Stereoselective synthesis of analogs of natural isoprenoids based on the reaction of alkyl 4-dialkoxyphosphoryl-3-methylbut-2-enoates with aldehydes in ionic liquids and in an imidazolium salt—benzene system

S. G. Zlotin, G. V. Kryshtal, G. M. Zhdankina, P. A. Belyakov, and E. P. Serebryakov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: zlotin@ioc.ac.ru

Condensation of alkyl 4-dialkoxyphosphoryl-3-methylbut-2-enoates with a number of aldehydes under the Horner—Emmons reaction conditions in 1-butyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate and in 1-butyl-3-methylimidazolium bromide—benzene and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate—benzene systems was studied. The *E*/*Z*-stereoisomer ratio of the olefination products for the reaction carried out in ionic liquids was 3 : 1, which corresponds to the values attained previously in the KOH—benzene—Bu_4^nNBr (cat.) system. Quantum-chemical calculations were used to determine the averaged radii (r_0) of the $[Bu_4^nN]$ and substituted imidazolium cations by means of the Gaussian 98 program package. The stereoselectivity of olefination in the KOH—PhH—phase-transfer catalyst system decreases with a decrease in the r_0 value for the catalyst cation. The possibility of recovery and reuse of ionic liquids is demonstrated.

Key words: alkyl 2,4-dienoates, isoprenoids, juvenoids, hydroprene, methoprene, Horner—Emmons reaction, ionic liquids, aldehydes.

The reactions of aldehydes with alkyl 4-dialkoxyphosphoryl-3-methylbut-2-enoate (**1**) are used in the synthesis of biologically active polyunsaturated isoprenoids for the elongation of the carbon chain by one functionalized isoprenoid unit.[1] This reaction is complicated by stereomutation of the double bond in compound **1** under the action of the base needed for the generation of the carbanion; as a result, even in the case of stereochemically pure starting compounds, the reactions result in binary mixtures of 2*Z* and 2*E* stereoisomers of the olefination products. As to the newly formed double bond in position 4, this always has the *E*-configuration. Development of methods for stereochemical control of this reaction is important, as the most active antikeratitis and immunoregulatory agents of the retinoic acid group and juvenoids (methoprene, hydroprene) containing polyene isoprenoid fragments available by olefination have *E*-configurations of all double bonds.[2]

Previously, it has been shown that in the condensation of ethyl 4-diethoxyphosphoryl-3-methylbut-2-enoate (**1a**) with 3-methylbutanal (**2**), the proportion of the 2*E*,4*E* isomer in the reaction product (**3**) increases on passing from hydrocarbon to polar aprotic solvents (MeCN, DMF, DMSO)[3] and also when the reaction is carried out in the presence of phase-transfer catalysts (in particular, tetraalkylammonium salts).[4] These data prompted the idea of using structurally related 1,3-dialkylimidazolium salts (currently well-known under the name "ionic liquids"[5,6]) as solvents and catalysts in the stereoselective synthesis of isoprenoid dienoic esters by the Horner—Emmons—Wadsworth reaction. Indeed, our preliminary results showed that ester **1a** reacts with 3-methylbutanal (**2**) or 3,7-dimethyloctanal (**4**) in 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] in the presence of $LiOH \cdot H_2O$ to give the corresponding 2*E*,4*E*-dienes **3** and **5** as the major products.[7]

The purpose of this work is to study in more detail the influence of the structure of the ionic liquid, phosphonate **1**, and the type of base used on the stereoselectivity of the reaction of alkyl 4-dialkoxyphosphoryl-3-methylbut-2-enoates **1a,b** with aldehydes in imidazolium salts and in imidazolium salt—benzene systems.

