

**STERIC EFFECTS IN ACID-CATALYZED DECOMPOSITION AND BASE-CATALYZED CYCLIZATION OF 1-(2-ALKOXYCARBONYL-PHENYL)-3-PHENYLTRIAZENES**Oldrich PYTELA<sup>1</sup> and Ales HALAMA<sup>2</sup>

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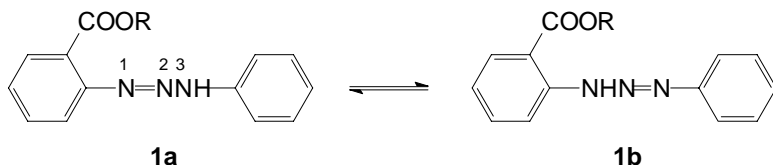
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Eight derivatives of 1-(2-alkoxycarbonylphenyl)-3-phenyltriazenes (R = methyl, ethyl, propyl, isopropyl, butyl, isobutyl, hexyl, and allyl) have been synthesized and their UV-VIS, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra measured. The NMR spectra have been interpreted in detail. The kinetics of acid-catalyzed decomposition and base-catalyzed cyclization of the title compounds have been measured in 52.1% w/w methanol at 25.0 °C. The unit reaction order has been verified and the cyclization product has been identified. The pH-profiles obtained have been used to calculate the catalytic rate constants  $k_A$  (acid-catalyzed decomposition) and  $k_B$  (base-catalyzed cyclization) of all the derivatives; the constants have been interpreted with regard to inductive and steric effects. The catalytic rate constant  $k_A$  has been found to be independent of the substituents. The catalytic rate constant  $k_B$  depends statistically significantly upon both inductive and steric effects, the sensitivity to the former being more significant. The experimental results and their interpretation confirm the base-catalyzed cyclization mechanism with formation of tetrahedral intermediate as the rate-limiting step.

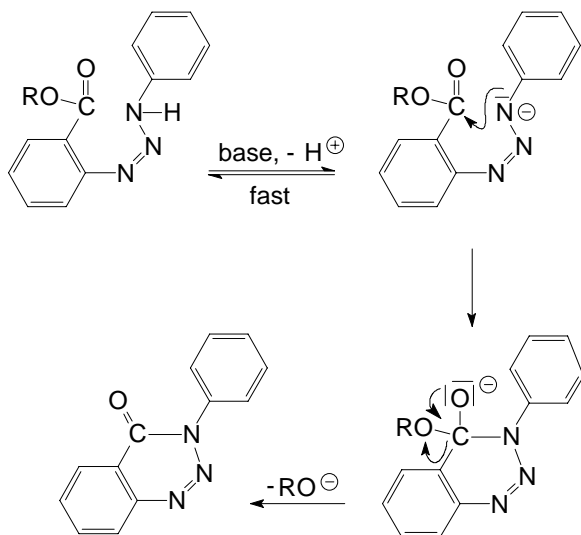
**Key words:** Triazenes, acid-catalyzed decomposition of; Triazenes, base-catalyzed cyclization of; Inductive effect; Steric effects.

The title 1-(2-alkoxycarbonylphenyl)-3-phenyltriazenes of general formula **1** (Scheme 1) have not been systematically studied yet, only the methyl and ethyl derivatives being known so far<sup>1-3</sup> (**1**, R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>). The cognate compounds so far synthesized and described involve 1-alkyl-3-(2-alkoxycarbonylphenyl)triazenes<sup>4</sup>, 1-(2-ethoxycarbonylphenyl)-3-aryltriazenes<sup>3</sup>, 1-(2-aryloxycarbonylphenyl)-3-phenyltriazenes<sup>5</sup>, and 1-(2-cyanophenyl)-3-phenyltriazenes<sup>6-8</sup>. The compounds of type **1** can undergo two different reactions depending on the catalyst type. In acid media they undergo acid-



SCHEME 1

catalyzed splitting of the triazene chain into the respective diazonium salt and amine. Due to the tautomerism between the two forms **1a** and **1b**, the splitting can produce either of the two possible diazonium salts along with the corresponding anilines. This type of reactions is relatively well known, for a survey see, e.g., our previous communications<sup>9-12</sup>. Depending on the substrate structure and on the reaction medium, the catalytic particles involve the proton, nondissociated general acid, and (in aprotic media) also dimer of general acid<sup>9-11</sup>. The decomposition connected with splitting of triazene chain can be described by two mechanisms expressing rather two limit states of a real process. The first of these mechanisms, which is called A1, involves a formation of protonated substrate in a rapid pre-equilibrium and its subsequent decomposition in the rate-limiting step. It is observed in polar protic media predominantly. Evidently, the reaction is co-assisted by the acid anion as a general base catalyst<sup>12</sup>. The second mechanism, referred to as A-S<sub>E</sub>2, is characterized by a proton transfer from a general acid to the substrate in the rate-limiting step, and it is likely to take place in little polar media. In basic media, the proton is dissociated from N<sup>3</sup> atom<sup>13</sup> to give an anion behaving as a nucleophile which attacks the carbonyl of ester group at *ortho* position to the triazene chain. This cyclization produces 3-phenyl-3*H*,4*H*-benzo[*e*]-1,2,3-triazin-4-one<sup>14</sup> (Scheme 2). The cyclization can also be spontaneous during crystallization from alcohols in the presence of small amount of water<sup>1,14</sup>. The mechanism of base-catalyzed cyclization of 1-(2-ethoxycarbonylphenyl)-3-aryltriazenes<sup>3</sup> and 1-(2-aryloxycarbonylphenyl)-3-phenyltriazenes<sup>5</sup> was dealt with in our previous communications. The reaction is likely to go by a B<sub>Ac</sub>2 type mechanism with formation of the tetrahedral intermediate as the rate-limiting step (Scheme 2). One of the symptoms supporting this



