Conformational Studies by Dynamic Nuclear Magnetic Resonance. Part 16.[1] The Mechanism of Tautomerism in Triazenes

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The kinetics of tautomerism of triazenes, $R^1NH-N=NR^2 \rightleftharpoons R^1N=N-NHR^2$, have been determined by means of line-shape analysis of the ^1H n.m.r. spectra at various temperatures. When $R^1 = R^2 =$ Me the equilibrium reaction is second-order whereas when $R^1 =$ Me, $R^2 =$ Ph or when $R^1 = R^2 = p$-MeC$_6$H$_4$ the reaction follows a first-order course. Thermodynamic activation parameters have been determined for both situations for a variety of solvents. Theoretical INDO calculations helped in understanding the switch from a bimolecular to a unimolecular reaction pathway when aliphatic are replaced by aromatic substituents. The absence of solvent effects suggests a radical mechanism, in agreement with the conclusion of a theoretical charge population analysis.

INFRARED studies of 1,3-disubstituted triazenes indicated that these molecules exist in solution as tautomeric forms in equilibrium.[2,3] Further evidence has been gained from low-temperature n.m.r. spectroscopy;[4-7] this technique also gave information on the effect of various substituents in shifting the equilibrium in favour of one of the two possible tautomers.[6,7] Despite the wealth of information available for the static situation (*i.e.* structure and ratio of tautomers) no dynamic study of this tautomerism has been carried out. To make good this deficiency we undertook to determine the order of the reaction, the thermodynamic parameters of activation, and also a possible mechanism for the equilibrium.

For this purpose we selected the three triazenes (1)—(3). Their kinetic processes at the equilibrium were followed by means of total line-shape analysis of the ^1H n.m.r. signals at various temperatures.

$R^1NH-N=NR^2$
(1) $R^1 = R^2 =$ Me
(2) $R^1 =$ Me, $R^2 =$ Ph
(3) $R^1 = R^2 = p$-MeC$_6$H$_4$

RESULTS AND DISCUSSION

The utmost care was required to avoid the catalytic effects of traces of impurity which greatly increased the rate of the tautomeric equilibrium (1) (see Experimental section). Despite all the precautions, we could not

$$R^1NH-N=NR^2 \rightleftharpoons R^1N=N-NHR^2 \qquad (1)$$

obtain reproducible results in some solvents. In addition, the different temperature ranges required for observing line-broadening effects required the use of solvents with different boiling points for different triazenes and, furthermore, the requirements for not having the solvent signals superimposed on those of the solute were not the same for (1)—(3). Because of these experimental limitations we were not able to find an unique solvent for the three molecules; as few solvents as possible were thus employed so that at least (1) and (2) and (2) and (3) could share the same medium.

The aliphatic 1,3-dimethyltriazene (1) showed line-broadening effects over a temperature range much higher than that for the aromatic derivatives (2) and (3). In Figure 1 the 60-MHz n.m.r. spectrum of a 1.12M solution of (1) in C$_6$D$_6$ is shown for various temperatures. The singlet for CH$_3$N= and the doublet for CH$_3$NH- first broaden and eventually coalescence into a single line upon raising the temperature. In order to make the two methyl groups isochronous a rapid exchange of protons between N(1) and N(3) is required, accompanied by a rehybridization of the two nitrogens from sp^3 to sp^2 and *vice versa*.

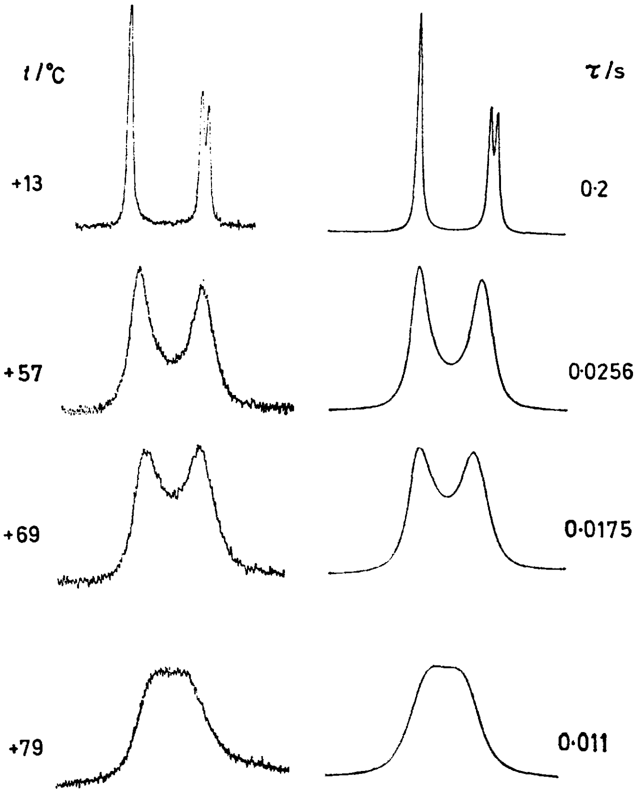
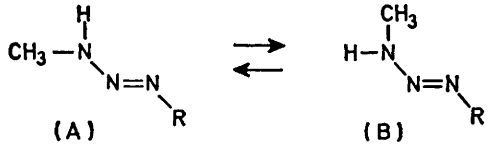


