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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>

Acetylene Phosphonates as Dienophiles: A Route to Carbocyclic and Aromatic Phosphonates and Diphos-Phonates

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To cite this Article Dogadina, A. V. , Senderickhin, A. I. , Ionin, B. I. and Petrov, A. A.(1990) 'Acetylene Phosphonates as Dienophiles: A Route to Carbocyclic and Aromatic Phosphonates and Diphos-Phonates', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 51: 1, 285

To link to this Article: DOI: 10.1080/10426509008040819

URL: <http://dx.doi.org/10.1080/10426509008040819>

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ACETYLENE PHOSPHONATES AS DIENOPHILES: A ROUTE TO CARBOCYCLIC AND AROMATIC PHOSPHONATES AND DIPHOSPHONATES

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Systematic research of unsaturated phosphonates, started at the end of the sixties, gave rise to a variety of acetylene phosphonic derivatives. The authors worked out two significant routes to these compounds, (1) action of PCl_5 upon some alkynes followed by HCl elimination which gives alkyne dichlorophosphonates. and (2) Arbuzov reaction of P^{III} esters with halo- and dihaloalkynes which gives different phosphono- and diphosphonoacetylenes. The phosphonic groups are electron-withdrawing, and acetylenephosphonates are typical dienophiles in Diels-Alder cycloaddition of diene-donor/dienophile-acceptor type. Phosphonic esters are less active than corresponding dichlorophosphonates, but diphosphonic esters expose high reactivity. Haloethyne- and dialkylaminoethynephosphonates are sufficiently active in the reaction with simple dienes (butadiene, isoprene, 2,3-dimethylbutadiene and piperylene), but we were not able to introduce alkyl- or arylacetylene phosphonic esters in the cycloaddition.

The 2-substituted cyclohexa-1,4-diene phosphonates either slowly convert to corresponding benzene derivatives under oxydizing action of air oxygen or suffer dehydrohalogenation. It is noteworthy that diene cycloaddition to t-butylacetylene dichlorophosphonate is followed by phosphonic group elimination and formation of t-butylbenzene derivatives.