# JOURNAL OF
# AGRICULTURAL AND FOOD CHEMISTRY

# Synthesis and Phytotoxicity of New Ionic Liquids Incorporating Chiral Cations and/or Chiral Anions

Piotr Bałczewski,*,†,§ Barbara Bachowska,§ Tomasz Białas,†
Robert Biczak,§ Wanda M. Wieczorek,§,# and Agnieszka Balińska§

Department of Heteroorganic Chemistry, Center of Molecular and Macromolecular Studies,
Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland; Institute of Chemistry and
Environmental Protection, Jan Długosz University, Armii Krajowej 13/15, 42-200 Częstochowa,
Poland; and Institute of General and Ecological Chemistry, Technical University of Łódź,
Żeromskiego 116, 90-924 Łódź, Poland

The aim of this work was to synthesize chiral ionic liquids as chiral solvents for organic synthesis and to evaluate the phyto(eco)toxicity of the new products and starting *N*-alkylimidazoles and their potential environmental influence on soil and plants. Chiral ionic liquids containing anions such as $Cl^-$, $Br^-$, $TsO^-$, $PF_6^-$, $NO_3^-$, $CF_3SO_3^-$, and (+)- and (−)-$C_6H_5CH(OH)C(O)O^-$ were synthesized using (−)-(1*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-ethyl [(−)-(1*R*)-nopyl] halides (X = Cl, Br) and tosylate in 62–100% yields. The chloride **7** and the nitrate **13** ionic liquids possessed a toxicity dependent on the applied concentration. The lowest concentration causing a distinct reduction in plant germination/ growth was 100 mg/kg. Spring barley better tolerated the ionic liquids (200 mg/kg) than common radish (100 mg/kg). The nitrate liquid did not exhibit an inhibiting effect on the germination ability of seeds. The starting *N*-methylimidazole used in lower concentrations (1 and 10 mg/kg of soil dry weight) was not phytotoxic, in contrast to higher doses (>1000 mg/kg).

## INTRODUCTION

Ionic liquids are cheap and versatile alternatives to volatile organic solvents, and their green character has usually been justified with their negligible vapor pressure (*1–3*). Being interesting targets in academic laboratories, ionic liquids have until recent years struggled to enter the industrial mainstream, when two leading chemical companies developed processes that used these new solvents. On the other hand, there is a little knowledge of environmental cumulative effects of ionic liquid use if they were to enter ecosystems via industrial effluents (*4, 5*). As a solution of this problem, very recently biodegradable ionic liquids have been engineered (*6*); however, also in this case investigations of phyto(eco)toxicity of biodegradation products should be carried out. Although there are a great number of publications devoted to different aspects of achiral ionic liquids, the literature of chiral ionic liquids is surprisingly very limited (*7–12*). Chiral ionic liquids, possessing combinations of chiral anions and/or cations, are attractive for their application in chiral discrimination including asymmetric synthesis and catalysis as well as optical resolution of racemates; however, the results obtained in this field are still at a

preliminary stage. In this context, a recent application of chiral alkoxyimidazolinium salts, as precursors of the corresponding carbenes in highly enantioselective copper-catalyzed conjugate addition to cyclic enones, is worthy of note (*13*). The aim of this work was to synthesize new chiral ionic liquids as new chiral solvents for organic asymmetric synthesis, structure elucidation, investigations of physicochemical properties, and application and finally phyto(eco)toxicity tests of the new products and starting *N*-methylimidazole for evaluation of the potential environmental impact on soil and plants.

## MATERIALS AND METHODS

The ¹H NMR (200 and 500 MHz) and ¹³C NMR (50 and 125 MHz) spectra were recorded using Bruker AC-200 and Bruker DRX-500 spectrometers. The IR spectra were recorded using an ATI Mattson Infinity FTIR 60 spectrometer. The mass spectra of pure compounds were obtained using a Finnigan Mat 95 spectrometer. Column chromatography was done using Merck silica gel ($F_{254}$ 60, 70–230 and 270–400 mesh). Organic solvents were distilled before use. All chemicals were purchased from Sigma-Aldrich and used directly.

Numbering of atoms applied in the experimental part is presented in the structure below:

(−)-**(1*R*)-Nopyl Chloride (2).** To a stirred solution of triphenylphosphine (25.3 g, 0.09 mol) dissolved in carbon tetrachloride (52 mL) was added (−)-(1*R*)-nopol (**1**) (14.6 g, 15 mL, 0.09 mol), and the reaction mixture was refluxed for 1 h. After the flask had cooled to ambient temperature, a white precipitate was removed by filtration.

* Author to whom correspondence should be addressed (e-mail pbalczew@bilbo.cbmm.lodz.pl; telephone +48 42 6803202; fax +48 42 6847126).
† Polish Academy of Sciences.
§ Jan Długosz University.
# Technical University of Łódź.

**1882**   *J. Agric. Food Chem.*, Vol. 55, No. 5, 2007

Bałczewski et al.
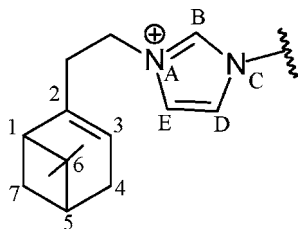
The filtrate was evaporated to give a yellowish oil. This oil was subsequently washed with *n*-hexane and further purified by filtration through a silica gel layer using *n*-hexane as an eluent to afford pure **2** (13.8 g, 85%): $[\alpha]_D^{25}$ −47 (*c* 0.6 in CHCl$_3$); $n_D^{25}$ 1.4987; IR (film) cm$^{-1}$ 2986 (m), 2917 (s), 2833 (m), 1468 (m), 1449 (m), 1432(m), 1382 (w), 1365 (m), 1330 (w), 1293 (w), 1265 (w), 1241 (w), 1219 (w), 1118 (w), 1099 (w), 1082 (w), 960 (w), 886 (w), 790 (w), 742 (m); $^1$H NMR (200 MHz; CDCl$_3$), $\delta$ 0.84 (s, 3, CH$_3$–C(6)), 1.16 (d, 1, *J* = 8.5 Hz, C(7)H$_{endo}$), 1.28 (s, 3, CH$_3$–C(6)), 1.98−2.13 (m, 2, C(1)H, C(5)H), 2.21−2.25 (m, 2, C(4)H$_2$), 2.32−2.46 (m, 2+1, CH$_2$CH$_2$Cl, C(7)H$_{exo}$), 3.49 (t, 2, *J* = 7.2 Hz, CH$_2$Cl), 5.32 (br s, 1, C(3)H); $^{13}$C NMR (50 MHz, CDCl$_3$), $\delta$ 21.15 (s, CH$_3$–C(6)), 26.21 (s, CH$_3$–C(6)), 31.26 (s, C(4)), 31.58 (s, C(7)), 37.99 (s, C(6)), 40.11 (s, CH$_2$CH$_2$Cl), 40.63 (s, C(5)), 42.52 (s, CH$_2$Cl), 45.48 (s, C(1)), 119.19 (s, C(3)), 144.35 (s, C(2)); *m/e* (CI, DB-1, 30 m, 50−250 °C, 10 °C/min) 93 (61), 105 (75), 149 (M$^+$ + 1 − Cl, 100), 185 (M$^+$($^{35}$Cl) + 1, 51), 186 (21), 187 (M$^+$($^{37}$Cl) + 1, 17). Calcd for C$_{11}$H$_{17}^{35}$Cl (M$^+$): 184.1018. Found: 184.1021.

**(−)-(1R)-Nopyl Bromide (3).** To a stirred mixture of NaBr (12 g, 116.6 mmol) in dry DMSO (50 mL) was added a solution of (−)-(1*R*)-nopyl tosylate (**4**) (12.5 g, 38.9 mmol) in dry DMSO (30 mL). After 5 h of stirring at 70 °C, the resulting emulsion was diluted with water and extracted with *n*-hexane (3 × 50 mL). The combined organic fractions were washed once again with water and brine and next dried over MgSO$_4$. After filtration of the drying agent and evaporation of hexane, the crude **3** was obtained (5.47 g, 60% yield). Then it was purified by filtration through the thin silica gel layer using *n*-hexane as an eluent to afford pure **3** (2.48 g, 30% yield) as a light-yellow liquid: $[\alpha]_D^{25}$ −30 (*c* 0.83 in CHCl$_3$); $n_D^{25..5}$ 1.5133; IR (film) cm$^{-1}$ 3420 (bw), 2983 (s), 2917 (m), 2882 (m), 2833 (m), 1462 (w), 1433 (m), 1381 (w), 1366 (w), 1266 (m), 1209 (w), 1047 (m), 887 (w), 790 (m); $^1$H NMR (200 MHz; CDCl$_3$), $\delta$ 0.84 (s, 3, CH$_3$–C(6)), 1.17 (d, 1, *J* = 8.6 Hz, C(7)H$_{endo}$), 1.27 (s, 3, CH$_3$–C(6)), 1.90−2.20 (m, 1+1, C(1)H, C(5)H), 2.20−2.30 (m, 2, C(4)H$_2$), 2.37 (dt, 1, *J* = 8.6 Hz, *J* = 5.6 Hz, C(7)H$_{exo}$), 2.51 (t, 2, *J* = 7.6 Hz, CH$_2$CH$_2$Br), 3.35 (t, 2, *J* = 7.6 Hz, CH$_2$Br), 5.20−5.40 (m, 1, C(3)H); $^{13}$C NMR (50 MHz, CDCl$_3$), $\delta$ 21.21 (s, CH$_3$–C(6)), 26.21 (s, CH$_3$–C(6)), 30.73 (s, CH$_2$Br), 31.24 (s, C(4)), 31.61 (s, C(7)), 38.90 (s, C(6)), 40.38 (s, CH$_2$CH$_2$Br), 40.62 (s, C(5)), 45.41 (s, C(1)), 119.10 (s, C(3)), 145.10 (s, C(2)); *m/e* (CI, isobutane) 149 (M$^+$ + 1 − Br, 41), 229 (M$^+$($^{79}$Br) + 1, 100), 231 (M$^+$($^{81}$Br) + 1, 96). Calcd for C$_{11}$H$_{18}^{79}$Br (M$^+$($^{79}$Br) + 1): 229.0592. Found: 229.0590.

