SYNTHESIS AND CYCLIZATION KINETICS AND MECHANISM OF 1-(2-ETHOXYCARBONYLPHENYL)-3-ARYLTRIAZENES. KINETIC ACIDITY FUNCTION OF SODIUM METHOXIDE IN METHANOL

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Eight 1-(2-ethoxycarbonylphenyl)-3-aryltriazenes have been synthetized and the rate constants of their sodium-metoxide-catalyzed cyclization have been measured in methanol at 25·0°C. The experimental rate constants k_{obs} have been adopted to construct the kinetic acidity function H_{KM} which has been shown to be identical with the $-\log [CH_3O^-]$ values. Two mathematical procedures have been used to determine the catalytic rate constants and their dependence on the Hammett substituent constants. A closer dependence is obtained with the σ values than with the σ_p^- values. The ϱ value found (0·3) indicates a compensation of the substituent effects upon the dissociation of the starting triazene and upon the subsequent reaction of the conjugated base. Out of the two mechanistic alternatives — E1cB and $B_{Ac}2$ — the latter appears to be more probable, the splitting of tetrahedral intermediate being its limiting step.

The ethyl esters of the given formula *I* have not been described in literature yet. On the other hand, the corresponding methyl esters are known: their synthesis and UV-VIS spectra are given in ref.[1]. Also studied were the methyl and ethyl esters having an alkyl group at the 3 position of triazene chain[2]. Structure of these com-

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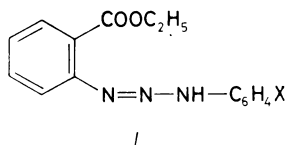
pounds was confirmed by ^{1}H NMR spectra, however, main attention was paid to cyclizations of these compounds on aluminium(III) oxide giving benzotriazinone. The highest activity was found with a catalyst of basic type and of the activity V. However, the cyclization already takes place during preparation of the compounds mentioned in the presence of sodium acetate, viz. in attempts of their purification by distillation. The cyclizations were also observed by other authors during crystal-

lizations of this type of esters from alcohols in the presence of small amounts of water[3,4]. Synthetic aspects of cyclizations of analogous 1-(2-cyanophenyl)-3-phenyl-triazenes were described by Stevens[5-7]. A possibility of decomposition of the cyclization products back to the starting triazenes was shown in ref.[8]. The same paper also describes products of photodecomposition of analogues of compound *I*: a compound with ketene group and also with ketonic group in quinoid arrangement is presumed as an intermediate.

The aim of the present paper is a study of kinetics and elucidation of the cyclization mechanism of the compounds of general formula *I* in methanol with catalysis of sodium methoxide. Another aim is construction of a kinetic acidity function and its interpretation with regard to the sodium methoxide concentration.

EXPERIMENTAL

Synthesis of 1-(2-Ethoxycarbonylphenyl)-3-aryltriazenes

Method A. A solution of 0·05 mol substituted aniline in 14 ml concentrated hydrochloric acid and 11 ml water was cooled below 5°C and treated with a solution of 3·5 g (0·05 mol) sodium nitrite in 14 ml water added drop by drop with stirring at a temperature below 5°C. The diazonium salt prepared in this way was added to an emulsion of 7·1 g (0·043 mol) ethyl anthranilate[9] in a solution of 20 g anhydrous sodium acetate and 80 ml water. The reaction mixture was stirred 2 h, the precipitated product was collected by suction, thoroughly washed with water, and dried in air. The raw product was purified by recrystallization from heptane.

Method B. An emulsion of 8·3 g (0·05 mol) ethyl anthranilate[9] in 17 ml concentrated hydrochloric acid and 13 ml water was cooled below 5°C, and a solution of 3·5 g (0·05 mol) sodium nitrite in 14 ml water was added thereto drop by drop with stirring at a temperature below 5°C. The diazonium salt prepared in this way was added to a mixture of 0·045 mol substiuted aniline suspended in a solution of 20 g anhydrous sodium acetate and 80 ml water, whereafter the reaction mixture was stirred 2 h and worked up similarly as in the Mehtod A. The synthetic method used, yields, and physical properties of the compounds prepared are given in Table I.

