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Formation of a New Zwitterionic Phosphorus Compound using Buⁿ₃P and COS

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We have recently reported the use of the crystalline tri-n-butylphosphine-carbon disulfide adduct to form a variety of heterocyclic compounds including dithiole-containing ylides, ¹ 2-alkylidene-1,3-dithiolanes, ² and dihydrotetrathiafulvalenes. ³ In particular reaction with DMAD gave the dithiole-containing ylide shown. ¹ We now describe the corresponding reaction of tributylphosphine and carbonyl sulfide, COS, with a variety of unsaturated systems which generally takes a completely different course as shown for the example of DMAD below. The structure of the unusual zwitterionic product has been confirmed by X-ray diffraction and is shown.

The difference is that tributylphosphine apparently does not form an adduct with COS but instead undergoes conjugate addition to two molecules of DMAD and only then does the resulting species interact with the COS. The product might alternatively be formed by addition of the phosphine to tetrakis(methoxycarbonyl)cyclopentadienone and this aspect is currently being examined. Although such an addition would normally be expected at the 3-position of the cyclopentadienone, it may occur at the 2-position in this case to give the more thermodynamically stable product.

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