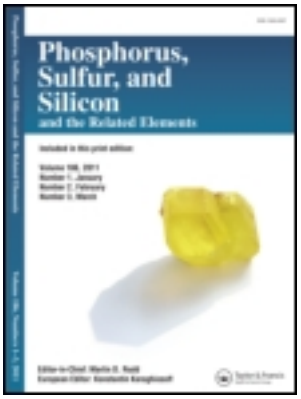


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

O,O-Dialkyldithiophosphoric Acids in the Reactions with Nonactivated α-Olefins

Lidiya I. Kursheva [a] , Ilyas S. Nizamov [a b] , 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
Accepted author version posted online: 12 Sep 2012.Published online: 29 May 2013.

To cite this article: Lidiya I. Kursheva , Ilyas S. Nizamov , Elvira S. Batyeva , Ilnar D. Nizamov , Farid D. Yambushev & Rafael A. Cherkasov (2013): O,O-Dialkyldithiophosphoric Acids in the Reactions with Nonactivated α-Olefins, Phosphorus, Sulfur, and Silicon and the Related Elements, 188:4, 487-489

To link to this article: http://dx.doi.org/10.1080/10426507.2012.727511

Phosphorus, Sulfur, and Silicon, 188:487–489, 2013

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2012.727511

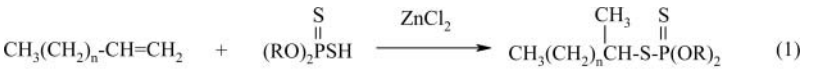
O,O-DIALKYLDITHIOPHOSPHORIC ACIDS IN THE REACTIONS WITH NONACTIVATED α-OLEFINS

Lidiya I. Kursheva,[1] Ilyas S. Nizamov,[1,2] Elvira S. Batyeva,[1] Ilnar D. Nizamov,[2] Farid D. Yambushev,[2] and Rafael A. Cherkasov[2]

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

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

GRAPHICAL ABSTRACT



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-1-ene; 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.

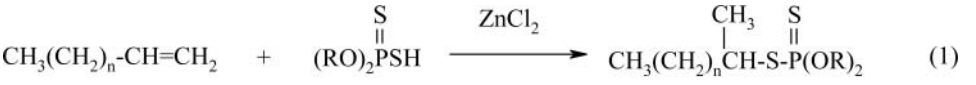
RESULTS AND DISCUSSION

In the series of nonactivated simple asymmetric olefins propylene, oct-1-ene, oct-2-ene, cyclohexene,[2] 2-metthyl-buth-2-ene, norbornene, racemic β-camphene[3], and

Received 27 June 2012; accepted 1 August 2012.

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

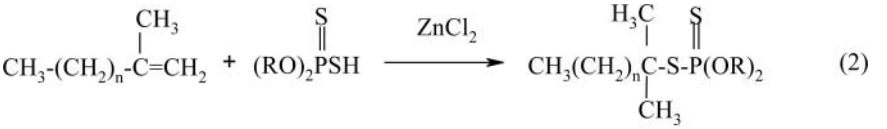
1-aryl-butadienes-1,3[4] have been reported to react with *O*,*O*-dialkyl dithiophosphoric acids to give adducts. The reactions of lower olefins were carried out at elevated temperature (100–110 °C). However, the chemical behavior of nonactivated simple higher (C_{16} and C_{18}) α-mono-olefins remained 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 ^{1}H 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*-2-methylalkyldithiophosphates as major products in yields of 63–88% in accordance with Markovnikov's rule (Equation (1)).



(1)

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

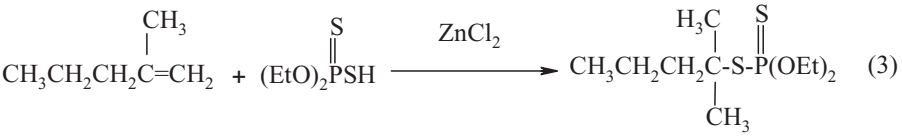
The impurities of 2-methylpentadec-1-ene and 2-methylheptadec-1-ene also react with dithiophosphoric acids to form *O*,*O*-dialkyl-*S*-1,1-dimethylalkyldithiophosphates as minor products (Equation (2)).



(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)).



(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

1. 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.

3. 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.
5. 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.