VINYLIC CATIONS FROM SOLVOLYSIS. XVI. [1]   HIGH k_{cis}/k_{trans} REACTIVITY RATIO

IN THE SOLVOLYSIS OF α-BROMO-β-tert-BUTYL-p-METHOXYSTYRENES

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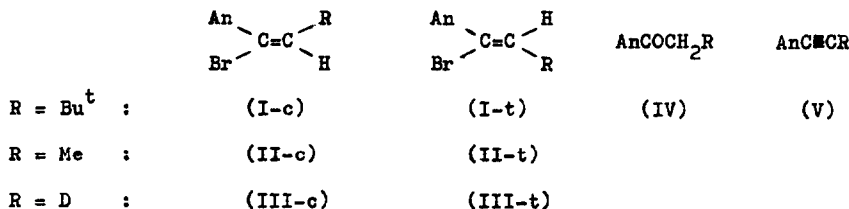Department of Organic Chemistry , The Hebrew University, Jerusalem, Israel

The introduction of two β-substituents into a vinylic system has a relatively

small effect on the rate of S_N1 solvolysis,[2] while with β-monomethyl α-activated vinyl

halides k_{cis}/k_{trans} values of 8.3 , [3] and ca. 9.5 ,[4] were found. The largest

k_{cis}/k_{trans} value observed to date is 49 , which was observed for a β-p-methoxyphenyl

substituent.[5] These rate differences were attributed to rate enhancement of the cis

isomer due to partial deconjugation of the activating group with the double bond, [3,5]

or to a relief of steric interaction between the cis methyl and activating groups. [4]

In order to test this hypothesis further we have compared the solvolysis rates

of cis and trans pairs of p-methoxy-α-bromostyrenes substituted with mono β-tert-butyl

group   [(I-c) : δ (CDCl$_3$) 0.88 (Bu^t) , 6.07 (:CH) , λ_{max}^{EtOH} 243 nm (ε 11,000) ;

(I-t) : δ (CDCl$_3$) 1.23 (Bu^t) , 6.03 (:CH) , λ_{max}^{EtOH} 262 nm (ε 12,600)]   , mono-β-methyl

group (II-c and II-t) [3] and mono-β-deuterium   [(III-c) : δ (CDCl$_3$) 5.60 ;

(III-t) : δ (CDCl$_3$) 5.94] in 50% EtOH containing NaOAc. The solvolysis products were

the substituted acetophenones (IV) and acetylenes (V). Rate and product data are

listed in the Table.

Our most significant result is the high k_{cis}/k_{trans} ratio of 1640 ($\Delta\Delta F^{\ddagger}$ [(I-c) -

(I-t)]   = -5.2 Kcal mol^{-1}) for the β-tert-butyl derivatives which is almost completely

due to the enhanced solvolytic reactivity of the cis isomer. This ratio is not due to

a competing E2 elimination as established by the following : (a) The reaction rates

of (I-c) and (I-t) are independent of the concentration of the NaOAc. (b) The reaction

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\begin{array}{ccccc}
\underset{Br}{\overset{An}{>}}C=C\underset{H}{\overset{R}{<}} & \underset{Br}{\overset{An}{>}}C=C\underset{R}{\overset{H}{<}} & AnCOCH_2R & AnC{\equiv}CR
\end{array}
$$

R = Bu^t	:	(I-c)	(I-t)	(IV)	(V)
R = Me	:	(II-c)	(II-t)		
R = D	:	(III-c)	(III-t)		

