor substituents deviate systematically and significantly downward from this correlation line, indicating the inadequacy of the σ^+-constant to this system. The line with a slope of 0.75 for *meta* substituents suggests that the stabilization of this cation by these substituents is smaller than that for **1C**$^+$. The resonance contribution of the *p*-π-donor substituents in cation **7C**$^+$ should be lower than those in **6C**$^+$ and **1C**$^+$. An application of the Eq. 1 to **7C**$^+$ (Fig. 7) provides an r value of 0.70, lower than 0.89 of **6C**$^+$ and unity of **1C**$^+$, and a ρ value of −6.6 which is significantly lower than those of **6C**$^+$ and **1C**$^+$.

$$\log(K/K_0) = (-\delta\Delta G^\circ_{7\mathrm{C}^+})/2.303RT = -6.6(\sigma^0 + 0.70\Delta\bar{\sigma}_\mathrm{R}^+) \quad (R = 0.997,\ \mathrm{SD} = \pm 0.18). \quad (6)$$

These r values 0.89 for **6C**$^+$ and 0.70 for **7C**$^+$ are in complete agreement with 0.91 and 0.70 obtained from the solvolyses of **6** and **7**, respectively. In addition, the gas phase stability of cation **2C**$^+$ can be correlated excellently with Eq. 1 to give an r of 0.81,[21] which is identical to the value observed for the 1-*t*-butyl-3,3-dimethyl-1-phenylbutyl solvolysis.[10] The identity of r values between the solvolysis and the gas phase stability is observed also for sterically twisted carbocations (Table 3). This reveals that the structure of the transition state of solvolysis should be quite close to that of the cationic intermediate.

Steric Loss of Resonance. The efficiency of resonance interaction can be expressed as in Eq. 3 as a function of $\cos^2\theta$, where θ is the dihedral angle between two overlapping p-orbitals.[11,12] An intrinsic r_max value may be taken

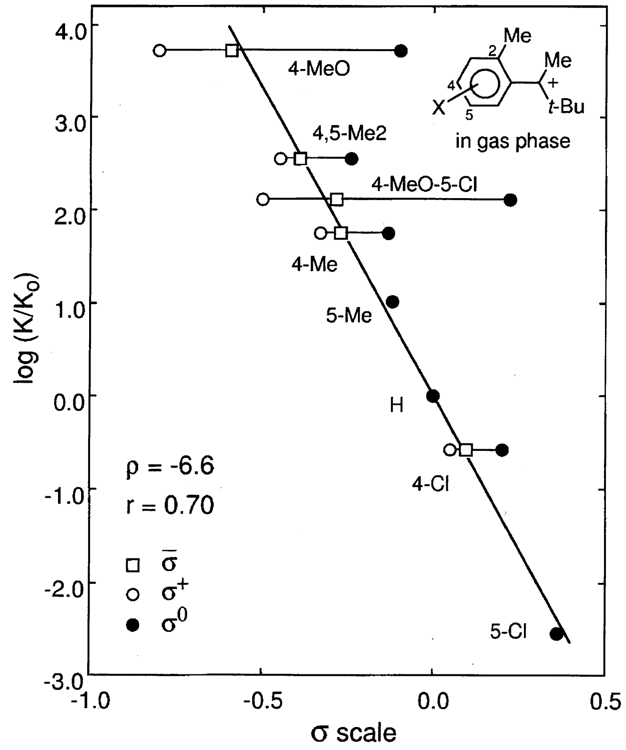
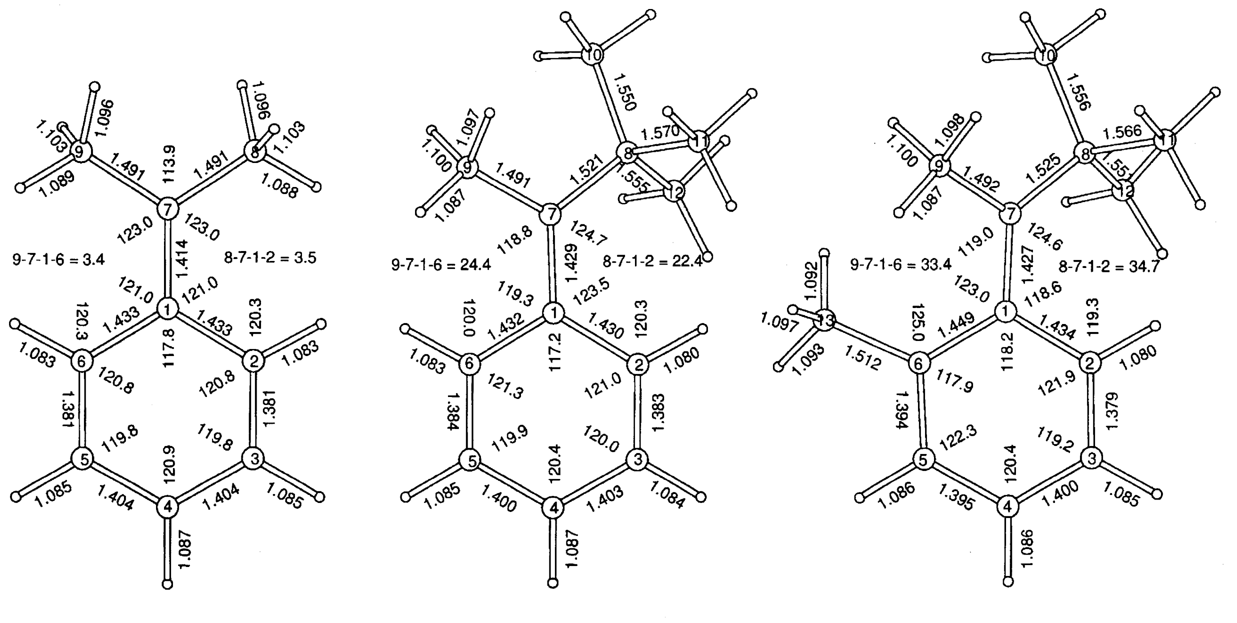