SCHEME 2

conclusion is the high sensitivity of this reaction to steric effects of substituents at 3-position of the cyclized aryl esters.

The term "steric effects" summarily describes nonbonding repulsion interactions between the reaction centre and substituent due to overlap of occupied molecular orbitals<sup>15-20</sup>. The term "kinetic steric effect" is most often understood as a hindrance to the reagent approach toward the reaction centre<sup>19</sup>. Steric effects usually result in an increase in the Gibbs activation energy and, hence, retardation of the reaction. On the other hand, in some reactions the steric requirements in educts are greater than those in the activated complex, which leads to the so-called steric acceleration of reaction. For the first time, the steric effect was quantitatively described by Taft<sup>15,21</sup> using the  $E_S$  constant. Correctness on the  $E_S$  constant has often been discussed, first of all from the point of view of involvement of other effects<sup>22-25</sup>. These drawbacks are avoided by the steric parameters  $\nu$  derived by Charton<sup>20,26</sup> using the van der Waals radii of atoms. The steric parameters  $\Omega_S$  were also derived from geometrical arrangement of atoms in the substituents<sup>27</sup>. However, differences between the  $E_S$  and  $\Omega_S$  parameters in their applications to selected reactions were not much significant<sup>27</sup>. Another, in principle different description of steric effect was derived from thermodynamic measurements and called  $S_f$ ; it is based on the difference between standard enthalpies of formation of the substituents bound to *tert*-butyl and methyl residues<sup>28</sup>. From the point of view of mechanistic studies, the quality differences between the parameters given are negligible; it must only be remembered that the  $E_S$  constants decrease with increasing steric requirements of substituent, hence the respective reaction constants have opposite signs to those in other scales. The correlation relations used for interpretation of experimental kinetic data evaluate the inductive and/or mesomeric effects along with steric effects.

The aim of the present communication is to evaluate the steric effects in base-catalyzed cyclization of compound **1** and therefrom to decide whether the reaction involves the formation or the decomposition of the tetrahedral intermediate as the rate-limiting step (Scheme 2).

## EXPERIMENTAL

### Syntheses of Alkyl Anthranilates by Reactions of Isatoic Anhydride with Alcohols (Method A)

Sodium (0.5 g, 22 mmol) was dissolved in the chosen alcohol (100 ml) and isatoic anhydride (16.3 g, 100 mmol) was added thereto. The reaction mixture was refluxed until the evolution of carbon dioxide (foaming) ceased. Then the excess alcohol was distilled off, and the raw alkyl anthranilate was extracted with benzene (25 ml). The benzene extract was shaken with the same volume of 5% aqueous potassium carbonate and then with the same volume of water, whereafter it was dried with anhydrous sodium sulfate. Benzene was evaporated in a vacuum evaporator, and the raw ester was refined by vacuum distillation. The yields and refractive indexes are presented in Table I.

## Syntheses of Alkyl Anthranilates from Alkyl 2-Nitrobenzoates (Method B)

The respective ester of 2-nitrobenzoic acid (100 mmol) was dissolved in the corresponding alcohol (in the ratio of ca 1 : 10 v/v) with addition of platinum(IV) oxide (0.2 g). Hydrogen (ca 1 mol) was introduced under mild pressure into the reaction mixture, and after the reduction was finished the catalyst and solvent were removed by filtration and distillation, respectively. The raw anthranilate was purified by vacuum distillation. The yields and refractive indexes are presented in Table I.

## Syntheses of 1-(2-Alkoxy-carbonylphenyl)-3-phenyltriazenes

In a beaker, alkyl anthranilate (25 mmol) was mixed with hydrochloric acid (20 ml) diluted with water in the ratio of 1 : 1, the mixture was cooled to 5 °C, and sodium nitrite solution (approximately 5 g NaNO<sub>2</sub> in 5 ml water) was added thereto drop by drop with continuous stirring and keeping the temperature below 5 °C. The end of diazotization was indicated with the help of potassium iodide-starch test paper. With intense stirring, the diazonium salt solution prepared was added in portions to a mixture of aniline (2 g, 22 mmol), ammonium acetate (30 g), and water (40 ml). The separated solid was collected by suction, washed with water, and dried in air. The raw product was purified by column chromatography (alumina, benzene) and recrystallized from hexane. The yields of 1-(2-alkoxy-carbonylphenyl)-3-phenyltriazenes (1) and their melting points are presented in Table II.

