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KINETIC STUDIES ON β-ARYL MIGRATION ACROSS THE DOUBLE BOND IN VINYL CATIONS

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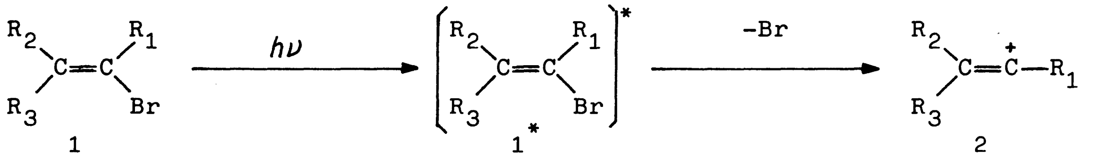
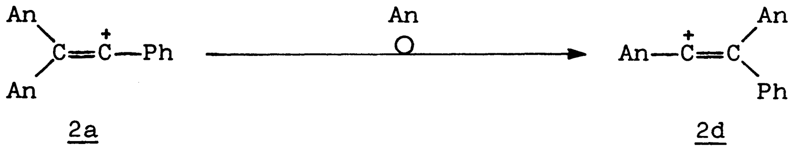
The rates of β-aryl migration in vinyl cations were determined by laser flash photolysis of the corresponding vinyl bromides in acetonitrile. β-Anisyl migration occurred very rapidly ($k \gtrsim 10^8\ s^{-1}$). β-Phenyl migration in $Ph(An)C{=}\overset{+}{C}{-}Ph \longrightarrow An{-}\overset{+}{C}{=}CPh_2$ was relatively slow process ($k=7.4 \times 10^6\ s^{-1}$ at 273 K).

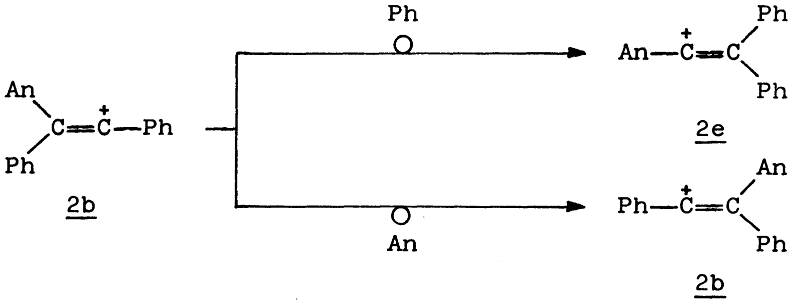
Because vinyl cations can be efficiently produced by photolysis of the corresponding vinyl halides,[1-4] the kinetics of reactions of these ions can conveniently be studied with laser flash photolysis.[5,6] This paper reports the kinetics of β-aryl migration in vinyl cations 2a-c.



a:R_1=Ph,R_2=R_3=An=p-$MeOC_6H_4$ b:R_1=R_2(or R_3)=Ph,R_3(or R_2)=An c:R_1=Me,R_2=R_3=An

β-Aryl migrations across the double bond during the solvolysis of triarylvinyl compounds have been extensively studied by Rappoport et al.[7] and Lee et al.[8] It has been reported in the excellent book of Stang et al.[9] that during solvolysis the rearrangement according to reaction (2) occurs so facile that ion 2a cannot be scavenged by nucleophiles added to the solution. It is well-known that an anisyl group can migrate more easily than a phenyl one. However, it was pointed out that

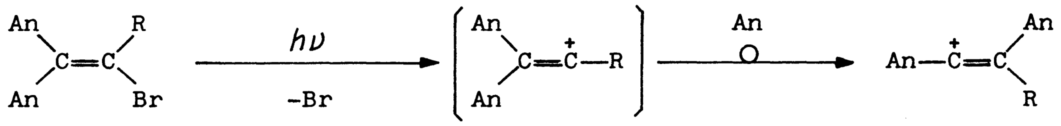




the rearrangement of ion 2b according to reaction (3) is suitable for studying the relative migratory aptitudes of different β-aryl groups because the migration of the β-phenyl group across the double bond of the ion 2b gives a more stable ion 2e, whereas the β-anisyl migration is degenerate. In non-nucleophilic solvent the phenyl migration was observed to some extent.7) However, there has been no report of an absolute rate of 1,2-aryl migration such as reaction (3a).

