Substituent Effects on Tautomerisation Constants of Alkylaryltriazenes

Migel A. Kelly, Martin Murray, and Michael L. Sinnott *
Department of Organic Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS

Both tautomers of propyl-*p*-nitrophenyl-, -*p*-cyanophenyl-, -3,5-dichlorophenyl-, -3,4-dichlorophenyl-, and -*p*-chlorophenyl-triazenes are directly observable by ^{1}H n.m.r. at 200 MHz in CD_3CN at 25 °C. In addition, lower temperature studies enable the two tautomers of propyl-*p*-methylphenyl- and-*p*-methoxyphenyl-triazenes to be quantitated. At −45 °C rotamers about the N–N bond of the conjugated tautomers are also separately observable. ^{13}C N.m.r. studies of the *p*-nitro- and *p*-chloro-compounds suggest tautomerisation involves the less abundant rotamer of the conjugated tautomer and the unconjugated tautomer. The position of equilibrium at 25 °C is described by log ($[C_3H_7N : NNHAr]/[C_3H_7NHN : NAr]$) = (0.67 ± 0.13) − (0.31 ± 0.04)pK_a ($ArNH_3^+$). ^{13}C, as well as ^{1}H n.m.r. studies indicate that change of solvent to $(CD_3)_2SO$, CD_3CN–$(CD_3)_2SO$, or CD_3CN–$(CD_3)_2SO$–H_2O has little effect. Neither, in the *p*-nitrophenyl case, does change of the propyl group for benzyl.

The question of whether alkylaryltriazenes exist predominantly in the unconjugated form (I) or the conjugated form (II) has been addressed for the past century: [1-11] more recently attention has also been focused on the mechanisms whereby this tautomerisation takes place.[5,9] Electron-withdrawing substituents in the aryl group appear to favour the unconjugated tautomer,[4,7,10] but no systematic, quantitative study of a range of compounds appears to have been presented.

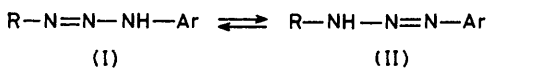
We now report a quantitative study of the effect of substituents and solvent on the position of this tautomeric equilibrium. The information is required in order to better understand the behaviour of alkylaryltriazenes as deamination precursors,[12] more particularly to interpret substituent effects on rates of triazene decomposition in water.[13] The behaviour of alkylaryltriazenes in water is in turn of interest since glycosylmethylaryltriazenes, are, by virtue of their properties as sources of glycosylmethanediazonium ions, highly selective k_{cat} inactivators and affinity labels for glycosidases, *in vitro* and *in vivo*.[14] For such 'exotic'[8] uses the available qualitative impressions of the effect of substituents on the equilibrium are inadequate.

Experimental

The syntheses and characterisation of unlabelled triazenes are described in the following paper.[13] The [1-^{13}C]propyltriazenes were made analogously, m.p. of the *p*-nitrophenyl compound 78—80 °C and of the *p*-chlorophenyl compound 35—38 °C.

[1-^{13}C]*Propylamine Hydrochloride*.—Finely powdered sodium [^{13}C]cyanide (1.0 g) was mixed with diethyl sulphate and distilled in an oil-bath; the fraction boiling between 90 °C and *ca.* 110 °C was collected. Redistilled propiononitrile (1.0 g) was added to facilitate handling and the product was redistilled to give labelled material (1.25 g) [ν (^{13}C≡N) 2 200, ν (^{12}C≡N) 2 250 cm^{-1} in the ratio 1 : 2]. This material was then reduced by the method of Secrist and Logue,[15] being dissolved in a mixture of dry ethanol (150 ml) and chloroform (11.3 ml) and being hydrogenated over 20% palladium on charcoal (775 mg) at 3.2 atmospheres pressure for 6 h. The catalyst was filtered off and the filtrate was evaporated, taken up in water, filtered, evaporated, and taken up in ethanol, whence [1-^{13}C]-propylamine hydrochloride (0.422 g), m.p. 153—156 °C (lit.,[15] 153—154 °C), was induced to crystallise by the addition of ether, *m/e* 59 (16.2%) and 60 (7.4%), corresponding to 31% ^{13}C enrichment.

200 MHz ^{1}H *and* 50.1 MHz ^{13}C *N.m.r. Spectra*.—These were measured on a JEOL FX 200 spectrometer using the Fourier transform technique. ^{1}H Spectra were routinely obtained on a sample (10 mg) in undried [$^2H_3$]acetonitrile (0.5 ml), using 1 500—2 000 pulses with a 2 s delay. The sharpness of the peak from trace water in the ^{1}H n.m.r. spectra (at δ 2.175 at 25 °C) is an indication of the stability of temperature control during spectral acquisition. Natural abundance proton-decoupled ^{13}C spectra were obtained on solutions containing 135 mg ml^{-1} of *p*-chlorophenylpropyltriazene and 100 mg ml^{-1} *p*-nitrophenyltriazene, using 3 000—9 000 data pulses with a 0.1 s delay. ^{1}H Spectra on partially aqueous solutions were obtained with gated homonuclear irradiation for solvent suppression.