## Identification of 1-(2-Alkoxy-carbonylphenyl)-3-phenyltriazenes

For identification and characterization of 1-(2-alkoxy-carbonylphenyl)-3-phenyltriazenes (1) we measured their UV-VIS, IR, <sup>1</sup>H, and <sup>13</sup>C NMR spectra. The UV-VIS spectra were measured in methanol using an HP 8452A (Hewlett-Packard, Diode Array Spectrophotometer). The IR spectra were measured in Nujol suspension using a Specord 75 IR (Zeiss, Jena) apparatus. The <sup>1</sup>H NMR measurements were carried out on an AMX-360 (Bruker) apparatus using a frequency of 360.14 MHz at the temperature of 298 K; the samples were dissolved in CDCl<sub>3</sub> (5% solutions). The chemical shifts are referenced to the signal of HMDSO standard ( $\delta = 0.05$  ppm). The <sup>13</sup>C NMR spectra were measured at the frequency of 90.57 MHz at 298 K in 5% solutions in CDCl<sub>3</sub>. The chemical shifts are referenced

TABLE I

Methods of preparation, reaction yields, and refractive indexes of the alkyl anthranilates 2-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>COOR synthesized

R	Method	Yield, %	$n_D^{20}$ (ref.)	R	Method	Yield, %	$n_D^{20}$ (ref.)
Methyl	A	66.2	1.5830 (1.582 <sup>a</sup> )	Butyl	A	40.3	1.5468 (1.545 <sup>b</sup> )
Ethyl	A	50.2	1.5640 (1.564 <sup>b</sup> )	Isobutyl	B	86.3	1.5423 (1.540 <sup>b</sup> )
Propyl	A	43.8	1.5562 (1.551 <sup>b</sup> )	Hexyl	B	50.8	1.5381 —
Isopropyl	B	75.9	1.5478 —	Allyl	A	45.7	1.5709 —

<sup>a</sup> Ref.<sup>29</sup>; <sup>b</sup> ref.<sup>30</sup>.

to the solvent signal ( $\delta = 77.0$  ppm). The  $\text{CDCl}_3$  used was rid of traces of hydrochloric acid to prevent destruction of the compound measured: deuteriochloroform was shaken with the same volume of 5% aqueous sodium carbonate and then with the same volume of water, dried with anhydrous sodium sulfate, filtered, and distilled.

#### Identification of Product of Base-Catalyzed Cyclization of 1-(2-Alkoxy-carbonylphenyl)-3-phenyltriazenes

In order to identify the product of base-catalyzed cyclization of the model triazenes we isolated a small amount of product from the reaction of 1-(2-alkoxy-carbonylphenyl)-3-phenyltriazene in aqueous-methanolic buffer of pH 11.94. The melting point of the product isolated was 149–151 °C in accordance with that of the expected 3-phenyl-3*H*,4*H*-benzo[*e*]-1,2,3-triazin-4-one (ref.<sup>31</sup> gives m.p. 151–152 °C). Similarly, the positions of UV absorption maxima  $\lambda = 291$  nm and  $\lambda = 315$  nm corresponded to the values published<sup>32</sup>  $\lambda = 290$  nm and  $\lambda = 314$  nm.

#### Kinetic Measurements

The reaction media used for the kinetic measurements were aqueous methanolic buffers containing 52.1% (w/w) methanol. The buffers in the range from pH 2.65 to pH 5.27 were obtained by mixing (at various volume ratios) the solutions of citric acid (0.01–0.1 M) and 0.01 M potassium carbonate. The buffers in the range from pH 7.53 to pH 9.79 were prepared by mixing various volumes of saturated solutions of sodium hydrogenphosphate and potassium dihydrogenphosphate. The buffers with pH above 9.79 were prepared by mixing various volumes of saturated sodium hydrogenphosphate and 0.2 M sodium hydroxide. The ionic strength of the buffers was not adjusted. Their pH values were measured by means of a glass electrode using an MV 870 Digital (VEB-Präcitronic) pH meter.

Before the measurement itself, about 2 ml of buffer in a cell was placed into the thermostated cell holder of the apparatus ( $25 \pm 0.1$  °C), and after reaching the said temperature, 1–10  $\mu\text{l}$  dioxane solution of triazene **1** of suitable concentration was added and the mixture was thoroughly mixed. The transmittance–time dependence was recorded for at least four half-lives. The observed rate constants were evaluated by a known procedure<sup>33</sup> and are presented in Table III.

