VINYLIC CATIONS FROM SOLVOLYSIS. XIV. ANISYL REARRANGEMENT IN

THE ACETOLYSIS OF β,β-DIANISYL-α-PHENYLVINYL BROMIDE

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1,2-Rearrangements across the double bond during the solvolysis of aryl-substituted

vinylic compounds are known for α,β-diaryl-β-arylthio (or alkylthio) 2,4,6-trinitrobenzene-

sulfonates,[1] and for β-phenyl-[2] and β,β-diphenyl-α-methylvinyl[3] systems. The only reported

rearrangements in triarylvinyl systems are in the acid-catalyzed decomposition of vinyl-

triazenes via vinyldiazonium and vinyl cations.[4] β,β-Dianisyl-α-phenylvinyl bromide (I-Br)

seemed to us a favourable system for rearrangement during the C-Br heterolysis.[5]

Reflux of 25 mM of I-Br with 35 mM of AgOAc in dry AcOH for 1 hr gave two acetates (> 90%

by nmr) with signals at δ 1.87 and 1.92 in a ratio of 1 : 1. No other acetoxy signal was

observed. These signals were assigned to the cis-acetate II-OAc (m.p. 117-8°, δ (CDCl$_3$): 1.87)[6]

and to its trans isomer III-OAc (m.p. 140°, δ 1.95).[6] A repeated crystallization (from EtOH) of

the 1 : 1 mixture obtained from 0.17 M of I-Br and 0.18 M of AgOAc gave a fraction , m.p. 130-1°

An Ph	An An	X An	An Ph	An X	Ph An
C=C	C=C	C=C	C=C	C=C	C=C
An X	X Ph	An Ph	Ph X	Ph Ph	Ph X
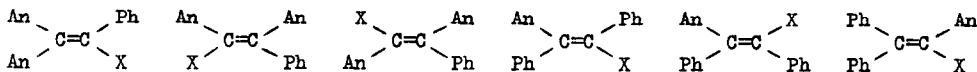
X=Br :	I-Br	II-Br	III-Br	IV-Br	V-Br	
X=OAc :	I-OAc	II-OAc	III-OAc	IV-OAc	V-OAc	VI-OAc

An = p-MeOC$_6$H$_4$

which was composed of 80% III-OAc and 20% of II-OAc, and another fraction , m.p. 111-2°, which

consisted of 70% of II-OAc and 30% of III-OAc (by nmr and ir). Acetolysis of 0.014 M of I-Br

in the presence of 0.84 M of NaOAc at 160° for 21 hrs (~20% reaction) gave only II-OAc and

III-OAc in a 1 : 1 ratio.

Acetolysis of IV-Br with two molar equivalents of AgOAc for 6 hrs (100% reaction by nmr

and tlc) gave exclusively two acetates with signals at δ 1.85 and 1.92 (in CDCl$_3$) in a ratio

Table. Solvolysis of $PhC(Br)=CR^1R^2$ [a]

R^1	R^2	Solvent	Base	10^2 [Base], M	T, °C	$10^6 k_1$, sec^{-1}
An	An	AcOH	NaOAc	84.0	160.4	4.13 ± 0.12
An	An	AcOH	NaOAc	8.4	160.4	2.26 ± 0.10
An	An	AcOH	LiOAc	8.4	160.4	2.62 ± 0.08
An	An	AcOH	NaOAc	8.4	160.4	3.20 ± 0.12 [b]
An	An	AcOH	NaOAc	8.0	140.0	0.7 [c]
An	An	80% EtOH	NaOAc	32.0	160.4	6.78 ± 0.19
Ph	Ph	AcOH	NaOAc	8.4	160.4	0.17 [c]
An	Ph [d]	AcOH	NaOAc	8.4	160.4	0.3 [c]
An	Ph [d]	AcOH	NaOAc	8.0	140.0	0.18 [c]

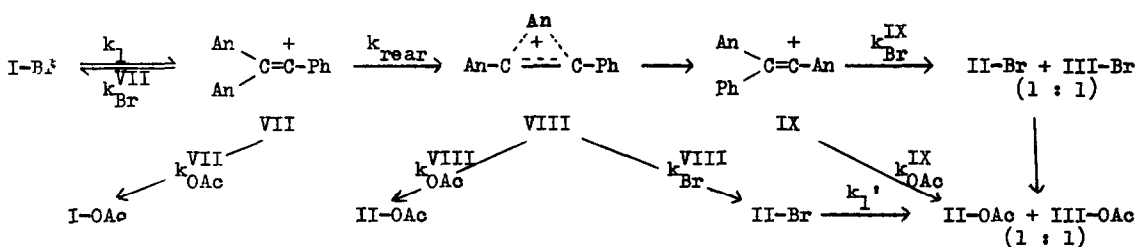[a] $[PhC(Br)=CR^1R^2] = 0.035$ M.   [b] In the presence of 0.035 M Bu$_4$NBr.   [c] Data for one point experiment at low reaction percentages.   [d] Data for IV-Br.

of 45 : 55 and two methoxy signals at δ 3.60 and 3.68 in the same ratio, indicating the exclusive formation of IV-OAc and V-OAc. Indeed, the other possible product VI-OAc , showed only one acetoxy and one methoxyl signals at δ 1.95 and 3.70. [7] The same 45 : 55 ratio was also obtained for partially solvolyzed reaction mixtures , and at 30% reaction the unreacted bromide consisted of 9 : 1 mixture of IV-Br to V-Br.

The kinetic data for the buffered acetolysis of I-Br and some approximate one-point experiments with IV-Br and Ph$_2$C=C(Br)Ph, which are too slow to follow completely at our reaction temperatures, are given in the Table. The reaction of I-Br is faster at higher NaOAc concentration, it shows no common ion rate depression in the presence of added Bu$_4$NBr (which accelerates the reaction as a salt with a Winstein's b value [8] of ca. 10) , and is slightly affected by changing the base from NaOAc to LiOAc.

