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O,O-Dialkyldithiophosphoric Acids in the Reactions with Nonactivated $\alpha\text{-Olefins}$

Lidiya I. Kursheva^a, Ilyas S. Nizamov^{ab}, Elvira S. Batyeva^a, Ilnar D. Nizamov^b, Farid D. Yambushev^b & Rafael A. Cherkasov^b

^a State Budgetary-Funded Institution of Science, A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, Russia

^b A.M. Butlerov Chemical Institute , Kazan Federal University , Kazan , Russia

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O,O-DIALKYLDITHIOPHOSPHORIC ACIDS IN THE REACTIONS WITH NONACTIVATED α -OLEFINS

Lidiya I. Kursheva,¹ Ilyas S. Nizamov,^{1,2} Elvira S. Batyeva,¹ Ilnar D. Nizamov,² Farid D. Yambushev,² and Rafael A. Cherkasov²

¹State Budgetary-Funded Institution of Science, A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, Russia

²A.M. Butlerov Chemical Institute, Kazan Federal University, Kazan, Russia

GRAPHICAL ABSTRACT

 $CH_{3}(CH_{2})_{n}-CH=CH_{2} + (RO)_{2}PSH \xrightarrow{ZnCl_{2}} CH_{3} \xrightarrow{CH_{3}} S_{\parallel} \\ H \xrightarrow{CH_{3}(CH_{2})_{n}-CH=CH_{2}} + CH_{3}(CH_{2})_{n}CH-S-P(OR)_{2}$ (1)

R = Et, n = 13; R = Pr-*i*, n = 13; R = Pr-*i*, n = 15; R = Bu-*i*, n = 13

Abstract Reactions of O,O-dialkyl dithiophosphoric acids with hexadec-1-ene, octadec-1-ene, and also 2-methylpentadec-1-ene and 2-methylheptadec-1-ene as impurities in commercial samples of hexadec-1-ene and octadec-1-ene, and pure 2-methylpent-1-ene were studied in the presence of zinc chloride and ultrasound irradiation.

Keywords Higher olefins; dithiophosphoric acids; zinc chloride; hexadec-1-ene; octadec-1ene; 2-methylpent-1-ene

INTRODUCTION

One of the actual problems of petroleum chemical industry is related to effective use of higher mono-olefins of industrial fractions of C_{16} – C_{18} , C_{20} – C_{26} , and C_{28} – C_{40} . The fraction of C_{16} – C_{18} mainly includes vinylidene α -olefins (25.6%), linear C_{16} and C_{18} α -olefins (61.6%), and inner C_{16} and C_{18} olefins (12.8%).¹ Taking into account the rather complicacy of content of industrial fraction of C_{16} – C_{18} of higher olefins, we have studied model reactions of hexadec-1-ene and octadec-1-ene as linear C_{16} and C_{18} α -olefins, and 2-methylpent-1-ene as vinylidene α -olefin with dithiophosphoric acids.

RESULTS AND DISCUSSION

In the series of nonactivated simple asymmetric olefins propylene, oct-1-ene, oct-2-ene, cyclohexene,² 2-methyl-buth-2-ene, norbornene, racemic β -camphene³, and

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Address correspondence to Ilyas S. Nizamov, Lab. of Organoelement Synthesis, State Budgetary-Funded Institution of Science, A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Arbuzov Str., 8, Kazan 420088, Russian Federation. E-mail: isnizamov@mail.ru

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1-aryl-butadienes-1,3⁴ have been reported to react with *O*,*O*-dialkyl dithiophosphoric acids to give adducts. The reactions of lower olefins were carried out at elevated temperature (100–110 °C). However, the chemical behavior of nonactivated simple higher (C_{16} and C_{18}) α -mono-olefins remained unknown in similar reactions. To increase low reactivity of long chain higher olefins, we have defined catalysts or initiators of these transformations. On the basis of ¹H NMR spectra, purchased commercial samples of hexadec-1-ene and octadec-1-ene contain 2% of 2-methylpentadec-1-ene and 2-methylheptadec-1-ene, respectively, as impurities of vinylidene alpha-olefins.⁵ The reactions of *O*,*O*-dialkyl dithiophosphoric acids with hexadec-1-ene and octadec-1-ene in the presence of zinc chloride (3.0 wt%) as Lewis acid catalyst at 80 °C over 2 h led to formation of *O*,*O*-dialkyl-*S*-2methylalkyldithiophosphates as major products in yields of 63–88% in accordance with Markovnikov's rule (Equation (1)).

$$CH_{3}(CH_{2})_{n}-CH=CH_{2} + (RO)_{2}PSH \xrightarrow{ZnCl_{2}} CH_{3} S | I \\ CH_{3}(CH_{2})_{n}-CH=CH_{2} + (RO)_{2}PSH \xrightarrow{I} CH_{3}(CH_{2})_{n}CH-S-P(OR)_{2}$$
(1)
$$R = Et, n = 13; R = Pr-i, n = 13; R = Pr-i, n = 15; R = Bu-i, n = 13$$

The impurities of 2-methylpentadec-1-ene and 2-methylheptadec-1-ene also react with dithiophosphoric acids to form *O*,*O*-dialkyl-*S*-1,1-dimethylalkyldithiophosphates as minor products (Equation (2)).

$$CH_{3}-(CH_{2})_{n}-C=CH_{2} + (RO)_{2}PSH \xrightarrow{ZnCl_{2}} CH_{3}(CH_{2})_{n}C-S-P(OR)_{2} \qquad (2)$$

$$R = Et, n = 12; R = Pr-i, n = 12; R = Pr-i, n = 14; R = Bu-i, n = 12$$

Reaction of di-*iso*-propyldithiophosphoric acid with hexadec-1-ene was also performed under ultrasound irradiation (frequency 22 kHz, power 400 W) to form the same adduct at 60 °C for 30 min. The reaction of pure 2-methylpent-1-ene as a model of vinylidene α -olefin with *O*,*O*-diethyl dithiophosphoric acid proceeds at 20 °C for 6 days to give *O*,*O*-diethyl *S*-1,1-dimethylbuthyl dithiophosphate in 97% yield (Equation (3)).

$$CH_{3}CH_{2}CH_{2}C=CH_{2} + (EtO)_{2}PSH \xrightarrow{ZnCl_{2}} CH_{3}CH_{2}CH_{2}C=S-P(OEt)_{2} \quad (3)$$

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%.

REFERENCES

- Nizamov, I. S.; Yermolaev, Ye. S.; Nizamov, I. D.; Sergeenko, G. G.; Batyeva, E. S.; Alfonsov, V. A. Chem. Techn.: An Indian J. 2007, 2, http://tsijournals.com/ctaij/Vol_2_3/Abs08.html.
- 2. Norman, G. R.; LeSuer, W. M.; Mastin, T. W. J. Am. Chem. Soc. 1952, 74, 161-163.

- Mebah, J. M. N.; Mieloszynski, J. L.; Paquer, D. Phosphorus Sulfur Silicon Relat. Elem. 1992, 73, 49-56.
- 4. Obushak, N. D.; Vovk, M. V.; Vengrzhanovskii, V. A.; Mel'nik, Y. I.; Ganushchak, N. I. *Russ. J. Gen. Chem. (Engl. Transl.)* **1987,** 57, 1078-1080.
- Nizamov, I. S.; Nizamov, I. D.; Popovich, Y. E.; Yambushev, F. D.; Cherkasov, R. A. Russ. J. Gen. Chem. (Engl. Transl.) 2012, 82, 27-32.