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Dedicated to the 90th Anniversary of Academician M.G. Voronkov

The Products of Phosphorylation of *N,N*-Dialkylureas and Dialkylcyanamides with Phosphorus Pentachloride. NMR Spectroscopy Study

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Abstract—The study by ^{1}H and ^{31}P NMR spectroscopy has shown that phosphorylation of *N,N*-dimethylurea and diethylcyanamide with phosphorus pentachloride results in the formation of *N'*-(*N,N*-dialkylchloroformamidino)trichlorophosphonium hexachlorophosphorates where the positive charge of the organyltrichlorophosphonium cation is delocalized over the system of the multiple bonds with participation of the lone electron pair of the nitrogen atom. Bis-*N'*-(*N,N*-dialkylchloroformamidino)dichlorophosphonium hexachlorophosphorates, dichlorides of *N,N*-dialkylchloroformamidinophosphonic and thiophosphonic acids are synthesized where the conjugation of the phosphorus-containing substituent with the chloroformamidinium part of the molecules is retained. Organyltetrachlorophosphoranes based on *N,N*-dimethylurea and diethylcyanamide exist in polar and nonpolar solvents as orhanyltrichlorophosphonium chlorides.

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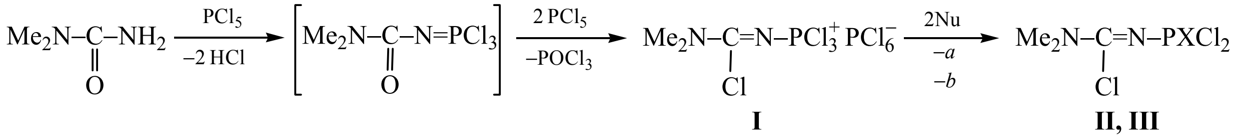
It is known that under the action of phosphorus pentachloride alkyl(aryl)ureas are converted either into *N*-dichlorophosphoryl-*N'*-alkyl(aryl)chloroformamidines [1], or the derivatives of urea containing the trichlorophosphazo group [2]. Earlier it was found that phosphorylation of unsubstituted urea with phosphorus pentachloride gave rise to 1-trichlorophosphazo-1-chloro-2-dichlorophosphoryl-2-azaethene [3] rather than bis(trichlorophosphazo)derivative as described in [4].

In the present work, we have found that *N,N*-dimethylurea is phosphorylated with phosphorus pentachloride with the formation of *N'*-(*N,N*-dimethylchloroformamidino)trichlorophosphonium hexachlorophosphorate (**I**), which is readily separated from the reaction mixture as a crystalline precipitate.

In the ^{31}P NMR spectrum of compound **I** we have observed an unusual resonance of the phosphorus atom of the trichlorophosphonium cation at δ_P 25.7 ppm instead of its conventional resonance range 80–100 ppm [5]. The observed location of the signal in the spectrum is more typical for the trichlorophosphazo compounds $R–N=PCl_3$.

When treated with sulfur dioxide, compound **I** is easily converted into *N'*-dichlorophosphoryl-*N,N*-dimethylchloroformamidine (**II**), which is not typical for phosphazo compounds [6]. Complex salt **I** also readily reacts with hydrogen sulfide being converted into *N'*-dichlorothiophosphoryl-*N,N*-dimethylchloro-formamidine (**III**). Such a behavior of compound **I** is indicative of the presence of a positive charge on the

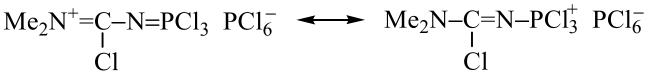


$$Me_2N\text{–}\underset{\underset{O}{\|}}{C}\text{–}NH_2 \xrightarrow[-2\,HCl]{PCl_5} \left[Me_2N\text{–}\underset{\underset{O}{\|}}{C}\text{–}N{=}PCl_3\right] \xrightarrow[-POCl_3]{2\,PCl_5} \underset{\mathbf{I}}{Me_2N\text{–}\underset{\underset{Cl}{|}}{C}{=}N\text{–}PCl_3^+\,PCl_6^-} \xrightarrow[-a \atop -b]{2Nu} \underset{\mathbf{II,\,III}}{Me_2N\text{–}\underset{\underset{Cl}{|}}{C}{=}N\text{–}PXCl_2}$$

II, Nu = SO_2, X = O, *a* = 2 $SOCl_2$, $POCl_3$; **III**, Nu = H_2S, X = S, *b* = $PSCl_3$, 4HCl.

