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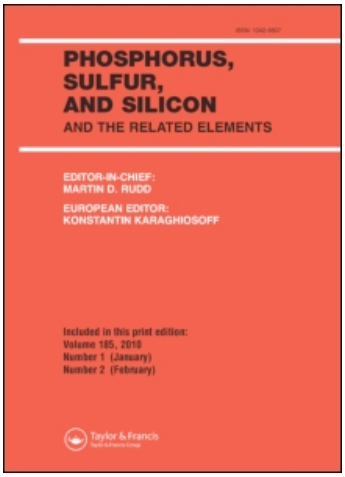

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SYNTHESIS OF MONO-AND DIALKYLPHOSPHATES BY THE REACTIONS OF HYDROXYCOMPOUNDS WITH THE PHOSPHORUS PENTAOXIDE UNDER MICROWAVE IRRADIATION

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To cite this Article Elias, Abdelhamid , Didi, M. Amine , Villemin, Didier , Semaoune, T. and Ouattas, S.(2004) 'SYNTHESIS OF MONO-AND DIALKYLPHOSPHATES BY THE REACTIONS OF HYDROXYCOMPOUNDS WITH THE PHOSPHORUS PENTAOXIDE UNDER MICROWAVE IRRADIATION', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 12, 2599 — 2607
To link to this Article: DOI: 10.1080/10426500490494705
URL: http://dx.doi.org/10.1080/10426500490494705

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Phosphorus, Sulfur, and Silicon, 179:2599–2607, 2004
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490494705

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SYNTHESIS OF MONO-AND DIALKYLPHOSPHATES BY THE REACTIONS OF HYDROXYCOMPOUNDS WITH THE PHOSPHORUS PENTAOXIDE UNDER MICROWAVE IRRADIATION

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(Received May 13, 2004; accepted May 26, 2004)

The reactions of phosphorus pentoxide with two alcohols and one phenol were performed in different conditions under microwave irradiation. The products (alkylphosphates and dialkylphosphates) were identical to those formed by classic heating and were obtained with better yields. The speed of the reaction was increased by a factor from 100 to 4000.

Keywords: Alkylphosphates; dialkylphosphate; microwave irradiation; solvent free

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Alkylphosphates are synthesized from alcohols by reaction with reactive phosphorus substances such as phosphorus pentoxide (P_2O_5), phosphorus oxychloride ($POCl_3$), phosphorus trichloride (PCl_3), and phosphorus pentachloride (PCl_5).[1]

The reaction of alcohols with the phosphorus pentoxide (P_2O_5) presents several advantages, such as the simplicity of the procedure, the availability of the reagent and the absence of volatile and potentially toxic products.[2] These reactions are schematized according to the Scheme 1.

The main products of this reaction of alcohols with phosphorus pentoxide are generally mono and dialkylphosphoric acids. However, small quantities of secondary products, such as orthophosphoric acid and trialkylphosphate, as well as intermediary products—essentially some dialkylpyrophosphoric acids [(RO) (OH) (O) P] $_2$(O)—can be found in the reactional mixture.

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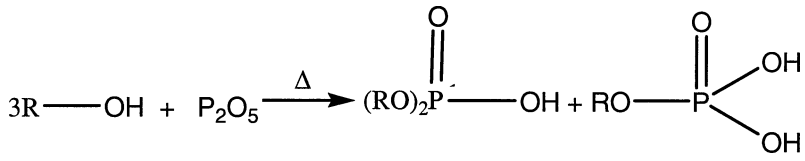
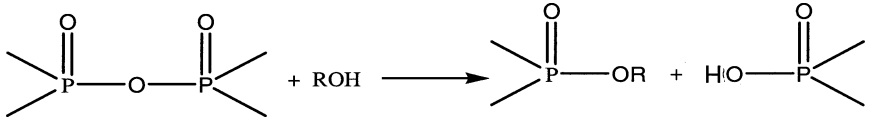


SCHEME 1

The action of the alcohol according to Scheme 1 consists of gradually breaking the bonds P—O—P in the polymeric structure of phosphorus anhydride according to the reaction in Scheme 2.[2]



SCHEME 2

This process can go on until all the bonds P—O—P of the anhydride are broken to form monophosphorus products.

