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REACTION OF 2-PHENYL(ACETYL)-5-METHYLDIAZAPHOSPHOLE WITH PHENYL AZIDE

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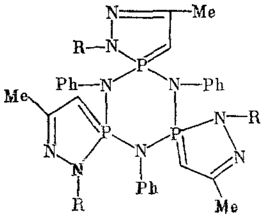
UDC 542.91:547.1'118

Continuing the study of cycloaddition at the P = C bond of the two-coordinate P atom [1, 2], in the present paper we have investigated the reactions of diazaphospholes with phenyl azide.

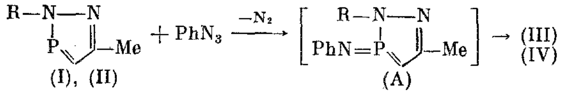
The reaction of 2-phenyl- (I) and 2-acetyl-5-methyldiazaphosphole (II) with phenyl azide was carried out both without a solvent and in ether, pentane, C_6H_6, and CCl_4 and was accompanied by vigorous evolution of nitrogen with the formation of unstable amorphous 1:1 adducts. A comparison of the IR spectra of the obtained adducts with the spectra of the starting diazaphospholes suggests that the diazaphosphole ring was retained in the adducts (presence of a band at 1300 cm^{-1} and pulsational vibrations of the diazaphosphole ring [3]).

The adduct with the phenyl substituent (III) was so unstable in the solvents that it could not be characterized by the ^1H and ^{31}P NMR spectra, although when the reaction was carried out in pentane, a solid product was obtained whose ^{31}P NMR spectrum (in CH_2Cl_2) contained two signals: + 32 and + 20 ppm. Apparently, the latter signal belonged to unchanged (III). Adduct (IV), obtained from (II), was found to be more stable in solvents and was characterized by ^1H and ^{31}P NMR spectra, $\delta^{31}P$ of +17 ppm* ($CHCl_3$). The PMR spectrum (in $CHCl_3$) contained signals with δ 2.3 ($CH_3C = N$) and 2.1 ppm (CH_3CO). However, the nature of the spectrum (broad absorption) indicated that the compound had a high molecular weight. Indeed, the molecular weight determined by cryoscopy in $CHBr_3$ confirmed this assumption, and adduct (IV) was apparently a trimer. The UV spectrum of (IV) contained absorption at 275 nm characteristic of the diazaphosphole ring



R = Ph (III), $\delta^{31}P$ + 20 ppm
R = CH_3CO (IV), $\delta^{31}P$ + 17 ppm

Apparently, the formation of trimers (III) and (IV) was preceded by the appearance of an adduct with diylide structure (A), which underwent trimerization at the P = N bond



With recrystallization of trimeric adduct (III) from alcohol, ethyl acetate, CH_3CN, or nitromethane without protection from moisture of air, crystalline 2-phenyl-3-oxo-3-anilino-5-methyl-1,2,3-diazaphospholine (Va) was obtained, $\delta^{31}P$ +32 ppm (in CH_2Cl_2). The IR spectrum of (Va) contained absorption bands of P = O (1211 cm^{-1}) and NH (3200 cm^{-1}) groups, absent in the spectrum of (III), and the PMR spectrum contained signals of the CH_3 group with δ 2.23 ppm and an H^4 doublet at δ 2.89 ppm, J_{PH} = 14 Hz. Apparently, trimer (III) was so sensitive to moisture that if there were traces of moisture in the solvent, (III) was converted to (Va)

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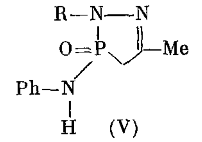
* The signals in the field which was weak with respect to H_3PO_4 are denoted with a plus sign.

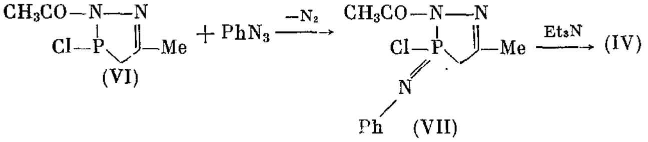
A. M. Butlerov Chemical Institute, V. I. Ul'yanov-Lenin Kazan State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1600-1602, July, 1981. Original article submitted July 8, 1980.