Kinetic Measurements

Procedure. The necessary volumes of the solutions of substrate and sodium methoxide in methanol were mixed in a 1 cm cell at the temperature of 25·0 ± 0·1°C. The decrease of the substance studied was monitored with a Specord UV VIS apparatus (Zeiss, Jena) at 360 nm (the triazene band) for a period of 4—5 half-lives. The results were evaluated according to our own program[10] using an EC 1033 computer.

Evaluation of catalytic constants. The catalytic constants were evaluated along with the kinetic acidity function according to an algorithm published earlier[11,12], the initial point was defined by the relationship $\log k_{obs}^0 = \log [CH_3O^-]$.

RESULTS AND DISCUSSION

The logarithms of observed rate constant k_{obs} obtained from the kinetic measure-

TABLE I

The methods used for synthesis, yields, and physical properties of 1-(2-ethoxycarbonylphenyl)-3-
-aryltriazenes $Ia-Ih$ 2-$C_2H_5OCOC_6H_4$—N=N—NH—C_6H_4X

Compound	X	Method Yield, %	Melting point, °C	Formula (M.w.)	Calculated/ Found, % N
Ia	4-NO_2	A 59	151—154	$C_{15}H_{14}N_4O_4$ (314·3)	17·83 17·79
Ib	3-NO_2	A 62	130—134	$C_{15}H_{14}N_4O_4$ (314·3)	17·83 17·78
Ic	3-Cl	B 67	97—100	$C_{15}H_{14}ClN_3O_2$ (303·7)	13·84 13·90
Id	4-Cl	B 61	116—119	$C_{15}H_{14}ClN_3O_2$ (303·7)	13·84 13·88
Ie	H	B 60	70—72	$C_{15}H_{15}N_3O_2$ (269·3)	15·60 15·54
If	3-CH_3	B 38	86—88	$C_{16}H_{17}N_3O_2$ (283·3)	14·83 14·80
Ig	4-CH_3	B 58	90—91	$C_{16}H_{17}N_3O_2$ (283·3)	14·83 14·87
Ih	4-OCH_3	B 47	94—96	$C_{16}H_{17}N_3O_3$ (299·3)	14·04 14·00

TABLE II

The slopes (a) of dependences $\log k_{obs}$ vs $\log [CH_3O^-]$, their standard deviations (s_a), logarithms of the catalytic rate constants determined from the shift ($\log k_B^S$) and from the kinetic acidity function ($\log k_B^H$), and numbers (n) of the concentrations used (sodium methoxide in methanol) in the reactions of the substituted derivatives $Ia—Ih$ at 25°C

Compound	a	s_a	$\log k_B^S$	$\log k_B^H$	n
Ia	1·316	0·054	0·269	0·264	13
Ib	1·012	0·036	0·214	0·273	14
Ic	1·191	0·025	0·186	0·163	16
Id	1·200	0·028	0·149	0·164	18
Ie	0·911	0·031	0·062	0·059	19
If	0·968	0·025	−0·023	−0·021	19
Ig	0·940	0·042	0·101	0·081	14
Ih	1·129	0·039	−0·039	−0·070	18

ments give (with the exception of 4-nitro derivative *Ia*) a linear dependence on the logarithm of the corresponding concentration of sodium methoxide. The slopes of these dependences are presented along with their standard deviations in Table II. As it can be seen from this table some of the slopes differ statistically significantly from the value of 1. In the given case this is evidently due to a specific sensitivity of the individual substituted derivatives to a change of medium. As it was shown earlier[13] this fact can negatively affect the correctness of the calculated catalytic constant k_B. The most suitable procedure of treating such dependences consists in constructing a kinetic acidity function H_{KM}. Its comparison with other acidity or basicity parameters of medium makes it possible to gain insight into the principles of the process[12,14] and, at the same time, to obtain the respective catalytic constants. The kinetic acidity function obtained from 131 kinetic measurements of the base--catalyzed reaction of eight substituted derivatives of *I* at altogether 67 concentrations of sodium methoxide in methanol depends linearly on the logarithm of sodium methoxide concentration as it is shown in Eq. (*1*).

