

SHORT COMMUNICATIONS

Reaction of *O,O*-Diisopropyl Hydrogen Dithiophosphate with (+)-Limonene

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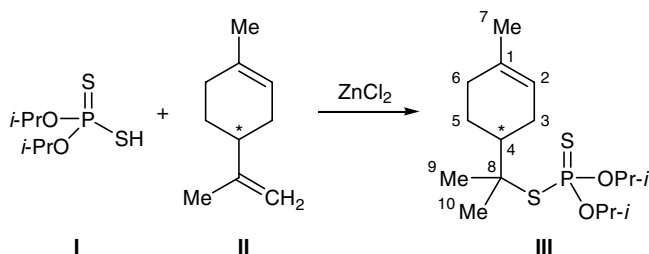
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A large number of practically important compounds for wood-chemical, petrochemical, pharmaceutical, and fragrance industries are prepared from such naturally occurring substances as terpenoids, including their phosphorus-containing derivatives [1–5]. According to early patent data [4, 5], reactions of *O,O*-dialkyl hydrogen dithiophosphates with pinenes and dipentene [racemic mixture of (+)- and (–)-limonenes] at 100–200°C lead to mixtures of phosphorus-containing compounds proposed as oil additives; however, the structure of the reaction products was not determined. Presumably, primary adducts formed in the above reactions are involved under severe conditions in various isomerizations and fragmentations typical of labile terpenoid molecules.

With a view to obtain stable adducts and determine their structure, we examined reactions of mono- and bicyclic monoterpenoids with dithiophosphoric acid derivatives in the presence of both proton-donor catalysts (such as strong mineral acids) and Lewis acids. The present communication reports on the results of our study on the reaction of *O,O*-diisopropyl hydrogen dithiophosphate (**I**) with (+)-limonene (**II**) as one of the most stable monocyclic terpenes. The presence in molecule **II** of exo- and endocyclic double bonds characterized by different reactivities could give rise to different directions of electrophilic addition.

We have found that the addition of *O,O*-diisopropyl hydrogen dithiophosphate (**I**) in the presence of a catalytic amount of anhydrous zinc(II) chloride under

solvent-free conditions occurs at the exocyclic double bond of (+)-limonene (**II**) according to the Markovnikov rule, yielding compound **III** as the only product. The conversion of *O,O*-diisopropyl hydrogen dithiophosphate (**I**) is 100%. When the reaction was carried out in acetonitrile under more severe conditions (60°C, 3 h), no other products were formed. The fact that the addition follows the Markovnikov rule (as in the reaction with sulfanylacetic acid [6]) reflects the ability of dithiophosphoric acid derivatives to react with electron-rich alkenes according to the electrophilic addition pattern. Dual reactivity of dithiophosphates in addition processes is well known: the presence of a labile proton and nucleophilic dithiophosphoryl fragment enables them to enter both nucleophilic and electrophilic addition reactions [7].



***O,O*-Diisopropyl S-[1-methyl-1-(4-methylcyclohex-3-en-1-yl)ethyl] dithiophosphate (**III**)**. Freshly calcined zinc(II) chloride, 0.056 g (0.4 mmol, 1 wt %), was added in portions to a mixture of 8.0 g (37.4 mmol) of *O,O*-diisopropyl hydrogen dithiophosphate (**I**) and 5.1 g (37.4 mmol) of (+)-limonene (**II**)

under stirring at $\sim 20^\circ\text{C}$ in a stream of dry argon. The mixture was stirred for 2 h at $\sim 20^\circ\text{C}$, diluted with 10 ml of diethyl ether, and washed with water (3×10 ml). The organic phase was separated and dried over CaCl_2 for 12 h. The drying agent was filtered off, and the filtrate was evaporated under reduced pressure at 40°C (1 h at 0.5 mm and 1 h at 0.06 mm) to isolate 11.1 g (85%) of adduct **III**. The product was purified by column chromatography on silica gel using carbon tetrachloride as eluent. R_f 0.24 (CCl_4), $n_D^{20} = 1.5079$. IR spectrum (neat), cm^{-1} : 2976 s, 2928 s, 2836 s [$\nu_{\text{as,s}}(\text{CH}_3)$, $\nu_{\text{as,s}}(\text{CH}_2)$]; 1450 m [$\delta_{\text{as}}(\text{CH}_3)$]; 1384 m, 1373 m [$\delta_{\text{s}}\text{C}(\text{CH}_3)_2$]; 968 v.s, br [$\nu(\text{POC})$]; 887 m, 775 m [$\nu(\text{PO}_2)$]; 650 m [$\nu(\text{P}=\text{S})$]; 548 m [$\nu(\text{P}-\text{S})$]. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.35 d and 1.37 d [12H, $(\text{CH}_3)_2\text{CHO}$, $^3J_{\text{HH}} = 6.0$ Hz]; 1.53 s and 1.59 s [6H, $(\text{CH}_3)_2\text{C}$]; 1.66 s (3H, 1- CH_3); 1.54–2.18 m (7H, CH_2 , CH); 4.91 m [2H, $(\text{CH}_3)_2\text{CH}$, $^3J_{\text{HH}} = 6.0$ Hz]; 5.37 m (1H, 2-H). ^{31}P NMR spectrum: δ_{P} 87.1 ppm. Mass spectrum (60 eV): m/z 350.2 (I_{rel} 20) $[M]^+$. Found, %: C 54.58; H 8.38; P 9.25; S 18.17. $\text{C}_{16}\text{H}_{31}\text{O}_2\text{PS}_2$. Calculated, %: C 54.82; H 8.94; P 8.84; S 18.26.

The IR spectrum was recorded on a Bruker Vector 22 spectrometer with Fourier transform using KBr plates. The ^1H NMR spectrum was measured on a Bruker Avance-600 spectrometer at 600.13 MHz, and

the ^{31}P NMR spectrum was obtained on a Bruker CXP-100 instrument at 36.5 MHz using 85% H_3PO_4 as reference. The mass spectrum (electron impact) was recorded on a Finnigan MAT-212 mass spectrometer.

REFERENCES

1. Grigor'eva, N.Ya. and Moiseenkov, A.M., *Khim.-Farm. Zh.*, 1989, p. 144.
2. Serebryakov, E.P. and Nigmatov, A.G., *Khim.-Farm. Zh.*, 1990, p. 104.
3. Vedernikov, D.N. and Roshchin, V.I., Abstracts of Papers, *II Vserossiiskaya konferentsiya "Kimiya i tekhnologiya rastitel'nykh veshchestv"* (IInd All-Russia Conf. "Chemistry and Technology of Plant Compounds"), Kazan, 2002, p. 39.
4. Barlett, J.H., Rud, H.W., and Cyphers, E.B., US Patent no. 2611728, 1952; *Chem. Abstr.*, 1953, vol. 47, p. 2930a.
5. Augustine, F.B., US Patent no. 2665295, 1954; *Chem. Abstr.*, 1954, vol. 48, p. 12807f.
6. Morgunova, V.A., Nikitina, L.E., Plemenkov, V.V., Chugunov, V.V., and Fazlyeva, M.G., *Russ. J. Org. Chem.*, 2000, vol. 36, p. 489.
7. Cherkasov, R.A., *Stroenie i reaktsionnaya sposobnost' organicheskikh soedinenii* (Structure and Reactivity of Organic Compounds), Moscow: Nauka, 1978, p. 107.