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# The development of technological method of manufactoring of O,O-dialkyl esters of long-chain alkylphosphonic acids on the basis of industrial fractions of higher monoolefins

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## ABSTRACT

The reactions of higher monoolefins of industrial fractions of $C_{16}$-$C_{18}$ and $C_{20}$-$C_{26}$ with O,O-dialkyl phosphites in the presence of benzoyl peroxide were studied. On the basis of these studies, the technological method of synthesizing o,o-dialkyl esters of mixed long-chain alkylphosphonic acids was developed.

## KEYWORDS

Higher industrial olefins;
Phosphonation;
O,O-dialkyl phosphates;
Long-chain alkylphosphonates.

## INTRODUCTION

Numerous derivatives of phosphonic acids are known to have a considerable commercial value as well as a great variety of useful application. Organic phosphonic acids as well as their esters and salts have found an expanding application as plasticizers for many plastics and resins, oil lubricant additives, corrosion inhibitors, surface-active agents, emollients, washing agents, wetting agents and detergents, dispersing agents, flame proofing agents, bonding agents for asphalt, general agricultural and household chemicals including pesticides etc[1-12]. Homolytical phosphorylation of non-activated individual lower aliphatic olefins by acidic phosphites are usually broadly used for preparing of organophosphorus compounds containing the P-C bond formed in accordance with anti-Markovnikow's rule[1-10]. O,O-Dialkyl esters of long-chain alkylphosphonic acids were previously synthesized by radical addition of O,O-dialkyl phosphites onto individual higher $\alpha$-olefins of $C_{12}$-$C_{22}$ in the presence of di(t-butyl)peroxide [11,12]. Non-terminally substituted O,O-dimethyl alkylphosphonates have been prepared by the reaction of individual internally unsaturated hydrocarbons of $C_{12}$-$C_{22}$ with O,O-dimethyl phosphite in the presence of organic peroxides[13]. However, the chemical behavior of O,O-dialkyl phosphites remained unstudied toward the complicated mixtures of various structure olefins of industrial fractions of $C_{16}$-$C_{18}$ and $C_{20}$-$C_{26}$. Consequently, in this article, an efficient method is presented for the synthesis of O,O-dialkyl esters of mixed long-chain alkylphosphonic acids directly from higher industrial olefins.

## EXPERIMENTAL

The $^{31}$P NMR spectra were recorded with a Bruker

CXP-100(36.47MHz) instrument. The $^1H$ NMR spectra were taken on a Bruker MSL-400(400MHz) spectrometer and an Avance-600(600MHz) spectrometer in $CDCl_3$. The $^{13}C$ NMR spectra were run on an Avance-600(100.6MHz) spectrometer in $CDCl_3$. The IR spectra were obtained with a Bruker Vector 22 infrared spectrometer. Mass spectra were determined on a Turbomass Gold Perkin Elmer chromatomass spectrometer, Finnigan MAT-212 spectrometer(60eV), TRACE MS Finnigan MAT(70eV) and laser mass spectrometer Dynamo Finnigan(method MALDI TOF with precession values of mass peaks). GC analyses were performed on a Turbomass Gold Perkin Elmer chromatomass spectrometer.

Olefins of industrial fractions of $C_{16}$-$C_{18}$(TU 2411-067-05766801-97) and $C_{20}$-$C_{26}$(TU 2411-068-05766801-97) were obtained from Join Stock Company "Nizhnekamskneftekhim"(Russia) and dried with $CaCl_2$. O,O-Dimethyl phosphite(TU 2435-430-057663441-2004) was purchased from join stock company "Khimprom"(Novocheboksarsk, Russia) and used without further purification. O,O-Di-*iso*-propyl phosphite was prepared according to literature[14]. Commercial available benzoyl peroxide was used without purification.

### Reaction of olefins of fraction of $C_{16}$-$C_{18}$ (1a-c) with O,O-dimethyl phosphite (3a) in molar ratio 1:1. typical procedure

The mixture of **(1a-c)**(15.0g, 62.9mmol), **3a**(6.5 g, 59.1 mmol) and **4**(0.4g, 0.8mmol) was stirred at 135-140$^0$C for 3h. The mixture was diluted with 10mL of $Et_2O$ and washed by third portions of 25mL of water. Organic layer was separated and dried with $CaCl_2$ for ~12 h. The mixture was filtered. The filtrate was evaporated at reduced pressure(0.5mm Hg) at 40$^0$Cfor 1 h and at 0.06 mm Hg at 40$^0$C for 1 h to give 16.4 g(81%) of crude **(5a-d)**. Pure **(5a-d)**(13.8g, 67%) was isolated from the residue by means of a falling-film distillation at 100-110$^0$C(0.02 mm Hg) and then distilled in vacuum with bp 110-115$^0$C(0.05 mm Hg)(See TABLES 3-8).

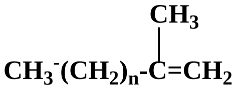
Crude products**(5a-d)** were also obtained similarly by the reaction of**(1a-c)** with **(3a)** in molar ratio 1:2 in the presence of benzoyl peroxide **(4)**(See TABLE 3) with the use of benzene(70mL) instead of $Et_2O$.

