REACTION OF SUBSTITUTED 5-METHYL 1,2,3-DIAZAPHOSPHOLES AND 1,2,3-DIAZAARSOLES WITH DIPHENYLDIAZOMETHANE AND NITRONES

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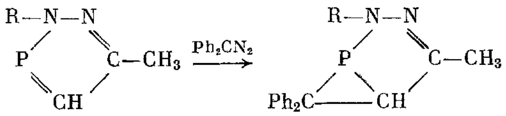
Earlier, by reaction of 5-methyl-2-phenyl(acetyl)-1,2,3-diazaphospholes (I) and (II) with diphenyldiazomethane in various solvents, bicyclic phosphiranes (III) and (IV) were obtained [1].

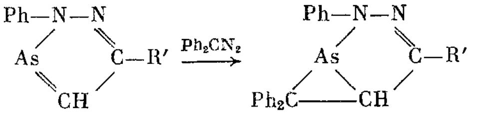


(I), (II) (III), (IV)

R = Ph(I), (III), Ac(II), (IV).

However, it is known that reaction of α,β-unsaturated carbonyl compounds with diazo compounds in pyridine leads to [2 + 3]-cycloaddition to diazaphospholes, the reaction of diazaphosphole (II) with diphenyldiazomethane in pyridine was carried out. It was found that also in this solvent 2-acetyl-5-methyl-6,6-diphenyl-1-phospha-2,3-diazabicyclo[3.1.0]-hex-3-ene (IV) is formed. Thus, the nature of the solvent does not influence the reaction of diazaphospholes with Ph_2CN_2.

Earlier [3] we found that heating 2,5-diphenyl-1,2,3-diazaarsole (V) with Ph_2CN_2 without solvent results in bicyclic arsirane (VI)



(V), (VII) (VI), (VIII)

R′ = Ph(V), (VI), CH_3(VII), (VIII).

It was of interest to study the behavior of 5-methyl-2-phenyl-1,2,3-diazaarsole (VII) in the reaction with Ph_2CN_2 and compare the reactivity of diazaphospholes and diazaarsoles. Diazaarsole (VII) reacts with Ph_2CN_2 without heating in the absence of solvent forming 4-methyl-2,6,6-triphenyl-1-arsa-2,3-diazabicyclo[3.1.0]hex-3-ene (VII) the structure of which was proved by its mass spectrum, elemental analysis, and IR and PMR spectra.

Thus, diazaphospholes (I) and (II) and diazaarsoles (V) and (VII) react with Ph_2CN_2 analogously. Comparison of the reactivity of 5-methyl-2-phenyl-1,2,3-diazaphosphole (I) and 5-methyl-2-phenyl-1,2,3-diazasrsole (VII), which have the same substituents, showed that diazaarsole (VII) is more active toward Ph_2CN_2. It is interesting that with methylphenyldiazomethane diazaphospholes (I) and (II) and diazaarsoles (V) and (VII) behave differently and form different products, which will be reported elsewhere.

The stabilities of phosphirane- and arsirane-containing bicycles are varied. Thus, 4-methyl-2-phenyl(acetyl)-6,6-diphenyl-1-phospha-2,3-diazabicyclo[3.1.0]hex-3-enes (III) and (IV) are stable in crystalline form and in solutions. They can be recrystallized from MeOH. 2,4,6,6-Tetraphenyl-1-arsa-2,3-diazabicyclo[3.1.0]hex-3-ene (VI) in unstable in solutions and upon prolonged storage it decomposes to the initial diazaarsole. 4-Methyl-2-phenyl-6,6-diphenyl-1-arsa-2,3-diazabicyclo[3.1.0]hex-3-ene (VIII) is stable in crystalline form. In benzene, $CHCl_3$, and CCl_4 it resinifies, but it can be recrystallized from EtOH/MeCN.

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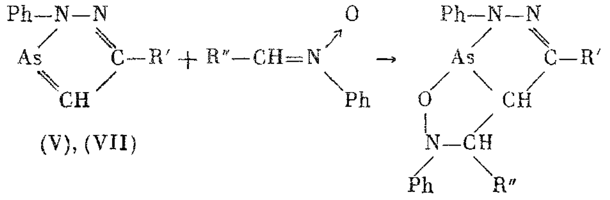
Cycloaddition of diazaarsoles to the As=C bond was first realized in 1979 [4] with the reaction of 2,5-diphenyl-1,2,3-diazaarsole (V) with nitrones. The structure of the product (IXb) was proved by X-ray analysis

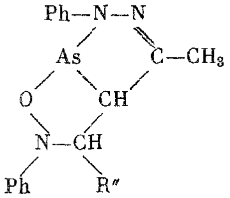


(V), (VII)

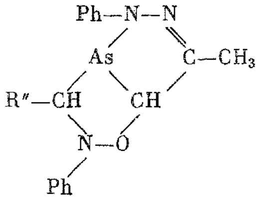
(IXa,b), (Xa,b)

R′ = Ph(V), (IX), Me(VII), (X); R″ = p-NO_2—C_6H_4(a), Ph(b).

