

Short Communications

1-Substituted 3,5-Diaryl-s-triazolo-
[3,4-c]-s-triazoles

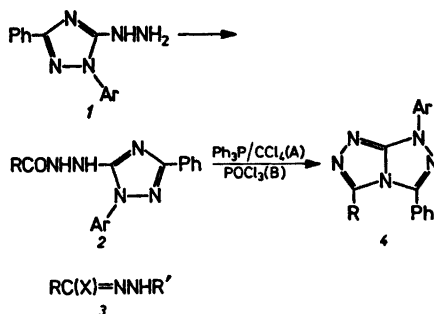
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Hydrazonyl halides (**3**, X = halogen) have been used extensively in the preparation of five-membered heterocyclic compounds *via* 1,3-dipolar cycloaddition reactions,¹ and by displacement reactions at the hydrazonyl carbon atom.² Internal dipolar cyclization reactions are also known,^{2,3} and recently internal 1,3-dipolar cycloaddition reactions have been reported.⁴

5-Hydrazino-1,2,4-triazoles (**1**) have now become readily available from the reaction of hydrazonyl halides with thiosemicarbazide in the presence of base,⁵ and these compounds were thought to be suitable as precursors, *via* the acylhydrazide (**2**) and the hydrazonyl halide (**3**), of the hitherto unknown 1,3,5-trisubstituted-s-triazolo[3,4-c]-s-triazoles (**4**). This ring system (3,5-disubstituted) has previously been reported in the literature.^{6,7}

The acylhydrazides (**2**) were easily prepared by acylation [aroyl chloride (**2a–c**) or acetic anhydride (**2d**)] of the free hydrazine. Treatment of the benzohydrazide (**2a**) with triphenylphosphine and carbon tetrachloride ($\text{Ph}_3\text{P}/\text{CCl}_4$) (Method A), did not give the expected⁸ hydrazonyl chloride, instead internal cyclization took place with formation of 1,3,5-triphenyl-s-triazolo[3,4-c]-s-triazole (**4a**) (*cf.*



Scheme 1. a, Ar = R = Ph; b, Ar = 2,4-Br₂C₆H₃ and R = Ph; c, Ar = Ph and R = 4-CH₃OC₆H₄; d, Ar = Ph and R = CH₃.

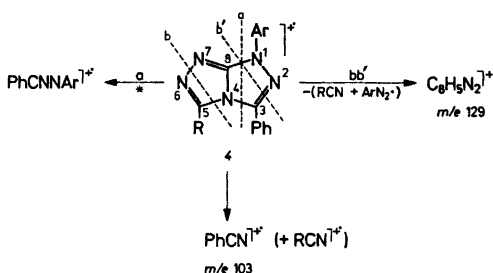
Ref. 9). Phosphoryl chloride (POCl_3) was also found to be a convenient reagent (Method B) for the conversion of **2** into **4**.

The mass spectra of **4** (see Table 1) are compatible with the structural assignment. The mass spectra are characterized by molecular ions, base peaks of the spectra, abundant $[\text{PhCN}]^+$ (also $[\text{RCN}]^+$ in case of **4c**), $[\text{PhCNNAr}]^+$ and $[\text{M} - (\text{ArN}_2 + \text{RCN})]^+$ ions. The latter two types of ions are of particular significance. The $[\text{PhCNNAr}]^+$ ions (route a) confirm the integrity of the original 1,2,4-triazole ring of **1**. The *m/e* 129 ion $[\text{C}_6\text{H}_5\text{N}_2]^+$ is present in all mass spectra and corresponds to the loss of $(\text{ArN}_2 + \text{RCN})$ from the molecular ion (route bb') (confirmed by metastable defocusing¹⁰). This ion may be formed also by a different route involving atoms C- (5 and 8) and N- (6 and 7) of the ring as seen by the

Table 1. The principal peaks^a in the mass spectra^b (70 eV) of compounds **4**.

| Compound | M ⁺ | $[\text{PhCNNAr}]^+$ | M ²⁺ | $[\text{C}_6\text{H}_5\text{N}_2]^+$ <i>m/e</i> 129 | $[\text{PhCN}]^+$ <i>m/e</i> 103 | $[\text{ArN}]^+$ |
|---------------------------------|----------------|----------------------|-----------------|--|-------------------------------------|----------------------|
| 4a (140 °C) ^c | 339 (100) | 194 (6) | (5) | (8) | (60) | 91 (17) |
| 4b (160 °C) | 497 (100) | 350 (1) | (5) | (13) | (33) | 249 (8) ^d |
| 4c (120 °C) | 369 (100) | 194 (9) | (7) | (5) | (11) | 91 (28) ^e |
| 4d (100 °C) | 275 (100) | 194 (1) | (4) | (18) | (67) | 91 (5) ^f |

^a *m/e* (rel. int.). ^b Recorded on an A.E.I. MS 902 mass spectrometer. ^c Ion source temperature. ^d $[\text{C}_7\text{H}_3\text{Br}_2\text{N}]^+$ 261 (46). ^e $[\text{C}_6\text{H}_7\text{N}_2\text{O}]^+$ 159 (1.5), 133 (35), 118 (4). ^f 117 (8).



