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Reaction of H-Phosphonate Diesters with Trityl Halides

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A study on the reaction of H-phosphonate diesters with trityl halides under different reaction conditions has been performed. The reactions were evaluated using ³¹P NMR spectroscopy. For the study we selected simple H-phosphonate diesters, *i.e.* diphenyl H-phosphonate and diethyl H-phosphonate. Depending on the reaction conditions used the products obtained differed substantially. Formation of C-phosphonate 1 vs 2 depended primarily on the kind of trityl derivative used for the reaction.

Reaction of diphenyl H-phosphonate with 2 equiv. DMT-Cl in pyridine, produced a compound of type 1. Contrary to this, diphenyl H-phosphonate in the presence of 2 equiv. Tr-Cl in pyridine afforded the 4-pyridylphosphonate 2 as product. This reaction proceeded via an intermediate, which was slowly transformed into the product upon standing or during attempted isolation. The 4 position in pyridine is activated for nucleophilic attack through reaction with an electrophile (Tr-Cl)^[1]. Reaction of diethyl H-phosphonate with 1.2 equiv. Tr-Br in the presence of 2.4 equiv. DBU in pyridine also produced the 4-pyridylphosphonate 2. In the reaction of diphenyl H-phosphonate with 2 equiv. MMT-Cl, two signals were present in the reaction mixture in about 1:1 proportions; these signals were assigned to the monomethoxytrityl derivative 1 and the 4-pyridylphosphonate 2.

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