STERIC EFFECTS IN THE BASE-CATALYZED CYCLIZATION OF 1-[2-(METHOXYCARBONYL)PHENYL]-3-(2-SUBSTITUTED PHENYL)TRIAZENES

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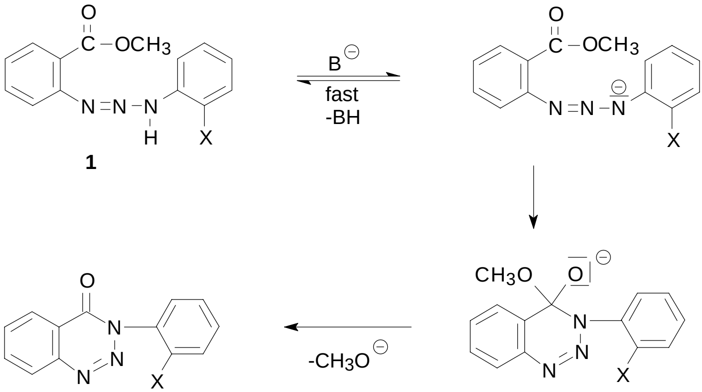
Eleven model 1-[2-(methoxycarbonyl)phenyl]-3-(2-substituted phenyl)triazenes were synthesized and their cyclization kinetics examined in aqueous-methanolic buffer solutions (51 wt.% methanol) at various pH values. 3(2-Substituted phenyl)benzo[*d*][1,2,3]triazin-4(3*H*)-ones were identified as the cyclization products. The log k_{obs} *vs* pH plot was linear with a slope of unity. Investigation of the steric and electronic effects of substituents in the *ortho* position revealed that substituents at the ring which is bonded to the N(3) nitrogen affect the cyclization rate through their steric effect only, while their electronic effects are statistically insignificant. This fact was explained in terms of the ring being tilted from the plane in which the remaining part of the conjugate base anion of the model substrate lies. The assumed and confirmed $B_{Ac}2$ mechanism involving specific base catalysis begins by deprotonation of the triazene giving rise to the conjugate base, continues with formation of a tetrahedral intermediate, and ends with elimination of the methanolate ion. Other mechanisms, such as the elimination-addition mechanism *via* a ketene intermediate or the mechanism involving general base catalysis, are unlikely.

Key words: Triazenes; Base catalyzed cyclization; Steric effect; Substituent effect; Reaction kinetics.

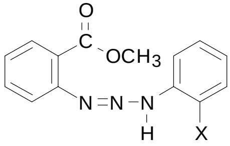
Although some triazene derivatives (**1**) have been described[1,2] (R = CH_3, X = H, CH_3, OCH_3, Cl, NO_2, $COOCH_3$, $NHCOCH_3$), only their physical constants and spectral properties have been published – UV-VIS spectra, vibrational spectra[3], and ^{13}C and ^{15}N NMR spectra[4]. As far as kinetic measurements are concerned, the acid-catalyzed decomposition and base-catalyzed cyclization have been studied for substances structurally related to the triazenes (**1**) (R = Me, Et, Pr, i-Pr, Bu, *s*-Bu, Hex, allyl; X = H) and the reaction has been modelled mathematically. The cyclization reaction has been observed to slow down with increasing steric demands of the substituent[5]. Other kinetic studies of structurally related 1,3-diaryltriazenes centered mainly on the elucidation of the mechanism of the decomposition reactions occurring in acid solutions[6–10]. With the model 1-[2-(methoxycarbonyl)phenyl]-3-(2-substituted phenyl)triazenes (**1**), intramolecular cyclization takes place in basic solutions giving rise to 3-(2-substituted phenyl)benzo[*d*][1,2,3]triazin-4(3*H*)-one[3,5,11,12]. In previous studies, the addition-elimination mechanism $B_{Ac}2$ associated with the formation of a tetrahedral intermediate as the rate-determining step was assumed to be the most likely mechanism of formation of the cyclization product (Scheme 1). Among features characteristic of this mechanism is a high susceptibility of the reaction to the steric demands of substituents near the reaction centre.