The reactions of alcohols with the phosphorus pentoxide in the usual conditions of synthesis were already studied.[2,3] The slowness (some hours) of these reactions, which constitutes the major drawback of this method of synthesis, generates interest in the activation of these reactions by microwave irradiation. We have already described the use of microwave activation in phosphorus chemistry.[4]

The reaction was studied in the synthesis of important industrial mono- and diesters of phosphoric acid used as metal extractant, such as MBP (monobutyl phosphoric acid), DBP (dibutyl phosphoric acid), M_2EHPA (mono-2-ethylhexyl phosphoric acid), D_2EHPA (di-2-ethylhexyl phosphoric acid), MOPPA (mono(4-(1,1′,3,3′-tetramethyl)butyl) phenyl phosphoric acid), and DOPPA(di(4-(1,1′,3,3′-tetramethyl)butyl)phenyl phosphoric acid).[5,6]

RESULTS AND DISCUSSION

In addition to its thermic effect, the effect of microwave irradiation on the proportions of mono- and dialkylphosphates formed were studied in different operating conditions (Table I).

The growth of microwave energy (increase of the power and the duration of microwave irradiation) increases the temperature of reaction mixtures. The temperature of mixtures of light alkylphosphates

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TABLE I Temperatures and Proportions of Alkylphosphates Obtained under Microwave Irradiation

Hydroxy compounds	Irradiation conditions and ratio of alkylphosphates							
R	3				4			
P (W)	270		450		270		450	
Butan-1-ol								
t (S)	5	10	5	10	5	10	5	10
T (°C)	55	95	67	116	50	82	60	110
N_D	1.2	1.0	1.2	1.0	1.2	1.0	1.2	1.1
N_M	0.7	1.0	0.8	1.0	0.7	1.0	0.7	0.8
2-Ethylhexan-1-ol								
t (min)	2	4	0.83	1.5	2	4	0.83	1.5
T (°C)	80	108	93	111	57	97	83	91
N_D	1.1	0.7	0.9	0.5	1.4	1.1	1.4	1.1
N_M	0.9	1.1	1.1	1.2	0.5	0.9	0.5	0.7
4(1,1′,3,3′) Tetramethyl Butylphenol								
t (min)	3	4	2	3	3	4	2	3
T (°C)	92	110	84	110	81	102	73	107
N_D	0.9	1.5	0.8	1.3	0.8	1.1	0.2	1.3
N_M	1.1	0.5	1.2	0.7	1.2	0.9	1.8	0.7

R, molar ratio: hydroxy compound/P_2O_5; P and t, power and time of microwave irradiation; T, temperature of the reactional mixture at the end of irradiation; N_D and N_M, number of moles of dialkylphosphates and monoalkylphosphates, obtained per mole of pentoxide used.

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increases more quickly than those of the heavy homologues, probably because of their weak calorific capacities, Cp (Table II).

A temperature variation, about 50°C, was observed after 5 s of irradiation in the case of MBP–DBP mixture, but for the other mixtures of product such a temperature variation required irradiations of some minutes. The temperatures observed with mixtures of alkylphosphates synthesized with an excess of alcohol (R = 4) were relatively lower, compared with those obtained with a stoichiometric quantity (R = 3).

The nature of synthetic products under microwave irradiation was confirmed by various techniques of analyses.[8,9] The ^{31}P NMR

TABLE II Calorific Capacities of Alkylphosphates

Products	Cp (cal/mole.K)	Products	Cp (cal/mole.K)	Products	Cp (cal/mole.K)
n-butanol	27	2-ethylhexanol	49	R-Ar-OH	70
MBP	40	M_2EHPA	62	MOPPA	83
DBP	62	D_2EHPA	106	DOPPA	147

Cp, calorific capacities at 25°C calculated by the Benson's method of contribution; R-Ar-OH, 4-(1,1′,3,3′,-tetramethyl butyl) phenol.[7]

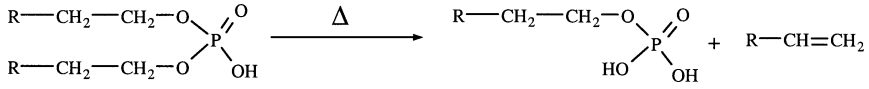
has shown the presence of two important signals corresponding to monoalkylphosphates and to dialkylphosphates (MBP ($\delta = 1.19$ ppm) and the DBP ($\delta = 0.02$ ppm), the M2EHPA ($\delta = 0.86$ ppm) and the D2EHPA ($\delta = 0.02$ ppm), the MOPPA ($\delta = -3.7$ ppm), and the DOPPA ($\delta = -9.4$ ppm)). Small signals corresponding to the secondary products (the orthophosphoric acid and trialkylphosphates ($\delta = 1.6$ ppm)) were also observed. On the other band, the signal of intermediary products (di- and polypyrophosphates) were not noticed.

