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Dithiophosphorylation of Cyclic Monoterpenes

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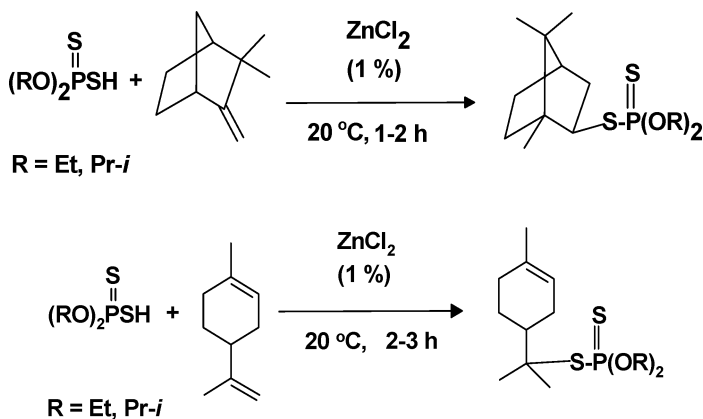
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New data are presented for the synthesizing terpene esters of dithiophosphoric acids and their structure.

Keywords Cyclic monoterpenes; Lewis acid catalysts; thiophosphorylation

We have carried out the reactions of dithiophosphoric acids with such terpenes as racemic camphene, (+)-limonene, (1S)-(–)-β-pinene and 3-carene under mild conditions. These reactions occur at 20 °C for 1–3 h in



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the presence of catalytic amounts of anhydrous ZnCl_2 to yield adducts formed in accordance with Markovnikov's rule. In the case of camphene the adduct formation is accompanied by skeleton transformation into norbornane structure. The reactions O,O-dialkyl dithiophosphoric acids with (+)-limonene proceed with the participation of the exocyclic C=C bond.

The reactions studied are facilitated by Lewis acid catalysts (NiCl_2 , CuCl , CuCl_2 , FeCl_3 , $\text{BF}_3\text{Et}_2\text{O}$, AlCl_3). The reactions of O,O-dialkyl dithiophosphoric acids with (1S)-(-)- β -pinene can also be performed non-catalytically.

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