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Synthesis of Aryl-Thiophosphonates via A [1,2] or [1,3] Phospho-Fries Rearrangement

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SYNTHESIS OF ARYL-THIOPHOSPHONATES VIA A [1,2] OR [1,3] PHOSPHO-FRIES REARRANGEMENT

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Abstract The synthesis of O,O-diethyl arylthiophosphonates is achieved following a baseinduced [1,2] or [1,3] phospho-Fries rearrangement that makes use of O,O-diethyl O-aryl thiophosphates as substrates. The coordination properties of O,O-diethyl arylthiophosphonates are also discussed.

Keywords Coordination; phospho-Fries; rearrangement; thiophosphate; thiophosphonate

Thiophosphonates are usually synthesized by making use of air- and/or water-sensitive intermediates (e.g., thiooxydation of P(III) species). On the other hand, the application of the phospho-Fries rearrangement (Scheme 1) requires less reactive and thus more convenient to handle P(V) intermediates. According to this method of synthesis, the rearrangement can



Scheme 1 Synthesis of *O*,*O*-diethyl arylthiophosphonate following either a [1,3] or a [1,2] phospho-Fries rearrangement.

be achieved on phenol¹ or pyrrole² derivatives, giving rise to diethyl arylthiophosphonates in high yields. The study of this rearrangement by NMR at low temperature indicates that the reaction proceeds first by an ortho-metallation (via a metal halogen exchange or a

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Figure 1 Palladium coordination complexes 4 and 5 synthesized, respectively, from compounds 2 and 3 and a palladium salt.

deprotonation step) followed by the migration of diethyl thiophosphonate group. For the [1,3] rearrangement performed on phenol derivatives, the first step is rapid at -78° C when the metallation is achieved by a halogen-metal exchange (typically with *n*-BuLi). The lithiated intermediate is not detectable, since the [1,3] rearrangement is immediate even at low temperature (-78° C). The chemical behavior is different for the [1,2] rearrangement on pyrrole. Indeed, the metallation occurs between -35 to -40° C by deprotonation (*n*-BuLi is used) while the rearrangement is very slow at this temperature. Consequently, a full characterization of the lithiated intermediate by low temperature NMR (COSY ¹H-¹H, HMBC ¹H-¹³C, HMBC ¹H-³¹P, HMBC ¹H-¹⁵N, and HMQC ¹H-¹³C) has been achieved.

Besides the synthetic aspect, coordination properties of thiophosphonates have been evaluated.³ Palladium and silver were selected as metal, and the compounds **2** and **3** as potential bidentate or tridentate ligands. With palladium as metal, the coordination complexes **4** and **5** were isolated (Figure 1).^{2,3} When a silver salt was associated with the bidentate ligand **2**, an unstable coordination complex was obtained, but its stabilization can be achieved by the addition of triphenylphosphine.

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