Products **(6a-d)** were obtained similarly(See TABLES 3-7), however, without water washing.

Products **(7a-d)** and **(8a-d)** were obtained similarly (See TABLES 3-8) with water washing, however, without use of a solvent. Crude **(8a-d)** were chromato graphed on a silica gel column with ethyl acetate as eluent to yield pure **(8a-d)**.

## RESULTS AND DISCUSSION

Taking into account the rather complicacy of content of industrial fractions of higher olefins, we have initially studied the content and structure of industrial fractions of $C_{16}$-$C_{18}$ and $C_{20}$-$C_{26}$ used in this work by $^1H$ NMR and mass spectral methods and GC analyses. Thus, the $^1H$ NMR spectrum of olefins of industrial fraction of $C_{16}$-$C_{18}$ **(1a-c)** in $CDCl_3$ solution shows four groups of signals of vinyl protons of three specimens of olefins. A singlet at δ 4.76ppm attributed to two vinyl protons $H_2C=C(CH_3)R$ at C-1 atom of 2-methyl substituted α-olefins **(1a)**. t-Vinyl proton at C-1 atom H(H)C=C(H)R of non-branched α-olefins **(1b)** gives a doublet at δ 4.98ppm($^3J_{HH}$ 10.2Hz), whereas a doublet at δ 5.05ppm is due c-vinyl proton H(H)C=C(H)R of **(1b)**($^3J_{HH}$ 16.9Hz). At δ 5.87ppm is situated a multiplet of the vinyl proton at C-2 atom of the C=C bond of linear α-olefins **(1b)**. Two vinyl protons at both C-1 and C-2 atoms of C=C bond of olefins **(1c)** containing the inner C=C bond appear as a small intensity characteristic multiplet at δ 5.47ppm. On the intensities of vinyl protons it was established that industrial fraction of $C_{16}$-$C_{18}$ includes isomeric α-olefins **(1a)** 25.6%, linear α-olefins **(1b)**-61.6% and inner unsaturated hydrocarbons **(1c)**-12.8%. Thus, on the basis of $^1H$ NMR spectral data,the general content of α-olefins of $C_{16}$ and $C_{18}$ in the fraction of $C_{16}$-$C_{18}$ is 87.2% including 1-alkenes of linear and branched structure.



$CH_3\text{-}(CH_2)_n\text{-}\overset{CH_3}{\overset{|}{C}}=CH_2$

**n=12,14**

**(1a)**

$CH_3\text{-}(CH_2)_n\text{-}CH=CH_2$

**n = 13,15**

**(1b)**

$CH_3(CH_2)_kCH=CH(CH_2)_mCH_3$

**($C_{16}$,$C_{18}$)**

**(1c)**

**TABLE 1 : The content of olefins of the fraction of $C_{16}$-$C_{18}$ on the basis of GC and chromatomass spectra**

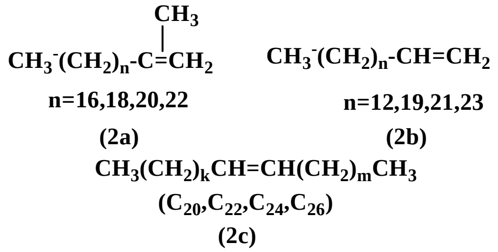
| Number of peaks | The GC bush | Retention time, min | The content, % | The appertaining |
|---|---|---|---|---|
| 1 | $C_{16}$ | 9.67 | 4.2 | 7-Methylenepentadecane |
| 2 | $C_{16}$ | 9.75 | 3.7 | 2-Methyl-1-pentadecene |
| 3 | $C_{16}$ | 10.03 | 8.8 | Methyl substituted 1-pentadecene |
| 4 | $C_{16}$ | 10.16 | 32.3 | 1-Hexadecene |
| 5 | $C_{16}$ | 10.27 | 5.8 | 7-Hexadecene |
| 6 | $C_{16}$ | 10.40 | 2.8 | 3-Hexadecene |
| 7 | $C_{18}$ | 12.01 | 7.1 | Methyl substituted 1-heptadecene |
| 8 | $C_{18}$ | 12.11 | 3.9 | 2-Methyl-1-heptadecene |
| 9 | $C_{18}$ | 12.35 | 9.4 | Methyl substituted 1-heptadecene(isomer) |
| 10 | $C_{18}$ | 12.44 | 14.7 | 1-Octadecene |
| 11 | $C_{18}$ | 12.55 | 5.2 | 5-Octadecene |
| 12 | $C_{18}$ | 12.68 | 2.1 | 9-Octadecene |
|  | In all |  | 100.0 |  |