FIGURE 1 Experimental (left) and computer simulated (right) 60-MHz spectrum of the methyl groups of MeHN–N=NMe (1) in C$_6$D$_6$ (1.12 mol) at various temperatures. The chemical shift difference at 10 °C is 49.7 Hz and $J_{Me,NH}$ is 4.2 Hz

It should be pointed out that trisubstituted triazenes such as 1,1-dialkyl-3-aryltriazene[8,9] do experience restricted rotation around the N–N bond: this motion however has not been detected in the disubstituted triazenes (1)—(3). In 1,3-derivatives restricted rotation would give two rotamers (A) and (B) with n.m.r. spectra



with two doublets of non-equal intensity, due to the methyl group bonded to NH: however, such doublets have not been detected for (1) or (2). This means that either only one of the two possible rotamers is populated in these triazenes, or the rotational barriers are much lower than in 1,1-dialkyltriazenes. In consequence the observed motion can only be attributed to tautomerism.

Computer simulation of the line shape of (1) gives the lifetime of the methyl group bonded to the imino-nitrogen, which is obviously the same as in CH_3NH. In more dilute solutions the lifetime was found to increase and in more concentrated solutions to decrease; the reciprocal lifetime was linearly dependent on the concentration at a given temperature, typical for a second-order reaction.

Thermodynamic parameters for tautomerism of triazenes (1)—(3)

Compound	Solvent	Reaction order	$\Delta H^\ddagger$/kcal mol^{-1}	$\Delta S^\ddagger$/cal mol^{-1} K^{-1}	E_a/kcal mol^{-1}	$\Delta G^\ddagger$/kcal mol^{-1} at 0 °C
(1)	C_6D_6	Second	$8.6 \pm 0.2_5$	-27 ± 1	$9.3 \pm 0.2_5$	16.0
	[$^2H_8$]Toluene		8.6 ± 0.9	-26 ± 3	9.3 ± 0.9	15.7
	$CDCl_3$		$8.5_5 \pm 0.2$	-27 ± 1	9.2 ± 0.2	15.9
(2)	[$^2H_8$]Toluene	First	12.6 ± 0.6	-7 ± 2	$12.5_5 \pm 0.6$	13.9
	$CDCl_3$		11.8 ± 0.5	-6 ± 2	12.3 ± 0.5	13.4
	CD_2Cl_2		12.2 ± 0.7	-5 ± 5	12.4 ± 0.7	14.0
	CS_2		13.0 ± 1.2	-4 ± 4	13.5 ± 1.3	14.1
(3)	CD_2Cl_2	First	$6.0 \pm 0.2_5$	-19 ± 5	$6.4 \pm 0.2_5$	11.2

From these line-shape investigations a second-order rate constant for the tautomerism was obtained and plotted as function of $1/T$ to yield the thermodynamic parameters of activation. Figure 2 gives a plot for four different concentrations in C_6D_6 in the temperature range +45 to +110°: the corresponding parameters are given in the Table.

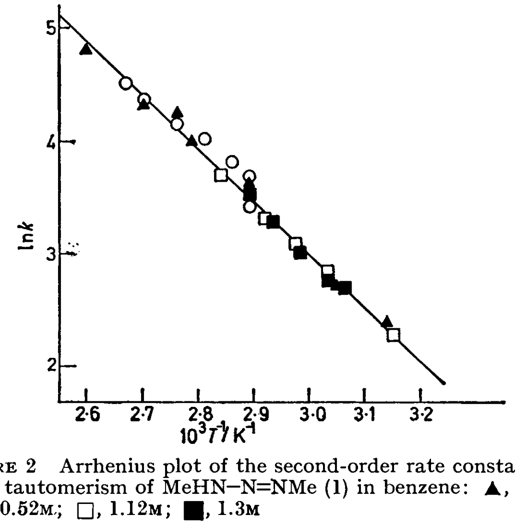


FIGURE 2 Arrhenius plot of the second-order rate constants for the tautomerism of MeHN–N=NMe (1) in benzene: ▲, 0.23M; ○, 0.52M; □, 1.12M; ■, 1.3M

Both the order of reaction and the parameters were checked in more polar solvents such as [$^2H_8$]toluene and $CDCl_3$. The reaction was confirmed to be second-order and the thermodynamic parameters were the same as in benzene (Table).

