REACTION OF 2,4,6-TRIISOPROPYL-1,3,5-DIOXAPHOSPHORINANE WITH PHENYL AZIDE

B. A. Arbuzov, O. A. Erastov,
S. N. Ignat'eva, I. P. Romanova,
O. V. Ovodova, and R. P. Arshinova

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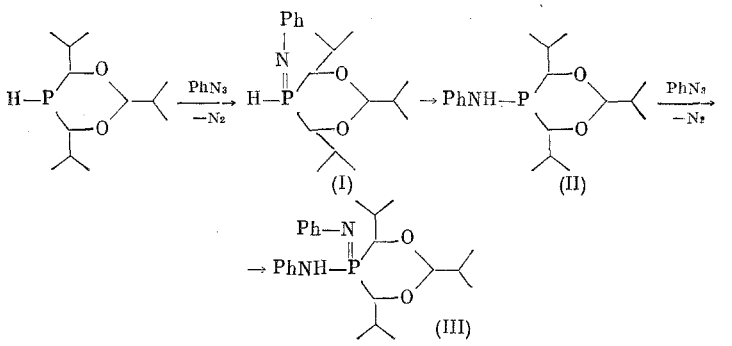
The Staudinger reaction with tertiary phosphines usually leads to the formation of the corresponding imides [1]. The conversions of primary and secondary phosphines have not been studied as extensively. Phenylphosphine reacts with azides to give complex mixtures which do not yield pure products [2]. Diethylphosphine reacts with phenyl azide through intermediate diethylphosphonous acid anilide to give the imidophosphonate [3].

We studied the reaction of 2,4,6-triisopropyl-1,3,5-dioxaphosphorinane with phenyl azide and isolated a product with $\delta^{31}P = -8$ and -24 ppm. The intensities of these signals varied depending on the reagent ratio



The formation of products (I), (II) and (III) might have been expected. The IR spectrum of the compound obtained did not have a band at 2300 cm^{-1} characteristic for P—H bond stretching but has bands at 3180 and 3315 cm^{-1} in the N—H bond stretching region, indicating isomerization of (I) and migration of a proton from phosphorus to nitrogen. Analogous behavior was proposed for diethylphenylphosphine [3]. Compounds (II) and (III) may have stereoisomers with different orientation of the substituents at the phosphorus atom as found for 2,4,6-triisopropyl-1,3,5-dioxaphosphorinane [4, 5]. The product with a strong signal at -24 ppm and weak signal at -8 ppm corresponds in elemental analysis to (II). Its derivatives and model compounds were obtained to confirm this hypothesis.

Compound (II) reacts with H_2O_2 in methanol to form a crystalline product with $\delta^{31}P$ 22 ppm and IR spectrum with strong stretching bands at 1090 cm^{-1} (P=O) and 3080 cm^{-1} (NH). The structure assigned on the basis of elemental analysis was 5-oxo-5-phenylamino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (IV). The reaction mixture obtained by heating (II) with sulfur at 130°C showed (IV) with $\delta^{31}P$ 22 ppm and the products of sulfur addition with $\delta^{31}P$ 45 and 52 ppm. Chromatography of this mixture on silica gel gave a crystalline product with $\delta^{31}P$ 45 ppm and IR bands at 760 cm^{-1} (P=S) and 3260 cm^{-1} (NH). The elemental analysis permitted assignment of the structure of 5-thio-5-phenylamino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (V).

Model compounds for (II) and its derivatives are 5-amino-1,3,5-dioxaphosphorinanes and their derivatives. 5-Diethylamino-, 5-piperidino- and 5-morpholino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinanes (VI)-(VIII) were obtained by the reaction of 5-chloro-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane with diethylamine, piperidine, and morpholine. Products (IV)-(VIII) are yellow, readily oxidized compounds with $\delta^{31}P = -24$, -24, and 26 ppm, respectively, which are similar to the value for (II). The starting 5-chloro-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane is a mixture of two stereoisomers [5], whose separation is complicated by the presence of hydrochloride salts of amines. Thus, these stereoisomers were identified as their derivatives.