Scheme 2. MS fragmentation of 4.

formation of m/e 159 in the spectrum of 4c.

Several attempts to convert (with nitrous acid) the hydrazino compounds (1) to azides, invariably resulted in decomposition to the corresponding amines (cf. Ref. 11).

Experimental. 5-(*N'*-Acylhydrazino-1-aryl-3-phenyl-1,2,4-triazoles (2). Crude hydrochloride of 1a⁵ (10.0 mmol) was stirred for 30 min in conc. ammonia (20 ml), filtered and dried to give the free hydrazine 1a (7.5 mmol). This was dissolved in pyridine (10 ml) and treated with benzoyl chloride (3.75 mmol). After 30 min the reaction mixture was poured into water and stirred. The precipitate was filtered off, dried and crystallized from ethanol to give 2a (40%), m.p. 164–165 °C. Anal. C₂₁H₁₇N₅O: C, H, N.

Compounds 2b and 2c were prepared in a similar manner. Compound 1b and benzoyl chloride gave 2b (40%), m.p. 241–243 °C (from ethanol). Anal. C₂₁H₁₅Br₂N₅O: C, H, N. Compound 1a and anisoyl chloride gave 2c (60%), m.p. 198–200 °C (from ethanol). Anal. C₂₂H₁₉N₅O₂: C, H, N.

Compound 1a (2.5 mmol) and acetic anhydride (2.5 mmol) were refluxed together in benzene (10 ml) for 30 min. Removal of the solvent by evaporation and crystallization of the residue from ethanol gave 2d (60%), m.p. 191–194 °C. Anal. C₁₆H₁₁H₂O: C, H, N.

1-Substituted 3,5-diaryl-s-triazolo[3,4-c]-s-triazoles (4). Method A. Carbon tetrachloride (1.50 mmol) was added to a stirred suspension of 2a (1.50 mmol) and Ph₃P (1.87 mmol) in dry acetonitrile (5 ml) as described previously.⁸ After 7 days at room temperature the mixture was filtered, and the solid was crystallized from acetonitrile (80 ml) to give 4a (23%), m.p. 244–246 °C. Anal. C₂₁H₁₅N₅: C, H, N.

Method B. The benzohydrazide 2a (0.31 mmol) and POCl₃ (1 ml) were refluxed together for 15 min, allowed to cool and followed by removal of the solvent. The residue was treated with ice-water, and the solid was crystallized from ethanol to give 4a (34%), m.p. 240–245 °C.

Compounds 4b, 4c and 4d were prepared in a similar manner. Compound 2b and POCl₃ gave 4b (70%), m.p. 198–200 °C. Anal. C₂₁H₁₃Br₂N₅:

C, H, N. Compound 2c and POCl₃ gave 4c (50%), m.p. 219–221 °C. Anal. C₂₂H₁₇N₅O: C, H, N. Compound 2d and POCl₃ gave 4d (60%), m.p. 158–160 °C. Anal. C₁₆H₁₁N₅: C, H, N.

Nitrosation of the hydrazines (1). Sodium nitrite (2.5 mmol) in water (0.5 ml), previously cooled, was added dropwise to a stirred suspension of the hydrochloride of 1a⁵ (1.0 mmol) in conc. hydrogen chloride (2.5 ml) cooled to 5–10 °C. After 30 min the solution was filtered, and the solid was crystallized from acetonitrile, containing a few drops of conc. HCl, to give the hydrochloride of the corresponding amine (45%), solvated as a hydrate. Anal. C₁₄H₁₂N₄.HCl.H₂O: C, H, N.

Treatment of this with conc. ammonia gave the free amine, m.p. 148–150 °C (from hexane/benzene, 1:1) (reported⁵ 148–150 °C).

Similarly, after work-up the hydrobromide of 1b⁵ gave the free amine, m.p. 226–229 °C (reported⁵ 219–221 °C); an IR spectrum was identical to that of an authentic specimen.⁵

Nitrosation of the free hydrazine 1b at 0 °C did not afford any reaction, the hydrochloride of 1b was recovered, m.p. 257–261 °C. Anal. C₁₄H₁₁Br₂N₅.HCl: C, H, N.

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