in a 3:1 AcOH−HCl mixture and worked up in the usual manner to give 2.4 g of 9-mercapto-m-carborane (64% when based on starting carborane) and 0.4 g of neutral fractions.

CONCLUSIONS

1. A simple method was proposed for obtaining the bis(9-o- and 9-m-carboranyl) disulfides from the o- and m-carboranes and S_2Cl_2 in the presence of $AlCl_3$, and also a simple method for reducing the latter to the 9-o- and 9-m-carboranylthiols.

2. When the o- and m-carboranes are reacted with SCl_2 in the presence of $AlCl_3$ the main products are the bis(o- and m-carboranyl) disulfides.

LITERATURE CITED

1. J. Plešek and S. Heřmánek, Collection 43, 1325, 1332 (1978).
2. J. Böeseken, Rec. Trav. Chim., 24, 209 (1905).
3. J. Böeseken and D. A. King, Rec. Trav. Chim., 30, 116 (1911).
4. W. W. Hartman, L. A. Smith, and J. B. Dickey, Org. Synthesis, 14, 26 (1934).
5. L. I. Zakharkin and I. V. Pisareva, Izv. Akad. Nauk SSSR, Ser. Khim., 1978, 2831.
6. L. I. Zakharkin and V. V. Korneva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1958, 852.

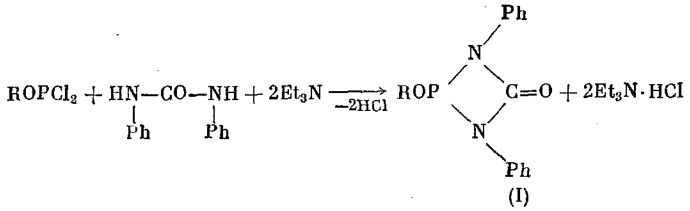
REACTION OF PHOSPHORUS ACID CHLORIDES WITH DIPHENYLUREA

K. V. Nikonorov, É. A. Gurylev,
L. A. Antokhina, and Z. Ya. Latypov

UDC 542.91:547.1'118

The direction of the reactions of carboxylic acid amides with the acid chlorides of phosphorus esters depends on the coordination number of the P atom: phosphorylation occurs in the case of the tricoordinated phosphorus atom [1], while the derivatives of the tetracoordinated phosphorus atom dehydrate carboxylic acid amides [2, 3]. It was interesting to determine if this rule extends to carbamic acid amides.

In the present paper we report the results of studying the reaction of the acid chlorides of phosphorous, phosphonous, and phosphoric esters with symmetrical diphenylurea (DPU) in the presence of HCl acceptors. 2-Alkoxy-4-oxo-1,3-diphenyl-1,3-diaza-2-phosphetidin-4-ones (I) were isolated in good yields when DPU is reacted with the dichlorides of alkylphosphorous acids in the presence of triethylamine.



(I)

R=Me (Ia), Et (Ib), i-Pr (Ic), n-Bu (Id).

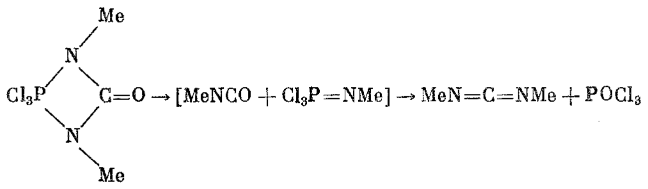
Compound (Ia) is a liquid that can be vacuum-distilled, while (Ib-d) are crystalline compounds. The IR spectra of the compounds lack the absorption band of the N−H group. The presence of the absorption band of the C=O group in the 1760-1770 cm^{-1} region indicates the presence of a ring carbonyl group [4]. The chemical shift of the signals of the P nuclei of (Ia-d) lies in the 90-95 ppm region. The PMR spectra of these compounds have only the signals of the protons of alkoxyl and phenyl groups. Based on the cryoscopy data, (Ia-d) are monomeric. The vacuum-distillation of (Ia) leads to partial decomposition and the liberation of diphenylcarbodiimide. The thermal decomposition of 2-trichloro-2-phospha-1,3-diazetidin-4-one was observed previously

