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THE INVOLVEMENT OF AZOCARBONIUM IONS IN SOME REACTIONS OF HYDRAZIDIC HALIDES

F. L. Scott and D. A. Cronin
Department of Chemistry, University College,
Cork, Ireland

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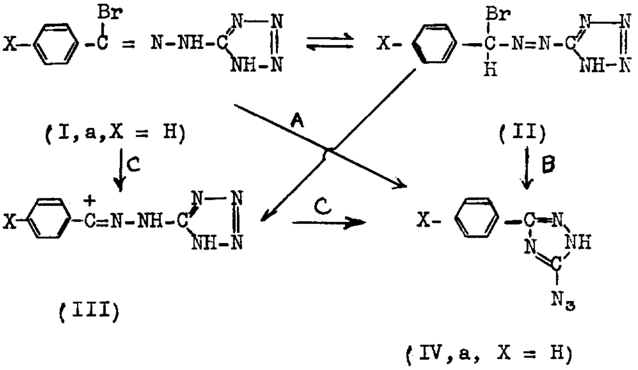
THE facile cyclization in aqueous ethanol of N-5-tetrazolylbenzhydrazidic bromide (Ia) to 5-azido-3-phenyl-1,2,4-triazole (IVa) has been described.[1] Table I summarizes some kinetic data pertaining to the effects of substituents on this process, together with the yields of substituted azides obtained in the various reactions.



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[1] F.L.Scott and M.N. Holland, Proc.Chem.Soc. 106 (1962).

Table I

Kinetics of Bromide ion Elimination from Substituted Tetrazolylhydrazidic Bromides[a]

Hydrazidic Bromide	k_1[b] (x10^4), sec.$^{-1}$	Yield[c] of Substituted Triazolyl Azide.
Ib, X = OCH_3	86.0	69
Ic, X = $CH(CH_3)_2$	6.6	65
Id, X = CH_3	5.5	72
Ie, X = H	2.9	65
If, X = Br	1.5	61
Ig, X = Cl	1.07	72
Ih, X = NO_2	(0.08)[d]	88

[a] In 95%(v/v) aqueous ethanol; [b] At 25(±0.1)°. All rate constants drifted downward during the runs; the k values reported were calculated by extrapolating the plot of k versus % reaction to 0% reaction. The values reported were replicated at least three times in separate runs. [c] Yields in separate product runs. [d] Rough rate constant as the insolubility of Ih made the determination of reliable rate data difficult.

From these data, a Hammett $\rho\sigma$ treatment (using σ values)[2] affords a ρ of -1.8 (with the point corresponding to p-methoxy far off the general curve). Use of σ^+ values[3] enables the p-methoxy value

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[2] D.H. McDaniel and H.C. Brown, J.Org.Chem. 23, 420 (1958).

[3] These were taken from the paper of H.C. Brown and Y.Okamoto, J.Amer.Chem.Soc. 79, 1913 (1957). All we wish to imply here is that we must use an 'exalted' σ value for p-methoxy to have it fit our data. We agree with recent criticisms (H.Van Bekkum, P.E. Verkade and B.M. Webster, Rec.Trav. chim. 78, 815 (1959) of a dualistic approach to σ values.

to fit the general pattern and leaves ρ virtually unchanged.

The conversion of compounds (I) to (IV) may proceed in one, or several, of the ways outlined in Figure I. Thus the 1-tetrazolyl moiety may directly participate in the expulsion of bromide ion (Path A).[4] This is akin to an aminolytic displacement at an acyl function. The rate sequence in Table I is, however, the opposite of that expected on this basis[5] and we provisionally eliminate Path A from consideration.

A second possibility involves a preliminary tautomerization[6] of Ia to the azobenzyl halide (II) which then undergoes tetrazolyl anchimerism to yield the azide (IV). A formally comparable reaction is the interaction of benzyl halides and **amines**,[7] for which however the ρ is only -0.12. Finally, there exists the possibility that an S_N1 process occurs to form the carbonium ion (III) - the conjugate acid of a nitrileimine[8] — which is then converted to substance (IV). This mechanism (Path C)

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[4] Compare the analogous reaction of the 2-tetrazolyl position with an imidic halide moiety, R.Huisgen, J. Sauer and M.Seidel, Chem.Ber. 93, 2885 (1960).

[5] Cf. E.W. Crunden and R.F.Hudson, J.Chem.Soc. 201 (1956), E.R.A. Peeling, J.Chem.Soc. 2307 (1959), I. Ugi and F. Beck, Chem.Ber. 94, 1839 (1961).

