Tetrahedron Letters,Vol.25,No.8,pp 815-816,1984
Printed in Great Britain

0040-4039/84 $3.00 + .00

PHOSPHORUS HETEROCYCLE SYNTHESIS USING PHOSPHENIUM IONS AND 1,4-DIENES

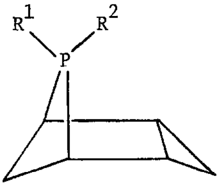
Alan H. Cowley*, Constantine A. Stewart, Bruce R. Whittlesey and Thomas C. Wright

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

The stabilized phosphenium ion, $[Pr^i{}_2NPCl]^+$, reacts readily with 1,4-dienes to afford high yields of bicyclic phosphonium salts, the structure of one of which has been determined by X-ray crystallography.

Complexes of the type $RPX_2 \cdot AlX_3$ (R = Me, Ph; X = Cl, Br) react with e.g. 1,4-dienes to afford phosphorus-containing heterocycles.[1] It has been suggested that the initial step in these reactions involves electrophilic attack of the diene by a two-coordinate phosphorus (phosphenium) cation, $[RPX]^+$. However, we have found no ^{31}P NMR evidence for phosphenium ion formation when $MePCl_2$ or $PhPCl_2$ is treated with Al_2Cl_6 in CH_2Cl_2 solution. The mechanism of this reaction is therefore not clear. It was thus important to determine whether stabilized phosphenium ions react with 1,4-dienes. We report (i) that such reactions take place rapidly in high yields using readily available starting materials, and (ii) definitive information on the configuration of one of the products.

Equimolar mixtures of $Pr^i{}_2NPCl_2$ and $AlCl_3$ units in CH_2Cl_2 exhibit a ^{31}P NMR chemical shift (+334 ppm) in the region characteristic of stabilized phosphenium ions.[2] Typically, 2.25 mmol of $[Pr^i{}_2NPCl]^+[AlCl_4]^-$ (1) was treated with 4.50 mmol of 1,4-pentadiene in 40 ml of CH_2Cl_2 at 0°C. Monitoring by ^{31}P NMR spectroscopy showed the reaction to be complete within 1 hour. Although the ^{31}P resonance of the product comprised a singlet (+118 ppm), the presence of two configurational isomers, (2a) and (2b), (in 10:3 ratio, respectively) was demonstrated by $^{13}C\{^1H\}$ NMR spectroscopy.† White, crystalline (2a) (mp 86-92°C) separated from a CH_2Cl_2/n-hexane solution of the mixture held at -20°C. Similar reaction of (1) with 1,4-cyclohexadiene afforded a 95% yield of a 50:50 mixture of (3a) (δ_P 54.3) and (3b) (δ_P 53.4).



(3a, 3b) R^1 or R^2 = Cl or $Pr^i{}_2N$

In order to establish the identity and configuration of (2a), an X-ray crystal structure was undertaken. Crystal Data: $C_{11}H_{22}AlCl_5NP$, M = 403.53, orthorhombic, space group $P2_12_12_1$, a = 8.309(4), b = 14.265(2), c = 14.936(2) Å, U = 2021.1 Å^3, z = 4, D_c = 1.223 g/cm^3, λ(Mo-Kα) = 0.71069 Å, μ(Mo-Kα) = 7.5 cm^{-1}. The structure, shown in Figure 1 along with the atom numbering scheme, was solved by a combination of direct[3] and Fourier methods using data

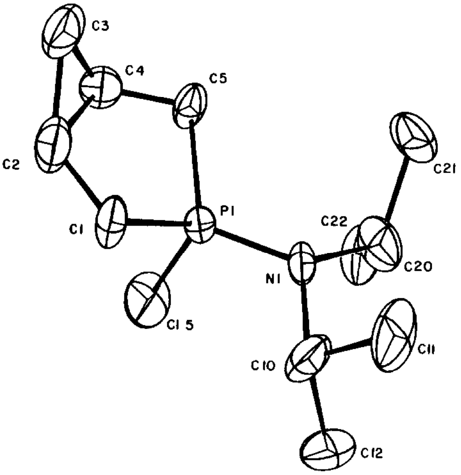


Figure 1. ORTEP of (2a)

collected on an Enraf-Nonius CAD-4 diffractometer. Refinement (full-matrix, least-squares) using 1014 unique observed data ($I > 2\sigma I$) converged smoothly to give final residuals $R = 0.0664$ and $R_w = 0.0841$.‡ The configuration of (2a) involves a proximal relationship between the $\mathrm{Pr}^i{}_2\mathrm{N}$ and cyclopropane moieties. Presumably, the positions of the Cl and $\mathrm{Pr}^i{}_2\mathrm{N}$ groups are interchanged in the less favored isomer, (2b). The structure of the phosphenium ion, $[\mathrm{ClPN}^i\mathrm{Pr}_2]^+$, is unknown hence it is difficult to quantify the changes that take place upon coordination. However, the P-N bond length and X-P-N bond angles in (2a) (1.636(7) Å, 112.6(3)°) are close to those in $[(\mathrm{Pr}^i{}_2\mathrm{N})_2\mathrm{P}]^+$ (1.611(4) Å, 114.8(2)°).[4]

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for generous financial support.

References

1 (a) Y. Kashman, Y. Menachem and E. Benary, Tetrahedron, 29, 4279 (1973); (b) Y. Kashman and A. Rudi, Tetrahedron Lett., 2819 (1976); (c) A. Rudi and Y. Kashman, Ibid., 2209 (1978).

2 A. H. Cowley, M. C. Cushner, M. Lattman, M. L. McKee, J. S. Szobota and J. C. Wilburn, Pure and Appl. Chem., 52, 789 (1980).

3 G. Germain, P. Main and M. M. Woolfson, Acta Crystallogr., A27, 368 (1971).

4 A. H. Cowley, M. C. Cushner and J. S. Szobota, J. Am. Chem. Soc., 100, 7784 (1978).

Footnotes

† All new compounds had correct analytical and spectroscopic characteristics.

‡ The atomic coordinates for this work are available on request from the Director of the Cambridge Data Centre, University Chemistry Laboratory, Lensfield, Rd., Cambridge CB2 1EW.

(Received in USA 15 December 1983)