25th International Symposium on the Organic Chemistry of Sulfur

Częstochowa, Poland, June 24-29, 2012

Chairman	**Józef Drabowicz**
Honorary Chairman	**Marian Mikołajczyk**

SYMPOSIUM MATERIALS

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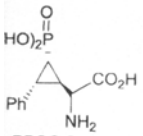

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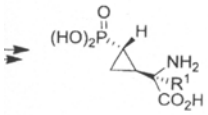

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PC-27

O,O-DIALKYLDITHIOPHOSPHORIC ACIDS IN THE REACTIONS WITH NON-ACTIVATED α-OLEFINS

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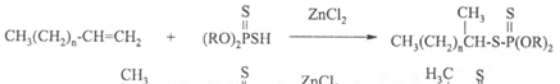
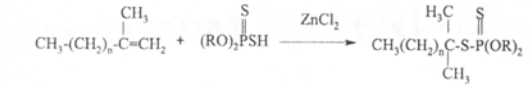
Synthetic result of the reactions of tetracoordinated phosphorus thioacids with olefins depends significantly on the regiochemistry of addition of thiophosphoric fragments to the double bonds of asymmetric olefins. We have studied reactions of *O,O*-dialkyl dithiophosphoric acids with the unactivated asymmetric olefins under milder conditions. It was found that in the absence of additives the reaction of 2-methylpent-1-ene with *O,O*-diethyl dithiophosphoric acid starts at 20°C and proceeds for six days to give *O,O*-diethyl *S*-1,1-dimethylbuthyl dithiophosphate in 97% yield. Spectral data indicate clearly the formation of a Markovnikov's adduct in the reaction studied. This reaction can be accelerated by carrying it out at 80°C for 2 h in the absence of additives. After stirring the mixture of 2-methylpent-1-ene with *O,O*-diethyl dithiophosphoric acid and 0.5 wt % of zinc chloride for 1 h at 20°C the amount of adduct reaches 50%.

In the reaction of *O,O*-diethyl dithiophosphoric acid with hexadec-1-ene at 80°C for 2 h in the absence of additives the conversion calculated on the phosphorus does not exceed 12%. The reactions of *O,O*-dialkyl dithiophosphoric acids with hexadec-1-ene, octadec-1-ene, and oct-1-ene in the presence of zinc chloride (3.0 wt %) at 80°C over 2 h led to formation of *O,O*-dialkyl-
S-2-methylalkyldithiophosphates as the major products in yields of 63–88%. The used commercial samples of hexadec-1-ene, octadec-1-ene, and oct-1-ene contain vinylidene α-olefins as impurities (2%), 2 methylpentadec-1-ene, 2-methylheptadec-1-ene, and 2-methylhept-1-ene, which react with dithiophosphoric acids to form *O,O*-dialkyl-*S*-1,1-dimethylalkyldithiophosphates as the minor products.





R = Et, n = 13; R = Pr-*i*, n = 13; R = Pr-*i*, n = 15; R = Pr-*i*, n = 5; R = Bu-*i*, n = 5
R = Et, n = 12; R = Pr-*i*, n = 12; R = Pr-*i*, n = 14; R = Pr-*i*, n = 4; R = Bu-*i*, n = 4

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