SCHEME 1

The term “steric effect” is usually defined as a hindrance to the access of the reagent to the reaction centre[13–18]. Such effects can be considerable, reducing the reaction rate and varying irregularly in dependence on the increasing steric demands. Steric effects of substituents were first described quantitatively by Taft[13,19], who characterized them by the E_s constants. Several corrections to the E_s constants have been suggested; among them are the E_s^C constants proposed by Hancock and coworkers[20]. An approach which is theoretically different has been applied by Charton[21,22], who defined steric constants υ based on the van der Waals radii. Additional, principally new steric constants Ω_s have been proposed by Komantsuzaki and coworkers[23]: the constants represent the relative area of the shadow cast by the substituent onto a spherical surface having a unit area. The constants have been reported nearly solely for alkyl groups.

The main aim of this work is to take advantage of synthesized 1-[2-(methoxycarbonyl)-phenyl]-3-(2-substituted phenyl)triazines (**1**) as model for studying of steric and ele-



1

1	X
a	H
b	CH_3
c	C_2H_5
d	CN
e	CF_3
f	OCH_3
g	F
h	Cl
i	Br
j	NO_2
k	SO_2CH_3

tronic effects of various substituents used on the rate of cyclization in basic media. This paper is a continuation of works published by our group on area of various types of triazenes reactions in various media and also works focused upon steric a *ortho* effects. Substitution of the aromatic ring in the *ortho* position to the side chain with the reaction centre exhibits very specific features compared with substitution in the remaining positions. Kinetic and mechanistic studies are conducted with the aim to describe discussed effects on model substances.

EXPERIMENTAL

Synthesis of 1-[2-(Methoxycarbonyl)phenyl]-3-(2-substituted phenyl)triazenes **1**

Methyl anthranilate (1.51 g, 0.01 mol) was mixed with 20 ml of hydrochloric acid diluted with water in the 1 : 1 ratio. The mixture was cooled to –5 °C, and a solution of sodium nitrite (0.69 g, 0.01 mol) in water (10 ml) was added dropwise to the stirred mixture while keeping the temperature below 5 °C. The diazotization end point was indicated by using iodine-starch paper. The diazonium salt solution was added dropwise to a vigorously stirred mixture of 2-substituted aniline (0.01 mol) and sodium acetate (12.8 g, 0.4 mol) in water (40 ml). The triazenes formed were purified by column chromatography (stationary phase: neutral aluminium oxide supplied by Woelm company; mobile phase: toluene–ethyl acetate–hexane 1 : 5 : 1, the crystallization from diethyl ether was done after chromatography) or by crystallization. The yields of the crude triazenes **1**, their melting points and purification procedures are given in Table I.

TABLE I
Yields, melting points and purification procedures of 1-[2-(methoxycarbonyl)phenyl]-3-(2-substituted phenyl)triazenes **1**

Substrate	Substituent X	Yield, %	Melting point ° C	Purification procedure
1a	H	31.5	64–66[a]	chromatography
1b	CH_3	60.1	70–71[b]	crystallization from methanol
1c	C_2H_5	38.2	62–64	crystallization from methanol
1d	CN	50.0	150–152	crystallization from methanol
1e	CF_3	34.0	130–132	chromatography
1f	OCH_3	31.6	95–97[c]	crystallization from methanol
1g	F	70.0	77–80	chromatography
1h	Cl	41.5	102–104[d]	chromatography
1i	Br	55.0	105–107	chromatography
1j	NO_2	29.0	164–166[e]	crystallization from diethyl ether
1k	SO_2CH_3	29.0	163–165	crystallization from methanol

[a] Ref.[25] 69–71 °C; [b] ref.[25] 69.5 °C; [c] ref.[2] 105 °C; [d] ref.[2] 109 °C; [e] ref.[3] 165–167 °C.

Identification of Triazenes **1**

The structure of the triazenes **1** was confirmed by the UV-VIS spectra of their methanolic solutions, measured on a Hewlett–Packard HP 8452 diode array spectrophotometer, and by the ^{1}H NMR spectra of their solutions in deuterated chloroform, scanned at 25 °C on a Bruker AMX spectrometer (360.14 MHz, standard: hexamethylenedisiloxane, δ 0.05 ppm). Since the triazenes are sensitive to acids present even in trace amounts, the solvent was freed from traces of HCl by extraction with the same volume of 5% aqueous sodium carbonate and with the same volume of water, dried with anhydrous sodium sulfate, and distilled.

