Meso-ionic 1,3,4-Thiadiazolium and 1,3,4-Triazolium-2-benzylidenehydrazinides

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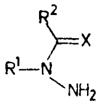
Summary The use of the 1,1-dihalogeno-2,3-diaza-1,3-dienes (IX) and (X) for the synthesis of the novel meso-ionic heterocycles (VI) and (VII) is described.

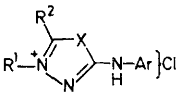
Isocyanide dichlorides have been used[1] as versatile intermediates for the rational synthesis of three new classes of meso-ionic heterocycles (III; X = O, S, or NAr) by the route (I) + (VIII) → (II) → (III). The existence of pairs of meso-ionic heterocycles (III) and (IV) has been established and their interconversion and relative thermodynamic stability have been explored.[1] As analogues of the isocyanide dichlorides (VIII), the 1,1-dihalogeno-2,3-diaza-1,3-dienes (IX)[2] and (X)[3] have been shown to have similar synthetic utility. The synthesis of a new class of meso-ionic heterocycle (VI) associated with a novel carbanionoid exocyclic substituent, Ar–CH–N–N, is now reported; examples of their base-catalysed isomerisation and 1,3-dipolar cycloaddition reactions are described.

The 1,1-dibromo-4-aryl-2,3-diazabuta-1,3-dienes[2] (IX; Ar = Ph, *p*-Me·C_6H_4, *p*-Cl·C_6H_4, or *p*-MeO·C_6H_4) and either *N*-methyl-*N*-thiobenzoylhydrazine[1,4,5] (I; R^1 = Me, R^2 = Ph, X = S) or *N*-phenyl-*N*-thiobenzoylhydrazine[5] (I; $R^1 = R^2$ = Ph, X = S) in boiling benzene yielded the corresponding yellow 1,3,4-thiadiazolium bromides (V; X = S). These salts (V; X = S) with anhydrous ammonia in methylene chloride at room temperature gave the orange-red crystalline meso-ionic 1,3,4-thiadiazolium-2-benzylidenehydrazinides (VI). These meso-ionic compounds (VI) with hydrogen bromide in benzene solution regenerated the 1,3,4-thiadiazolium bromides (V).

An analogous sequence of reactions with *N*-amino-*N*-methyl-*N'*-phenylbenzamidine[6] (I; $R^1 = \mathrm{Me}$, $R^2 = \mathrm{Ph}$, $X = \mathrm{NPh}$) and the above 1,1-dibromo-4-aryl-2,3-diazabuta-1,3-dienes (IX) gave the intermediate 1,3,4-triazolium bromides (V; $X = \mathrm{NPh}$) and the yellow meso-ionic 1,3,4-triazolium-2-benzylidenehydrazinides (VI; $X = \mathrm{NPh}$).



(I)



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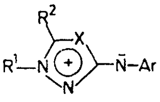

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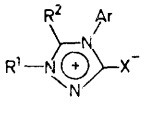

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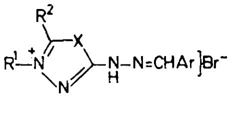

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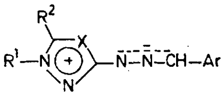

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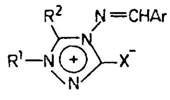


(VII)

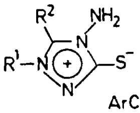
(VIII) $\mathrm{Ar{-}N{=}CCl_2}$

(IX) $\mathrm{Ar{-}CH{=}N{-}N{=}CBr_2}$

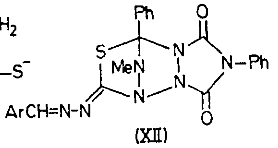
(X) $\mathrm{Ar{-}CCl{=}N{-}N{=}CCl_2}$

The isomerisation (VI) ⟶ (VII; $X = \mathrm{S}$) takes place during 10 days in boiling ethanol continuously saturated with anhydrous ammonia. For example, the *p*-chlorobenzylidene derivative (VI; $R^1 = \mathrm{Me}$, $R^2 = \mathrm{Ph}$, $\mathrm{Ar} = p\text{-}\mathrm{Cl{\cdot}C_6H_4}$, $X = \mathrm{S}$) gave the rearrangement product (VII; $R^1 = \mathrm{Me}$, $R^2 = \mathrm{Ph}$, $\mathrm{Ar} = p\text{-}\mathrm{Cl{\cdot}C_6H_4}$, $X = \mathrm{S}$). A second product from this reaction was the *N*-amino-meso-ionic heterocycle (XI; $R^1 = \mathrm{Me}$, $R^2 = \mathrm{Ph}$) whose structure was confirmed by an independent synthesis.[7] The *N*-amino-meso-ionic heterocycle and *p*-chlorobenzaldehyde gave the *p*-chlorobenzylidene derivative (VII; $R^1 = \mathrm{Me}$, $R^2 = \mathrm{Ph}$, $\mathrm{Ar} = p\text{-}\mathrm{Cl{\cdot}C_6H_4}$, $X = \mathrm{S}$).

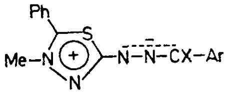
The meso-ionic 1,3,4-thiadiazolium-2-benzylidenehydrazinides (VI; $X = \mathrm{S}$) do not give isolable products with many 1,3-dipolarophiles. However, with 4-phenyl-1,2,4-triazoline-3,5-dione in acetone solution at room temperature the orange adducts (XII) are formed and precipitated very rapidly.



(XI)



(XII)



(XIII)

Two side-chain variants (XIII; $X = \mathrm{Cl}$) and (XIII; $X = \mathrm{CN}$) of the mesoionic systems (VI) have also been synthesised. The meso-ionic compound (XIII; $X = \mathrm{Cl}$, $\mathrm{Ar} = p\text{-}\mathrm{Cl{\cdot}C_6H_4}$) was prepared from (I; $R^1 = \mathrm{Me}$, $R^2 = \mathrm{Ph}$, $X = \mathrm{S}$) and the compound (X; $\mathrm{Ar} = p\text{-}\mathrm{Cl{\cdot}C_6H_4}$)[3] and reaction with potassium cyanide in dimethylformamide gave the cyano-derivative (XIII; $X = \mathrm{CN}$, $\mathrm{Ar} = p\text{-}\mathrm{Cl{\cdot}C_6H_4}$).

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