DIPHENOXYTHIOPHOSPHORYLIMIDOPHOSPHORUS TRICHLORIDE, ITS THERMAL ISOMERIZATION AND REACTION WITH PHENOL AND DIMETHYLAMINE

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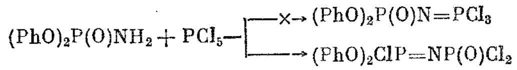
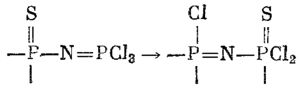
Previously [1] we had shown that the reaction of diphenylphosphoramide with PCl_5 proceeds to give diphenyl (dichlorophosphorylimido)chlorophosphate, and not diphenoxyphosphorylimidophosphorus trichloride, i.e., rearrangement involving the O atom takes place.



$$(PhO)_2P(O)NH_2 + PCl_5 - \begin{cases} \xrightarrow{\times} (PhO)_2P(O)N{=}PCl_3 \\ \rightarrow (PhO)_2ClP{=}NP(O)Cl_2 \end{cases}$$

A similar rearrangement was studied previously by other authors [2, 3].

The analogous rearrangement involving the thiono sulfur atom in the series of thiophosphorylimidophosphorus compounds of type



$$-\overset{\overset{S}{\|}}{\underset{|}{P}}-N{=}PCl_3 \rightarrow -\overset{\overset{Cl}{|}}{\underset{|}{P}}{=}N-\overset{\overset{S}{\|}}{\underset{|}{P}}Cl_2$$

is unknown up to now.

It was shown by us on the example of diphenoxythiophosphorylimidophosphorus trichloride (I) that the S atom migrates at high temperature:

$$\underset{(I)}{(PhO)_2P(S)N{=}PCl_3} \xrightarrow{220°;\ 8\text{–}10\ h} \underset{(II)}{(PhO)_2ClP'{=}N-{''}P(S)Cl_2}$$

Imidophosphate (I) was obtained as described in [4], and its structure was proved by the ^{31}P NMR and IR spectral data. The ^{31}P NMR spectrum has signals at 43.4 and −6.9 ppm, which confirms the presence of the $(PhO_2)_2P(S)N-$ and $Cl_3P=N-$ groups in the molecule. The constants of (I) are given in Table 1.

Imidophosphate (I) can be distilled in a high vacuum, but the ^{31}P NMR spectrum of the distillate has, besides the intense signals of the starting (I), signals at 13.1 and 30.8 ppm ($J_{PNP} = 31.7$ Hz), which are characteristic for diphenyl(dichlorophosphorylimido)chlorophosphate (II), a compound that we had obtained previously [5]. When (I) is heated at 220°C for 8-10 h, it is converted completely (data of ^{31}P NMR spectra) to imidophosphate (II), which was isolated in satisfactory yield from the reaction mixture and whose structure was confirmed by the ^{31}P NMR and IR spectral data, and also by direct comparison with the previously obtained (II) [5].

Imidophosphate (II), obtained by the thermal isomerization of (I), reacts with phenol, taken in a 1 : 1 ratio, to give triphenyl (dichlorothiophosphorylimido)phosphate (III), whose constants coincide with the constants of the triphenoxy derivative of (III), which had been obtained from dichlorothiophosphorylimidophosphorus trichloride and phenol using a 1 : 3 ratio of the reactants [5].

$$Cl_3P{=}NP(S)Cl_2 + 3PhOH \xrightarrow[-3HCl]{} \underset{(III)}{(PhO)_3P{=}NP(S)Cl_2}$$

Besides the thermal isomerization, we studied the reaction of (I) with phenol and dimethylamine using a variable ratio of the reactants. The Cl atoms in (I) are successively replaced by the phenoxy group when a mixture of (I) and phenol, taken in a ratio of 1 : 1, 1 : 2, and 1 : 3, is heated, in which connection each successive insertion of the phenoxy group into (I) requires more drastic conditions, similar to the replacement of the Cl atoms in the "thiopentachloride" by the phenoxy group [5].

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TABLE 1. Derivatives of $(PhO)_2{}'P(S)N={}''PRR'R''$