Identification of the Product of Base-Catalyzed Cyclization of Triazenes **1**

A small amount of the product was isolated from the reaction mixture of 1-[2-(methoxycarbonyl)phenyl]-3-phenyltriazene (substrate **1a**) and aqueous-methanolic buffer at pH 11.68. The UV-VIS spectrum of this substance was measured in methanol, and the wavelengths of the observed absorption maxima (λ_1 292 nm, λ_2 314 nm) were compared with published data (290 and 314 nm) pertaining to a different reaction pathway starting from anthranilanilide[26]. The isolated product melted at 148–150 °C, which also agrees well with published data (151–152 °C, ref.[27]).

Kinetic Measurements

Aqueous-methanolic buffers containing 51.1 wt.% methanol were used. Buffers for the range of pH 7.54–8.75 were obtained by mixing saturated solutions of disodium hydrogen phosphate and potassium dihydrogen phosphate (both in 51.1 wt.% methanol) in various proportions, whereas buffers for the range of pH 9.13–11.68 were obtained by mixing a saturated solution of disodium hydrogen phosphate and a 0.2 M solution of sodium hydroxide in the same solvent (ref.[28]). The pH values were read on a Radiometer TITRALAB 3 pH-meter using a glass electrode combined with a modified calomel electrode.

Kinetic measurements were performed on a Hewlett–Packard HP 8452A instrument; an HP DURRUM D-150 instrument of the same manufacturer was employed for systems with half-lives below 3 s. Prior to the measurement, the buffer (approximately 2 ml) was thermostatted to 25 ± 0.1 °C in a quartz cell, and a solution of triazene **1** in dioxane (approximately 4 μl) was added with a Hamilton 701 N syringe so that its concentration in the cell was about 5 μmol l^{-1}. The cell contents were stirred thoroughly, and the decrease in absorbance was monitored in dependence on time for a period no shorter than four half-lives. In the measurements on the DURRUM instrument, following thermostatting to 25 ± 0.1 °C, the buffer solution was mixed with an aqueous-methanolic solution of the triazene **1** at a concentration of 2.5 μmol l^{-1} by means of the injecting device. The results of measurement were evaluated by non-linear regression using an optimizing program. The observed rate constants are given in Table II.

RESULTS AND DISCUSSION

Spectra of 1-[2-(Methoxycarbonyl)phenyl]-3-(2-substituted phenyl)triazenes

The UV-VIS spectra of methanolic solutions of the model substances **1** exhibited two absorption peaks: one at 202 nm and the other, characteristic of triazenes, in the 360 nm range. The absorption peak wavenumbers and molar absorptivities are given in Table III.

TABLE II
Reaction medium pH and observed rate constants k_{obs} for the base-catalyzed cyclization of triazenes **1** in 51 wt.% methanol at 25 °C