The reactions were carried out with aldehydes of the isoprenoid series, 3-methylbutanal (**2**), 3,7-dimethyloctanal (**4**), and 7-methoxy-3,7-dimethyloctanal (**6**), and with benzaldehyde (**7**). Readily available 1-butyl-3-methylimidazolium salts that are now under intensive research were used as ionic liquids, namely, 1-butyl-3-methylimidazolium bromide ([bmim][Br]),[8] hexafluorophosphate ([bmim][PF_6]),[9] and tetrafluoroborate

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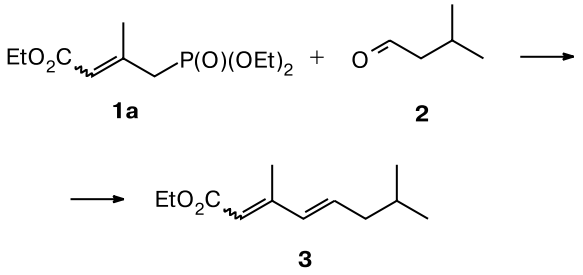
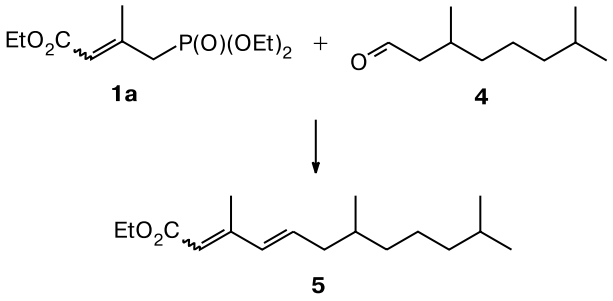
([bmim][BF_4])[10] and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([bdmim][PF_6]).[11] Deprotonation of CH-acids **1a,b** was accomplished by treatment with LiOH, KOH, and 1-butyl-3-methylimidazolium hydroxide ([bmim][OH])[12] (LiOH was taken as the monohydrate). It should be noted that the ester group in the allylic phosphonates **1a,b**, unlike that in triethyl phosphonoacetate,[7] is not saponified by KOH in the ionic liquid and, hence, this base can be used for olefination.

It was found that the use of ionic liquids changes the regularities of olefination established previously for reactions carried out in molecular organic solvents.[1] For example the nature of the base does not influence the yield or the ratio of 2*E*,4*E* to 2*Z*,4*E* stereoisomers (3 : 2) in product **3** when 3-methylbutanal (**2**) is olefinated with ethyl 4-diethoxyphosphoryl-3-methylbut-2-enoate (**1a**) in [bmim][PF_6] (Table 1). The *E*-selectivity of the reaction in ionic liquids is higher than that in benzene but is lower than in DMSO.[3]



The stereochemical outcome of the reactions of esters **1a,b** with aldehydes depends on whether the reaction is carried out directly in an ionic liquid medium or in the imidazolium salt—benzene system. Whereas the ratio of 2*E*,4*E* to 2*Z*,4*E* stereoisomers in product **5** formed upon olefination of 3,7-dimethyloctanal (**4**) with phosphonate **1a** in [bmim][PF_6] equals 3 : 1, in the reaction carried out in benzene in the presence of a catalytic amount [bmim][Br], this ratio decreases to ~2 : 1. Under these conditions, [bmim][Br] acts apparently as a phase-transfer catalyst, which carries the anion of CH-acid **1a** into the organic phase. The effect of the imidazolium salt on the transition state of the reaction follows from different stereochemical outcomes of the reaction of phosphonate **1a** with 3,7-dimethyloctanal (**4**) carried out in benzene and in the benzene—[bmim][Br] system (Table 2).



Similar regularities also hold in the reaction of ethyl 4-diethoxyphosphoryl-3-methylbut-2-enoate (**1a**) with

Table 1. Influence of the base on the yield and stereochemistry of dienoic ester **3** in various solvents

Base	τ[a]/h	The yield of **3** in [bmim][PF_6] (%)	Ratio of 2*E*,4*E* to 2*Z*,4*E* stereoisomers in diene **3**		
			[bmim][PF_6]	DMSO[b]	benzene[b]
KOH	2	58	3 : 2	7 : 3	44 : 56
LiOH · H_2O	6	48	3 : 2	4 : 1	3 : 2
[bmim][OH]	6	52	3 : 2	—[c]	—[c]

[a] τ is the reaction time.
[b] Data from Ref. 3.
[c] No data are available.