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TABLE 1. Dipole Moments of (IX), (X), and (XI)

Compound	α*	γ*	μ_{exp}, D	μ_{calc}, D	
				P=S_a	P=S_e
(IX)	9,0478	0,2514	3,90	6,15	3,44
(X)	6,5360	0,3094	3,34	6,18	3,45
(XI)	3,0695	0,0031	3,14	5,34	3,57

* Coefficients of the calculation equations.

The reaction of (VI)-(VIII) with sulfur at 140°C yields 5-thio-5-diethylamino-, 5-thio-5-piperidino-, and 5-thio-5-morpholino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinanes (IX)-(XI) which were separated by column chromatography on silica gel ($\delta^{31}P$ = 48, 50, and 44 ppm, respectively). As in the case of P(III), a change in the substituent at P(IV) does not produce any significant shift in $\delta^{31}P$ and the chemical shifts of these compounds are similar to that observed for (V).

The reaction of 5-oxo-5-chloro-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane with piperidine and morpholine yields 5-oxo-5-piperidino- and 5-oxo-5-morpholino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinanes (XII) and (XIII) with $\delta^{31}P$ 18 and 16 ppm, respectively, which are close to that observed for (IV). This is further evidence in support of the assignment of structure (II).

Treatment of (VI) with excess phenyl azide yields 5-diethylamino-5-phenylimino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (XIV). A pure sample isolated by column chromatography on silica gel has $\delta^{31}P = -5$ ppm and an IR band at 1390 cm^{-1} characteristic for the P=N bond [6].

A correlation of the data for the model compounds and (IV) and (V) permits assignment of the signals in the ^{31}P NMR spectrum of the products of the reaction of 2,4,6-triisopropyl-1,3,5-dioxaphosphorinane with phenyl azide. In the case of equivalent amounts of the reactants or a slight excess of phenyl azide, we largely obtain the product of the addition of one phenyl azide molecule (II) with $\delta^{31}P = -24$ ppm. In the case of excess phenyl azide, (III) is formed with $\delta^{31}P = -8$ ppm. This product could not be isolated as a pure compound.

The dipole moment method was used to determine the structures of (IX)-(XI). The dipole moment calculation was carried out for the two chair forms by analogy with the method of Gololobov et al. [6]. The cyclic bond parameters and molecular geometry of 1,3,5-dioxaphosphorinane were taken as in the work of Gololobov et al. [6]. An intermediate value of 3.65 D was taken for the dipole moment of the highly polar and electron-labile thiophosphoryl group which is between the dipole moments for the environment at P(IV): $C^3P=S$ and $N^3P=S$ [7, 8]. The moment of the N→P bond (0.25 D) was calculated previously from the dipole moment of a bicyclic derivative. In accord with our previous work [9], the dipole moment of the morpholine ring is 0.81 D and it is aligned along the bisector of the CNC angle toward the oxygen atom. The results obtained are given in Table 1 and indicate predominance of the isomer with equatorial orientation of the thiophosphoryl group.

Compounds (VI), (VIII), and (IX) were obtained from the mixture of stereoisomers of 5-chloro-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane under thermodynamic control (traces of acid). Compounds (X)-(XII) are also the products of thermodynamic control. Thus ^{31}P NMR spectroscopy and the dipole moment measurements indicate that the equilibrium of these compounds as well as of (II) and (IV) are almost entirely shifted toward the stereoisomer with axial orientation of the amino group.

A study of the equilibrium of the stereoisomers of 5-phenyl-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane and its sulfide [11] indicated that the form with axial orientation of the phenyl group accounts for 22% of the mixture in the case of P(III) but is absent in the case of P(IV) (which has 50% twist form and 48% of the stereoisomer in the chair form with equatorial orientation of the phenyl group). The replacement of the phenyl group by a methyl group at P(III) does not affect the equilibrium [4]. For comparison, we determined the position of the equilibrium of 5-methyl-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane sulfide, whose synthesis was described in our previous work [4]. The equilibrium was achieved in 12 h upon heating in benzene at 80°C in the presence of p-toluenesulfonic acid (Fig. 1). The twist form and the stereoisomer in the chair conformation with equatorial orientation of the methyl group are found in 1:1 ratio. As in the case of P(III), the replacement of the phenyl group by methyl for P(IV) does not affect the equilibrium.