($NPCl_3$) group, whereas the trichlorophosphazo group is electroneutral.

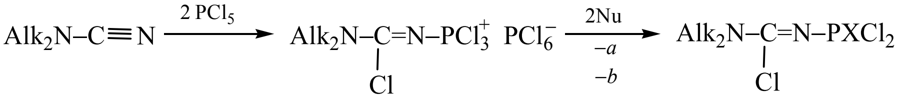
The reason for the upfield shift of the resonance signal of the phosphorus atom of compound **I** is, apparently, the delocalization of the positive charge due to direct polar conjugation of the lone electron pair (LEP) of the nitrogen atom of the dimethylamino group with the trichlorophosphonium cation.



$$\mathrm{Me_2N^+{=}\underset{\displaystyle Cl}{C}{-}N{=}PCl_3\ PCl_6^-} \longleftrightarrow \mathrm{Me_2N{-}\underset{\displaystyle Cl}{C}{=}N{-}PCl_3^+\ PCl_6^-}$$

The structure of compound **I** must be similar to that of the products formed by the addition of phosphorus pentachloride to dialkylcyanamides [7].

Since [7] does not contain the data on the NMR spectra of synthesized compounds, we have synthesized *N'*-(*N,N*-diethylchloroformamidino)trichloro-phosphonium hexachlorophosphorate (**IV**) by the action of phosphorus pentachloride on diethylcyanamide. The modification of the reaction conditions as compared to those recommended in [7] (the phosphorylation was performed under homogeneous conditions) allowed us doubling the yield of compound **IV**.



$$\mathrm{Alk_2N{-}C{\equiv}N} \xrightarrow{2\,\mathrm{PCl_5}} \underset{\textbf{IV}}{\mathrm{Alk_2N{-}\underset{\displaystyle Cl}{C}{=}N{-}PCl_3^+\ PCl_6^-}} \xrightarrow[\substack{-a\\-b}]{2\mathrm{Nu}} \underset{\textbf{V, VI}}{\mathrm{Alk_2N{-}\underset{\displaystyle Cl}{C}{=}N{-}PXCl_2}}$$

IV **V, VI**

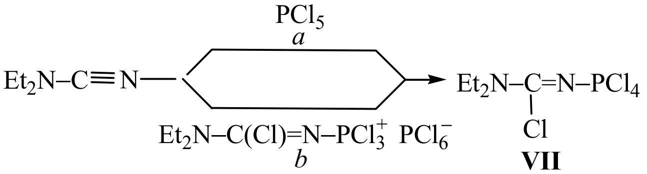
Alk = Et; **V**, Nu = SO_2, X = O, *a* = 2 $SOCl_2$, $POCl_3$; **VI,** Nu = H_2S, X = S, *b* = $PSCl_3$, 4 HCl.

Spectral characteristics of compound **IV** and its derivatives **V, VI** presented in the Table are close to the corresponding characteristics of dimethylchloroformamidinotrichlorophosphonium hexachlorophosphorate **I**, *N'*-dichlorophosphoryl- and *N'*-dichlorothiophosphoryl-*N,N*-dimethylchloroformamidines **II** and **III**, which proves the identical structure of the products of phosphorylation of dimethylurea and dialkylcyanamides.

Another reason for the upfield shift of the resonance signal of the phosphorus atom of compound **IV** is the delocalization of the positive charge due to the direct polar conjugation of the LEP of the nitrogen atom of the dimethylamino group with the trichlorophosphonium cation.

An additional evidence of the double bond between the nitrogen atom of the dimethylamino group and the chloroformamidine carbon atom is the splitting of the signals of the *N*-methyl and *N*-ethyl groups in the ^1H NMR spectra, which is indicative of their nonequivalence.