TABLE II

Yields of syntheses, melting points, and spectral characteristics in UV-VIS and IR spectra of 1-(2-alkoxy-carbonylphenyl)-3-phenyltriazenes **1**

R	Yield, %	M.p., °C	$\lambda_1$ , nm	$\epsilon_1 \cdot 10^{-4}$ $\text{l mol}^{-1} \text{cm}^{-1}$	$\lambda_2$ , nm	$\epsilon_2 \cdot 10^{-4}$ $\text{l mol}^{-1} \text{cm}^{-1}$	$\nu(\text{NH})$ $\text{cm}^{-1}$	$\nu(\text{CO})$ $\text{cm}^{-1}$
Methyl	32	64–66	224	2.683	358	2.416	3 250	1 678
Ethyl	35	70–72	220	2.220	358	2.512	3 230	1 677
Propyl	28	76–77	220	1.647	358	2.485	3 217	1 693
Isopropyl	33	77–79	220	1.492	358	2.429	3 222	1 690
Butyl	26	64–66	220	2.023	358	2.553	3 227	1 695
Isobutyl	32	57–60	220	2.013	358	2.579	3 240	1 692
Hexyl	24	53–56	220	2.365	358	2.397	3 222	1 677
Allyl	52	65–68	222	2.504	360	2.557	3 237	1 677

TABLE III  
pH dependence of observed rate constant  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) of reactions of 1-(2-alkoxycarbonylphenyl)-3-phenyltriazenes **1**

pH	$k_{\text{obs}}$	pH	$k_{\text{obs}}$	pH	$k_{\text{obs}}$	pH	$k_{\text{obs}}$
R = Methyl							
2.65	$3.123 \cdot 10^{-2}$	3.90	$1.968 \cdot 10^{-3}$	7.96	$3.185 \cdot 10^{-4}$	9.06	$4.624 \cdot 10^{-3}$
2.84	$1.994 \cdot 10^{-2}$	4.32	$8.222 \cdot 10^{-4}$	8.08	$4.609 \cdot 10^{-4}$	9.20	$6.445 \cdot 10^{-2}$
3.15	$9.256 \cdot 10^{-3}$	4.73	$3.293 \cdot 10^{-4}$	8.27	$7.812 \cdot 10^{-4}$	9.47	$1.021 \cdot 10^{-2}$
3.31	$5.760 \cdot 10^{-3}$	5.27	$9.455 \cdot 10^{-5}$	8.50	$1.278 \cdot 10^{-3}$	9.79	$1.826 \cdot 10^{-2}$
3.52	$3.756 \cdot 10^{-3}$	7.53	$1.532 \cdot 10^{-4}$	8.83	$3.232 \cdot 10^{-3}$		
R = Ethyl							
2.65	$2.576 \cdot 10^{-2}$	3.90	$1.821 \cdot 10^{-3}$	8.50	$2.017 \cdot 10^{-4}$	9.47	$1.440 \cdot 10^{-3}$
2.84	$1.843 \cdot 10^{-2}$	4.32	$7.698 \cdot 10^{-4}$	8.68	$3.047 \cdot 10^{-4}$	9.79	$3.865 \cdot 10^{-3}$
3.15	$9.978 \cdot 10^{-3}$	4.73	$3.192 \cdot 10^{-4}$	8.83	$4.065 \cdot 10^{-4}$	10.93	$4.020 \cdot 10^{-2}$
3.31	$6.668 \cdot 10^{-3}$	5.27	$1.074 \cdot 10^{-4}$	9.06	$7.001 \cdot 10^{-4}$	11.29	$7.051 \cdot 10^{-2}$
3.52	$4.132 \cdot 10^{-3}$	8.27	$1.158 \cdot 10^{-4}$	9.20	$9.319 \cdot 10^{-4}$		
R = Propyl							
2.65	$2.620 \cdot 10^{-2}$	3.90	$1.863 \cdot 10^{-3}$	8.83	$2.728 \cdot 10^{-4}$	10.26	$8.570 \cdot 10^{-3}$
2.84	$2.074 \cdot 10^{-2}$	4.32	$9.219 \cdot 10^{-4}$	9.06	$4.819 \cdot 10^{-4}$	10.48	$6.717 \cdot 10^{-3}$
3.15	$9.593 \cdot 10^{-3}$	4.73	$3.656 \cdot 10^{-4}$	9.20	$5.976 \cdot 10^{-4}$	10.93	$2.618 \cdot 10^{-2}$
3.31	$6.429 \cdot 10^{-3}$	5.27	$1.014 \cdot 10^{-4}$	9.47	$8.948 \cdot 10^{-4}$	11.41	$5.556 \cdot 10^{-2}$
3.52	$3.790 \cdot 10^{-3}$	8.68	$1.841 \cdot 10^{-4}$	9.79	$2.395 \cdot 10^{-3}$		
R = Isopropyl							
2.65	$2.692 \cdot 10^{-2}$	3.90	$1.839 \cdot 10^{-3}$	9.79	$2.555 \cdot 10^{-4}$	11.29	$9.077 \cdot 10^{-3}$
2.84	$1.814 \cdot 10^{-2}$	4.32	$7.219 \cdot 10^{-4}$	10.26	$7.761 \cdot 10^{-4}$	11.42	$1.467 \cdot 10^{-2}$
3.15	$9.821 \cdot 10^{-3}$	4.73	$3.086 \cdot 10^{-4}$	10.48	$1.197 \cdot 10^{-3}$	11.84	$3.155 \cdot 10^{-2}$
3.31	$6.602 \cdot 10^{-3}$	5.27	$1.320 \cdot 10^{-4}$	10.72	$1.994 \cdot 10^{-3}$	11.94	$4.471 \cdot 10^{-2}$
3.52	$3.934 \cdot 10^{-3}$	9.47	$1.101 \cdot 10^{-4}$	10.93	$4.353 \cdot 10^{-3}$		