We should note the pronounced difference in the conformational behavior of the phenyl and methyl groups relative to amino groups, which are similar to the chlorine atom. The equilibrium of the stereoisomers of

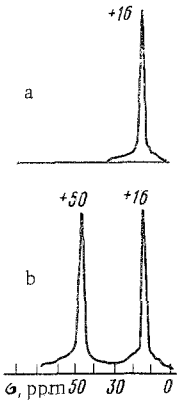

Fig. 1. ^{31}P NMR spectra of 5-methyl-5-thio-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane in benzene: a) prior to isomerization and b) after isomerization.

5-chloro-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane and its sulfide [5] is also shifted toward the form with axial orientation of the substituent. The axial preference of the chlorine atom is attributed to a weakening of the steric interactions with the isopropyl groups relative to the phenyl group [5].

As proposed by Hoth and Vetter [12], the oxidative imination of compounds with P(III) is independent of substituent steric effects. Indeed, the reaction of phenyl azide with 5-phenyl-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane, which is a mixture of three stereoisomers, yields a mixture of three stereoisomers of 5-phenyl-5-phenylamino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane with $\delta^{31}P$ +8, −16, and −22 ppm.

EXPERIMENTAL

The ^{31}P NMR spectra were taken on a YaMR-KGU-4 spectrometer at 10.2 MHz. The dipole moments were determined in benzene at 25°C.

5-Phenylamino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (II). A sample of 1.5 g (0.12 mole) freshly distilled phenyl azide was added with cooling in an argon atmosphere to 3 g (0.12 mole) 2,4,6-triisopropyl-1,3,5-dioxaphosphorinane. After cessation of nitrogen liberation, the excess phenyl azide was removed in vacuum. The product was a thick yellow oil with $\delta^{31}P = -8$ and −24 ppm. IR spectrum (ν, cm^{-1}): 3180, 3315 (NH). Found: C, 66.59; H, 9.60; P, 9.57; N, 4.39%. Calculated for $C_{18}H_{30}PNO_2$: C, 66.87; H, 9.28; P, 9.59; N 4.33%.

5-Oxo-5-phenylamino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (IV). Hydrogen peroxide was added dropwise with cooling to a solution of 2 g (II) in 10 ml abs. methanol until the completion of the exothermic reaction. The crystalline precipitate was filtered and recrystallized from methanol−DMSO to give a quantitative yield of (IV), mp 228°C, $\delta^{31}P$ 22 ppm (DMSO). Found: C, 63.61; H, 9.03; P, 8.80; N, 4.15%. Calculated for $C_{18}H_{30}PO_3N$: C, 63.71; H, 8.84; P, 9.14; N, 4.12%.

5-Thio-5-phenylamino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (V). Excess sulfur was added to a solution of 2.5 g (II) in 10 ml abs. benzene and the reaction mixture was heated at 130°C until the completion of the reaction, which was monitored by ^{31}P NMR spectroscopy. A pure sample was isolated by chromatography on silica gel with 40:1 petroleum ether−ether eluent, mp 134°C, $\delta^{31}P$ 45 ppm (benzene). Found: 60.87; H, 8.43; P, 9.15; N, 4.10%. Calculated for $C_{18}H_{30}PO_2NS$: C, 60.84; H, 8.45; P, 8.73; N, 3.94%.

5-Diethylamino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (VI). A solution of 10.2 g (0.04 mole) 5-chloro-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane in 25 ml abs. ether was added dropwise to 5.47 g (0.08 mole) diethylamine in 100 ml abs. ether. At the completion of the addition, the reaction mixture was stirred for 1.5 h at reflux. The precipitate was filtered, twice washed with ether and dried in vacuum. All the operations were carried out in an argon atmosphere. The yield was 5 g (43%), bp 107°C (0.5 mm), n_D^{20} 1.4665, $\delta^{31}P$ 24 ppm. Found: P, 10.14; N 3.95%. Calculated for $C_{16}H_{34}PO_2N$: P, 10.23; N, 4.62%.