We have found that olefins of industrial fractions of $C_{16}$-$C_{18}$ and $C_{20}$-$C_{26}$ involve in exclusively even number of carbon atoms. GC-chromatomass spectra of olefins of fraction of $C_{16}$-$C_{18}$ reveal two bushes of peaks with retention times of 9.67-10.40 and 12.01-12.68 min belong to unsaturated hydrocarbons of $C_{16}$ and $C_{18}$ respectively(TABLE 1). The appertaining of GC peaks obtained was carried out on the basis of Perkin Elmer electronic chromatogram and mass spectral library. It was established that general content of $\alpha$-olefins of $C_{16}$ is 44.8% involving 32.3% of 1-hexadecene, 3.7% of 2-methyl-1-pentadecene and 8.8% of methyl substituted 1-pentadecene(no site of situation of methyl group determined). Four peaks of $\alpha$-olefins were found in the bush of $C_{18}$ that corresponds to 35.1% with respect to general content of $\alpha$-olefins. $\alpha$-Olefins of $C_{18}$ involve 14.7% of 1-octadecene and 20.4% of three methyl substituted 1-heptadecenes including 2-methyl-1-heptadecene. Thus, the general content of $\alpha$-olefins of $C_{16}$ and $C_{18}$ in the fraction of $C_{16}$-$C_{18}$ is 79.9%. Taking into account 4.2% of 7-methylenepentadecane, the general content of $\alpha$-olefin is increased to 84.1%. On the other hand, 3- and 7-hexadecenes as olefins of $C_{16}$ with the inner C=C bond are included in the fraction of $C_{16}$-$C_{18}$ in the overall quantity of 8.6%, whereas the mutual content of 5- and 9-octadecenes as inner unsaturated hydrocarbons of $C_{18}$ is no more 7.3%. Thus, the general content of olefins of $C_{16}$ and $C_{18}$ with the inner C=C bond in the fraction $C_{16}$-$C_{18}$ is 15.9%.

**TABLE 2 : The content of olefins of the fraction of $C_{20}$-$C_{26}$ on the basis of GC and chromatomass spectra**

| Number of peaks | The GC bush | Retention time, min | The content, % | Found MS peaks *m/z* | The appertaining |
|---|---|---|---|---|---|
| 1 | $C_{20}$ | 14.06 | 5.5 | 280 | 2-Methyl-7-nonadecene |
| 2 | $C_{20}$ | 14.10 | 4.0 | 280 | 2-Methyl-7-nonadecene(isomer) |
| 3 | $C_{20}$ | 14.18 | 3.0 | 280 | 2-Methyl-1-nonadecene |
| 4 | $C_{20}$ | 14.41 | 7.2 | 280 | 3,7,11,15-Tetramethyl-2- hexadecene |
| 5 | $C_{20}$ | 14.47 | 6.3 | 280 | 1-Eicosene |
| 6 | $C_{20}$ | 14.51 | 1.5 | 280 | Unidentified |
| 7 | $C_{20}$ | 14.56 | 2.6 | 280 | 5-Eicosene |
| 8 | $C_{20}$ | 14.70 | 1.6 | 280 | 9-Eicosene |
| 9 | $C_{22}$ | 15.95 | 8.3 | 308 | 2-Methyl-1-uncosene |
| 10 | $C_{22}$ | 15.99 | 3.8 | 308 | 2-Methyl-7-uncosene |
| 11 | $C_{22}$ | 16.07 | 2.2 | 308 | 2-Methyl-7-uncosene(isomer) |
| 12 | $C_{22}$ | 16.28 | 5.5 | 308 | 9-Methyl-1-uncosene |
| 13 | $C_{22}$ | 16.33 | 3.7 | 308 | 1-Docosene |
| 14 | $C_{22}$ | 16.41 | 1.6 | 308 | 5-Docosene |
| 15 | $C_{22}$ | 16.55 | 0.9 | 308 | 9-Docosene |
| 16 | $C_{24}$ | 17.68 | 6.6 | 336 | 2-Methyl-1-tricosene |
| 17 | $C_{24}$ | 17.73 | 2.5 | 336 | 2-Methyl-7-tricosene |
| 18 | $C_{24}$ | 17.80 | 1.1 | 336 | 2-Methyl-1-tricosene(isomer) |
| 19 | $C_{24}$ | 17.99 | 3.1 | 336 | Methyl substituted 1-tricosene |
| 20 | $C_{24}$ | 18.03 | 1.7 | 336 | 1-Tetracosene |
| 21 | $C_{24}$ | 18.10 | 0.8 | 336 | 5-Tetracosene |
| 22 | $C_{24}$ | 18.25 | 0.6 | 336 | 9-Tetracosene |
| 23 | $C_{26}$ | 19.27 | 9.3 | 364 | 2-Methyl-1-pentacosene |
| 24 | $C_{26}$ | 19.33 | 1.2 | 364 | 2-Methyl-7-pentacosene |
| 25 | $C_{26}$ | 19.40 | 0.6 | 364 | 10-Methyl-2-pentacosene |
| 26 | $C_{26}$ | 19.58 | 1.2 | 364 | 9-Methyl-1-pentacosene |
| 27 | $C_{26}$ | 19.61 | 0.6 | 364 | 9-Methyl-1-pentacosene(isomer) |
| 28 | $C_{28}$ | 20.75 | 6.6 | 392 | Methyl substituted heptacosene |
| 29 | $C_{28}$ | 20.89 | 0.3 | 392 | Unidentified |
| 30 | $C_{28}$ | 20.95 | 0.4 | 392 | Unidentified |
| 31 | $C_{28}$ | 21.05 | 0.5 | 392 | Unidentified |
| 32 | $C_{30}$ | 22.14 | 3.3 | 420 | A triacontene |
| 33 | $C_{32}$ | 23.43 | 1.3 | 448 | A dotriacontene |
| 34 | $C_{34}$ | 24.65 | 0.6 | 476 | A tetratriacontene |
|  | In all |  | 100.0 |  |  |