TABLE III  
(Continued)

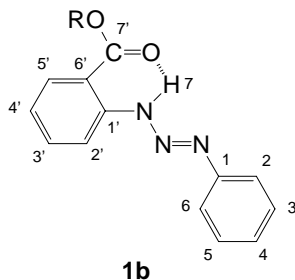
pH	$k_{\text{obs}}$	pH	$k_{\text{obs}}$	pH	$k_{\text{obs}}$	pH	$k_{\text{obs}}$
R = Butyl							
2.65	$2.577 \cdot 10^{-2}$	3.90	$1.552 \cdot 10^{-3}$	9.06	$3.707 \cdot 10^{-4}$	10.48	$8.474 \cdot 10^{-3}$
2.84	$1.863 \cdot 10^{-2}$	4.32	$7.301 \cdot 10^{-4}$	9.20	$4.557 \cdot 10^{-4}$	10.72	$1.521 \cdot 10^{-2}$
3.15	$8.264 \cdot 10^{-3}$	4.73	$3.051 \cdot 10^{-4}$	9.47	$8.923 \cdot 10^{-4}$	10.93	$3.091 \cdot 10^{-2}$
3.31	$5.087 \cdot 10^{-3}$	5.27	$7.110 \cdot 10^{-5}$	9.79	$1.957 \cdot 10^{-3}$	11.29	$7.092 \cdot 10^{-2}$
3.52	$3.467 \cdot 10^{-3}$	8.83	$2.291 \cdot 10^{-4}$	10.26	$4.973 \cdot 10^{-3}$		
R = Isobutyl							
2.65	$2.806 \cdot 10^{-2}$	3.90	$1.604 \cdot 10^{-3}$	9.43	$3.814 \cdot 10^{-4}$	10.93	$1.329 \cdot 10^{-2}$
2.84	$2.021 \cdot 10^{-2}$	4.32	$9.044 \cdot 10^{-4}$	9.79	$8.457 \cdot 10^{-4}$	11.26	$2.885 \cdot 10^{-2}$
3.15	$8.878 \cdot 10^{-3}$	4.73	$3.208 \cdot 10^{-4}$	10.26	$2.203 \cdot 10^{-3}$	11.41	$4.770 \cdot 10^{-2}$
3.31	$5.852 \cdot 10^{-3}$	5.27	$1.039 \cdot 10^{-4}$	10.48	$3.613 \cdot 10^{-3}$		
3.52	$3.455 \cdot 10^{-3}$	9.20	$1.725 \cdot 10^{-4}$	10.72	$6.143 \cdot 10^{-3}$		
R = Hexyl							
2.65	$2.752 \cdot 10^{-2}$	3.90	$1.431 \cdot 10^{-3}$	9.06	$2.924 \cdot 10^{-4}$	10.48	$5.227 \cdot 10^{-3}$
2.84	$1.972 \cdot 10^{-2}$	4.32	$7.821 \cdot 10^{-4}$	9.20	$3.092 \cdot 10^{-4}$	10.93	$2.325 \cdot 10^{-2}$
3.15	$8.644 \cdot 10^{-3}$	4.73	$3.143 \cdot 10^{-4}$	9.47	$8.094 \cdot 10^{-4}$	11.29	$4.460 \cdot 10^{-2}$
3.31	$6.221 \cdot 10^{-3}$	5.27	$1.060 \cdot 10^{-4}$	9.79	$1.771 \cdot 10^{-3}$		
3.52	$3.412 \cdot 10^{-3}$	8.83	$1.971 \cdot 10^{-4}$	10.26	$4.277 \cdot 10^{-3}$		
R = Allyl							
2.65	$2.562 \cdot 10^{-2}$	3.90	$1.570 \cdot 10^{-3}$	8.08	$4.980 \cdot 10^{-4}$	9.06	$4.590 \cdot 10^{-3}$
2.84	$2.093 \cdot 10^{-2}$	4.32	$6.825 \cdot 10^{-4}$	8.27	$7.725 \cdot 10^{-4}$	9.20	$4.978 \cdot 10^{-3}$
3.15	$9.185 \cdot 10^{-3}$	4.73	$3.011 \cdot 10^{-4}$	8.50	$1.132 \cdot 10^{-3}$	9.47	$1.102 \cdot 10^{-2}$
3.31	$6.362 \cdot 10^{-3}$	5.27	$1.064 \cdot 10^{-4}$	8.68	$2.043 \cdot 10^{-3}$	9.79	$2.680 \cdot 10^{-2}$
3.52	$3.315 \cdot 10^{-3}$	7.96	$3.251 \cdot 10^{-4}$	8.83	$3.083 \cdot 10^{-3}$	10.26	$5.902 \cdot 10^{-2}$

## RESULTS AND DISCUSSION

*Spectra of 1-(2-Alkoxy carbonylphenyl)-3-phenyltriazenes*

The UV-VIS spectra of the triazenes studied were measured in methanol; they show two absorption maxima: one in the region of 220 nm and the other (which is characteristic of triazenes) in the region of 360 nm. The values of individual derivatives are presented in Table II. The IR spectra are characterized by valence vibrations  $\nu(\text{N-H})$  in the region from  $3\,217\text{ cm}^{-1}$  to  $3\,250\text{ cm}^{-1}$  and  $\nu(\text{C=O})$  in the region from  $1\,677\text{ cm}^{-1}$  to  $1\,695\text{ cm}^{-1}$  (see Table II).