Fig. 7. The Y–T plots of substituent effect on the gas phase stabilities of 1,2,2-trimethyl-1-(2-methylphenyl)propyl cations: Open circles, σ^+, closed, σ^0, and squares, $\bar{\sigma}$ for $r = 0.70$.

to be unity for solvolyses forming coplanar tertiary dialkyl(phenyl)methyl cations.[8] Thus, from the ratios $r/r_{\max}$ for these solvolyses, which can be related to the efficiency of benzylic resonance interaction, the torsion angles θ in the transition states may be estimated by Eq. 3. In Table 3, the r values and the calculated dihedral angles θ between aryl and tertiary carbenium sp^2 planes are compared for a series of dialkyl(aryl)methyl solvolyses. The torsion angles θ in the gas-phase cations **6C$^+$** and **7C$^+$** are identical to those derived from the corresponding solvolyses.

The structures of carbenium ions can be precisely and unambiguously estimated by the most advanced molecular orbital calculation. The geometry optimizations of parent benzylic cations **6C$^+$** and **7C$^+$** have been carried out by means of ab initio method with the RHF/6-31G*, MP2/6-31G*, and Becke3LYP/6-31G* (hereafter B3LYP/6-31G*) levels. Structures of **1C$^+$**, **6C$^+$**, and **7C$^+$** optimized at the B3LYP/6-31G* level are shown in Fig. 8. Olah et al.[22] reported $\theta = 8\pm2°$ for the dihedral angle of **1C$^+$** from crystallographic study, which agrees with our $\theta_{\text{calcd}} = 3°$ (Table 3). The calculated structure also reproduces their crystallographic data within experimental error. Small intramolecular steric hindrance in **1C$^+$** seems to be reduced in two ways. (a) α-Alkyl groups and aromatic ring moved far apart from each other; angles of $\angle C_8C_7C_1$, $\angle C_9C_7C_1$, $\angle C_7C_1C_2$, and $\angle C_7C_1C_6$ are increased in 1—3° from normal sp^2 trigonal angle (120°). (b) The side chain which includes α-alkyl groups is rotated around C_1–C_7 axis; the dihedral angle θ_{calcd} is increased in 3° from coplanar structure. α-*t*-Bu group in the cations **6C$^+$** and **7C$^+$** brings about larger steric hindrance compared to **1C$^+$**. Effect (a) in **6C$^+$** and **7C$^+$** does not seem to differ much from that in **1C$^+$**. Effect (b) is important to reduce steric hindrance; θ_{calcd} is increased to 23° for **6C$^+$** and 34° for **7C$^+$**.