Table 2. Influence of the ionic liquid on the yield and stereochemistry of the diene ester **5** (hydroprene)

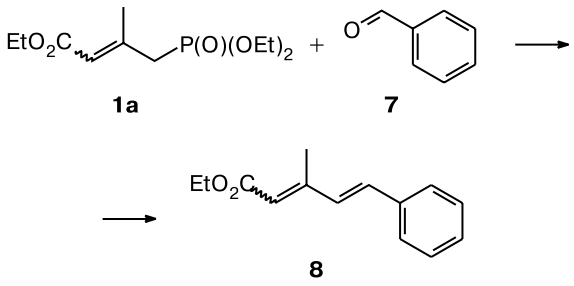
Base	Solvent	Catalyst	τ/h	The yield of **5** (%)	Ratio of 2*E*,4*E* to 2*Z*,4*E* isomers in diene **5**
KOH	Benzene	—	6	60	44 : 56*
KOH	Benzene	[bmim][Br] (0.1 equiv.)	6	63	65 : 35
LiOH · H_2O	[bmim][PF_6]	—	10	75	3 : 1

* Data from Ref. 4.

Table 3. Reaction conditions, product yield, and isomer ratio in dienoic ester **8**

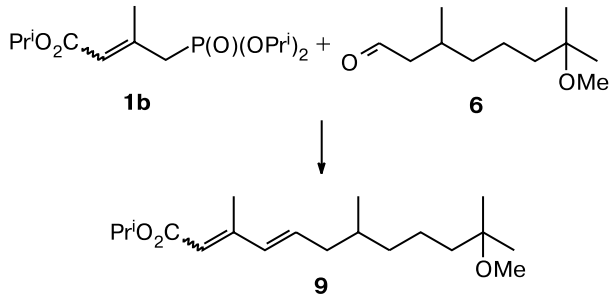
Base	Solvent	Catalyst (equiv.)	τ/h	The yield of **8** (%)	Ratio of 2*E*,4*E* to 2*Z*,4*E* isomers in diene **8**
KOH	Benzene	[bmim][Br] (0.1)	5	74	7 : 3
KOH	Benzene	[bmim][Br] (1.0)	4	70	7 : 3
KOH	[bmim][PF_6]	—	4	65	3 : 1
[bmim][OH]	[bmim][PF_6]	—	6	67	3 : 1

benzaldehyde (**7**) (Table 3). In this case, too, replacement of the [bmim][PF_6] ionic solvent by the benzene—imidazolium salt system results in somewhat lower ratio of the 2*E*,4*E* to 2*Z*,4*E* stereoisomers in the reaction product **8**. The increase in the amount of the imidazolium salt [bmim][Br] from a catalytic (~0.1 equiv.) to equimolar amount with respect to the reactants does not affect noticeably the stereochemical outcome of the reaction.



We studied the reaction of isopropyl 4-di(isopropoxy)phosphoryl-3-methylbut-2-enoate (**1b**) with 3,7-dimethyl-7-methoxyoctanal (**6**) in most detail (Table 4). The addition of the imidazolium salt [bmim][Br] to the solid KOH—benzene system inverts again the reaction stereochemistry, resulting in the predominant formation of the 2*E*,4*E* isomer of compound **9**. The ratio of 2*E*,4*E* to 2*Z*,4*E* isomers remains the same, irrespective of whether the system contains a catalytic or an equimolar amount of the imidazolium salt, although an increase in the amount of the catalyst results in a higher overall yield of the olefination product **9**. In both cases, the proportion of the 2*E*,4*E* isomer **9** is lower than that obtained in the olefination in the solid KOH (2 equiv.)—benzene—[Bu_4^nN][Br] (2 equiv.) system (the ion pair extraction method).[4] The replacement of the 1-butyl-3-methylimidazolium cation by the 1-butyl-2,3-dimethylimidazolium cation does not result either in a higher 2*E*,4*E*- to 2*Z*,4*E* ratio in product **9**.