It was shown that the variation of the ratio of dialkylcyanamide and phosphorus pentachloride makes it possible to obtain not only complex salts but also organyltetrachlorophosphoranes **VII** (route *a*) [8]. It was also suggested to prepare compounds **VII** by the treatment of dialkylcyanamides with the corresponding organyltrichlorophosphonium hexachlorophosphorate (route *b*).



$$\mathrm{Et_2N{-}C{\equiv}N} \xrightarrow[\substack{\mathrm{Et_2N{-}C(Cl){=}N{-}PCl_3^+\ PCl_6^-}\\ b}]{\substack{\mathrm{PCl_5}\\ a}} \mathrm{Et_2N{-}\underset{\displaystyle Cl}{C}{=}N{-}PCl_4}$$

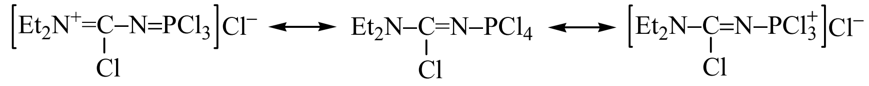
VII

Parameters of NMR spectra of phosphorylation products obtained from *N,N*-dimethylurea, *N,N*-diethylcyanamide, and their derivatives $Alk_2N–C(Cl)=N–R$

Compound	Alk	R	δ_P, ppm	δ_H, ppm
I	Me	PCl_3^+ PCl_6^-	25.7 –297.0	3.62 3.68
II	Me	$POCl_2$	–0.6[a]	3.15 3.21
III	Me	$PSCl_2$	44.2	
IV	Et	PCl_3^+ PCl_6^-	25.0 –296.5	1.24[b] 3.81[c]
V	Et	$POCl_2$	–0.5[d] –2.2[f]	1.21[e] 3.56[g]
VI	Et	$PSCl_2$	43.1	
$Et_2N–C{\equiv}N$	δ_H, ppm: 1.21 t (CH_3, $^3J_{HH}$ 7.4 Hz), 2.99 q (CH_2, $^3J_{HH}$ 7.9 Hz)			

[a] In $CDCl_3$. [b] Two triplets: 1.26 and 1.21 ppm (CH_3, $^3J_{HH}$ 7.2 Hz). [c] Two overlapped quartets (CH_2, J_{HH} 7.3 Hz). [d] In nitromethane. [e] Two triplets: 1.23 and 1.18 ppm (CH_3, $^3J_{HH}$ 7.4 Hz). [f] In deuterobenzene. [g] Two overlapped quartets (CH_2, J_{HH} 7.3 Hz).

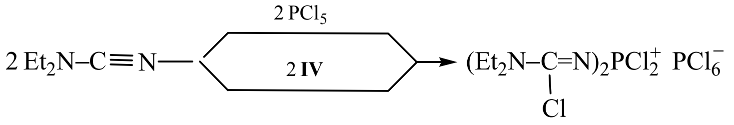
However, we failed to isolate tetrachlorophosphorane **VII** using the procedure described for its preparation in [7]. An atempt to synthesize the phosphorane by route *a* led to the formation of two compounds. The ^{31}P NMR spectrum of the products of the reaction obtained by the addition to a stirred suspension of phosphorus pentachloride in dichloroethane of the equimolar amount of diethylcyanamide contains two singlets of approximately equal intensity at δ_P 25.3 and 4.0 ppm The observed singlets resonate in the field, which is not typical for compounds of pentacoordinate phosphorus, the low-field signal being coincident with the value of the chemical shift of trichlorophosphonium cation of complex salt **IV**. Apparently, the low-field signal belongs to compound **VII**, which, unexpectedly, is easily ionized and exists in solutions not as a phosphorane but as an ion pair. The structure of this ion pair can be represented as a mesomeric form between the resonance structure **VIIA** and **VIIB** with delocalized positive charge as in compounds **I** and **IV**.



$$\left[\mathrm{Et_2N^+{=}\underset{\displaystyle Cl}{C}{-}N{=}PCl_3}\right]\mathrm{Cl^-} \longleftrightarrow \mathrm{Et_2N{-}\underset{\displaystyle Cl}{C}{=}N{-}PCl_4} \longleftrightarrow \left[\mathrm{Et_2N{-}\underset{\displaystyle Cl}{C}{=}N{-}PCl_3^+}\right]\mathrm{Cl^-}$$