$$H_{KM} = (0.001 \pm 0.035) - (1.000 \pm 0.015) \log [CH_3O^-] , \qquad (1)$$

$$r = 0.992 , \quad s = 0.031 , \quad n = 67$$

This finding fully agrees with the usually applied relationship[15] $H_M = -\log . [CH_3O^-]$, where H_M is the acidity function of sodium methoxide in methanol. As it can be seen from the slope of Eq. (*1*) the original non-unity slopes of the dependence of $\log k_{obs}$ vs $\log [CH_3O^-]$ were equalized in the statistical set.

Table II gives the catalytic rate constants k_B^S determined from the shift of the individual dependences of $\log k_{obs}$ vs $\log [CH_3O^-]$ during construction of the kinetic acidity function. These constants have the advantage in being independent, in their relative mutual magnitude, of the basicity characteristics of medium. With application of the kinetic acidity function H_{KM} it is possible to determine another set of catalytic constants, k_B^H, according to Eq. (*2*).

$$\log k_B^H = n^{-1} \sum_{i=1}^{n} (\log k_{obs} + H_{KM})_i , \qquad (2)$$

where n means the number of concentrations of methoxide at which the reaction was measured. These constants are given in Table II too. By plotting the catalytic constants in the dependence on the Hammett substituent constant according to Exner[16] (σ_{Ex}) we obtain the relationships

$$\log k_B^S = (0.064 \pm 0.019) + (0.256 \pm 0.046) \sigma_{Ex} , \qquad (3)$$

$$r = 0.915 , \quad s = 0.048 , \quad n = 8 ;$$

$$\log k_B^H = (0.055 \pm 0.018) + (0.296 \pm 0.044)\,\sigma_{Ex}, \tag{4}$$

$$r = 0.940, \quad s = 0.046, \quad n = 8.$$

Slightly better correlations are obtained with application of the substituent constants derived for nonaqueous media[17] which proved suitable earlier[14].

