

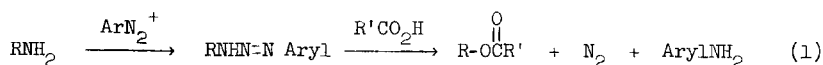
CARBONIUM IONS FORMED IN THE TRIAZENE METHOD OF DEAMINATION

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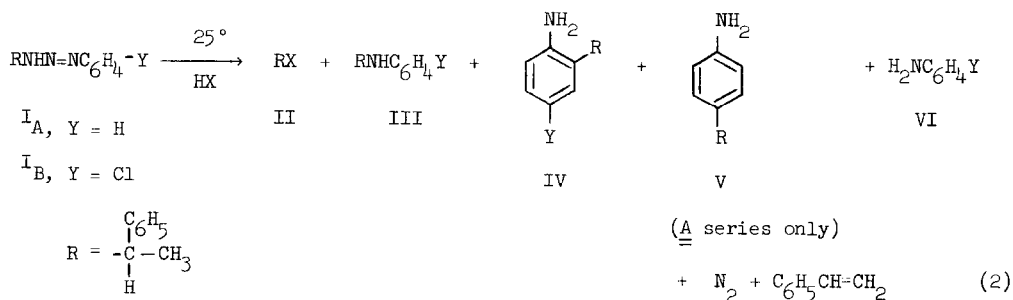
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(Received in USA 20 March 1969; received in UK for publication 2 April 1969)

We have been able to show that interceptible carbonium ions are formed in the triazene method (1) of deamination (eq. 1).



The chief evidence is the intramolecular formation with retention of configuration of substitution products III, IV, and V of the arylamine.



The configuration of III_A was established by a synthesis from optically active 1-phenylethylamine and diphenyliodonium bromide, and that of IV_B by conversion into 2-(1-phenylethyl)-4-chlorophenol, which had been correlated previously with 1-phenylethyl chloride and hence with 1-phenylethylamine (2), the precursor of I. The correlations show that S (-) 1-phenylethylamine, (+) III_A, and (+) IV_B have the same configuration. It seems quite certain that (+) III_B and (+) IV_A, which were isolated from the corresponding triazene reactions, also have this configuration. Compound V, the para isomer, was formed optically active, and in

view of the sign of rotation, (+), it is probable that this compound was also formed with retention of configuration.

The A and B series (eq. 2) gave similar results, essentially independent of the acid used (Table I). Also, similar yields of amines were obtained from the reaction of 1-benzhydryl-3-(4-chlorophenyl)triazene with benzoic acid in ethanol. The reaction of I_B with hydrogen chloride in ether led to no detectible amount of ethyl 1-phenylethyl ether (3a). Furthermore, no ethylbenzene or 2,3-diphenylbutane (4) were formed, thus ruling out free radicals as reaction intermediates (5). In the presence of 0.4 M thiophenol, the reaction of 0.05 M I_B with 0.1 M HCl in ether yielded less than 1% ethylbenzene, indicating again the negligible importance of free radicals in the reaction (6).

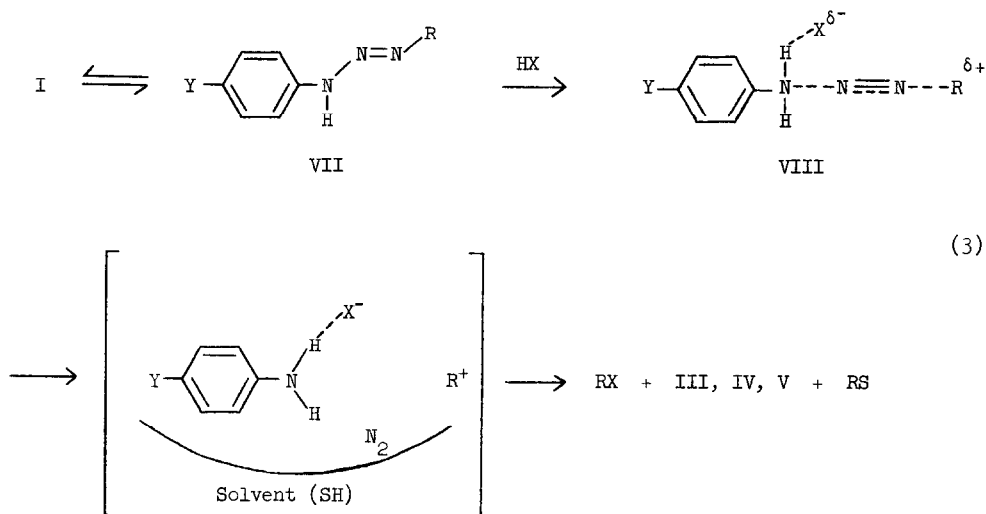
Table I
Products From The Reaction of Triazene I (eq. 2)