VIIA **VII** **VIIB**

It turned out that the ratio of the intensities of the signals can be changed by performing the reaction under homogeneous conditions and with the inverse order of mixing of the reagents. Thus, addition of the solution of phosphorus pentachloride in benzene to the benzene solution of diethylcyanamide (at the equimolar amounts of the reagents) led to a product having only one signal in the ^{31}P NMR spectrum at δ_P 4.0 ppm. Apparently, this signal corresponds to compound **VIII** having two organic substituents bound to phosphorus.



$$2\,\mathrm{Et_2N{-}C{\equiv}N} \xrightarrow[2\,\mathbf{IV}]{2\,\mathrm{PCl_5}} \mathrm{(Et_2N{-}\underset{\displaystyle Cl}{C}{=}N)_2PCl_2^+\ PCl_6^-}$$

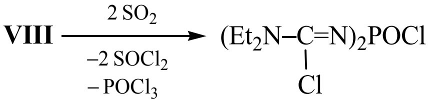
VIII

Such a sensitivity of the reaction to variation of the ratio and the order of mixing of the reagents is typical, for example, for aromatic and tertiary nitriles [8] and can be ascribed to the easy addition of the organyltrichlorophosphonium cation to the nitrile group containing a donor substituent. We believe that this underlie the failure of our atempt to synthesize the phosphorane by route *b* [7]. In this event in the ^{31}P spectrum of the product of the reaction of diethylcyanamide and complex salt **IV** the signal of trichlorophosphonium cation (δ_P 25.4 ppm) disappears, and only the singlets at δ_P (ppm) 296.4 ($\mathrm{PCl_6^-}$) and 4.0 ($\mathrm{Org_2PCl_2^+}$) are observed. The signals characteristic of the pentacoordinate phosphorus atom are lacking.

The position of the signals remains practically unchanged when recording the NMR spectra in highly ionizing solvent ($\mathrm{C_6D_5NO_2}$: δ_P 4.0 ppm) or in low polar solvents (mixture of benzene with dichloroethane: δ_P 3.0 ppm). This is not typical for chlorophosphoranes and suggests the stability of the ion pair $\mathrm{Org_2PCl_2^+\ PCl_6^-}$.

An additional factor that hampered interpretation of the results of [7] is that the purity of compound **VII** has been controlled using the elemental analysis. However, close values of the calculated and experimentally obtained mass fractions of chlorine presented in the paper cannot guarantee the individuality of compound **VII**, since for compounds **VII** and **VIII** the mass fractions of the elements are the same.

When treated with sulfur dioxide, compound **VIII** is converted into bis(*N,N*-diethylchloroformamidino) chlorophosphorate **IX**, which is characterized by a singlet at δ_P 0.3 ppm in the ^{31}P NMR spectrum.



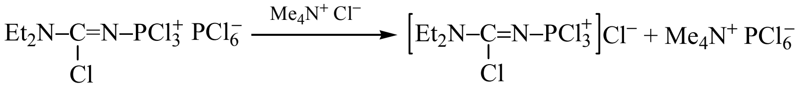
$$\mathbf{VIII} \xrightarrow[\substack{-2\,\mathrm{SOCl_2}\\ -\,\mathrm{POCl_3}}]{2\,\mathrm{SO_2}} \mathrm{(Et_2N{-}\underset{\displaystyle Cl}{C}{=}N)_2POCl}$$

IX

Compounds **V** and **IX** have different composition, therefore, the purity and individuality of compound **VIII** can be indirectly proved by the data of elemental analysis of compound **IX**, which is practically quantitatively formed from complex salt **VIII**. The data of elemental analysis of compound **IX** were consistent with the structure we suggested.

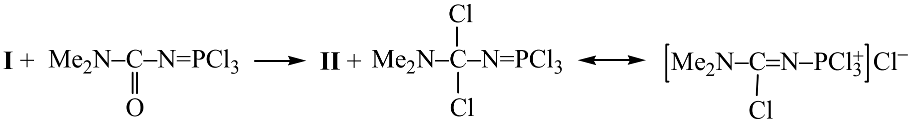
It is known that tetraalkylammonium chlorides can be used for the conversion of organyltrichlorophosphonium hexachlorophosphorates into organyltetrachlorophosphoranes [9]. This method turned out to be the most suitable for the synthesis of compound **VII** from complex salt **IV**. Compound **I** reacts with tetraalkylammonium chloride similarly.