^{1}H NMR confirmed the formation of alkylphosphates with characteristic signals corresponding to the protons CH_2—O—P ($\delta = 3.9$–4 ppm) and P—O—H from $\delta = 7$ ppm.[10]

The infrared spectra has presented absorption corresponding to alkylphosphates groups: P═O ($\nu = 1200$–1240 cm^{-1}), P—OC and P—OH ($\nu = 950$–1045 cm^{-1}), and the PO—H ($\nu = 2250$–2370 cm^{-1}).[11]

The acid nature of monoalkylphosphates and dialkylphosphates was confirmed by the titration of these products. The titration curves presented two slope shifts. The first one corresponds to the neutralization of the dialkylphosphate and one of the protons of the monoalkylphosphate (pH = 6). The second one (pH = 10.5) marks the neutralization of the second proton of the monoalkylphosphate.[12]

All the results of these analyses have shown that the products of the reaction of alcohol with the phosphorus pentoxide, obtained under microwave irradiation, were identical to those obtained with the classic method of heating. These products were essentially monoalkylphosphates and dialkylphosphates. Dialkylphosphates (DBP, D_2EHPA, DOPPA) were generally the main products. However, the proportions of monoalkylphosphates (MOPPA, M_2EHPA) can surpass those of the dialkylphosphates. When the temperature was higher than 90°C under microwave irradiation or under usual conditions, the side products were attributed to the well-known thermal elimination of alkene during the pyrolysis of phosphate esters at a temperature superior to 100°C according to Schemes 3 and 4.[13,14]



SCHEME 3

In the case of 4-(1,1,3,3′-tetramethylbutyl)phenylphosphates (MOPPA and DOPPA), this reaction is not possible. MOPPA and DOPPA are thermically more stable, so the quantity of the diester

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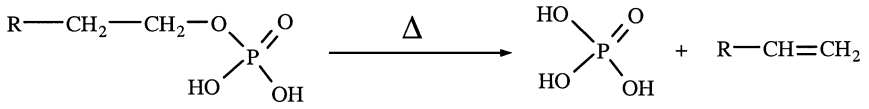

SCHEME 4

(DOPPA) was found to be higher than with other alcohols after longer irradiation time. The comparative study of the results of syntheses under classic heating condition and under microwave irradiation has shown that in the case of the usual heating, monoalkylphosphates always dominated (N_M = 1.0–1.6 moles/mole of pentoxide), and that the quantities of dialkylphosphate do not exceed, in the best of cases, 0.8 moles per mole of pentoxide. Under microwave irradiation, the amounts of monoalkylphosphates and dialkylphosphates can respectively reach the ratio of 1.8 and 1.5 per mole of P_2O_5. The difference between the two activations can be explained by the higher speed of heating under microwave condition and consequently the reduction of reaction time and degradation products (Table III).

In the classic conditions and under microwave irradiation, the temperature was the most important parameter that influences the ratio and the speed of formation of alkylphosphates.[15] The domain of the temperatures between 70 and 95°C was recommended for the synthesis of alkylphosphates. Under microwave irradiation, a control of the temperature in this domain of temperatures (70–95°C) during the reaction allows the best formation of alkylphosphates (N > 1 mole of product/mole of pentaoxide).

The molar ratio of alcohol/pentaoxide fixed between 3–4 as adequate for the synthesis of mono- and dialkylphosphates. The excess of alcohol does not considerably influence the proportions of products in both methods of heating.

TABLE III Proportions of Alkylphosphates in the Classic Conditions of Synthesis

Produit	MBP-DBP				M_2EHPA-D_2EHPA				MOPPA-DOPPA			
T (°C)	80		95		80		95		80		93	
R	3	4	3	4	3	4	3	4	3	4	3	4
N_D	0.7	0.8	0.3	0.4	0.7	0.7	0.6	0.6	0.6	0.6	0.6	0.5
N_M	1.3	1.1	1.6	1.4	1.0	1.1	1.0	1.3	1.1	1.4	1.4	1.5

R, molar ratio alcohol/P_2O_5; T, temperature of the reactional mixture; N_D and N_M, number of moles of di- and of monoalkylphosphates obtained per mole of pentoxide used.