The content, mass distribution and appertaining of olefins involved in the fraction of $C_{20}$-$C_{26}$ **(2a-c)** is summarized in TABLE 2. It should be emphasized that the fraction trade marked as $C_{20}$-$C_{26}$ mostly consists from the olefins of $C_{20}$(the overall consist of $C_{20}$ is 31.7%), $C_{22}$(26.0%), $C_{24}$(16.4%) and $C_{26}$(12.9%) involving $C_{28}$(7.8%), with more than half of unsaturated hydrocarbons(57.7%) being the olefins of $C_{20}$ and $C_{22}$ in summa. On the basis of GC, 8 peak bushes were found in the fraction of $C_{20}$-$C_{26}$. In the fraction of $C_{20}$-$C_{26}$ the most of a-olefins were established to be 2-methyl substituted branched 1-alkenes such as 2-methyl-1-nonadecene, -uncosene, -tricosene and pentacosene(in general of ~35%). Such α-olefins of linear structure as 1-eicosene, 1-docosene and 1-tetracosene are situated in general quantity of 11.7% in the fraction of $C_{20}$-$C_{26}$. The general content of inner unsaturated hydrocarbons of branched(mostly methyl substituted) and linear structure(such as 2-methyl-7-nonadecene, 2-methyl-7-uncosene, 2-methyl-7-tricosene, 2-methyl-7-pentacosene, 5- and 9-eicosenes, 5- and 9-docosenes and 5- and 9-tetracosenes) reaches to ~28%. Thus, industrial fractions of olefins of $C_{16}$-$C_{18}$ and $C_{20}$-$C_{26}$ mostly involve in 2-methyl substituted α-olefins **(1a)** and **(2a)** and linear α-olefins**(1b)** and **(2b)**. Minor amounts of spatially hindered olefins with inner C=C bond **(1c)** and **(2c)** seem to possess low reactivity with respect to O,O-dialkyl phosphites.



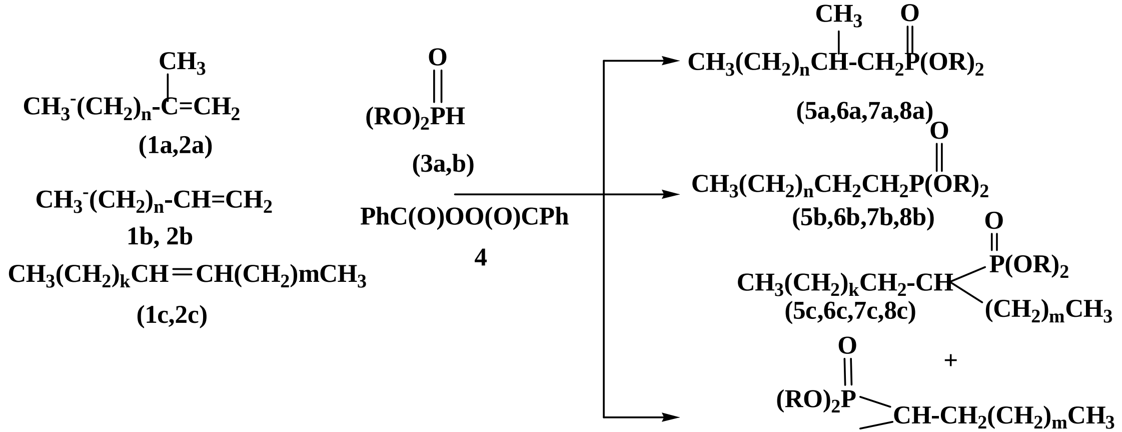
$CH_3^-(CH_2)_n$-$C(CH_3)$=$CH_2$ n=16,18,20,22 (2a)

$CH_3^-(CH_2)_n$-CH=$CH_2$ n=12,19,21,23 (2b)

$CH_3(CH_2)_kCH$=$CH(CH_2)_mCH_3$ ($C_{20}$,$C_{22}$,$C_{24}$,$C_{26}$) (2c)

It should be expected that complicacy of content of industrial fractions of olefins of $C_{16}$-$C_{18}$ and $C_{20}$-$C_{26}$ can lead to intricate mixture of the addition products of O,O-dialkyl phosphites into the C=C bond. We were deciding for use effectively method of promoting of addition reaction of O,O-dialkyl phosphites with non-activating olefins by involving benzoyl peroxide. Indeed, the reaction of olefins of industrial fractions of $C_{16}$-$C_{18}$ **(1a-c)** and $C_{20}$-$C_{26}$ **(2a-c)**with O,O-dialkyl phosphites **(3a,b)** in molar ratio 1:1 in the presence of benzoyl peroxide **(4)** has been shown to bring about the formation of O,O-dialkyl esters of long chain alkylphosphonic acids **(5a-d), (6a-d), (7a-d)** and **(8a-d)** as a mixture of homologues and isomers at 125-140$^0$C for 3-12 h(TABLES 3-8).

