Conversion of a 1,2,3-dithiazole into a 3H-pyrrrole-3-thione and a 3H-pyrrl-3-ylidenephosphorane

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Treatment of the readily available dicyanomethylenedithiazole 1 with excess of morpholine or triphenylphosphine gives the 3-azacyclopentadienethione (3H-pyrrrole-3-thione) 5 and the 3-azacyclopentadienylphosphorane (3H-pyrrl-3-ylidenephosphorane) 16 respectively. Both products are deeply coloured and highly stabilised by extensive electron delocalisation: $^1$H and $^{13}$C NMR spectra show that rotation of the morpholine groups in 5 is hindered. Structure 16, the first azacyclopentadienylphosphorane reported, is proved by X-ray crystallography. Mechanisms are reported for these transformations in which the initial step is considered to be opening of the dithiazole ring of 1 by nucleophilic attack by the amine or the phosphine at the central heteroatom.

We recently reported the synthesis of dicyanomethylene-dithiazole 1 from 4,5-dichloro-1,2,3-dithiazolium chloride (Appel salt) 2 and malononitrile or tetracyanoethylene oxide (TCNEO), and from 4-chloro-5H-1,2,3-dithiazole-5-thione 3 and tetracyanoethylene oxide, together with the conversion of 1 into 4,5-dicyano-3-morpholinoisothiazole 4 with morpholine in boiling benzene.¹

In an attempt to improve the yield of isothiazole 4, in what could be a very direct and attractive route to this ring system, the dithiazole 1 was treated with an excess of morpholine (10 equiv.) in boiling toluene. A yellow precipitate was formed immediately, the reaction mixture rapidly darkened and within 10–15 min a new deep red product was formed together with an unidentified black precipitate. TLC also showed the presence of isothiazole 4, dimorpholino sulfide 6 and sulfur, but these were not isolated. After chromatography and purification the red compound was shown to be 4-cyano-2,5-dimorpholino-3H-pyrrole-3-thione (30%) as follows.

HRMS gave the formula C$_2$H$_6$N$_2$O$_2$S, the 16 hydrogens and two oxygens suggesting the presence of two morpholino substituents. The parent ion m/z 292 (100%) was by far the strongest in the mass spectrum, which revealed little else of value. The IR spectrum showed a nitrile stretch at 2197 cm$^{-1}$ strongly in the mass spectrum, which revealed little else of value. The IR spectrum showed a nitrile stretch at 2197 cm$^{-1}$ indicating extensive electron release from the morpholino groups and electron withdrawal by the other three heteroatoms results in a highly delocalised structure, imparting the observed stability. The resulting iminium ion character of the morpholino nitrogen atoms also accounts for their hindered rotation.

The 3-thione structure 5 was assigned to the product on the basis of a more rational mechanism for its formation (see below) and by comparison with the related 4-cyano-3H-pyrrole 16 formed from 1 and triphenylphosphine, the structure of which was proved by X-ray crystallography (see below). The 3H-pyrrle-3-thione ring of the deep red product 5 is formally 4π anti-aromatic, but extensive electron release from the morpholino groups and electron withdrawal by the other three heteroatoms results in a highly delocalised structure, imparting the observed stability. The resulting iminium ion character of the morpholino nitrogen atoms also accounts for their hindered rotation.

On the basis of structure 5, the $^1$H NMR spectrum can be assigned more completely. The environment of all the CH$_2$O protons will be very similar and they should have similar chemical shifts, close to the value for this methylene in morpholine itself (3.67 ppm). The multiplet at 3.66–3.55 ppm with the integral ratio of 8 is assigned to these protons. The remaining, CH$_2$N, proton resonances at 4.94, 3.92 and 3.81–3.76 ppm are strongly deshielded compared to the same protons in morpholine (2.87 ppm) because of the electron withdrawal mentioned above. The local environment of the CH$_2$N protons A and C is similar and they can be assigned to the multiplet at 3.81–3.76 ppm, with an integral ratio of 4. One of the two remaining CH$_2$N resonances (4.94) is shifted 1 ppm downfield from the other (3.92 ppm). This extra deshielding could arise from the local environment of the protons where the hindered rotation of the morpholine ring could bring the protons at B into the deshielding zone of the cyano group; the protons at D are assigned to the 3.92 ppm signal.