pH	k_{obs} (s^{-1}) for substrate with substituent X										
	1a H	**1b** CH_3	**1c** C_2H_5	**1d** CN	**1e** CF_3	**1f** OCH_3	**1g** F	**1h** Cl	**1i** Br	**1j** NO_2	**1k** SO_2CH_3
7.54	$1.77 . 10^{-4}$	$1.15 . 10^{-4}$	$8.08 . 10^{-5}$	$7.31 . 10^{-5}$			$1.89 . 10^{-4}$	$9.60 . 10^{-5}$	$8.46 . 10^{-5}$	$1.84 . 10^{-4}$	
7.78	$3.18 . 10^{-4}$	$1.93 . 10^{-4}$	$1.32 . 10^{-4}$	$1.28 . 10^{-4}$		$6.86 . 10^{-5}$	$3.44 . 10^{-4}$	$1.78 . 10^{-4}$	$1.47 . 10^{-4}$	$3.31 . 10^{-4}$	
8.03	$5.48 . 10^{-4}$	$3.37 . 10^{-4}$	$2.12 . 10^{-4}$	$2.33 . 10^{-4}$	$6.36 . 10^{-5}$	$1.17 . 10^{-4}$	$5.71 . 10^{-4}$	$3.01 . 10^{-4}$	$2.49 . 10^{-4}$	$5.74 . 10^{-4}$	
8.33	$9.81 . 10^{-4}$	$5.92 . 10^{-4}$	$3.82 . 10^{-4}$	$4.18 . 10^{-4}$	$1.16 . 10^{-4}$	$2.09 . 10^{-4}$	$1.07 . 10^{-3}$	$5.34 . 10^{-4}$	$4.59 . 10^{-4}$	$1.08 . 10^{-3}$	$6.36 . 10^{-5}$
8.42	$1.24 . 10^{-3}$	$7.38 . 10^{-4}$	$4.54 . 10^{-4}$	$5.20 . 10^{-4}$	$1.41 . 10^{-4}$	$2.50 . 10^{-4}$	$1.31 . 10^{-3}$	$6.57 . 10^{-4}$	$5.56 . 10^{-4}$	$1.31 . 10^{-3}$	$7.86 . 10^{-5}$
8.60	$1.73 . 10^{-3}$	$1.02 . 10^{-3}$	$6.14 . 10^{-4}$	$6.99 . 10^{-4}$	$1.86 . 10^{-4}$	$3.47 . 10^{-4}$	$1.82 . 10^{-3}$	$9.31 . 10^{-4}$	$7.32 . 10^{-4}$	$1.80 . 10^{-3}$	$1.05 . 10^{-4}$
8.75	$2.30 . 10^{-3}$	$1.39 . 10^{-3}$	$8.04 . 10^{-4}$	$9.57 . 10^{-4}$	$2.57 . 10^{-4}$	$4.45 . 10^{-4}$	$2.46 . 10^{-3}$	$1.21 . 10^{-3}$	$9.85 . 10^{-4}$	$2.45 . 10^{-3}$	$1.35 . 10^{-4}$
9.13	$5.54 . 10^{-3}$	$2.19 . 10^{-3}$	$1.86 . 10^{-3}$	$2.24 . 10^{-3}$	$5.52 . 10^{-4}$	$1.19 . 10^{-3}$	$5.19 . 10^{-3}$	$2.75 . 10^{-3}$	$2.02 . 10^{-3}$	$5.25 . 10^{-3}$	$3.09 . 10^{-4}$
9.58	$2.08 . 10^{-2}$	$8.10 . 10^{-3}$	$7.22 . 10^{-3}$	$1.06 . 10^{-2}$	$2.33 . 10^{-3}$	$3.91 . 10^{-3}$	$1.46 . 10^{-2}$	$1.07 . 10^{-2}$	$8.73 . 10^{-3}$	$1.63 . 10^{-2}$	$1.25 . 10^{-3}$
9.83	$3.04 . 10^{-2}$	$1.30 . 10^{-2}$	$9.70 . 10^{-3}$	$1.15 . 10^{-2}$	$3.37 . 10^{-3}$	$5.15 . 10^{-3}$	$2.53 . 10^{-2}$	$1.47 . 10^{-2}$	$1.17 . 10^{-2}$	$2.40 . 10^{-2}$	$1.65 . 10^{-3}$
10.66	$2.32 . 10^{-1}$	$1.27 . 10^{-1}$	$1.21 . 10^{-1}$	$1.03 . 10^{-1}$	$2.54 . 10^{-2}$	$6.53 . 10^{-2}$	$2.32 . 10^{-1}$	$1.26 . 10^{-1}$	$1.32 . 10^{-1}$	$2.00 . 10^{-1}$	$7.91 . 10^{-3}$
11.15	$5.33 . 10^{-1}$	$3.01 . 10^{-1}$	$2.64 . 10^{-1}$	$2.20 . 10^{-1}$	$9.63 . 10^{-2}$	$1.35 . 10^{-1}$	$6.03 . 10^{-1}$	$3.01 . 10^{-1}$	$2.31 . 10^{-1}$	$5.78 . 10^{-1}$	$4.52 . 10^{-2}$
11.52	$1.65 . 10^{0}$	$7.70 . 10^{-1}$	$4.33 . 10^{-1}$	$5.60 . 10^{-1}$	$2.04 . 10^{-1}$	$2.67 . 10^{-1}$	$1.51 . 10^{0}$	$7.88 . 10^{-1}$	$6.54 . 10^{-1}$	$1.28 . 10^{0}$	$9.77 . 10^{-2}$
11.68	$2.24 . 10^{0}$	$1.20 . 10^{0}$	$6.93 . 10^{-1}$	$8.66 . 10^{-1}$	$2.31 . 10^{-1}$	$4.33 . 10^{-1}$	$2.24 . 10^{0}$	$1.20 . 10^{0}$	$1.02 . 10^{0}$	$1.98 . 10^{0}$	$1.41 . 10^{-1}$