---

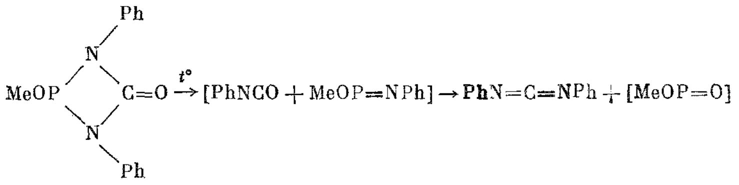
A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2796-2800, December, 1981. Original article submitted April 29, 1981.

0568-5230/81/3012-2330$07.50

[5] and went by the following scheme:



Thermal decomposition by an analogous scheme probably also occurs in the case of (Ia) during distillation.

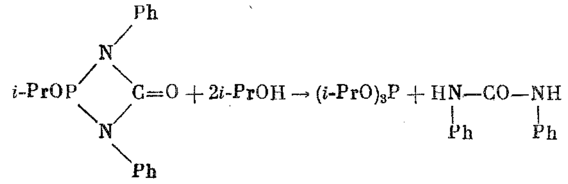


(Ia)

Diphenylcarbodiimide was isolated and characterized. Methyl metaphosphite could be neither isolated nor identified by physical methods due to decomposition under the distillation conditions [6]. The formation of 2-phenyl-4-oxo-1,3-diphenyl-1,3-diaza-2-phosphetidin-4-one with $\delta^{31}P$ 97 ppm could be recorded by the ^{31}P NMR method when phenylphosphonous dichloride is reacted with DPU in the presence of an HCl acceptor.

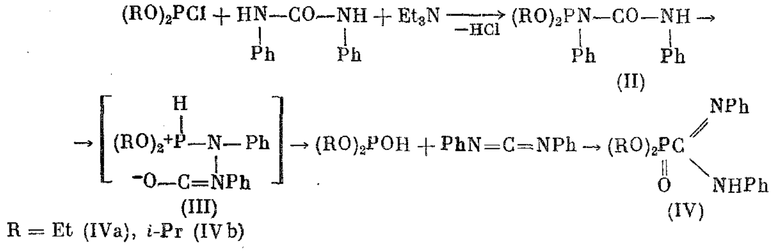
The reaction of PCl_3 with DPU gives a complex mixture of reaction products (six according to the ^{31}P NMR data), from which pure compounds could not be isolated.

A study of the chemical properties of the phosphetidines (I) disclosed that they are inert in some reactions that are typical for tricoordinated phosphorus derivatives; they do not add sulfur when heated, are not oxidized by nitrogen oxides, and do not react with chloral and CH_3Br. A decrease in the nucleophilicity of the P atom in these compounds is apparently related to the presence of electron-withdrawing groups (phenyl and carbonyl) in the four-membered ring. However, when reacted with atmospheric moisture or alcohols both of the P–N groups in (Ia-d) are easily cleaved, for example



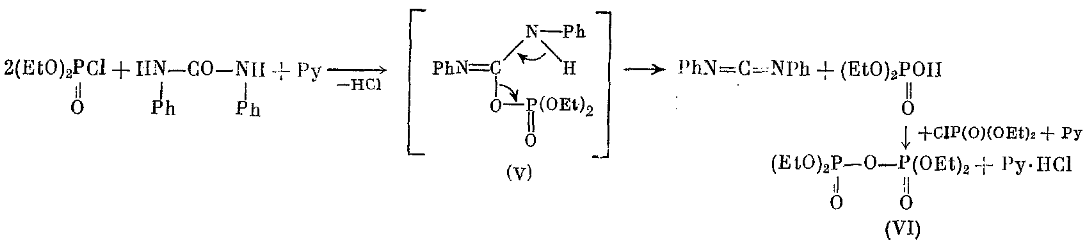
(Ic)

