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SHORT COMMUNICATION

NONPLANAR PHENYL RING AND INVERSE ORDER OF SOLVOLYTIC REACTIVITY FOR TERTIARY BENZYLIC SUBSTRATES

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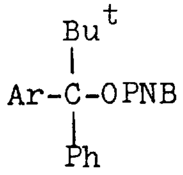
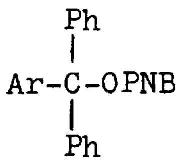
ABSTRACT

The rates of solvolysis of 1-aryl-1-phenyl-2,2-dimethylpropyl(**1**) *p*-nitrobenzoates and of aryldiphenylmethyl-*p*-nitrobenzoates (**2**) were measured in 80% acetone. An inverse order of reactivity, $k_{p\text{-CF}_3}/k_{m\text{-CF}_3} > 1$ was observed for **1** but not for **2**. The X-ray crystallogoraphic study of the parent compounds, 1,1-diphenyl-2,2-dimethylpropyl-*p*-nitrobenzoate (**1b**) and triphenylemethyl benzoate (**3b**), and of 2-phenyl-2-propyl-*p*-nitrobenzoate (*4*) indicated that in the highly congested system **1** both phenyl rings were nonplanar, whereas the phenyl rings in **3** and **4** were essentially planar.

In a recent communication[1] we reported that the observation of an inverse order of solvolytic reactivities, $k_p/k_m > 1$, for substrates containing electron-attracting α-aryl substituents could be used as a probe for the lack of significance of resonance contribution in the cationic transition states. We now wish to report an additional evidence of such an abnormal reactivity, i.e. $k_{P\text{CF}_3}/k_{m\text{-CF}_3} = 1{\cdot}12$ for 1-aryl-1-phenyl-2,2-dimethylpropyl-*p*-nitrobenzoates (**1**) at 25 °C. Moreover, X-ray crystallographic data reveal significant deviations from planar structure for phenyl rings in **1b**, and not for triphenylmethyl benzoate (**3b**) or 2-phenyl-2-propyl-*p*-nitrobenzoate (**4**). This is the first illustration of the nonplanarity of monosubstituted benzene


$\mathrm{Ar{-}\overset{\overset{Bu^t}{|}}{\underset{\underset{Ph}{|}}{C}}{-}OPNB}$

1
a: Ar = *p*—CH$_3$
b: Ar = H
c: Ar = *m*—CF$_3$
d: Ar = *p*—CF$_3$


$\mathrm{Ar{-}\overset{\overset{Ph}{|}}{\underset{\underset{Ph}{|}}{C}}{-}OPNB}$

2
a; Ar = *m*—CH$_3$
b: Ar = H
c: Ar = *m*—CF$_3$
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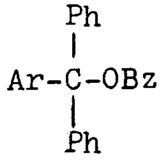
$\mathrm{Ar{-}\overset{\overset{Ph}{|}}{\underset{\underset{Ph}{|}}{C}}{-}OBz}$

3
a; Ar = *m*—CH$_3$
b: Ar = H

PNB: *p*-nitrobenzoate; Bz: benzoate

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with a severe crowding at the benzylic carbon, which accounts for the abnormal rate ratio $k_p/k_m > 1$.

The preparation of aryldiphenylmethyl-*p*-nitrobenzoates (**2**) and benzoates (**3**) was accomplished by using the newly developed one-pot procedure.[2] The solvolyses were carried out in 80% acetone at appropriate temperature, and the rates were followed titrimetrically in duplicate, with an experimental error of less than 2%. For the isomeric pairs**1c**/**1d** and **2c**/**2d** the rates were measured by running the reactions side by side in the same thermostat. The rates for the reactive *p*-nitrobenzoates **2a** and **2b** were calculated by multiplying the rates of the benzoates **3a** and **3b**, respectively, by a factor of 20·8.[3] The results are shown in Table 1.

Table 1. Rate constants for solvolysis of some benzylic esters[a]

Substrate	10^5k, s^{-1}	T, °C	k_p/k_m(25 °C)
1a	50·3	75	
	2·34	50	
	$6{\cdot}50 \times 10^{-2}$[b]	25	
1b	25·7	90	
	4·52	75	
	$3{\cdot}89 \times 10^{-3}$[b]	25	
1c	25·5	125	
	2·04	100	
	$8{\cdot}21 \times 10^{-5}$[b]	25	1·12
1d	26·5	125	
	2·15	100	
	$9{\cdot}17 \times 10^{-5}$[b]	25	
2a	99·2[c]	25	
2b	69·3[d]	25	
2c	5·21	25	
2d	3·06	25	0·587

[a] In 80% acetone.

