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Mendeleev Commun., 1993, **3**(2), 68–70
Mendeleev Communications

Phosphirenes and Diphosphetenes: the Products of the Reaction of λ^3-Iminophosphines with 1-Alkoxy- and 1-Aminoalkynes

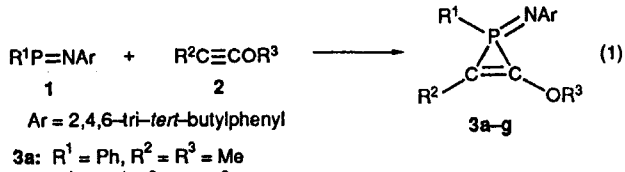
Alexei D. Averin, Nikolai V. Lukashev,* Marina A. Kazankova and Irina P. Beletskaya

Department of Chemistry, M. V. Lomonosov Moscow State University, 117899 Moscow, Russian Federation.
Fax: +7 095 939 0156

The reaction path in cycloaddition reactions of λ^3-iminophosphines with alkoxy- and amino-alkynes depends on the type of starting compound and solvents employed and leads to the formation of phosphirenes or 1,2-diphosphetenes.

Work by Schoeller[1,2] and Niecke[3,4] provides evidence that cycloaddition reactions of λ^3-iminophosphines with double and triple bonds can result in products of [2+2]- and [2+1]-cycloaddition that are dependent on the type of substituent in the λ^3-iminophosphine. Using tolan (diphenylacetylene) and tert-butylphosphaalkyne the corresponding λ^5-phosphirene[3] and λ^5-diphosphirenes[4] were obtained. Here we report on the influence of the type of alkyne, λ^3-iminophosphine and solvent used upon the reaction path of cycloaddition.

The reactions of dilute solutions of λ^3-iminophosphines **1** in pentane with alkylalkoxyalkynes **2** give the corresponding

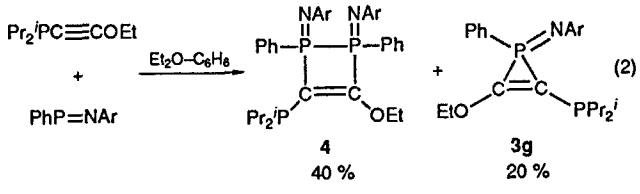


Ar = 2,4,6-tri-*tert*-butylphenyl

3a: R^1 = Ph, R^2 = R^3 = Me
3b: R^1 = Bu^t, R^2 = Et, R^3 = Me
3c: R^1 = Bu^t, R^2 = Pr^i_2P, R^3 = Et
3d: R^1 = Bu^t, R^2 = Me_3Si, R^3 = Et
3e: R^1 = Bu^t, R^2 = Me_3Ge, R^3 = Et
3f: R^1 = Cl, R^2 = Et, R^3 = Me
3g: R^1 = Ph, R^2 = Pr^i_2P, R^3 = Et

phosphirenes **3a–g**† *via* [2+1] cycloaddition in yields of 70–95%, reaction (1).

The phosphirenes thus obtained are stable either in the free state or in solutions of hydrocarbons and neither change nor isomerize to 1,2-azaphosphetenes, even after prolonged (12 h) heating in toluene at 100°C. When a more polar mixture of diethyl ether and benzene (1:1) is used instead of pentane, 1,2-diphosphetene[5] **4**‡ along with phosphirene **3g** can be formed [reaction (2)] and in the case of PhP=NAr more polar solvents (THF, CH_2Cl_2) diminish the selectivity of these reactions whereas ClP=NAr and Bu^{t}P=NAr react smoothly in more polar solvents to give alkoxy-substituted phosphirenes. The formation of **4** might be explained by the possible reaction of an intermediate of unknown structure with the second molecule of iminophosphine. This probable non-chelotropic pathway coincides with the chelotropic formation of **3g**.