The tautomerism of (1) thus occurs through a collision between two molecules: the large and negative $\Delta S^\ddagger$ value is also indicative of an ordered cyclic transition state [see Scheme, (E)].

Different behaviour is observed for (2), where one of the two methyls is replaced by a phenyl group. The tautomerism is first order in all the solvents examined, even in those ([$^2H_8$]toluene, $CDCl_3$) where (1) gave a second-order reaction (Table).

Because of the asymmetry of the molecule two different tautomers (C) and (D) are present at the equilibrium which does not now require a collison between two molecules. Species (C) was more abundant (63.5%) in toluene, $CDCl_3$, and CD_2Cl_2 whereas in CS_2 (D) was slightly favoured (52.5%). Again the effect of solvent on the thermodynamic parameters does not significantly exceed the experimental error. The data reported in the Table for (2) refers to the transformation of (C) into (D).

$$\underset{\text{(C)}}{CH_3NH{-}N{=}NPh} \rightleftarrows \underset{\text{(D)}}{CH_3N{=}N{-}NHPh}$$

In order to check whether the change in the order of reaction was somehow dependent on the molecular symmetry [(1) is symmetrical whereas (2) is not] a symmetrical aromatic triazene was investigated. However, whereas in (1) and (2) the kinetics are followed simply by monitoring the methyl signals, it is not so when two phenyl groups are present, owing to their complex spectral patterns. We thus selected 1,3-di-*p*-tolyltriazene (3) in order to have simpler spectra. The tolyl methyl groups did not give sufficiently separated lines in the low exchange region, but the aromatic protons did.

At room temperature down to −30° a unique A_2B_2 pattern was observed for the eight protons of the phenyl groups, but at −105° different groups of lines for the two pairs of *ortho*-, as well as for the two pairs of *meta*-protons, were detectable (Figure 3). Owing to the absence of the couplings with NH we could not assign the signals of the phenyl group bonded to NH or to N=N, but this was immaterial for the kinetic study. As in the case of (2) the appearance of the spectrum was in-dependent of the concentration at a given temperature, thus indicating a first-order reaction. The thermodynamic parameters obtained from the line-shape analysis are reported in the Table. Because of the difficult experimental conditions (see Experimental section), the $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values are much less reliable than those of (2).

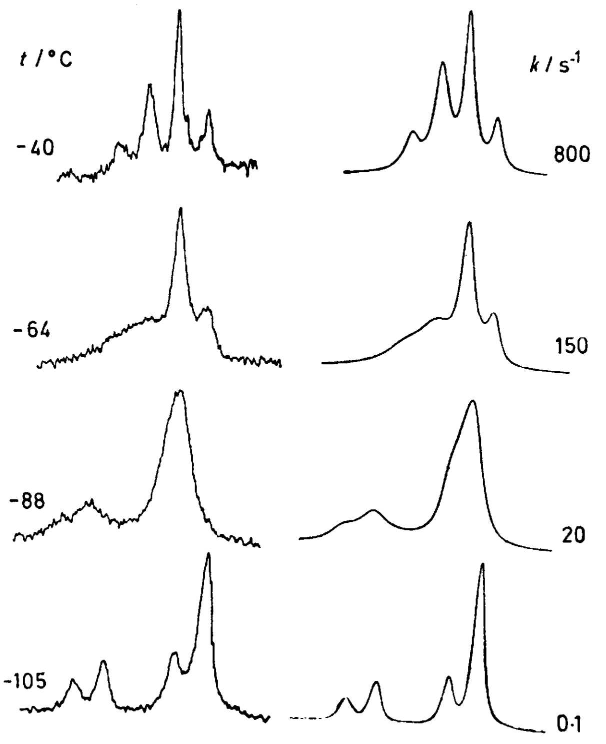


FIGURE 3 Experimental (left) and computer simulated (right) 100-MHz spectrum of p-$MeC_6H_4NH-N=NC_6H_4Me$-p (3) at various temperatures in CD_2Cl_2. At -105 °C the chemical shifts of the two *ortho*-signals differ by 30.2 Hz and those of *meta* by 5.7 Hz; $J_{o,m}$ is 8 Hz