It should be noted that the initial O,O-dialkyl phosphites **(3a,b)** are good dissolved in water. That is why



R=Me(2a,5a-d, 6a-d), Pr-*i* (2b,7a-d,8a-d);

n=12,14(5a,7a); 13,15(5b,7b); 16,18,20,22(6a,8a); 17,19,21,23(6b,8b) (5d,6d,7d, 8d)

**TABLE 3 : Experimental data and yields of the products obtained**

| Initial compounds quantity(g(mmol)) | Reaction conditions temp.($^o$C)/Time(h) | Product yield(g(%)) |
|---|---|---|
| **3a** 6.5(59.1)/**1a-c** 15.0(62.9)/**4** 0.4(0.8) | 135-140/3 | **5a-d** 16.7(81)$^a$/13.8(67)$^b$ |
| **3a**$^d$ 87.3(793.6)/**1a-c** 100(419.5)/**4** 0.9(3.7) | 120-130/3 | **5a-d** 120.5(87)$^a$ |
| **3a** 4.5(40.9)/**2a-c** 13.2(40.9)/**4** 0.2(3.7) | 130-140/10.5 | **6a-d** 11.6(66)$^b$ |
| **3b** 17.6(106.0)/**1a-c** 25.3(106.1)/**4** 4.8(19.8) | 135-140/10 | **7a-d** 31.4(73)$^e$/24.4(57)$^c$ |
| **3b** 7.7(46.7)/**2a-c** 15.0(46.5)/**4** 1.0(4.1) | 135-140/12 | **8a-d** 14.0(62)$^{b, f}$ |

[a]Yield of crude products, [b]Yield of products isolated by means of a thin layer distillation, [c]Yield of product isolated by vacuum distillation, [d]In molar ratio of 1a-c:3a as 1:2, [e]Yield of product isolated by vacuum evaporation(0.06 mm Hg) of non-reacted olefins, [f]Products were purified by column chromatography

**TABLE 4 : Physical, analytical and $^{31}$P NMR spectral data of products obtained**

| Prod. | B.p.($^0$C) (mm Hg)$^a$/m.p($^0$C) | $n_D^{20}$ | $d_4^{20}$ | Molecular *formula* (mol. mass) | Found/(calc.), %P | $^{31}$P NMR δppm (ratio) |
|---|---|---|---|---|---|---|
| **5a-d**$^{c,d}$ | 110-115(0.05)$^b$/15-20 | 1.4659 | 0.9945 | $C_{18}H_{39}O_3P$(334.4)<br>$C_{20}H_{43}O_3P$(362.4)<br>$C_{22}H_{47}O_3P$(390.4) | 9.27/<br>(9.26-8.55) | 33.8, 35.0, 37.1<br>(12:84:4) |
| **6a-d** | 170(0.02) | 1.4628 | 0.9088 | $C_{24}H_{51}O_3P$(418.5)<br>$C_{26}H_{55}O_3P$(446.5)<br>$C_{28}H_{59}O_3P$(474.4) | 6.72/<br>(7.93-6.53) | 35.9, 34.1(2.5:1.0) |
| **7a-d** | 170-180(0.02) | 1.4580 | | $C_{22}H_{47}O_3P$(390.4)<br>$C_{24}H_{51}O_3P$(418.5)<br>$C_{28}H_{59}O_3P$(474.6) | 7.63/<br>(7.93-7.40) | 29.3, 30.0, 31.4, 31.8(80:5:7:7) |
| **8a-d**$^{e,f}$ | | 1.4399 | | $C_{30}H_{63}O_3P$(502.6)<br>$C_{32}H_{67}O_3P$(530.6)<br>$C_{34}H_{71}O_3P$(558.7) | 6.16/<br>(6.53-5.54) | 28.7, 30.2, 33.2, 35.4(3:20:76:10) |

**$^a$Temperature of thermal element of a thin layer distillation apparatus, $^b$Bp of vacuum distillation, $^c$GC retention time, min: 15.88-19.18, $^d$Kinematic viscosity $\eta^{20}$, ñSt: 17.88, $^e$R$_f$ 0.74(AcOEt), $^f$GC retention time, min: 12.78-16.91**