The chlorides of dialkylphosphorous acids react with DPU in the presence of an HCl acceptor to initially give the phosphorylated urea (II) with $\delta^{31}P$ 136-138 ppm, which after some time rearranges to the phosphorylated amidine (IV) with $\delta^{31}P$ 2-3 ppm. The rearrangement is accelerated by heat. A similar rearrangement of (II) to (IV) was observed previously [7] when (II) was obtained from the anilide of diethylphosphorous acid and phenyl isocyanate.



Apparently, the intermediate bipolar ion (III) is formed in the first step, which decomposes on the type of the Staudinger–Wittig reaction to the dialkylphosphorous acid and diphenylcarbodiimide; their reaction leads to (IV); the yields are low and the reaction is ill-defined.

The chloride of diethylphosphoric acid reacts with DPU in the presence of pyridine the same as with carboxylic acid amides, i.e., with the formation of tetraethyl pyrophosphate (VI) and diphenylcarbodiimide by the following scheme:



Apparently, the reaction proceeds with the iso form of DPU; the unstable phosphorylated isourea (V) is formed here, which decomposes to diphenylcarbodiimide and diethylphosphoric acid. The latter reacts with a second mole of diethyl chlorophosphite and gives (VI).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer, the PMR spectra on a Varian T-60 instrument (60 MHz, internal standard = TMS), and the ^{31}P NMR spectra on a KGU-4 NMR instrument (10.2 MHz, standard = 85% H_3PO_4).

2-Ethoxy-4-oxo-1,3-diphenyl-1,3-diaza-2-phosphetidin-4-one (Ib). To 6.36 g of DPU and 4.4 g of ethyl dichlorophosphite in 30 ml of dry ether was added at ~20°C an ether solution of 6.46 g of Et_3N. The temperature of the reaction mixture rose to 35°. After separating the precipitate and removing the solvent we obtained 6 g [70% of crude (Ib)]. The crystals were dissolved in CCl_4, the solution was decanted from the insoluble tar, and the solvent was removed in vacuo. The residue was dissolved in ether, the solution was cooled in liquid nitrogen, and the obtained crystals of (Ib) were filtered, mp 79-80°. Found: P 10.73; N 9.51%. $C_{15}H_{15}N_2O_2P$. Calculated: P 10.84; N 9.79%. Infrared spectrum (ν, cm^{-1}): 1500, 1605, 3040 (C_6H_5), 1765 (C=O). δ ^{31}P 93 ppm.

2-Isopropoxy-4-oxo-1,3-diphenyl-1,3-diaza-2-phosphetidin-4-one (Ic). The compound was obtained and purified the same as (Ib). Yield 55%, mp 74-75°. Found: P 9.92; N 9.42%. $C_{16}H_{17}N_2O_2P$. Calculated: P 10.33; N 9.33%. Infrared spectrum (ν, cm^{-1}): 1500, 1600, 3050 (C_6H_5), 1760 (C=O). δ ^{31}P 92 ppm.

2-n-Butoxy-4-oxo-1,3-diphenyl-1,3-diaza-2-phosphetidin-4-one (Id). Obtained and purified the same as (Ib). Yield 50%, mp 40-42°. Found: P 10.11; N 8.75%. $C_{17}H_{19}N_2O_2P$. Calculated: P 9.87; N 8.91%. Infrared spectrum (ν, cm^{-1}): 1500, 1605, 3045 (C_6H_5), 1765 (C=O), δ ^{31}P 93 ppm.