Compound	R	R′	R″	Yield, %	bp, °C (p, mm Hg); mp, °C	n_D^{20}	d_4^{20}	Found/Calculated, %			Empirical formula	IR (ν, cm⁻¹)		PMR (δ, ppm)		^{31}P NMR (δ, ppm)		
								Cl	P	S		P=N	P=O	Me_2N	PhO	P′	P″	J_{PNP}, Hz
(I)	Cl	Cl	Cl	94	–*	1,6016	1,4484	26,5 26,6	15,4 15,5	8,1 8,0	$C_{12}H_{10}Cl_3NO_2P_2S$	1325	690	–	7,2–7,3	43,4	–6,9	29,3
(IV)	PhO	Cl	Cl	65	162–164 (0,005)	1,6029	1,3751	15,4 15,5	13,6 13,5	–	$C_{18}H_{15}Cl_2NO_3P_2S$	1335	695	–	7,2–7,4	45,1	–3,1	48,8
(V)	PhO	PhO	Cl	53	192–196 (0,005)	1,6033	–	7,4 6,9	12,0 12,0	5,9 6,2	$C_{24}H_{20}ClNO_4P_2S$	1335	690	–	7,2–7,4	45,9	–10,1	61,0
(VI)	PhO	PhO	PhO	41	97–98, cf. [4]	–	–	–	10,8 10,8	6,0 5,6	$C_{30}H_{25}NO_5P_2S$	1330	690	–	7,2–7,4	46,6	–23,3	65,9
(VII)	Me_2N	Cl	Cl	56	142–145 (0,008)	1,5918	1,3505	17,8 17,3	15,1 15,1	8,0 7,8	$C_{14}H_{16}Cl_2N_2O_2P_2S$	1320	695	2,68	7,2–7,4	—	–	–
(VIII)	Me_2N	Me_2N	Cl	60	155–159 (0,003)	1,5811	1,2556	7,4 7,7	–	–	$C_{16}H_{22}ClN_3O_2P_2S$	1305	700	2,58	7,2–7,3	48,1	24,1	51,3
(IX)	Me_2N	Me_2N	Me_2N	74	48	–	–	–	14,5 14,5	7,9 7,5	$C_{18}H_{28}N_4O_2P_2S$	1295	700	2,54	7,2–7,4	—	–	–
				65†	158–160 (0,001) (48–49)	1,5723‡	–	–	14,3 14,5	–		1295	700	–	–	46,6	22,2	64,7

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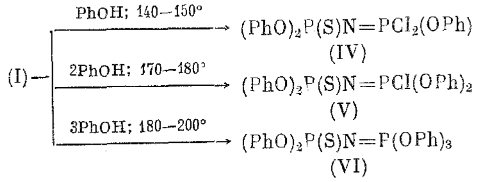
*The compound was purified by microdistillation at 0.0001 mm of Hg.

†Obtained by the reaction of diphenyl azidothiophosphate with hexamethylphosphorous triamide.

‡Supercooled liquid.



$$(I)-\begin{cases}\xrightarrow{\text{PhOH; 140–150°}} (PhO)_2P(S)N{=}PCl_2(OPh) & (IV)\\ \xrightarrow{\text{2PhOH; 170–180°}} (PhO)_2P(S)N{=}PCl(OPh)_2 & (V)\\ \xrightarrow{\text{3PhOH; 180–200°}} (PhO)_2P(S)N{=}P(OPh)_3 & (VI)\end{cases}$$

The reaction of (I) with dimethylamine, using a reactant ratio of 1 :2 and 1 :4, is also accompanied by the replacement of either one or two Cl atoms, as is shown below.

$$(I) + 2nMe_2NH \rightarrow (PhO)_2P(S)N{=}PCl_{3-n}(NMe_2)_n$$
$$n = 1\ (VII);\ n = 2\ (VIII)$$

The reaction of acid chloride (VIII) with excess dimethylamine gave hexamethyltriamido(diphenoxythiophosphorylimido)phosphoric acid (IX), which was also obtained independently from hexamethylphosphorous triamide and diphenyl azidothiophosphate.

$$(VIII) \xrightarrow{Me_2NH} \underset{(IX)}{(PhO)_2P(S)N{=}P(NMe_2)_3} \xleftarrow{N_3P(S)(OPh)_2} (Me_2N)_3P$$

EXPERIMENTAL

The IR spectra were obtained on a UR-20 instrument as a film, and for imidophosphates (VI) and (IX) as KBr pellets; the PMR spectra were obtained on a Perkin–Elmer R-12 instrument in CCl_4 solution relative to TMS; the ^{31}P NMR spectra were obtained on a Brucker HX-90 instrument (operating frequency 36.43 MHz), with suppression of the spin–spin coupling of the P and H atoms, and using 85% H_3PO_4 as the external standard. The characteristics of compounds (I) and (IV)-(IX) are given in Table 1.

Thermal Isomerization of Diphenoxythiophosphorylimidophosphorus Trichloride (I). Compound (I) (9.5 g) was heated in an argon stream for 8-10 h at 220°. Distillation gave 2.9 (31%) of (II) with bp 120-122° (0.003 mm); n_D^{20} 1.5943; d_4^{20} 1.4400. Found: P 14.9; S 8.1%. $C_{12}H_{10}Cl_3NO_2P_2S$. Calculated: P 15.4; S 8.0%. ^{31}P NMR spectrum (δ, ppm): −13.1 (P'); 30.8 (''P); J_{PNP}=31.7 Hz, cf. [5].

Triphenyl (Dichlorothiophosphorylimido)phosphate (III). A mixture of 9.5 g of (II), obtained by the thermal isomerization of (I), and 2.5 g of phenol was heated for 5 h at 180-200° until the gas evolution ceased. Distillation gave 6.4 g (58%) of (III) with bp 165-168° (0.003 mm), n_D^{20} 1.5976, d_4^{20} 1.3591. Found: Cl 15.4; P 13.5%. $C_{18}H_{15}Cl_2NO_3P_2S$. Calculated: Cl 15.5; P 13.5%, cf. [5].