The ^{1}H NMR spectra of the substances were measured in deuterated chloroform. The chemical shifts $\delta(^1H)$ are given in Table IV.

Reaction Order and Catalytic Rate Constants

The reaction order was calculated by applying the method of two different starting concentrations[29] to the fluoro (**1g**) and ethyl (**1c**) derivatives (pH 8.03 and 8.75, respectively). The n values were 0.967 and 0.981, respectively; hence, the reaction is first order with respect to substrate.

The catalytic rate constant logarithms ($\log k_B$) were calculated as the average differences between the observed rate constant logarithms ($\log k_{obs}$) and pH. The $\log k_B$ values are given in Table V.

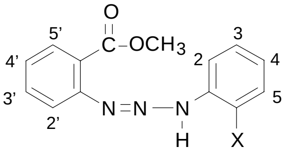
Substituent Effects and Mechanism of Base Catalyzed Cyclization of 1-[2-(Methoxycarbonyl)phenyl]-3-(2-substituted phenyl]triazenes

To investigate the substituent effects, the $\log k_{obs}$ values were subjected to analysis by the PCA (ref.[30]) and CDA (ref.[31]) methods; a completely full matrix 11 × 11 was used. (Note: for some substituents, the k_{obs} values in three buffers at the lowest pH could not be determined due to the long reaction half-life.) Although the F-test gave a value of 3 for the number of necessary latent variables, the 2nd and 3rd latent variables lay at the

TABLE III
Wavelengths of absorption maxima λ_1, λ_2, related molar absorptivities ε_1, ε_2 of methanolic solutions and elemental analyses of triazenes **1**

Substrate	Substituent X	λ_1, nm	ε_1 l mol^{-1} cm^{-1}	λ_2, nm	ε_2 l mol^{-1} cm^{-1}	Calculated/Found % N
1a	H	202	$1.206 . 10^5$	358	$2.638 . 10^4$	16.47/16.62
1b	CH_3	202	$1.370 . 10^5$	362	$2.587 . 10^4$	15.61/15.45
1c	C_2H_5	202	$1.424 . 10^5$	360	$2.830 . 10^4$	14.84/14.72
1d	CN	202	$1.285 . 10^5$	368	$2.512 . 10^4$	20.00/19.96
1e	CF_3	202	$1.695 . 10^5$	356	$3.055 . 10^4$	13.00/12.95
1f	OCH_3	202	$1.377 . 10^5$	370	$2.422 . 10^4$	14.73/14.68
1g	F	202	$1.266 . 10^5$	360	$2.606 . 10^4$	16.09/15.88
1h	Cl	202	$1.679 . 10^5$	360	$2.937 . 10^4$	14.51/14.62
1i	Br	202	$1.508 . 10^5$	360	$2.244 . 10^4$	13.05/13.02
1j	NO_2	202	$1.513 . 10^5$	362	$2.219 . 10^4$	18.66/18.62
1k	SO_2CH_3	202	$1.611 . 10^5$	362	$2.367 . 10^4$	12.61/12.49

