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(Hydroxyimino)Phosphonoacetic Acids: Synthesis, Stereochemistry and Reactivity

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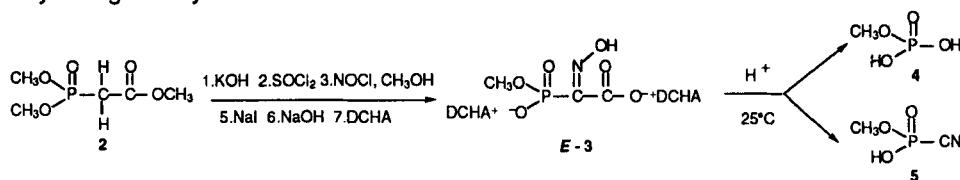
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(HYDROXYIMINO)PHOSPHONOACETIC ACIDS: SYNTHESIS, STEREOCHEMISTRY AND REACTIVITY

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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%; ³¹P NMR δ 2.1 ppm) and methyl phosphorocyanidate **5** (85 %; ³¹P 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* \rightleftharpoons *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 (³¹P 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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