# MECHANISM OF THE REACTION OF BIS(α-HYDROXYALKYL)PHENYL-PHOSPHINE SULFIDES WITH DIMETHYLFORMAMIDE DIMETHYLACETAL

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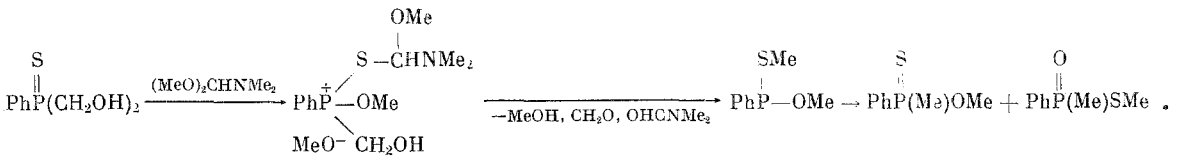
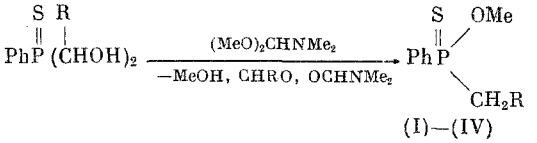
The reaction of bis(hydroxymethyl)phenylphosphine sulfide with dimethylformamide dimethylacetal leads to O-methyl methylphenylthiophosphinate [1]. It can be assumed that the reaction proceeds via the intermediate formation of the phosphonium salt, which decomposes with the cleavage of MeOH, $CH_2O$, $Me_2NCHO$, and O,S-dimethyl phenylthiophosphonite. When the last is acted on by $(MeO)_2CHNMe_2$, it isomerizes to O-methyl methylphenylthiophosphinate. The other route of the isomerization should lead to S-methyl methylphenylthiophosphinate. In the first case, the methyl at the P atom is taken from $(MeO)_2CHNMe_2$; in the second case, it is taken from the bis(hydroxymethyl)phenylphosphine sulfide. The transfer of the O atom of the hydroxyl group to the P atom in α-hydroxyalkylphosphonium compounds is well known [2]. The alkylating action of dimethylformamide acetals with the isolation of dimethylformamide has been described [3].



The O-derivatives of thioacids of phosphorus are usually obtained by the alkylation of the thioacids of phosphorus or their salts; these possess dual reactivity, and give the S-derivatives as the main reaction product [4]. The reaction route depends on the structure of the reagents and the conditions [5-8]. However, the reaction route could only be shifted in favor of the O-derivative by the reaction of the salts of dialkyl thiophosphoric acid with aromatic diazo compounds and the alkylation of the salts of monothioacids of phosphorus with alkyl tosylates in the solution of hexamethylphosphorotriamide [4, 9].

The variation of the substituents in the hydroxyalkyl groups of bis(α-hydroxyalkyl)-phenylphosphine sulfides was accomplished in the present work. Apart from bis(hydroxymethyl)-phenylphosphine sulfide, the following were taken as the initial compounds: bis(α-hydroxyethyl)-, bis(α-hydroxyisobutyl)-, and bis(α-hydroxybenzyl)phenylphosphine sulfides. Their reactions with $(MeO)_2CHNMe_2$ were started by heating. The reaction products were separated by chromatography on silica gel. The monitoring of the course of the reactions was performed using the $^{31}P$ NMR spectra. The reactions were completed after 30 min, and the signal of one product was observed in the spectra of the reaction mixtures. The structure of the O-methyl alkylphenylthiophosphinates (I)-(IV) was assigned to the products on the basis of the IR, $^1H$ NMR, and $^{31}P$ NMR spectral data.



R = H (I), Me (II), Pr-*i* (III), Bz (IV).