(I) (II)

Results and Discussion

A *Identification and Quantification of Tautomers*.—The ^{1}H n.m.r. spectra at 25 °C of CD_3CN solutions of propyl-*p*-nitrophenyl-, -*p*-cyanophenyl-, -3,5-dichlorophenyl-, and -3,4-dichlorophenyl-triazenes are clearly those of two species whose interconversion is slow on the n.m.r. time scale: Figure 1a illustrates this for the *p*-cyano-compound. At the high fields involved, proton resonances in the aromatic region (δ 7—8) appear as $|AX|_2$ systems. From integration of the highest field aromatic protons a tautomerisation constant of 1.5—1.73 can be estimated.

More accurate measurement comes from the integration of the resonances of the most deshielded peaks, due to the NH protons: this gives a value of 1.63. Which set of peaks pertained to which tautomer was determined by homonuclear decoupling: irradiation of the multiplet centred on δ 1.68, assignable to the central methylene protons of the propyl group, results in the collapse of the complex multiplet centred on δ 3.6 to a singlet and a doublet, relative intensities 1.66 : 1 (Figure 1b). The most abundant tautomer is thus the unconjugated one. Therefore, as is reasonable, the unconjugated tautomer has the lower field N–H resonance and the higher field benzenoid *ortho*-C–H resonance. This decoupling experiment results in the collapse of the methyl signal around δ 0.95 to two lines of unequal intensity separation *ca.* 6 Hz, rather than a singlet (*i.e.* the lifetime of each tautomer is > *ca.* 0.2 s).

There is no evidence, in these spectra, of the presence of species other than the two tautomers, which we assume to have