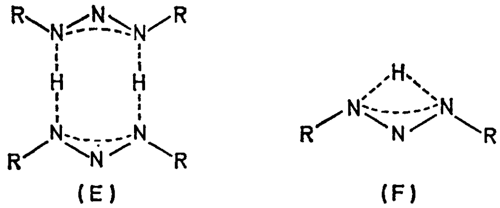
We do not yet understand why the order of reaction changes for the aromatic with respect to the aliphatic triazenes. In principle two reaction pathway are available by which triazenes can undergo tautomeric equilibrium, a bimolecular mechanism with a transition state like (E) (see Scheme) and an unimolecular mechanism with a transition state like (F).

The choice of one rather than the other depends on the relative values of the free energies of activation ($\Delta G^{\ddagger}$) corresponding to the two possible transition states. Because of the lower probability, the entropy relative to the bimolecular mechanism (E) ($\Delta S^{\ddagger}_{\mathrm{E}}$) is expected to be more negative than for (F) [compare, for instance, the experimental $\Delta S^{\ddagger}$ values of (1) and (2)]. In consequence, the choice of the bimolecular pathway (E) as followed by (1) (*i.e.* $\Delta G^{\ddagger}_{\mathrm{E}} < \Delta G^{\ddagger}_{\mathrm{F}}$) implies that, with $-T\Delta S^{\ddagger}_{\mathrm{A}} > 0$, the activation enthalpy for mechanism (E) is much smaller than for (F) (*i.e.* $\Delta H^{\ddagger}_{\mathrm{E}} \ll \Delta H^{\ddagger}_{\mathrm{F}}$). This has been confirmed by approximate INDO calculations [10] on the relative stability of (E) and (F). On the other hand the choice of a unimolecular mechanism as followed by the aromatic derivations (2) and (3) (*i.e.* $\Delta G^{\ddagger}_{\mathrm{F}} < \Delta G^{\ddagger}_{\mathrm{E}}$) requires either an increase n $\Delta H^{\ddagger}_{\mathrm{E}}$ or a decrease of $\Delta H^{\ddagger}_{\mathrm{F}}$ (or both) with respect to the values for (1).

It is conceivable that $\Delta H^{\ddagger}_{\mathrm{E}}$ for (2) and (3) is larger than for (1), owing to the mutual repulsive forces of the phenyl hydrogens when R = Ph (see Scheme). To check whether $\Delta H^{\ddagger}_{\mathrm{F}}$ might also be smaller for (3) than for (1), an INDO calculation was carried out on the ground state and on the transition state (F) of both (3) and (1).

Whereas no limitations are expected for tautomerism involving the transition state (E), a suprafacial, 1,3-intramolecular sigmatropic shift of the mechanism (F) is forbidden by symmetry.[11] Our INDO calculations confirmed this fact, since an exceedingly large activation enthalpy (>70 kcal mol⁻¹) was obtained for this forbidden pathway. However, if the intramolecular mechanism (F) takes place within the plane defined by the three nitrogen atoms, the presence of the nitrogen lone pairs does allow a 1,3-sigmatropic shift to occur. The enthalpies $\Delta H^{\ddagger}_{\mathrm{F}}$ computed for such a process are 35.5 and 28.1 kcal mol⁻¹ for (1) and (3), respectively. This large difference comes from the stabilisation of the allylic-type π molecular orbitals due to interactions with the molecular orbitals of the phenyl ring in (3). Standard bond lengths and angles were used for (1) and (3), except for $N(sp^2)-N = 1.259$ and $N(sp^3)-N = 1.338$ Å, taken from ref. 9. In the symmetrical transition state (F) partial optimisation was also carried out and the resulting values for (1) and (3) respectively, are as follows: NH = 1.72, 1.72 Å; NN = 1.285, 1.29 Å; $\widehat{NNN} = 95.2, 95.2°$; $\widehat{NNC} = 123, 124°$.

Even taking into account the large errors likely to occur in the experimental determination of $\Delta S^{\ddagger}$, there is no doubt that the experimental enthalpy values (Table) are quite different from those calculated in this way. This depends both on the approximations in the calculations (neglect of configurational interactions) and on the approximate model employed (solvent effects could not be considered). The difference, however, is certainly indicative, and it is thus clear that for mechanism (F) the activation enthalpy $\Delta H^{\ddagger}_{\mathrm{F}}$ for the aromatic derivative (3) is much smaller than for the aliphatic compound (1) ($\Delta\Delta H^{\ddagger}_{\mathrm{F}}$ 7.4 kcal mol⁻¹).