The absorption in the region of 3100-3700 $cm^{-1}$, which is characteristic of hydroxyl groups, is absent from the IR spectra of (I)-(IV). The values of the chemical shifts (CSs)

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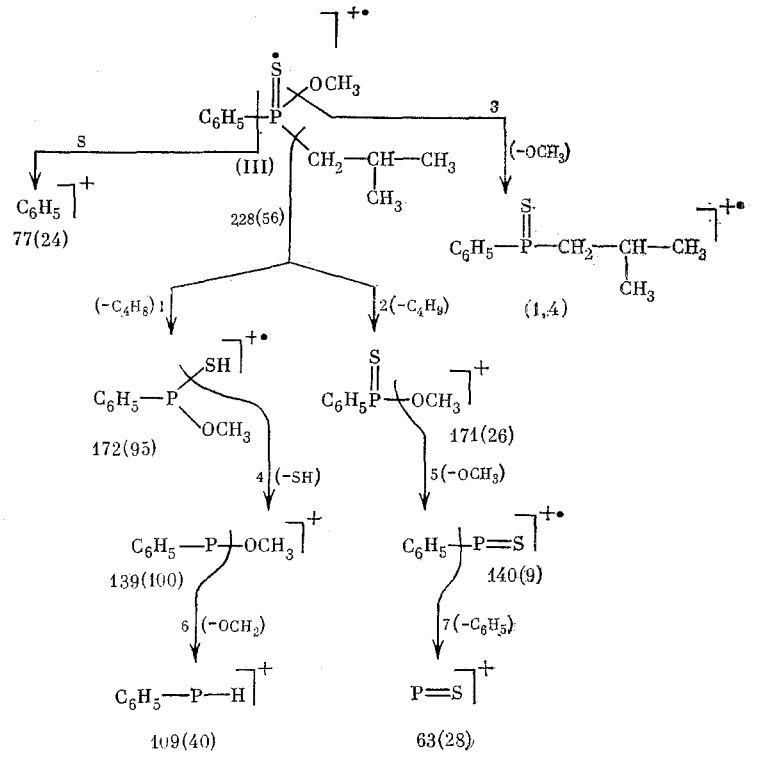
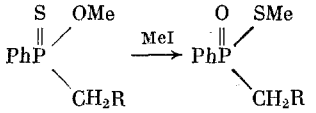
Scheme




of the signals in the $^{31}P$ NMR spectra indicate the nonidentity of (I)-(IV), and correspond with the thione isomers [10]. The values of the CSs of the signals of the methyl protons of (I)-(IV) in the PMR spectra clearly indicate the presence of a methyl group connected to an O atom [5]. The methyl group at the P atom of the thiophosphoryl group has the CS value of 1.88-1.95 ppm [11]. A signal with such a shift is observed in the PMR spectrum of (I). The refractive index of (I) agrees with the value in [12] for the thione isomer, and differs from the value in [13] for the thiol isomer.

The isomerization of (I) and (III) by the action of MeI was carried out, as described for (II) in [14], for the confirmation of the structure of (I)-(IV); the CSs in the $^{31}P$ and $^{1}H$ NMR spectra were determined. The complete conversion of the thione isomer to the thiol isomer was observed after 10 min at 150°C. In the case of (I), a signal at 40 ppm appeared in the $^{31}P$ NMR spectrum instead of the signal at 89 ppm. In the case of (III), the signal at 95 ppm was replaced by the signal at 45 ppm. In the PMR spectrum of the thiol isomer of (I), the CS of the methyl protons at the S atom equals 3.09 ppm; the corresponding CS at the P atom is 1.53 ppm. This is in accord with the data of [6].

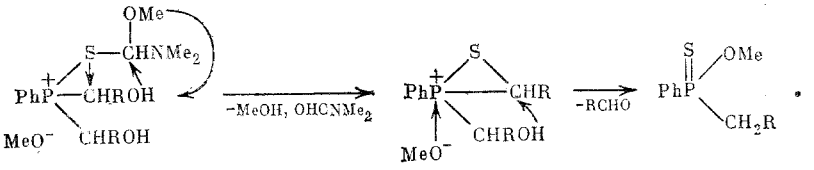



(I), (III)

The structure of the products of the reaction of bis(α-hydroxyalkyl)phenylphosphine sulfides with $(MeO)_2CHNMe_2$, which was obtained from the analysis of their IR, $^{1}H$ NMR, and $^{31}P$ NMR spectra, is fully confirmed by the data of the mass spectra of (I)-(IV) as well as O-methyl methylphenylselenophosphinate (V). In the mass spectra of (I)-(V), the peaks of the molecular ions are very intense owing to their stabilization by the phenyl ring. The substitution of the S atom by Se leads to an incrase in the intensity of the peaks of the molecular ions. Thus, the peak with the m/z 234 is the most intense one in the mass spectrum of (V), although it is caused by the compound with the content of the isotope $^{80}Se$ comprising 50%. Consequently, the total intensity of the peaks of the molecular ions for compound (V) comprises 200%. The elemental composition of the molecular ions, calculated from the precision-measured value of their mass, proved to be as follows: $C_8H_{11}O_1S_1P_1$ for (I), $C_9H_{13}O_1S_1P_1$ for (II), $C_{11}H_{17}O_1S_1P_1$ for (III), $C_{14}H_{15}O_1S_1P_1$ for (IV), and $C_8H_{11}O_1P_1Se_1$ for

