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SOLVOLYSIS OF (*E*)- AND (*Z*)-2-ARYL-2-CHLORO-5-FLUOROADAMANTANES. EVIDENCE FOR A COMPETITION BETWEEN SIGMA-PARTICIPATION AND PI-RESONANCE

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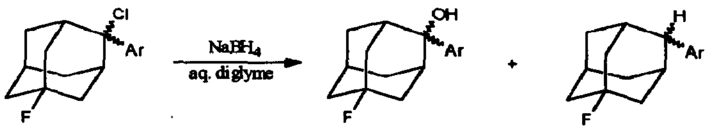
Abstract: Competition between sigma-participation by C_β-C_γ and pi-resonance by α-aryl group could be illustrated from the decreasing of (*Z*)/(*E*) rate ratios with increasing electron releasing of aryl substituent in the solvolysis of titled substrates. Product studies gave rise to the question about the efficiency of the tool of borohydride trapping.

Adamantane derivatives have generally been employed as reference standards in the correlation analyses for solvolytic reactivities.[1] Recent studies by le Noble,[2,3] Adcock,[4] Kelly,[5] and their coworkers provided several pieces of evidence for sigma-participation by C_3-C_4 in reactions in 2-adamantyl systems. Such an effect was considered not to be swamped by pi-resonance from 2-aryl group based on borohydride trapping experiment.[2] However, our kinetic and borohydride trapping studies on the solvolysis of isomeric 2-aryl-2-chloro-5-fluoroadamantates (**1-3**) indicated a competition between sigma-participation and pi-resonance. Moreover, the observed product ratios cast a doubt about the efficiency of the tool of borohydride trapping.

Both isomers of 2-chloro-5-fluoro-2-(4-trifluoromethyl)phenyladamantanes (**1**), 2-chloro-5-fluoro-2-phenyladamantanes (**2**) and 2-chloro-5-fluoro-2-(4-methyl)phenyladamantanes (**3**) were prepared from alcohols with $SOCl_2$ and were separated by HPLC. Rates of solvolysis in various solvent systems were measured at least in duplicate by conductimetry. Excellent linear log k - mY_{BnCl}[4] plots ($R > 0.990$, e.g. **Figure 1**) were realized. The rate constants (Table 1) were about 10^{-2} to 10^{-3} times that for the analogous 2-aryl-2-



1. Ar = 4-$CF_3C_6H_4$
2. Ar = C_6H_5
3 Ar = 4-$CH_3C_6H_4$

4. Ar = 4-$CF_3C_6H_4$
5. Ar = C_6H_5
6. Ar = 4-$CH_3C_6H_4$

7. Ar = 4-$CF_3C_6H_4$
8. Ar = C_6H_5
9 Ar = 4-$CH_3C_6H_4$

Table 1. Pertinent rate data for the solvolysis of chlorides **1-3**.

Solvent	k, /s, at 25°C					
	(*E*)-**1**	(*Z*)-**1**	(*E*)-**2**	(*Z*)-**2**	(*E*)-**3**	(*Z*)-**3**
	[(*Z*)/(*E*)]		[(*Z*)/(*E*)]		[(*Z*)/(*E*)]	
90E			1.06×10^{-4}	2.25×10^{-4}	5.53×10^{-3}	8.27×10^{-3}
			[2.12]		[1.50]	
80E	2.25×10^{-7}	6.88×10^{-7}	5.41×10^{-4}	1.06×10^{-3}	2.26×10^{-2}	3.16×10^{-2}
	[3.06]		[1.96]		[1.40]	
70E	6.85×10^{-7}	2.25×10^{-6}	1.77×10^{-3}	3.15×10^{-3}		
	[3.29]		[1.78]			
80A			4.14×10^{-5}	8.02×10^{-5}	1.85×10^{-3}	2.67×10^{-3}
			[1.94]		[1.44]	
70A	1.86×10^{-7}	5.53×10^{-7}	2.96×10^{-4}	6.13×10^{-4}	1.24×10^{-2}	1.65×10^{-2}
	[3.29]		[2.07]		[1.33]	
60A			1.48×10^{-3}	3.41×10^{-3}		
			[2.30]			
80M			4.56×10^{-3}	1.03×10^{-2}		
			[2.22]			
80T-20E	7.39×10^{-6}	2.53×10^{-5}	3.05×10^{-2}	5.15×10^{-2}		
	[3.42]		[1.69]			
60T-40E			3.75×10^{-3}	6.17×10^{-3}		
			[1.65]			

chloroadamantanes.[6]

