Pyrazolotrithiadiazepines and their Unexpected Rearrangement to 1,2,3-Dithiazoles

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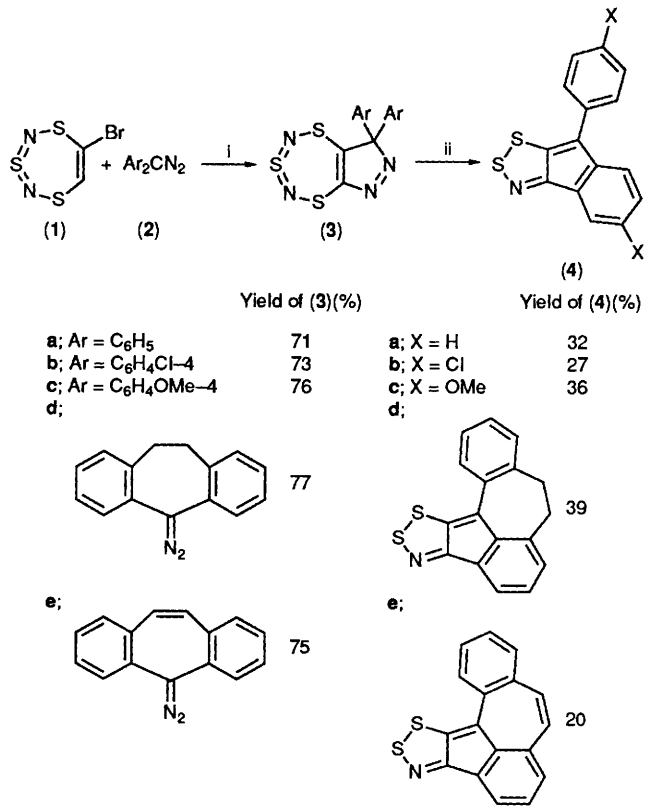
Treatment of 6-bromotrithiadiazepine (**1**) with Hünig's base in the presence of diaryldiazomethanes (**2**) gives the trithiadiazepyne cycloadducts (**3**) which undergo a deep-seated thermal rearrangement to give fused 1,2,3-dithiazoles (**4**), for which a mechanism is proposed.

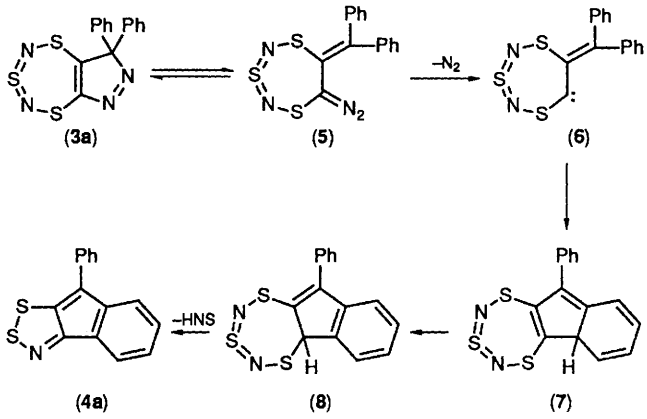
We have described the generation of trithiadiazepyne and its reactions with nucleophiles and dienes.[1] We now show that this intermediate can be intercepted by diaryldiazomethanes, and the resulting 1,3-dipolar cycloadducts undergo a deep-seated molecular rearrangement on heating.

When 6-bromotrithiadiazepine (**1**) and the diazo compounds (**2**) were treated with Hünig's base in methanol at room temperature the stable hetaryne cycloadducts (**3**) were formed in good yield. Since these are cyclic azo compounds they could on pyrolysis, lose nitrogen to form other fused trithiadiazepines. The diphenyl compound (**3a**) decomposed above its m.p. to form a deep-red product; gas evolution was almost instantaneous at 210 °C and the red product (**4a**) was isolated in modest yield. Its mass spectrum showed M^+ at 267 and a peak for loss of S_2; the IR spectrum showed a stretch at 1120 cm^{-1} (NS), the UV spectrum was too complex for a trithiadiazepine, and the ^{13}C NMR spectrum showed one mono- and one di-substituted benzene ring. Elemental analysis indicated the formula, $C_{15}H_9NS_2$, in agreement with the mass spectrum. Clearly the trithiadiazepine ring has not survived extrusion of nitrogen, the element of HNS having also been lost. Crystals of the red product were not suitable for *X*-ray analysis but on treatment with N_2O_4 in dichloromethane it gave an oxide in high yield which was shown by *X*-ray crystallography[2] to be the $S_{(2)}$-oxide of (**4a**), thus, confirming the structure of the latter, and particularly the rearranged SSN heteroatom sequence (Scheme 1).