The formed phosphorane **VII** is poorly soluble in benzene because it is readily ionized. Compound **VII** can be extracted from the reaction mixture with dichloroethane. The ^{31}P NMR spectrum of the extract contains a single signal at δ_P 25.2 ppm characteristic of trichlorophosphonium cation. The spectrum of the solution of the crystalline residue in nitromethane contains the single singlet at δ_P –296.2 ppm belonging to tetramethylammonium hexachlorophosphorate **X**.



$$\underset{\textstyle \mathbf{IV}}{Et_2N{-}\underset{\underset{\textstyle Cl}{|}}{C}{=}N{-}PCl_3^+\,PCl_6^-} \xrightarrow{Me_4N^+\,Cl^-} \underset{\textstyle \mathbf{VII}}{\left[Et_2N{-}\underset{\underset{\textstyle Cl}{|}}{C}{=}N{-}PCl_3^+\right]Cl^-} + \underset{\textstyle \mathbf{X}}{Me_4N^+\,PCl_6^-}$$

We have found that the results of phosphorylation of *N,N*-dimethylurea depend on the conditions of the process. The maximum yield of compound **I** is achieved when finely powdered phosphorus pentachloride and *N,N*-dimethylurea are mixed in benzene. If dimethylurea reacts with the benzene solution of phosphorus pentachloride, the fraction of diorganyldichlorophosphonium hexachlorophosphorate substantially increases. In both cases, according to the NMR spectroscopy data, *N*-dichloro-phosphoryl-*N'*,*N'*-dimethylchloroformamidine (**II**) is formed as a side product, apparently, by the following scheme.



$$\mathbf{I} + Me_2N{-}\underset{\underset{\textstyle O}{\|}}{C}{-}N{=}PCl_3 \longrightarrow \mathbf{II} + Me_2N{-}\overset{\overset{\textstyle Cl}{|}}{\underset{\underset{\textstyle Cl}{|}}{C}}{-}N{=}PCl_3 \longleftrightarrow \left[Me_2N{-}\underset{\underset{\textstyle Cl}{|}}{C}{=}N{-}PCl_3^+\right]Cl^-$$

Therefore, the reaction of *N,N*-dimethylurea with phosphorus pentachloride leads to compounds whose structure is similar to that of the product of phosphorylation of dialkylcyanamides. The synthesized organyltrichlorophosphonium hexachlorophosphorates are characterized by an unusual position of the resonance signal of the phosphorus atom in the NMR spectrum caused by delocalization of the positive charge over the system of multiple bonds with the participation of the LEP of the nitrogen atom. In the reaction of phosphorus pentachloride or organyltrichlorophosphonium hexachlorophosphorates with dialkylcyanamides, bis-*N*-(*N'*,*N'*-dialkylchloroformamidino)dichlorophosphonium hexachlorophosphorates are formed. Organyltetrachlorophosphoranes prepared by the action of tetramethylammonium chloride on *N*-(*N'*,*N'*-dimethylchloro-formamidino)trichlorophosphonium hexachlorophosphorates **I** and **IV** are readily ionized and exist in the form of organyltrichlorophosphonium chlorides.

EXPERIMENTAL

^{1}H and ^{31}P NMR spectra of the studied compounds were registered on a Bruker AV 400 spectrometer (400.13 and 161.98 MHz) in nitrobenzene-d_5 (**I, IV**) or $CDCl_3$ (**II, V**). 75% aqueous solution of H_3PO_4 was used as an external standard for recording ^{31}P NMR spectra. IR spectra were taken in the range 4000–400 cm^{-1} on a Specord IR-75 spectrometer.

***N*-(*N'*,*N'*-Dimethylchloroformamidino)trichlorophosphonium hexachlorophosphorate (I).** To a vigorously stirred suspension of 28.4 g of finely powdered phosphorus pentachloride in 50 ml of benzene 3.4 g of ground *N,N*-dimethylurea was added. The dissolution of the precipitate is followed by evolution of hydrogen chloride. After some time light oil is separated, which on the next day crystallized. Crystals of **I** were separated from the solution, twice washed with anhydrous benzene, and dried in a vacuum. Light-green prisms from dichloroethane. Yield 12.5 g (66.4%).