**(−)-(1R)-Nopyl Tosylate (4).** (−)-(1*R*)-Nopol (**1**) (4.49 g, 27 mmol) was dissolved in dry pyridine (7 mL), and to this solution was added *p*-toluenesulfonyl chloride (5.91 g, 31 mmol). The resulting mixture was placed in a refrigerator for 20 h. Then, the reaction mixture containing a white precipitate was treated with aqueous solution of HCl (prepared from 7.5 mL of 36% aqueous solution of HCl and 15 mL of water) and extracted with diethyl ether (3 × 50 mL). Combined ethereal layers were dried for 24 h over K$_2$CO$_3$, filtered, and evaporated to afford **4** as a yellow oil (7.77 g, 88% yield) from which white crystals were obtained after a few minutes: $[\alpha]_D^{25}$ −26 (*c* 1.03 in CHCl$_3$); mp 46−48 °C; IR (film) cm$^{-1}$ 2999 (m), 2971 (m), 2915 (s), 2892 (m), 2864 (m), 2832 (m), 1598 (m), 1460 (m), 1357 (s), 1203 (m), 1189 (s), 1174 (s), 1096 (m), 981 (s), 962 (m), 935 (m), 911 (s), 814 (s), 804 (m), 795 (m), 773 (s), 665 (s), 571 (m), 555 (s); $^1$H NMR (500 MHz; CDCl$_3$), $\delta$ 0.75 (s, 3, CH$_3$–C(6)), 1.06 (d, 1, *J* = 8.7 Hz, C(7)H$_{endo}$), 1.22 (s, 3, CH$_3$–C(6)), 1.92 (dd, 1, $J_{H(1)-H(7)}$ = 5.3 Hz, $J_{H(1)-H}$ = 5.3* Hz, C(1)H), 2.04 (br s, 1, C(5)H), 2.17 (AB system, $\delta_{H1}$ 2.11, $\delta_{H2}$ 2.23, *J* = 17.7 Hz, C(4)H$_2$), 2.25−2.38 (m, 2+1, CH$_2$CH$_2$O, C(7)H$_{exo}$), 2.44 (s, 3, Ar–CH$_3$), 4.01 (t, 2, *J* = 7.0 Hz, CH$_2$O), 5.23 (br s 1, C(3)H), 7.33 (d, 2, *J* = 8.1 Hz, C$_{Ar}$H), 7.77 (d, 2, *J* = 8.1 Hz, C$_{Ar}$H) (*, $J_{H(1)-H}$ could not

be unambiguously attributed); $^{13}$C NMR (126 MHz, CDCl$_3$, $\delta$ 21.01 (s, CH$_3$–C(6)), 21.59 (s, Ar–CH$_3$), 26.12 (s, CH$_3$–C(6)), 31.22 (s, C(4)), 31.46 (s, C(7)), 36.03 (s, CH$_2$CH$_2$O), 37.95 (s, C(6)), 40.49 (s, C(5)), 45.45 (s, C(1)), 68.55 (s, CH$_2$O), 119.63 (s, C(3)), 127.81 (s, C$_{Ar}$H), 129.75 (s, C$_{Ar}$H), 133.17 (s, C$_{Ar}$–CH$_3$), 142.55 (s, C(2)), 144.62 (s, C$_{Ar}$–SO$_2$O). *m/e* (CI, NH$_3$) calcd for C$_{18}$H$_{28}$NSO$_3$ (M + NH$_4^+$): 338.1790. Found: 338.1779.

**(−)-1-[(1R)-Nopyl]-3-methylimidazolium Chloride (7).** (−)-(1*R*)-Nopyl chloride (**2**) (1.85 g, 0.01 mol) was dissolved in 1-methylimidazole (0.83 g, 0.01 mol), and the resulting mixture was heated (NOT refluxed) to 80−90 °C through 72 h. After cooling to ambient temperature, a viscous brownish substance was washed with ethyl acetate (3 × 10 mL). After evaporation of the last portion of the solvent, the crude ionic liquid was kept under vacuum at 70 °C for 30 min to afford a pure light brown product, **7** (2.53 g, 85% yield): $[\alpha]_D^{25}$ −18 (*c* 1.23 in CHCl$_3$); IR (film) cm$^{-1}$ 3377 (bm), 3145 (m), 3073 (m), 3034 (m), 2983 (m), 2935 (s), 2916 (s), 2832 (s), 1712 (m), 1672 (m), 1572 (m), 1466 (m), 1432 (m), 1382 (m), 1365 (m), 1169 (m), 1036 (m), 624 (m); $^1$H NMR (200 MHz; CDCl$_3$), $\delta$ 0.68 (s, 3, CH$_3$–C(6)), 0.94 (d, 1, *J* = 8.6 Hz, C(7)H$_{endo}$), 1.19 (s, 3, CH$_3$–C(6)), 1.99 (m, 2, C(1)H, C(5)H), 2.10 (br s, 2, C(4)H$_2$), 2.26−2.36 (m, 1, C(7)H$_{exo}$), 2.51 (m, 2, CH$_2$CH$_2$N(A)), 4.05 (s, 3, N(C)–CH$_3$), 4.25 (2 × t, 2, *J* = 7.4 Hz, *J* = 8.6 Hz, CH$_2$CH$_2$N(A)), 5.28 (m, 1, C(3)H), 7.33, 7.57 (2 × br t, 2 × 1, *J* = 1.7 Hz, *J* = 1.5 Hz, C(D)H, C(E)H), 10.37 (br s, 1, C(B)H); $^{13}$C NMR (126 MHz, CDCl$_3$), $\delta$ 20.76 (s, CH$_3$–C(6)), 25.85 (s, CH$_3$–C(6)), 31.02 (s, C(4)), 31.41 (s, C(7)), 36.27 (s, N(C)–CH$_3$), 36.88 (s, CH$_2$CH$_2$–N(A)), 37.79 (s, C(6)), 40.22 (s, C(5)), 44.88 (s, C(1)), 47.67 (s, CH$_2$CH$_2$N(A)), 120.5 (s, C(3)), 121.8, 123.6 (2 × s, C(D)H, C(E)H), 137.3 (s, C(B)H), 142.2 (s, C(2)). *m/e* (FAB(+), LSI, Cs$^+$, 13 keV) calcd for C$_{15}$H$_{23}$N$_2$ (M$^+$): 231.1861. Found 231.1867 *m/e* (FAB(−), LSI, Cs$^+$, 13 keV) 301, 303, 305 (M$^+$ + 2 × Cl$^-$, 90, 60, 9); 35, 37 (100, 31, Cl$^-$).

**(−)-1-[(1R)-Nopyl]-3-n-butylimidazolium Chloride (8).** (−)-(1*R*)-Nopyl chloride **2** (1.69 g, 9.15 mmol) was dissolved with 1-butylimidazole (1.15 g, 9.3 mmol), and the resulting mixture was heated (NOT refluxed) to 70−80 °C through 72 h. After cooling to ambient temperature, a yellowish precipitate of **8** was washed with ethyl acetate (3 × 10 mL). After evaporation of the last portion of the solvent, the crude ionic liquid was kept under vacuum at 70 °C for 30 min to afford a pure beige product **8** (1.98 g, 63% yield): $[\alpha]_D^{25}$ −14 (*c* 1.16 in CHCl$_3$); mp 64−67 °C (hygroscopic); IR (film) cm$^{-1}$ 3406 (bs), 3265 (s), 3134 (s), 3077 (s), 2959(bs), 2832 (s), 1714 (m), 1677 (m), 1635 (m), 1568 (s), 1466 (s), 1365 (m), 1167 (s), 947 (m), 891 (m), 625 (m); $^1$H NMR (200 MHz; CDCl$_3$), $\delta$ 0.63 (s, 3, CH$_3$–C(6)), 0.82 (t, 3, *J* = 7.3 Hz, N(C)–(CH$_2$)$_3$CH$_3$), 0.87 (1 H, d, $J_{H-H}$ = 8.1 Hz, C(7)-H$_{endo}$), 1.14 (s, 3 CH$_3$–C(6)), 1.22 (m, 2, N(C)-(CH$_2$)$_2$CH$_2$CH$_3$), 1.77 (m, 2, N(C)-CH$_2$CH$_2$CH$_2$CH$_3$), 1.96 (m, 2, C(1)H, C(5)H), 2.05 (br s, 2, C(4)H$_2$), 2.25 (m, 1, C(7)H$_{exo}$), 2.50 (m, 2, CH$_2$CH$_2$N(A)), 4.26 (m, 4, CH$_2$CH$_2$–N(A), N(C)–CH$_2$(CH$_2$)$_2$CH$_3$), 5.24 (m, 1, C(3)H), 7.38, 7.48 (2 × br s, 2 × 1, C(D)H, C(E)H), 10.32 (br s, 1, C(B)H); $^{13}$C NMR (50 MHz, CDCl$_3$,), $\delta$ 13.18 (s, N(C)–(CH$_2$)$_3$CH$_3$), 19.10 (s, N(C)–(CH$_2$)$_2$CH$_2$CH$_3$), 20.72 (s, CH$_3$–C(6)), 25.82 (s, CH$_3$–C(6)), 31.00, 31.42, 31.92 (3 × s, C(4), C(7), N(C)–CH$_2$CH$_2$CH$_2$CH$_3$), 36.79 (s, CH$_2$CH$_2$–N(A)), 37.76 (s, C(6)), 40.19, 44.80 (2 × s, C(1), C(5)), 47.62, 49.41 (2 × s, CH$_2$CH$_2$–N(A), N(C)–CH$_2$(CH$_2$)$_2$CH$_3$), 120.47 (s, C(3)), 121.85 (s, C(D)H, C(E)H), 137.01 (s, C(B)H), 142.23 (s, C(2)). *m/e* (FAB(+), LSI, Cs$^+$, 13 keV) calcd for C$_{18}$H$_{29}$N$_2$ (M$^+$): 273.2331. Found: 273.2336. *m/e* (FAB(−), LSI, Cs$^+$, 13 keV) 343, 345, 347 (M$^+$ + 2 × Cl$^-$, 90, 60, 9); 35, 37 (100, 31, Cl$^-$).

**(−)-1-[(1R)-Nopyl]-3-methylimidazolium Bromide (9).** (−)-(1*R*)-Nopyl bromide (**3**) (1.15 g, 5 mmol) was dissolved in 1-methylimidazole (0.41 g, 5 mmol). After 10 days of stirring at ambient temperature, the mixture was heated to 50 °C for 66 h. Three-fold extraction of the crude reaction mixture with AcOEt followed by drying over MgSO$_4$, filtration of the drying agent, and evaporation of the solvent gave the pure product **9** (1.06 g, 74% yield): $[\alpha]_D^{25}$ −15 (*c* 2.60 in CHCl$_3$); IR (film) cm$^{-1}$ 3435(bs), 3140 (s), 3063 (s), 2983 (s), 2915 (s), 2832 (s), 1732 (m), 1571 (m), 1466 (s), 1431 (s), 1379 (m), 1365 (m), 1244 (m), 1169 (s), 753 (m), 622 (m); $^1$H NMR (200 MHz; CDCl$_3$), $\delta$ 0.65 (s, 3, CH$_3$–C(6)), 0.91 (d, 1, *J* = 8.6 Hz, C(7)H$_{endo}$), 1.16 (s, 3, CH$_3$–C(6)), 1.95−2.00 (m, 1, C(5)H), 2.07 (2 × br s, 2 C(4)H$_2$), 2.20−2.40

(m, 1, C(7)$H_{egzo}$), 2.50 (t, 2, $J$ = 7.4 Hz, C$H_2$CH$_2$N(A)), 4.02 (s, 3, N(C)-CH$_3$), 4.23 (t, 2, $J$ = 7.4 Hz, CH$_2$C$H_2$N(A)), 5.27 (s, 1, C(3)H), 7.37, 7.61 (2 × s, 2 C(D)H, C(E)H), 10.10 (s, 1, C(B)H); $^{13}$C NMR (50 MHz, CDCl$_3$), $\delta$ 20.79 (s, C$H_3$-C(6)), 25.88 (s, C$H_3$-C(6)), 31.06 (s, C(4)), 31.47 (s, C(7)), 36.50, 36.90, 37.83 (3 × s, C(6), N(C)-CH$_3$, C$H_2$CH$_2$-N(A)), 40.31 (s, C(5)), 45.00 (s, C(1)), 47.82 (s, CH$_2$C$H_2$N(A)), 120.63 (s, C(3)), 121.88, 123.50 (2 × s, C(D)H, C(E)H), 137.03 (s, C(B)H), 142.13 (s, C(2)). *m/e* (FAB(+), LSI, Cs$^+$, 13 keV) calcd for C$_{15}$H$_{23}$N$_2$ (M$^+$): 231.1861. Found: 231.1855. *m/e* (FAB(−), LSI, Cs$^+$, 13 keV) 79 (M$^-$($^{79}$Br), 95), 81 (M$^-$($^{81}$Br), 93).

