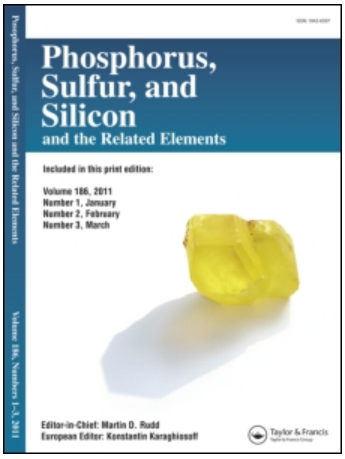

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(Hydroxyimino)Phosphonoacetic Acids: Synthesis, Stereochemistry and Reactivity

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(HYDROXYIMINO)PHOSPHONOACETIC ACIDS: SYNTHESIS, STEREOCHEMISTRY AND REACTIVITY

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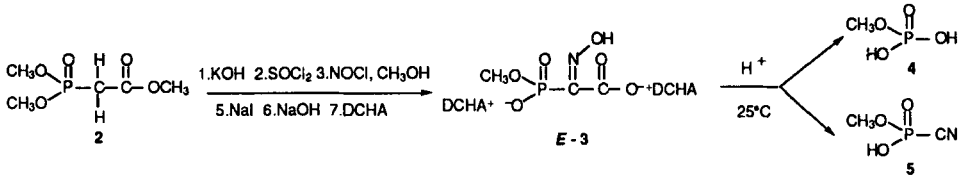
Individual *E*/*Z* isomers of the C-methyl ester **1** of α-(hydroxyimino)phosphonoacetic acid ("troika acid") were recently prepared as dicyclohexylammonium salts and found to be stable at neutral pH.[1] On alkaline demethylation followed by pH adjustment to 6–7, *E*-**1** and *Z*-**1** stereospecifically undergo P-C_α and C_α-C_β cleavage, respectively.[1] Herein we report synthesis of the corresponding P-methyl ester from trimethyl phosphonoacetate **2**. The product was isolated as its bis-DCHA$^+$ salt *E*-**3**, with stereochemistry assigned by NMR.[2]



Like **1**, *E*-**3** was stable at pH 7 for 24 h (25°C). However, in contrast to **1**, which is also stable at low pH, *E*-**3** decomposed over 2.5 h at pH 1.5 to a mixture of methyl phosphate **4** (15%; ^{31}P NMR δ 2.1 ppm) and methyl phosphorocyanidate **5** (85 %; ^{31}P NMR δ –17.4 ppm). Formation of these products suggests that two fragmentation pathways are available to *E*-**3**: 1) P-C_α cleavage to **4**; 2) *E* ➡ *Z* isomerization followed by C_α-C_β cleavage to **5**. Process (2) overall is more rapid than process (1). Further evidence of dual fragmentation pathways was observed (^{31}P NMR) when *E*-**3** was heated in ethanol or acetonitrile: **5** (81-84%) was obtained in both solvents in addition to the expected phosphorylation products ethyl methyl phosphate (ethanol; 19%) and P,P'-dimethyl pyrophosphate (acetonitrile; 16%).

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