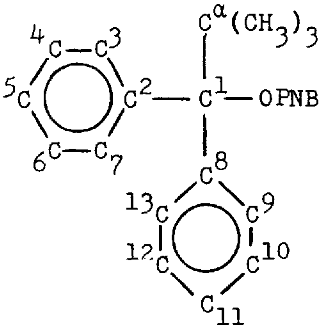
[b] Extrapolated from data at higher temperature.

[c] By multiplying the rate constant of **3a**, $4{\cdot}77 \times 10^{-5}s^{-1}$, by 20·8(Reference 3)

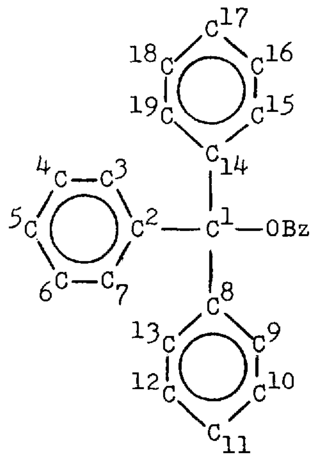
[d] By multiplying the rate constant of **3b**, $3{\cdot}33 \times 10^{-5}s^{-1}$, by 20·8 (Reference 3)

Hammett–Brown treatment[4] of the rate data gave excellent linear plots for both systems, $\rho = -3{\cdot}18$ (correlation coefficient 0·993) for **1** and $\rho = -2{\cdot}20$ (correlation coefficient 0.999) for **2**. However, an inverse order of reactivity, $k_p/k_m > 1$, was realized in the case of **1c** vs **1d**. Obviously, it is in line with the proposal[1] that the substrate has a highly crowded reaction center, and the deactivated aryl ring in **1**, deviates appreciably from the cationic sp^2 plane developed in the transition state. Moreover, the inherent drawback[1] in the simple linear free energy treatment is once again observed.

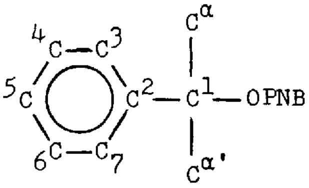
The results obtained from X-ray structural analyses are also remarkable. Single crystals of **1b**, **3b** and **4** were subjected to the diffraction study on a 4-circle diffractometer. The data processing was performed by using NRCC-SDP programs.[5] Each structure was fully refined and yielded agreement indices R of 0·08, 0·04 and 0·05, respectively. The bond lengths, bond angles and torsional angles in **4** are in good agreement with those observed by Tidwell and co-workers.[6] The detailed analyses of the crystal structure will be reported elsewhere, and the



1b



3b



4

Table 2. Pertinent bond lengths (Å) for some benzylic esters

Bond	**1b**	**3b**	**4**
C^1—C^α	1·592(6)		1·511(4)
C^1—$C^{\alpha'}$			1·530(4)
C^1—O	1·463(5)	1·465(3)	1·487(3)
C^1—C^2	1·539(7)	1·521(4)	1·509(3)
C^1—C^8	1·535(7)	1·540(4)	
C^1—C^{14}		1·536(4)	

pertinent data are listed in Tables 2,3, and 4. The variations of bond angles at the carbinyl carbon (C^1 in Scheme 2) are nearly the same in all three cases. The significant lengthening of $C(sp^3)$—$C(sp^3)$ in **1b**, 1·592 Å, is an indication of the steric crowding at C^1, although it is less profound than that in the tri-*tert*-butylmethyl system in which the C—C distance at the carbinyl carbon is 1·618Å.[7]

The result of examining the torsional angles for carbon atoms that define the phenyl rings (Table 3) is especially noteworthy. In **4** the planarity of the phenyl moiety could be assured by the observation of small torsional angles, $\phi \leq 1·8°$. The deviation of carbon atoms from the least-square plane is in the order of 10^{-3}Å. The two phenyl rings in **3b** are also essentially planar, whereas the third one is slightly puckered ($\phi \leq 2·6°$). On the other hand, both phenyl rings in the highly congested substrate **1b** deviate from the planar structure, as are shown by the larger torsional angle of 3·5–4°, as well as by larger displacement, 0·039 Å, from the least-squares plane of the ring. This is the first correlation noted for a nonplanar monosubstituted benzene ring in a substrate with the inverse order of solvolytic reactivity due to the steric crowding at the benzylic carbon atom.