**(−)-1-[(1R)-Nopyl]-3-methylimidazolium Tosylate (10).** (−)-(1R)-Nopyl tosylate (**4**) (1.6 g, 6.9 mmol) was dissolved in 1-methylimidazole (0.41 g, 5 mmol), and the resulting mixture was heated under argon atmosphere (NOT refluxed) to 70−80 °C through 72 h. Then the crude product was kept under vacuum at 70 °C for 30 min to afford a brownish product **10** (1.9 g, 95% yield): [$\alpha$]$_D^{25}$ −9 (*c* 2.38 in MeOH); IR (film) cm$^{-1}$ 3455 (bm), 3148 (m), 3104 (m), 2983 (m), 2916 (m), 2832 (m), 1720 (w), 1574 (w), 1468 (w), 1427 (w), 1382 (w), 1365 (w), 1218 (s), 1194 (s), 1123 (s), 1034 (s), 1012 (s), 816 (m), 683 (s), 625 (w), 569 (m); $^1$H NMR (500 MHz; CDCl$_3$), $\delta$ 0.66 (s, 3, CH$_3$-C(6)), 0.90 (d, 1, $J$ = 8.7 Hz, C(7)H$_{endo}$), 1.17 (s, 3, CH$_3$-C(6)), 1.90−1.96 (m, 1, C(1)H), 1.96−2.02 (m, 1, C(5)H,), 2.08 (AB system, $\delta_{H1}$ = 2.11, $\delta_{H2}$ = 2.06, $J$ = 17.7 Hz, C(4)H$_2$), 2.23−2.30 (m, 1, C(7)-H$_{exo}$), 2.27 (s, 3, CH$_3$-C$_{Ar}$), 2.32−2.45 (m, 2, C$H_2$CH$_2$-N(A)), 3.84 (s, 3, N(C)-CH$_3$), 4.05−4.20 (m, 2, CH$_2$C$H_2$-N(A)), 5.17 (s, 1, C(3)H), 7.08 (d, 2, $J$ = 7.9 Hz, C$_{Ar}$H), 7.24, 7.41 (2 × s, 2, C(D)H, C(E)H), 7.69 (d, 2, $J$ = 7.9 Hz, C$_{Ar}$H), 9.46 (s, 1, C(B)H); $^{13}$C NMR (50 MHz, CDCl$_3$), $\delta$ 20.79 (s, C$H_3$-C(6)), 21.12 (s, CH$_3$-Ar), 25.90 (s, C$H_3$-C(6)), 31.08 (s, C(4)), 31.46 (s, C(7)), 35.35, 36.07, 36.82 (3 × s, C(6), N(C)-CH$_3$, C$H_2$CH$_2$-N(A)), 40.31 (s, C(5)), 44.87 (s, C(1)), 47.57 (s, CH$_2$C$H_2$-N(A)), 120.30 (s, C(3)), 125.63 (s, C$_{Ar}$H), 128.54 (s, C$_{Ar}$H), 122.21 (2 × s, C(D)H, C(E)H), 137.30 (s, C(B)H), 139.35, 142.33, 143.33 (3 × s, C$_{Ar}$-CH$_3$, C$_{Ar}$-O, C(2)). *m/e* (FAB(+), LSI, Cs$^+$, 13 keV) calcd for C$_{15}$H$_{23}$N$_2$ (M$^+$): 231.1861. Found: 231.1871. *m/e* (FAB(−), LSI, Cs$^+$, 13 keV) 171 (M$^-$, 100).

**(−)-1-[(1R)-Nopyl]-3-methylimidazolium Hexafluorophosphate (11).** To a stirred solution of the ionic liquid **7** (0.53 g, 2 mmol) in water (3 mL) was added an aqueous solution of HPF$_6$ (0.63 g, 2.6 mmol, *c* = 60%), and the mixture was stirred for 12 h at ambient temperature. The resulting viscous mixture was washed with water (10 × 5 mL) to gain the neutral pH and afforded a brownish yellow product **11** (0.49 g, 63% yield): [$\alpha$]$_D^{25}$ −10 (*c* 1.94 in MeOH); IR (film) cm$^{-1}$ 3340 (bm), 3158 (m), 3118 (m), 2962 (m), 1703 (w), 1575 (w), 1169 (s), 1109 (m), 1042 (s), 1007 (s), 884 (m), 754 (m), 580 (m); $^1$H NMR (200 MHz; CDCl$_3$), $\delta$ 0.71 (s, 3, CH$_3$-C(6)), 0.97 (d, 1, $J$ = 8.4 Hz, C(7)H$_{endo}$), 1.22 (s, 3, CH$_3$-C(6)), 2.00−2.06 (m, 2, C(1)H, C(5)H), 2.13 (br s, 2, C(4)H$_2$), 2.28−2.38 (m, 1, C(7)H$_{exo}$), 2.48 (t, 2, $J$ = 7.0 Hz, C$H_2$CH$_2$-N(A)), 3.83 (s, 3, N(C)-CH$_3$), 4.12 (t, 2, $J$ = 7.1 Hz, CH$_2$C$H_2$-N(A)), 5.28 (br s, 1, C(3)H), 7.26 (br s, 2, C(D)H, C(E)H), 8.40 (br s, 1, C(B)H); $^{13}$C NMR (50 MHz, CDCl$_3$), $\delta$ 20.91 (s, C$H_3$-C(6)), 25.90 (s, C$H_3$-C(6)), 31.16 (s, C(4)), 31.51 (s, C(7)), 35.96 (s, N(C)-CH$_3$), 36.71 (s, C$H_2$CH$_2$-N(A)), 37.90 (s, C(6)), 40.37 (s, C(5)), 44.85 (s, C(1)), 47.86 (s, CH$_2$C$H_2$N(A)), 120.69 (s, C(3)), 122.15, 123.43 (2 × s, C(D)H, C(E)H), 135.62 (s, C(B)H), 142.25 (s, C(2)). *m/e* (FAB(+), LSI, Cs$^+$, 13 keV) calcd for C$_{15}$H$_{23}$N$_2$ (M$^+$): 231.1861. Found: 231.1868. *m/e* (FAB(−), LSI, Cs$^+$, 13 keV): 145 (PF$_6^-$, 100).

**(−)-1-[(1R)-Nopyl]-3-n-butylimidazolium Hexafluorophosphate (12).** To a stirred solution of the ionic liquid **8** (0.86 g, 2.8 mmol) in water (3 mL) was added an aqueous solution of HPF$_6$ (0.88 g, 3.6 mmol, *c* = 60%), and the mixture was stirred through 12 h at ambient temperature. The resulting viscous mixture was washed with water (10 × 5 mL) to neutral pH to afford a viscous brownish yellow liquid of the product **12** (1.01 g, 87% yield): [$\alpha$]$_D^{25}$ −9 (*c* 2.35 in MeOH); mp 64−67 °C (hygroscopic); IR (film) cm$^{-1}$ 3161 (w), 2962 (w), 2936 (w), 2877 (w), 1566 (w), 1463 (w), 1163 (w), 840 (s), 750 (w), 557 (m); $^1$H NMR (200 MHz; CDCl$_3$), $\delta$ 0.68 (s, 3, CH$_3$-C(6)), 0.82−0.94 (m, 4, N(C)-(CH$_2$)$_3$C$H_3$, C(7)H$_{endo}$), 1.19 (s, 3, CH$_3$-C(6)), 1.15−1.31 (m, 2, N(C)-(CH$_2$)$_2$C$H_2$CH$_3$), 1.54−1.84 (m, 2, N(C)-CH$_2$C$H_2$-CH$_2$CH$_3$), 1.97−2.03 (m, 2, C(1)H, C(5)H), 2.09 (br s, 2, C(4)H$_2$), 2.27−2.37 (m, 1, C(7)H$_{exo}$), 2.48 (m, 2, C$H_2$CH$_2$N(A)), 4.10 and 4.14 (2 × t, 4, $J$ = 6.9 Hz, $J$ = 7.2 Hz, CH$_2$C$H_2$-N(A), N(C)-C$H_2$(CH$_2$)$_2$-

CH$_3$), 5.24 (br s, 1, C(3)H), 7.29 (s, 1, C(D)H, C(E)H), 8.47 (br s, 1, C(B)H); $^{13}$C NMR (50 MHz, CDCl$_3$), $\delta$ 14.11 (s, N(C)-(CH$_2$)$_3$CH$_3$), 20.08 (s, N(C)-(CH$_2$)$_2$C$H_2$CH$_3$), 21.87 (s, C$H_3$-C(6)), 26.85 (s, C$H_3$-C(6)), 32.15, 32.52, 32.72 (3 × s, C(4), C(7), N(C)-CH$_2$CH$_2$CH$_2$CH$_3$), 37.67 (s, C$H_2$CH$_2$-N(A)), 38.86 (s, C(6)), 41.33 (s, C(5)), 45.72 (s, C(1)), 48.80, 50.62 (2 × s, CH$_2$C$H_2$-N(A), N(C)-C$H_2$(CH$_2$)$_2$CH$_3$), 121.76 (s, C(3)), 123.23, 123.31 (2 × s, C(D)H, C(E)H), 135.89 (s, C(B)H), 143.32 (s, C(2)). *m/e* (FAB(+), LSI, Cs$^+$, 13 keV) calcd for C$_{18}$H$_{29}$N$_2$ (M$^+$): 273.2331. Found: 273.2333. *m/e* (FAB(−), LSI, Cs$^+$, 13 keV) 145 (PF$_6^-$, 100).

**(−)-1-[(1R)-Nopyl]-3-methylimidazolium Nitrate (13).** To the ionic liquid **7** (3.87 g, 14.5 mmol) dissolved in acetone (30 mL) was added an aqueous solution of AgNO$_3$ (2.47 g, 14.5 mmol), and the mixture was stirred for 24 h at ambient temperature. A white precipitate of AgCl was filtered off, and acetone was evaporated. The resulting crude ionic liquid was washed with hexane to give **13** (4.42 g , 99% yield): [$\alpha$]$_D^{25}$ −16 (*c* 2.13 in CHCl$_3$); IR (film) cm$^{-1}$ 3478 (bm), 3147 (m), 3101 (m), 2984 (m), 2916 (m), 2833 (w), 1573 (m), 1465 (m), 1352 (s), 1168 (m), 830 (w), 624 (w); $^1$H NMR (200 MHz; CDCl$_3$), $\delta$ 0.73 (s, 3, CH$_3$-C(6)), 0.99 (d, 2, $J$ = 8.6 Hz, C(7)H$_{endo}$), 1.24 (s, 3, CH$_3$-C(6)), 1.95−2.10 (m, 1, C(5)H), 2.16 (br s, 2, C(4)H$_2$), 2.25−2.45 (m, 1, C(7)H$_{egzo}$), 2.54 (t, 2, $J$ = 7.2 Hz, C$H_2$CH$_2$N(A)), 3.98 (s, 3, N(C)-CH$_3$), 4.24 (t, 2, $J$ = 7.2 Hz, CH$_2$C$H_2$N(A)), 5.31 (s, 1, C(3)H), 7.38, 7.49 (2 × s, 2, C(D)H, C(E)H), 9.67 (s, 1, C(B)H); $^{13}$C NMR (50 MHz, CDCl$_3$), $\delta$ 20.87 (s, C$H_3$-C(6)), 25.99 (s, C$H_3$-C(6)), 31.19 (s, C(4)), 31.57 (s, C(7)), 36.13, 36.99, 37.94 (3 × s, C(6), N(C)-CH$_3$, CH$_2$-CH$_2$-N(A)), 40.38 (s, C(5)), 44.98 (s, C(1)), 47.87 (s, CH$_2$CH$_2$N(A)), 120.64 (s, C(3)), 122.03, 123.46 (2 × s, C(D)H, C(E)H), 137.56 (s, C(B)H), 142.34 (s, C(2)). *m/e* (FAB(+), LSI, Cs$^+$, 13 keV) calcd for C$_{15}$H$_{23}$N$_2$ (M$^+$): 231.1861. Found: 231.1861. *m/e* (FAB(−), LSI, Cs$^+$, 13 keV) 355 (M$^+$ + 2 × NO$_3^-$, 44), 62 (NO$_3^-$, 100).