(2)

† All products obtained gave satisfactory analytical figures. NMR spectra were recorded in C_6D_6, CD_2Cl_2 and $CDCl_3$ and chemical shifts were referenced to 85% H_3PO_4 (^{31}P, 121.5 MHz) and Si Me_4 (^1H, 300 MHz, ^{13}C, 75 MHz). Chemical shifts are given in ppm, coupling constants in Hz.

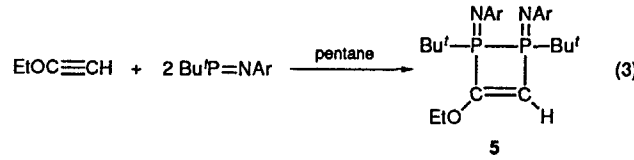
3a: R^1 = Ph, R^2 = R^3 = Me; ^{31}P NMR (C_6D_6) δ_P −78; ^{13}C NMR (C_6D_6) $\delta_C(J_{PC})$ 10.7 (d, 5.0, CH_3C=), 31.5 [s, *o*-C(CH_3)$_3$], 31.7 [s, *p*-C(CH_3)$_3$], 34.3 [d, 1.2, *o*-C(CH_3)$_3$], 36.0 [s, *p*-C(CH_3)$_3$], 60.2 (d, 8.6, CH_3O), 131.0 (d, 6.0, C_1-Ph), 133.8 (d, 11.4, C_2-Ph), 128.2 (d, 15.3, C_3-Ph), 128.1 (s, C_4-Ph), 142.3 (d, 9.2, *C*-Ar), 139.0 (d, 5.1, C_2-Ar), 121.4 (d, 3.9, C_3-Ar), 133.1 (s, C_4-Ar), 120.9 (d, 12.0, CH_3C=), 162.3 (d, 11.5, CH_3OC=).

For the rest of the compounds in the series **3** ^{13}C NMR chemical shifts of aryl carbons are omitted because these are essentially the same as those reported for **3a**.

3b: R^1 = Bu^t, R^2 = Et, R^3 = Me; ^{31}P NMR (C_6D_6) δ_P −46.5; ^{13}C NMR $\delta_C(J_{PC})$ 14.9 (d, 2.3, CH_3CH_2), 20.9 (d, 3.4, CH_3CH_2), 60.6 (d, 6.0, OCH_3), 126.1 (d, 3.4, CH_2C=), 163.1 (d, 19.9, CH_3OC); ^1H NMR (C_6D_6), $\delta_H(J_{PH})$ 0.75 (3H, t, CH_3CH_2), 1.25 [9H, d, 18, (CH_3)$_3$CP], 1.32, [9H, s, *p*-C(CH_3)$_3$], 1.72 (18H, s, o-C(CH_3)$_3$], 3.1 (3H, s, CH_3O), 7.4 (2H, d, 1.0, *H*-Ar). **3c**: R^1 = Bu^t, R^2 = Pr$^i_2$P, R^3 = Et; ^{31}P NMR (C_6D_6) δ_P −42, −3, J_{PP} 22; ^{13}C NMR (C_6D_6) $\delta_C(J_{PC})$ 20.3 [d, 10.7, (CH_3)$_2$CHP], 19.7 [d, 13.4, (CH_3)$_2$CHP], 20.8, [d, 16.4, (CH_3)$_2$CHP], 15.3 (s, CH_3CH_2O), 71.2 (s, CH_3CH_2O), 119.4 (dd, 17.0, 76.5, P*C*=), 180.5 (d, 42.4, CH_2C=). **3d**: R^1 = Bu^t, R^2 = Me_3Si, R^3 = Et; ^{31}P NMR (C_6D_6) δ_P −48, ^{13}C NMR (C_6D_6) $\delta_C(J_{PC})$ 0.53 (s, CH_3Si), 15.0 (s, CH_3CH_2), 69.4 (d, 4.5, CH_3CH_2O), 125.1 (d, 19.7, Si*C*=), 180.3 (d, 28.0, CH_2OC=). **3e**: R^1 = Bu^t, R^2 = Me_3Ge, R^3 = Et; ^{31}P NMR (C_6D_6) δ_P −45, ^{13}C NMR (C_6D_6) $\delta_C(J_{PC})$ 0.44 (d, 0.8, CH_3Ge), 14.8 (s, CH_3CH_2O), 68.5 (d, 4.9, CH_3CH_2O), 125.4 (d, 7.7, Ge*C*=), 178.6 (d, 25.4, CH_2OC=). **3f**: R^1 = Cl, R^2 = Et, R^3 = Me; ^{31}P NMR (C_6D_6) δ_P −80, ^{13}C NMR (C_6D_6) $\delta_C(J_{PC})$ 12.8 (d, 5.6, CH_3CH_2), 19.5 (d, 5.0, CH_3CH_2), 60.1 (d, 8.8, OCH_3), 130.5 (d, 9.2, CH_2C=), 165.7 (d, 14.6, CH_3OC=). **3g**: R^1 = Ph, R^2 = Pr$^i_2$P, R^3 = Et; ^{31}P NMR (C_6D_6) δ_P −74.5, −0.5, J_{PP} 9.5. **6**: ^{31}P NMR (CD_2Cl_2) δ_P −55; ^{13}C NMR (CD_2Cl_2) $\delta_C(J_{PC})$ 13.5 (s, CH_3CH_2N), 15.3 (s, CH_3CH_2C), 20.0 (s, CH_3CH_2C), 46.6 (s, CH_3CH_2N), 109.1 (d, 12.6, CH_2C=), 156.7 (d, 29.8, N*C*=).