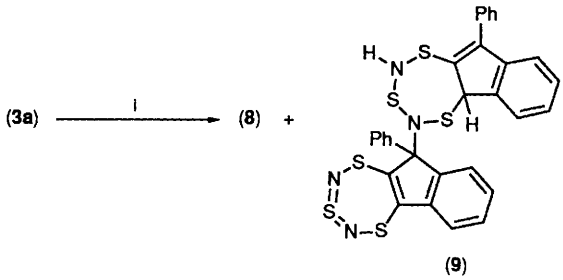
The other diaryldiazomethane cycloadducts (**3b—e**) were thermolysed similarly to give analogues (**4b—e**) of the unusual compound (**4a**). Crystals of the dibenzocycloheptadiene product were suitable for *X*-ray crystallography which confirmed structure (**4d**).[2] All the thermolysis products (**4**) have



Scheme 1. *Reagents and conditions:* i, Et NPr^i_2, MeOH, 20 °C, 20 min, ii, 210 °C, 5 s.



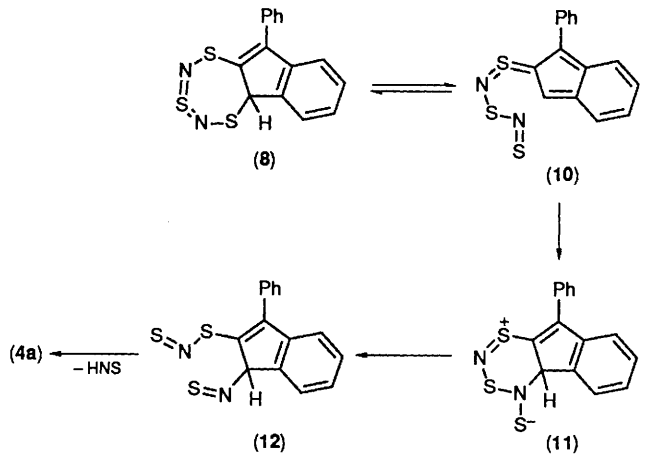
Scheme 2



Scheme 3 *Conditions:* i, Xylene, reflux, N_2, 25 min.

similar spectroscopic properties and undoubtedly the same ring structure. This benzo 5,5-fused ring system is new, and only one example of the 5,5-system, 4,6-di-t-butylcyclopenta-1,2,3-dithiazole, has been previously reported.[3] A partial mechanism for this molecular rearrangement is shown, for compound (**3a**), in Scheme 2. Diazo compound (**5**) and carbene (**6**) are both stabilised by extensive delocalisation. The next intermediate (**7**) has an aromatic trithiadiazepine ring which could be disrupted by a 1,5-hydrogen shift to give (**8**) with an aromatic benzene ring and a more reactive array of heteroatoms. Exactly how the heteroatoms rearrange and extrude HNS is more speculative (see below).

In the neat, high temperature, pyrolysis conditions described above no intermediates were detected, and so the thermolysis was carefully studied under milder conditions in solution. When the diphenyl compound (**3a**) was boiled in xylene (140 °C for 20 min), bromobenzene (156 °C for 6 min), or 1,2-dichlorobenzene (180 °C for 3 min), the red product (**4a**) was again obtained though in lower yield (20, 16 and 15% respectively). However, TLC monitoring showed the presence of an orange product in solution which appeared to be an intermediate in the rearrangement, but which decomposed on silica and was difficult to isolate pure. However, thermolysis of (**3a**) in a dilute (0.75 mg ml^{-1}), deoxygenated



Scheme 4

xylene solution for 25 min allowed the isolation of two new products, the proposed intermediate (**8**) (46%) and its dimer (**9**) (20%) (Scheme 3). The dimer structure was established by *X*-ray crystallography[2] and the monomer structure by its spectroscopic properties and its relation to the dimer, to which it was rapidly converted on silica or Florisil, possibly by an ene-type reaction.

The isolation and structure determination of intermediate (**8**) and its conversion into the red product (**4a**) lend strong support to the mechanism of Scheme 2. A possible mechanism for the final stages of the rearrangement are shown in Scheme 4. Compound (**8**) could undergo reversible ring opening to (**10**), facilitated by electron donation from the electron-rich sulphur diimide to the indene ring which can stabilise a negative charge. The indene ring of (**10**) is nucleophilic and could react with the terminal thionitroso group to form (**11**); opening of the new heterocyclic ring could give (**12**) followed by collapse with loss of HNS to form the stable 1,2,3-dithiazole (**4a**).

The high thermal stability and deep colour of the indenodithiazoles (**4**), made available by this unprecedented rearrangement, suggest that they may be delocalised 14 π systems in spite of the formal S–S single bond.

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