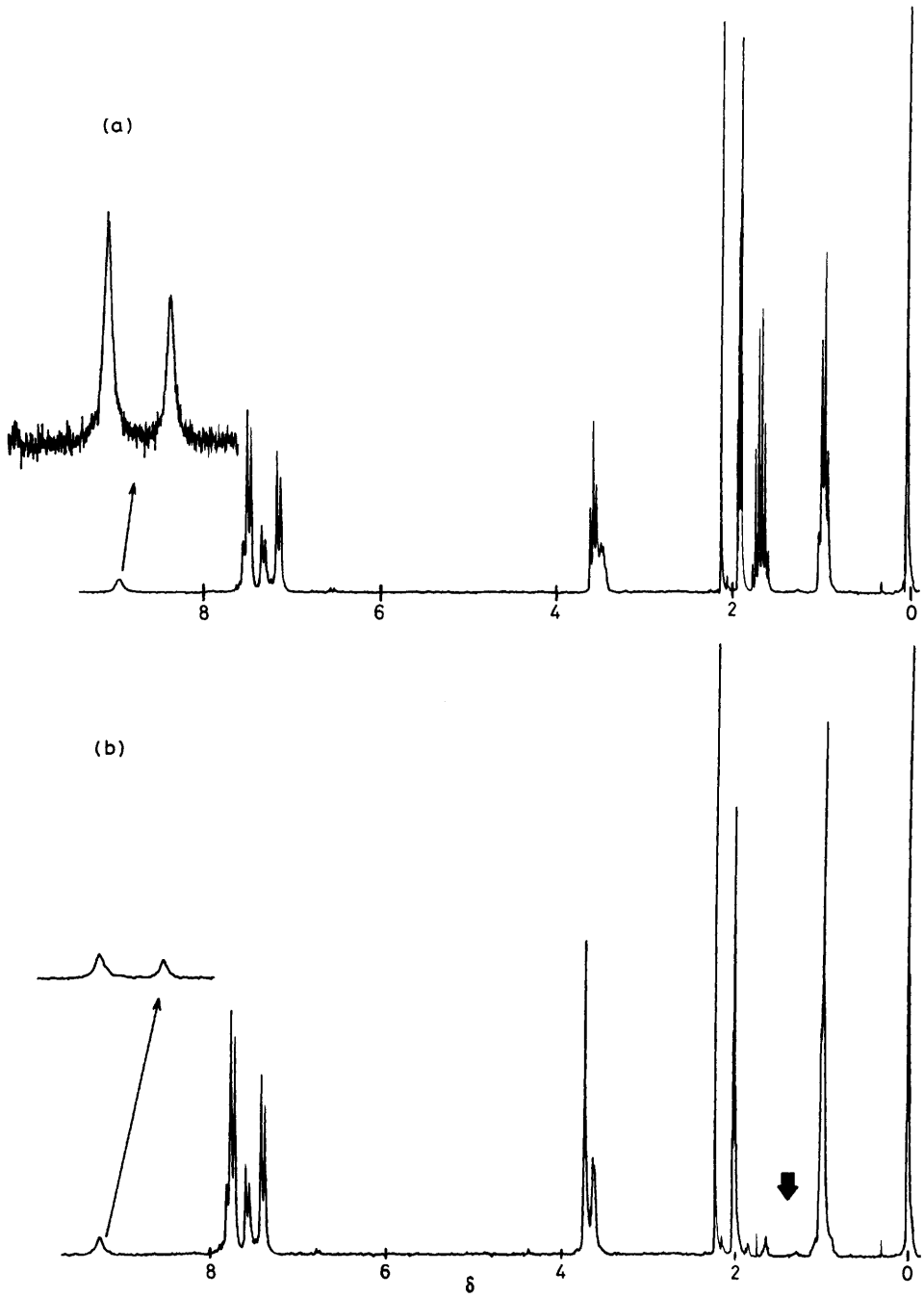


Figure 1. (a) 200 MHz ^{1}H N.m.r. spectrum of propyl-*p*-cyanophenyltriazene (20 mg ml^{-1}) in CD_3CN at 25 °C. The inset shows a vertica expansion of the NH region. (b) Effect of homonuclear decoupling by irradiation as shown

the *trans*-configuration about the N=N double bond. There are two grounds for this assumption, apart from the well known property of arenediazonium ions of giving *trans*-azo-compounds exclusively in those coupling reactions where the stereochemistry can be directly determined. First, studies of aliphatic azoalkanes indicate a surprisingly constant value of 6—8 kcal mol^{-1} for the ' intrinsic ' energy difference between *cis*- and *trans*-azoalkanes,[16] in the absence of any additional steric interaction between the alkyl groups. Secondly, the *cis*-form of the conjugated tautomer of an alkylaryltriazene cannot become planar because of steric interactions between the N–H group and the *ortho*-hydrogen atoms of the aromatic ring.

As the substituents in the phenyl ring become less electron-withdrawing, the rate of the tautomerisation increases. An intermediate situation is observed with the propyl-*p*-chlorophenyltriazene, where two separate well resolved but broad peaks are observed for the NH protons (at δ 8.8 and 9.8), a sharp triplet for the methyl group, and a broad peak at δ 7.32 (width at half-height, *ca.* 30 Hz) for the C-1 protons of the propyl group, *i.e.* the tautomerisation process is fast compared with the frequency separation of the methyl resonances, slow compared with the frequency separation of the NH resonances, and comparable to the frequency separation of the C-1 methylene resonances.

