Tetrahedron Letters No. 34, pp 2927 - 2930, 1974. Pergamon Press. Printed in Great Britain.

CONVERSION OF α,α'-DICHLOROAZOALKANES TO DIAZOALKANES VIA A BRIDGED INTERMEDIATE

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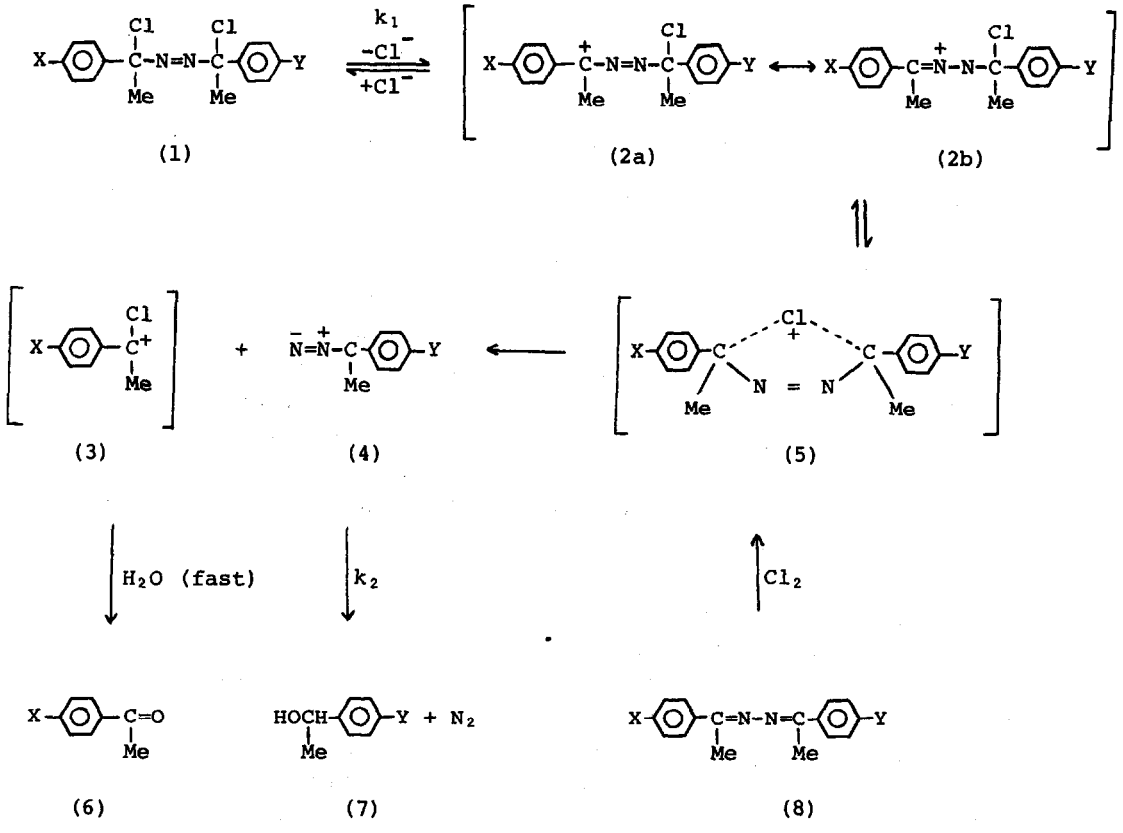
(Received in UK 21 June 1974; accepted for publication 3 July 1974)

α,α'-Dichloroazoalkanes are converted into free radical species with loss of nitrogen on heating and as such have attracted interest as radical initiators.[1] However, (1) can also undergo rapid ionic reactions in which nitrogen is either lost or retained. Examples of this type of reaction are the replacement of both chlorides in (1) by the nucleophiles cyanide, acetate[2] or alkylation using alkyl aluminium salts.[3] When (1) is solvolysed in mixed aqueous organic solvents in the absence of other nucleophiles, rapid loss of nitrogen occurs and the final products are the ketone (6) and the alcohol (7). We report that these solvolyses occur via a novel mechanism involving an isolable diazoalkane intermediate which is formed on rearrangement of an azocarbonium ion.