**(−)-1-[(1R)-Nopyl]-3-n-Butylimidazolium Nitrate (14).** To a stirred solution of the ionic liquid **8** (0.31 g, 1 mmol) in acetone (10 mL) was added an aqueous solution of AgNO$_3$ (0.2 g, 1.2 mmol), and the mixture was stirred through 24 h at ambient temperature. A white AgCl precipitate was filtered under reduced pressure. The filtrate was concentrated, affording oil, which was heated to 70 °C through 30 min on a vacuum pump to give the brownish yellow viscous liquid 14 (0.33 g, 100% yield); [$\alpha$]$_D^{25}$ −16 (*c* 0.81 in CHCl$_3$); $n_D^{30}$ = 1.4903; IR (film) cm$^{-1}$ 3450 (bw), 3138 (m), 3098 (m), 3044 (m), 2959 (m), 2934 (m), 2876 (m), 2833 (w), 1565 (m), 1468 (m), 1365 (s), 1345 (s), 1220 (w), 1165 (m), 1034 (w), 753 (m); $^1$H NMR (200 MHz; CDCl$_3$), $\delta$ 0.73 (s, 3, CH$_3$-C(6)), 0.80−1.00 (m, 3+1 N(C)-(CH$_2$)$_3$C$H_3$, C(7)H$_{endo}$), 1.24 (s, 3, CH$_3$-C(6)), 1.31 (septet, 2, $J$ = 7.5 Hz, N(C)-(CH$_2$)$_2$C$H_2$CH$_3$), 1.83 (quint, 2, $J$ = 7.5 Hz, N(C)-CH$_2$C$H_2$CH$_2$CH$_3$), 1.90−2.10 (m, 2, C(1)H, C(5)H), 2.10−2.20 (br s, 2, C(4)H$_2$), 2.25−2.50 (m, 1, C(7)-H$_{exo}$), 2.55 (m, 2, C$H_2$CH$_2$-N(A)), 4.15−4.35 (m, 4, CH$_2$C$H_2$-N(A), N(C)-C$H_2$(CH$_2$)$_2$CH$_3$), 5.28 (s, 1, C(3)H), 7.25−7.45 (m, 2, C(D)H, C(E)H), 9.74 (s, 1, C(B)H); $^{13}$C NMR (50 MHz, CDCl$_3$), $\delta$ 13.30 (s, N(C)-(CH$_2$)$_3$CH$_3$), 19.30 (s, N(C)-(CH$_2$)$_2$C$H_2$CH$_3$), 20.91 (s, C$H_3$-C(6)), 26.03 (s, C$H_3$-C(6)), 31.26, 31.67, 32.04 (3 × s, C(4), C(7), N(C)-CH$_2$CH$_2$CH$_2$CH$_3$), 36.99 (s, C$H_2$CH$_2$-N(A)), 37.99 (s, C(6)), 40.43, 45.00 (2 × s, C(1), C(5)), 47.91, 49.74 (2 × s, CH$_2$C$H_2$-N(A), N(C)-C$H_2$(CH$_2$)$_2$CH$_3$), 120.71 (s, C(3)), 121.89, 122.05 (2 × s, C(D)H, C(E)H), 137.28 (s, C(B)H), 142.50 (s, C(2)). *m/e* (FAB(+), LSI, Cs$^+$, 13 keV) 171 (54), 187 (37). Calcd for C$_{18}$H$_{29}$N$_2$ (M$^+$): 273.2331. Found: 273.2323. *m/e* (FAB(−), LSI, Cs$^+$, 13 keV) 397 (M$^+$ + 2 × NO$_3^-$, 100).

**(−)-1-[(1R)-Nopyl]-3-n-butylimidazolium Trifluoromethylosulfonate (15).** To a stirred solution of the ionic liquid **8** (0.31 g, 1 mmol) in acetone (10 mL) was added a solid AgCF$_3$SO$_3$ salt (0.31 g, 1.2 mmol), and the mixture was stirred through 24 h at ambient temperature. A white precipitate of AgCl was filtered off under reduced pressure. The filtrate was concentrated, affording oil, which was heated to 70 °C through 30 min on a vacuum pump to give the brownish yellow viscous liquid 15 (0.26 g, 62% yield): [$\alpha$]$_D^{25}$ −8 (*c* 0.83 in MeOH); IR (film) cm$^{-1}$ 3492 (bw), 3145 (w), 3110 (w), 2963 (m), 2937 (m), 2878 (w), 1566 (w), 1462 (w), 1274 (s), 1258 (s), 1225 (s), 1163 (s), 1030 (s), 757 (w), 638 (s), 518 (w); $^1$H NMR (200 MHz; CDCl$_3$), $\delta$ 0.74 (s, 3, CH$_3$-C(6)), 0.80−1.15 (m, 3+1, N(C)-(CH$_2$)$_3$C$H_3$, C(7)-H$_{endo}$), 1.26 (s, 3, CH$_3$-C(6)), 1.15−1.50 (m, 2, N(C)-(CH$_2$)$_2$C$H_2$-

**1884** *J. Agric. Food Chem.,* Vol. 55, No. 5, 2007

Bałczewski et al.

CH₃), 1.65−2.00 (m, 2, N(C)−CH₂C*H₂*CH₂CH₃), 2.00−2.10 (m, 2, C(1)H, C(5)H), 2.10−2.25 (m, 2, C(4)H₂), 2.25−2.50 (m, 1, C(7)-H_exo), 2.50−2.65 (m, 2, C*H₂*CH₂−N(A)), 4.05−4.35 (m, 4, CH₂C*H₂*−N(A), N(C)−C*H₂*(CH₂)₂CH₃), 5.33 (br s, 1, C(3)H), 7.30−7.35 (m, 2, C(D)H, C(E)H), 9.07 (s, 1, C(B)H); ¹³C NMR (50 MHz, CDCl₃), δ 13.25 (s, N(C)−(CH₂)₃*C*H₃), 19.27 (s, N(C)−(CH₂)₂*C*H₂CH₃), 20.90 (s, *C*H₃−C(6)), 25.98 (s, *C*H₃−C(6)), 31.32, 31.87, 31.93 (3 × s, C(4), C(7), N(C)−CH₂*C*H₂CH₂CH₃), 36.99 (s, *C*H₂CH₂−N(A)), 38.04 (s, C(6)), 40.45, 45.02 (2 × s, C(1), C(5)), 47.96, 49.80 (2 × s, CH₂*C*H₂−N(A), N(C)−*C*H₂(CH₂)₂CH₃), 120.18 (s, C(3)), 120.81 (q, *J* = 318 Hz, CF₃), 122.03, 122.21 (2 × s, C(D)H, C(E)H), 136.18 (s, C(B)H), 143.07 (s, C(2)); *m/e* (FAB(+), LSI, Cs⁺, 13 keV) 125 (26, M⁺ − Nop + H). Calcd for C₁₈H₂₉N₂ (M⁺): 273.2331. Found: 273.2324. *m/e* (FAB(−), LSI, Cs⁺, 13 keV) 149 (M⁻, 100).

**(−)-1-[(1R)-Nopyl]-3-methylimidazolium (R)-Mandelate (16).** To a stirred solution of sodium salt of (−)-*(R)*-mandelic acid [obtained from Na (0.034 g, 1.48 mmol) dissolved in methanol (10 mL) and (−)-*(R)*-mandelic acid (0.225 g, 1.48 mmol)] was added the ionic liquid **7** (0.40 g, 1.48 mmol). The mixture was stirred for 24 h at ambient temperature. Next, methanol was evaporated, acetone was added, and a precipitate of NaCl was filtered off. The filtrate was evaporated to afford the ionic liquid **16** (0.39 g, 70% yield): [α]_D²⁵ −39 (*c* 1.06 in MeOH); IR (film) cm⁻¹ 3381 (bm), 3148 (m), 3086 (m), 3063 (m), 3030 (m), 2984 (m), 2914 (m), 2832 (m), 1614 (s), 1574 (m), 1451 (m), 1431 (m), 1364 (s), 1169 (m), 1086 (m), 1057 (m), 737 (m), 700 (m), 622 (w); ¹H NMR (200 MHz; CDCl₃), δ 0.70 (s, 3, CH₃−C(6)), 0.94 (d, 2, *J* = 8.6 Hz, C(7)H_endo), 1.21 (s, 3, CH₃−C(6)), 1.80−2.10 (m, 2, C(1)H, C(5)H), 2.11 (br s, 2, C(4)H₂), 2.15−2.50 (m, 3, C(7)-H_egzo, C*H₂*CH₂N(A)), 3.74 (s, 3, N(C)−CH₃), 3.95−4.25 (m, 2, CH₂C*H₂*N(A)), 4.48 (br s, 1, OH), 4.79 (s, 1, CH−COO⁻), 5.26 (s, 1, C(3)H), 6.80−7.30 (m, 5, C₆H₅), 7.41, 7.45 (2 × s, 2, C(D)H, C(E)H), 10.01 (s, 1,C(B)H); ¹³C NMR (50 MHz, CDCl₃), δ 20.86 (s, *C*H₃−C(6)), 25.99 (s, *C*H₃−C(6)), 31.16 (s, C(4)), 31.52 (s, C(7)), 35.97 (s, C(6)), 36.90 (s, N(C)−CH₃), 37.91 (s, *C*H₂CH₂N(A)), 40.43 (s, C(5)), 45.09 (s, C(1)), 47.61 (s, CH₂*C*H₂N(A)), 74.50 (s, CH−OH), 120.45, 121.39, 122.83 (3 × s, C(3), C(D), C(E)), 126.30 (s, Ar_para), 126.48, 127.58 (2 × s, Ar_ortho, Ar_meta), 138.45 (s, C(B)), 142.36, 143.58 (2 × s, C(2), *Ar*−C), 176.82 (s, COO⁻). *m/e* (FAB(+), LSI, Cs⁺, 13 keV) calcd for C₁₅H₂₃N₂ (M⁺): 231.1861. Found: 231.1868. *m/e* (FAB(−), LSI, Cs⁺, 13 keV) calcd for C₈H₇O₃ (Migd⁻): 151.0395. Found 151.0397.

