CONCLUSIONS

1. The corresponding aluminum dialkyl chlorides were obtained by the reaction of aluminum trialkyls with $CuSO_4 \cdot 2HC1$ at 20° .

2. The corresponding monoalkylaluminum dichlorides and dialkylaluminum chlorides are formed when the Gustavson complexes are reacted with a trialkylaluminum at $0-60^{\circ}$.

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DECOMPOSITION OF CYCLIC AND LINEAR N-ACETYL-N-TRIMETHYLSILYL-

AMIDOPHOSPHITES

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While studying the reaction of N,N-bis(trimethylsilyl)acetamide (I) with trivalent phosphorus acid chlorides in solution at room temperature or using heat we either isolated or identified in the crude form both the cyclic and linear N-acetyl-N-trimethylsilylamidophosphites.

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 $(EtO)_2PCl + CH_3CON(SiMe_3)_2 \rightarrow (EtO)_2PNCOCH_3$ (I)
(II)

SiMe.

Thus, in the case of diethyl chlorophosphite the yield of diethyl N-acetyl-N-trimethylsilylamidophosphite (II) was 70%. The IR spectrum of (II) has the intense band of amido carbonyl at 1650 cm⁻¹. In the NMR spectrum of (II) the protons of the trimethylsilyl group appear as a singlet at 0.33 ppm, while the protons of the acetyl group appear as a doublet at 2.03 ppm, $^{4}J_{HP} = 3$ Hz. However, when the trivalent phosphorus acid chlorides are reacted with (I) at elevated temperatures, with removal of the Me₃SiCl by distillation, the end products are silyl phosphites. This is because the cyclic and linear N-acetyl-N-trimethylsilylamidophosphites that are formed in the first step undergo decomposition, which proceeds by the mechanism of a four-center rearrangement with the formation of the corresponding silyl phosphites and CH₃CN [1].

A convenient method was proposed by us previously [2], and then later also in [3], for the preparation of silyl phosphites by the reaction of acid phosphites with aminosilanes and aminosilazanes. However, this method is inconvient for the synthesis of cyclic silyl

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. 3, pp. 672-675, March, 1977. Original article submitted July 2, 1976.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise; without written permission of the publisher. A copy of this article is available from the publisher for \$7.50. phosphites, since the cyclic acids, as a rule, are thermally unstable. By starting with the appropriate acid chlorides and (I), the reaction discovered by us makes it possible to obtain in one step various cyclic and acyclic silyl phosphites in good yield (Table 1).



In the discussed reaction the decomposition of the phosphorus atom plays the role of the electrophilic center, and the ease of intramolecular substitution depends on the properties of the substituents at this center. In the case of the five-membered cycles the decomposition should go more easily than in the case of the acyclic derivatives with the same type of environment at the phosphorus atom, while in the case of the six-membered cycles this difference should be slight. The differential-thermal analysis data are given in Table 2, which confirm this postulation. If the acyclic silylamidophosphite (II) is thermally quite stable and can be purified by vacuum-distillation then 2-trimethylsiloxy-1,3,2-dioxaphospholane (VII) is formed and CH₃CN is distilled off in quantitative yield when 2-(N-acetyl-N-trimethylsily1amido)-1,3,2-dioxaphospholane (III) is heated. As was to be expected, dioxaphosphorinane (IV) occupies an intermediate position. As can be seen from Table 2, a quite distinct tendency to hinder the decomposition can be traced in the series of five-membered derivatives when the cyclic oxygen atoms are replaced by nitrogen atoms, which are more effective π -donors. The N-silylated acetamides cannot be obtained even in the crude form from pyracatechol chlorophosphite and 2-chloro-3-acety1-4,5-benzo-1,3,2-oxazaphospholane in ether using cooling. The ³¹P NMR spectra record the formation of the 2-siloxy derivatives, which are decomposition products. This is due to the increased electrophilicity of the phosphorus atom in the given compounds. It is known that the 2-substituted 4,5-benzo-1,3,2-dioxa-(oxaza)phospholanes, when compared with other trivalent phosphorus derivatives, react more easily with dienes [4].