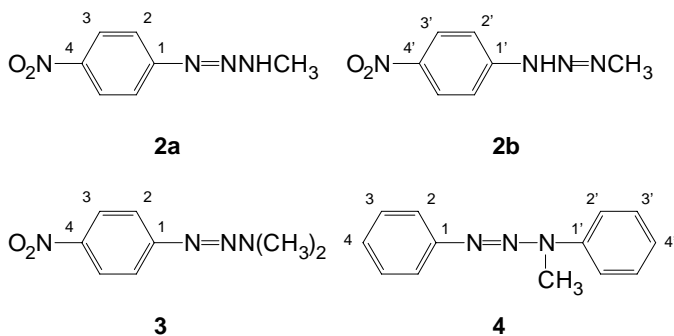
The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Tables IV and V) are of primary importance for proving and characterizing the 1-(2-alkoxycarbonylphenyl)-3-phenyltriazenes **1**. For an unambiguous assignment of  $^1\text{H}$  and  $^{13}\text{C}$  signals in the NMR spectra of the 1-(2-ethoxycarbonylphenyl)-3-phenyltriazenes we used the H,H-COSY, H,C-COSY technique and two INEPT  $^{13}\text{C}$  experiments with selective transfer of polarization from H-2' and H-5' protons. For the remaining derivatives the assignment was carried out on the basis of analogy between the individual spectra. From the NMR spectra it is obvious that the variation of alkyl groups does not affect the values of chemical shifts of signals of protons and carbon atoms in the aromatic region and those of carbonyl carbon atom signals.



However, it is possible to make an important conclusion with respect to the possible tautomeric forms of the model triazenes. For this purpose, it is possible to adopt the known spectral data ( $^{13}\text{C}$  NMR) on the tautomers of 3-methyl-1-(4-nitrophenyl)triazenes (**2a**, **2b**, ref. <sup>34</sup>) and on the triazenes whose tautomerism is prevented by substituents (**3**, **4**, refs<sup>34,35</sup>). The tautomerism of triazenes mostly affects the chemical shifts of carbons separated by the least number of bonds from the  $-\text{N}=\text{N}-\text{NHR}$  or  $-\text{NH}-\text{N}=\text{NR}$  group ( $\text{R} = \text{alkyl or aryl}$ ). These particularly include the carbons C-1, C-2, and C-1' and C-2'. The following chemical shifts are given<sup>34</sup> for the tautomer **2a**:  $\delta(\text{C-1}) = 148.81$ ,  $\delta(\text{C-2}) = 120.48$ , and for the tautomer **2b**:  $\delta(\text{C-1}') = 140.74$ ,  $\delta(\text{C-2}') = 112.86$ . For the triazenes whose tautomerism is prevented by substituents at N-3 atom, e.g., the following  $^{13}\text{C}$  NMR spectra are known: 3,3-dimethyl-1-(4-nitrophenyl)triazenes **3** ( $\delta(\text{C-1}) = 155.84$ ,  $\delta(\text{C-2}) =$



120.34, ref.<sup>35</sup>) and 1-phenyl-3-methylphenyltriazene **4** ( $\delta(\text{C-1}) = 150.2$ ,  $\delta(\text{C-2}) = 121.2$ ,  $\delta(\text{C-1}') = 145.0$ ,  $\delta(\text{C-2}') = 116.8$ , ref.<sup>34</sup>). From the  $\delta(\text{C-1})$  and  $\delta(\text{C-2})$  values of compounds **2a**, **3**, **4** it follows that the chemical shifts of carbon atoms close to  $-\text{N}=\text{N}-\text{NR}^1\text{R}$  group ( $\text{R} = \text{H}$  or alkyl,  $\text{R}^1 = \text{alkyl}$  or aryl) are found approximately in the intervals of 148–156 ppm and 120–121 ppm for C-1 and C-2, respectively. On the other hand, in the cases of **2b** and **4** the values of  $\delta(\text{C-1}')$  and  $\delta(\text{C-2}')$  of the carbon atoms close to  $-\text{NR}-\text{N}=\text{NR}^1$  group ( $\text{R} = \text{H}$  or alkyl,  $\text{R}^1 = \text{alkyl}$  or aryl) are approximately in the regions of 141–145 ppm and 113–117 ppm for C-1' and C-2', respectively. From the spectral data obtained by us it follows that 1-(2-alkoxycarbonylphenyl)-3-phenyltriazenes **1** ( $\delta(\text{C-1}) = 149.5$ – $149.7$ ,  $\delta(\text{C-2}) = 121.6$ – $121.7$ ,  $\delta(\text{C-1}') = 143.9$ – $144.1$ ,  $\delta(\text{C-2}') = 114.4$ – $114.5$ ) exist in the tautomeric form **1b** under the conditions of measurements. This statement is directly supported also by the found high values of  $\delta(\text{NH})$  (12.36–12.46) in the  $^1\text{H}$  NMR spectra which indicate the participation of H-7 hydrogen in intramolecular hydrogen bond with the free electron pair at the carbonyl oxygen atom resulting in formation of a six-membered cycle (**1b**).