TABLE IV
Chemical shifts δ(^{1}H) of triazenes **1**



Substrate (Substituent)	Protons			
	aliphatic δ, ppm	aromatic δ, ppm		other δ, ppm
1a (H)	3.93 s, 3 H (–OCH_3)	8.01 d, 1 H (H-5′) 7.94 d, 1 H (H-2′) 7.51 t, 1 H (H-3′) 7.01 t, 1 H (H-4′)	7.56 d, 2 H (H-2,6) 7.42 t, 2 H (H-3,5) 7.29 t, 1 H (H-4)	12.37 s, 1 H (–NH)
1b (CH_3)	3.93 s, 3 H (–OCH_3) 2.48 s, 3 H (–CH_3)	8.00 d, 1 H (H-5′) 7.95 d, 1 H (H-2′) 7.50 t, 1 H (H-3′) 6.99 t, 1 H (H-4′)	7.53 t, 1 H (H-3) 7.17–7.24 m, 3 H (H-2,4,5)	12.35 s, 1 H (–NH)
1c (C_2H_5)	3.93 s, 3 H (–OCH_3) 2.92 k, 2 H (–CH_2–) 1.22 t, 3 H (–CH_3)	8.01 d, 1 H (H-5′) 7.96 d, 1 H (H-2′) 7.49 m, 1 H (H-3′) 7.01 t, 1 H (H-4′)	7.53 m, 1 H (H-3) 7.18–7.27 m, 3 H (H-2,4,5)	12.36 s, 1 H (–NH)
1d (CN)	3.93 s, 3 H (–OCH_3)	8.04 d, 1 H (H-5′) 7.98 d, 1 H (H-2′) 7.55 m, 1 H (H-3′) 7.09 t, 1 H (H-4′)	7.69–7.73 m, 2 H (H-2,5) 7.59 m, 1 H (H-3) 7.33 t, 1 H (H-4)	12.72 s, 1 H (–NH)
1e (CF_3)	3.96 s, 3 H (–OCH_3)	8.02 d, 1 H (H-5′) 7.93 d, 1 H (H-2′) 7.52 m, 1 H (H-3′) 7.05 t, 1 H (H-4′)	7.67–7.72 m, 2 H (H-2,5) 7.54 m, 1 H (H-3) 7.34 t, 1 H (H-4)	12.58 s, 1 H (–NH)
1f (OCH_3)	3.95 s, 3 H (–OCH_3) 3.91 s, 3 H (X = OCH_3)	7.99 d, 1 H (H-5′) 7.93 d, 1 H (H-2′) 7.50 t, 1 H (H-3′) 6.98 m, 1 H (H-4′)	7.57 d, 1 H (H-2) 7.29 d, 1 H (H-5) 6.97–7.01 m, 2 H (H-3,4)	12.58 s, 1 H (–NH)
1g (F)	3.92 s, 3 H (–OCH_3)	7.99 d, 1 H (H-5′) 7.90 d, 1 H (H-2′) 7.51 t, 1 H (H-3′) 7.05 t, 1 H (H-4′)	7.63 t, 1 H (H-4) 7.22 m, 2 H (H-2,5) 7.13 t, 1 H (H-3)	–
1h (Cl)	3.94 s, 3 H (–OCH_3)	8.02 d, 1 H (H-5′) 7.93 d, 1 H (H-2′) 7.52 t, 1 H (H-3′) 7.04 t, 1 H (H-4′)	7.60 d, 1 H (H-5) 7.45 d, 1 H (H-2) 7.19–7.26 m, 2 H (H-2,5)	12.57, 1 H (–NH)
1i (Br)	3.94 s, 3 H (–OCH_3)	8.02 d, 1 H (H-5′) 7.93 d, 1 H (H-2′) 7.52 t, 1 H (H-3′) 7.04 t, 1 H (H-4′)	7.64 d, 1 H (H-5) 7.56 d, 1 H (H-2) 7.31 t, 1 H (H-3) 7.12 t, 1 H (H-4)	12.57, 1 H (–NH)

TABLE IV
(*Continued*)

Substrate (Substituent)	Protons			
	aliphatic δ, ppm	aromatic δ, ppm		other δ, ppm
1j (NO_2)	3.92 s, 3 H ($–OCH_3$)	7.97 d, 1 H (H-5′) 7.80 m, 1 H (H-2′) 7.55 m, 1 H (H-3′) 7.14 t, 1 H (H-4′)	7.77 m, 1 H (H-5) 7.69 d, 1 H (H-2) 7.58 m, 1 H (H-3) 7.31 t, 1 H (H-4)	12.57, 1 H (–NH)
1k (SO_2CH_3)	3.95 s, 3 H ($–OCH_3$) 3.42 s, 3 H ($–SO_2CH_3$)	8.08 d, 1 H (H-5′) 7.93 d, 1 H (H-2′) 7.58 t, 1 H (H-3′) 7.11 t, 1 H (H-4′)	8.18 d, 1 H (H-5) 7.76 d, 1 H (H-2) 7.64 t, 1 H (H-3) 7.43 t, 1 H (H-4)	12.78, 1 H (–NH)

limit of statistical significance, while the 1st latent variable accounted for 98.74% of the source matrix variability. The values of the first score t_1 vector calculated by the CDA method of conjugate deviations with 2 latent variables are given in Table V.