**(+)-1-[(1R)-Nopyl]-3-methylimidazolium (S)-Mandelate (17).** The procedure used was analogous to that decribed for **16** except that (+)-*S*-mandelic acid was used: yield (0.33 g, 86%); [α]_D²⁵ +14 (*c* 0.86 in MeOH); IR (film) cm⁻¹ 3347 (bm), 3146 (m), 3084 (m), 3062 (m), 3029 (m), 2983 (m), 2915 (s), 2832 (m), 1618 (s), 1573 (m), 1451 (m), 1431 (m), 1358 (s), 1170 (m), 1085 (m), 1055 (m), 737 (m), 701 (m); ¹H NMR (200 MHz; CDCl₃), δ 0.74 (s, 3, CH₃−C(6)), 0.98 (d, 1, *J* = 8.6 Hz, C(7)H_endo), 1.25 (s, 3, CH₃−C(6)), 1.95−2.10 (m, 2, C(1)H, C(5)H), 2.15 (br s, 2, C(4)H₂), 2.25−2. (m, 3,C(7)H_egzo, C*H₂*CH₂N-(A)), 3.80 (s, 3, N(C)−CH₃), 4.11 (m, 2, CH₂C*H₂*N(A)), 4.64 (br s, 1, OH), 4.85 (s, 1, CH−COO⁻), 5.26 (s, 1, C(3)H), 7.00−7.30 (m, 5, C₆H₅), 7.47, 7.50 (2 × s, 2, C(D)H, C(E)H), 10.17 (s, 1, C(B)H); ¹³C NMR (50 MHz, CDCl₃), δ 20.87 (s, *C*H₃−C(6)), 26.00 (s, *C*H₃−C(6)), 31.18 (s, C(4)), 31.53 (s, C(7)), 35.98 (s, C(6)), 36.90 (s, N(C)−CH₃), 37.93 (s, *C*H₂CH₂N(A)), 40.44 (s, C(5)), 45.11 (s, C(1)), 47.64 (s, CH₂*C*H₂N(A)), 74.47 (s, CH−OH), 120.47, 121.41, 122.82 (3 × s, C(3), C(D), C(E)), 126.38 (s, Ar_para), 126.50, 127.62 (2 × s, Ar_ortho, Ar_meta), 138.35 (s, C(B)), 142.37, 143.44 (2 × s, C(2), *Ar*-C), 176.88 (s, COO⁻). *m/e* (FAB(+), LSI, Cs⁺, 13 keV) calcd for C₁₅H₂₃N₂ (M⁺): 231.1861. Found: 231.1861. *m/e* (FAB(−), LSI, Cs⁺, 13 keV) calcd for C₈H₇O₃ (Migd⁻): 151.0395. Found 151.0400.

**Crystallographic Data for (1R)-(−)-6,6-Dimethylbicyclo[3.1.1]-hept-2-ene-2-ethyl-*N*-methyl-3-*H*-imidazol-1-ium Toluene-4-sulfonate (4):** C₁₈H₂₄O₃S, colorless, needle 0.56 × 0.11 × 0.05 mm from chloroform, orthorhombic, space group *P*2₁2₁2₁, *a* = 6.062(2)Å, *b* = 14.896(4)Å, *c* = 18.347(5)Å, *V* = 1656.7(8)Å³, *M*_r = 320.44, *Z* = 4, *d*_calcd = 1.285 g/cm³, μ = 0.206 mm⁻¹, *T* = 90(2) K, *F*(000) = 688.

*Data collection* was performed with an Xcalibur PX CCD κ-geometry (Oxford Diffraction) diffractometer with graphite monochromatized Mo Kα radiation. Measured reflections were 33818 (θ_max 38.0°) and 8931 independent (*R*_int 0.062).

*Structure solution* was determined via a direct method with aniso-tropic refinement on *F*² for all non H atoms; hydrogen atoms attached to C atoms were included by using a riding model. The structure was refined over 5900 reflections with *I* > 2σ (*I*) (202 refined parameters with 29.2 reflections on parameter). The correct absolute structure was proved by Flack parameter (*22*) *x* = 0.02(6). For all data the final *wR*2 was 0.118, *R*1 = 0.061, *S* = 0.996, max Δρ = 0.82 eÅ⁻³.

Data processing was carried out with the Oxford Diffraction (*23, 24*), structure solution with SHELXS (*25*), and structure refinement with SHELXL (*26*).

Full details (excluding the structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Center, as supplementary publication CCDC-602211, and can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, United Kingdom (e-mail deposit@ccdc.cam.ac.uk).

**Materials and Methods Used in Phytotoxicity Tests (*21*).** The phytotoxicity tests for ionic liquids **7** and **13** were carried out in a plant house using spring barley (*Hordeum vulgare*)—a monocotyledonous plant—and common radish (*Raphanus sativus* L. subvar. *radicula* Pers.)—a dicotyledonous plant. In four repetitions, pots made of nonporous plastic of a 90 mm diameter were filled, respectively, with the control soil and with the soil containing tested ionic liquids in relevant concentrations. The grain size analysis of the soil used in the experiment showed that this was a light argillaceous sand containing 10% of flotable particles and 0.9% of organic carbon and having pH (KCl) = 5.8. The salinity of the soil was about 70 mg of KCl/1 dm³ of the soil. Twenty identical seeds of the selected plant species, originating from the same source, were planted to the prepared pots (**Figures 4i** and **5i**). Constant parameters such as humidity, light intensity, and temperature (20 ± 2 °C) were maintained throughout the whole period of the 14 day test.
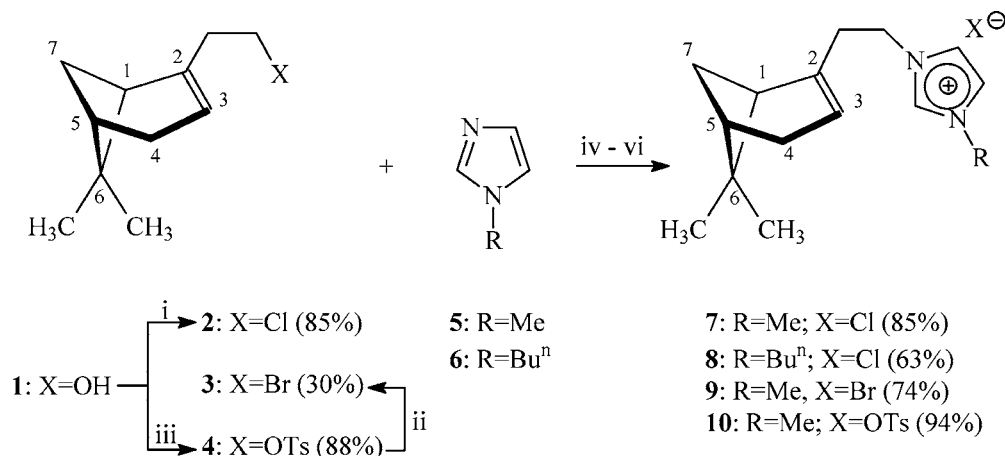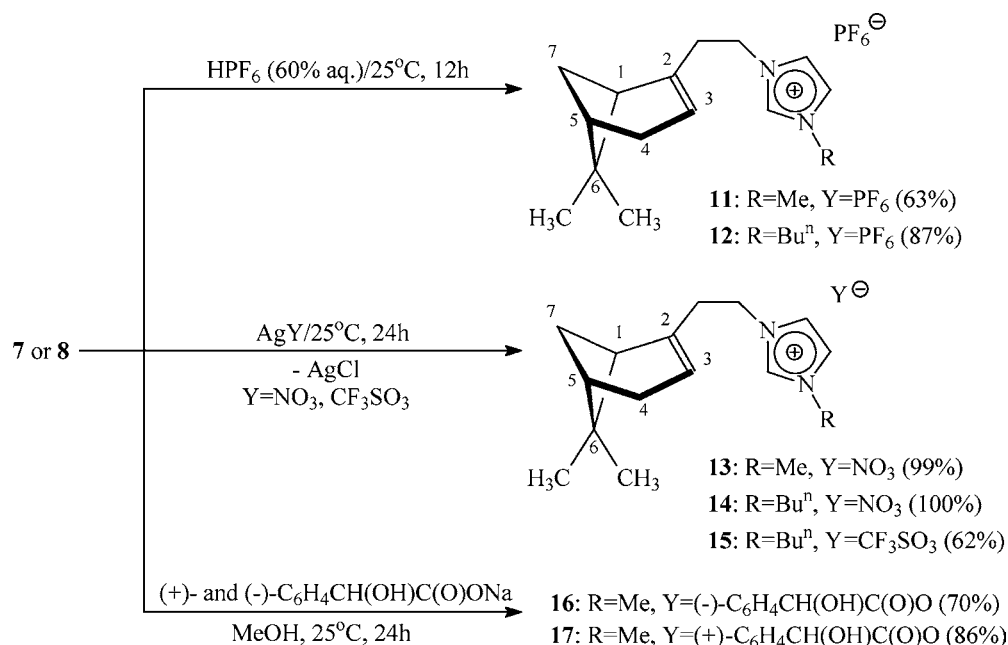
The phytotoxicity test comprised two testing cycles: a preliminary test and a final test. The preliminary test was carried out to determine the range of concentrations of compounds affecting the soil quality; therefore, in accordance with the standard, the tested ionic liquids **7** and **13** were introduced to the soil in the following concentrations: 0 mg (control) and 1, 10, 100, and 1000 mg/kg of the soil dry weight. In the final test, concentrations were arranged in a geometric progression with a factor of 2, starting from the lowest concentration that reduced germination and growth of plants. This concentration was found to be 100 mg of the tested compounds per kilogram of the soil; therefore, concentrations equal to 200, 400, and 800 mg/kg of the soil dry weight were used in final tests. The ionic liquids were introduced to the soil in the form of water solutions.

To evaluate the phytotoxicity of ionic liquids **7** and **13** in the applied concentrations, the germination and (dry and fresh) weights of control plant sprouts were determined and compared with germination and (dry and fresh) weight of the sprouts of plants grown in the soil containing the relevant amounts of the tested chemicals. Visual assessment of any types of damages of the tested species, such as growth inhibition, chlorosis, and necrosis, was also carried out and was depicted by digital photographs of the tested plants. On the basis of the obtained results, the magnitudes of the the lowest observed effect concentration (LOEC)—the lowest concentration causing observable effects in the form of a reduction in growth and germination compared with the control—and the no observed effect concentration (NOEC)—the highest concentration not causing any observable toxic effects—were also determined.

Evaluation of the significance of the obtained results was performed using the analysis of variance (Fisher−Snedecor's *F* test), whereas the values of LSD₀.₉₅ were calculated using Tukey's test.

## RESULTS AND DISCUSSION

**Synthesis and Properties of New Chiral Ionic Liquids.** In the course of our studies on the synthesis, properties, and application of chiral ionic liquids, we synthesized a new series of these compounds based on imidazolium cation containing

**Scheme 1.** Synthesis of (–)-(1*R*)-Nopyl Chloride **2**, Bromide **3**, and Tosylate **4**; Quaternization of 1-Alkylimidazoles **5** and **6**



|  |  |  |
|---|---|---|
| **i** → **2**: X=Cl (85%) | **5**: R=Me | **7**: R=Me; X=Cl (85%) |
|  | **6**: R=Bu$^n$ | **8**: R=Bu$^n$; X=Cl (63%) |
| **1**: X=OH → **3**: X=Br (30%) ← |  | **9**: R=Me, X=Br (74%) |
| **iii** → **4**: X=OTs (88%) → **ii** |  | **10**: R=Me; X=OTs (94%) |

**Scheme 2.** Synthesis of Ionic Liquids from Chlorides **7** and **8** via the Anion Exchange Reaction



HPF$_6$ (60% aq.)/25°C, 12h

**11**: R=Me, Y=PF$_6$ (63%)
**12**: R=Bu$^n$, Y=PF$_6$ (87%)

**7 or 8**

AgY/25°C, 24h
- AgCl
Y=NO$_3$, CF$_3$SO$_3$

**13**: R=Me, Y=NO$_3$ (99%)
**14**: R=Bu$^n$, Y=NO$_3$ (100%)
**15**: R=Bu$^n$, Y=CF$_3$SO$_3$ (62%)

(+)- and (-)-C$_6$H$_4$CH(OH)C(O)ONa
MeOH, 25°C, 24h

**16**: R=Me, Y=(-)-C$_6$H$_4$CH(OH)C(O)O (70%)
**17**: R=Me, Y=(+)-C$_6$H$_4$CH(OH)C(O)O (86%)

the (−)-(1*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-ethyl [(−)-(1*R*)-nopyl] moiety.