The case of the propyl-*p*-methylphenyltriazene is worth

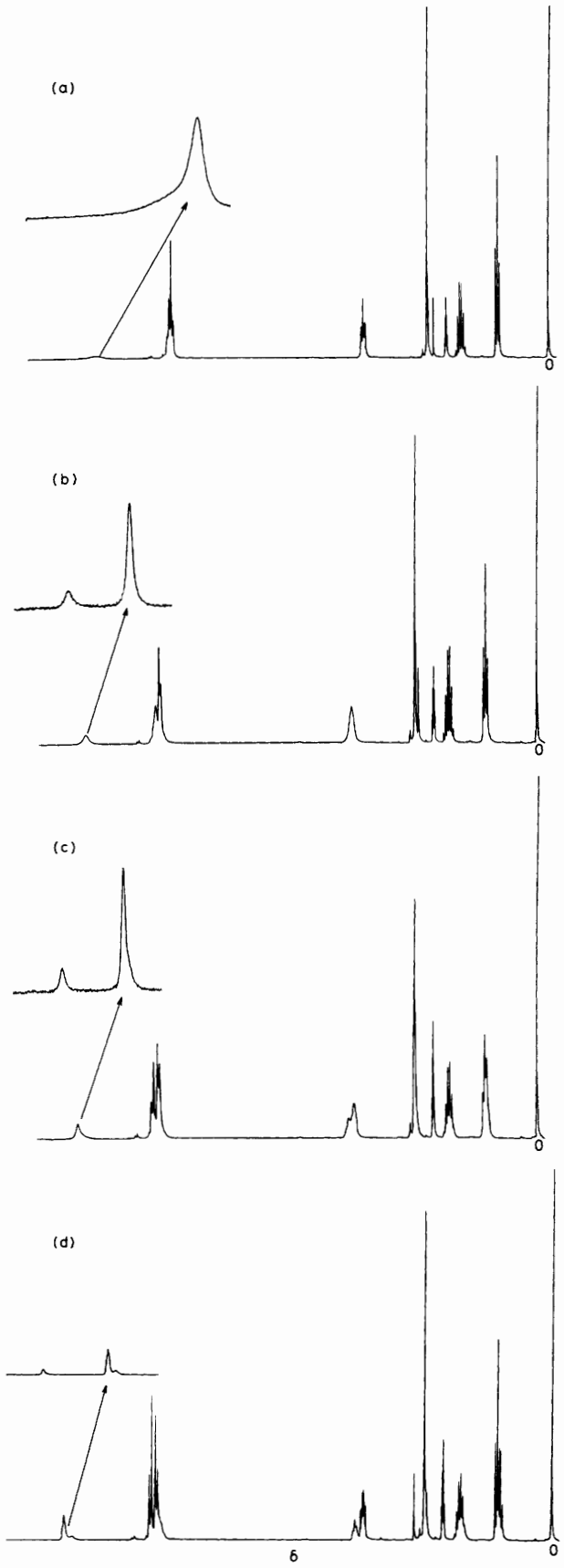


Figure 2. 200 MHz ^{1}H N.m.r. spectrum of propyl-*p*-methylphenyltriazene (46 mg ml^{-1}) in CD_3CN. The insets show vertical expansions of the NH region. (a) at 25 °C, (b) at 0 °C, (c) at −22 °C, and (d) at −45 °C

considering in detail in the light of the literature confusion about the methyl compound.[2,3,5,10] ^{1}H N.m.r. spectra are displayed in Figure 2. At 25 °C the N–H resonances are clearly in the intermediate exchange region, whereas others are in the fast exchange region. At 0 °C the situation is similar to that of the *p*-chloro-compound at 25 °C: the NH resonances are in the slow exchange region, and the C-1 methylene resonances in the intermediate exchange region. However, at −45 °C three species are detectable. The least abundant one is the unconjugated tautomer, but it is seen that the NH and CH_2 methylene resonances of the conjugated tautomer have now each separated into two distinct signals. The simplest explanation for this is that at −45 °C there is slow rotation about the N–N single bond of the conjugated tautomer, and the two most abundant species correspond to its cisoid (III) and transoid (IV) forms in the ratio 1 : 3.

The *p*-methoxy-compound behaves similarly, except that at 25 °C even the N–H resonances are in the fast exchange region, and the minor tautomer can be detected only at −45 °C. Restricted rotation about the N–N single bond of *NN*-dialkyl-*N'*-aryltriazene, which cannot tautomerise, has been observed, with energy barriers in the region of those necessary for the separate observation of (III) and (IV).[17] [In principle the unconjugated tautomer also could exhibit slow rotation about both the NH–Ar and the N–N bonds. However, the cisoid rotamer about the N–N bond of this tautomer (V) experiences steric clashes between the nitrogen lone pair and the benzenoid *ortho*-hydrogen, and is thus unlikely to be present in significant concentration. Since all the triazenes here considered (except the 3,4-dichlorophenylpropyltriazene) have symmetrically substituted aryl groups, the two rotamers about the N–Ar bond of the unconjugated tautomer are identical, and this type of restricted rotation would result only in the non-equivalence of the two *ortho*- and *meta*-hydrogens.

Table 1 gives data on ^{13}C chemical shifts for propyl-*p*-nitrophenyl- and -*p*-chlorophenyl-triazenes. Chemical shifts of the aromatic carbons of the two tautomers of the *p*-nitrophenylpropyltriazene correspond closely to those reported Hooper and Vaughan [10] for the *p*-nitrophenylmethyltriazene, except that their assignment of peaks at 149 and 156 to C-1 of the conjugated tautomer, and the *para*-carbon of the conjugated tautomer, respectively, is reversed. The peak at 149 p.p.m. in our system clearly arose from the unconjugated tautomer, both because of its intensity and the fact that it was broadened, like most peaks assignable to the unconjugated tautomer. This broadening we attribute to exchange with the minor rotamer of the conjugated tautomer, which is present in small concentration (<10%) and within this particular system is not observed, because of low intensity, broadness of the signals, and similar chemical shifts to the major rotamer. Such a process would account for the absence of proton–proton coupling between the NH and C-1 methylene in the minor rotamer of the conjugated tautomer of propyl-*p*-methylphenyltriazene at −45 °C (Figure 2d). A peak at 57.8 attributable to C-1 of the minor rotamer of the conjugated tautomer is however observed at −50° C in the spin-decoupled ^{13}C n.m.r. spectrum of *p*-chlorophenylpropyltriazene.

