

SHORT
COMMUNICATIONS

Esterification of Phosphorus Electrophiles with 3,4-Dichloro-5-hydroxyfuran-2(5H)-one

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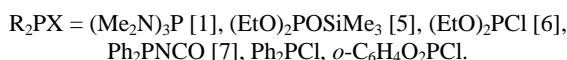
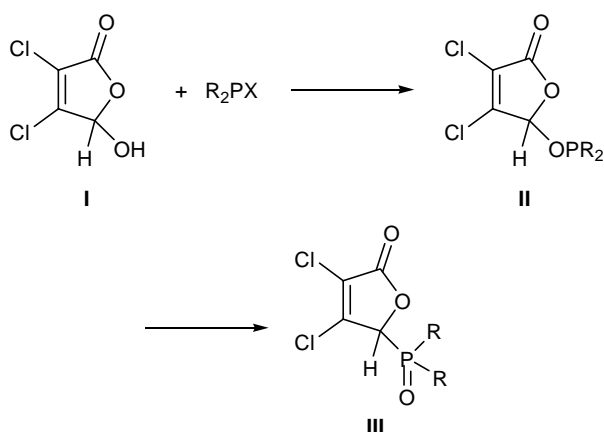
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We previously showed that the results of reactions of 3,4-dichloro-5-hydroxyfuran-2(5H)-one (**I**, mucochloric acid) and some its functional derivatives with phosphorus(III) compounds strongly depend on the substituents at the phosphorus atom and that mucochloric acid can act as both nucleophilic and electrophilic reagent. In keeping with the results of numerous studies, two main reaction paths are possible, which eventually lead to different 4- and 5-phosphorylated furanones. As a rule, initial attack by nucleophilic σ^3 -P atom is directed at the C⁴ atom which occupies β -position with respect to the carbonyl group [1]. This reaction path was substantiated by quantum-chemical calculations [2]. The structure of several products was proved by X-ray analysis [3, 4]. Some phosphorylation reactions were accompanied by esterification involving the 5-hydroxy group in the mucochloric acid molecule; such process is typical of electrophilic σ^3 -P derivatives having readily departing groups. For example, analogous pattern was observed in the reactions with hexamethylphosphorous triamide [1], substituted silyl phosphites [5], and diethyl phosphorochloridite [6]; as a result, C⁴- and C⁵-phosphorylated products were isolated. Phosphorylation of mucochloric acid with isocyanato(diphenyl)phosphine also follows the esterification pathway [7]. The structure of the only product of this reaction was proved by X-ray analysis. We proposed a general two-step scheme for all reactions occurring at the hydroxy group of mucochloric acid. This scheme includes intermediate formation of a three-coordinate phosphorus derivative having a P–O–C⁵ moiety and its subsequent rearrangement into a $\sigma^4\lambda^5$ -phosphoryl compound [1, 5–7]. However, up to now we have not succeeded in detecting intermediate esterification product containing a σ^3 -phosphorus atom.

The present communication describes the reaction of mucochloric acid (**I**) with *o*-phenylene phosphorochloridite. The latter was selected due to its pronounced electrophilicity; nucleophilic reactions with participation of this compound (e.g., those leading to quaternization of the σ^3 -P atom) are almost unknown. In addition, *o*-phenylene phosphites do not tend to undergo Arbuzov rearrangement. Therefore, phosphorylation of mucochloric acid with *o*-phenylene phosphorochloridite was expected to afford the first O-phosphorylated furanone, as well as to gain unambiguous proofs for the proposed scheme of esterification of mucochloric acid with phosphorus-containing electrophiles.

We have found that the reaction occurs under fairly severe conditions, on heating of the reactants for 10 h at 70–80°C without a solvent and with a large excess of the phosphorylating agent. As the reaction mixture cooled, a colorless solid crystallized therefrom (mp 58–60°C). The ³¹P NMR spectrum of the product contained a signal at δ_p 131 ppm, i.e., in a region typical of phosphites. In the IR spectrum we observed characteristic absorption bands at 1800 (C=O) and 1650 cm⁻¹ (C=C), while bands assignable to P=O and OH groups were absent. These data led us to conclude that the reaction of *o*-phenylene phosphorochloridite with mucochloric acid (**I**) afforded 3,4-dichloro-5-oxo-2,5-dihydro-2-furyl *o*-phenylene phosphite (**II**). The product turned out to be stable, and it did not undergo rearrangement into phosphonate **III**.