The starting materials were 1-alkylimidazoles **5** (R = Me), **6** (R = Bu$^n$), and (−)-(1*R*)-nopol (**1**), which was converted to the corresponding chloride **2** and tosylate **4** in 85 and 88% yields, respectively. The bromide **3** was synthesized from the tosylate **4** in 30% yield (**Scheme 1**).

In particular, (−)-(1*R*)-nopyl chloride **2** was obtained as a very pure product according to the modified literature workup without requiring distillation (*14*). Both the chloride **2** and the bromide **3** turned out to be stable liquids for at least half a year at 5 °C. Only the tosylate **4** was a solid, which enabled the X-ray analysis. All starting materials **2**−**4** were quaternized with 1-alkylimidazoles **5** and **6**, leading to the formation of the corresponding ionic liquids **7**−**10** in 63−94% yields. The bromide **3** was more reactive than the chloride **2**. Thus, at room temperature the ratio of **9** to **5** continuously increased from 1:3 and 1:5 to 9:10 after 24 h, 48 h, and 10 days, respectively, but only at 50 °C/66 h was the imidazole **5** totally consumed. In contrast, no traces of the product **7** were obtained at 25 °C/8 days, 60 °C/54 h, and 70 °C/31 h; only at 90 °C/29 h was the majority of the chloride **2** consumed.

Further ionic liquids **13**−**17** were obtained from **7** or **8** via the anion exchange reactions with silver (NO$_3^-$, CF$_3$SO$_3^-$) and sodium salts [(+)-(*S*)- and (-)-(*R*)-mandelates] as well as with 60% solution of HPF$_6$ (PF$_6^-$) in overall 62−100% yields (**Scheme 2**).

All new compounds **7**−**17**, with the exception of **8**, were yellow or yellow-brownish viscous liquids. The compound **8** was a hygroscopic beige solid with mp 64−67 °C. The remaining ionic liquids contained some small amount of water, which could be removed at elevated temperatures under vacuum or atmospheric pressure. For instance, **7** lost water within 30 min at 100 °C (atmospheric pressure) as determined by $^1$H NMR monitoring.

The latter was thermally stable up to 150 °C (first 100 °C/30 min and then 150 °C/30 min). Decomposition of **7** began at 200 °C after 30 min as deteremined by $^1$H NMR spectra (*15*). Other properties of the obtained ionic liquid are reported in **Tables 1** and **2**. **Table 1** shows viscosities of selected ionic liquids as a function of temperature. In comparison to polyethylene glycol (PEG 400), the values of viscosities were rather high, but they decreased rapidly upon warming by 15−20 °C,

**1886** *J. Agric. Food Chem.,* Vol. 55, No. 5, 2007

Bałczewski et al.

**Table 1.** Viscosities[a] of the Selected Ionic Liquids Measured with a Brookfield DV-II+ Viscometer

| compd | $\eta$ (mPa·s) at | | | | | |
| | 30 °C | 35 °C | 40 °C | 45 °C | 50 °C | 55 °C |
|---|---|---|---|---|---|---|
| 7 | 2700 | 1570 | 1037 | 675 | 470 | 333 |
| 9 | 1600 | 1100 | 770 | 510 | 353 | 255 |
| 10 | 1160 | 755 | 500 | 349 | 250 | 186 |
| 12 | 5441 | 3510 | 2345 | 1588 | 1108 | 800 |
| 16 | 8600 | 4700 | 2650 | 1600 | 1020 | 654 |
| PEG 400 | 74 | 60 | 49 | 40.5 | 34 | 29 |

[a] $\eta$ was measured after storage of samples under vacuum.

**Table 2.** Miscibility[a] with Water and Organic Solvents

| ionic liquid | $H_2O$ | AcOEt | $CHCl_3$ | acetone |
|---|---|---|---|---|
| 7 | + | − | + | + |
| 9 | + | − | + | + |
| 8 | + | − | + | + |
| 10 | − | + | + | + |
| 11 | − | + | ± | + |
| 12 | − | + | ± | + |
| 14 | + | - | + | + |
| 15 | − | ± | + | + |
| 16 | + | ± | + | + |
| 17 | ± | ± | + | + |

[a] +, miscible; −, immiscible; ±, partially miscible.

enabling stirring. Application at low temperatures required dilution with classical solvents or with ionic liquids of lower viscosity.

Analysis of **Table 1** shows that all ionic liquids are miscible with acetone and chloroform with the exception of two hydrophobic ionic liquids **11** and **12** containing the $PF_6^-$ anion, which are partly miscible with chloroform. Three ionic liquids, **7**, **8**, and **14**, containing $Cl^-$ and $NO_3^-$ anions were simultaneously miscible with water and chloroform and immiscible with ethyl acetate, which was utilized in purification and product separation techniques. Unreacted reagents and nonionic byproducts were, for instance, removed with ethyl acetate during the purification of **7** and **8** (Materials and Methods). Simultaneous miscibility with water and chloroform may be also utilized in the application of these ionic liquids in enantioselective phase transfer catalysis reactions.

**Spectroscopic Analysis.** In-depth NMR studies of the starting **2**−**4** and the obtained ionic liquids were carried out for a detailed analysis of the (−)-(1R)-nopyl framework, which was not solved unambigously in the literature, at least for (−)-(1R)-nopyl chloride (**2**) (*14*). At the outset ${}^1$H NMR (200 MHz) spectra of the obtained ionic liquids showed that H-1 and H-5 methine protons of the (−)-(1R)-nopyl moiety in **7** were shielded almost identically and resonated at $\delta_H = 1.96$−2.01. Locations of H-7 axial and H-7 equatorial methylene protons were much more differentiated ($\delta_H = 1.36$). On the other hand, the H-4 pseudoaxial and H-4 pseudoequatorial protons of the second methylene group in the nopyl ring did not show such a great differentiation and resonated at $\delta_H = 2.10$, appearing in the spectrum as a broad singlet. It was also noteworthy that signals of $N^+{=}CH$ protons were shifted downfield ($\delta_H = 10.32, 10.37$) in a series of the chloride ion containing ionic liquids (**7** and **8**) and upfield ($\delta_H = 8.40, 8.47$) in the $PF_6$ series (**11** and **12**). Moreover, in the latter, signals of $N^+{-}CH{=}CH{-}N$ protons were indistinguishable singlets at $\delta_H = 7.26$ and 7.29, respectively.

Because unambiguous assignment of some ${}^{13}$C NMR resonances in the (−)-(1R)-nopyl moiety in **2** was not done in the

**Scheme 3.** ${}^1$H–${}^{13}$C NMR (HMQC) Correlation for **10**
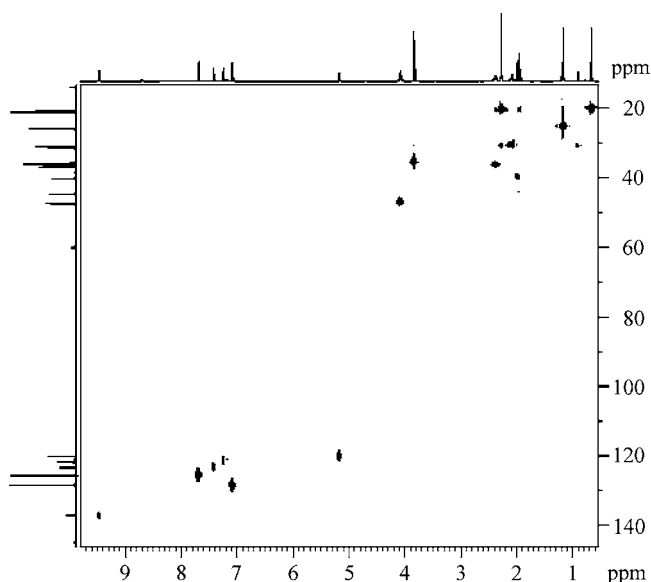


literature (*14*), we decided to carry out a full spectroscopic analysis of this rigid structure. This analysis was done on the basis of correlation spectra and similarity of the signal pattern in the range of 0.5−2.5 ppm of the **2** and **4** spectra as well as the X-ray analysis of the latter. In the COSY (${}^1$H−${}^1$H) spectrum of **4**, the 4.01 ppm triplet corresponding to the $CH_2CH_2O$ group was coupled with the 2.25−2.38 ppm multiplet, of which integration indicated one additional proton (vide infra). A very clear HMQC (${}^1$H−${}^{13}$C) spectrum of **3** showed that this ${}^1$H NMR multiplet was coupled with two peaks in the ${}^{13}$C NMR spectrum at $\delta = 31.5$ and 40.0. The latter peak could be assigned to the $CH_2CH_2O$ carbon.

A DEPT spectrum of **4** showed that the 31.5 ppm peak corresponded to a secondary carbon, which meant that there should be another group of signals belonging to the second proton bound to this carbon. It was well illustrated with the HMQC (${}^1$H−${}^{13}$C) spectrum of **2**. In this spectrum, the corresponding signal at $\delta = 31.6$ was coupled with two groups of ${}^1$H NMR signals: the 2.25−2.40 multiplet mentioned earlier for **4** and a one-proton doublet at $\delta = 1.16$. A very large difference of these chemical shifts might indicate two geminal protons of the ${}^7CH_2$ group of a sterically restrained cyclobutane ring in the nopyl moiety. A lack of visible couplings of the latter with ${}^1$CH and ${}^5$CH methine protons meant that a dihedral angle between a ${}^7$C−H proton and ${}^1$C−H or ${}^5$C−H bonds was close to 90° (proton endo). Due to the rigidity of the bicyclo nopyl moiety, preserved both in liquid and in solid, this finding might be compared with the dihedral angles calculated from the X-ray analysis of **4** (vide infra). The corresponding torsion angles $\theta = 99°$ for H−${}^5$C−${}^7$C−H$_{endo}$ and $\theta = -99°$ for H−${}^1$C−${}^7$C−H$_{endo}$ were in good agreement with those obtained from NMR. Two multiplets in the ${}^1$H NMR spectrum of **4** at $\delta = 1.92$ and 2.04 corresponded to ${}^1$CH and ${}^5$CH methine protons, respectively, on the basis of the finding that the first multiplet did not correlate (${}^1$H−${}^{13}$C/COSY) with the 2.17 ppm AB system of the ${}^4CH_2$ methylene group, whereas the second one correlated very strongly.