### *Verification of Reaction Molecularity and Evaluation of Catalytic Rate Constants*

The reaction order of acid-catalyzed decomposition and base-catalyzed cyclization of the triazenes **1** studied were evaluated, with maintaining the reaction conditions, by the method of two initial concentrations in the case of the methyl derivative (pH 3.90), ethyl derivative (pH 4.73), hexyl derivative (pH 9.20), and allyl derivative (pH 9.06). The corresponding  $n$  values are 1.033, 1.033, 1.045, and 0.961, hence the reactions are of the first order in the substrate.

The pH dependence of observed rate constants (Table III), i.e. the pH profile, is characterized by two line segments corresponding to the acid and base catalyses (negative and positive slopes, respectively). The catalytic rate constants of the two processes were calculated as the average value of sum of ( $k_A$ , acid catalysis) or difference between

( $k_B$ , base catalysis) the values of the observed rate constants  $k_{\text{obs}}$  and pH: the respective results are given in Table VI.

### Interpretation of Steric Effects

The catalytic rate constants  $k_A$  of acid-catalyzed decomposition of 1-(2-alkoxycarbonylphenyl)-3-phenyltriazenes **1** given in Table VI gave no statistically significant correlation with any combination of substituent constant  $\sigma^*$  and some other of the constants describing the steric effects in the same Table. This conclusion is not unexpected since the change of alkyl group practically changes neither the electron density at the nitrogen atoms of the triazene chain nor steric situation in its environment.

On the other hand, correlations of the catalytic constants  $k_B$  with a combination of the substituent constant  $\sigma^*$  and steric constants from Table VI were statistically significant as it can be seen from Eqs (1) through (4).

TABLE IV  
Values of  $^1\text{H}$  and  $^{13}\text{C}$  NMR shifts ( $\delta$ , ppm) of protons and carbon atoms of the basic skeleton of 1-(2-alkoxycarbonylphenyl)-3-phenyltriazenes **1b**

Atom	Methyl	Ethyl	Propyl	Isopropyl	Butyl	Isobutyl	Hexyl	Allyl
H-2/H-6	7.60	7.59	7.59	7.59	7.59	7.59	7.60	7.59
H-3/H-5	7.40	7.39	7.38	7.39	7.37	7.38	7.40	7.40
H-4	7.28	7.26	7.26	7.26	7.25	7.26	7.27	7.25
H-7	12.36	12.41	12.41	12.46	12.40	12.40	12.41	12.36
H-2'	7.91	7.89	7.89	7.90	7.88	7.89	7.91	7.89
H-3'	7.50	7.48	7.47	7.47	7.46	7.47	7.50	7.47
H-4'	6.99	6.98	6.97	6.98	6.95	6.97	7.00	6.96
H-5'	7.99	7.99	7.99	7.98	7.96	7.99	8.00	8.00
C-1	149.5	149.6	149.6	149.7	149.6	149.6	149.7	149.6
C-2/C-6	121.6	121.7	121.7	121.7	121.6	121.6	121.7	121.7
C-3/C-5	128.9	128.9	129.0	129.0	128.9	129.0	129.0	129.0
C-4	127.7	127.8	127.8	127.8	127.7	127.8	127.8	127.8
C-1'	143.9	144.0	144.0	144.0	143.9	144.0	144.0	144.1
C-2'	114.4	114.4	114.4	114.4	114.4	114.4	114.5	114.4
C-3'	134.4	134.3	134.3	134.2	134.3	134.3	134.4	134.5
C-4'	120.9	121.0	121.0	120.9	120.9	121.0	121.0	121.0
C-5'	131.0	131.1	131.0	131.0	131.0	131.1	131.1	131.0
C-6'	111.8	112.1	112.1	112.5	112.1	112.1	112.3	112.7
C-7'	167.7	167.3	167.3	166.8	167.3	167.2	167.4	166.9

$$\log k_B = -(11.33 \pm 0.07) + (7.11 \pm 0.89)\sigma^* + (0.545 \pm 0.131)E_S^{\text{C}} \quad (1)$$

$$n = 7, s = 0.079, R = 0.9941$$

$$\log k_B = -(10.83 \pm 0.20) + (8.52 \pm 0.88)\sigma^* - (0.995 \pm 0.339)\nu \quad (2)$$

$$n = 7, s = 0.103, R = 0.9900$$

$$\log k_B = -(7.56 \pm 0.43) - (18.4 \pm 1.6)\Omega_S \quad (3)$$

$$n = 7, s = 0.123, R = 0.9821$$

$$\log k_B = -(11.41 \pm 0.05) + (6.33 \pm 0.70)\sigma^* - (0.337 \pm 0.054)S_f \quad (4)$$

$$n = 7, s = 0.056, R = 0.9971$$

TABLE V

Values of  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts ( $\delta$ , ppm) of protons and carbon atoms in alkyl chain of 1-(2-alkoxycarbonylphenyl)-3-phenyltriazenes **1**