A protonation–deprotonation sequence may not be a major pathway for triazene tautomerisation: separate NH resonances are observable for the two tautomers of propyl-*p*-nitrophenyltriazene in solutions containing 20% water, and for the two tautomers of the *p*-chlorophenyl compound in solutions containing 10% water. Conversely, as noted by Lunazzi *et al.*,[9] the presence of impurities greatly accelerates the tautomerisation. Whereas at 25 °C, with a freshly made up solution of freshly recrystallised *p*-chlorophenylpropyltriazene in CD_3CN, two separate NH resonances are observable at δ

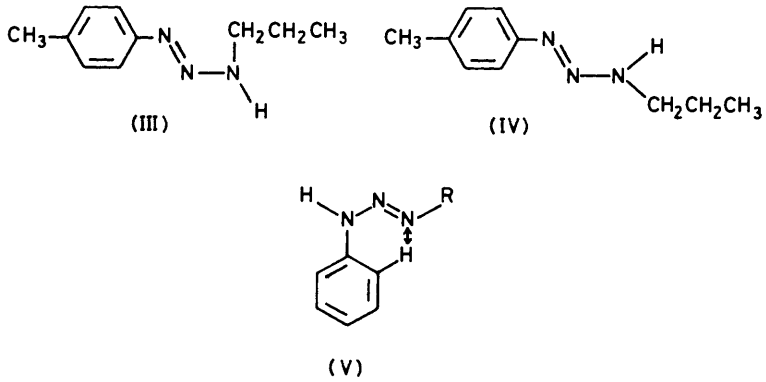


Table 1. ^{13}C Chemical shifts (p.p.m. relative to tetramethylsilane)

Carbon		Propyl-*p*-nitrophenyltriazene CD_3CN–$(CD_3)_2SO$ (1 : 1 v/v) at 8 °C ArN=N–NHPr^n	Propyl-*p*-nitrophenyltriazene CD_3CN–$(CD_3)_2SO$ (1 : 1 v/v) at 8 °C ArNH–N=NPr^n	Propyl-*p*-chlorophenyltriazene (CD_3CN at −50 °C, see text) ArN=N–NHPr^n	Propyl-*p*-chlorophenyltriazene (CD_3CN at −50 °C, see text) ArNH–N=NPr^n
CH_3		12.0	12.1	11.8	11.8
2-CH_2	propyl group	19.6	22.3	19.7	22.7 (b)
1-CH_2		46.3	63.2 (b)	46.0 + 47.8 (b)	62.8 (b)
C-1		157.0	141.2 (b)		
ortho	benzene ring	120.9	112.9 (b)	122.2	114.7 (b)
meta		125.3	126.3	129.3	129.5
para		144.6	149.0 (b)	also sharp signals at 130.3, 150.1, and 165.1	

9.8 and 8.8, in the ratio 0.3 : 1, in the n.m.r. spectrum of a less pure sample the well separated peak at δ 9.8 had become a broad hump around δ 9.2. Likewise, a sample of [1-^{13}C]-propyl-*p*-chlorophenyltriazene in CD_3CN at −10 °C exhibited an average signal (at δ 57.1 p.p.m.) for the 1-^{13}C resonance of the unconjugated tautomer and the minor rotamer of the conjugated tautomer. Linewidths increased with increasing concentration, as noted previously,[10] but not as rapidly as would be expected for a bimolecular exchange process. Lunazzi *et al.*[9] reported that the tautomerisation of rigorously purified methyl-*p*-methylphenyltriazene was unimolecular. The transition state they drew for this process, involving a simple shift of hydrogen from N-1 to N-3, is aromatic only if it has Möbius geometry. A 1,3-shift with Möbius geometry would result in direct interconversion of the transoid rotamer of the unconjugated tautomer and the cisoid rotamer of the conjugated tautomer, the process we propose (in addition to various impurity-catalysed reactions).

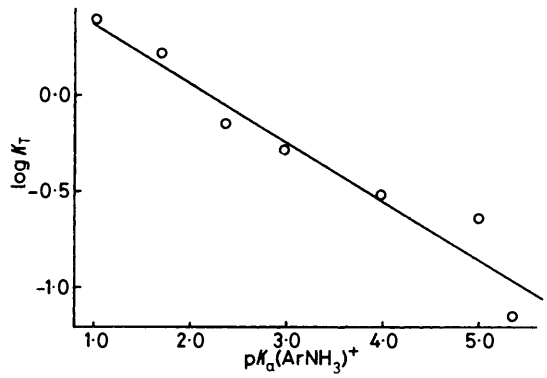


Figure 3. Linear free energy relationship between the tautomerisation equilibrium of arylpropyltriazenes and the acid dissociation of the corresponding anilinium ions in water, at 25 °C. The line is the least squares best fit, log K_T = 0.674 − 0.306 pK_a

B *Correlation of Tautomerisation Constants with Structure.*— Table 2 gives measured tautomerisation constants for various triazenes. The two tautomers of propyl-*p*-methylphenyltriazene are separately observable only below 25 °C: the temperature variation of K_T gives ΔH° *ca.* 0.4 kcal mol^{-1}, ΔS° *ca.* −1.5 cal mol^{-1} K^{-1} at 25 °C, in agreement with the value of 0.3 kcal mol^{-1} Hadzî and Jan [2] obtained for methylphenyltriazene by i.r. spectroscopy.