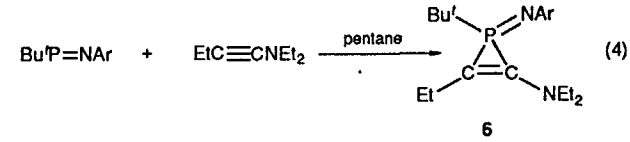
‡ The ^{13}C NMR chemical shifts of the most important carbon atoms are presented for compounds **4**, **5** and **7**. **4**: m.p. 212–215°C (decomp.); ^{31}P NMR ($CDCl_3$) δ_P 29.6, 8.9, 4.1, J_{PP} 118.4, 70.2, 4.3; ^{13}C NMR ($CDCl_3$) $\delta_C(J_{PC})$ 15.2 (s, CH_3CH_2O), 21.0 [dd, 28.8, 18.3, (CH_3)$_2$CHP], 22.0 [dd, 17.7, 5.9, (CH_3)$_2$CHP], 23.9 [dd, 15.8, 6.0, (CH_3)$_2$CHP], 25.3 [dd, 17.8, 3.6, (CH_3)$_2$CHP], 69.5 (s, OCH_2), 124.9 (ddd, 72.0, 43.0, 5.5, Pr$^i_2$P*C*=), 185.5 (ddd, 108.8, 11.6, 4.5, CH_2OC=). **5**: m.p. 230°C (decomp.); ^{31}P NMR ($CDCl_3$) δ_P 46.2, 41.7, $^1J_{PP}$ = 216; ^1H NMR ($CDCl_3$) $\delta_H(J_{PH})$ 0.94 [d, 18.0, 18H, (CH_3)$_3$P], 1.26 (t, 3H, CH_3CH_2O), 1.27 [*s*, 18H, *p*-C(CH_3)$_3$], 1.32 [s, 36H, *o*-C(CH_3)$_3$], 3.9 (m, 4.1, 2H, CH_3CH_2O), 6.2 (dd, 62.3, 17.3, 1H, C*H*=), 7.1 (m, 4H, *H*-Ar); ^{13}C NMR ($CDCl_3$) $\delta_C(J_{PC})$ 113.5 (dd, 72.0, 43.0, H*C*=), 175.2 (dd, 84.7, 33.0, CH_2OC=).