In harmony with the proposed scheme, the decomposition of Nsilylated acetamido derivatives should be hindered by adding electrondonor substituents to the phosphorus atom. Actually, the decomposition is sharply hindered when going from (II) to diethyl N-acetyl-Ntrimethylsilylamidophosphinite. The latter does not decompose when heated to 200°. However, in reactions with nucleophilic reagents, for example (I), alcohols, etc., where the phosphorus atom, the same as in the decomposition reaction, plays the role of an electrophilic center, diethylchlorophosphine proved to be more reactive than diethyl chlorophosphite. The abnormally high reactivity of diethylchlorophosphine was also mentioned in the reaction of trivalent phosphorus chlorides with acetals [5]. The authors postulated that in this case a qualitative change occurs in the nature of the reagent and the diethylchlorophosphine plays the role of an nucleophile, due to an increase in the p-character of the free electron pair of phosphorus. The catalytic effect of HCl, which is always present in acid chlorides, must be taken into account in these cases. The HCl protonates diethylchlorophosphine at low temperatures, which is recorded by the ³¹P NMR method. The creation of a positive charge on the phosphorus atom in the protonated form facilitates nucleophilic attack at this atom, with subsequent substitution and formation of the end products. The N-silylated amidophosphinites are efficient silylating agents, in which acid impurities are absent. Consequently, the manifestation of the electronic effect of alkyl substituents on the

TABLE 1. Silyl Phosphites RR'POSiMe₃

1,55

33,33 37,30 -49,06

«NO₃PS

5,31 4,30

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48,64

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Empirical formula

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Yield, %

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57 55 55,5 78,5

CH.

Р,

Calculated,

TABLE 2. Thermographic Parameters of Decomposition of N-Acetyl-N-trimethylsilylamidophosphites RR'PN(COCH₃)SiMe₃

Com-	R and R'	Т₀,	T _{max} ,
pound		°С *	℃†
(II)	R=R'=OEt	95	135
(III)	O(CH ₂) ₂ O	35	88
(IV)	O(CH ₂) ₃ O	52	128
(V)	O(CH ₂) ₂ NMe	70	130
(VI)	O(CH ₂) ₂ NPh	65	108

 ${}^{*}T_{o}$ is the temperature at which the exo peak starts. ${}^{\dagger}T_{max}$ is the maximum temperature of the exo peak.

process of nucleophilic substitution at the trivalent phosphorus atom can be observed on the example of their tendency to decompose.

EXPERIMENTAL

The ³¹P NMR spectra were taken on a KGU-4 NMR instrument at a frequency of 10.2 MHz, using 85% H₃PO₄ as the standard. The PMR spectra were recorded on a Varian T-60 instrument, using TMS as the internal standard. The thermographic study of the decomposition was run on equipment that consisted of a two-coordinate TsDS-021 potentiometer, an I-37 amplifier, a linear heating data unit, and a thermal block furnace. A Chromel—Alumel thermocouple was used. The heating rate was 2.5 deg/min. The experiments were run in glass Stepanov cups.

<u>Diethyl N-Acetyl-N-trimethylsilylamidophosphite (II).</u> A solution of 7.8 g of diethyl chlorophosphite and 10.2 g of N,N-bis(trimethylsilyl)acetamide (I) in 30 ml of benzene was heated for 1 h. After removing the solvent the residue was fractionally distilled in vacuo to give 8.8 g (70%) of amidophosphite (II), bp 97-98° (8 mm); $n_D^{2°}$ 1.444; $d_4^{2°}$ 0.9774. Found: C 42.60; H 8.72; P 12.02; Si 10.66%. C₉H₂₂NO₃PSi. Calculated: C 43.02; H 8.76; P 12.35; Si 11.15%.

Synthesis of Silyl Phosphites (VII)-(XI). The cyclic and linear silyl phosphites were obtained by heating equimolar amounts of the P(III) acid chlorides and disilylated acetamide (I) at 120-160°C for 1-2 h until the liberation of $(CH_3)_3$ SiCl and CH_3 CN ceased. The products were vacuum-distilled (see Table 1).

CONCLUSIONS

N-Acetyl-N-trimethylsilylamidophosphites when heated undergo decomposition to give the corresponding silyl phosphites, which decomposition is facilitated by adding electron-ac-ceptor substituents to the phosphorus atom.

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