Calculated dihedral angles (θ_{calcd}) of the optimized structures are summarized in Table 3 together with those for rel-



1C$^+$　**6C$^+$**　**7C$^+$**

Fig. 8. Some geometric parameters of 1-methyl-1-phenylethyl **1C$^+$**, 1,2,2-trimethyl-1-phenylpropyl **6C$^+$**, and 1,2,2-trimethyl-1-(2-methylphenyl)propyl **7C$^+$** cations optimized at the B3LYP/6-31G* level. Lengths are given in angstroms, angles in degrees. The C atoms are labeled by their numbers.

evant benzylic carbenium ions (**1C**$^+$–**5C**$^+$). The calculated dihedral angles of the optimized structures are, even though slightly dependent on the theories, in good agreement with the experimental angles based on Eq. 3 of the solvolysis transition state and/or of the gas-phase carbenium ions.

Steric Effects on the Yukawa–Tsuno Correlations. The value $\theta_{\rm calcd}$ of 23° for cation **6C**$^+$ is in good agreement with the above experimental value of $\theta_{\rm sol} = 17°$ for the solvolysis transition state and $\theta_{\rm gas} = 19°$ for the gas-phase cation of **6C**$^+$. Similarly, the dihedral angle 34° of the optimized cation **7C**$^+$ is in good agreement with that (33°) obtained from the r value for the solvolysis and the gas phase carbocation formation. In addition, all $\theta_{\rm calcd}$ agree well with $\theta_{\rm sol}$ and $\theta_{\rm gas}$ available for benzylic systems **1C**$^+$–**7C**$^+$.

Thus the twisting angle $\theta = 17°$ for **6** and $\theta = 33°$ for **7** is estimated for the transition state by Eq. 3, and are identical to the angle $\theta = 19°$ and 33° calculated from the corresponding gas-phase cations, respectively. This further leads to a conclusion that the cation can be used as a model of resonance structure of the transition state of benzylic solvolysis. This identity of r value between the solvolysis reactivity and the corresponding gas-phase cation stability provides quite important information concerning the real picture of the solvolysis transition state. Although ρ values of gas phase cations are twice as large as those for the solvolysis, the degree of charge-delocalization into the aryl ring will remain essentially the same in the gas phase as in the solution.[3,15] The solvation of the cation lowers the response to substituent perturbation, essentially without any change in intramolecular charge-delocalization. Furthermore, the charge delocalization in the $\rm S_N1$ transition state in the benzylic solvolysis should also be quite close to that of the carbocation intermediate. The structure of the carbenium ion can model that of the transition state as well as of the solvolysis intermediate which follows closely after the transition state. This confirms that the observed decrease in the r value should be ascribed to a loss of the resonance interaction due to a deviation out of the coplanarity between the carbenium center and the benzene π-system rather than to a shift in the transition state coordinate.

The close agreement between theoretically calculated and empirically derived dihedral angles assigned for twisted benzylic systems provides a theoretical basis for characterization of the r value in the Yukawa–Tsuno equation as the empirical parameter reflecting the degree of π-delocalization interaction between the aryl group and the reaction site.

The appreciable decrease in the ρ value in these congested solvolyses has been observed to be always accompanied by a decrease in r value, compared with that for the uncongested benzylic solvolysis. The reduced ρ value may be related to the shift of this transition state toward an earlier position along the reaction coordinate. However, the present work clearly demonstrates that a significant decrease in the ρ value is observed in the sterically twisted bulky carbenium ion system in the gas phase. This argues against the explanation in terms of the Hammond shift towards an earlier transition state. It follows that either the extended π-delocalization to the incipient carbenium p-orbital or the exalted π-bond order of aryl-$\rm C_\alpha$ bond plays an important part in the attenuation of the polar effect of substituents. This point will be considered further for a wider series of congested carbenium systems.