An = $\underline{p}$-MeOC$_6$H$_4$ -

rate of (I-c) is slightly enhanced , and that of (I-t) is moderately enhanced in the presence of the stronger base NaOH. A small contribution from an E2 route with NaOH for the _trans_ isomer is possible. (c) The product composition from both isomers is reasonably close, and the ketone (IV, R=Bu^t), which is expected only from the S_N1 reaction, was formed in $>50\%$ yield under conditions in which the acetylene (V, R = Bu^t) was stable to hydration. The higher percentage of acetylene with the stronger base has a precedent in a related system.[6] (d) The isotope effect $k_{\beta-H}/k_{\beta-D}$ of 1.10 for (I-c) is close to the value predicted for an S_N1 solvolysis of the α-($\underline{p}$-methoxyphenyl)vinyl system,[7] while the $k_{\beta-H}/k_{\beta-D}$ of 1.26 for (I-t) is still in the range assigned for S_N1 solvolyses.[6,8] For comparison, the isotope effect $k_{(III-c)}/k_{(III-t)}$ which is based on the unchanged composition of a partially solvolysed 65 : 35 mixture of (III-c) to (III-t) after 48% reaction , is $\underline{ca}$. 1. (e)The Grunwald-Winstein m value [9] of 0.83$\pm$0.03 at 30° which was found for (I-c) in aqueous EtOH is in the range assigned for S_N1 reactions.[9a,c]

The negligible effect of the _trans_-β-alkyl groups [relative reactivity : D(1) $\sim$ Me(0.81)$\sim$Bu^t(0.83)] may result from a cancellation of a steric acceleration due to a relief of the ground state crowding by steric retardation by R to the expulsion of Br$^-$. The telescopic increase in the k_{cis}/k_{trans} ratios in the series β-D(1)$<$ β-Me(7.65)$<$ β-An(49)$<$ β-Bu^t(1640) substantiate the suggestion that the ratios are mainly determined by steric effects. Models show that while the distortion from planarity in the _trans_ isomers is small , the α-aryl group of the _cis_ isomers is twisted out of the plane of the double bond. The increased steric interaction between the _cis_-$\underline{p}$-methoxyphenyl and R groups for the bulkier R's results in increasing π(Ar) - π(C=C) deconjugation , and consequently a rise in the ground state energy. Simultaneously , the transition state energy decreases by the increase in the π(Ar) - p (C$^+$)

Table. Solvolysis of AnC(Br)=CHR in 50% EtOH.

Substrate[a]	Base	Concn., 10^3 mol l^{-1}	T, °C	$10^5 k_1$, s^{-1}	Relative k_1 (80°)	Products (IV)	(V)
I-c	NaOAc	13.9	30	125±0.3		75[b]	25[b]
	NaOAc	51	30	122±0.7			
	NaOAc	146	30	140±1.0			
	NaOAc	26	80	9200 [c]	1362 [c]		
	NaOH	8.3	30	129±1.1		57[d]	43[d]
	NaOH	20.6	30	152±1.1			
I-t	NaOAc	26	80	5.61±0.08	0.83	81[e]	19[e]
	NaOAc	103	80	5.85±0.09			
	NaOH	51	80	8.26±0.13			
II-c	NaOAc	26	80	42.0±0.18	6.2[f]	68[g]	16[g]
II-t	NaOAc	26	80	5.49±0.12	0.81[f]	83[h]	17[h]
III-c	NaOAc	26	80	6.80±0.11	1.0	67[i]	11[i]
III-t	NaOAc	26	80	6.80±0.11	1.0[j]		

[a] $[AnC(Br)=CHR]$ = 1.5–1.8 x 10^{-4} mol l^{-1} for (I-c) and 0.009–0.021 mol l^{-1} for the other compounds. [b] With 0.028 mol l^{-1} of NaOAc. [c] Extrapolated from data at lower temperatures: $\Delta H^* $ = 17.6 Kcal mol^{-1}; ΔS^* = -10 cal K^{-1}mol^{-1}. [d] With 0.051 mol l^{-1} of NaOH. [e] At 70°. [f] k_1(II-c)/k_1(AnC(Br)=CH$_2$)=6.7 and k_1(II-t)/k_1(AnC(Br)=CH$_2$) = 0.83 in 80% EtOH at 80° with 0.1 M Et$_3$N. [g] After 5 half-lives. Also formed are 12% of (II-t) and 4% of the vinyl ether. [h] After 7 half-lives. [i] At 50% reaction. Also formed are 11% of the vinyl ether and 11% of the vinyl acetate. After 30 half-lives the products are 45% of (IV), 36% of AnCOCH$_2$D, 16% of (V) and 3% of the vinyl acetate. [j] Within the accuracy of the nmr determination.

conjugation. Attempts to evaluate the difference in ground state energy between (I-c) and (I-t) by their thermal equilibration have so far failed due to the formation of (V, R = Bu^t) and HBr.

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