

ANIONIC REARRANGEMENTS FOLLOWING DECARBOXYLATION OF BENZOPHENONE DERIVATIVES
WITH CRYOGENIC IR SPECTROSCOPY

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Carbanions are highly reactive intermediates that are commonly used in organic synthesis. Here, we investigate the fundamental gas phase spectroscopy and isomerization of substituted aromatic phenides (deprotonated benzene derivatives) using isomer-selective cryogenic ion vibrational predissociation spectroscopy (1000 cm^{-1} – 4200 cm^{-1}). The phenide is formed by the decarboxylation of the 4-benzoyl benzoate anion (4BBA^- , $\text{C}_{14}\text{H}_9\text{O}_3^-$), a substituted benzophenone, in a commercial Orbitrap mass spectrometer before being transferred to the triple focusing time-of-flight photofragmentation mass spectrometer. The resulting spectra are congested, suggesting the presence of multiple isomers. They are revealed by quantum chemical calculations in conjunction with two color IR-IR photobleaching spectroscopy to be the expected phenide, and a new molecule formed by multiple steps of isomerization that end in ring-closed product. The identities of these compounds and the proposed mechanism are confirmed by additional experiments using 4BBA^- - d_9 and 2BBA^- .