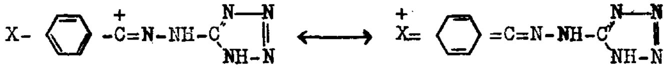
[6] In some recent papers, (see R. O'Connor, J.Org.Chem. 26, 4375 (1961); R.O'Connor and W. Rosenbrook Jr., J. Org.Chem. 26, 5208 (1961)), the tautomerism of hydrazones has been examined.

[7] C.G.Swain and W.P.Langsdorf Jr., J.Amer.Chem.Soc. 73, 2813 (1951).

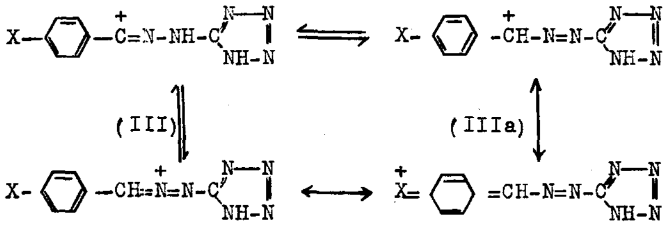
[8] Compare R.Huisgen, M.Seidel, G.Wallbillich and H.Knupfer, Tetrahedron 17, 3 (1962).

is similar to that proposed recently[9] for the hydrolysis of substituted imidic halides (for which we calculate from the data reported a ρ of -1.25).[10]

The carbonium ion (III) would be stabilized by such resonance as



or perhaps after a preliminary tautomerization, thus



(III) (IIIa)

(IIIc) (IIIb)

The species (III,etc.) above are also derivable from a preliminary ionization of substance II. Stabilization of the carbonium ion utilizing the α-aso function as in (IIIc) is related to the delocalization of charge operative in such carbonium ion

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[9] I.Ugi, F.Beck and U.Fetzer, Chem.Ber. 95, 126 (1962).

[10] Further support for the ionization mechanism is the fact that we have found that the entropy of activation for the cyclization of compound (Ia) to compound (IVa) is + 10 e.u.; compare F.A.Long, J.C. Pritchard and F.E. Strafford, J.Amer.Chem.Soc. 79, 2362 (1957).

species as oxocarbonium,[11a] aminocarbonium,[11b] aminoacylium[11c] and amidocarbonium ions.[11d]

The good yields of substituted triazolyl azides which are obtained from compounds of type (I) suggest that the tetrazolyl function is product-determining, if not rate-determining, and thus the carbonium ion involved cannot be completely free. A transition state for the cyclization process which has considerable carbonium ion character on the arylidene carbon atom and yet which has weak bonding between this same electron-deficient carbon and the 1-tetrazolyl moiety best accomodates our data so far.

In very preliminary runs, the solvolyses of 4-substituted-N-(2'-bromo-4'-nitrophenyl)benzhydrazidic bromides i.e. p-X-C_6H_4-C(Br)=N-NH-$C_6H_3Br(NO_2)$, o (p), (V), show a substituent response similar to that of Table I. Thus, when X in formula (V) is varied from $(CH_3)_2CH$ to H to Br, the rate constants for the ethanolyses (at 50°) of the respective compounds are roughly 6.4, 3.4 and 0.6 ($\times 10^{-3}$, sec.$^{-1}$) respectively, for which an approximate ρ of -2.9 may be derived. In

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[11a] See the following papers for example for leading references: (a) P.Ballinger, P.B.D. de la Mare, G. Kohnstam and B.M. Prestt, *J.Chem.Soc.* 3641 (1955);

[11b] (b) H. Bohme, L.Koch and E.Kohler, *Chem.Ber.* *95,* 1849 (1962);

[11c] (c) H.K.Hall, Jr., *J.Amer.Chem.Soc.* *77,* 5993 (1955);

[11d] (d) these are most likely involved in the acid-catalysed reactions of methylolamides with aryl compounds; a reaction which one might call the Einhorn reaction; for some references to this reaction see R.O'Cinneide, *Nature* *175,* 47 (1955).

these reactions the formation of an intermediary carbonium ion again appears very possible.

Finally, while the rate of cyclization of compound (Ia) is unaffected by its being run in 95% ethanol in the presence of acid, e.g. when the starting solution is 10N in sulphuric acid, the rate is extremely sensitive to the presence of bases. Attempts to buffer the cyclization of substance (Ia) to compound (IVa) in 95% ethanol using either sodium acetate, or sodium acetate- acetic acid, results in a sharp increase in the rate of bromide ion evolution (it is 95% complete after 10 minutes at 25°), and the yield of the material (IVa) drops to *ca.* 35%. In 1N sodium hydroxide solution (at 25°), the reaction of the halide (Ia) is complete in two minutes, only 5% of the azide (IVa) being formed. The major reaction product (possibly a dihydrotetrazine derivative) has not been identified unequivocally.

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