Having obtained an experimental proof for the formation of O-phosphorylation product in the reaction with *o*-phenylene phosphorochloridite, we focused again on the reaction of 3,4-dichloro-5-hydroxyfuran-2(5H)-one with chloro(diphenyl)phosphine. Previously



[6], the product of this reaction was assigned the structure of 4-phosphorylated furanone which contradicts the general scheme of phosphorylation of mucochloric acid, following from the available experimental data and assuming phosphorylation at the 5-position. For instance, the reaction with isocyanato(diphenyl)phosphine [7] leads to replacement of the isocyanato group by the furanone hydroxyl. The chlorine atom in diphenylchlorophosphine is a better leaving group, which suggests an analogous esterification process with formation of 5-substituted furanone. Our results have confirmed the above assumptions: the structure of 3,4-dichloro-5-diphenylphosphinoylfuran-2(5H)-one (**III**, R = Ph) was rigorously proved by the IR and ^{31}P , 1H , and ^{13}C NMR spectra and X-ray diffraction data.

Chloro(diphenyl)phosphine reacted with mucochloric acid (**I**) in diethyl ether at room temperature. The isolated crystalline product had mp 169–171°C and showed one signal at δ_P 28.9 ppm in the ^{31}P NMR spectrum, indicating the presence of a phosphine oxide fragment $Ph_2P(O)R$ in the molecule. The IR spectrum contained the following absorption bands, ν , cm^{-1} : 1000, 1190 (P=O); 1580, 1600, 1770 (C=C_{arom}, C=C, C=O). In the mass spectrum of the product we observed a strong peak from the molecular ion, m/z 353, which corresponds to the formula $C_{16}H_{11}Cl_2O_3P$. The base peak in the mass spectrum was that with m/z 201 $[Ph_2P=O]^+$. Compound **III** (R = Ph) showed in the 1H NMR spectrum a doublet at δ 5.73 ppm ($J_{PH} = 6.3$ Hz) from the 5-H proton. The C^5 signal appears in the $^{13}C\{-^1H\}$ NMR spectrum as a doublet at δ_C 80.2 ppm due to coupling with the phosphorus atom ($^1J_{PC} = 70.1$ Hz). In addition, the presence in the $^{13}C\{-^1H\}$ NMR spectrum of two doublets belonging to each of the C^p , C^o , and C^m atoms unambiguously indicates that

the two phenyl groups on the phosphorus are diastereotopic, which is a fairly rare thing. According to the X-ray diffraction data, the product has the structure of 5-phosphorylated 3,4-dichlorofuranone **III** (R = Ph) which is fully identical to a sample obtained by the reaction of mucochloric acid (**I**) with isocyanato(diphenyl)phosphine [7].

Thus our results showed that reactions of mucochloric acid (**I**) with phosphorus-containing electrophiles involve intermediate formation of P(III) derivatives **II** having a P–O–C⁵ bond. Phosphite **II** (R₂ = *o*-C₆H₄O₂) obtained from furanone **I** and *o*-phenylene phosphorochloridite is quite stable under the reaction conditions, while the reaction of mucochloric acid (**I**) with chloro(diphenyl)phosphine gives phosphinite **II** (R = Ph) which cannot be detected due to ready rearrangement into phosphine oxide **III** (R = Ph).

3,4-Dichloro-5-oxo-2,5-dihydrofuran-5-yl *o*-phenylene phosphite (II). Yield 63%, mp 58–60°C. IR spectrum (mineral oil), ν , cm^{-1} : 1800 (C=O), 1650 (C=C). ^{31}P NMR spectrum (CHCl₃): δ_P 131 ppm. Found, %: C 39.09; H 1.84. C₁₀H₅Cl₂O₅P. Calculated, %: C 39.22; H 1.63.

3,4-Dichloro-5-diphenylphosphinoylfuran-2(5H)-one (III). Yield 89%, mp 169–171°C. IR spectrum (mineral oil), ν , cm^{-1} : 1000, 1190 (P=O); 1580 (C=C_{arom}); 1600 (C=C); 1770 (C=O). 1H NMR spectrum (CDCl₃), δ , ppm: 5.73 d (CH, $J_{PH} = 1.7$ Hz), 7.4–8.0 m (C₆H₅). $^{13}C\{-^1H\}$ NMR spectrum (DMCO), δ_C , ppm: 165.5 s (C²), 149.7 d (C⁴, $^2J_{PC} = 5.7$ Hz), 128.0 d (C³, $^3J_{PC} = 23.3$ Hz), 80.2 d (C⁵, $^1J_{PC} = 70.1$ Hz), 134.0 d and 138.8 d (C^p, $^4J_{PC} = 2.0$ Hz), 132.0 d and 131.8 d (C^o, $^2J_{PC} = 9.0$ Hz), 129.8 d and 129.7 d (C^m, $^3J_{PC} = 12.0$ Hz). ^{31}P NMR spectrum (CHCl₃): δ_P 28.9 ppm. Mass spectrum: m/z 353 $[M]^+$. C₁₆H₁₁Cl₂O₃P. Calculated: M 353.

The spectral data were acquired using Varian Unity-300 (300 MHz) (NMR), Specord IR-75 (IR), and Hitachi M-80B (GC–MS) instruments.

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