5-Thio-5-diethylamino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (IX). A sample of 2.5 g (VI) was heated for 1 h with excess sulfur in an argon atmosphere at 120-140°C bath temperature. The reaction was monitored by ^{31}P NMR spectroscopy. A pure sample was isolated by chromatography on silica gel using 40:1 petroleum ether−ether eluent. The yield was 0.4 g (15%), n_D^{20} 1.4996, $\delta^{31}P$ 48 ppm. Found: C, 56.79; H, 9.92; P, 9.02; N, 4.06%. Calculated for $C_{16}H_{34}PO_2NS$: C, 57.31; H, 10.15; P, 9.25; N, 4.17%.

5-Thio-5-piperidino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (X). A sample 5.5 g (0.025 mole) 5-chloro-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane was added dropwise with cooling and stirring in an argon atmosphere to 4.5 g (0.05 mole) piperidine in 100 ml abs. ether. The reaction mixture was stirred for 3 h at reflux. The precipitate was separated and the ether was removed in vacuum. The yellow oil obtained (VII) ($\delta^{31}P$ 24 ppm) was heated for 1 h with excess sulfur in an argon atmosphere at 140°C bath temperature. The reaction was monitored by ^{31}P NMR spectroscopy. A pure sample was separated by chromatography on silica gel with 40:1 petroleum ether–ether eluent. The yield was 1.6 g (25%), mp 83.5°C, $\delta^{31}P$ 50 ppm (benzene). Found: C, 58.50; H, 9.72; P, 8.80; N, 3.98%. Calculated for $C_{17}H_{34}PO_2NS$: C, 58.78; H, 9.79; P, 8.93; N, 4.03%.

5-Thio-5-morpholino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (XI). (VIII) and (XI) were obtained analogously to (VII) and (X) by the reaction of morpholine with 5-chloro-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane and subsequent heating of the product with sulfur to yield 1.5 g (45%) (XI), mp 28°C, $\delta^{31}P$ 44 ppm. Found: C, 55.08; H, 9.10; P, 9.03; N, 3.99%. Calculated for $C_{16}H_{32}PO_3NS$: C, 55.01; H, 9.16; P, 8.88; N, 4.01%.

5-Oxo-5-piperidino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (XII). A sample of 0.59 g (0.006 mole) piperidine was added to a solution of 1 g (0.003 mole) 5-oxo-5-chloro-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane in 10 ml abs. benzene. The reaction mixture was heated for 1 h at reflux. The precipitate was filtered and the benzene was removed in vacuum. The product was recrystallized from acetonitrile. The yield was quantitative, $\delta^{31}P$ 18 ppm, mp 152°C. Found: P, 9.58; N, 4.22%. Calculated for $C_{17}H_{34}PO_3N$: P, 9.58; N, 4.47%.

5-Oxo-5-morpholino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (XIII). A sample of 0.67 g (0.008 mole) morpholine was added to a solution of 1.1 g (0.004 mole) 5-oxo-5-chloro-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane in 15 ml abs. benzene and the reaction mixture was heated for 1 h at reflux. The precipitate was filtered and the benzene was removed in vacuum. The product was recrystallized from acetonitrile. The yield was quantitative, mp 155°C, $\delta^{31}P$ 16 ppm. Found: P, 9.19; N, 4.50%. Calculated for $C_{16}H_{32}PO_4N$: P, 9.31; N, 4.20%.

5-Diethylamino-5-phenylimino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (XIV). Excess freshly distilled phenyl azide was added with cooling in an argon atmosphere to 1.5 g (VI). After cessation of nitrogen liberation, the excess phenyl azide was removed in vacuum. The residual oil was subjected to chromatography on silica gel with 4:1 petroleum ether–ether eluent. The yield was 0.6 g (20%), mp 67°C, $\delta^{31}P = -5$ ppm (ether). Found: C, 67.00; H, 9.90; P, 7.67; N, 7.19%. Calculated for $C_{22}H_{39}PO_2N_2$: C, 67.00; H, 9.89; P, 7.86; H, 7.10%.