Experimental

Materials. 3,3-Dimethyl-2-phenyl-2-butanols and 3,3-Dimethyl-2-(2-methylphenyl)-2-butanols: Under nitrogen, bromobenzene or 2-methylbromobenzene (0.12 mol) in ether (100 cm^3) was added to 15% butyllithium in hexane solution (75 cm^3, 0.12 mol) at −40 °C. After stirring for 1 h at room temperature, 3, 3-dimethyl-2-butanone (0.12 mol) in ether (100 cm^3) was added to the reaction mixture at −30 °C. The 3,3-dimethyl-2-phenyl-2-butanols obtained were purified by distillation, column chromatography or recrystallization. 3,3-Dimethyl-2-(2-methylphenyl)-2-butanols were used to the next step without purification to prepare p-nitrobenzoates **7** and 3,3-dimethyl-2-(2-methylphenyl)-1-butenes (**9**).

1,2,2-Trimethyl-1-phenylpropyl chlorides (6): Into a solution of 3,3-dimethyl-2-phenyl-2-butanol in ether in the presence of anhydrous $\rm CaCl_2$ was bubbled dry hydrogen chloride at 0 °C for 4 h. The reaction mixture was filtered after drying with anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. This procedure was repeated till excess HCl was completely removed. For derivatives having more electron-attracting groups than m-Cl, $\rm CH_2Cl_2$ was used as a solvent at room temperature to prevent generation of rearranged olefin.[23] All chlorides obtained are used for rate measurements without further purification.

1,2,2-Trimethyl-1-(2-methylphenyl)propyl *p*-Nitrobenzoates (7):[4,10,24] Under argon, a 15% butyllithium solution in hexane (9.2 cm^3, 15 mmol) was added to 3,3-dimethyl-2-(2-methylphenyl)-2-butanols (10 mmol) in THF 10 cm^3 at −30 °C and the mixture was heated under reflux for 2 h. p-Nitrobenzoyl chloride (1.9 g, 10 mmol) in THF 10 cm^3 was added to the above alkoxide solution at −30 °C over 20 min with stirring. The reaction mixture was allowed to stand overnight at room temperature and then treated with ice water. The crude ester was extracted with ether and was purified through column chromatography and recrystallized from benzene–hexane.

3,3-Dimethyl-2-phenyl-1-butenes (8): 3,3-Dimethyl-2-phenyl-2-butanol was passed over activated alumina at 275 °C, under 40 mmHg (1 mmHg = 133.322 Pa) for 1 h.[25] The product was dried with anhydrous magnesium sulfate in ether. The crude olefin was obtained by evaporation of solvent, and was purified by column chromatography on $\rm SiO_2$. Olefins were subjected to several freeze-pump-throw cycles on the ICR inlet system to remove any volatile impurities.

3,3-Dimethyl-2-(2-methylphenyl)-1-butenes (9): Into a solution of 3,3-dimethyl-2-(2-methylphenyl)-2-butanol in ether in the presence of anhydrous $\rm CaCl_2$ was bubbled dry hydrogen chloride at 0 °C for 4 h. The reaction mixture was stirred overnight at room temperature, and then the solvent and excess HCl were removed to give the crude olefin **9**, which was purified in the same procedure as that of **8**.

The physical data of 3,3-dimethyl-2-phenyl-2-butanols, p-nitrobenzoates **7**, and olefins **8** and **9** are listed in Tables 5, 6, and 7.

Solvents: Ethanol, acetone, and water were purified by the established method as described before.[10,26] Fifty % (v/v) aq ethanol was prepared by mixing equal volumes of ethanol and water at 25 °C. Eighty % (v/v) aq acetone was prepared by mixing 80 : 20

