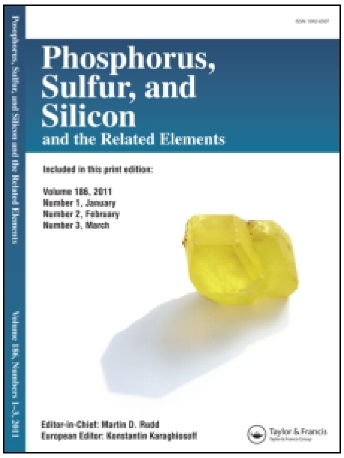

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Spontaneous Aromatization of Diels-Alder Adducts in the Reaction of Alkatrienyl Phosphonates with Alkyl Esters of Acetylencarboxylic Acids

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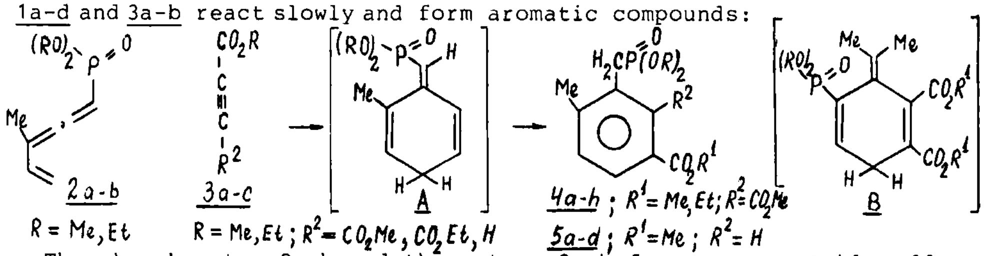
The subject of this study was the Diels-Alder reaction involving dialkyl(3-methylpenta-1,2,4-trienyl)phosphonates 1a-d, dialkyl(5-methylhexa-1,3,4-trienyl)phosphonates 2a-b, and dienophiles (esters of acetylencarboxylic acids) 3a-c, at 65-90°C, in chloroform or with no solvent. The reaction between 1a-d and 3a-b led to the benzyl phosphonates 4a-h, while with 3c it proceeds to a mixture of 5a-d (90%) and 6a-d (10%), which are dialkyl esters of the 3-carboalkoxy (or 2-carboalkoxy)-6-methylbenzyl phosphonic acid. The intermediate Diels-Alder adducts (A) are not even spectroscopically observable, i.e. in the course of the reaction a 1,5-sigmatropic isomerization occurs, accompanied by aromatization of (A). The isomerization is spontaneous: at ambient temperature 1a-d and 3a-b react slowly and form aromatic compounds:



The phosphonates 2a-b and the esters 3a-b form a more stable adduct (B), which can be spectroscopically (NMR) observed in the course of the reaction, together with the obtained dialkyl esters of 2-isopropyl-3,4-dicarboalkoxy-phenyl phosphonic acid 7a-d. 4a-h, 5a-d, 6a-d, and 7a-d were isolated by precrystallization, or by chromatography. Their structures were confirmed by IR, MS and NMR spectra.

The above Diels-Alder reaction is a new original method for the synthesis of benzyl and phenyl phosphonates, which differs from the known methods in that the benzol nucleus is formed during the reaction.