$$\log k_B^S = (0.057 \pm 0.019) + (0.268 \pm 0.046)\,\sigma_{F6}, \tag{5}$$

$$r = 0.922, \quad s = 0.046, \quad n = 8;$$

$$\log k_B^H = (0.047 \pm 0.018) + (0.311 \pm 0.043)\,\sigma_{F6}, \tag{6}$$

$$r = 0.947, \quad s = 0.043, \quad n = 8.$$

When using both the sets of substituent constants, somewhat closer correlations are obtained from the catalytic rate constants determined from the acidity function according to Eq. (2), which is in accordance with our earlier paper[13]. Irrespective of the way of treatment it can be stated that the Hammett relationship is fulfilled with an accuracy comparable with or better than 0·06 units usually given for $\log k$ (see ref.[16], p. 88). Low correlation coefficients are due to small slope. On the other hand, application of the dual substituent parameters σ_p^- for the 4-nitro derivative results in worsening of fit of the correlation for both k_B^S ($s = 0.055$) and − predominantly − k_B^H ($s = 0.063$). This conclusion is surprising since in the given medium the substrate is undoubtedly dissociated, which is indicated by the plateau found for the 4-nitro derivative *Ia* in the experimental region of sodium methoxide concentrations from $7.0 . 10^{-3}$ to $12.6 . 10^{-3}$ mol dm^{-3}. The break in the pH profile corresponds to the methoxide concentration comparable with the hydroxide ion concentration at the point of half ionization of triazenes in the medium of 20% ethanol[18]. As there is no direct conjugation between the reaction centre and substituent (which is usually strenghtened in nonaqueous solvents[19]), the free electron pair must be extensively delocalized into the second benzene ring too. The anion formed can be subsequently cyclized into benzotriazinone (see Introduction) by two mechanisms[20], viz. E1cB type and $B_{Ac}2$ type (Scheme 1). These mechanisms cannot be differentiated kinetically. Although formation of compound *III* is less probable (decomposition of aromatic system of benzene ring usually has high energy demands), nevertheless compounds of similar structure were described[8] during photodecompositions of analogues of compound *I*. On the other hand, formation of structure *IV* is usually preferred in cyclizations of this type (e.g. the cyclization of ethyl 3-(N'-alkyl-ureido)-2-butenoates[21] and ethyl 3-ureido-2-butenoates[20]). For both the mechanisms, however, it is substantial that splitting off of ethoxide anion most likely represents the rate-limiting step in both cases[22]. As this process takes place in the first step
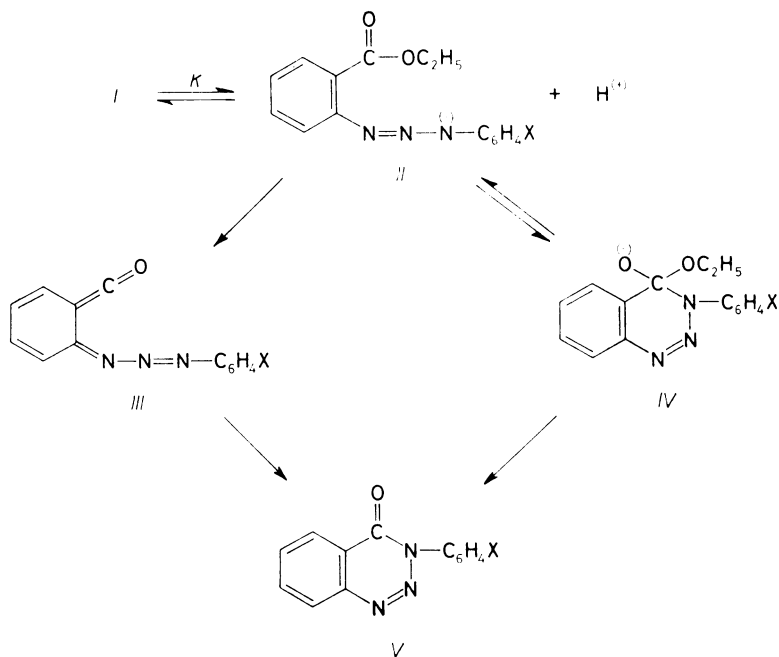
SCHEME 1

in the E1cB type of mechanism, whereas it occurs in the second step in the $B_{Ac}2$ type, there exists a possibility of lowering of the concentration of the starting anion *II* due to the equilibrium with the intermediate *IV*, whereby also the mechanism of $B_{Ac}2$ type is preferred. The mechanism of E1cB type exhibits high sensitivity to the nature of leaving group[23] and it is insignificant with bad leaving groups. Another criterion consists in the value of the reaction constant of the Hammett equation which represents a superposition of the reaction constants of the rate-limiting step and all preceding steps. The magnitude of the ϱ constant is about 1·5 for dissociation of triazenes[18]. The decompositions by the mechanism of E1cB type exhibit high sensitivity to substituents not only in the leaving group but also in the ring adjacent to the group undergoing the ionization, e.g. $\varrho = -2·75$ for 3-(N-arylcarbamoyl)-1,3-diphenyltriazenes in water at 25°C (ref.[24]). Hence the reaction constants for dissociation and for splitting of the conjugated base are mutually practically compensated, in our case we would expect a ϱ value near to zero. On the other hand, formation of the tetrahedral intermediate in the mechanism of $B_{Ac}2$ type (unless it represents the rate-limiting step) will be less sensitive to substituents and so will be its decomposition, too. Hence, there will be no full compensation of the reaction constants, and the resulting ϱ value will be nonzero and positive. From the rate constant values found

in Eqs $(3)-(6)$ it is impossible to univocally decide about the type of mechanism, however, the mechanism of $B_{Ac}2$ type appears to be more likely.

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