The *E*-stereoselectivity of the reaction of phosphonate **1b** with aldehyde **6** was somewhat increased by conducting the olefination directly in the medium of the 1-butyl-3-methylimidazolium salts [bmim][PF_6] or [bmim][BF_4], which are liquid under ordinary conditions. Irrespective of the nature of the anion, the ratio of the 2*E*,4*E* to 2*Z*,4*E* isomers in olefination product **9** was 3 : 1, which is similar to the values attained in the solid KOH—benzene—[Bu_4^nN][Br] (cat.) system.[4]



The moderate stereoselectivity of the reactions of alkyl 4-dialkoxyphosphoryl-3-methylbut-2-enoates (**1a,b**) with isoprenoid aldehydes carried out in the imidazolium

Table 4. Influence of the ionic liquid and reaction conditions on the yield and stereochemistry of diene ester **9** (methoprene)

Base (equiv.)	Solvent	Catalyst (equiv.)	τ/h	The yield of **9** (%)	Ratio of 2*E*,4*E* to 2*Z*,4*E* isomers in diene **9**
KOH (1.0)	Benzene	—	2	61	30 : 70*
KOH (1.0)	Benzene	[Bu_4^nN][Br] (0.1)	3	79	75 : 25*
KOH (2.0)	Benzene	[Bu_4^nN][Br] (2.0)	3	85	93 : 7*
KOH (1.0)	Benzene	[bmim][Br] (0.1)	8	72	65 : 35
KOH (1.0)	Benzene	[bmim][Br] (1.0)	8	81	65 : 35
$LiOH \cdot H_2O$ (1.0)	Benzene	[bdmim][PF_6] (1.0)	8	68	65 : 35
KOH (1.0)	[bmim][PF_6]	—	6	77	75 : 25
KOH (1.0)	[bmim][BF_4]	—	6	75	75 : 25

* Data from Ref. 4.

salt—benzene system compared to the corresponding reactions in the [Bu_4^nN][Br]—benzene system is apparently due to the different geometric parameters of the [bmim], [bdmim], and [Bu_4^nN] cations. The influence of the size of the cation of the phase-transfer catalyst on the transition state of olefination reaction has been hypothesized previously.[1] In order to verify this assumption, we carried out quantum-chemical calculations for the geometry of the [bmim], [bdmim], and [Bu_4^nN] cations. Their optimized geometries thus obtained are shown in Fig. 1.