(V)

R = Ph (Va), CH_3CO (Vb)

Trimer (IV) was much more stable in the solvents, and prolonged heating was necessary for it to be converted to phospholine (Vb). Trimer (IV) was obtained by reverse synthesis



2-Acetyl-3-chloro-5-methyl-1,2,3-diazaphospholine (VI) reacted with phenyl azide with evolution of nitrogen and the formation of unstable acid chloride (VII), which was easily dehydrohalogenated. The IR spectrum of (VII) contained lines of amide carbonyl (1700 cm^{-1}), lines at 1190 and 1270 cm^{-1}, which could be assigned to absorption of the P = N bond [4], and an intense band below 500 cm^{-1}, which was assigned to vibration of the P–Cl bond [3]; $\delta^{31}P$ + 36 ppm ($CHCl_3$). By reaction with Et_3N, acid chloride (VII) was converted to trimer (IV), which was identified according to the IR spectra. Compound (Vb) was obtained by the hydrolysis of (IV).

EXPERIMENTAL

The PMR spectra of 5% solutions in $CHCl_3$ were recorded with a Varian HA-100 D spectrometer. The δH chemical shifts were measured with respect to TMS as the internal standard with a precision of ± 0.005 ppm. The IR spectra were recorded with a UR-10 spectrophotometer.

Reaction of 2-Phenyl-5-methyldiazaphosphole (I) with Phenyl Azide. Without a Solvent. To 2.95 g of (I) [5] in a box was gradually added 2 g of phenyl azide, after which the temperature of the mixture rose to 110°C, and vigorous evolution of nitrogen occurred. The solidified mass was treated with ether. Obtained: 4.4 g (98%) of a residue of (III) with an undistinct melting point of 215-220°C. Found: C 67.19; H 4.85; P 11.41; N 15.43%. $(C_{15}H_{14}N_3P)_3$. Calculated: C 67.49; H 5.27; P 11.59; N 15.72%.

The product of recrystallization from alcohol, dioxane, ethyl acetate, and CH_3NO_2 was converted to colorless crystals of (Va), mp 179-180°C. IR spectrum (ν, cm^{-1}): 455 medium, 480, 500 strong, 700, 720 medium, 760 very strong, 960, 1000 strong, 1020 medium, 1060, 1090 medium, 1155 strong, 1215 very strong, 1270 strong, 1290, 1310 medium, 1340, 1380 strong, 1420, 1460 medium, 1500, 1600 strong, 3200 broad. $\delta^{31}P$ +32 ppm (CH_2Cl_2). Found: C 63.30; H 5.69; P 10.99; N 14.88%. $C_{15}H_{16}N_3PO$. Calculated: C 63.14; H 5.65; P 10.86; N 14.72%.

In Ether. A solution of equimolar amounts of (I) and phenyl azide in ether was kept for 48-72 h at 20°C. Compound (III) was formed quantitatively with a wide melting-point range. Found: mol. wt. 760.03 (cryoscopically in $CHBr_3$). $(C_{15}H_{14}N_3P)_3$. Calculated: mol. wt. 801.85. After chromatography of (III) on silica gel (KSK brand, 0.25 mesh) with elution with abs. ether, (Va) was isolated, mp 179-180°C; $\delta^{31}P$ + 32 ppm (CH_2Cl_2).

Reaction of 2-Acetyl-5-methyldiazaphosphole (II) with Phenyl Azide. An ether solution of 0.5 g of phenyl azide was added to a solution of 0.6 g of (II) [6] in ether in a box. In several minutes, a lemon-yellow precipitate began to appear, which was filtered off the next day. Obtained: 1 g of (IV) with mp 127-129°C, $\delta^{31}P$ +17 ppm (CH_2Cl_2). IR spectrum (ν, cm^{-1}): 700 medium, 722 weak, 753 medium, 950, 1035, 1080, 1230, 1285, 1500, 1600, 1675 strong, etc. Found: P 12.85; N 18.61%. $(C_{11}H_{12}ON_3P)_3$. Calculated: P 13.29; N 18.01%. A similar product was obtained from equimolar amounts of the starting reagents at 20°C in ether, CCl_4, and C_6H_6.