The difference between the logarithms of the catalytic rate constants $\Delta \log k_B = \log k_{BX} - \log k_{BH}$ was used to quantify and evaluate the substituent effects on the reaction kinetics

TABLE V
Logarithms of catalytic rate constants log k_B, steric constants υ_{eff}, and 1st score vectors t_1 calculated by the CDA method for triazenes **1**

Substrate	Substituent X	log k_B	υ_{eff}	t_1
1a	H	–11.33	0.00	1.000
1b	CH_3	–11.59	0.52	0.772
1c	C_2H_5	–11.76	0.56	0.625
1d	CN	–11.71	0.40	0.683
1e	CF_3	–12.27	0.90	0.231
1f	OCH_3	–12.02	0.36	0.421
1g	F	–11.33	0.27	0.994
1h	Cl	–11.61	0.55	0.761
1i	Br	–11.69	0.65	0.692
1j	NO_2	–11.35	0.35	0.983
1k	SO_2CH_3	–12.57	1.13	0.000

and mechanism. The differences were processed by linear regression analysis with different independently variables characterizing the substituent, *viz*. σ_0^i, σ^i, σ_I, σ_R, and σ_p (refs[32,33]). Correlation with those substituent constants appeared invariably to be statistically insignificant. A considerably better correlation was achieved with the parameters characterizing the steric demands of the substituents, *viz*. with Charton's υ_{eff} constants[22]. The correlation of the $\Delta \log k_B$ values with the υ_{eff} constants was made with all points included, as well as with the exclusion of two outliers (triazenes **1a** and **1f**). The correlation coefficient improved thereby from 0.845 ($n = 11$) to 0.962 ($n = 9$), and the explained variability then was 92.49%. Logically, then, the best statistical characteristics ($r = 0.9995$, explained variability 99.91%) were obtained if the $\Delta \log k_B$ values were correlated with the $\boldsymbol{t_1}$ vector calculated by the CDA method. The use of other steric parameters such as σ_s^i (ref.[32]) did not lead to statistically significant results because the parameters did not cover the range of substituents used by us and thus were unusable. The results were also processed by multiple linear regression using various combinations of the substituent constants[32]. Not a single suitable multiparameter model describing the variability of the experimental results was found.

Physical meaning can be attached to the 1st latent variable, characterized by the score vector $\boldsymbol{t_1}$, if a vector of the substituent constants correlating well with the score vector can be identified. The best correlation was observed with Charton's constants υ_{eff}, describing the steric demands of the substituents. After eliminating two outliers (H and OCH_3 substituents), 92.49 per cent of variability of the experimental data set was explained ($r = 0.962$). An attempt was also made to correlate the 2nd score vector $\boldsymbol{t_2}$ with some constants accounting for the inductive and mesomeric substituent effects but all of the correlations were statistically insignificant. The fact that no inductive or mesomeric substituent effect was observed can be due to the long distance between the substituent and the reaction centre (for the inductive effect) or to the non-planarity of the molecule (for the mesomeric effect). This can be explained by the ring at the N(3) nitrogen being more or less tilted from the plane in which the remaining part of the molecule lies. The degree of tilting is related with the substituent bulk: a bulky substituent hinders the attack of the negatively charged nitrogen on the carbon in the $COOCH_3$ group carbonyl, and its electronic effects do not manifest themselves.

On the basis of the slowing-down of the reaction of some related substrates observed when a sterically more demanding substituent was present in the vicinity of the reaction centre, it has been suggested recently[3,5,11,12] that the $B_{Ac}2$ mechanism, with the second step as the rate determining step, is the most likely mechanism of their cyclization. The model 1-[2-methoxycarbonyl)phenyl]-3-(2-substituted phenyl)triazenes studied in this work exhibit similar dependences, and so the above mechanism can be regarded as confirmed for them as well.

