Kinetics and Mechanism of the Decomposition of 3-Alkyl-1-aryltriazenes by Carboxylic Acids

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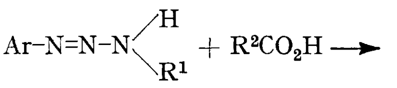
A kinetic study of reactions between a series of 3-alkyl-1-aryltriazenes with benzoic acids to yield alkyl benzoates supports a mechanism in which proton transfer and departure of an alkyl cation are rate-determining and synchronous. The resulting alkyl cation–carboxylate ion-pair may suffer nucleophilic attack or Wagner–Meerwein rearrangement before collapsing to product.

3-ALKYL-1-ARYLTRIAZENES (I) are known to react readily with carboxylic acids to form the corresponding alkyl esters [reaction (1)] in high yield.[1] Indeed, the readily accessible 3-methyl-1-*p*-tolyltriazene (I; Ar = *p*-Me-C_6H_4, R^1 = Me), has been recommended as a reagent for the preparation of methyl esters under mild conditions.[2] The reaction provides a route to the deamination of aliphatic amines.[3]



$$\mathrm{Ar{-}N{=}N{-}N}\begin{matrix}\diagup\mathrm{H}\\ \diagdown\mathrm{R^1}\end{matrix} + \mathrm{R^2CO_2H} \longrightarrow \mathrm{ArNH_2 + N_2 + R^2CO_2R} \quad (1)$$

(I)

Biologically, triazenes may act as carcinogens or tumour inhibitors and have been proposed as insecticides (particularly the 3,3-dialkyl derivatives), no doubt on account of their alkylating action.[4] To date, no systematic study has been made of these reactions which are of interest as examples of acid-induced reactions which will take place in a wide variety of media. Since the decomposition of triazenes by acids plausibly involves an initial proton transfer the reaction may be used as a model to study the effects of medium on this process both in protic and aprotic solvents, as reported in the following paper. Here we describe the characteristics of the reaction and the mechanistic conclusions which can be drawn.

EXPERIMENTAL

The triazenes were prepared by the method of White and Scherrer,[3] *i.e.*, the addition of a primary amine to a solution of aryldiazonium tetrafluoroborate in dimethyl sulphoxide at −20° in the presence of sodium carbonate. They were purified by repeated sublimation *in vacuo* until no further change in m.p. occurred. The physical properties are tabulated (Table 1). The molecular weights were checked by mass spectrometry, and the structures by n.m.r. spectroscopy. All showed u.v. maxima at *ca.* 278 and 305 nm and loss from the parent ion of 30, 42, and 68 mass units as the principal mass spectral fragmentations. Substituted benzoic acids were commercial samples and were purified to constant m.p. by recrystallisation. Chloroform was fractionated over collidine and then over P_2O_5 under nitrogen, collecting a middle fraction each time. Samples were stored in the dark and were discarded after a week to avoid the possibility of contamination by HCl. Products were determined qualitatively and quantitatively by g.l.c. (Apiezon on Chromosorb P); it was established in all cases that the reactions were clean and obeyed the stoicheiometry (1).

TABLE 1

Physical properties of some triazenes *p*-$XC_6H_4N{=}NNHR$

X	R	M.p. (°C)	[Lit m.p. (°C)]	τ Values
H	Me	37·5	[37—37·5]	
Me	Me	79	[79—81]	1·7br (s), 2·9 (m), 6·80br (s), 7·70 (s)
MeO	Me	39		
Br	Me	88	[86—87]	
F	Me	63		
Me	Et	36		2·85 (m), 6·35 (q), 7·62 (s), 8·72 (t)
Me	Pr^i	28		2·95 (m), 6·10 (septet), 7·8 (s), 8·8 (d)
Me	Bu^t	Liquid (not obtained pure)		2·90 (m), 7·70 (s), 8·60 (s)