**TABLE 5 : IR spectral data of the products obtained**

| Product | ν, cm$^{-1}$ |
|---|---|
| **5a-d** | 2940, 2925, 2854 ν($CH_3$ as, s; $CH_2$ as, s); 1464 δ($CH_3$ as), δ($CH_2$); 1378 δ($CH_3$ s); 1199 ν(P=O); 1034 ν[(P)O-C)]; 995 ν(OC-C); 842 ν($PO_2$ as, s). |
| **6a-d** | 2924, 2853 ν($CH_3$ as, s; $CH_2$ as, s); 1464 δ($CH_3$ as); δ($CH_2$); 1378 δ($CH_3$ s); 1203 ν(P=O); 1052 ν [(P)O-C)]; 989 ν(OC-C); 888 ν($PO_2$ as, s). |
| **7a-d** | 2940, 2926, 2854 ν($CH_3$ as, s; $CH_2$ as, s); 1464 δ($CH_3$ as); δ($CH_2$); 1380 δ($CH_3$ s); 1247 ν(P=O); 1008 ν[(P)O-C)]; 983 ν(OC-C); 891 ν($PO_2$ as, s). |
| **8a-d** | 2940, 2926, 2855 ν($CH_3$ as, s; $CH_2$ as, s); 1466 δ($CH_3$ as); δ($CH_2$); 1374 δ($CH_3$ s); 1242 ν(P=O); 1009 ν [(P)O-C)]; 984 ν(OC-C); 894 ν($PO_2$ as, s). |

**TABLE 6 : $^1$H NMR spectral data of the products obtained**

| Product | $CDCl_3$, δ, ppm , J, Hz |
|---|---|
| **5a-d** | 0.88(t, 3H, $CH_3CH_2CH_2$, $^3J_{HH}$ 7.0); 1.27 [broad s, $C(CH_2)_nC$); 1.37[d, 3H, $CH_3C(H)P$]; 1.62(m, 2H, $PCH_2CH_2CH_2$); 1.74(m, 2H, $PCH_2CH_2$); 1.96(m, 1H, $PCHR_2$]; 2.04(m, 2H, $PCH_2$]; 3.64[m,$(CH_3O)_2PCHR_2$]; 3.73 and 3.74 [two d, 6H,$(CH_3O)_2P$, $^3J_{PH}$ 10.71 and $^3J_{PH}$ 10.98]. |
| **6a-d** | 0.83(t, 3H, $CH_3CH_2$, $^3J_{HH}$ 7.0); 1.27 [broad s, $C(CH_2)_nC$)]; 1.38(d, 3H, $CH_3C(H)CH_2P$); 1.59(m, 2H, $PCH_2CH_2CH_2$); 1.92(m, 2H, $PCH_2CH_2$); 1.99(m, 2H, $PCH_2CH_2$); 3.71 [d, 6H,$(CH_3O)_2P$, $^3J_{PH}$ 11.0]; 3.74 [d, 6H,$(CH_3O)_2P$, $^3J_{PH}$ 11.0]. |
| **7a-d** | 0.85(t, 3H, $CH_3C$, $^3J_{HH}$ 6.5); 1.23 [broad s, $C(CH_2)_nC$]; 1.27 {d, 12H, $[(CH_3)_2CHO]_2P$, $^3J_{HH}$ 5.8}; 1.45(m, 2H, $PCH_2CH_2CH_2$); 1.50(m, 2H, $PCH_2CH_2$); 1.97(m, 2H, $PCH_2CH_2$); 2.34(m, 1H, $PCH_2CH(CH_3)CH_2$); 4.66 {m, 2H, $[(CH_3)_2CHO]_2P$}. |
| **8a-d** | 0.80(t, 3H, $CH_3CH_2CH_2$, $^3J_{HH}$ 7.0); 1.18 [broad s, $C(CH_2)_nC$]; 1.22(d, 12H, $[(CH_3)_2CHO]_2P$, $^3J_{HH}$ 6.2); 1.30(m, 2H, $PCH_2CH_2CH_2$); 1.54(m, 2H, $PCH_2CH_2$); 1.94(m, 2H, $PCH_2CH_2$); 4.59(m, 2H, $[(CH_3)_2CHO]_2P$). |

we have used the water washing of crude reaction mixtures for the removing of non-reacted amounts of **(3a,b)**. An organic solvent has often used so that destroy an emulsion formed. On the basis of GC, IR and $^{31}$P, $^1$H and $^{13}$C NMR spectroscopy(TABLES 4-8), it was established that the products **(5a-d)**, **(6a-d)**, **(7a-d)** and **(8a-d)** were formed in high purity after water washing, drying with $CaCl_2$ and vacuum evaporating that increased the technological level of method developed. These compounds do not requiring further purification by vacuum distillation for they to find practical use.

The products **(5a-d)**, **(6a-d)**, **(7a-d)** and **(8a-d)** were obtained in rather high yields(62-81%)(TABLE 3) before the purification by vacuum distillation. To obtain analytically pure specimens of **(5a-d)**, **(6a-d)**, **(7a-d)** and **(8a-d)** they were further isolated by means of a falling-film distillation and then vacuum distillation. After removing of olefin admixtures the products **(5a-d)**, **(6a-d)**, **(7a-d)** and **(8a-d)** were solidified as white wax-like substances with lower melting points.