1,2-Diphosphetene **5**‡ is formed solely provided terminal ethoxyacetylene is used [reaction (3)].



(3)

A low-temperature ^{31}P NMR study of this reaction demonstrated that no phosphirene was formed *via* [2+1] cycloaddition at any stage of the process. An intermediate was registered at −60°C (δ_P 91; 105, J_{PP} 139 Hz) that transformed quantitatively into 1,2-diphosphetene **5** on heating, and whose structure is to be determined in further experiments. Finally, the use of ClP=NAr (which has not been hitherto investigated in cycloaddition reactions) in place of Bu^{t}P=NAr for the reaction with 1-aminoalkyne results in a dramatic change in the process. λ^5-Phosphirene **6**‡ in a yield of 75–80% was obtained in the case of Bu^{t}P=NAr [reaction (4)] whereas azaphosphetene **7**§ (80% yield) was formed using ClP=NAr [reaction (5)]. A low-temperature ^{31}P NMR investigation of reaction (5) showed the successive formation of two intermediates to precede the formation of azaphosphetene **7**, the first having δ_P 134 and the second having δ_P 12; −10; J_{PP} 8 Hz. On heating, the last intermediate transformed into **7**. A possible explanation for the fact that reaction (5) is non-chelotropic and that the reaction of the same iminophosphine with EtC≡COMe [reaction (1)] proceeds in a chelotropic manner giving phosphirene **3f** is the higher activation of a C≡C bond to nucleophilic addition in the case of EtC≡CNEt$_2$ which could proceed faster than [2+1] cycloaddition.



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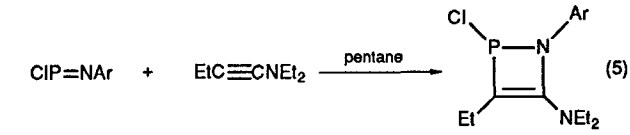

(5)

To sum up, all these data show that the change of reagents and solvents mentioned above can result in the changeover of the reaction mechanism and that azaphosphetenes can form not only *via* the concerted [2+2] cycloaddition pathway.

The general procedure employed was as follows. Pentane [reactions (1), (3), (4) and (5)] or diethyl ether–benzene (1:1) [reaction (2)] solutions of iminophosphines (0.5–1.0 mmol in 10 ml) were treated with equimolar quantities of the appropriate alkyne under an atmosphere of argon at room temperature. After completion of the reactions, solvents were evaporated under reduced pressure and the final products were obtained as oils or crystals. Crystalline products **3b**, **4** and **5** were recrystallized from pentane whereas attempts to further purify the oils were unsuccessful. Nevertheless, the spectral data of the oily products as well as satisfactory microanalytical data indicate reasonable purity of the products.

We are glad to thank Dr. V. D. Romanenko and coworkers for the sample of iminophosphine **4a**. We also thank Professor J. Bunnet for his profound interest in our work and for important linguistic improvements.

§ **7**: ^{31}P NMR ($CDCl_3$) δ_P 141; ^{13}C NMR ($CDCl_3$) $\delta_C(J_{PC})$ 50.4 (d, 29.8, CH_2C=), 159.1 (d, 20.5, N*C*=).

References

1 W. W. Schoeller and E. Niecke, *J. Chem. Soc., Chem. Commun.*, 1982, 569.
2 E. Niecke, D. Gudat, W. W. Schoeller and P. Rademacher, *J. Chem. Soc., Chem. Commun.*, 1985, 1050.
3 E. Niecke and M. Lysek, *Tetrahedron Lett.*, 1988, **29**, 605.
4 E. Niecke and D. Barion, *Tetrahedron Lett.*, 1989, **30**, 459.
5 A novel structure; for related λ^3-diphosphetenes, see L. Ricard, N. Maigrot, C. Charrier and F. Mathey, *Angew. Chem.*, 1987, **99**, 590.

Received: Moscow, 9th September 1992
Cambridge, 11th November 1992; Com. 2/04924D