Tetrahedron Letters,Vol.24,No.19,pp 2039-2040,1983 0040-4039/83/192039-02$03.00/0
Printed in Great Britain

THE ORTHO-LITHIATION OF N,N,N´,N´-TETRAMETHYLPHENYLPHOSPHONIC DIAMIDE

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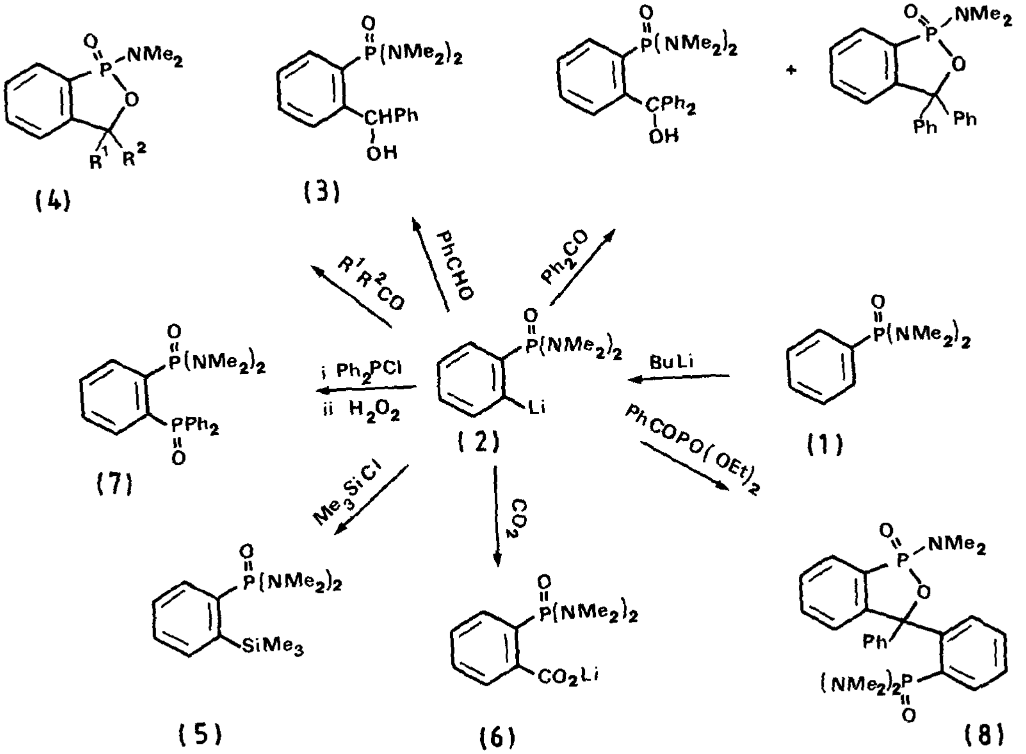
Summary *N,N,N´,N´-Tetramethylphenylphosphonic diamide has been ortho-lithiated and the resulting aryl-lithium reacted with a series of electrophiles. Benzonitrile (2 moles) gave 8-bis(dimethylamino)phosphinyl-2,3a-diphenyl-1,3a-dihydrocycloheptimidazole (12).*

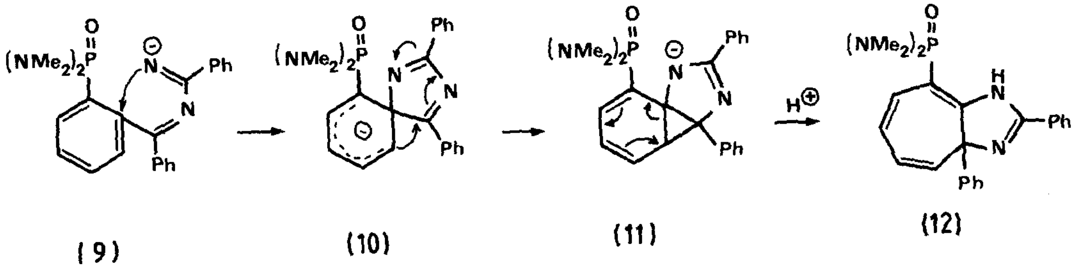
Numerous carbocyclic aromatic systems having a substituent capable of co-ordinating to lithium are ortho-lithiated on treatment with an alkyl-lithium or N-lithio-amine.[1] The substituents include NR_2, OR, SR^2, $CONR_2$, SO_2R, and 2-oxazolyl. Among organophosphorus compounds only triarylphosphine oxides and imides have been o-lithiated.[1] We now report the successful o-lithiation of N,N,N´,N´-tetramethylphenylphosphonic diamide (1) and subsequent reaction with a range of electrophiles.

Treatment of the phosphonic diamide (1) in THF at -5°C with butyl-lithium gave a deep-red solution containing the aryl-lithium (2). With benzaldehyde this gave the alcohol (3; 72%)[3]; other carbonyl compounds, such as acetaldehyde, acetone, and cyclohexanone, gave the benzoxaphospholes (4; 32, 53, and 67% respectively), whereas benzophenone gave a mixture of the cyclised (26%) and uncyclised (25%) products. The benzoxaphosphole (4; R^1 = H, R^2 = Me) derived from acetaldehyde probably has the ring hydrogen cis to the phosphoryl oxygen ($^3J_{PH}$ 3 Hz).[4] Chlorotrimethylsilane and (2) gave the silane (5; 74%), carbon dioxide led to the lithium salt (6; 87%) whereas chlorodiphenylphosphine gave the phosphine oxide (7; 81%) after oxidation of the crude product. With methyl iodide the aryl-lithium (2) gave a complex mixture of arylphosphonic diamides which, from its ^1H n.m.r. and mass spectra contained ortho ethyl and isopropyl groups as well as the expected methyl. Whereas benzoyl chloride led to no identifiable product, treatment of (2) with diethyl benzoylphosphonate gave the benzoxaphosphole (8; 52%), of unknown geometry, presumably formed by further addition of (2) to the initial o-benzoylphenylphosphonic diamide followed by cyclisation.

With benzonitrile, (2) gave a pale yellow crystalline 1:2 adduct (83%), m.p. 116-118°C, which from its spectra[5] was clearly not a straightforward product. X-Ray analysis showed it to be the 1,3a-dihydrocycloheptimidazole (12). A plausible route for its formation involves nucleophilic attack of nitrogen on the aromatic ring in the initial 1:2-adduct (9) to give the spiro-compound (10) followed by formation of the cyclopropane (11), electrocyclic ring opening, and protonation. Such a product has not previously been obtained from the reaction of an aryl-lithium with benzonitrile.

We have been unable to effect ortho-lithiation of diethyl phenylphosphonate.





References and Notes

1. H.W. Gschwend and H.R. Rodriguez, Organic Reactions, 1979, 26, 1.
2. L. Horner, A.J. Lawson, and G. Simons, Phosphorus and Sulfur, 1982, 12, 353.
3. All new compounds showed the expected mass spectra and elemental analysis.
4. J.A. Miles, R.C. Grobiak, and C. Cummins, J. Org. Chem., 1982, 47, 1677.
5. δ1.9 (1H, br, exchangeable with D_2O), 2.4 (6H, d, J 10 Hz), 2.6 (6H, d, J 10 Hz), 5.8-6.5 (4H, m), 6.9-7.4 (8H, m), and 7.8 (2H, m); δP 34.0; m/e 418, 329, 283.

We thank Drs J.A. Fawcett and D.R. Russell for the X-ray analysis and the Government of the People's Republic of China for support.

(Received in UK 25 February 1983)