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IMIDAZOLE NEIGHBOURING GROUPS IN THE SOLVOLYSIS OF HYDRAZIDIC HALIDES

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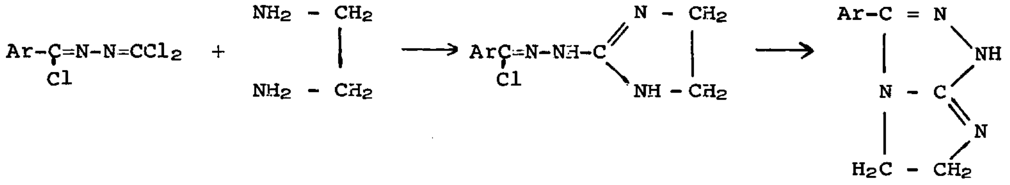
In the reaction of bromine with basic arylidene heterocyclic hydrazones (e.g. the 2-pyridyl compounds)[1] methine bromination to yield the desired hydrazidic halides is inhibited and instead N-bromination occurs. We describe herein how in a similar situation namely the bromination of basic dihydroimidazolyl hydrazones where perbromide formation occurs, we circumvent this difficulty. We have prepared the desired hydrazidic halide systems (II) using instead of direct halogenation, our recently described[2] reactive aryl trichloro-diazabutadienes (I) as precursors. We also describe the facile conversion of compounds (II) to the fused ring systems (III).

Reaction of a series of 4-(p-substituted-phenyl)-1,1,4-trichloro-diazabutadienes (I) with two equivalents of ethylenediamine in benzene for several hours at ambient temperatures forms the dihydroimidazolyl hydrazidic chlorides (II) in good (70-80%) yields. Using the p-chlorophenyl compound as a model, we attempted to make these hydrazidic halides by a direct method. When p-chlorobenzylidene dihydroimidazolylhydrazine (IV) was treated with bromine in glacial acetic acid, the product was the hydrazone (IV) perbromide which reverted to starting hydrazone on distribution between ether and aqueous base. Thus the indirect route to compounds (II) was necessary.



I II III

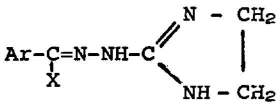
These materials (II) were solvolytically reactive, the compounds cyclising very rapidly in 80% aqueous dioxan to yield the fused dihydroimidazolotriazoles (III) in high (ca. 90%) yields. We measured the rates

(Table 1) of this process by u.v. spectroscopy and found these were correlated by a Hammett ρ = -2.9 (r = 0.997). This value is consistent with these solvolyses involving an intermediary azocarbonium ion. Despite this the internal nucleophilic imidazolinyl group competes most effectively with external nucleophiles for this carbonium ion. We have examined the solvolysis solutions carefully using t.l.c. for any traces of the corresponding hydrazides (V) but found none. Using an efficient, external nucleophile together with conditions where ionisation is minimised can defeat this imidazolinyl competition. For example, refluxing compounds (II) with two equivalents of aniline in benzene yields the anilino derivatives (VI) in high (90%) yields.

Table 1

Rates of Solvolysis of the Hydrazidic Chlorides, II, Ar = p-XC_6H_4

Substrate, X	i-C_3H_7	CH_3	H	Cl	Br	NO_2
10^4k (13°, 80% aqueous dioxan)	v.rapid	177	70.8	20.5	14.1	0.35



IV, X = H, Ar = p-ClC_6H_4
V, X = OH
VI, X = NHC_6H_5

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References

1. M. S. Gibson, Tetrahedron, 19, 1587 (1963).

2. F. L. Scott, J. Donovan and J. K. O'Halloran, Tetrahedron Letters, in press.