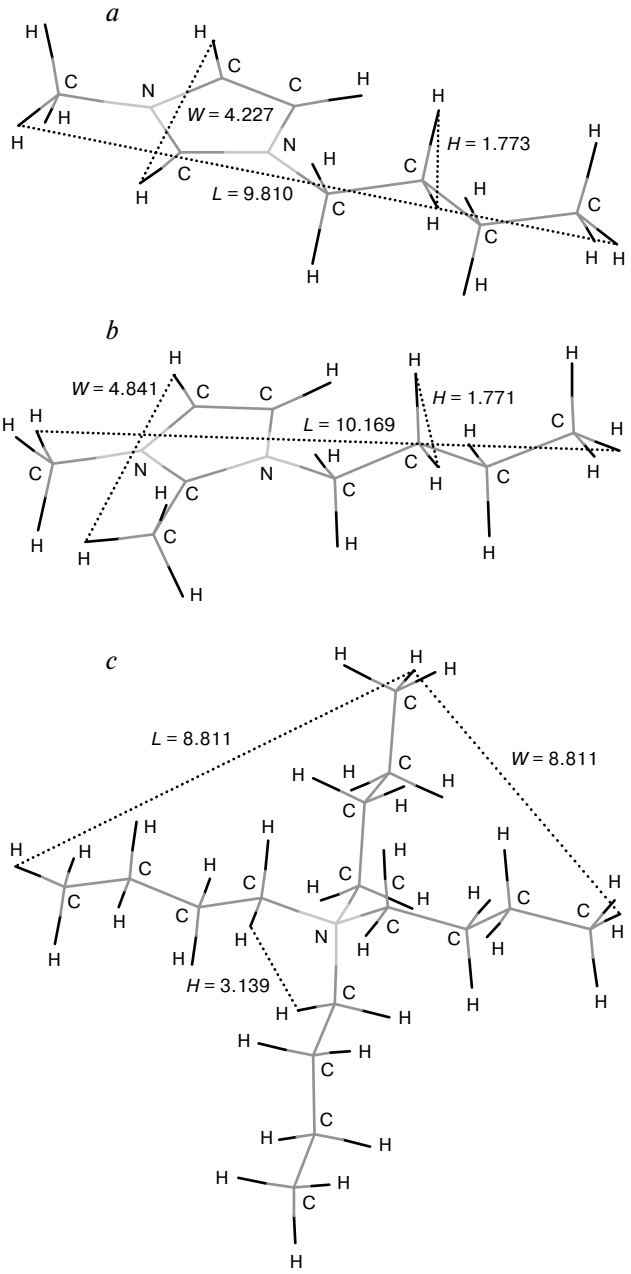


Fig. 1. Results of quantum-chemical calculations for the geometry of 1-butyl-3-methylimidazolium ([bmim]) (*a*), 1-butyl-2,3-dimethylimidazolium ([bdmim]) (*b*), and tetrabutylammonium ([Bu_4^nN]) cations (*c*).

The averaged radii (r_0) of the [bmim], [bdmim], and [Bu_4^nN] cations determined with account of the maximum distances between the terminal atoms (*L*, *H*, and *W*) using Eq. (1) were 2.6, 2.8, and 3.9 Å, respectively.

$$r_0 \approx (3HWL)^{1/3}/4\pi \quad (1)$$

The agreement between the resulting r_0 = 3.9 Å and the Stokes radius of the [Bu_4^nN] cation in methanol determined experimentally[13] (~4.3 Å) may be regarded as satisfactory, in view of the fact that the calculation did not take into account the effect of the medium, which is known to change somewhat the geometric parameters of cations.[14] Thus, of the three cations studied, the [Bu_4^nN] cation has the largest radius, which markedly exceeds those of [bmim] or [bdmim].

The results of calculations are consistent with the assumption that the ratio of the 2*E*,4*E* to 2*Z*,4*E* isomers in the Horner—Emmons reaction products changes in parallel with the linear dimensions of the cation in the phase-transfer catalyst used. The shape of the cation (flattened in the case of the [bmim] and [bdmim] cations[13] and three-dimensional for [Bu_4^nN]) (see. Fig. 1) may also exert a certain influence on the stereoselectivity. The somewhat higher stereoselectivity of olefination when carried out directly in ionic liquids is apparently due to the change in the medium polarity, which influences the geometric parameters of the transition state.[14]

The use of imidazolium salts with fluorinated anions as the solvents has a number of advantages, in particular, the ease of isolation of the products, avoidance of toxic benzene in operation, and the possibility of recovery and reuse of the ionic solvent. Dienoic esters **3**, **5**, **8**, and **9** can be separated from nonvolatile liquid imidazolium salts, [bmim][BF_4] and [bmim][PF_6], by direct distillation under reduced pressure (0.1—1.0 Torr). Ionic liquids are easily recovered after the reaction by filtering from inorganic salts followed by washing with water (in the case of [bmim][PF_6], which is immiscible with water) and removal of volatile compounds (water, $CHCl_3$) under reduced pressure. The yield of ionic liquids is 89—95%. The [bmim][BF_4] and [bmim][PF_6] salts recovered in this way are identical, according to the ^1H, ^{13}C, and ^{19}F NMR spectra to fresh ionic liquids[7,9,10] and can be used in olefination once again. An increase in the number of "olefination—regeneration" cycles to 10 does not entail a decrease in the yields or stereochemical purity of the dienoic esters **3**, **5**, **8**, and **9**.