Since the minor tautomer of propyl-*p*-methoxyphenyltriazene is observable as a separate species only at −45 °C, the value of the tautomerisation constant at 25 °C was estimated assuming the same value of ΔH° as for the methyl compound. Since this value is small the errors involved in this assumption are likely to be less than those inevitably associated with n.m.r. integration.

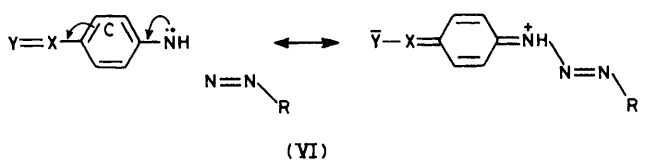
The correlation of the logarithm of the tautomerisation constant, K_T, with σ, σ$^+$, or σ$^-$ constants [18] for the substituents in the aryl group is not all it might be (*r* 0.905, 0.936, and 0.957, respectively). A better correlation is obtained with the aqueous pK_a of the anilinium ion [19] (*r* 0.967). This correlation is illustrated in Figure 3: it is seen that the scatter is largely attributable to the values of the tautomerisation constants for the *p*-methyl and *p*-methoxy-compounds, which are, experimentally, the least reliable. Some improvement in the correlation (to *r* 0.982) is obtained if σ$^-$ constants are used for *p*-nitro- and *p*-cyano-substituents and σ$^+$ constants for the mesomerically electron-releasing *p*-methyl, *p*-methoxy-, and *p*-chloro-substituents.

Such a correlation would be expected, if, in addition to delocalisation of the NH lone pair of the unconjugated tautomer into the aromatic ring (VI) there were also delocalisation of substituent lone pairs into the N=N bond of the conjugated tautomer (VII).

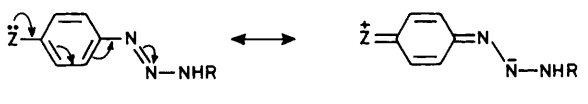
Table 2. Tautomerisation constants K_T ([RN=NNHAr]/[RNHN=NAr]) for alkylaryltriazenes

R (Measured by ^{1}H n.m.r. integration)	Ar	Solvent	t/°C	K_T
Pr^n	*p*-$C_6H_4NO_2$	CD_3CN	25	2.4_3
Pr^n	*p*-C_6H_4CN	CD_3CN	25	1.6_3
Pr^n	3,5-$C_6H_3Cl_2$	CD_3CN	25	0.71
Pr^n	3,4-$C_6H_3Cl_2$	CD_3CN	25	0.52
Pr^n	*p*-C_6H_4Cl	CD_3CN	25	0.30
Pr^n	*p*-C_6H_4Cl	CD_3CN	−50	0.20_7
Pr^n	*p*-C_6H_4Me	CD_3CN	25 [a]	0.22_5
Pr^n	*p*-C_6H_4Me	CD_3CN	0	0.21_5
Pr^n	*p*-C_6H_4Me	CD_3CN	−22	0.19_2
Pr^n	*p*-C_6H_4Me	CD_3CN	−45	0.18_4
Pr^n	*p*-C_6H_4OMe	CD_3CN	−45	0.057
Pr^n	*p*-C_6H_4OMe	CD_3CN	25 [b]	0.07
$PhCH_2$	*p*-$C_6H_4NO_2$	CD_3CN	25	2.1_7
Pr^n	*p*-$C_6H_4NO_2$	$(CD_3)_2SO$	25	2.7_2
Pr^n	*p*-$C_6H_4NO_2$	$(CD_3)_2SO$–CD_3CN (1 : 1 v/v)	25	2.8_4
Pr^n	*p*-$C_6H_4NO_2$	$(CD_3)_2SO$–CD_3CN (1 : 1 v/v)	−8	2.8_1
Pr^n	*p*-$C_6H_4NO_2$	$(CD_3)_2SO$–CD_3CN–H_2O (9 : 9 : 2 v/v)	−8	2.8_6
Pr^n	*p*-$C_6H_4NO_2$	$(CD_3)_2SO$–CD_3CN–H_2O (2 : 2 : 1 v/v)	−8	2.3
Pr^n	*p*-C_6H_4Cl	$(CD_3)_2SO$–CD_3CN (1 : 1 v/v)	−8	0.37
Pr^n	*p*-C_6H_4Cl	$(CD_3)_2SO$–CD_3CN–H_2O (9 : 9 : 2 v/v)	−8	0.33
Pr^n	*p*-C_6H_4Cl	$(CD_3)_2SO$–CD_3CN–H_2O (9 : 9 : 2 v/v)	−8	0.33
Pr^n	*p*-$C_6H_4NO_2$	CD_3CN–CH_3CN (1 : 1 v/v)	−30	2.1 [c]
Pr^n	*p*-$C_6H_4NO_2$	CD_3CN–CH_3CN–H_2O (9 : 9 : 2 v/v)	−30	2.0 [c]
Pr^n	*p*-$C_6H_4NO_2$	CD_3CN–CH_3CN–H_2O (9 : 9 : 2 v/v)	−45	2.2 [c]
Pr^n	*p*-$C_6H_4NO_2$	CD_3CN–$(CD_3)_2SO$ (1 : 1 v/v)	−8	3.0 [d]
Pr^n	*p*-$C_6H_4NO_2$	CD_3CN–$(CD_3)_2SO$–H_2O (9 : 9 : 2 v/v)	−8	2.4 [d]
Pr^n	*p*-$C_6H_4NO_2$	CD_3CN–$(CD_3)_2SO$–H_2O (9 : 9 : 2 v/v)	−30	2.6 [d]
Pr^n	*p*-C_6H_4Cl	CD_3CN	−50	0.22_5