The $^{31}$P NMR spectra of**(5a-d)**, **(6a-d)**, **(7a-d)** and **(8a-d)**(TABLE 3) reveal a few singlets in the region of $\delta_{Ð}$ 28-37 ppm in the practically same region as observed in other phosphonates with the structural fragment C-P=O[15]. In the $^{31}$P NMR spectrum of crude **(5a-d)** obtained in the reaction of olefins of fraction of $C_{16}$-$C_{18}$ **(1a-c)** with O,O-dimethyl phosphite **(3a)** after water washing there are three singlet signals at $\delta_{Ð}$ 33.8, 35.0

**TABLE 7 : $^{13}C$ NMR spectral data of the products obtained$^a$**

| Product | $CDCl_3$, δ, ppm , J, Hz |
|---|---|
| **5a-d** | 14.1[s(q) $CH_3CH_2$, $^1J_{HC}$ 124.4]; 22.5[s(d) $PCH_2CH_2$, $^2J_{PC}$ 8.0]; 22.8 [s(t) $CH_3CH_2$, $^1J_{HC}$ 124.4]; 24.8 [d(m) $PCH_2CH_2$, $^1J_{PC}$ 139.9]; 26.3 [d(m) $CH_3CH_2CH_2P$, $^3J_{PC}$ 7.7]; 26.8[d(m) $PCH_2CH_2CH_2$, $^3J_{PC}$ 7.7]; 29.4[d(m) $PCH_2CH_2CH_2$, $^4J_{PC}$ 9.4]; 29.5 [s(t) $CH_3CH_2CH_2CH_2$, $^1J_{HC}$ 124.4]; 29.85[broad s(t) $CCH_2C$, $^1J_{HC}$ 124.4]; 32.1 [s(t) $CH_3CH_2CH_2$, $^1J_{HC}$ 124.4]; 33.5[d(m) $PCH_2CH$, $^1J_{PC}$ 140.0]; 34.1 [d(m) $PCH_2CH$, $^2J_{PC}$ 17.4]; 34.6[d(m) $PCH_2CHCH_2$, $^3J_{PC}$ 9.0]; 51.4 [m(m) $POCH_3$]; 52.2 [d(d.q) $POCH_3$, $^1J_{HC}$ 147.2, $^2J_{PC}$ 27.6]. |
| **7a-d** | 13.7[s(q) $CH_3CH_2CH_2$, $^1J_{HC}$ 124.7]; 22.3[s(t) $CH_3CH_2CH_2$, $^1J_{HC}$ 124.7]; 23.67[s(t) $CH_3CH_2CH_2P$, $^1J_{HC}$ 126.1]; 23.69 and 23.73 [two s(two t) $[(CH_3)_2CHO]_2P$, $^1J_{HC}$ 127.4]; 26.7 [d(m) $PCH_2CH_2$, $^1J_{PC}$ 142.0, $^1J_{HC}$ 127.4]; 29.4 [broad s(t) $CCH_2C$, $^1J_{HC}$ 124.7]; 31.6 [s(t) $CH_3CH_2CH_2$, $^1J_{HC}$ 127.4]; 33.3[d(m) $PCH_2CHCH_3$, $^1J_{PC}$ 138.0]; 69.3 {d(d.d) $[(CH_3)_2CHO]_2P$, $^1J_{HC}$ 149/9, $^2J_{PC}$ 7.3}. |
| **8a-d** | 13.7[s(q) $CH_3CH_2CH_2$, $^1J_{HC}$ 124.7]; 22.3 [s(t) $CH_3CH_2CH_2$, $^1J_{HC}$ 124.7]; 23.67[s(t) $CH_3CH_2CH_2P$, $^1J_{HC}$ 126.1]; 23.69 and 23.73 [two s(two t) $[(CH_3)_2CHO]_2P$, $^1J_{HC}$ 127.4]; 26.7 [d(m) $PCH_2CH_2$, $^1J_{PC}$ 142.0, $^1J_{HC}$ 127.4]; 29.4 [broad s(t) $CCH_2C$, $^1J_{HC}$ 124.7]; 31.6 [s(t) $CH_3CH_2CH_2$, $^1J_{HC}$ 127.4]; 33.3 [d(m) $PCH_2CHCH_3$, $^1J_{PC}$ 138.0]; 69.3 {d(d.d) $[(CH_3)_2CHO]_2P$, $^1J_{HC}$ 149.9, $^2J_{PC}$ 7.3}. |

$^a$($^{13}C$-{$^{31}$Đ}) spectra, signal form in the $^{13}C$-{$^1H$} NMR spectrum was brought in braces

**TABLE 8 : Mass spectral data of the products obtained**

| Product$^a$ | i-$C_4H_{10}$, m/e($I_{rel}$, %) |
|---|---|
| **5a-d** | 334.4$[M]^{+\cdot}$(18); 362.4$[M]^{+\cdot}$(14). |
| **6a-d** | 390.3$[M]^{+\cdot}$(2), 418.3$[M]^{+\cdot}$(3), 446.3$[M]^{+\cdot}$(3), 474.4$[M]^{+\cdot}$(2). |
| **7a-d** | 391.439$[M]^{+\cdot}$(46), 418.171$[M]^{+\cdot}$(34). |
| **8a-d** | 475$[M]^{+\cdot}$(2), 503 $[M]^{+\cdot}$(2). |

and 37.1ppm in ratio 12:84:41(on the basis of signal integral intensities). It is of interest that the $^{31}P$ NMR spectrum of **(7a-d)** prepared by the reaction of O,O-di-*iso*-propyl phosphite **(2b)** with olefins of fraction of $C_{16}$-$C_{18}$ **(1a-c)** show four singlets at $\delta_P$ 29.3, 30.0, 31.4 and 31.8ppm in ratio 80:5:7:7. These resonances are shifted toward high field in comparison with the $^{31}P$ NMR data of **(5a-d)**.