Thus, we studied for the first time the reaction of alkyl 4-dialkoxyphosphoryl-3-methylbut-2-enoates **1a,b** with isoprenoid aldehydes and benzaldehyde in imidazolium salts that are liquid under ordinary conditions and in imidazolium salt—benzene systems. This reaction was

employed to synthesize a number of biologically active substances, analogs of natural isoprenoids, including dienoic ester **3**, which is an efficient chemosterilant for the arachnoid mite, and environmentally safe insecticides, hydroprene **5** and methoprene **9**, which are structural analogs of insect juvenile hormones.[15,16] The results obtained can be used to develop stereoselective and environmentally safe methods for the deliberate synthesis of natural products using ionic liquids as solvents and catalysts.

Experimental

^{1}H NMR spectra were recorded on Bruker AM-300 (300.13 MHz {^{1}H}) and Bruker DRX-500 (500.13 MHz {^{1}H}, 125.76 MHz {^{13}C}, 470.4 MHz {^{19}F}, 202.4 MHz {^{31}P}) instruments in DMSO-d_6 and acetone-d_6. The ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR chemical shifts were referred to Me_4Si, acetone-d_6, $CFCl_3$, and H_3PO_4, respectively. GLC analysis was carried out on a LKhM-80 chromatograph with a flame ionization detector using N_2 as the carrier gas and a 1.5×0.003 m glass column with 5% SE-30 or OV-17 on Chromaton N-AW-DMCS. Phosphonates **1a,b**[17] and imidazolium salts, [bmim][Br],[8] [bmim][PF_6],[9] [bmim][BF_4],[10] and [bdmim][PF_6],[11] were synthesized by known procedures.

The geometry of the 1-butyl-3-methylimidazolium and 1-butyl-2,3-dimethylimidazolium cations was optimized using the B3LYP hybrid functional[18—20] in the standard 6—31G* basis set.[21] The calculations were carried out using the Gaussian 98 program package.*[22] The molecular structures and vibrations were visualized using the MOLDEN graphics package.[23] The geometry of the tetrabutylammonium cation was optimized using the PRIRODA program[24] with the PBE functional in the 3z full-electron basis set.

Reaction of aldehydes 2, 4, 6, and 7 with phosphonates 1a,b in the KOH/[bmim][PF_6], KOH/[bmim][BF_4], and LiOH·H_2O/[bmim][PF_6] systems (general procedure). The finely ground base (7.5 mmol), phosphonate **1a** or **1b** (5.0 mmol), and aldehyde **2**, **4**, **6**, or **7** (5.0 mmol) were added successively with vigorous stirring at 20 °C to an ionic liquid (15 mmol). The reaction mixture was stirred at 20 °C for 2—10 h and products **3**, **5**, **8**, and **9** were extracted with diethyl ether (4×10 mL) and distilled *in vacuo* (0.1—12 Torr), or directly distilled off from the ionic liquid under reduced pressure.

Reaction of aldehydes 4, 6, and 7 with phosphonates 1a,b in the KOH/PhH/[bmim][Br] and LiOH·H_2O/PhH/[bmim][PF_6] systems (general procedure). Phosphonate **1a** or **1b** (5.0 mmol) and aldehyde **4**, **6**, or **7** (5.0 mmol) were added successively with vigorous stirring to a suspension of powdered KOH (0.40 g, 7.5 mmol) and imidazolium salt (0.5—5.0 mmol) in benzene (10 mL). The reaction mixture was stirred for 4—8 h at 20 °C and filtered. The benzene solution was concentrated on a rotary evaporator and compounds **5**, **8**, and **9** were distilled under reduced pressure.