There are few reports in the literature on 3H-pyrrle-3-ones (3-azacyclopentadienones), the oxygen analogues of 5, but only one example of a 3H-pyrrle-3-thione. 2,4,5-Tris(dimethyl-
Mechanism for the formation of 5
5-((N-Arylimino)-4-chloro-5H-1,2,3-dithiazoles 14 (see below) have been shown to undergo nucleophilic attack at S-1, S-2 and C-5, with S-2 being the usual electrophilic centre in intermolecular reactions. Kim has shown that secondary aliphatic amines displace the 4-chlorine atom by a ring opening-ring closing mechanism initiated by attack at S-2. In the reaction of the dicyanomethylenedithiazole 1 with morpholine it seems entirely reasonable that the first reaction (arrows in 8) should be the same to give the disulphide 9 where the relatively weak S–N bond has been broken and a new cyano group formed (Scheme 1).

The powerfully electron withdrawing tricyanovinyl group in 9 will activate the S–S bond to further nucleophilic attack by the excess of morpholine (arrows in 9) to give the dimorpholino sulphide 6 and tricyanovinyl thiol 10.† This last species, in equilibrium with the thione and possibly the ketenimine forms, could add morpholine and cyclise to the pyrrole derivative 12 (cf. ref. 6). Tautomerism and amine exchange with more morpholine would then give the product 5 isolated (Scheme 1).

For the earlier conversion of the dithiazole 1 into isothiazole 4 with one equivalent of morpholine in benzene,¹ we proposed that the first step could be addition of morpholine to a cyano group, followed by opening of the dithiazole ring by the amidine so formed to give 4. In view of the mechanism of Scheme 1 and the evidence for ready nucleophilic attack at S-2 in the aryliminodithiazole compounds 14,¹⁴ we now consider that the first step for 1→4 is more likely to be the attack at S-2, as in 8, to give the same intermediate 9 (Scheme 1). It is then possible that with only one equivalent of morpholine present, the chloride generated in this displacement competes effectively with morpholine in adding to 9, as shown in 13, to give 3-chloro-4,5-dicyanoisothiazole as we found before.¹ We also found that this chloro compound reacted in high yield (80%) with morpholine to give the 3-morpholinoisothiazole 4.¹

Reaction of dithiazole 1 with triphenylphosphine
Triphenylphosphine abstracts the 2-sulfur atom from aryliminodithiazoles 14 with the formation of a cyano group to give cyanothioformanilides 15 in high yield under very mild conditions.⁷

This reaction appears to involve initial nucleophilic attack by phosphorus at S-2, of the type described above (cf. 8). It was therefore of interest to apply this reaction to the dicyanomethylenedithiazole 1, to see if triphenylphosphine acted similarly to morpholine by a pathway analogous to 8→9→10 (Scheme 1) to generate the same tricyanovinyl thiol species.

Upon addition of triphenylphosphine (1 equiv.) to a toluene solution of 9 a black precipitate was formed which did not dissolve even at reflux. Chromatography gave triphenylphosphine oxide and sulfide and a very dark red crystalline compound (mp >250°C) which dissolved readily in DCN to give a deep blue solution. The red compound was shown by single crystal X-ray analysis to be the ylide [4-cyano-5-tricyanovinyl-2-(triphenylphosphoranylideneamino)-3H-pyrrolyl-3-ylidenepyrophosphanor 16 (24%); Fig. 1, the first 3H-pyrrolo-3-ylidenephosphorane, as follows.