(V). The route of the dissociative ionization with the breaking of the P–C bond and the loss of the R radical from the molecular ion was characteristic of the compounds $(C_6H_5)(R)\cdot P(O)OR_1$ [15]. The intense peaks of the $[M - CH_3]^+$ ion (40%) for (I), the $[M - C_2H_5]^+$ ion (41%) for (II), the $[M - C_4H_9]^+$ ion (14%) for (III), the $[M - CH_2C_6H_5]^+$ ion (100%) for (IV), and the $[M - CH_3]^+$ ion (17%) for (V) indicate the direct linkage of the indicated radicals to the phosphorus atom. The other main route of the dissociative ionization of (II) and (III) is also associated with the breaking of the P–C bond. However, the migration of a hydrogen atom of the radical R to the charged fragment thereby occurs, and the molecular ion loses a molecule of olefin. This process is dominant for (II) and (III). All the other intense peaks of the ions are explained by the further decomposition of the $[M - olefin]^+$ ion; the mass spectra of (II) and (III) are therefore very similar. The presence of the $OCH_3$ group at the P atom leads to the $[M - OCH_3]^+$ ions in the mass spectra of all the compounds; they are, however, of low intensity due to the competition of the decomposition of the molecular ions with the breaking of the P–C bond. The intense peaks are caused by the ions of the composition $[C_6H_5–P–OCH_3]$, $[C_6H_5P]$, $C_6H_5$, and $C_6H_5PS$, and correspond to the structure (I)-(V). The decomposition of the molecular ion of (III) is shown below as an example.

The isolation of O-methyl alkylphenylthiophosphinates in the reaction of bis(α-hydroxyalkyl)phenylphosphine sulfides with $(MeO)_2CHNMe_2$ shows that the reaction proceeds by the following path. The O atom of the hydroxyalkyl group of the phosphonium compound passes to the C atom of the acetal fragment prior to the cleavage of methanol and dimethylformamide. The closure of the five-membered ring favors the transfer. The resulting phosphonium salt is stabilized on account of the addition of the methoxide anion to the P atom, the addition of a proton to the C atom of the ring, and the separation of the aldehyde.




The transfer of the O atom of the hydroxyalkyl group to the C atom of the acetal fragment is dominant among the reactions considered.

## EXPERIMENTAL

The $^{31}P$ NMR spectra were recorded on the NMR-KGU-4 spectrometer at the frequency of 10.2 MHz with the noise suppression of the protons at the frequency of 24.3 MHz relative to 85% $H_3PO_4$. The PMR spectra were recorded on a Varian T-60 spectrometer at 34.5°C. The IR spectra were recorded on the UR-10 spectrometer at ~20°C. The mass spectra were obtained on the MX-1310 mass spectrometer with the resolving power of $1\cdot10^4$, the ionizing voltage of 50 V, the electron current of the collector at 30 mA, and the inlet temperature of 90°C. The registration and treatment of the mass spectra and the precision determination of the ion masses were accomplished using the complex MX-1310 system of information treatment. The relative accuracy (ΔM/M) of the determination of the ion masses was of the order of $1\cdot10^{-6}$.