Table 5. Physical and Analytical Data of 3,3-Dimethyl-2-phenyl-2-butanols

Subst. X	Mp[°C] or bp (°C/mmHg)	Carbon/% Found	Carbon/% Calcd	Hydrogen/% Found	Hydrogen/% Calcd
p-MeO-*m*-Me	Liq.	75.52	75.60	9.91	9.91
p-MeO	[53.4—53.9]	74.79	74.96	9.73	9.68
p-MeS	[41.9—42.6]	69.51	69.56	8.99	8.98
p-PhO	[56.2—57.2]	79.87	79.96	8.20	8.26
3,4,5-Me$_3$	Liq.	81.41	81.76	10.69	10.98
p-MeO-*m*-Cl	Liq.	64.48	64.32	7.89	7.89
3,4-Me$_2$	Liq.	81.31	81.50	10.65	10.75
p-Me	Liq.[a)]	81.06	81.20	10.47	10.48
p-*t*-Bu	[83.6—85.6]	81.72	81.99	11.02	11.18
p-MeS-*m*-Cl	[75.5—76.0]	60.35	60.33	7.29	7.40
p-Ph	[70.5—71.6]	84.85	84.99	8.67	8.72
2-Naph	[75.7—76.9]	84.08	84.16	8.83	8.83
3,5-Me$_2$	(88.0—91.0/0.5)	81.36	81.50	10.70	10.75
m-Me	Liq.	81.05	81.20	10.49	10.48
p-F	Liq.	73.17	73.44	8.69	8.73
H	Liq.[b)]	80.75	80.85	10.15	10.18
p-Cl	(97.0—99.0/1)	67.96	67.76	8.10	8.16
p-Br	Liq.	56.08	56.05	6.64	6.66
m-F	(75.0—76.0/1)	73.28	73.44	8.76	8.73
m-Cl	Liq.	67.77	67.76	8.16	8.06
m-CF$_3$	[30.5—31.2]	63.53	63.40	6.89	6.96
p-CF$_3$	(109—111/9)[c)]	63.42	63.40	6.95	6.96

a) Lit,[23)] bp 98 °C/2.5 mmHg (1 mmHg = 133.322 Pa). b) Lit,[23)] bp 95.5 °C/4.5 mmHg. c) Lit,[23)] bp 85 °C/1.7 mmHg.

Table 7. Physical and Analytical Data of 3,3-Dimethyl-2-phenyl-1-butenes and 3,3-Dimethyl-2-(2-methylphenyl)-1-butenes

Subst. X	Carbon/% Found	Carbon/% Calcd	Hydrogen/% Found	Hydrogen/% Calcd
3,3-Dimethyl-2-phenyl-1-butenes				
p-MeO	81.88	82.06	9.45	9.53
p-MeS	75.82	75.67	8.82	8.79
p-MeO-*m*-Cl	69.28	69.48	7.53	7.63
p-Me	89.48	89.51	10.29	10.41
3,5-Me$_2$	89.28	89.29	10.77	10.71
m-Me	89.75	89.51	10.44	10.41
H	89.69	89.94	9.95	10.06
p-F	80.80	80.86	8.41	8.41
m-Cl	73.83	74.03	7.72	7.77
m-F	80.95	80.86	8.47	8.48
m-CF$_3$	68.28	68.41	6.61	6.62
p-CF$_3$	68.22	68.41	6.68	6.62
3,3-Dimethyl-2-(2-methylphenyl)-1-butenes				
4-MeO	82.23	82.30	9.98	9.87
4,5-Me$_2$	88.90	89.04	11.07	10.96
4-MeO-5-Cl	70.66	70.43	7.87	8.02
4-Me	89.26	89.30	10.65	10.71
5-Me	89.21	89.30	10.64	10.71
H	89.73	89.59	10.19	10.41
4-Cl	74.76	74.81	8.21	8.21
5-Cl	74.72	74.81	8.37	8.21

volumes of acetone and water at 25 °C.

Kinetic Measurement.[10,26)] Solvolysis rates of the chlorides **6** in 80% (v/v) aq acetone (80A) at 45 °C and the *p*-nitrobenzoates **7** in 50% (v/v) aq ethanol (50E) at 75 °C were determined conductimetrically. Conductance measurements were made using approximately 50 cm^3 of 10^{-4}—10^{-5} mol dm^{-3} solution of the starting substrates (1—2 mg) in a thermostatted bath controlled within ±0.02 °C. In case of **7**, excess lutidine (2—5 μl) was added. For the conductivity measurement in 50E, complete dissolution of substrate can be attained relatively quickly by first dissolving the starting **7** in a small amount of absolute ethanol and then adding it to the 50E solvent together with the adjustable amount of water. Conductance readings were taken automatically by using a conductivity meter (CM-60S, Toa Electronics Ltd.) connected to a computer. Solvolyses were followed by taking at least 100 readings at appropriate intervals for 2.5 half-lives; the infinity reading was taken after 10 half-lives. The precision of fit to first-order kinetics was generally satisfactory over 2.5 half-lives ($R > 0.99995$). The experimental errors in individual runs were generally less than 1.5% and rate constants from repeated runs were reproducible within an accuracy of 3%.