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The speed of the reaction of alcohols with the phosphorus pentoxide was 6 h in the classic conditions of heating, whereas under microwave irradiation, reaction took place in 4 min; the ratio of speed increasing was 100 to 4000.

CONCLUSION

The products of the reaction of alcohols with the phosphorus pentoxide under microwave irradiation were identical to those obtained by classic heating—monoalkylphosphates and dialkylphosphates according to reaction 1. The effects of the temperature and the excess of alcohol were comparable in both methods of heating. The activation of reaction 1 by microwaves allows better yields and a higher amount of dialkylphosphate. The decrease of the reaction time and the decrease of degradation products of dialkylphosphates are the main advantages of microwave irradiation.

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EXPERIMENTAL

The infrared spectra were made on a FT IR Perkin Elmer 16 PC spectrometer. Samples were analyzed in the form of films deposited between two windows in KBr. NMR spectrometry analyses were carried out on a spectrometer with Fourier Bruker AC 250 multinuclear. Samples of the products were diluted in $CDCl_3$, with tetramethylsilane (TMS) as the internal reference.

Densities and refractive indexes were measured at 25°C using a Supelco pycnometer and a Euromax Honland refractometer.

The titrations of mono- and dialkylphosphates were made on a Tacussel Mini 80 pH-meter provided with an electrode (calomel). The procedure of titration by NaOH 0.1N is classic after dissolution of 0.1 g of the reaction mixture in water–acetone (volumic ratio: acetone/water = 3). The reactions of synthesis under microwave irradiation were performed in a microwave oven Delonghi MW 715 working with the frequency of 2450 MHz.

Reagent

Reagents used—phosphorus pentaoxide (P_2O_5, 98%), n-butanol (C_4H_9OH, 98%), 2-ethyl-1-hexanol ($C_8H_{17}OH$, 98%) and 4-(1,1,3,3,-tetramethylbutyl) phenol (C_8H_{17}-C_6H_4-OH, 90%), sodium hydroxide 99%, hydrochloric acid 32%, and acetone 99.5%—are Merck (Darmstadt) products.

General Procedure

Hydroxycompounds used in these reactions were n-butanol, 2-ethyl-1-hexanol, and 4-(1,1′,3, 3′, -tetramethylbutyl)phenol.

Solid phosphorus pentoxide (2 g (0.014 mole)) and the hydroxycompounds (molar ratio: hydroxyl compounds/pentaoxide: R = 3–4) were stirred and heated at 40°C under dry nitrogen.

Microwave Irradiation

The mixture above was irradiated in a glass cylinder reactor (diameter = 3 cm) fitted by a cooler filled with cooled octane (0–5°C) according to the conditions (power and time) reported in Table I.

Classic Conditions of Heating

The mixture was heated and stirred under dry nitrogen at 80–95°C for 6 h according to the conditions reported in Table III.

The separation of monoalkylphosphates and dialkylphosphates was performed by liquid–liquid extraction with an aqueous solution of soda according to the classic procedure described in the literature.[16]

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Physical Properties of the Alkylphosphates*

Monobutylphosphate (MBP)

(n-C_4H_9O)(O)P$(OH)_2$, $d_4^{25} = 1.198$, $\eta_D^{25} = 1.447$.
IR: ν (cm^{-1}) = 1025 (vS, L), 1200 (S, L), 1370 (w), 1460 (m), 1620 (w, L), 2330 (w, L), 2850 (S), 2940 (S, L).
^{1}H NMR: δ/TMS (ppm) = 0.94 (t, 3H, CH_3), 1.43 (sext, 2H, CH_2), 1.64 (quint, 2H, CH_2), 4.03 (m, 2H, CH_2O—P), 8.73 (s, 2H, P$(OH)_2$).
^{31}P NMR: δ/H_3PO_4 (ppm) = 1.19.