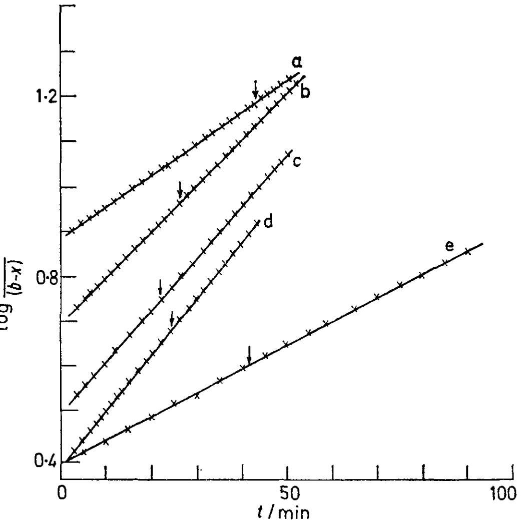


FIGURE 1 Representative second-order kinetic plots for reactions of some triazenes with benzoic acid (all at 30°): a, methyl-*p*-bromophenyltriazene; b, methylphenyltriazene; c, methyl-*p*-tolyltriazene; d, methyl *p*-methoxyphenyltriazene; e, methyl *p*-fluorophenyltriazene. Arrows mark one half-life

Reaction rates were measured in chloroform solution using concentrations of both reagents in the range 10^{-2}—10^{-3}M and following the reactions by the change in absorption at 340 nm, the measurements being carried out in a thermostatted cell within a Unicam SP 1800 spectrophotometer. Satisfactory second-order kinetics were observed to at least 70% reaction (Figure 1). Least squares procedures were applied to all linear relationships. Measured second-order rate constants are given in Table 2. The reaction between (I; Ar = *p*-MeC_6H_4, R^1 = Me) and benzoic

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[1] (*a*) V. Ya. Pochinok and O. I. Shevchenko, *Ukrain. Khim. Zhur.*, 1954, **20**, 289; (*b*) V. Ya. Pochinok and A. P. Limarenko, *ibid.*, 1955, **21**, 496, 628.

[2] E. H. White, A. H. Baum, and D. E. Eitel, *Org. Synth.*, 1968, **48**, 102.

[3] E. H. White and H. Scherrer, *Tetrahedron Letters*, 1961, 758.

[4] T. Zsolnai, *Biochem. Pharmacol.*, 1962, **11**, 995; 1965, **14**, 1325.

acid was studied over the temperature range 20—40° giving Arrhenius activation parameters E_a 11·5 kcal mol^{-1} and log A 7·23.

TABLE 2

Rate constants for reactions of alkyl(aryl)triazenes *p*-$XC_6H_4N_3HR$ with benzoic acids *p*-$XC_6H_4CO_2H$ in chloroform at 30° (unless otherwise stated)

X	Y	R	k_2/ l mol^{-1} s^{-1}
MeO	H	Me	0·0724
Me	H	Me	0·0669
H	H	Me	0·0509
F	H	Me	0·0347
Br	H	Me	0·0264
Me	MeO	Me	0·0340
Me	Me	Me	0·0407
Me	H	Me	0·0669
Me	Br	Me	0·130
Me	NO_2	Me	0·436
Me	H	Me	0·0669
Me	H	Et	0·118
Me	H	Pr^i	0·496
Me	H	Bu^t	>0·5 *
Me	H	Me (20)	0·0331
Me	H	Me (25)	0·0495
Me	H	Me (30)	0·0669
Me	H	Me (35)	0·0936
Me	H	Me (40)	0·138
Me	H	Me (+PhCOOD)	0·0271

* The Bu^t compound was not obtained sufficiently pure for kinetic studies: qualitatively it reacted considerably faster than the isopropyl analogue.

DISCUSSION

Effect of Substituents.—Structural variations in the aryl portions of triazene and of benzoic acid indicate that the measured rates increase by electron donation in the former case and electron withdrawal in the latter. The values of the respective Hammett reaction constants[5] ρ are −0·92 and +1·14 (Figure 2). These are of quite modest magnitude and are clearly consistent with proton transfer playing a kinetically significant role.