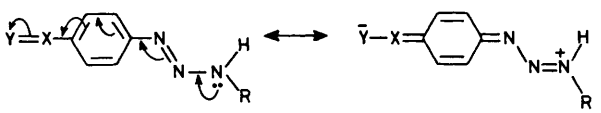
[a] Extrapolated from data at lower temperatures which gave $\Delta H^\ominus$ and $\Delta S^\ominus$. [b] Extrapolated from data at −45 °C, assuming a $\Delta H^\ominus$ valve identical to that of the *p*-methyl compound. [c] Measured on a 1-^{13}C enriched sample at a concentration of 3 mg ml^{-1}. [d] Measured with natural abundance ^{13}C at a concentration of 100 mg ml^{-1}.



(VI)



(VII)



(VIII)

However, the improvement in the correlation produced by adumbrating the phenomenon depicted in (VII) is not marked, and to explain the correlation with the pK_a of $ArNH_3^+$ only delocalisation as in (VI) is necessary. The gradient of the log K_T *versus* pK_a plot (β) is low (−0.3), indicating that delocalisation of this type is only 0.3 times as effective in preferentially stabilising the unconjugated tautomer as in promoting the dissociation of $ArNH_3^+$. This is readily understood, since delocalisation of the NH lone pair of the conjugated tautomer in the same sense as (VI) is also possible [(VIII)].

The substituent effect on the tautomeric equilibrium thus measures the differential strength of the two phenomena represented by (VI) and by (VIII).

If the effects of substituents in the aryl group on the tautomeric equilibrium of alkylaryltriazenes are very largely a consequence of conjugative interactions, then the electronic effect of substituents in the alkyl group should be negligible. This is so. The tautomerisation constants of benzyl- and propyl-*p*-nitrophenyltriazenes are indeed very similar (Table 2) despite the inductive effect of the phenyl group (aqueous pK_a values of the benzylammonium and propylammonium ions differ by 1.4 pK units). An upper limit of 0.03 can then be put on any β value correlating K_T and the pK_a of the alkylammonium ion.

The apparently very substantial difference in tautomerisation constant obtained for methyl- and benzyl-*p*-methylphenyltriazenes by Curci and Luccini [3] [*e.g.* 0.14 and 0.46 in $(CD_3)_2CO$ at −40 °C] suggests that what these authors were really quantitating were the two rotamers about the N–N bond of the conjugated tautomer, rather than the two tautomers. This idea receives support from the discrepancy between $\Delta H^\ddagger$ obtained for the tautomerisation of methyl-*p*-methylphenyltriazene by these authors (1 kcal mol^{-1}) and that obtained by Hadzi and Jan [2] (0.3 kcal mol^{-1}) and ourselves for the propyl compound (*ca.* 0.4 kcal mol^{-1}).

C *Effect of Change of Solvent.*—It is apparent from the data in Table 2 that change of solvent from CD_3CN to $(CD_3)_2SO$ alters the tautomerisation constant of propyl-*p*-nitrophenyltriazene by an amount comparable with the uncertainties in

n.m.r. integration. The same is true of the effect of change of the solvent for the *p*-chloro-compound from CD_3CN to 1 : 1 (v/v) CD_3CN–$(CD_3)_2SO$.

These solvents were chosen so that the effect of addition of water on the K_T values could be examined. Because of possible errors introduced into integrals of proton resonances by the solvent suppression procedure, ^{13}C integrals were also used to quantitate tautomers. These integrals of ^{13}C resonances were obtained on proton-decoupled spectra; the absence of a differential nuclear Overhauser effect on the propyl C-1 and C-2 carbons of the two tautomers was confirmed by the conformity of K_T to that measured by integration of N–H resonances in the absence of water.

