

Calculated (%): C, 56.24; H, 6.29; N, 29.15.

5,7-Dimethyl-6-(2-acetoxyethyl)-1,2,4-triazolo[1,5-*a*]pyrimidine was obtained in 46 % yield, b.p. 220 °C (2 Torr), m.p. 83–84 °C. ^1H NMR (CD_3OD), δ : 1.95 (s, 3 H, COCH_3), 2.65 and 2.80 (s, 6 H, CH_3), 3.10 (t, $J = 7$ Hz, 2H, CH_2), 4.20 (t, $J = 7$ Hz, 2H, CH_2), 8.30 (s, 1 H, $=\text{CH}$). IR, ν/cm^{-1} : 1620, 1740. MS, m/z : 234 (M^+). Found (%): C, 56.40; H, 6.13; N, 23.78. $\text{C}_9\text{H}_{12}\text{N}_4\text{O}$. Calculated (%): C, 56.40; H, 6.02; N, 23.92.

References

1. L. Ya. Yanovskaya, V. A. Dombrovskii, and A. Kh. Khusid, *Tsyklopropany s Funktsional'nymi Gruppami: Sintez i Prime-nenie* [Cyclopropanes with Functional Groups: Synthesis and Application], Nauka, Moscow, 1980 (in Russian).
2. N. S. Zefirov, S. I. Kozhushkov, and T. S. Kuznetsova, *Tetrahedron*, 1982, **38**, 1693.

Received July 2, 1993

The ability of 5- and 6-membered cyclic boron complexes formed by 4-amino-4-(2-pyridyl)-3-buten-2-one to interconvert in solution

L. S. Vasil'ev, B. S. Bogdanov, E. M. Shashkova, Nguyen Ky Khoa, K. L. Cherkasova, and V. A. Dorokhov*

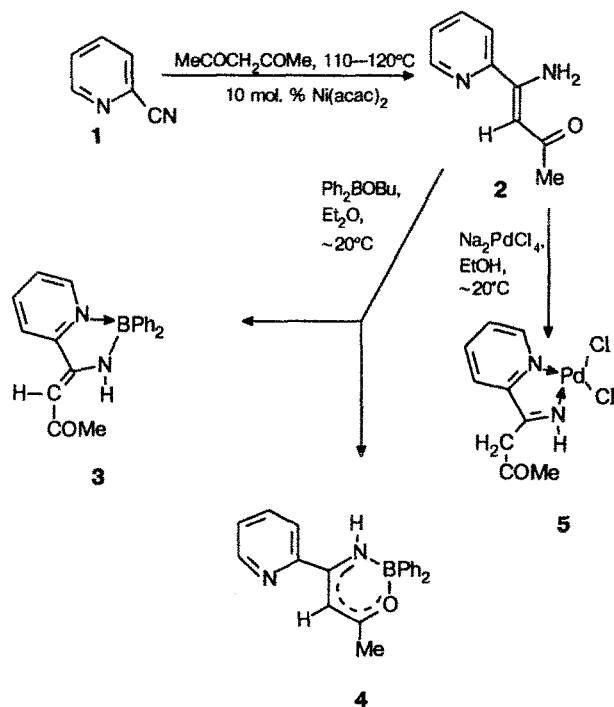
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

The reaction of acetylacetone with 2-cyanopyridine (**1**) in the presence of $\text{Ni}(\text{acac})_2$ after heating (110–120 °C, 15 h) has been investigated. The addition of acetylacetone to the $\text{C}\equiv\text{N}$ bond of heterocyclic nitrile **1** is accompanied by deacetylation and affords 4-amino-4-(2-pyridyl)-3-buten-2-one (**2**), a compound with potential chelating properties.

The reaction of compound **2** with Ph_2BOBu (~20 °C, 3 days) was found to give a mixture of isomeric cyclic boron complexes: **3** (a five-membered boron-containing ring with *N,N*-coordination) and **4** (a six-membered boron-containing ring with *N,O*-coordination) in a ~2 : 1 ratio. Chelates **3** and **4** were isolated as pure crystalline substances, however, ^1H and ^{13}C NMR spectroscopy show that in solution (CDCl_3 and $\text{DMSO}-d_6$) they are capable of interconversion, which occurs until a dynamic equilibrium is established ($3:4 \approx 2:1$). Interestingly, the reaction of **2** with Na_2PdCl_4 in EtOH (~20 °C, 1 h) yields complex **5**, in which, unlike **3** and **4**, the ligand is not deprotonated.

4-Amino-4-(2-pyridyl)-3-buten-2-one (**2**) was isolated by chromatography on SiO_2 (benzene as the eluent) and purified by sublimation *in vacuo* (b.p. 74–76 °C, yield 40 %). ^1H NMR (CDCl_3), δ : 2.21 (s, Me), 5.82 (s, $=\text{CH}$), 7.38 (m, H-5), 7.7–7.8 (m, H-3 и H-4), 8.65 (m, H-6, Py), 7.1 and 7.7 (both s, NH_2).