In our investigation bromides 1a-c were irradiated in the aerated acetonitrile solution at concentration10) of ca. 1×10^{-5} mol l^{-1} with single 15 ns flash of 265 nm light, and the optical absorbance was followed. The absorbed dose was about 6×10^{-6} einstein l^{-1}flash^{-1}. Dissociation of the electronically excited molecules occurred very rapidly and the rate constant for the dissociation was greater than 1×10^{8} s^{-1}, which was inferred from the fact that the electrical conductivity of the solution increased already to its maximum value during the flash. In case of irradiation of 1a and 1c the optical absorption measurements yielded almost identical transient spectra with a maximum at ca. 345 nm, as shown in Fig. 1.

The spectra were assigned respectively to ions 2d and 2f, which were formed by the migration of the anisyl group during the flash ($k \geq 10^{8}$ s^{-1}). This assignment emerges from the following consideration: the spectra are very similar to the spectrum of tris(p-methoxyphenyl)vinyl cation.6) If the spectra were due to ions



1a:R=Ph
1c:R=Me

2a:R=Ph
2c:R=Me

2d:R=Ph
2f:R=Me

(4)

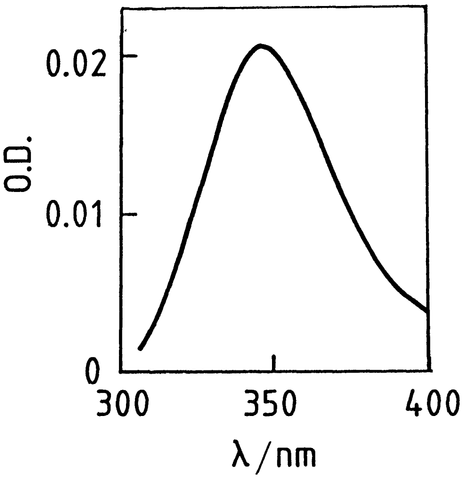


Fig.1. Transient optical absorption spectrum recorded at the end of irradiation of an acetonitrile solution of 1a (1×10^{-5} mol l^{-1}) at room temperature with a flash of λ_{inc}=265 nm. D_{abs}:ca. 6×10^{-6} einstein l^{-1}.

An almost identical transient spectrum was observed in the case of 1c.

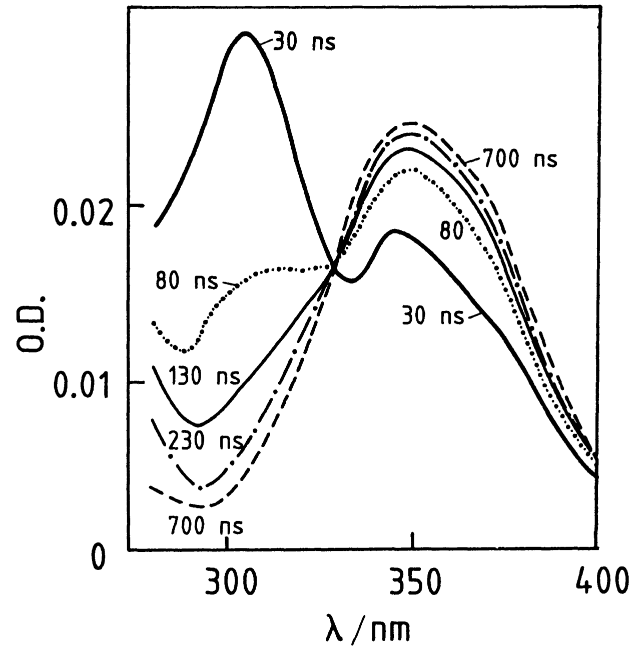
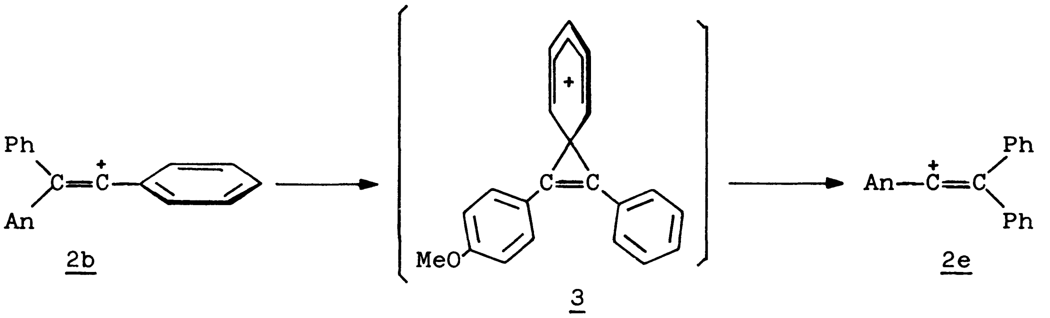


Fig.2. Time-dependent transient optical absorption spectra recorded after irradiation of E-1b in acetonitrile (1×10^{-5} mol l^{-1}) at room temperature. D_{abs}:ca. 6×10^{-6} einstein l^{-1}.