Phenyl (Diphenoxythiophosphorylimido) dichlorophosphate (IV). A mixture of 10 g of (I) and 2.5 g of phenol was heated at 140-150° until the HCl evolution ceased. Distillation gave 7.4 g of (IV).

Diphenyl (Diphenoxythiophosphorylimido) chlorophosphate (V). A mixture of 8.8 g of (I) and 4.6 g of phenol was heated at 170-180° until HCl evolution ceased. Distillation gave 6.0 g of (V).

Triphenyl (Diphenoxythiophosphorylimido)phosphate (VI). A mixture of 7.1 g of (I) and 5.0 g of phenol was heated for 7-10 h at 180-200° until the HCl evolution ceased. Then the mixture was cooled, 10 ml of MeOH was added, and 4.2 g of crystalline (VI) was isolated.

Dimethylamido(diphenoxythiophosphorylimido)dichlorophosphoric Acid (VII). With stirring, to a solution of 16.6 g of (I) in 100 ml of abs. ether at 0-5° was added 3.8 g of Me_2NH in 50 ml of ether, after which the mixture was stirred for 2 h at ~20°, the precipitate was separated, the filtrate was evaporated, and the residue was distilled to give 9.6 g of (VII).

Tetramethyldiamido(diphenoxythiophosphorylimido)chlorophosphoric Acid (VIII). With stirring, to a solution of 20.9 g of (I) in 100 ml of abs. ether at 0-5° was added 9.5 g of Me_2NH in 50 ml of ether. The mixture was stirred for another 2 h at ~20°, the precipitate was separated, the filtrate was evaporated, and the residue was distilled to give 13.1 g of (VIII).

Hexamethyltriamido(diphenoxythiophosphorylimido)phosphoric Acid (IX). a) Reaction of (VIII) with Me_2NH. To a solution of 3.8 g of (VIII) in 5 ml of abs. ether at ~20° was added a 2- to 3-fold excess of Me_2NH and the mixture was let stand at 20-22° in an airtight closed flask for 2 days. The hydrochloride was separated, the filtrate was evaporated, the volatiles were removed by distillation, and the residue was recrystallized from a 1 :1 heptane–CCl_4 mixture to give 2.9 g of (IX).

b) Reaction of hexamethylphosphorous triamide with diphenyl azidothiophosphate. To a solution of 3.0 g of hexamethylphosphorous triamide in 5.0 ml of abs. benzene at 40-50° was cautiously added 2.9 g of diphenyl azidothiophosphate in 5 ml of benzene. Immediately after adding the first drops of the azide a yellor color appears (formation of the triazene) and nitrogen is evolved vigorously. At the end of reaction the volatiles were vacuum-distilled and the residue was distilled to give 3.1 g of imidophosphate (IX).

CONCLUSIONS

1. Diphenoxythiophosphorylimidophosphorus trichloride undergoes thermal isomerization to diphenyl (dichlorothiophosphorylimido)chlorophosphate.

2. The reactions of diphenoxythiophosphorylimidophosphorus trichloride with phenol and dimethylamine were studied.

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REGIOSELECTIVE SYNTHESES OF α-FUNCTIONALLY SUBSTITUTED KETONES

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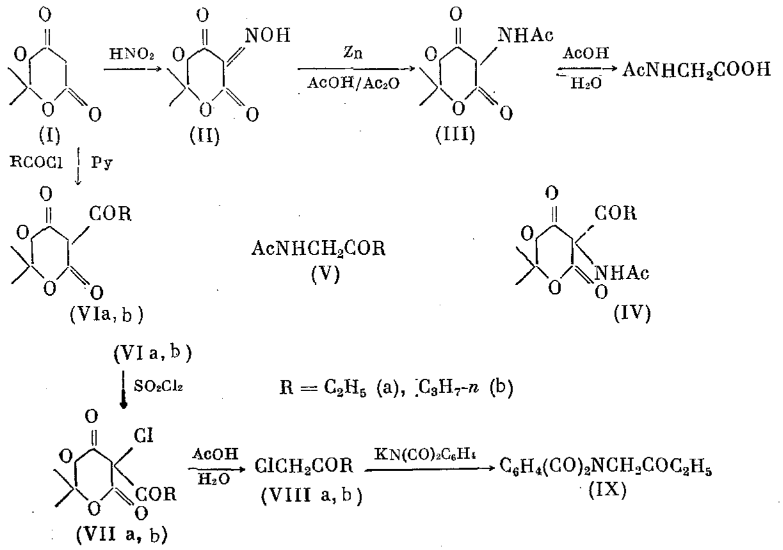
α-Functionally substituted ketones (FK) serve as important synthones for obtaining heterocyclic compounds. The most widely used method for synthesizing FK is based on the α-halogenation of ketones. A serious disadvantage of this method is the formation of mixtures of α-halo derivatives in the case of unsymmetrical ketones [1].

In the present paper we studied regioselective paths for the synthesis of FK using Meldrum's acid (I) [2].



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