Methoxy-4-oxo-1,3-diphenyl-1,3-diaza-2-phosphetidin-4-one (Ia). Obtained the same as (Ia). Two fractions were isolated when distilled in vacuo. The first fraction (26%), bp 168-170° (11 mm) and IR spectrum (ν, cm^{-1}): 2140 cm^{-1} (N = C = N), is diphenylcarbodiimide [8]. DPU is obtained quantitatively when this fraction is treated with water. The mixed melting point with an authentic specimen was not depressed. The second fraction (25%), bp 128-130° (0.03 mm), is (Ia). Found: P 10.72; N 9.44%. $C_{14}H_{13}N_2O_2P$. Calculated: P 11.39; N 10.29%. Infrared spectrum (ν, cm^{-1}): 1480, 1595, 3010 (C_6H_5), 1755 (C = O). According to the IR spectrum, (Ia) is contaminated with a small amount of diphenylcarbodiimide. δ ^{31}P 95 ppm.

Reaction of Diphenylurea with Chloride of Diethylphosphorous Acid. To a mixture of 10.6 g of DPU and 9.22 g of the chloride of diethylphosphorous acid in dry ether was added at ~20° an ether solution of 5.05 g of Et_3N. The mixture was stirred for 1 h at 25-30°. A thick liquid was obtained after removal of the precipitate and solvent. The ^{31}P NMR spectrum of this liquid has intense signals at 137-139 ppm and a signal at 2 ppm. The peak with δ 137 ppm decreases with time, while the peak with δ 2 ppm increases. The liquid deposited 4 g (25%) of diethylphosphoryl-N,N'-diphenylformamidine (IVa), mp 107-108° (from xylene). Found: P 9.25; N N 8.52%. $C_{17}H_{21}N_2O_3P$. Calculated: P 9.63; N 8.43%. Infrared spectrum (ν, cm^{-1}): 1255 (P = O), 1630 (C = N), 3260 (N − H). δ ^{31}P 2 ppm; cf. [7]. The peak with δ 139 ppm does not change with time, but the substance to which this peak belongs could not be identified due to decomposition when vacuum-distilled.

Diisopropylphosphoryl-N,N'-diphenylformamidine (IVb) was obtained in a similar manner. Yield 23%, mp 105-107° (hexane−benzene). Found: P 9.07; N 7.36%. $C_{19}H_{25}N_2O_3P$. Calculated: P 8.61; N 7.77%. Infrared spectrum (ν, cm^{-1}): 1240 (P = O), 1635 (C = N), 3260 (N − H). δ ^{31}P 3 ppm.

Reaction of Diphenylurea with Chloride of Diethylphosphoric Acid. To 10.6 g of DPU and 9.6 g of pyridine in dry ether was added 17.25 g of the chloride of diethylphosphoric acid. The mixture warmed up slightly and a dark-red oil deposited. The mixture was heated for another 30 min at 30-35°. The obtained oil was separated from the ether solution to give 21.9 g of product, which represented a mixture of Py · HCl and diphenylcarbodiimide, contaminated with a small amount of tetraethyl pyrophosphate (VI). The IR spectrum of the oil has bands at 2150 (N=C=N) and 2500 cm^{-1} ($-\overset{+}{N}\langle$ of pyridine); the ^{31}P NMR spectrum of the oil has a signal at −15 ppm, which belongs to (VI). Diphenylcarbodiimide was identified as DPU; treatment of the oil with water gave 8.2 g (74%) of DPU. The solvent was removed from the ether solution in vacuo and the residue was distilled to give 3.8 g of (VI), bp 127-129° (0.2 mm), n_D^{20} 1.4270. Found: C 32.93; H 6.45; P 20.76%. $C_8H_{20}O_7P_2$. Calculated: C 33.10; H 6.85; P 21.40%. δ ^{31}P; −15 ppm. (cf. [9]).

CONCLUSIONS

1. The reaction of diphenylurea with the chlorides of phosphorous and phosphonous esters gives phosphorylated urea derivatives, whereas reaction with the chloride of diethylphosphoric acid leads to tetraethyl pyrophosphate and diphenylcarbodiimide.

