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SHORT COMMUNICATIONS

2-Chloro-3-(Tetrachlorophosphoranyloxy)succinyl Dichloride

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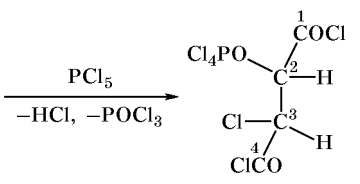
We previously synthesized new optically active diamines of the dioxolane series by aminolysis of diethyl tartrate or its cyclization product, diethyl 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate [1]. Sterically hindered aromatic amines may be promising from the viewpoint of asymmetric synthesis; however, the aminolysis does not occur because of their low basicity. We made an attempt to increase the nucleofugality of departing group via conversion of diethyl tartrate to tartaroyl dichloride. Here, it was not clear whether the chlorination of tartaric acid will occur at carboxy or hydroxy group. Strangely enough, we have found no unambigous published data on the selectivity of chlorination at the carboxy or hydroxy group in reactions of hydroxy acids with chlorinating agents (PCl_5, $SOCl_2$). There are only very early publications, according to which the reaction of tartaric acid with a 4–5-fold excess of PCl_5 yields chlorofumaric acid HOCOCH=C(Cl)COOH [2] or its mixture with 2,3-dichlorosuccinic acid [3].

We have found that the reaction of tartaric acid with 2 equiv of PCl_5 results in formation of 2-chloro-3-(tetrachlorophosphoranyloxy)succinyl dichloride (**I**) as the only product.

(*R*,*R*)-HOCOCH(OH)CH(OH)COOH



I

The structure of compound **I** was proved by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The ^1H NMR spectrum of **I** contained two signals, each being split due to coupling with the neighboring proton and phosphorus atom. In the ^{31}P NMR spectrum we observed a doublet due to coupling with one proton ($^3J_{PH}$; coupling with 3-H through four bonds was not observed). In the ^{13}C NMR spectrum recorded without decoupling from protons, two signals from sp^3-hybridized carbon atoms (C^2 and C^3) were present, and each signal was split due to coupling with two protons and phosphorus. Also, there were two signals from carbonyl carbon atoms, one of which (C^1) was coupled with two protons, and the other (C^4), with two protons and phosphorus. Presumably, the difference between our results and those obtained in [2, 3] is explained by the different reaction conditions.

Compound **I** may be regarded as an $ROPCl_4$-like intermediate. It is commonly believed that such intermediates (e.g., $ROPCl_3^+$ or $ROPOCl_2$) are formed in nucleophilic substitution of hydroxy group by chlorine under the action of PCl_5. Compounds like $ArOPCl_4$ (R = Ar) are formed by direct reaction of phenols with PCl_5 [4]; however; no published data are available on their alkyl-containing analogs $AlkOPCl_4$.

Thus our attempt to activate the carboxy group in tartaric acid without involving the hydroxy group was unsuccessful. Nevertheless, we obtained a new product which was not described in early publications on the reaction of tartaric acid with PCl_5. This product is likely to be the first stable intermediate in the chlorination of aliphatic alcoholc with phosphorus(V) chloride.

2-Chloro-3-(tetrachlorophosphoranyloxy)succinyl dichloride (I). A mixture of 10 g (0.067 mol) of (+)-tartaric acid and 30 g (0.15 mol) of PCl_5 in 40 ml of carbon tetrachloride was heated under reflux until hydrogen chloride no longer evolved (4–5 h). The solvent and $POCl_3$ were removed under reduced pressure (10 mm), and the residue was distilled at 96°C (0.5 mm). Yield 2.5 g (45%), n_D^{20} = 1.530.

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^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.30 d.d (1H, 2-H, $^3J_{HH}$ = 3.8, $^4J_{HP}$ = 1.5 Hz), 5.75 d.d (1H, 3-H, $^3J_{HH}$ = 3.8, $^3J_{PH}$ = 13.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 62.79 d.d.d (C^2, $^1J_{CH}$ = 157.6, $^2J_{CH}$ = 6.9, $^2J_{CP}$ = 4.2 Hz), 82.20 d.d.d (C^3, $^1J_{CH}$ = 158.3, $^2J_{CH}$ = 8.4, $^2J_{CP}$ = 2.7 Hz), 166.27 t (C^1, $^2J_{CH}$ = 6.3, $^3J_{CH}$ = 6.3 Hz), 166.69 d.t (C^4, $^2J_{CH}$ = 4.8, $^3J_{CH}$ = 4.8, $^3J_{CP}$ = 3.1 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 12.16 ppm, d, $^3J_{PH}$ = 12.9 Hz). Found, %: C 12.88; H 0.89; Cl 65.13; P 8.62. $C_4H_2Cl_7O_3P$. Calculated, %: C 12.74; H 0.53; Cl 65.79; P 8.21.

The NMR spectra were recorded on a Bruker DPX-400 instrument at 400 (^{1}H), 100 (^{13}C), and 162 MHz (^{31}P) using hexamethyldisiloxane as internal reference. The chemical shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) or H_3PO_4 (^{31}P).

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