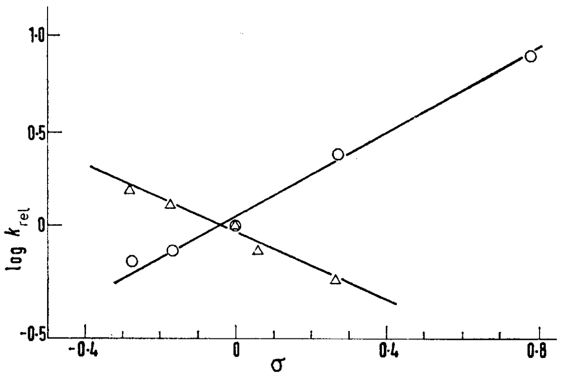
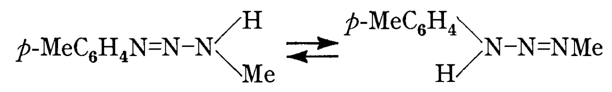


FIGURE 2 Hammett plot for 1-methyl-3-aryltriazenes with benzoic acids: ○ *para*-substituted benzoic acids; △ *para*-substituted triazenes

Little is known of acid–base reactions in aprotic solvents such as chloroform so it is difficult to predict the magnitude of ρ which would be expected for either an equilibrium or a rate process. In polar media, values of ρ for benzoic acid dissociations range from 1·00 (water) to *ca.* 1·5 (aqueous organic solvents).[6] Reaction constants for the decomposition of diphenyldiazomethane by benzoic acids have been determined in many solvents; typical values are 1·93 (acetone), 2·10 (ethyl acetate), and 2·00 (dioxan).[7] These are likely to be relevant to the present case since the reactions are known to be initiated by a proton transfer which is inferred to be rate determining.[8]

Position of Protonation.—3-Methyl-1-*p*-tolyltriazene (I; Ar = *p*-MeC_6H_4, R^1 = Me), exists in a state of rapid tautomeric equilibrium (A ⇌ B) as shown by the broad NH proton resonance at τ *ca.* 2 at room temperature. At lower temperatures this signal sharpens and becomes identifiable as a quartet while at the same time the *N*-methyl resonance becomes a doublet (Figure 3) confirming structure A as the more stable tautomer.



$$p\text{-}MeC_6H_4N{=}N{-}N(H)(Me) \rightleftharpoons p\text{-}MeC_6H_4(H)N{-}N{=}NMe$$

A B

This type of tautomerism is well established for 1,3-diaryltriazenes.[9] While N(1) must most plausibly bear two protons in order for the aniline to split out, there is little evidence in favour of either N(1) or N(3) as the site of primary protonation. It would be expected that N(3) would be the more basic site in (I; Ar = *p*-MeC_6H_4, R^1 = Me) and, furthermore, the rather low value of ρ for substitution in the triazene indicating protonation at the nitrogen most remote from the aromatic ring.* This interpretation however is complicated by the possible effects of substituents on the tautomerism of the triazene and the lack of knowledge of the separate reactivities of the tautomers.

Intermediacy of Carbonium Ions.—Previous workers have proposed carbonium ions as intermediates in triazene decomposition. Thus, Maskill *et al.*[10] obtained all isomeric octanes from the acetolyses of phenyloctyl- and phenyl-1-methylheptyl-triazenes. Even vinyl cations have been inferred as intermediates in the acetolysis of diarylvinyl-triazenes.[11]

The effects of alkyl group substitution upon rate supports the contention that the alkyl group leaves as a cation in a rate-determining step. The observed rate order, Me < Et < Pr^i < Bu^t, is clearly one of increasing stabilisation of a cation and the reverse order to that expected for a bimolecular substitution at carbon. The rate ratio may be compared with that for a typical S_N1 reaction. For triazene decomposition, Me : Et : Pr^i = 1 : 1·764 : 7·41 while for the formolysis of alkyl bromides

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* ρ For protonation of anilines is in the range −3·0 to −4·0.[5]

[5] P. R. Wells, ‘ Linear Free Energy Relationships,’ Academic Press, New York, 1968, ch. 2.1.