In continuation of these investigations we studied the reaction of nitrones with 5-methyl-2-phenyl-1,2,3-diazaarsole (VII). Crystalline products were obtained which by mass spectrum and elemental analysis are the 1:1 adducts (X) and (XI)



(X)



(XI)

The PMR spectra of the obtained compounds are analogous to the spectra of the compounds (IXa, b) synthesized earlier, in which the methine proton signals appeared as singlets because the C—H bonds lie in mutually perpendicular planes. Therefore, for the reaction products of 5-methyl-2-phenyl-1,2,3-diazaarsole with nitrones, 2,7-diphenyl-4-methyl-6-R″-1-arsa-8-oxa-2,37-triazabicyclo[3.3.0]oct-3-ene (X) is the preferred structure. Moreover, if products of type (XI) were formed, then the methine signals in the spectrum would not differ so strongly. PMR spectrum (acetone-d, δ, ppm) of compound (Xa): 2.16 s (CH_3), 4.60 s (H—C—N), 6.23 s (H—C—As), 7.16 m (C_6H_5). PMR spectrum (acetone-d, δ, ppm) of compound (Xb): 2.12 s (CH_3), 4.53 s (H—C—N), 6.03 s (H—C—As), 7.14 m (C_6H_5).

EXPERIMENTAL

IR spectra were recorded on a Specord 75 IR instrument, PMR spectra on a Tesla BS-467 NMR spectrometer (working frequency 60 MHz) relative to HMDS. Mass spectra were recorded on a Finnegan MAT-212 instrument at 50-120°C and Vu = 50 V.

2-Acetyl-5-methyl-6,6-diphenyl-1-phospha-2,3-diazabicyclo-[3.1.0]hex-3-ene (IV). To 1.5 g Ph_2CN_2 in 10 ml Py at 10°C, 1.1 g diazaphosphole (II) was added dropwise in an atmosphere of dry nitrogen. In 4 h the color of the mixture changed from crimson to yellow. After 24 h the crystalline product was filtered off and washed with ether. There was obtained 2.1 g (88%) of compound (IV) with m.p. 143-145°C.

Mixing with an authentic sample does not decrease the melting point. IR spectrum (ν, cm, white mineral oil): 515 w, 710 s, 725 s, 780 m, 1000 w, 1040 w, 1208 m, 1279 w, 1320 s, 1350 s, 1400 v. s, 1498 m, 1605 m (Ph), 1660 v. s (C=O), and others. Found: M 308 (mass spectrum). $C_{18}H_{17}N_2OP$. Calculated: M 308.

4-Methyl-2-phenyl-6,6-diphenyl-1-arsa-2,3-diazabicyclo[3.1.0]hex-3-ene (VIII). To 1.6 g Ph_2CN_2 1.8 g of diazaarsole (VII) was added dropwise. Evolution of nitrogen occured and a crystalline product was formed. The mixture was kept for 1.5 days, then the crystals were filtered off and washed with petroleum ether. There was obtained 2.2 g (69%) of compound (VIII) with m.p. 129-131°C (from EtOH/MeCN). IR spectrum (ν, cm^{-1}, white mineral oil): 475 w, 495 w, 505 w, 555 w, 630 s, 787 v. s, 830 v. s, 977 w, 1000 w, 1019 w, 1190 m, 1285 s, 1480 v. s, 1578 s, and others. PMR spectrum (acetone-d, δ, ppm): 2.00 s (CH_3), 4.65 s (CH), 7.06 m (C_6H_5). Found, %: C 68.32, H 4.90, N 7.16; M 386. $C_{22}H_{19}AsN_2$. Calculated, %: C 68.40, H 4.96, N 7.25; M 386.

Reaction of 5-Methyl-2-phenyl-1,2,3-diazaarsole (VII) with C-p-nitrophenyl-N-phenylnitrone. To a suspension of 0.42 g nitrone in CH_2Cl_2 0.38 g of diazaarsole (VII) was added dropwise. The mixture was kept for 3 days, then the crystals were filtered off and washed with CH_2Cl_2. There was obtained 0.65 g (81%) of compound (Xa) with m.p. 156.5-157.5°C. IR spectrum (ν, cm^{-1}, white mineral oil): 505 w, 575 m, 630 m, 668 m, 695 s, 740 s, 815 m, 985 w, 1025 w, 1170 w, 1248 m, 1310 s, 1485 s, 1505 s, 740 s, 815 m, 985 w, 1025 w, 1170 w, 1248 m, 1310 s, 1485 s, 1505 s, 1587 s, and others. Found, %: C 56.59, H 4.22, N 11.70. $C_{22}H_{19}AsN_4O_3$. Calculated, %: C 57.11, H 4.13, N 12.11. The mass spectrum has an intense signal at M 220 (diazaarsole (VII)) and M 242 (nitrone).

Reaction of 5-Methyl-2-phenyl-1,2,3-diazaarsole (VII) with C,N-diphenylnitrone. To a suspension of 1.28 g nitrone in CH_2Cl_2 1.43 g of diazaarsole (VII) was added dropwise. The mixture was kept for 40 days and then alcohol was added until dissolution. Upon cooling crystals precipitated which were filtered off and washed with EtOH. There was obtained 1.3 g (48%) of (Xb) with m.p. 109-111.5°C (from MeOH–petroleum ether). IR spectrum (ν, cm^{-1}, white mineral oil): 500 w, 570 m, 687 s, 730 s, 740 s, 1020 w, 1070 w, 1170 w, 1238 m, 1305 m, 1480 s, 1577 m, and others. Found, %: C 63.23, H 4.89, N 10.00. $C_{22}H_{20}AsN_3O$. Calculated, %: C 63.32, H 4.83, N 10.07.

CONCLUSIONS

1. Reaction of 2-acetyl-5-methyl-1,2,3-diazaphosphole and 5-methyl-2-phenyl-1,2,3-diazaarsole with diphenyldiazomethane leads to formation of phosphirane- and arsirane-containing bicyclic compounds.

2. In reaction with nitrones 5-methyl-2-phenyl-1,2,3-diazaarsole, as well as 2,5-diphenyl-1,2,3-diazaarsole, forms analogous [2 + 3]-cycloadducts.

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