Table 3. Pertinent bond and torsional angles (°) in some benzylic esters[a]

Angle	**1b**	**3b**	**4**
O—C^{1}—C$^{\alpha}$	102·4		109·3
O—C^{1}—C$^{\alpha'}$			101·4
O—C^{1}—C$^{\alpha}$	106·9	108·6	108·9
O—C^{1}—C^{8}	107·8	103·2	
O—C^{1}—C^{14}		109·8	
C^{2}—C^{1}—C$^{\alpha}$	111·7		115·6
C^{2}—C^{1}—C$^{\alpha'}$			110·7
C^{2}—C^{1}—C^{8}	117·1	111·3	
C^{2}—C^{1}—C^{14}		115·8	
C^{8}—C^{1}—C$^{\alpha}$	109·8		
C^{8}—C^{1}—C^{14}		107·4	
C$^{\alpha}$—C^{1}—C$^{\alpha'}$			109·9
C^{2}—C^{3}—C^{4}—C^{5}	−1·72	−0·67	1·48
C^{3}—C^{4}—C^{5}—C^{6}	3·50	0·91	−1·76
C^{4}—C^{5}—C^{6}—C^{7}	2·81	0·54	1·36
C^{5}—C^{6}—C^{7}—C^{2}	0·27	−0·07	−0·72
C^{6}—C^{7}—C^{2}—C^{3}	1·48	0·30	0·43
C^{7}—C^{2}—C^{3}—C^{4}	−0·75	0·06	−0·80
C^{8}—C^{9}—C^{10}—C^{11}	−0·71	−1·00	
C^{9}—C^{10}—C^{11}—C^{12}	−0·98	1·23	
C^{10}—C^{11}—C^{12}—C^{13}	0·12	−0·27	
C^{11}—C^{12}—C^{13}—C^{8}	2·51	1·13	
C^{12}—C^{13}—C^{8}—C^{9}	−4·03	−0·19	
C^{13}—C^{8}—C^{9}—C^{10}	3·12	−0·91	
C^{14}—C^{15}—C^{16}—C^{17}		1·69	
C^{15}—C^{16}—C^{17}—C^{18}		0·77	
C^{16}—C^{17}—C^{18}—C^{19}		−2·29	
C^{17}—C^{18}—C^{19}—C^{14}		1·34	
C^{18}—C^{19}—C^{14}—C^{15}		1·09	
C^{19}—C^{14}—C^{15}—C^{16}		−2·58	

[a] With standard deviations of 0·2–0·4° for bond angles.

Table 4. Pertinent crystal data for some benzylic esters

Compound Space group System	**1b** *P*2$_1$/*c* monoclonic	**3b** *P*na2$_1$ monoclinic	**4** *P*2$_1$/*c* monoclinic
a (Å)	14·720(3)	8·936(4)	6·404(2)
b (Å)	9·906(1)	14·928(5)	10·941(4)
c (Å)	15·194(6)	14·350(13)	20·468(5)
α (°)	90·0	90·0	90·0
β (°)	110·85(3)	90·0	91·74(2)
γ (°)	90·0	90·0	90·0
Volume (Å^{3})	2072·52	1914·12	1433·46
2θ max(°)	50	60	60
μ (cm^{-1})	0·80	0·73	0·89
R, *R*$_w$ (%)	8·50, 6·70[a]	4·14, 2·74	5·25, 3·63

[a] The NO_2 part is partially disordered.

The correlation of chemical reactivities with bond angles and/or bond lengths has been advanced as a new development in physical organic chemistry.[8–11] Our finding suggests an additional criterion to correlate crystal structures and solvolytic reactivities that an inverse order of reactivity for the highly crowded tertiary benzylic substrate would be accompanied by the observation of the lengthening of the C^1—C^α bond and of the nonplanarity of the phenyl moiety in the cryastal form. In the two systems previously reported,[1] 1,l-diphenyl-2,2-trifluoroethyl tosylate was too reactive for diffraction study, and the attempts at preparing single crystals of 3-phenyl-2,2,4,4-tetramethyl-3-pentyl-*p*-nitrobenzoate for structural study have not yet succeeded. More work on this aspect is in progress.

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