[6] H. H. Jaffe, *Chem. Rev.*, 1954, **54**, 191.

[7] A. Buckley, N. B. Chapman, M. R. J. Dack, J. Shorter, and H. M. Wall, *J. Chem. Soc.* (*B*), 1968, 631.

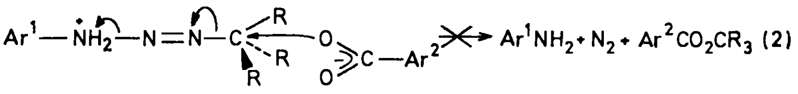
[8] R. A. More O'Ferrall, W. K. Kwok, and S. I. Miller, *J. Amer. Chem. Soc.*, 1964, **84**, 5553.

[9] S. Weckherlin and W. Luttke, *Tetrahedron Letters*, 1964, 1711.

[10] H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Comm.*, 1965, 496.

[11] W. M. Jones and T. W. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 1960.

the corresponding values are 1 : 1·71 : 44·7,[12] a more steeply increasing series but this is possibly due to the different medium. These results seem to exclude both the S_N2 attack (2) of carboxylate ion on the alkyl group and the expulsion (3) of alkyldiazonium ion.


$$Ar^1{-}\overset{+}{N}H_2{-}N{=}N{-}CR_3 \;\; {}^{-}O_2C{-}Ar^2 \not\rightleftarrows Ar^1NH_2 + N_2 + Ar^2CO_2CR_3 \quad (2)$$


$$Ar{-}\overset{+}{N}H_2{-}N{=}NCR_3 \not\rightleftarrows ArNH_2 + \overset{+}{N}_2CR_3 \quad (3)$$

While carbonium ion rearrangements would be expected in an ionising medium such as acetic acid, it was of interest to determine whether this feature occurred in less polar solvents. Accordingly 3-propyl-1-*p*-tolyltriazene was prepared and decomposed by the addition of acetic acid at 20° in a variety of media. The proportions of propyl and isopropyl acetates formed was determined by g.l.c. In all cases examined, Wagner–Meerwein rearrangement was found to have occurred but the extent of rearrangement depended markedly upon the solvent polarity (Table 3). These results are best interpreted in terms of a carbonium ion–carboxylate ion-pair (IV) whose lifetime and consequently opportunity to rearrange, increases with solvent polarity. Trapping of the carbonium ion may also be accomplished; the addition of sodium iodide to a mixture of triazene and benzoic acid results in the formation of a considerable amount of methyl iodide (acetone solution).