I-Br was recovered unchanged (m.p. , nmr , tlc) from reflux for 24 hrs in formic acid containing 0.04 M of sodium formate.

The kinetics and the product distribution of the reaction fit an S_N1 mechanism which will be discussed in terms of the following scheme. VII , VIII and IX are the unrearranged, the bridged and the rearranged ions , respectively; k_{Br} and k_{OAc} are the rate coefficients for the capture of the various cationic species (which appear in the superscripts) by bromide and acetate ions , respectively. The Br$^-$ and OAc$^-$ were ommitted from the scheme for

$$I\text{-Br} \underset{k_{Br}^{VII}}{\overset{k_1}{\rightleftharpoons}} \underset{An}{\overset{An}{>}}C = C\text{-Ph} \xrightarrow{k_{rear}} An\text{-}C \overset{\overset{An}{\cdot+\cdot}}{=\!=\!=} C\text{-Ph} \longrightarrow \underset{Ph}{\overset{An}{>}}C = C\text{-An} \xrightarrow{k_{Br}^{IX}} \begin{array}{c} II\text{-Br} + III\text{-Br} \\ (1 : 1) \end{array}$$

$$\quad VII \qquad\qquad\qquad VIII \qquad\qquad\qquad IX \qquad\qquad \downarrow$$

$$\overset{k_{OAc}^{VII}}{\searrow} \qquad \overset{k_{OAc}^{VIII}}{\swarrow}\quad \overset{k_{Br}^{VIII}}{\searrow} \qquad \overset{k_1'}{} \quad \overset{k_{OAc}^{IX}}{\swarrow}$$

$$I\text{-OAc} \qquad II\text{-OAc} \qquad\qquad II\text{-Br} \xrightarrow{k_1'} \begin{array}{c} II\text{-OAc} + III\text{-OAc} \\ (1 : 1) \end{array}$$

convenience.

The formation of a 1 : 1 mixture of II-OAc and III-OAc argues strongly that the products are derived from the linear cation IX, which gives the same acetate mixture when formed directly from the solvolysis of II-Br or III-Br.[6] The alternative possibility , i.e. , VIII $\xrightarrow{k_{Br}^{VIII}}$ II-Br $\xrightarrow{k_1'}$ II-OAc + III-OAc (1:1) is unlikely: capture of VIII by bromide and acetate ions would give a $[II\text{-Br}] / [II\text{-OAc}]$ ratio equal to $(k_{Br}^{VIII}/k_{OAc}^{VIII})$ $([Br^-]/[OAc^-])$ At our concentrations $[Br^-] / [OAc^-]$ is always lower than 0.017 , and $k_{Br}^{VIII}/k_{OAc}^{VIII}$ is not likely to be greater than 8 , which is the value found for k_{Br}^{IX}/k_{OAc}^{IX}.[9] The justification for using IX as a limiting model for VIII is that k_{Br}/k_{OAc} ratios for α-arylvinyl cations increase with the crowding of the substituents around the cationic orbital,[10,11] and VIII is less hindered from its unbridged side than IX. Hence, the main product from VIII would be II-OAc , contrary to what was found. Moreover, the capture of VIII by Br^- should be depressed in the presence of AgOAc, conditions under which the II-OAc to III-OAc ratio is still 1 : 1 .

Since neither common ion rate depression was observed, nor I-OAc formed, the rearrangement of VII (k_{rear}) is much faster than its reactions with both bromide (k_{Br}^{VII}) and acetate (k_{OAc}^{VII}) ions. Both the transition state of the rearrangement and the rearranged ion IX are stabilized by anisyl groups, causing complete rearrangement in AcOH , in trifluoroethanol[12] and in 60% EtOH.[12] In contrast, the β ,β -di-p-tolyl-α -phenylvinyl cation rearranges only partially in AcOH and is completely captured by excess acetate ion before rearrangement.[4]

The 13-fold higher reactivity of I-Br compared with $Ph_2C = C(Br)Ph$ (similar ratios were found also in trifluoroethanol and in 60% EtOH)[12] may suggest that the _trans_-β -anisyl group participates in the transition state of the heterolysis , i.e., that the I-Br $\longrightarrow$ VIII transformation has only one transition state. However, II-Br and III-Br solvolyze with similar rates[13] and both _cis_ and _trans_ β -monoanisyl substrates (e.g. , IV-Br and V-Br) solvolyze with similar rates and 3-4 times faster than $Ph_2C = C(Br)Ph.$[12] It is not yet clear why both _cis_ and _trans_ anisyl groups enhance the solvolytic reactivity. However, the additivity of the effects of the _cis_ and the _trans_ anisyl groups can account for the enhanced reactivity of I-Br

without invoking β-anisyl participation.

The absence of phenyl migration in the acetolysis of IV-Br is in contrast to the phenyl migration which occurs in trifluoroethanol.[12] The possibility of a degenerate β-anisyl migration in the intermediate ion $Ph(An)C=\overset{+}{C}Ph$ is now being investigated with a labelled compound. The occurrence of IV-Br ⟶ V-Br isomerization concurrently with the acetolysis suggests that bromide ion return to covalent bromide from the AgBr molecule - vinyl cation pair is possible. Such behaviour has precedents in vinylic systems.[9,14]

The unreactivity of I-Br in HCOOH under conditions in which II-Br is solvolytically reactive [13a] argues strongly against an electrophilic addition-elimination [15] as a competing route in the formolysis of II-Br , since II-Br should be less reactive in electrophilic addition than I-Br.

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