O-Methyl Methylphenylthiophosphinate (I). This was obtained as in [1]. The yield was 30%. It had the $n_D^{20}$ 1.5757 and $\delta^{31}P$ 89 ppm. The PMR spectrum (δ, ppm) was as follows: 1.88 ($^2J_{PH}$ = 14 Hz) and 3.45 ($^3J_{PH}$ = 14 Hz) in $CCl_4$. The mass spectrum* (m/z) was as follows: 188 (8.0), 187 (16), 186 (100) $[C_8H_{11}O_1S_1P_1]$, 173 (2.1), 172 (3.7), 171 (40) $[C_7H_8O_1\cdot S_1P_1]$, 158 (4.8), 157 (9.2), 156 (83) $[C_7H_9S_1P_1]$, 155 (9.7), 142 (1.2), 141 $[C_6H_6S_1P_1]$, 140 (3.7) $[C_6H_5S_1P_1]$, 139 (16) $[C_7H_8O_1P_1]$, 139 (10) $[C_6H_4S_1P_1]$, 124 (13), 123 (17), 121 (9.8), 109 (30) $[C_6H_6P]$, 109 (7), 107 (11), 91 (19) $[C_7H_7]$, 78 (11) $[C_6H_6]$, 77 (40) $[C_6H_5]$, 63 (49) [PS], 51 (33), 47 (13) $[CH_3S]$, 47 (10) [PO], 45 (9.7), 39 (7.7), 31 (2.0).

O-Methyl Ethylphenylthiophosphinate (II). The mixture of 9.61 g (0.0418 mole) of bis-(α-hydroxyethyl)phenylphosphine sulfide and 4.98 g (0.0418 mole) of $(MeO)_2CHNMe_2$ was boiled for 30 min; it was chromatographed on silica gel with the 1:1 mixture of benzene–petroleum ether as the eluent. The yield was 2.13 g (25%); the product had the $\delta^{31}P$ 97 ppm. The

*Here and subsequently, the elemental composition of the ions is presented in the square brackets.

PMR spectrum was characterized at 3.48 ppm ($OCH_3$), $J_{PH}$ = 14 Hz ($CCl_4$); the ratio of the integral intensities $C_6\underline{H}_5$:$O\underline{CH}_3$:$\underline{CH}_2\underline{CH}_3$ = 5:2.9:5. Found, %: C 53.86, H 6.76, P 15.73. $C_9H_{13}OSP$. Calculated, %: C 54.00, H 6.5, P 15.5. The mass spectrum was as follows: 202 (6.6), 201 (19), 200 (86) [$C_9H_{13}O_1S_1P_1$], 174 (4.9), 173 (9.7), 172 (78) [$C_7H_9O_1S_1P_1$], 171 (41) [$C_7H_8 \cdot O_1S_1P_1$], 170 (3.5), 169 (8.4), 142 (12) [$C_6H_6S_1P_1$], 141 (12), 140 (12) [$C_8H_8O_1P_1C_1{}^{13}$], 140 (8.8) [$C_6H_5S_1P_1$], 139 (100) [$C_7H_8O_1P_1$], 139 (10) [$C_6H_4S_1P_1$], 133 (1.7), 125 (3.4), 124 (10), 110 (5.4), 109 (50) [$C_6H_6P$], 108 (5.3), 107 (9.8), 105 (2.2), 95 (3.0), 91 (9.0) [$C_7H_7$], 78 (19) [$C_6H_6$], 77 (37) [$C_6H_5$], 65 (7.5), 63 (60) [PS], 51 (28), 47 (16), 39 (6.1).

O-Methyl Isobutylphenylthiophosphinate (III). The mixture of 9.23 g (0.032 mole) of bis(α-hydroxyisobutyl)phenylphosphine sulfide and 3.84 g (0.032 mole) of $(MeO)_2CHNMe_2$ was boiled for 30 min; it was chromatographed on silica gel with the 1:1 mixture of benzene–petroleum ether as the eluent. The yield was 3.48 g (47%); the product had the $\delta^{31}P$ 95 ppm. The PMR spectrum was characterized by the δ 3.45 ppm ($OCH_3$), $^3J_{PH}$ = 14 Hz ($CCl_4$); the ratio of the integral intensities $C_6\underline{H}_5$:$O\underline{CH}_3$:$\underline{CH}_2\underline{CH}(\underline{CH}_3)_2$ = 5:3:9.1. Found, %: C 57.91, H 7.66, P 13.16. $C_{11}H_{17}OSP$. Calculated, %: C 57.90, H 7.46, P 13.60. The mass spectra was as follows: 230 (4.5), 228 (56) [$C_{11}H_{17}O_1S_1P_1$], 197 (1.4) [$C_{10}H_{14}S_1P_1$], 196 (1.4) [$C_{11}H_{17}O_1P_1$], 174 (7.0), 173 (14), 172 (95) [$C_7H_9O_1S_1P_1$], 171 (26) [$C_7H_8O_1S_1P_1$], 157 (2.2), 156 (6.6), 142 (3.6) [$C_6H_6S_1P_1$], 141 (8.9), 140 (14) [$C_6H_8O_1P_1C_1{}^{13}$], 140 (9) [$C_6H_5S_1P_1$], 139 (100) [$C_7H_8O_1P_1$], 139 (5.7), 125 (3.1), 124 (12), 109 (40) [$C_6H_6P$], 108 (3.4), 107 (5.2), 91 (11), 83 (2.7), 79 (5.4), 78 (7.3), 77 (24), 65 (5.0), 63 (28) [PS], 51 (13), 57 (4.2), 41 (14), 29 (15), 39 (6.3).