In the $^1H$ NMR spectra(TABLE 6) of purified **(5a-d)**, **(6a-d)**, **(7a-d)** and **(8a-d)** no vinyl proton signals of initial olefins in the region of δ4.76-5.88ppm were practically detected. On the basis of the $^1H$ NMR spectra, adducts **(5a,b)**, **(6a,b)**, **(7a,b)** and **(8a,b)** were formed in accordance with anti-Markovnikow's rule as well as other radical addition of acidic phosphites into non-activated olefins with the inner C=C bond [1-10]. The $^1H$ NMR spectrum of 6a-d in $CDCl_3$ solution shows two doublets at $\delta_1$ 3.71 and $\delta_2$ 3.74ppm of the methyl protons of the$(CH_3O)_2P$ group($^3J_{PH}$ 11.0Hz). Two small intensity multiplets at δ4.66 and 4.59ppm the $^1H$ NMR spectra of **(7a-d)** and **(8a-d)** were assigned to the methine protons of two *iso*-propoxy groups at the phosphorus atom $POCHC_2$. The $^{13}C$ NMR spectrum of **(5a-d)** in $CDCl_3$ solution(TABLE 7) reveals a doublet at 24.8ppm of two protons of methylene group at the phosphorus atom $PCH_2CH_2$($^1J_{PC}$ 139.9Hz) that indicates about the addition of the phosphoryl fragment into the terminal carbon atom of the C=C bond of α-olefins **(1a)** and **(1b)**. In the case of non-terminally substituted adducts 5c,d, **(6c,d)**, **(7c,d)** and **(8c,d)**, it is difficult to exactly establish site of addition of the phosphoryl group into the inner C=C bond of olefins **(1c)** and **(2c)**.

The electron impact mass spectrum of **(5a-d)** (TABLE 8) exhibits the mass peaks m/e 334.4 and 362.4 that being attributable to the molecular ions$[M]^{+\cdot}$ of two specimens of 5 formed from the olefins of $C_{16}$ and $C_{18}$(calculated M: 334.4 and 362.4, respectively). Precession values of mass peaks m/e 391.439 and 418.171 were attributed to the molecular ions$[M]^{+\cdot}$ of 7a-d obtained by addition reaction of olefins of $C_{22}$ and $C_{24}$ with O,O-di-*iso*-propyl phosphite**(2b)** (calculated M: 390.4 and 418.5, respectively).

Broad bands of large intensity presented at ν 1185-1247Cì$^{-1}$ in the IR spectra of**(5a-d)**, **(6a-d)**, **(7a-d0** and**(8a-d)**(TABLE 5) are due to the valence vibrations of the P=O bond. Symmetric and antisymmetric valence vibrations of the $PO_2$ group appear as bands of medium intensity at ν 808-891cm$^{-1}$.

When 2-fold excess of the initial O,O-dimethyl phosphite **(3a)** was involved in the reaction mixture with olefins **(1a-c)**, the yield of **(5a-d)** is increased to 87% (TABLE 3). The optimal reaction conditions (reaction time and temperature) were determined by the $^{31}P$ NMR spectroscopy. Products **(5a-d)**, **(6a-d)**, **(7a-d)** and **(8a-d)** were formed up to 70-75% in the during of 3h. The further heating of the reaction mixtures up to 9-10 h results in the increasing of the yields of **(5a-d)**,

**(6a-d)**, **(7a-d)** and **(8a-d)** to 4-6%. When the prolonging heating of the reaction mixtures more than 16 h were performed, the decreasing of yields of products**(5a-d)**, **(6a-d)**, **(7a-d)** and **(8a-d)** and partially decomposition of initial phosphites **(2a,b)** were observed. On the basis of kinetic study and the $^{31}$P NMR spectra it was established that products**(5a-d)** were initially appeared in the reaction mixture of O,O-dimethyl phosphite**(3a)** with olefins**(1a-c)** at 110$^0$C. No reaction is observed below 110$^0$C. This reaction is mostly completed for 30min at 130$^0$C. Thus, very thin temperature region of 135-140$^0$C was established that leads to maximum of product yields.

## COCLUSIONS

Thus, it was shown that one of the efficient approaches of utilization of higher olefins of industrial fractions $C_{16}$-$C_{18}$ and $C_{20}$-$C_{26}$ as waste materials of olygomerization of ethylene involves development of convenient methods of their phosphorylation by use of O,O-dialkyl phosphites. The phosphorylation of higher olefins seems to be readily monitored by spectral means especially by $^{31}$P NMR. Advantages of method developed may be ecologically pure processes of manufacturing of non-toxic phosphorylated products possessed properties of practical use(steel corrosion inhibitors, fireproof agents, plasticizers in food polymer films, surface-active agents etc).

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