Dibutylphosphate (DBP)

(n-$C_4H_9O)_2$(O)P(OH), $d_4^{25} = 1.058$, $\eta_D^{25} = 1.426$.
IR: ν (cm^{-1}) = 895 (w), 1010 (vS, L), 1210 (vS,L), 1365 (w), 1440 (m), 1630 (w, L), 2250 (w, L), 2875 (vS), 2960 (vS, L).
^{1}H NMR: δ/TMS (ppm) = 0.96 (t, 6H, CH_3), 1.39 (sext, 4H, CH_2), 1.63 (quint, 4H, CH_2), 4.03 (m, 4H, CH_2O—P), 8.87 (s, 1 H, PO—H).
^{31}P NMR: δ/H_3PO_4 (ppm) = −0.02.

*δ, chemical shift; ν, wave number; s, singulet; d, doublet; t, triplet; q, quadruplet; quint, quintuplet; sext, sextuplet; m, multiplet; J, coupling constante; S, strong; L, large; w, weak.

Mono 2-Ethylhexyl Phosphate (M_2EHPA)

$(C_8H_{17}O)(O)P(OH)_2$, $d_4^{25} = 0.987$, $\eta_D^{25} = 1.435$.
IR: ν (cm^{-1}) = 1005 (vS, L), 1235 (vS, L), 1375 (f), 1475 (m), 1615 (w), 2370 (w, L), 2880, 2970 (vS).
^{1}H NMR: δ/TMS (ppm) = 0.89 (t, 6H, CH_3), 1.28 (m, 8H, CH_2), 1.57 (m, 1H, CH), 3.92 (m, 2H, CH_2O—P), 8.13 (s, 2 H, $P(OH)_2$).
^{31}P NMR: δ/H_3PO_4 (ppm) = 0.86.

Di 2-Ethylhexyl Phosphate (D2EHPA)

$(C_8H_{17}O)_2(O)P(OH)$, $d_4^{25} = 0.977$, $\eta_D^{25} = 1.442$.
IR: ν (cm^{-1}) = 895 (w), 1045 (vS, L), 1240 (S, L), 1380 (w), 1470 (m), 1685 (w, L), 2275 (w, L), 2855 (S), 2955 (vS).
^{1}H NMR: δ/TMS (ppm) = 0.89 (t, 12H, CH_3), 1.28 (m, 16H, CH_2), 1.57 (m, 2H, CH), 3.93 (m, 4H, CH_2O—P), 7.11 (s, 1 H, P(OH)).
^{31}P NMR: δ/H_3PO_4 (ppm) = 0.02 ppm.

Mono[4-(1,1,3,3,-Tetramethylbutyl)phenyl] Phosphate (MOPPA)

$[C_8H_{17}(C_6H_4)O](O)P(OH)_2$.
IR: ν(cm^{-1}) = 825 (S), 960 (vS, L), 1005 (S, L), 1090 (w), 1165 (S), 1200 (vS, L), 1353 (m), 1375 (w), 1450 (S, L), 1490, 1585 (m), 1870 (w, L), 2300 (w, L), 2880, 2930 (vS).
^{1}H NMR: δ/TMS (ppm) = 0.64 (s, 9H, CH_3), 1.26 (s, 6H, CH_3), 1.62 (s, 2H, CH_2), 6.68 (d, 2H, CH_{meta}, J^3 H—H = 8.65 Hz), 7.14 (d, 2H, CH_{ortho}, J^3 H—H = 8.65 Hz).
^{31}P NMR: δ/H_3PO_4 (ppm) = −3.7.

Di [4-(1,1,3,3,-Tetramethylbutyl)phenyl] Phosphate (DOPPA)

$[C_8H_{17}(C_6H_4)O]_2(O)P(OH)$.
IR: ν (cm^{-1}) = 820 (S), 950 (vS, L), 1000 (S, L), 1080 (w, L), 1155 (S), 1210 (vS, L), 1350 (m), 1370 (w), 1440 (S, L), 1580 (m), 1860 (w, L), 2300 (w, L), 2850, 2880, 2940 (vS).
^{1}H NMR: δ/TMS (ppm) = 0.71 (s, 18H, CH_3), 1.33 (s, 12H, CH_3), 1.68 (s, 4H, CH_2), 6.76 (d, 4H, CH_{meta}, J^3 H—H = 8.64 Hz), 7.2 (d, 4H, CH_{ortho}, J^3 H—H = 8.65 Hz).
^{31}P NMR: δ/H_3PO_4 (ppm) = −9.4.

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