O-Methyl Benzylphenylthiophosphinate (IV). The mixture of 11.26 g (0.0318 mole) of bis(α-hydroxybenzyl)phenylphosphine sulfide and 3.79 g (0.0318 mole) of $(MeO)_2CHNMe_2$ was boiled for 30 min; it was chromatographed on silica gel with the 1:1 mixture of benzene–petroleum ether as the eluent. The yield was 1.72 g (20%); the product had the $\delta^{31}P$ 91 ppm. The PMR spectrum (δ, ppm, $CCl_4$) was as follows: 3.48 ($OCH_3$, $^3J_{PH}$ = 14 Hz) and 3.40 ($C\underline{H}_2Ph$, $^2J_{PH}$ = 16 Hz). The ratio of the integral intensities ($C_6\underline{H}_5$–$C_6\underline{H}_5$):($OC\underline{H}_3$–$C\underline{H}_2Ph$) = 2:1. Found, %: C 65.11, H 5.8. $C_{14}H_{15}OSP$. Calculated, %: C 64.12, H 5.73. The mass spectrum was as follows: 264 (2.3), 263 (6.7), 262 (43) [$C_{14}H_{15}O_1S_1P_1$], 231 (0.56) [$C_{13}H_{12}S_1P_1$], 173 (5.5), 172 (11.4), 171 (100) [$C_7H_8O_1S_1P_1$], 141 (2.8), 139 (4.2), 124 (6.2), 109 (12), 106 (2.4), 91 (19) [$C_7H_7$], 77 (15) [$C_6H_5$], 65 (14), 63 (7) [PS], 51 (4), 39 (1.1).

O-Methyl Methylphenylselenophosphinate (V). This was obtained as in [1]. The yield was 20%; the product has the $\delta^{31}P$ 90 ppm. The PMR spectrum (δ, ppm, $CCl_4$) was as follows: 1.91 ($^2J_{PH}$ = 14 Hz) and 3.28 ($^3J_{PH}$ = 14 Hz). The mass spectrum was as follows: 272 (2.0), 236 (20), 235 (11), 234 (100) [$C_8H_{11}O_1P_1{}^{80}Se_1$], 233 (7.2), 232 (53), 231 (20), 230 (22), 229 (1.9), 228 (3.3), 221 (3.4), 220 (3.4), 219 (17) [$C_7H_8O_1P_1{}^{80}Se_1$], 217 (8.8), 216 (3.2), 215 (3.6), 206 (5.3), 205 (3.0), 204 (30) [$C_7H_9P_1{}^{80}Se_1$], 203 (7.4) [$C_7H_8P_1{}^{80}Se_1$], 202 (14.5), 201 (8.6), 200 (7.4), 199 (1.2), 190 (2.3), 189 (2.7), 187 (6.2), 185 (3.0), 173 (1.2), 172 (5.4), 170 (2.4), 168 (1.1), 140 (2.2), 139 (21) [$C_7H_8O_1P_1$], 128 (2.3), 126 (12), 125 (2.1), 125 (4.9), 124 (4.9), 124 (6.4), 123 (53), 121 (18), 111 (11), 109 (23), 107 (11), 91 (15), 77 (25) [$C_6H_5$], 77 (21) [$C_2H_6O_1P_1$], 65 (5.0), 51 (18), 47 (9), 47 (6.0), 45 (6.8), 45 (3.4), 39 (3.8).

Absorption in the region of 3100-3700 $cm^{-1}$ is absent from the IR spectra of (I)-(IV).