Obviously, (*Z*)-chlorides showed slightly higher reactivities than the isomeric (*E*)-chlorides. The (*Z*)/(*E*) rate ratios are smaller than those found for the secondary 5-fluoro-2-adamantyl tosylates.[7] The presence of a

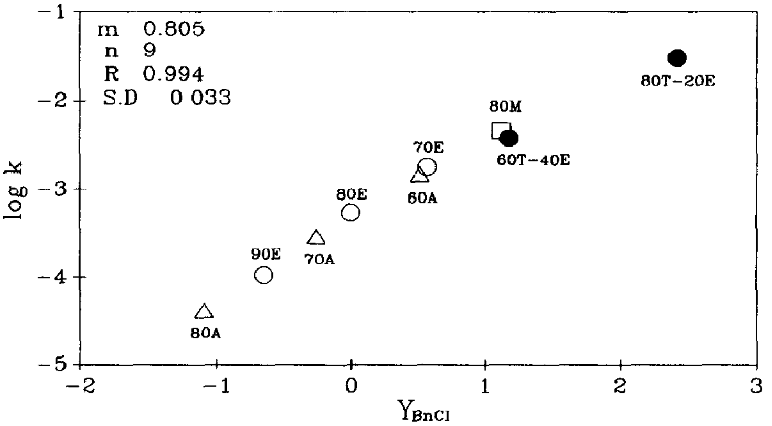


Figure 1. Correlation of logk s for (*E*)-**2** against Y_{BnCl}.

weak sigma-participation for (*Z*)- over (*E*)- chlorides in the cationic transition state at rate-determining step could then be concluded.[8] The (*Z*)/(*E*) rate ratios decreased from **1** to **2**, and to **3**, as the 2-aryl group became more electron releasing. Contrary to le Noble's observation,[2] the tool of increasing electron demand[9] is applicable in this study. The linear $\sigma^{+}\rho$ plots observed for both (*E*)- and (*Z*)-series in 80% ethanol (Figure 2) and in 70% acetone (Figure 3) showed crossing points at σ^{+} of about -0.72. Therefore, the isomeric pair containing 2-aryl group with σ^{+} near -0.72 would exhibit equal rates. In other words, the importance of C_3-C_4 sigma-participation in 2-adamantyl system will be suppressed by pi-resonance if a sufficiently strong electron releasing 2-aryl group is present. Unfortunately, such an aryl group would make the corresponding chloride too reactive to be prepared in a pure state for kinetic measuremnets.

Solvolysis products from **1**-**3** were also studied. The major product formed

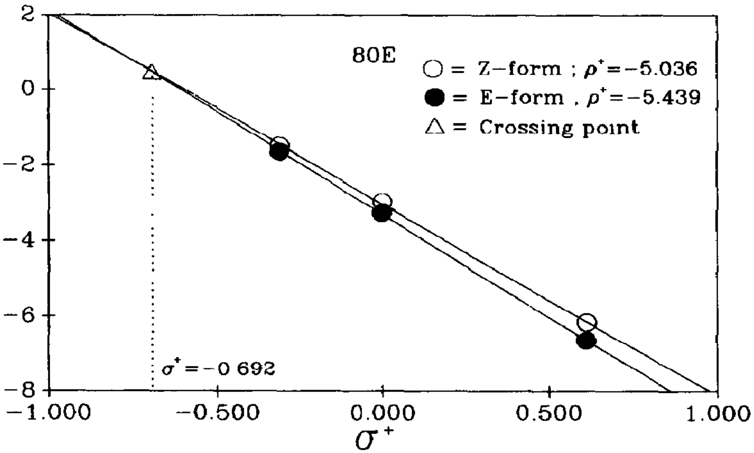


Figure 2. Logk–σ^{+} plot for solvolysis in 80E.