Gas Phase Measurements. The equilibrium-constant measurements for 1,2,2-trimethyl-1-phenylpropyl system were performed on a homemade pulsed ion cyclotron resonance mass spectrometer and an Extrel FTMS-2001 used for 1,2,2-trimethyl-1-(2-methylphenyl)propyl system. Details concerning the experimental techniques used for the measurements of the equilibrium constants (K) of the proton-transfer reaction (7), where B refers to a given olefin and B$_0$ is a reference base, were described previously.[15)]

$$\mathrm{B} + \mathrm{B_0H^+} \rightleftarrows \mathrm{BH^+} + \mathrm{B_0} \tag{7}$$

$$\Delta G^\circ = -RT\ln K = -RT\ln\,[\mathrm{B_0/B}][\mathrm{BH^+/B_0H^+}]. \tag{8}$$

All measurements were performed at 70 °C at a constant magnet field strength of 1.3 Tesla (or at 3.0 Tesla on the Extrel FTMS-2001). The overall pressures of the reagents were maintained at

Table 6. Physical and Analytical Data of 1,2,2-Trimethyl-1-(2-methylphenyl)propyl *p*-Nitrobenzoates

Subst. X	Mp/°C	Carbon/% Found	Carbon/% Calcd	Hydrogen/% Found	Hydrogen/% Calcd	Nitrogen/% Found	Nitrogen/% Calcd
4-MeO	165.0—166.0	67.61	67.91	6.81	6.78	3.68	3.77
4,5-Me$_2$	130.5—132.0	71.70	71.52	7.41	7.37	3.77	3.79
4-MeO-5-Cl	141.0—142.0	62.15	62.15	5.91	5.96	3.41	3.45
4-Me	109.0—110.2	71.00	70.97	7.11	7.09	3.94	3.94
5-Me	98.0—99.3	71.05	70.97	7.03	7.09	3.93	3.94
H	136.5—137.1	70.10	70.36	6.77	6.79	4.08	4.10
4-Cl	138.8—140.0	64.06	63.91	5.82	5.90	3.70	3.73
5-Cl	114.5—115.5	64.20	63.91	5.93	5.90	3.71	3.73

$(1—3)\times10^{-4}$ Pa. After a reaction period of several hundred ms to 1 s, depending upon the reactant, equilibrium was attained. Then the relative abundances of BH^+ and B_0H^+ were measured by the signal intensities of the ICR spectra. Each experiment was performed at several ratios of the partial pressures and at different overall pressures. The arithmetic-mean values of K from Eq. 8 were used to calculate ΔG° at 343 K with an average uncertainty of ±0.2 kcal mol^{-1} (1 cal = 4.184 J). More than two reference compounds were used in most cases in order to ensure the internal consistency of the data.

MO Calculations. All ab initio LCAO-MO calculations[27] have been performed on the Digital UNIX workstation (Dragon Alpha, Scientists' Paradise, Inc.) with GAUSSIAN-94 suite of programs.[28] Geometries have been optimized completely by the gradient procedure at the C_1 symmetry. The closed-shell restricted Hartree–Fock calculation with 6-31G* basis sets has been applied to find stationary points on the potential energy surface for **7C**$^+$. At the RHF/6-31G* level, optimized structure has been checked by the analysis of harmonic vibrational frequencies obtained from diagonalization of force constant matrices. For cations **1C**$^+$–**6C**$^+$, the same level of calculations was reported before.[12,16] Since the electron correlation may become important for congested molecules, Møller–Plesset perturbation theory[29] was applied to these benzylic cations. MP2 optimizations were carried out for **1C**$^+$–**7C**$^+$ at the 6-31G* basis set using the frozen-core approximation. The geometries were further optimized by means of a hybrid density-functional theory; Becke's three-parameter hybrid method using the LYP correlation functional (Becke3-LYP)[30] is performed with the 6-31G* basis set for these cations.

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