A UV absorption at λmax 594 nm (log ε 4.41) indicated an extensive chromophore. The FAB (glycerol) mass spectrum showed a strong protonated molecular ion of m/z 729 (MH⁺, 100%) and little other structural information. HRMS supported the molecular formula, C44H36N8P6S, of a highly unsaturated molecule. The IR data showed aromatic C–H stretching at 3150 and 3060 cm⁻¹, strong ethene or imine stretching at 1515 cm⁻¹ and a strong broad nitrile band at 2294 cm⁻¹. The ¹H NMR spectrum showed three complex aromatic multiplets of the triphenylphosphines groups. ³¹P NMR showed two similar phosphorus environments at 15.4 and 13.3 ppm, in the range for phosphonium ylides, Ph₃P=CR₂, with no ³¹P–³¹P coupling. The proton decoupled ¹³C NMR data was not clear; all the aromatic C–H resonances were assigned and confirmed by a C–H DEPT, with the ³¹P–³¹C coupling values. One of the aromatic quaternary carbons directly attached to phosphorus was not visible. The ³¹P–³¹C coupling values for such carbons are very large (1'JPC = 80–100 Hz) and we could only identify one peak of doublets (128.8 ppm, 1'JPC 101 Hz) we assume that both aromatic quaternary carbon signals overlap at this resonance. Two significantly higher field signals (121.1 and 120.7 ppm) gave the appearance of being coupled (∼1'JPC 94 Hz) but their assignment has not been confirmed. Four non-coupled carbon signals were in the nitrile region (117.2, 115.5, 114.5 and 113.1 ppm) and a signal at 71.2 ppm was typical for the central carbon in dicyanomethylene compounds. The remaining sp² carbon resonances were weak and complex signals, presumably caused by ³¹P–³¹C coupling between both phosphorus atoms and nearby carbon atoms.

The ylide nature of 16 is further demonstrated by the patterns of bonding in the molecule. The P(2)–C(3) linkage has clear partial double bond character [1.755(4) Å] though it is noticeably longer than that reported for triphenylphosphonium cyclopentadienyldiyl [1.718(2) Å].⁸ The bond lengths within the pyrrole ring indicate a pattern of delocalisation extending between P(2) and N(6) via N(1), the C(2)–C(3) bond having pronounced single bond character [1.440(6) Å]. This delocalisation also includes, to a lesser degree, the cyano carbon C(7) and the carbon atom C(6) of the tricyanoethylene group. The P–N double bond length is typical at 1.577(4) Å and the bond lies close to the plane of the pyrrole ring, the average torsion angle about the C(2)–N(6) bond being ca. 22°. The only intermolecular packing interaction of note is an edge-to-face

† Whilst this sulfur compound 10 appears to be unknown, its highly acidic oxygen analogue has been prepared in aqueous solution by hydrolysis of tetracyanoethylene and characterised as various salts.³
C–H⋯π aromatic⋯aromatic interaction between one of the phenyl rings attached to P(1) in one molecule and one of the phenyl rings attached to P(2) in another [the H⋯π distance is 2.80 Å and the C⋯H angle is 170°].

**Mechanism for the formation of ylide 16**

Although the structure of ylide 16 is somewhat analogous to that of 5, the reaction of dithiazole 1 with triphenylphosphine is more complex than its reaction with morpholine. Two molecules of both starting materials are incorporated into the product and all the sulfur and chlorine atoms are removed as triphenylphosphine sulfide and, after chromatographic work up, triphenylphosphine oxide. The simplest overall stoichiometry is shown in Scheme 2, and the key problem is how the two dithiazole derived portions combine together.

![Scheme 2](image)

We again assume that the reaction starts by attack of triphenylphosphine at S-2, with cleavage of the S–N bond to give 17 which is analogous to the intermediate 9 in the morpholine reaction. Then either sulfur atom of 17 could suffer further attack by triphenylphosphine (Scheme 3). Attack at the same sulfur as before would lead to the tricyanovinyl species 10, exactly as described in Scheme 1; in its thiocarbonyl tautomer this could be attacked yet again by the phosphine to give the zwitterion 18. Attack at the other sulfur atom in 17, as shown in 19 could lead to the tricyanovinylphosphonium salt 20 with its cis cyan groups being susceptible to nucleophilic addition and cyclisation to a pyrrole derivative. Such attack of 20 by the carbanionic centre of 18, analogous to 11 in Scheme 1, could lead to the highly delocalised product 16 isolated, as shown in Scheme 4.