5-Phenyl-5-phenylimino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane (XV). Excess freshly distilled phenyl azide was added to 3 g 5-phenyl-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane. The reaction was carried out with cooling and in an argon atmosphere. The yield was quantitative, mp 80-104°C, $\delta^{31}P = 8, -16,$ and -22 ppm, which corresponds to three stereoisomers. Found: C, 71.66; H, 8.33; P, 7.72; N, 3.13%. Calculated for $C_{24}H_{34}PO_2N$: C, 72.18; H, 8.52; P, 7.77; N, 3.51%.

CONCLUSIONS

1. The reaction of 2,4,6-triisopropyl-1,3,5-dioxaphosphorinane with phenyl azide yields 5-phenylamino-2,4,6-triisopropyl-1,3,5-dioxaphorinane and 5-phenylimino-5-phenylamino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane in yields depending on the reagent ratio.

2. The stereoisomer with axial orientation of the amino group predominates in the equilibrium of 5-phenylamine, 5-diethylamino-, 5-piperidino-, and 5-morpholino-2,4,6-triisopropyl-1,3,5-dioxaphosphorinane and their sulfides.

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REACTION OF PRIMARY ALIPHATIC AMINES IN OXIDATION SYSTEMS CONTAINING SODIUM PEROXYDISULFATE

E. I. Troyanskii, V. A. Ioffe, I. V. Svitan'ko, and G. I. Nikishin

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Among the large class of nitrogen-centered free radicals, aminyl radicals occupy an important place, in particular, because of their wide use during recent years in organic synthesis [1, 2]. Great progress has been made in the development of methods for the production of these radicals, based on the reactions of amines and some of their derivatives with free radicals [3], in redox systems [4], and under electrochemical conditions [5]. Among the reactions in oxidation systems, the transformations of secondary and tertiary amines has been studied most. The oxidation of primary amines has been studied much less [6-8].

In continuation of our studies on the reactions of nitrogen-centered amidyl and aminyl radicals in the $Na_2S_2O_8-CuCl_2$ and $K_3Fe(CN)_6-NaOH$ systems [9, 10], we studied the oxidation reactions of primary amines and aminyl radicals produced from them in systems containing sodium peroxydisulfate.*

It is known that during oxidation by peroxydisulfates in an alkaline medium catalyzed by Ag^+ ions, primary aliphatic amines transform into Schiff bases [12]. We found that nitriles (IIa-e), 2,3-dichloroalkanals (IIIa-e), alkanoic acids (IVa-e) and chloroalkanes (Va-e) are formed from amines $RCH_2CH_2NH_2$ (Ia-e) by the action of the $Na_2S_2O_8-CuCl_2$ system, using equimolar amounts of the substrate and the oxidation system components in water at 70-80°C (Table 1)

$$\underset{(Ia-e)}{RCH_2CH_2NH_2} \xrightarrow{Na_2S_2O_8-CuCl_2} \underset{(IIa-e)}{RCH_2CN} + \underset{(IIIa-e)}{RCCl_2CHO} + \underset{(IVa-e)}{RCH_2COOH} + \underset{(Va-e)}{RCH_2CH_2Cl}$$

$$R = C_3H_7\,(a),\ C_4H_9\,(b),\ C_5H_{11}\,(c),\ C_6H_{13}\,(d),\ C_7H_{15}\,(e)$$

The transformations of amines (I) into 2,2-dichloroalkanals (III) and chloroalkanes (V) are new reactions of oxidative substitution of the amino group in primary aliphatic amines. The contribution of different oxidation paths of amines (Ia-d) is practically independent of the length of the alkyl fragment in the amine. The main products are the corresponding nitriles (IIa-d) (see Table 1). During the oxidation of (Ie), the selectivity of the oxidation reactions decreases, and products (IIe)-(Ve) are formed in almost the same amounts. It is probable that this is due to a change in the reaction conditions as the result of the decreased solubility of (Ie) in water (compared with other amines studied), as manifested in the nonhomogeneous character of the reaction medium.

* Preliminary article, see [11].

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