## CONCLUSIONS

The reaction of bis(α-hydroxyalkyl)phenylphosphine sulfides with dimethylformamide dimethylacetal proceeds with the formation of the O-methyl alkylphenylthiophosphinates.

## LITERATURE CITED


1. B. A. Arbuzov, A. S. Ionkin, Yu. Ya. Efremov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 232 (1978).
2. O. A. Erastov and G. N. Nikonov, Usp. Khim., 53, 625 (1984).
3. V. G. Granik, A. M. Zhidkova, and R. G. Glushkov, Usp. Khim., 46, 685 (1977).
4. T. A. Mastryukova, G. K. Genkina, R. M. Kalyanova, and T. M. Shcherbina, Chemistry and Application of Organophosphorus Compounds; Trans. VI Conf. [in Russian], Naukova Dumka, Kiev (1980), pp. 95-101.
5. T. A. Mastryukova, M. Orlov, D. Eremich, and M. I. Kabachnik, Zh. Obshch. Khim., 44, 2403 (1974).
6. T. A. Mastryukova, M. Orlov, L. S. Butorina, et al., Zh. Obshch. Khim., 44, 1001 (1974).

7. T. A. Mastryukova, A. B. Uryupin, and M. I. Kabachnik, Zh. Obshch. Khim., 48, 2174 (1978).
8. T. A. Mastryukova, L. S. Butorina, A. B. Uryupin, et al., Zh. Obshch. Khim., 48, 257 (1978).
9. N. N. Mel'nikov, Ya. A. Mandel'baum, and V. I. Lomakina, Zh. Obshch. Khim., 28, 476 (1958).
10. T. A. Mastryukova, R. M. Kalyanova, G. K. Genkina, et al., Zh. Obshch. Khim., 47, 2723 (1977).
11. N. J. De'ath, K. Ellis, D. J. H. Smith, and S. Trippett, J. Chem. Soc. Chem. Commun., No. 13, 714 (1971).
12. M. Mikolajczyk, M. Para, J. Omelanczuk, et al., Tetrahedron, 28, 4357 (1972).
13. H. P. Benschop, G. R. Van den Berg, and H. L. Boter, Requeil, 87, No. 5, 387 (1968).
14. M. Mikolajczyk and J. Drabowicz, J. Chem. Soc. Chem. Commun., No. 10, 382 (1975).
15. H. Budzikiewicz and Pelah, Monatsh. Chem., 96, 1739 (1966).

# MOLECULAR STRUCTURE OF THE REACTION PRODUCT OF TRIMETHYL PHOSPHITE WITH 3,4,5-TRICHLORO-2(5H)-FURANONE

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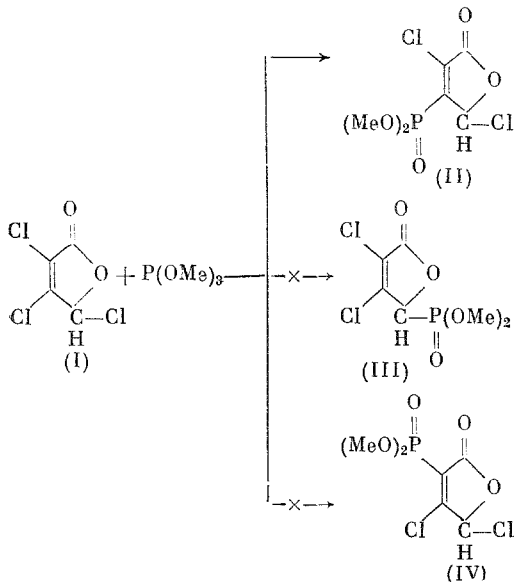
We studied the reaction of the cyclic quasichloride of mucochloric acid, 3,4,5-trichloro-2(5H)-furanone (I), with trimethyl phosphite. It is known [1] that the Cl atom at $C^5$ has lower reactivity: it practically does not enter into reaction with CuCN (200°C for 5 h) and does not react with magnesium in the presence of iodine and with benzene in the presence of $AlCl_3$. Secondary amines replace the Cl atom at $C^4$ and $C^5$, and in some cases the lactone ring is cleaved [2].

Similarly, the reaction of chloride (I) with trimethyl phosphite could afford phosphonate (II) or (III); it is also impossible to rule out completely the formation of phosphonate (IV).

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