The reaction of compound **2** with Ph_2BOBu was carried out in absolute ether (under N_2). The precipi-



tated crystals of chelate **3** were filtered off and washed with heptane, yield 68.5 %. ^1H NMR (CDCl_3) δ : 2.21

(s, Me), 5.81 (s, =CH), 8.02 (m, H-3), 8.18 (m, H-4), 7.65 (m, H-5), 8.60 (m, H-6), 10.12 (s, NH), 7.25 (m, 2Ph). ^{13}C NMR ($\text{DMSO}-d_6$) δ : 29.27 (Me), 88.72 (=CH), 126.48, 127.47, 132.04 (2 Ph, the C—B signal is significantly broadened), 154.06 (C-2), 121.13 (C-3), 143.24 (C-4), 127.28 (C-5), 143.12 (C-6, Py), 150.66 (CNH), 194.94 (C=O).

The volatile compounds were evaporated from the filtrate *in vacuo*, and the residue was treated with hexane and cooled to -18°C . The precipitate of chelate **4** was then filtered off and washed with hexane, yield 30.8 %. ^1H NMR (CDCl_3), δ : 2.26 (s, Me), 5.8 (d, =CH), 7.15–7.55 (m, 2Ph), 7.78–7.87 (m, H-3, H-4), the signal from H-5 is covered by the signals from Ph, 8.73

(H-6), 9.05 (s, NH). ^{13}C NMR (CDCl_3), δ : 24.32 (Me), 91.58 (=CH), 126.18, 127.23, 131.75 (Ph, the C—B signal is significantly broadened), 161.46 (m, C-2), 121.73 (C-3), 137.47 (C-4), 126.74 (C-5), 149.72 (C-6, Py), 147.41 (CNH), 181.64 (C=O).

Chelate **5** was isolated from the reaction mixture by treating it with water (after the evaporation of EtOH), m.p. > 265 (dec.), yield 99 %. The structure of **5** was confirmed by the data from the IR and ^1H NMR spectra. The ^1H NMR spectrum exhibits a characteristic singlet with δ 4.30 (2 H, CH_2), and the IR spectrum displays an adsorption band at 1712 cm^{-1} (C=O).

The elemental analysis data for compounds **2**–**5** correspond to the calculated values.

Received July 7, 1993

New phosphaaalkenes with small rings as substituents

A. B. Kostitsyn,^a H. Heydt,^b M. Regitz,^{*b} and O. M. Nefedov^{*a}

^a N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.

Fax: (095) 135 5328

^b University Kaiserslautern, Erwin-Schroedinger Strasse, D-67633, Germany

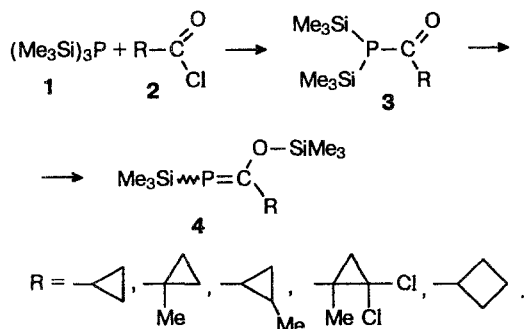
At this time a great number of phosphaaalkenes containing various substituents at the phosphorus or carbon atom are known.¹ However, phosphaaalkenes having small rings as substituents are practically uninvestigated, and are represented in the literature by only one example.²

We have found the conditions for the preparation of these labile compounds and have synthesized for the first time phosphaaalkenes with various cyclopropane and cyclobutane substituents at the carbon atom of the $\text{P}=\text{C}$ bond. Thus, the addition of a 1.1 mol excess of acyl chlorides (**2**) to tris(trimethylsilyl)phosphane (**1**) in ben-

zene at -3°C under Ar affords in all cases acylphosphanes (**3**) which undergo a 1,3-shift of the Me_3Si -group at 25°C to yield the corresponding phosphaaalkenes in 75–95 % yields (NMR data).

The thermal lability of compounds **4** does not allow their isolation, however, their solutions in benzene are stable below zero under argon and can be stored under these conditions for several days.

The NMR characteristics of **4** as well as the intermediate compounds **3**, which are detectable by NMR spectroscopy even at -20°C , are in agreement with those presented in the literature.^{1,3}



References

1. R. Appel, F. Knoll, and J. Ruppert, *Angew. Chem.*, 1981, **93**, 771; *Angew. Chem.*, Int. Ed. Engl., 1981, **20**, 731; R. Appel, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Eds. M. Regitz and O. J. Scherer, Thieme, Stuttgart, 1990, 157.
2. R. Appel, P. Folling, W. Schuh, and F. Knoch, *Tetrahedron Lett.*, 1986, **27**, 1661.
3. T. Allspach, M. Regitz, G. Becker, and W. Becker, *Synthesis*, 1986, 31.

Received July 12, 1993

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1324–1325, July, 1993.

1066-5285/93/4207-1267 \$12.50 © 1994 Plenum Publishing Corporation