Similar relationships were found for the (−)-(1R)-nopyl moiety in ionic liquids on the basis of the similarity of the corresponding signal patterns. The example of ${}^1$H−${}^{13}$C NMR correlation for the ionic liquid **10** is shown in **Scheme 3**. None of the obtained ionic liquids could be X-ray analyzed due to the reasons below.
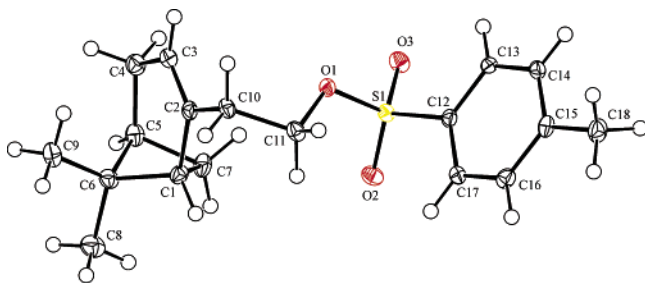
Ionic Liquids

*J. Agric. Food Chem.,* Vol. 55, No. 5, 2007 **1887**



**Figure 1.** Molecular structure of **4**, showing 50% probability ellipsoids.

**Table 3.** Selected Geometric Parameters (Ångstroms, Degrees) in **4**

| S1–O1 | 1.5728 (11) | S1–O3 | 1.4282 (12) |
|---|---|---|---|
| S1–O2 | 1.4253 (12) | S1–C12 | 1.7572 (16) |
| O2–S1–O1 | 109.64 (7) | O2–S1–C12 | 108.87 (7) |
| O2–S1–O3 | 119.49 (7) | O3–S1–C12 | 109.33 (7) |
| O3–S1–O1 | 104.00 (7) | C11–O1–S1 | 118.63 (9) |
| O1–S1–C12 | 104.43 (7) | | |
| C11–O1-S1–O2 | 44.12 (12) | C11–O1–S1–C12 | −72.39 (12) |
| C11–O1–S1–O3 | 173.00 (10) | | |

**X-ray Analysis of (−)-(1*R*)-Nopyl Tosylate (4).** The tosylate **4**, as the only solid among the starting materials, was synthesized for full NMR resolution of the rigid nopyl moiety based on comparison of dihedral angles obtained from NMR and X-ray analyses. It is worth noting that the ionic liquid **8** was the only solid among the obtained ionic liquids; however, it was too hygroscopic to give suitable crystals for X-ray analysis.

The molecular structure of **4** is shown in **Figure 1**, and selected geometric parameters are given in **Table 3**.

The S—C, S—O, and S=O bond lengths were close to standard values. The configuration at the C1 atom was *R*. The six-membered rings C1, C2, C3, C4, C5, and C6 and C1, C2, C3, C4, C5, and C7 had envelope conformations. Atoms C6 and C7 deviated from the plane of C1, C2, C3, C4, and C5 by −1.067(2) and 1.088(2), respectively. The puckering angle for the four-membered ring was 139.7(1)° and was already observed in ref *16*.

**Figure 2** shows a Newman projection along the S—O1 bond, taking C11 as reference. The C12—S1—O1—C11 torsion angle was −72.39(12)°, which corresponded to a synclinal conformation. Such a situation was also observed for aromatic sulfonates (*17*). Packing in the unit cell is shown in **Figure 3**.

**Application of New Chiral Ionic Liquids.** The synthesized ionic liquids **7**, **16**, and **17** were employed in the model Diels—Alder reaction of ethyl acrylate and cyclopentadiene (*18*) used in a ratio of 1:2, respectively (**Scheme 4**). The electron-rich double bond in the (−)-(1*R*)-nopyl moiety is unreactive in this reaction, and we expected a good endo/exo selectivity at low temperature, assuming the donor (dien)—acceptor (dienophile)—donor (ionic liquid) model involving electron-rich and electron-deficient double bonds of cyclopentadiene, acrylate, and chiral ionic liquid in a highly ordered self-organized transition state.
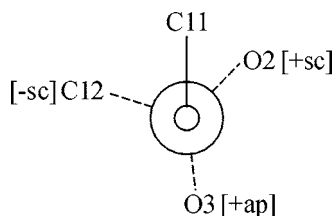


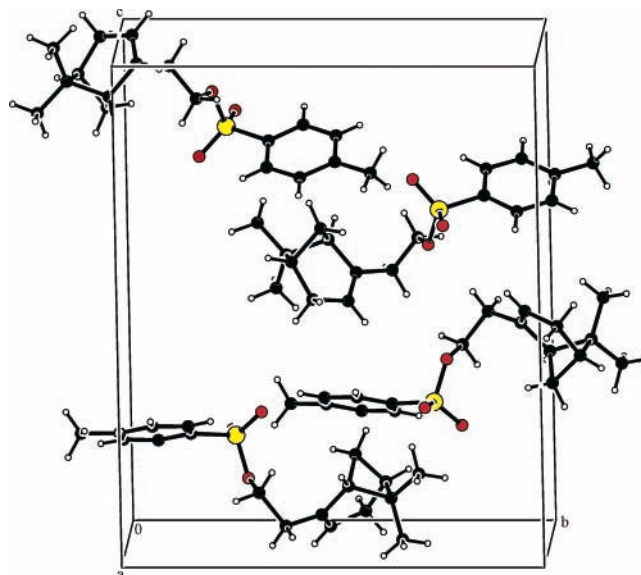**Figure 2.** Newman projection along the S–O1 bond in **4**.



**Figure 3.** Packing of molecules of **4** in the unit cell.

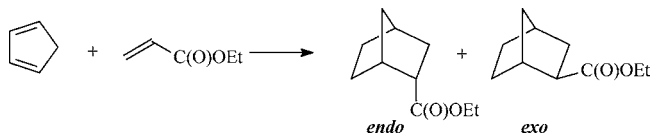**Scheme 4.** Model Diels–Alder Reaction of Cyclopentadiene with Ethyl Acrylate



**Table 4.** Diels–Alder Reaction of Cyclopentadiene with Ethyl Acrylate in the Molar Ratio 2:1

| entry | ionic liquid/ solvent system, ratio | time (h) | temperature (°C) | endo/exo[a] |
|---|---|---|---|---|
| 1 | **7**/CH$_2$Cl$_2$, 1.1:1 | 2.5 | 25 | 3.7 |
| 2 | **7**/CH$_2$Cl$_2$, 1.1:1 | 24 | 25 | 3.7 |
| 3 | MIMBF$_4$ only | 24 | 0 | 4.1 |
| 4 | **7**/MIMBF$_4$,[b] 1:4.1 | 24 | 0 | 5.1 |
| 5[c] | **7**/CH$_2$Cl$_2$, 1.8:1 | 1.5 | 45 | 3.9 |
| 6 | **7**/CH$_2$Cl$_2$, 1.8:1 | 26 | 0 | 4.2 |
| 7 | CH$_2$Cl$_2$ only | 24 | 25 | 3.8 |
| 8 | CH$_2$Cl$_2$ only | 24 | 0 | 4.1 |
| 9 | CH$_2$Cl$_2$ only | 2.5 | 35 | 3.5 |
| 10 | **16**/CH$_2$Cl$_2$, 1:1.3 | 24 | 0 | 4.0 |
| 11 | **16**/THF, 1.2:1 | 25 | 0 | 3.6 |
| 12 | **16**/C$_6$H$_6$, 1.2:1 | 25 | 0 | 3.4 |
| 13 | **17**/CH$_2$Cl$_2$, 1:1.3 | 23 | 0 | 2.9 |
| 14 | **17**/C$_6$H$_6$, 1.1:1 | 23 | 0 | 2.7 |

[a] Ratios obtained after deconvolution of signals due to endo/exo isomers at δ = 3.20/3.03[18]. [b] *N*-Methylimidazolium tetrafluoroborate (MIMBF$_4$). [c] Experiment carried out with evaporation of CH$_2$Cl$_2$ during the reaction.

This model might be supported by a Lewis acid type complexation and hydrogen bonding involving the OH group of the mandelates.

Depending on temperature (0−45 °C) and the solvent system used, the endo/exo ratios oscillated around 3.6/1 and were similar to those obtained in classical organic solvents or water (*18−20*) (**Table 4**). The best ratio of 5.1/1 was obtained in a mixture of the chiral **7** and achiral MIMBF$_4$ ionic liquids at 0 °C (entry 4, **Table 4**). The interesting result was an observation of a measurable difference in endo/exo ratios for reactions carried out in the (*R*)-mandelate **16** versus the (*S*)-mandelate **17** at 0 °C (1.4-fold increase), showing a certain modest contribution of complexation, hydrogen bonding, and the chiral environment of ionic liquid in the transient electron donor−

**1888** *J. Agric. Food Chem.,* Vol. 55, No. 5, 2007

Bałczewski et al.

**Table 5.** Changes in Basic Parameters of the Phytotoxicity Test for Spring Barley Following the Introduction of **7** (in Milligrams per Kilogram of Soil Dry Weight) to the Soil

| sample | no. of seeds planted | no. of plants | % germination relative to control | crop fresh wt (g/pot) | % crop relative to control | mean wt of single plant (g) | % of single plant wt relative to control | dry wt (mg/g of fresh wt) | % dry wt relative to control |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Preliminary Test | | | | | |
| 0, control | 20 | 18 | 100 | 2.017 | 100 | 0.114 | 100 | 0.0819 | 100 |
| 1 | 20 | 18 | 100 | 2.014 | 100 | 0.112 | 98 | 0.0806 | 98 |
| 10 | 20 | 19 | 106 | 2.270 | 113 | 0.120 | 105 | 0.0819 | 100 |
| 100 | 20 | 18 | 100 | 1.606 | 80 | 0.090 | 79 | 0.0934 | 114 |
| 1000 | 20 | 16 | 89 | 0.324 | 16 | 0.020 | 18 | 0.1519 | 185 |
| | | | | Final Test | | | | | |
| 200 | 20 | 18 | 100 | 1.485 | 74 | 0.084 | 74 | 0.1003 | 122 |
| 400 | 20 | 18 | 100 | 0.926 | 46 | 0.053 | 46 | 0.1161 | 142 |
| 800 | 20 | 16 | 89 | 0.461 | 23 | 0.028 | 25 | 0.1403 | 171 |
| | | $LSD_{0.95} = 1$ | | | $LSD_{0.95} = 0.285$ | | $LSD_{0.95} = 0.009$ | | $LSD_{0.95} = 0.0022$ |

**Table 6.** Changes in Basic Parameters of the Phytotoxicity Test for Common Radish Following the Introduction of **7** (in Milligrams per Kilogram of Soil Dry Weight) to the Soil

| sample | no. of seeds planted | no. of plants | % germination relative to control | crop fresh wt (g/pot) | % crop relative to control | mean wt of single plant (g) | % of single plant wt relative to control | dry wt (mg/g of fresh wt) | % dry wt relative to control |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Preliminary Test | | | | | |
| 0, control | 20 | 18 | 100 | 2.571 | 100 | 0.146 | 100 | 0.0617 | 100 |
| 1 | 20 | 18 | 100 | 2.721 | 105 | 0.148 | 102 | 0.0600 | 97 |
| 10 | 20 | 18 | 100 | 2.464 | 96 | 0.140 | 96 | 0.0619 | 100 |
| 100 | 20 | 17 | 94 | 2.036 | 79 | 0.133 | 91 | 0.0698 | 113 |
| 1000 | 20 | 5 | 28 | | | | | | |
| | | | | Final Test | | | | | |
| 200 | 20 | 15 | 83 | 1.066 | 41 | 0.070 | 48 | 0.1005 | 163 |
| 400 | 20 | 12 | 67 | 0.487 | 19 | 0.039 | 27 | 0.1555 | 252 |
| 800 | 20 | 10 | 56 | | | | | | |
| | | $LSD_{0.95} = 2$ | | | $LSD_{0.95} = 0.261$ | | $LSD_{0.95} = 0.013$ | | $LSD_{0.95} = 0.0067$ |