In the reaction of the arylimino derivatives 14 with triphenylphosphine, the species analogous to the thione 10 are the thioamides 15 which are isolated in high yield. The thione is

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**Fig. 1** The molecular structure of 16. Selected bond lengths (Å) are: N(1)–C(2) 1.336(6), C(2)–C(3) 1.440(6), C(3)–C(4) 1.403(6), C(4)–C(5) 1.417(6), C(5)–N(1) 1.374(6), C(2)–N(6) 1.360(5), N(6)–P(1) 1.577(4), C(3)–P(2) 1.755(4), C(4)–C(7) 1.414(6), C(5)–C(8) 1.412(7).
expected to be more reactive than the thioamide and not surprisingly it reacts further with triphenylphosphine, as proposed in Scheme 3. Our suggested mechanism agrees with the stoichiometry of Scheme 2, where the small amount of water required is assumed to be introduced during work up and chromatography.

The very rare 3-azacyclopentadienethione 5 and the previously unknown 3-azacyclopentadienylphosphorane 16 systems are thus readily available from the dithiazole 1 in one step, and are worthy of further examination.

Experimental

Light petroleum refers to the fraction, bp 60–80 °C. Reactions and column eluents were monitored by TLC using aluminium backed thin layer chromatography plates (Merck Kieselgel 60 F254) viewed under UV light at 254 and 350 nm. Dry flash chromatography on Sorbsil C60 M40 silica was used for separations. UV and IR spectra were measured on Perkin-Elmer Lambda II and Perkin-Elmer 1710 FT spectrometers respectively. 1H, 13C and 31P NMR spectra were measured on Bruker AM300WB and RX-400 machines. J Values are given in Hz.

Mass spectra were recorded on VG micromass 7070E or Perkin-Elmer 2400 CHN Analyser. Crystal data for 

Crystal structure determination

Crystal data for 16—C6H3P=N=P; C6H5OH; M = 774.8, monoclinic, space group P21/c (no. 14). a = 13.560(1), b = 22.508(7), c = 13.934(1) Å, β = 91.83(1)°, V = 4251(1) Å3. Z = 4, Dc = 1.211 g cm−3, µ(Cu-Kα) = 12.7 cm−1, F(000) = 1616, T = 293 K, red needles, 0.57 × 0.17 × 0.10 mm.

Data collection and processing—Data were measured on a Siemens P4/PC diffractometer with graphite monochromated Cu-Kα radiation using o-scans. 6311 Independent reflections were measured [20° < 2θ] of which 4203 had [F2] > 4σ(F2) and were considered to be observed. The data were corrected for Lorentz and polarisation factors, and an empirical absorption correction was applied; the maximum and minimum transmission factors were 0.64 and 0.16 respectively.

Structure analysis and refinement.—The structure was solved by direct methods and the pendant phenyl rings were refined as idealised rigid bodies. Disorder was found in the terminal nitrogen atom, unit and in one of the triphenylphosphine phenyl rings with, in both instances, two partial occupancy orientations being identified. In each case only the major occupancy non-hydrogen atoms were refined anisotropically. The included ethanol solvent molecule was found to be disordered over three partial occupancy sites with only the major occupancy non-hydrogen atoms being refined anisotropically. The remaining, full occupancy, non-hydrogen atoms were refined anisotropically and the C–H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, [U(H) = 1.2Ueq(C), U(H) = 1.5Ueq(C–Me)], and allowed to ride on their parent atoms. The C–H hydrogen atoms of the disordered ethanol molecule could not be located. Refinements were by full matrix least-squares based on F2 to give R = 0.079, wR = 0.213 for the observed data and 553 parameters. The maximum and minimum residual electron densities in the final AF map were 0.44 and −0.35 e Å−3 respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.000 and 0.000 respectively. All computations were carried out using the SHELXTL PC program system.

Full crystallographic details, including structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme see ‘Instructions for Authors’, J. Chem. Soc., Perkin Trans. 1, available via the RSC Web Pages (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207248.

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