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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

A Simple Synthesis of 3H- λ^5 -Phosphole Derivatives from Alkyldiphenylphosphine Imines and Dimethyl Acetylenedicarboxylate

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To cite this Article Barluenga, José and López, Fernando(1987) 'A Simple Synthesis of 3H- λ^5 -Phosphole Derivatives from Alkyldiphenylphosphine Imines and Dimethyl Acetylenedicarboxylate', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 30: 3, 759

To link to this Article: DOI: 10.1080/03086648708079251

URL: <http://dx.doi.org/10.1080/03086648708079251>

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A Simple Synthesis of 3H- λ^5 -Phosphole Derivatives from Alkyldiphenylphosphine Imines and Dimethyl Acetylenedicarboxylate

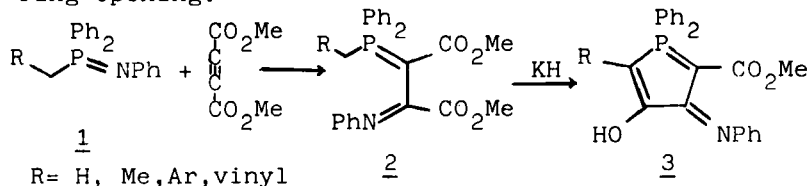
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Whereas several procedures have been developed for synthesizing λ^3 -phospholes and their oxides and sulphides¹, access to 2H- λ^5 -Phospholes is limited to the reaction of phosphines² with Dimethyl Acetylenedicarboxylate (DMAD) and only unstable 3H- λ^5 -Phospholes were detected² when diphenylvinylphosphine were used.

Recently we report the synthesis of 4-Aza- λ^5 -phosphinines³ from β -enaminophosphine imines⁴ and DMAD and we describe here the first synthesis of stable 3H- λ^5 -Phospholes by reaction of simple alkyldiphenylphosphine-N-phenylimines with DMAD.

The reaction of alkyldiphenylphosphine imines 1 with DMAD in THF at room temperature gave the 1:1 adduct 2 in excellent yield. Compounds 2 are formed through 2+2 cycloaddition of the P=N linkage of 1 to the carbon-carbon triple bond of DMAD, to give the non-isolable 1-aza-phosphete followed by an electrocyclic ring opening.



When a mixture of 2 and KH in THF was heated at 50°C followed by methanolysis and aqueous work-up, cyclocondensation and formation of 3H- λ^5 -phospholes 3 took place.

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