[1,2,3]Triazolo[4,5-*d*][1,3,2]thiazaphospholes: a new fused NPS ring system from a cycloaddition–rearrangement sequence with Lawesson's reagent, a super dipolarophile

Richard N. Butler,* Elaine C. McKenna and (in part) Denise C. Grogan

Chemistry Department, University College, Galway, Ireland

A new fused NPS ring system has been obtained from the reaction of substituted 1,2,3-triazolium-1-imide 1,3-dipoles with Lawesson's reagent

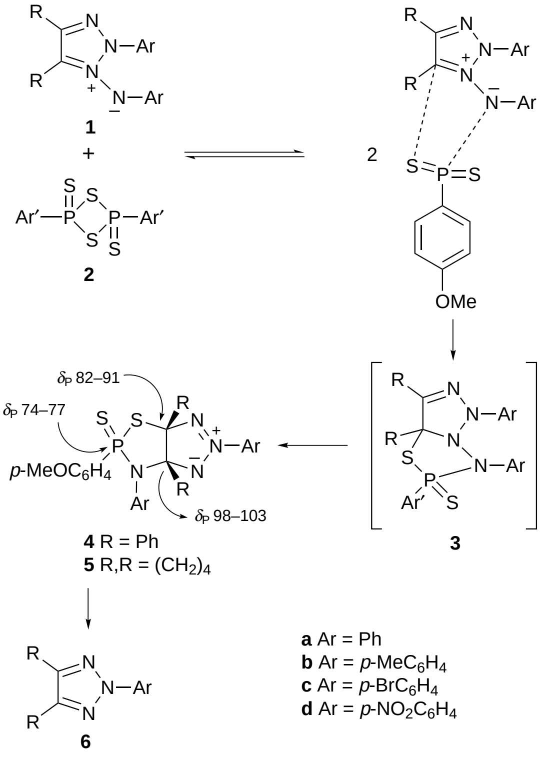
Recently there has been renewed interest in sulfur–nitrogen and sulfur–nitrogen–phosphorus containing ring systems.[1,2] The use of Lawesson's reagent as a possible P=S 1,3-dipolarophile has been established by Bertrand.[2] The cycloaddition–1,4-sigmatropic rearrangement sequences which we developed[3,4] for the triazolium imide 1,3-dipole system **1** opened the prospect of possible new fused nitrogen–phosphorus–sulfur ring systems such as **4** if these would be stable. Herein we describe routes to the new ring system **4** and the new tricyclic structure **5**, both of which proved to be reasonably stable in the solid state but unstable in solution, where they broke down rapidly to 1,2,3-triazoles **6** and uncharacterised N–P–S compounds. Kinetic studies on the rate of consumption of the dipole **1** by Lawesson's reagent showed it to be 2000 times faster than for acrylonitrile and twice as fast as the C=S dipolarophile of MeSC(S)CN, indicating that Lawesson's reagent is a super-dipolarophile comparable to thiones.[5–7]

