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VINYLIC CATIONS FROM SOLVOLYSIS. VIII. SOLVOLYSIS OF CIS AND TRANS α-BROMO-p,p'-DIMETHOXYSTILBENES.[1]

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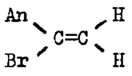
For the S_N1 solvolysis of α-bromo-p-methoxystyrene 1 [2] and of trianisylvinyl bromide 2 [3] $k_2/k_1 = 1.7$ in 80% EtOH. In buffered AcOH $k_2/k_1 = 4.2$ and 2 shows an extensive bromide ion return, while 1 shows no return.[4] The later difference is attributed to the presence of the bulky aryl groups in the ion derived from 2 which are absent in the ion derived from 1. The study of cis (3) and trans (4) α-bromo-p,p'-dimethoxystilbenes was therefore initiated in order to obtain additional information concerning this point.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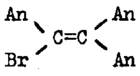
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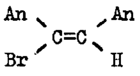
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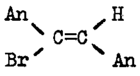
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An=p-MeOC_6H_4-

Addition of an equimolar amount of HBr to p,p'-dimethoxytolan (5) in AcOH during three hrs., followed by evaporation of the solvent and crystallization of the oil from EtOH gave 80% of 3,[5] less than 5% of 4 (the limit of detection by n.m.r.), and at most 1.5% of α-acetoxy-p,p'-dimethoxystilbene (6).[5] Over 70% of 3 is obtained by using an equimolar ratio of 5 and HBr in CCl_4.

AnC≡CAn
5

AnC(OAc)=CHAn
6
(a) cis ; (b) trans

The trans isomer 4 was obtained in AcOH by using a 2:1 ratio of HBr to 5. It was also obtained in 53% yield in CCl_4 by using excess HBr, or in 70% yield by refluxing a solution of pure 3 for 2 hrs. The geometrical assignment is based on the higher m.p., higher λ_{max} and ϵ,[6] the lower field OMe, CH: and Ar,[6] and the simpler I.R. spectra of 4 compared with 3, and on the acid-catalyzed 3 → 4 isomerization. The arguments are similar to those used for 1,2-dianisyl-2-phenylvinyl halides.[7]

Solvolysis of 3 and 4 in 80% EtOH in the presence of NaOH and NaOAc is summarized in the Table. The relatively large error is due to a combination of low solubility and high reactivity. The reaction of 4 was too fast to measure at 120°, but 84% of the Br^- was liberated in 6 min. at 97°, giving an approximate second order coefficient of 10^{-2} l/mole.sec. The rate coefficients remained constant during the runs. The main reaction product (>90%) is 5, but in the presence of NaOAc, the i.r. and the n.m.r. showed the formation of ca. 8% acetates. Both 5 and desoxyanisoin are formed in 90% EtOH. Their ratio remained constant at 36-73% reaction, the ketone being 37% of the product from 4 and 16% from 3. Based on k_1 values in 80% and 90% EtOH, Grunwald-Winstein's m values are 0.67 for 3 and 0.62 for 4 at 120°.

In acetolysis, k_1 decreases with the progress of the reaction (due to bromide ion return[4]), and its extrapolated value to zero reaction time ($k_1^{\,o}$) is given in the Table. The ratios of k_1 at half-life to the initial value $k_1^{50\%}/k_1^{\,o}$ for 3 are 0.75 and 0.74 in the presence of 0.08M and 0.16M NaOAc, and 0.69 for 4 in the presence of 0.08M NaOAc. The main isolated product (> 90%) is 5, and ca. 2% of 6 are also formed.

Reflux of equimolar amounts of AgOAc with 3 or 4 in AcOH for 1 hr. gave the same products distribution from both: 25-50% of 5 and 75-50% of two vinylic acetates, probably 6a and 6b. The ratio of 6a (Me at 128 cps) to 6b (Me at 136 cps) is 86-90 to 14-10. Reflux for 1 hr. of a mixture of 62% 5, 33% 6a and 5% 6b gave 61% 5 , 30% 6a and 9% 6b.