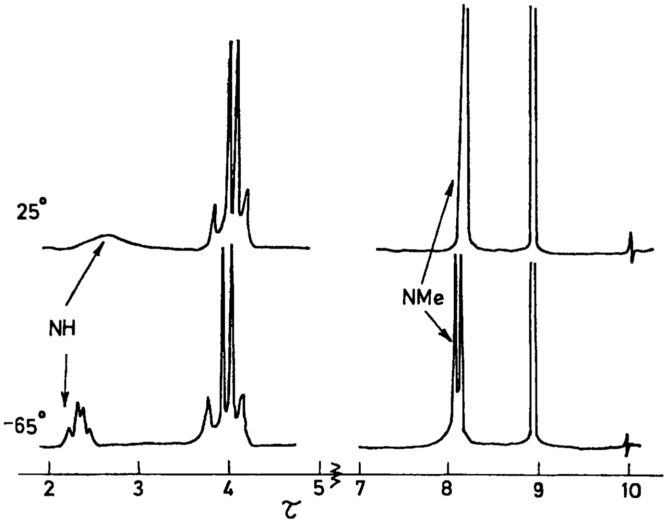


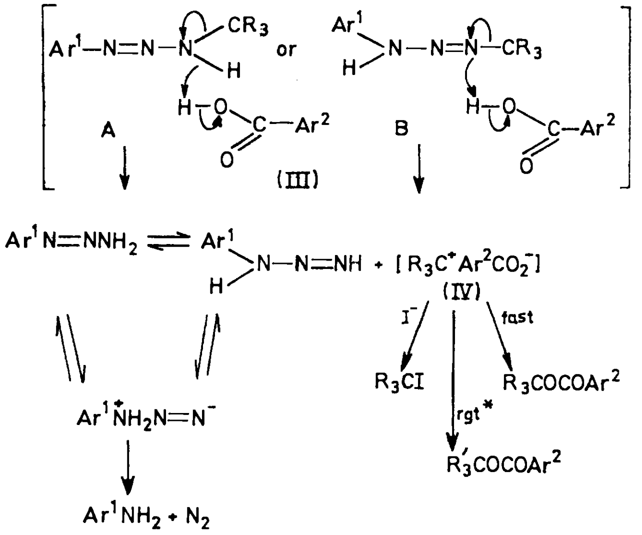
FIGURE 3 60 MHz ^{1}H N.m.r. spectra of 3-methyl-1-*p*-tolyltriazene at 25 and at −65° in dichloromethane solution

TABLE 3

Rearrangement in reactions of 3-propyl-1-*p*-tolyltriazene with acetic acid

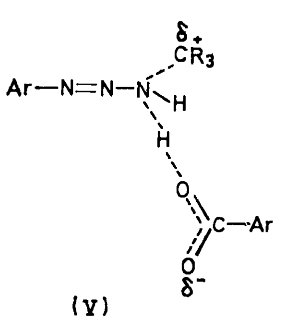
Solvent	Rearranged product (1-methylethyl acetate) (%)
Nitromethane	48
Acetic acid	40
Acetonitrile	32
Nitrobenzene	21
Nitropropane	15
Chloroform	12
cis-Pent-2-ene	14
Toluene	9
Diethyl ether	8
Dioxan	6
Carbon tetrachloride	2

Deuterium Isotope Effect. The observation of a substantial deuterium isotope effect on the reaction between triazene (I; Ar = *p*-MeC$_6$H$_4$, R^1 = Me) and [^{2}H]-benzoic acid, the magnitude of which indicates it to be a primary kinetic effect, requires the proton transfer to occur in a rate-determining step. The value of k_H/k_D (2·47) is of the same order as that observed for the decomposition of diphenyldiazomethane in ethanol (k_H/k_D 3·5).[8] Our further studies show that the value increases with solvent polarity,[13] and also that any equilibrium isotope effect is very small.



* rgt = Carbonium rearrangement.

SCHEME



(V)

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[12] L. C. Bateman and E. D. Hughes, *J. Chem. Soc.*, 1937, 1187; 1940, 935, 940; I. Dostrovsky and E. D. Hughes, *ibid.*, 1946, 171.

[13] N. S. Isaacs and E. Rannala, following paper.

Our results, as discussed above, require both proton transfer and the expulsion of an alkyl cation to occur in a rate-determining step. The isotope effect is inconsistent with pre-equilibrium protonation of the triazene while the effects of alkyl substitution are inconsistent with a rapid breakdown of protonated triazene. Accordingly we propose that the mechanism of this interesting reaction involves a concerted electrophilic substitution at nitrogen (Scheme) in which NH bond making and NC bond breaking are synchronous and the transition state is similar to (V). In this way, the reaction would respond both to the strength of the benzoic acid, the basicity of the triazene [affected by aryl substituents but not significantly by varying the N(3)-alkyl group], and the leaving ability of the N(3)-alkyl group. The latter may be equated with carbonium ion stability as found for displacements of alkyl cations at saturated carbon.[14]

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[14] E. M. Arnett and R. D. Bushick, *J. Amer. Chem. Soc.*, 1964, **86**, 1564.