Solutions of the dipoles **1** (*ca.* 0.4 mmol) in dry THF under an atmosphere of dry nitrogen were treated with Lawesson's reagent **2** (0.5 equiv.) and stirred at ambient temperature for *ca.* 1 h. The solvent was removed under reduced pressure and the flaky residue leached with cold Et_2O until the ethereal extracts were colourless. Evaporation of the ethereal extracts gave the products **4** and **5** as low melting yellow–orange solids. A single product only was obtained in each case. Due to the instability of the fused ring system in solution low temperatures (−30 °C) and a carefully chosen number of scans were necessary to obtain good NMR spectra since the products **4** and **5** readily broke down to **6** in NMR solvents. The compounds were fully characterised by their ^1H and ^{13}C NMR spectra measured in $CDCl_3$, which showed all of the expected signals. Key signals were the two bridgehead carbon signals (see Table 1 and Scheme 1). We have previously established[4] that the N–C–N fused bridgehead ^{13}C NMR signal for related systems without P occurs at δ 95–105 and the N–C–S bridgehead occurs at δ 80–95. These quaternary bridgehead signals were particularly weak and were made more difficult to detect because of the ongoing decomposition of the products. Small splittings (*ca.* 3–10 Hz) of the bridgehead carbon signals were observed due to the phosphorus. This is in agreement with the structures **4** and **5**, where P is not bonded directly to the bridgehead carbons. The *endo* or *exo* alignment of the substituents on the P atom has not been established. The ^{31}P signal for **4** and **5** appeared at δ 74–77 (downfield from H_3PO_4) and the P-bonded *p*-methoxyphenyl group showed the expected ^{31}P splittings although precise J_{PC} values could not be measured in all cases due to signal spreading caused by the ongoing decomposition. Despite the fact that they could not be recrystallised and only cold washing procedures could be used for purification, the solid compounds **4** and **5** gave satisfactory CHN microanalyses. Energy dispersive X-ray analyses (EDAX) of the solid compounds using a scanning electron microscope confirmed the presence of sulfur and phosphorus in **4** and **5** in the expected atomic ratio of 2 : 1.

Table 1 Substituted [1,2,3]triazolo[4,5-*d*][1,3,2]thiazaphospholes

			Chemical shifts (ppm)		
	Mp/°C	Yield (%)	P	NCN	NCS
4a	unstable oil	83	74.0	100.2	91
4b	45–47	65	75.4	99.6	92
4c	48–49	84	75.3	100.2	91.4
4d	55–58	71	73.9	100.4	90
5a	42–43	64	75	100.4	90.3
5b	34–36	80	75.4	100.2	91.4
5c	35–36	90	75.3	100.5	92
5d	55–57	74	73.9	99.4	89.2

UV spectral measurements of the disappearance of the dipole **1a** (R = Ph) at 37 °C in acetone were carried out using pseudo-first-order conditions with 10–1000-fold excesses of dipolarophile giving k_1 values. Second-order rate constants k_2 were obtained from plots of these k_1 values against the dipolarophile concentration, giving the following k_2 values at 37 °C: dimethyl maleate = 0.108×10^{-3}; ethyl acrylate = 0.57×10^{-3}, acrylonitrile = 1.47×10^{-3}, dimethyl acetylene-



Scheme 1

dicarboxylate = 0.80, MeSC(S)CN = 1.65 and Lawesson's reagent = 2.2 l mol^{-1} s^{-1}. Hence the P=S bond reacted with the dipole **1** at a rate which is faster than a C=S bond, and Lawesson's reagent is a superdipolarophile.[7]

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Footnote and References

* E-mail: r.debuitleir@ucg.ie

1 C. W. Rees, *J. Heterocyclic Chem.,* 1996, **33**, 1419.

2 N. Dubau-Assibat, A. Baceiredo and G. Bertrand, *J. Org. Chem.,* 1995, **60**, 3904.

3 For a review, see R. N. Butler and D. F. O'Shea, *Heterocycles,* 1994, **37**, 571.

4 R. N. Butler, A. M. Evans, A. M. Gillan, J. P. James, E. McNeela, D. Cunningham and P. McArdle, *J. Chem. Soc., Perkin Trans. 1,* 1990, 2537; R. N. Butler, A. M. Evans, E. McNeela, G. A. O'Halloran, P. D. O'Shea, D. Cunningham and P. McArdle, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2527.

5 R. Sustmann, W. Sicking and R. Huisgen, *J. Am. Chem. Soc.,* 1995, **117**, 9679.

6 R. Huisgen, L. Fisera, H. Giera and R. Sustmann, *J. Am. Chem. Soc.,* 1995, **117**, 9671.

7 L. Fisera, R. Huisgen, I. Kalwinsch, E. Langhals, X. Li. G. Mloston, K. Polborn, J. Rapp, W. Sicking and R. Sustmann, *Pure Appl. Chem.,* 1996, **68**, 789.

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