It is clear from Table 2 that addition of water to propyl-*p*-chlorophenyl- and -*p*-nitrophenyl-triazenes in CD_3CN–$(CD_3)_2SO$ mixture has no effect on the position of tautomeric equilibrium. [The three-component mixture was used since the triazenes decompose in aqueous solutions at ambient temperatures, CD_3CN and water are only partially miscible below 0 °C, and pure $(CD_3)_2SO$ freezes well above 0 °C.] An analysis by ^{13}C n.m.r. integration, of the effect of water on K_T for the *p*-chloro-compound was obtained as follows. Although the 1-^{13}C resonance of the unconjugated tautomer of propyl-*p*-chlorophenyltriazene is too broad to be accurately integrated, the ^{13}C-enriched sample of this compound exhibited a sharp resonance at δ 30.9 p.p.m., probably due to contaminating *N*-methyl-*N*-ethyl-*N'*-*p*-chlorophenyltriazene arising, originally, from labelled ethyl isocyanide formed in the reaction of $K^{13}CN$ with diethyl sulphate. The relative intensities of this peak and the sharp peak of C-1 of the conjugated tautomer of the monoalkyltriazene in CD_3CN at −10 °C did not alter on addition of 10% water.

D *Conclusions.*—The position of tautomeric equilibrium of primary alkylaryltriazenes depends, to a first approximation, only on aryl group substituents: solvent and alkyl group have no effect.

Acknowledgements

We thank the S.E.R.C. for provision of the spectrometer and the A.R.C. for a graduate research assistantship.

References

1 References to early work on triazene tautomerisation are given in T. W. Campbell and B. F. Day, *Chem. Rev.*, 1951, **48**, 299.
2 D. Hadzi and J. Jan, *Spectrosc. Lett.*, 1968, **1**, 139.
3 R. Curci and V. Lucchini, *Spectrosc. Lett.*, 1973, **6**, 293.
4 N. S. Isaacs and E. Rannala, *J. Chem. Soc., Perkin Trans. 2*, 1974, 899.
5 H. Iwamura, K. Albert, and E. Riecker, *Tetrahedron Lett.*, 1976, 2627.
6 K. Albert, K.-M. Dangel, A. Rieker, H. Iwamura, and Y. Imahashi, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2537.
7 K. Vaughan, *J. Chem. Soc., Perkin Trans. 2*, 1977, 17.
8 K. Vaughan and M. F. G. Stevens, *Chem. Soc. Rev.*, 1978, **7**, 377.
9 L. Lunazzi, G. Panciera, and M. Guerra, *J. Chem. Soc., Perkin Trans. 2*, 1980, 52.
10 D. L. Hooper and K. Vaughan, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1161.
11 J. M. Tronchet and F. Rachidzadeh, *Helv. Chim. Acta*, 1976, **59**, 2855.
12 E. H. White and H. Scherrer, *Tetrahedron Lett.*, 1961, 758.
13 C. C. Jones, M. A. Kelly, M. L. Sinnott, P. J. Smith, and G. T. Tzotzos, following paper.
14 (*a*) M. L. Sinnott, *CRC Critical Rev. Biochem.*, 1982, **12**, 327; (*b*) M. L. Sinnott and P. J. Smith, *Biochem. J.*, 1978, **715**, 525; (*c*) P. J. Marshall, M. L. Sinnott, P. J. Smith, and D. Widdows, *J. Chem. Soc., Perkin Trans. 1*, 1981, 366; (*d*) O. P. van Diggelen, H. Galjaard, M. L. Sinnott, and P. J. Smith, *Biochem. J.*, 1980, **188**, 337; (*e*) O. P. van Diggelen, A. W. Schram, M. L. Sinnott, P. J. Smith, D. Robinson, and H. Galjaard, *ibid.*, 1981, **200**, 143.
15 J. A. Secrist and M. W. Logue, *J. Org. Chem.*, 1972, **37**, 335.
16 P. S. Engel, *Chem. Rev.*, 1980, **80**, 99.
17 L. Lunazzi, G. Cerioni, E. Foresti, and D. Macciantelli, *J. Chem. Soc., Perkin Trans. 2*, 1978, 686.
18 Taken from T. H. Lowry and K. S. Richardson, ' Mechanism and Theory in Organic Chemistry,' Harper and Row, New York, 1981, 2nd. edn., p. 131.
19 pK_a Values of 1.02 for *p*-nitroaniline, 1.70 for *p*-cyanoaniline, 2.37 for 3,5-dichloroaniline, 2.97 for 3,4-dichloroaniline, 3.98 for *p*-chloroaniline, 5.08 for *p*-toluidine, and 5.36 for *p*-anisidine are taken from D. D. Perrin, ' Dissociation Constants of Organic Bases in Aqueous Solution, Supplement,' Butterworths, London, 1972.

Received 23rd *March* 1982; *Paper* 2/505