Alkyl	Nuclide	CH <sub>3</sub>	CH <sub>2</sub>	CH <sub>2</sub>	CH <sub>2</sub>	CH <sub>2</sub>	CH <sub>2</sub>	CH	CH=	CH <sub>2</sub> =
Methyl	$^1\text{H}$	3.92	–	–	–	–	–	–	–	–
	$^{13}\text{C}$	52.1	–	–	–	–	–	–	–	–
Ethyl	$^1\text{H}$	1.38	4.36	–	–	–	–	–	–	–
	$^{13}\text{C}$	14.2	61.2	–	–	–	–	–	–	–
Propyl	$^1\text{H}$	1.01	1.77	4.26	–	–	–	–	–	–
	$^{13}\text{C}$	10.5	22.0	66.7	–	–	–	–	–	–
Isopropyl	$^1\text{H}$	1.37	–	–	–	–	–	5.24	–	–
	$^{13}\text{C}$	21.9	–	–	–	–	–	68.8	–	–
Butyl	$^1\text{H}$	0.95	1.45	1.72	4.29	–	–	–	–	–
	$^{13}\text{C}$	13.7	19.2	30.6	64.9	–	–	–	–	–
Isobutyl	$^1\text{H}$	1.00	4.08	–	–	–	–	2.07	–	–
	$^{13}\text{C}$	19.7	71.1	–	–	–	–	27.8	–	–
Hexyl	$^1\text{H}$	0.90	1.33	1.33	1.44	1.76	4.31	–	–	–
	$^{13}\text{C}$	14.0	22.6	25.7	28.6	31.5	65.4	–	–	–
Allyl	$^1\text{H}$	–	4.79	–	–	–	–	–	6.00	5.24 5.39
	$^{13}\text{C}$	–	65.6	–	–	–	–	–	131.9	118.6

From the equations it is obvious that except for Eq. (3) the correlations are very good, both electronic and steric effects being interpreted. The multicollinearity between the interpreting variables is small (Eq. (2)) to medium (Eqs (1) and (4)), hence the reaction constants (regression coefficients) obtained can be considered valid. The negative sign of reaction constant  $\rho^*$  means that the cyclization is accelerated by electron acceptor substituents, the effect of substituents on dissociation of N–H bond (Scheme 1) being negligible in similar way as that in the acid-catalyzed decomposition. Therefrom it unequivocally follows that the attack of carbon atom of ester carbonyl group by the nitrogen atom  $N^3$  is rate limiting. The sensitivity of this elementary reaction expressed by the reaction constant is roughly twice as large as that in the aminolysis of alkyl acetates<sup>38</sup> and as much as three times as large as that of the base-catalyzed hydrolysis of methyl carboxylates<sup>36</sup>. Therefrom it can be deduced that the negative charge is little localized at the nitrogen atom  $N^3$  and this nitrogen atom is a weak nucleophile only. The sign at the rate constants describing the sensitivity to steric effect (in all the relations (1) through (4)) leads to an unequivocal conclusion that increased steric demands of substituents at the reaction centre retard the reaction. This fully agrees with the above-mentioned conclusions concerning the formation of tetrahedral intermediate as the rate-limiting step. The magnitude of steric reaction constants indicates a small to medium sensitivity to steric effect<sup>17,26,27,28,39</sup>. This conclusion is somewhat different from those obtained earlier for the cyclizations of 1-(2-aryloxycarbonylphenyl)-3-phenyltriazenes<sup>5</sup> where the sensitivity to steric effect was very high due obviously to the bulkiness of aromatic nucleus.

TABLE VI

Catalytic rate constants  $\log k_A$  for acid-catalyzed decomposition and  $\log k_B$  for base-catalyzed cyclization of 1-(2-alkoxycarbonylphenyl)-3-phenyltriazenes **1** in 52.1% (w/w) aqueous methanol at 25 °C and the corresponding constants  $\sigma^*$  (refs<sup>36,37</sup>),  $E_S^c$  (ref.<sup>25</sup>),  $\nu$  (ref.<sup>20</sup>),  $\Omega_S$  (ref.<sup>27</sup>), and  $S_f$  (ref.<sup>28</sup>) used for their interpretation

R	$\log k_A$	$\log k_B$	$\sigma^*$	$E_S^c$	$\nu$	$\Omega_S$	$S_f$
Methyl	1.163	-11.41	0.000	-0.059	0.52	0.206	0.00
Ethyl	1.165	-12.25	-0.100	-0.353	0.56	0.256	0.86
Propyl	1.178	-12.47	-0.115	-0.626	0.68	0.273	0.89
Isopropyl	1.169	-13.35	-0.190	-1.024	0.76	0.304	2.29
Butyl	1.103	-12.51	-0.130	-0.624	0.68	0.272	0.86
Isobutyl	1.153	-12.87	-0.125	-1.236	0.98	0.295	1.86
Hexyl <sup>a</sup>	1.140	-12.62	-0.140 <sup>b</sup>	-0.628	0.68	0.272	0.85
Allyl	1.138	-11.41	-0.180				

<sup>a</sup> The values for pentyl were used; <sup>b</sup> assessed value.

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