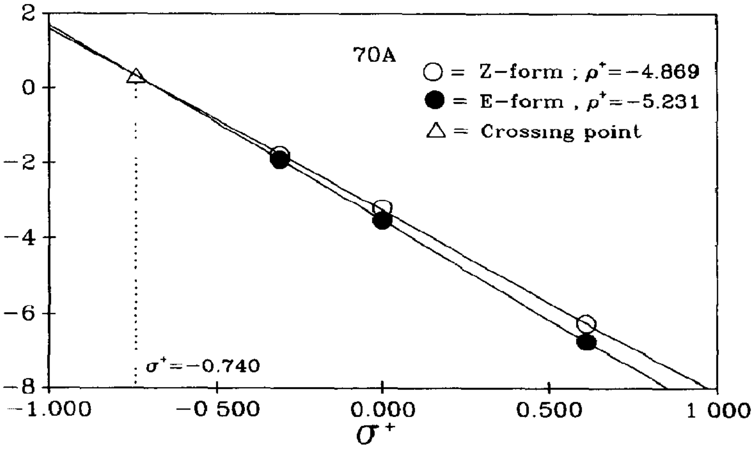


Figure 3. Logk–σ^{+} plot for solvolysis in 70A.

Table 2. Product analyses of solvolyses in aqueous acetone and with $NaBH_4$ trapping in aqueous diglyme.

Substrate	Solvolysis products	Products in $NaBH_4$ trapping experiment	
	4, **5** or **6** [(*Z*)/(*E*)]	**4**, **5** or **6** [(*Z*)/(*E*)]	**8** or **9**, [(*E*)/(*Z*)]
(*E*)-**1**	[78.2/21.8]		
(*Z*)-**1**	[93.8/6.2]		
(*E*)-**2**	[77.5/22.5]	43.7% [74.1/25.9]	56.3% [74.7/25.3]
(*Z*)-**2**	[92.8/7.2]	58.2% [89.9/10.1]	41.8% [74.1/25.9]
(*E*)-**3**	[90.5/9.5]	21.5% [75.4/24.6]	78.5% [74.1/25.9]
(*Z*)-**3**	[93.4/6.6]	27.6% [98.7/1.3]	72.4% [75.4/24.6]

in aqueous acetone was always the (*Z*)-alcohol, **4**, **5**, and **6**, respectively, but with different extent.[10] In 70 or 80% acetone, very close (*Z*)-/(*E*)-alcohol ratios, 93/7 to 94/6, were found in the cases of the more reactive (*Z*)-**1**, **2**, and **3**. The (*Z*)/(*E*) ratio of the solvolysis products from (*E*)-**3**, 90/10, was significantly larger than that from (*E*)-**1** and (*E*)-**2**, 78/22. The borohydride trapping[11] study in 80% diglyme could only be applied to **2** and **3**, because **1** was too unreactive to yield appreciable amount of the corresponding 5-fluoro-2-(4-trifluoromethyl)phenyladamantanes (7). The results are shown in **Table 2**.[12] Again, higher (*Z*)/(*E*) ratios for alcoholic products (**5** and **6**) were found from the more reactive (*Z*)-chlorides, which suggested the catonic intermediate was efficiently trapped by water. The (*E*)-/(*Z*)-2-aryl-5-fluoroadamantane (**8** and **9**) ratios, 74/26 to 75/25, were in agreement with those observed by le Noble and coworkers.[2] However, the total amount of hydride-trapping products was smaller from the more reactive (*Z*)-chloride, and even became the minor product (42%) in the case of (*Z*)-**2**. Thus, borohydride seems to be not an effective trap for carbocations, against what has been stated.[11] Further study is in progress.

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12. The amount of the isomeric (*E*)- and (*Z*)-**8** or -**9** were determined by GC and by F-19 NMR (2% error).

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