Reaction of aldehyde 7 with phosphonate 1a in the [bmim][OH]/[bmim][PF_6] system. Powdered KOH (0.40 g, 7.5 mmol) was added to a solution of [bmim][Br] (1.60 g, 7.5 mmol) in water (2 mL). Water was evaporated *in vacuo* and the residue was dissolved in MeOH (5 mL) and filtered. The filtrate was concentrated, and [bmim][PF_6] (4.25 g, 15 mmol) was added to the residue, which represented imidazolium hydroxide [bmim][OH].[12] Then phosphonate **1a** (1.30 g, 5.0 mmol) and aldehyde **7** (0.53 g, 5.0 mmol) were added with vigorous stirring. The reaction mixture was stirred for 6 h at 20 °C, and product **8** was distilled off under reduced pressure.

The reactions were monitored and the isomeric composition of the products was determined by GLC and ^{1}H NMR spectroscopy (based on the ratio of the signals for the methylene group protons at C(3) and olefinic protons at C(2) in the stereoisomers of **3**, **5**, **8**, and **9**).[3,4] The two methods gave similar results. The boiling points and the refractive indices of dienoic esters **3**, **5**, **8**, and **9** corresponded to published data: ethyl 3,7-dimethylocta-2,4-dienoate (**3**), b.p. 125—128 °C (12 Torr), n_D^{20} 1.4800 [25]; ethyl 3,7,11-trimethylundeca-2,4-dienoate **5** (hydroprene), b.p. 99—101 °C (0.1 Torr), n_D^{20} 1.4815 [4]; ethyl 3-methyl-5-phenylpenta-2,4-dienoate (**8**), b.p. 138—140 °C (0.8 Torr), n_D^{20} 1.5880 [26]; isopropyl 11-methoxy-3,7,11-trimethylundeca-2,4-dienoate (**9**) (methoprene), b.p. 144—146 °C (0.5 Torr), n_D^{20} 1.4835 [4].

Recovery of [bmim][PF_6]. The liquid remained after the reaction and the product isolation was filtered to remove inorganic salts, washed with water (2×10 mL), and evacuated (2 Torr) at 60 °C for 2 h to give a yellowish liquid identical, according to ^{1}H, ^{31}P, and ^{19}F NMR spectra in acetone-d_6, to the freshly prepared salt [bmim][PF_6]. ^{1}H NMR, δ: 0.93 (t, 3 H, J = 7.5 Hz); 1.36 (sext, 2 H, J = 7.5 Hz); 1.89 (quint, 2 H, J = 7.5 Hz); 4.00 (s, 3 H); 4.30 (t, 2 H, J = 7.5 Hz); 7.62 (d, 1 H, J = 1.8 Hz); 7.68 (d, 1 H, J = 1.8 Hz); 8.82 (s, 1 H). ^{31}P NMR, δ: −142.4 (sept, $^1J_{P,F}$ = 708 Hz). ^{19}F NMR, δ: −71.0 (d, $^1J_{P,F}$ = 708 Hz). The yield of recovered [bmim][PF_6] was 89—94%.

Recovery of [bmim][BF_4]. The salt left after the reaction and the product isolation was diluted with $CHCl_3$ (10 mL) and the resulting solution was filtered to remove inorganic salts and dried with $MgSO_4$. The solvent was evaporated *in vacuo* and the remaining oil was kept for 2 h at 60 °C (2 Torr) to give a yellowish liquid identical, according to ^{1}H, ^{13}C, and ^{19}F NMR spectra in acetone-d_6, to the freshly prepared salt [bmim][BF_4]. ^{1}H NMR, δ: 0.93 (t, 3 H, J = 7.5 Hz); 1.36 (sext, 2 H, J = 7.5 Hz); 1.89 (quint, 2 H, J = 7.5 Hz); 4.00 (s, 3 H); 4.30 (t, 2 H, J = 7.5 Hz); 7.62 (d, 1 H, J = 1.8 Hz); 7.68 (d, 1 H, J = 1.8 Hz); 8.82 (s, 1 H). ^{13}C NMR, δ: 13.73 (CH_3); 19.95 (CH_2); 32.75 (CH_2); 36.52 (CH_2); 50.09 (N—CH_3); 123.36 (CH); 124.68 (CH); 137.68 (CH). ^{19}F NMR, δ: −150.5. The yield of recovered [bmim][BF_4] was 90—95%.

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