In neutral water-dioxan (30:70) solution at 25° we have found that the α,α'diaryl azoalkanes (1) show consecutive reactions with the formation of an intermediate. The two reactions could be followed separately at different wavelengths in the ultraviolet. Under these conditions, the formation of the intermediate from (1, X = Y = Cl) is more rapid (k_1 = 1.1 x 10^{-2} s^{-1}) than its decomposition (k_2 = 4.5 x 10^{-3} s^{-1}). The relative magnitudes of the two rate constants, can, however, be varied, since the first step (k_1) is very sensitive to the ionizing power of the solvent (Grunwald-Winstein m = 1.2) whereas k_2 remains relatively unchanged when the aqueous content of the solvent is increased. Alternatively, changing the pH of the medium can also affect the balance between k_1 and k_2 - k_1 is insensitive, while k_2 is greatly increased in acid and tends to zero in basic solution. The "intermediate" under such basic conditions is then the final product of reaction. We have shown that this intermediate is the diazoalkane (4) by (a) actual isolation of the more stable materials (e.g. (4), Y = p-NO_2), (b) u.v. and i.r. identification in solution, and (c) comparison of the subsequent rate (k_2 values) obtained with the rate of hydrolysis of the same diazoalkanes, prepared and studied independently.

The mode of formation of the diazoalkane (4) is also of interest. The first step (k_1) most likely represents rate determining formation



(1) (2a) (2b) (3) (4) (5) (6) (7) (8)

of a stabilized azocarbonium ion (2). This is consistent with the large rate enhancing effect shown by electron donating substituents. (Hammett $\rho = -3.5$, when log k_1 is plotted against $2\sigma_X$ when the substituents X and Y are the same). However, when the two aryl rings do not have the same substituent (1, $X \neq Y$), then a similar plot *vs.* $\sigma_X + \sigma_Y$ shows surprisingly wide scatter. We have interpreted this in terms of preferential loss of of Cl^- in (1) from the site which yields the most stable azocarbonium ion (2). Thus, when X is more electron-donating than Y, the major pathway is through (2) which has the positive charge located adjacent to XC_6H_4. When Y is held constant as a strongly electron-withdrawing group (e.g. Y = p-NO_2) then the azocarbonium ion formed preferentially is (2) since in this

case a good plot of log k_1 *vs.* σ_X is obtained (X = p-Me, H, p-Br, p-Cl, m-Br); the substituent sensitivity is high (ρ = -2.5) consistent with a good deal of charge localization on the XC_6H_4-ring. On the other hand, when a strongly electron donating substituent is present (e.g. p-Me), then the other substituent (e.g. Y in (2)) has a relatively small effect on reactivity (ρ = -1.1, with Y = H, p-Br, p-Cl, m-Br, p-NO_2). There is thus clear evidence for the formation of an open unsymmetrical carbonium ion (such as (2)) on the reaction pathway; an alternative symmetrically bridged intermediate (such as (5)) would show the same sensitivity to both substituents X and Y.

On the basis of these results one would expect that the unsymmetrical carbonium ion (2) would break down to give the diazoalkane $XC_6H_4CMeN_2$ (9) and ketone YC_6H_4COMe (10). Unexpectedly, however, the isomeric materials (3) and (4) (and ultimately (7)) are actually obtained as the major products. It is difficult to visualize how the carbonium ion (2) could give rise directly to these products ((3) and (4)); we, therefore propose that the open carbonium ion (2) fragments via the bridged intermediate (5), which is formed *after* the rate-determining step. The driving force for this rearrangement is provided by the formation of the most stable carbonium ion (3) and diazoalkane (4) when X is more electron donating than Y. It is interesting that when the substituents X and Y do not differ greatly in electron-donating or withdrawing power (e.g. X or Y = H, p-Br, p-Cl) then both ketones ((6) and (10)) and diazoalkanes ((4) and (9)) are formed; moreover, the relative amounts of each is proportional to the difference between the σ values of the substituents (i.e. log {(6)/(10)} is proportional to $\sigma_X-\sigma_Y$ with ρ = +1.70).

It has previously been reported by Malament and McBride[4] that the ionic chlorination of diazabutadienes of type (8) is stereospecific in that only one of the possible isomeric α,α'-dichloro compounds (1) is actually obtained. This is explicable in terms of the proposed reaction scheme as follows. If the chlorination of (8) shares the same bridged intermediate (5) on the reaction pathway, then chloride ion attack on the side remote from the bridged chloronium ion would yield (1) with the observed stereospecificity.

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