SCHEME

Therefore not only $\Delta H^{\ddagger}_{\mathrm{E}}$ (because of steric effects) is larger, but also $\Delta H^{\ddagger}_{\mathrm{F}}$ is smaller for (3) with respect to (1). In consequence whereas in the aliphatic compound (1) the difference $\Delta H^{\ddagger}_{\mathrm{F}} - \Delta H^{\ddagger}_{\mathrm{E}}$ is large enough to overcome the contribution of $-T\Delta S^{\ddagger}_{\mathrm{E}}$ and to make $\Delta G^{\ddagger}_{\mathrm{E}} < \Delta G^{\ddagger}_{\mathrm{F}}$, in the aromatic derivative (3) the difference is greatly reduced; the entropy term now exceeds the difference in enthalpy, and thus $\Delta G^{\ddagger}_{E} > \Delta G^{\ddagger}_{F}$. This explains why (2) and (3) follow the unimolecular mechanism.

Finally, we comment on the mechanism of this tautomeric equilibrium: is it an ionic or a radical reaction? No appreciable effect of solvent polarity on the activation parameters has been observed (Table). Also, charge population analysis of the results of the INDO computations indicates that the transition state (F) can properly be described as a σ-triazenyl radical[12] interacting with a hydrogen atom: the electronic density of the latter is very close to 1, as expected for a hydrogen radical [0.797 and 0.803 in the case of (1) and (3), respectively]. If we add to that the fact that radicals are easily generated from triazenes by hydrogen abstraction (e.s.r. evidence[12]) or by thermolysis (CIDNP evidence[13]) the hypothesis of a radical rather than an ionic mechanism for this tautomerism does not seem unreasonable, at least for the unimolecular pathway.

EXPERIMENTAL

Kinetic Measurements.—Samples were carefully degassed by thawing and freezing the solutions in n.m.r. tubes connected to a vacuum line. Some barium oxide was added and the sealed tubes warmed at *ca.* 100 °C to ensure complete elimination of any catalytic traces of acidic impurities. For any concentration at least two samples were prepared to check the reproducibility of the measurements. Solvents where this could not be properly achieved $\{CD_3CN$ or $[^2H_5]$pyridine for (1) or $[^2H_6]$acetone for (2) and (3)$\}$ were not used.

N.m.r. spectra were run either at 60 MHz (JEOL) for (1) and (2) or 100 MHz for (3) (Varian XL-100). A dynamic n.m.r. computer program was employed for the simulation of the spectral patterns. For (1) and (2) very accurate results could be gathered, but this was much less the case for (3). The low temperature required to reach the slow exchange region made the line-width very dependent on viscosity; in addition the complex and only partially resolved spectral patterns made the n.m.r. parameters for the two A_2B_2 spectra less accurate than desirable. Therefore, whereas the reaction order and the $\Delta G^{\ddagger}$ value are still reliable, the values of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ for (3) are much less accurate than for (1) and (2), despite the seemingly small errors in the Table. In consequence, we must regard the $\Delta S^{\ddagger}$ value of (2) rather than that of (3) as typical for first-order tautomerism of triazenes.

Syntheses.—1, 3-*Dimethyltriazene* (1). Methyl azide (50 mmol) was condensed at −20° in a flask containing methylmagnesium iodide (*ca.* 50 mmol) in ether. The system was left to reach room temperature and allowed to reflux for *ca.* 0.5 h. To the cooled solution was slowly added freshly sublimed $AlCl_3$ (12 mmol) in ether (25 ml). Pentane (*ca.* 50 ml) was also added and the upper layer was separated. After vacuum elimination of the solvent, the remaining solid was sublimed at *ca.* 70 °C (3 mmHg) to yield tris-(1,3-dimethyltriazenyl)aluminium (1.5 g).[14] Using a dry box, 1,3-diphenyltriazene (5 g)[15] was added to the above-mentioned compound and the mixture warmed at *ca.* 100 °C and 3 mmHg. Free 1,3-dimethyltriazene was collected in a trap cooled at −40 °C.[14]

1-*Methyl*-3-*phenyl*- (2) *and* 1,3-*bis*-(4-*methylphenyl*)*triazene* (3). These were prepared, with appropriate modifications, by the method of ref. 15. Compound (2) had m.p. 41—42° and (3) 122—123°. The triazenes gave the expected molecular weight (mass spectrometry) and appropriate n.m.r. spectra.

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