2a and 2c, they should possess the absorption maxima at lower wavelengths. In case of the ion 2a the maximum should be at ca. 310 nm, where triphenylvinyl cation has its absorption maximum.11) In case of the ion 2c, which has a methyl group in α-position, the maximum should be below 310 nm. Thus in either case the absorption spectra should not be identical. It is, therefore, concluded that the migration of the type (4) occurs very rapidly ($k \geq 10^8$ s^{-1}).

A different situation was encountered with irradiation of E and Z isomers of 1,2-diphenyl-2-(p-methoxyphenyl)vinyl bromide 1c. While irradiating these compounds in acetonitrile at temperatures between -40 and 25 °C, we observed time-dependent absorption spectra. The absorption at 305 nm decreased and the one at 345 nm increased by appearance of an isosbestic point at 330 nm, as is illustrated in Fig. 2.12) The spectral changes after the flash reflect the occurrence of reaction (5), since the ion 2e has the absorption maximum at 345 nm, which is



(5)

formed during the flash of 2,2-diphenyl-1-(p-methoxyphenyl)vinyl bromide.6) A similar time-dependent figure was obtained in 2,2,2-trifluoroethanol and the rate was almost the same as the one obtained in acetonitrile. However, in the ethanol solution there was no absorption between 300 and 500 nm. This means that the rate of the β-phenyl migration in the ion 2b may be slower than the rate for nucleophilic attack of ethanol to the ion 2b (k 10^8 s^{-1}).13) The rate constants measured for both the Z and E isomers of 1c in acetonitrile at various temperatures are shown in Table 1. The relatively high negative activation entropy can be interpreted in terms of a rather rigid structure of the transition state, in which the mobility of all three aryl rings is hindered, similarly to the unstable reactive intermediate 3, whereas in the case of 2b this holds only for the α-phenyl group.

Table 1. The first-order rate constants for the β-phenyl migration in 2b produced by flash irradiation of Z or E isomer of 1b in acetonirile

Temperature K	k for Z-1b s^{-1}	k for E-1b s^{-1}
233.2	2.1×10^6	2.3×10^6
243.1	3.0×10^6	3.2×10^6
253.0	3.9×10^6	4.1×10^6
263.1	5.1×10^6	6.2×10^6
273.1	7.4×10^6	

$\Delta H^{\ddagger} = 12$ kJ mol^{-1} and $\Delta S^{\ddagger} = -69$ J $mol^{-1}K^{-1}$ at 298.15 K from Z-1a and
$\Delta H^{\ddagger} = 12$ kJ mol^{-1} and $\Delta S^{\ddagger} = -71$ J $mol^{-1}K^{-1}$ at 298.15 K from E-1b.

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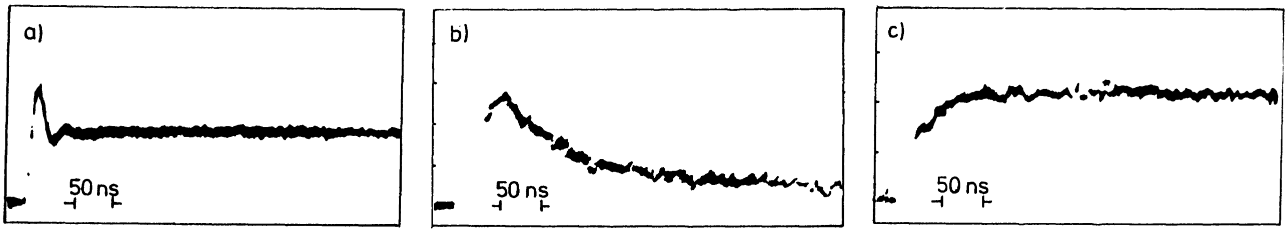
10) The solution was prepared so that the absorbance at 265 nm was 0.1 with 1 cm light path.

11) Our unpublished results.

12) Some oscilloscope traces are shown below. a) A photo-current was formed under electric field of D.C. 700 V. The current was kept constant during 500 ns after the flash. Optical measurement: b) at 305 nm. c) at 345 nm.



13) This value is reasonable, because the decay rate constant for tris(p-methoxyphenyl)vinyl cation, which is more stable than ion 2b, in ethanol is 1.03×10^7 s^{-1} at 25 °C.

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