***N*-(*N'*,*N'*-Diethylchloroformamidino)trichlorophosphonium hexachlorophosphorate (IV)**. To the solution of 10.6 g of phosphorus pentachloride in 75 ml of benzene at 15–20°C 2.0 g of diethylcyanamide in 10 ml of benzene was added dropwise at stirring. The formation of a crystalline precipitate starts even in the process of mixing of the reagents. On the next day the precipitate was filtered off, washed twice with anhydrous benzene, and dried in a vacuum. Yield of compound **IV** 9.8 g (93.2%), white fine crystalline powder.

***N*-Dichlorophosphoryl-*N'*,*N'*-dimethylchloroformamidine (II)**. Through the suspension of 10.6 g of complex salt **I** in 10 ml of benzene cooled with a water bath, dry sulfur dioxide was bubbled until the precipitate was dissolved. The solvent and volatile compounds were removed in a vacuum, the residual yellowish oil was distilled in a vacuum. Yield 3.1 g (63.7%), colorless liquid, bp 142–145°C (0.1 mm Hg) {165–167°C (0.02 mm Hg) [8]}. IR spectrum, ν, cm^{-1}: 1620 (C=N), 1250 (P=O), 550 (P–Cl). Found, %: C 16.13; H 3.00; Cl 48.61; N 12.31; P 13.90. $C_3H_6Cl_3N_2OP$. Calculated, %: C 16.12; H 2.71; Cl 47.61; N 12.54; P 13.86.

***N*-Dichlorophosphoryl-*N'*,*N'*-diethylchloroformamidine (V)**. Through the suspension of 4.0 g of complex salt **IV** in 10 ml of benzene cooled with a water bath, dry sulfur dioxide was bubbled until the crystals were dissolved. After removal of volatile compounds in a vacuum the residue crystallized. Yield 1.9 g (97.3%), white needles (hexane with addition of benzene), m.p. 77–79°C (74–75°C [8]). IR spectrum, ν, cm^{-1}: 1600 (C=N), 1270 (P=O), 530 (P–Cl). Found, %: C 24.80; H 5.22, Cl 41.74; N 10.51; P 11.72. $C_5H_{10}Cl_3N_2$ OP. Calculated, %: C 23.87; H 4.02; Cl 42.29; N 11.14; P 12.31.

***N*-Dichlorothiophosphoryl-*N'*,*N'*-dimethylchloroformamidine (III)**. To the suspension of 2.0 g of complex salt **I** in 10 ml of benzene dry hydrogen sulfide was passed. The precipitate gradually got softer, then solidified again. After drying in a vacuum, 0.7 g (71.2%) of compound **III** was obtained as greenish powder.

***N*-Dichlorothiophosphoryl-*N'*,*N'*-diethylchloroformamidine (VI)** was prepared similarly from 2.5 g of compound **IV**. Yield 1.2 g (92.4%). Viscous yellowish liquid.

***N*-(*N'*,*N'*-Diethylchloroformamidino)trichlorophosphonium chloride (VII)**. 4.0 g of complex salt **IV** and 0.85 g of finely powdered tetraalkylammonium chloride (dried in a vacuum) were mixed in 10 ml of benzene. The suspension was stirred for a day, the precipitate was filtered off. The precipitate was successively extracted with dry chloroform and dichloroethane. After removal of solvent from the combined extract 2.0 g (84%) of compound **VII** was obtained. Yellowish crystalline powder.

Bis-*N*-(*N'*,*N'*-diethylchloroformamidino)dichlorophosphonium hexachlorophosphorate (VIII). To the solution of 1.0 g of diethylcyanamide in 5 ml of benzene the solution of 2.1 g of phosphorus pentachloride in 15 ml of benzene was added dropwise at stirring and cooling with a water bath. During the mixing of the reagents a light yellowish oil is formed, which after 24 h was separated from the solution. After removal of volatile compounds the residue crystallized. Yield of compound **VIII** 2.6 g (83.1%). Greenish crystalline powder.

Using method [8, *a*], a mixture of compounds **VII** and **VIII** was obtained; using method [8, *b*], from 4.2 g of the complex salt and 0.8 g of diethylcyanamide, without reflux of the solution, after crystallization, compound **VIII** rather than tetrachlorophosphorane **VII** was obtained. Yield 3.1 g (62%).

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