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REFERENCES

1. Grammaticakis P.: *Bull. Soc. Chim. Fr*. **1957**, 129.
2. Grammaticakis P.: *Bull. Soc. Chim. Fr*. **1957**, 139.
3. Stevens H. N. E., Stevens M. F. G.: *J. Chem. Soc*. **1970**, 765.
4. Axenrod T., Mangiaracina P.: *Helv. Chim. Acta* **1976**, *59*, 1655.
5. Pytela O., Halama A.: *Collect. Czech. Chem. Commun*. **1996**, *61*, 751.
6. Benes J., Beranek V., Zimpirich J., Vetesnik P.: *Collect. Czech. Chem. Commun*. **1977**, *42*, 702.
7. Svoboda P., Pytela O., Vecera M.: *Collect. Czech. Chem. Commun*. **1986**, *51*, 553.
8. Isaacs N. S., Rannala E.: *J. Chem. Soc., Perkin Trans. 2* **1974**, 899.
9. Nevecna T., Pytela O., Ludwig M., Kavalek J.: *Collect. Czech. Chem. Commun*. **1990**, *55*, 147.
10. Pytela O., Nevecna T., Ludwig M.: *Collect. Czech. Chem. Commun*. **1990**, *55*, 156.
11. Pytela O., Dlouhy V.: *Collect. Czech. Chem. Commun*. **1990**, *55*, 2468.
12. Pytela O., Bahnik Z.: *Collect. Czech. Chem. Commun*. **1990**, *55*, 2692.
13. Taft R. W. in: *Steric Effects in Organic Chemistry* (M. S. Newman, Ed.). Wiley, New York 1956.
14. Unger N. R., Hansch C.: *Prog. Phys. Org. Chem*. **1976**, *12*, 91.
15. Shorter J.: *Correlation Analysis of Organic Reactivity*, Chap. 4. Wiley, New York 1982.
16. Gallo R.: *Prog. Phys. Org. Chem*. **1983**, *14*, 115.
17. Exner O.: *Correlation Analysis of Chemical Data*. Plenum, New York 1988.
18. Charton M. in: *Similarity Models in Organic Chemistry, Biochemistry and Related Fields* (R. I. Zalewski, T. M. Krygowski and J. Shorter, Eds), p. 629. Elesevier, Amsterdam 1991.
19. Taft R. W.: *J. Am. Chem. Soc*. **1950**, *72*, 4783.
20. Hancock C. K., Meyers E. A., Yager B. J.: *J. Am. Chem. Soc*. **1961**, *83*, 4211.
21. Charton M.: *J. Am. Chem. Soc*. **1975**, *97*, 1522.
22. Charton M.: *J. Am. Chem. Soc*. **1975**, *97*, 3691.
23. Komantsuzaki T., Akai I., Sakakibara K., Hirota M.: *Tetrahedron* **1992**, *48*, 1539.
24. Campbell T. W., Day B. F.: *Chem. Rev. (Washington, D. C.)* **1951**, *48*, 299.
25. Mehner J.: *J. Prakt. Chem*. **1901**, *63*, 241.
26. Suschitzky H., Price D.: *Justus Liebigs Ann. Chem*. **1976**, 946.
27. Mair A. C., Stevens M. F. G.: *J. Chem. Soc*. **1970**, 2317.
28. Sykora V., Zatka V.: *Prirucni tabulky pro chemiky*, p. 64. SNTL, Praha 1967.
29. Tockstein A.: *Zaklady fyzikalni chemie*, Vol. 2. (Texts for students of the Institute of Chemical Technology), Pardubice 1988.
30. Wold S., Esbensen K., Geladi P.: *Chemom. Intell. Lab. Syst*. **1987**, *2*, 37.
31. Pytela O.: *Collect. Czech. Chem. Commun*. **1990**, *55*, 42.
32. Pytela O., Liska J.: *Collect. Czech. Chem. Commun*. **1994**, *59*, 2005.
33. Exner O.: *Korelacni vztahy v organicke chemii*. SNTL/ALFA, Praha 1981.