Triazene	Solvent	HX	% Yield (Stereochemistry)						Styrene
			II	III	IV	V	VI		
I _A (Y = H)	CH ₃ CO ₂ H	CH ₃ CO ₂ H	27	18	11	1	35	14	
			(58% Retn.)	(86% Retn.)	(+17°) ^a	(+4°) ^a			
I _B (Y = Cl)	CH ₃ CO ₂ H	3,5-Dinitro- benzoic acid	4 ^b	24	11	-	33	17	
			(61% Retn.)	(+10°) ^a	(+44- 60°) ^a				
	C ₂ H ₅ OC ₂ H ₅	HCl	29	12	14	-	59	29	
			(61- 68% Retn.)	(+8- 10°) ^a	(+55- 66°) ^a				

^a[α]_D in CCl₄. In all cases, the triazene was prepared from optically pure S (-) 1-phenylethylamine. ^bAlso 25% of 1-phenylethylacetate (57% Retn.).

The results can best be accounted for by a reaction mechanism (eq. 3) closely related to those of other methods of deamination (the nitrosoamide decomposition and the nitrous acid deamination) (7).

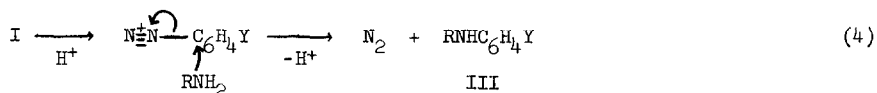
The formation of tautomer VII is thought to be necessary because of the relative stability of trisubstituted triazenes such as 1-phenyl-3,3-dimethyltriazene to acids (8). Protonation of the tautomer (\rightarrow VIII) would appear to be a reasonable second step in the reaction, followed



by N-N and C-N bond cleavage to give nitrogen (the role of the diazonium ion pair (RN_2^+X^-) is unknown at present). From the stereochemical data, it seems unlikely that intimate carbonium ion-carboxylate (or halide) pairs are intermediates in the formation of the amines (7). The special features of deamination suggest strongly that for a large fraction of the intermediates, the force between the cation and anion is considerably attenuated in deamination relative to solvolysis; this results, presumably, from either the physical presence of nitrogen between the two ions, or the formation of the ions at a greater internuclear separation than that which occurs in the corresponding intimate ion pair (3b,7,9). In any event, the carbonium ion is able to react with fairly inert molecules in the solvent cage in competition with the formation of a species in metastable equilibrium with the environment, the intimate ion pair R^+X^- (3b). Specifically with regard to the triazene reaction, the breaking of the carbon-nitrogen bond would lead to a carbonium ion in the same solvent cage with the counterion and the aromatic amine; a rapid reaction with either species (with retention of configuration) completes the process.

Various alternative reaction pathways can be eliminated from consideration by the data.

A displacement pathway for the formation of the secondary amine III (eq. 4) cannot be important



since (a) 1,3-diphenyltriazene on reaction with hydrochloric acid does not yield diphenylamine, but instead, aniline and products derived from the benzenediazonium ion (10a), (b) 1-phenyl-3,3-dimethyltriazene on reaction with hydrogen chloride in benzene does not yield N,N-dimethylaniline, but instead 91% of dimethylamine hydrochloride (10b), and (c) the reaction of acetic acid with I_B in the presence of aniline leads to negligible amounts of amines derived from aniline. Suitable controls have also eliminated cyclic concerted reactions from consideration.

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Acknowledgement. We thank the National Science Foundation (Grant GP-5446) for its support of this work, and Dr. H. Hart for kindly furnishing samples of compounds III_A, IV_A, and IV_B.