LITERATURE CITED

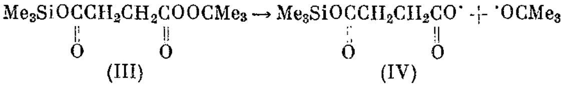
1. P. I. Alimov and L. N. Levkova, Izv. Akad. Nauk SSSR, Ser. Khim., 1964, 1801.
2. P. I. Alimov, L. N. Levkova, L. A. Antokhina, and I. V. Cheplanova, Izv. Akad. Nauk SSSR, Ser. Khim., 1972, 147.
3. L. V. Razvodovskaya, N. I. Mel'nikov, N. V. Lebedeva, and A. F. Grapov, Zh. Obshch. Khim., 41, 1446 (1971).
4. L. J. Bellamy, Infrared Spectra of Complex Molecules, Wiley (1958).
5. H. Ulrich and A. Sayigh, Angew. Chem., 76, 647 (1964).
6. R. Schwarz and H. Geulen, Ber., 90, 952 (1957).
7. R. F. Hudson and A. Mancuso, Phosphorus, 1, 265 (1972).
8. Beilstein, Vol. 12, p. 449 (1918).
9. D. F. Toy, J. Am. Chem. Soc., 70, 3882 (1948).

THERMAL DECOMPOSITION OF TRIMETHYLSILYL tert-BUTYL PERSUCCINATE

G. A. Razuvaev, G. V. Basova,
O. S. D'yachkovskaya, V. A. Dodonov,
and S. V. Krasnodubskaya

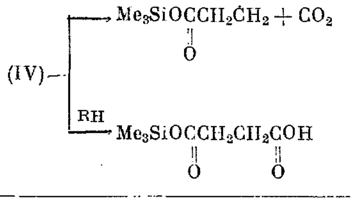
UDC 541.11:542.92:547.1'128

As a continuation of studying the reactivity of silicon-containing radicals, formed during the thermal decomposition of trimethylsilyl tert-butyl perphthalate (I) and trimethylsilyl tert-butyl permaleate (II), we made a study of the thermal decomposition of trimethylsilyl tert-butyl persuccinate (III) without a solvent and in either benzene or cumene. The purpose of the study was to ascertain the effect of varying the hydrocarbon fragment in the acyl portion of the peroxide on the behavior of the formed radicals. The complete decomposition of (III) proceeds at 110-115°C in 25 h. On the basis of the kinetic studies and the thermal decomposition products (Table 1) it may be concluded that the initial reaction act is homolysis of the peroxyester at the O—O bond.



$$\underset{\text{(III)}}{\mathrm{Me_3SiO\underset{\overset{\|}{O}}{C}CH_2CH_2\underset{\overset{\|}{O}}{C}OOCMe_3}} \rightarrow \underset{\text{(IV)}}{\mathrm{Me_3SiO\underset{\overset{\|}{O}}{C}CH_2CH_2\underset{\overset{\|}{O}}{C}O^{\cdot}}} + {}^{\cdot}\mathrm{OCMe_3}$$

The formed Si-containing acyloxy radicals (IV) are unstable and mainly undergo fragmentation with the elimination of CO_2, whose yield reaches 79-88%. Only a small part of (IV) cleaves hydrogen and is converted to the acid trimethylsilyl succinate.



$$\text{(IV)} \longrightarrow \mathrm{Me_3SiO\underset{\overset{\|}{O}}{C}CH_2\dot{C}H_2} + CO_2$$

$$\text{(IV)} \xrightarrow{\mathrm{RH}} \mathrm{Me_3SiO\underset{\overset{\|}{O}}{C}CH_2CH_2\underset{\overset{\|}{O}}{C}OH}$$

Institute of Chemistry, Academy of Sciences of the USSR, Gorki. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2800-2803, December, 1981. Original article submitted April 29, 1981.