Reaction of 2-Acetyl-3-chloro-5-methyl-1,2,3-diazaphospholine (VI) with Phenyl Azide. A solution of 2 g of phenyl azide in abs. ether was added to a solution of 3 g of (VI) in abs. ether in a box. Nitrogen was evolved, and a fine hygroscopic precipitate appeared. Obtained: 3.5 g of (VII) with mp 118-120°C (in a sealed capillary). Found: C 48.70; H 5.11; N 15.29; P 11.67%. $C_{11}H_{13}N_3POCl$. Calculated: C 48.97; H 4.85; N 15.57; P 11.49%. IR spectrum (ν, cm^{-1}): 400, 525, 580, 625 medium, 700, 760 strong, 1000 very strong, 1190 strong, 1270 very strong, 1350 strong, 1500 very strong, 1600 strong, 1700 strong.

Reaction of Acid Chloride (VII) with Triethylamine. A threefold excess of Et_3N was added to a solution of (VII) in $CHCl_3$ cooled with snow with salt, and the mixture was left at 20°C overnight and evaporated in vacuo. The residue was triturated with hexane into a powder, which was treated with water. The residue, which did not dissolve in water, was filtered off and was dried for several days in a vacuum desiccator. Obtained: (IV) with mp 127-129°C. Found: mol. wt. 702.4 (cryoscopically in $CHBr_3$). $(C_{11}H_{12}N_3PO)_3$. Calculated: mol. wt. 699.6. $\delta^{31}P$ +20 ppm (C_2H_5OH). The IR spectrum was similar to the spectrum of (IV) obtained from (II) and phenyl azide. Compound (Vb) was isolated with heating of (IV) with a reflux condenser in benzene in the presence of H_2O.

Methylation of 2-Phenyl-3-oxo-3-anilino-5-methyldiazaphospholine (Va). [7]. An equimolar amount of (Va) was added to a suspension of metallic Na in abs. xylene. Hydrogen was evolved. The reaction mixture was heated at 90-100°C for 1 h, CH_3I was added to the cooled solution, and the mixture was heated for 30 min more at 80°C. After xylene was removed, a viscous mass remained, whose IR spectrum contained no band of the NH group at 3200 cm^{-1}. IR spectrum (ν, cm^{-1}): 700, 750, 780, 800, 1500, 1600 (Ph), 1220 (P = O), 1620 (C = N), etc.

CONCLUSIONS

The reaction of 2-phenyl(acetyl)-5-methyldiazaphospholes with phenyl azide results in the formation of trimers which form 2-phenyl(acetyl)-3-oxo-3-anilino-5-methyl-1,2,3-diazaphospholines during hydrolysis.

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CHEMICAL PROPERTIES OF ORGANOTITANIUM COMPOUNDS CONTAINING A "SILANEOPENTYL" GROUP

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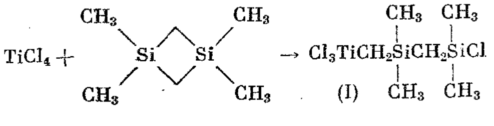
UDC 542.91:547.258.2'128

At the present time a fairly large number of relatively stable organic compounds of group IVA metals (Ti, Zr, Hf) containing a M−C σ bond are known [1]. They are benzyl, norbornyl, and neopentyl derivatives. In recent years silicon-, germanium-, and tin-containing organic radicals having a structure of the neopentyl type CH_2ER_3 have been widely used as stabilizing ligands at the transition-metal atom. The introduction of such groups at the atoms of transition metals is realized, as a rule, through organolithium, organosodium, organomagnesium, and organoaluminum compounds [2].

We have proposed a fundamentally new method for the synthesis of organometallic compounds with a group of the neopentyl type by the reaction of transition-metal halides with strained four-membered heterocycles, i.e., derivatives of 1,3-disila- or 1,3-digermacyclobutanes [3-5]. The method is simple and gives high yields of the desired products. Thus, the possibility of synthesizing organotitanium compounds with high yields by the reaction


(I)

$$TiCl_4 + (CH_3)_2Si(CH_2)_2Si(CH_3)_2 \rightarrow Cl_3TiCH_2Si(CH_3)_2CH_2Si(CH_3)_2Cl$$

A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1603-1606, July, 1981. Original article submitted October 24, 1980.