Several mechanistic points emerge from the data: a) In 80% EtOH the k_{cis}/k_{trans} ratio is base-dependent. This is interpreted as a result of a competition of E1 mechanism (operating for 3), with E2-elimination induced by the strong base NaOH (operating for the structurally biased 4). Indeed, k_{trans}/k_{cis} =208 was observed for the elimination of α-chlorostilbenes with NaOH.[8] In aqueous EtOH containing NaOAc the E1 mechanism predominates for both 3 and 4, in line with the independence of k_1 on the base used. In AcOH both compounds probably react via the E1 route.[9] The high k_{cis}/k_{trans} ratio in the E1 process is reminiscent of the AgOAc-catalyzed acetolysis of 1-iodo-1-cyclopropylpropenes where $k_{cis}/k_{trans} \gg 9.5$[10]. The explanation of relief of steric strain in the ground state holds also for 3 and 4. 3 has a higher ground state energy than 4 due to the interaction of the cis aryl groups, a known

Table. Solvolysis of 0.04M of 3 and 4 at 120.2° ± 0.2°

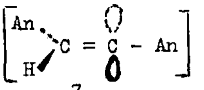
Compound	Solvent	Added base	Conc., M	10^5k_1,sec^{-1}	k_3/k_4
3	80% EtOH	NaOH	0.5	113 ± 21	ca. 0.06[a]
		NaOAc	0.5	132 ± 9	43.5
		NaOAc	0.043	137 ± 4	49
4		NaOH	0.5	b	
		NaOAc	0.5	3.03 ± 0.12	
		NaOAc	0.043	2.78 ± 0.17	
3	90% EtOH	NaOAc	0.043	44.4 ± 4.2	45
4		NaOAc	0.043	0.99 ± 0.007	
3	AcOH	NaOAc	0.08	8.25[c]	19.7
		NaOAc	0.16	10.8[c]	
4		NaOAc	0.08	0.42[c]	

[a] Estimated value. [b] Too fast to measure. [c] Extrapolated to zero reaction time from k_1 vs. time curves.

phenomenon in other stilbenes, which is supported by the 3 → 4 isomerization. At the same time the energy of the transition state decreases, since deconjugation of the α-aryl group and the double bond results in increased overlap of the aryl group with the incipient cationic p-orbital. The difference of 2.3-3 kcal/mole for the reactions of 3 and 4 suggests that a fair amount of the steric interactions still remains in the transition states.

b) 3 is 2.8-times and 1.23-times more reactive than 2 in 80% EtOH and in AcOH, respectively.[4] The small effect probably results from a balance of increased ground state energy by the β-Ar - Br interaction, and decreased energy due to a buttressing effect of the α-aryl group into the plan of the double bond (caused by the presence of the trans stilbene system) in 2. The k_3/k_4 ratio is not due to neighbouring group participation, as shown by the similar solvolysis rates of cis and trans-1,2-dianisyl-2-phenylvinyl bromides,[11a] both having similar ground states.

c) The $k_1^{50\%}/k_1^{o}$ values in AcOH decrease on increasing the number of the aryl groups, being 1 for 1,[4] 0.69-0.75 for 3 and 4, and 0.25-0.28 for 2.[4] This is in agreement with the assumption[4] that the selectivity of the vinyl cation is due to steric inhibition to ion return. 3 differs from 1,2-dianisyl-2-phenylvinyl bromides[11b] by showing very little isomerization to 4 concurrent with the solvolysis. Return by the formed bromide ion (as shown by the kinetics) without isomerization is possible only if the vinyl cation 7 is captured exclusively from the less hindered side. This was found in the formation of 3



7

from 5 and HBr, in the preferential formation of 6a over 6b, and in the hydrochlorination of 1-phenylpropyne.[12] The Br^- probably assists in the elimination of the proton from 7, since when it is captured by AgOAc 6 is the main product, and different 6a/6b ratios are formed from 3 and 4 in 90% EtOH.

d) The higher m values for 3 and 4, compared with 2, are in accordance with the suggestion of decreasing m values with the increase in the steric inhibition to solvation, on increasing the number of aryl groups.[13] The closer reactivity of 3 and 4 in AcOH suggests that this effect is less important when electrophilic solvation is the decisive factor.

e) 7 is probably the intermediate in the addition of HBr to 5. This is consistent with the stereochemistry of the addition, and the small amounts of formed vinylic acetates.

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5. All the new compounds gave satisfactory analyses and showed the expected spectra.
6. For 3 , λ_{max} 243 mμ (ϵ=18200), 296 mμ (ϵ=13000) in EtOH ; MeO at 224 and 229, CH: at 412 and the lower half AB quartet at 439 cps downfield from TMS. For 4 , λ_{max} 300 mμ (ϵ=26800), MeO at 230, CH: at 426 and lower half of the AB quartet at 426 cps.
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