**Table 7.** Changes in Basic Parameters of the Phytotoxicity Test for Spring Barley Following the Introduction of **13** (in Milligrams per Kilogram of Soil Dry Weight) to the Soil

| sample | no. of seeds planted | no. of plants | % germination relative to control | crop fresh wt (g/pot) | % crop relative to control | mean wt of single plant (g) | % of single plant wt relative to control | dry wt (mg/g of fresh wt) | % dry wt relative to control |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Preliminary Test | | | | | |
| 0, control | 20 | 18 | 100 | 1.793 | 100 | 0.102 | 100 | 0.0805 | 100 |
| 1 | 20 | 19 | 106 | 2.023 | 113 | 0.106 | 105 | 0.0805 | 100 |
| 10 | 20 | 18 | 100 | 1.870 | 104 | 0.104 | 103 | 0.0806 | 100 |
| 100 | 20 | 18 | 100 | 1.566 | 87 | 0.085 | 84 | 0.0950 | 118 |
| 1000 | 20 | 19 | 106 | 0.556 | 31 | 0.029 | 28 | 0.1234 | 185 |
| | | | | Final Test | | | | | |
| 200 | 20 | 20 | 111 | 1.361 | 76 | 0.069 | 68 | 0.1019 | 127 |
| 400 | 20 | 19 | 106 | 0.980 | 55 | 0.052 | 52 | 0.1102 | 137 |
| 800 | 20 | 19 | 106 | 0.638 | 36 | 0.033 | 33 | 0.1214 | 151 |
| | | $LSD_{0.95} = 1$ | | | $LSD_{0.95} = 0.115$ | | $LSD_{0.95} = 0.006$ | | $LSD_{0.95} = 0.0013$ |

acceptor−donor model. The Diels−Alder reaction performed in the system of **7**/CH$_2$Cl$_2$ (1.8/1) did not occur at −28 °C within 2.5 days.

**Effect of Selected Ionic Liquids 7 (Chloride) and 13 (Nitrate) on Germination and Growth of Superior Plants. Phytotoxicity Test.** The influence of selected ionic liquids **7** (chloride) and **13** (nitrate) introduced to the soil on germination and early stages of growth and development of superior plants was investigated using the phytotoxicity test based on the ISO-11269-2:1995 International Standard (*21*). In this test, the seeds of selected species of land superior plants [spring barley (*Hordeum vulgare*) and common radish (*Raphanus sativus* L. subvar. *radicula* Pers.] were planted in pots containing soil to which a test chemical compound had been added and in pots

with control soil. Optimum conditions for growth and development of the selected plant species were maintained for the duration of the experiment.

The ionic liquids were introduced to the soil in the form of water solution in the following concentrations: 0, 1, 10, 100, and 1000 mg/kg of the soil dry weight in a preliminary test and also in concentrations of 200, 400, and 800 mg/kg of the soil dry weight in the final test.

The obtained results concerning the effect of ionic liquids **7** and **13** on the germination and growth of spring barley and common radish at early stages are shown in **Tables 5−8** and in **Figures 4** and **5** (see also the Supporting Information).

Preliminary tests showed that ionic liquids used in concentrations of 1 and 10 mg/kg of the soil dry weight did not have any

Ionic Liquids

*J. Agric. Food Chem.,* Vol. 55, No. 5, 2007 **1889**

**Table 8.** Changes in Basic Parameters of the Phytotoxicity Test for Common Radish Following the Introduction of **13** (in Milligrams per Kilogram of Soil Dry Weight) to the Soil

| sample | no. of seeds planted | no. of plants | % germination relative to control | crop fresh wt (g/pot) | % crop relative to control | mean wt of single plant (g) | % of single plant wt relative to control | dry wt (mg/g of fresh wt) | % dry wt relative to control |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Preliminary Test | | | | | |
| 0, control | 20 | 18 | 100 | 3.091 | 100 | 0.170 | 100 | 0.0698 | 100 |
| 1 | 20 | 18 | 100 | 3.346 | 108 | 0.182 | 107 | 0.0651 | 93 |
| 10 | 20 | 18 | 100 | 2.825 | 91 | 0.155 | 91 | 0.0686 | 98 |
| 100 | 20 | 19 | 106 | 1.877 | 61 | 0.101 | 59 | 0.0930 | 133 |
| 1000 | 20 | 15 | 83 | | | | | | |
| | | | | Final Test | | | | | |
| 200 | 20 | 19 | 106 | 1.340 | 43 | 0.072 | 42 | 0.1044 | 150 |
| 400 | 20 | 17 | 94 | 1.098 | 19 | 0.066 | 37 | 0.1498 | 215 |
| 800 | 20 | 15 | 83 | | | | | | |
| | | $LSD_{0.95} = 2$ | | | $LSD_{0.95} = 0.469$ | | $LSD_{0.95} = 0.016$ | | $LSD_{0.95} = 0.0055$ |

significant effect on the germination and growth of either plant tested, which was indicated by the percentage of germination, the magnitude of fresh and dry weight of sprouts, and the crop fresh weight calculated per plant (**Tables 5−8**). This observation was in accordance with the standard for tested substances that were considered to be nontoxic, if the rate of germinated seeds and the overall fresh weight of the plants differed by not more than ±10% compared to the control sample. Also, in the case of the visual assessment, no visible differences in the appearance of the plants were observed for the above concentrations compared to the control objects; that is, no growth inhibition or chlorotic and necrotic changes were found (**Figures 4** and **5**). The early signs of a potential toxicity of the ionic liquid **7** (chloride) could be observed after application of 100 mg of the tested substance per kilogram of soil, which was reflected chiefly by a drop in the fresh weight of sprouts of approximately 20%

for spring barley and 22% for common radish. The ionic liquid **13** (nitrate), applied in the identical concentration, also brought about reductions in the crop of the experimental plants by approximately 13 and 39% for barley and radish, respectively, compared with the control. Similar correlations could be found when the effect of the tested substances, applied in a concentration of 100 mg/kg of soil, on the crop fresh weight per plant was analyzed. At the same time, neither changes in the appearance of the plants nor differences in their germinations were found at this concentration of the ionic liquids. The highest of the applied concentrations—1000 mg/kg of the soil dry weight—turned out to be highly toxic for both experimental plants, which was evidenced by substantial changes in all phytotoxicity test parameters discussed and by the presented digital photos of barley and radish plants (**Tables 5−8**; **Figures 4** and **5**; Supporting Information).
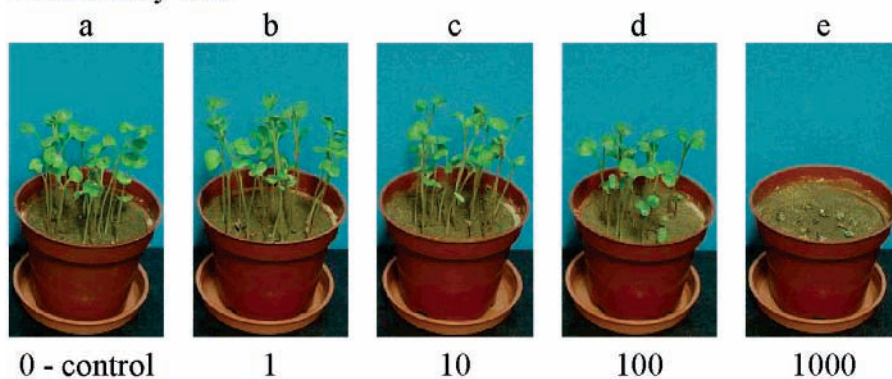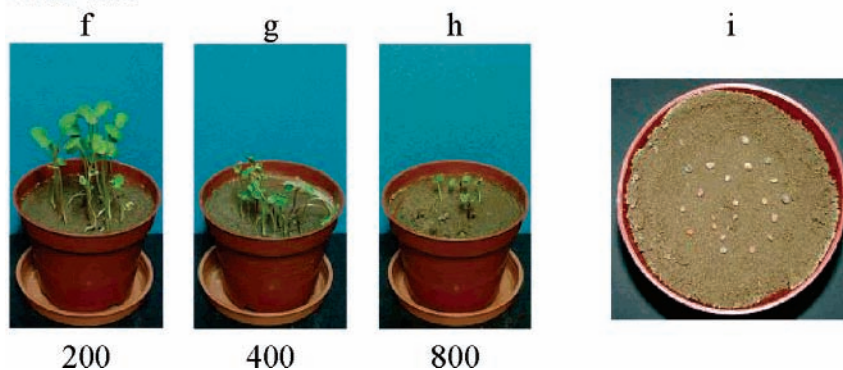


**Figure 4.** Digital photographs of common radish on the 14th day (**a–h**) after introducing to the soil specific amounts of **7** (in mg/kg of soil dry weight); (**i**) planted radish seeds, the 1st day.
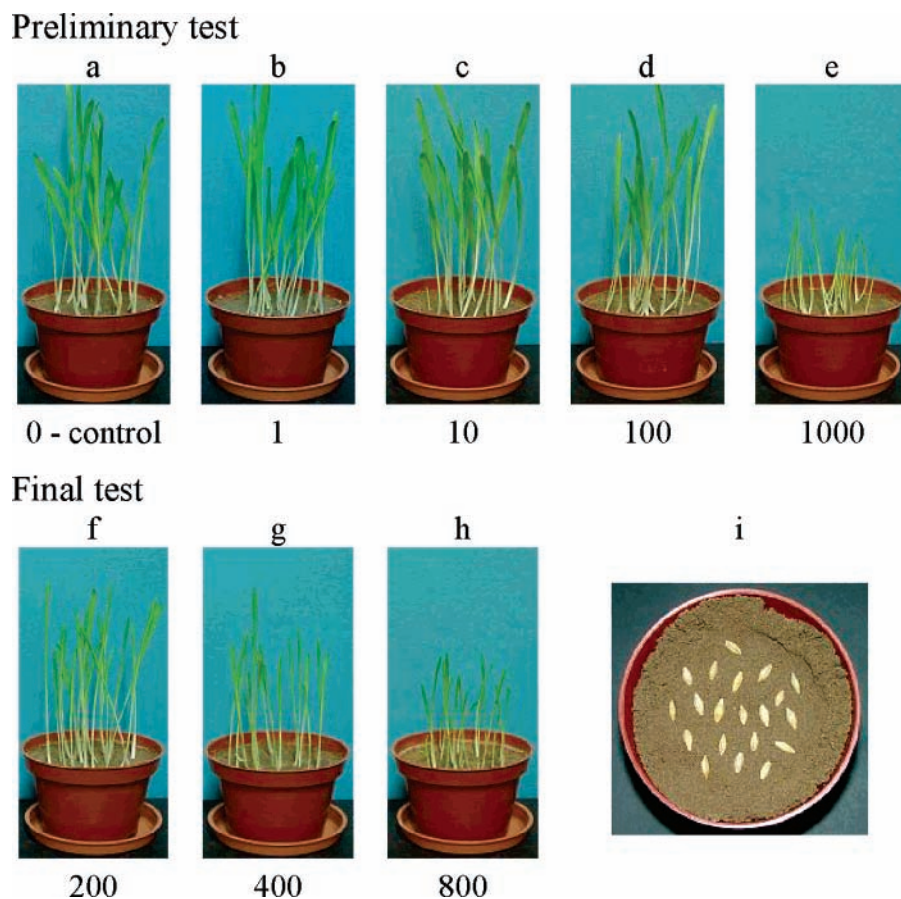
**Figure 5.** Digital photographs of spring barley on the 14th day (**a**–**h**) after introducing to the soil specific amounts of **13** (in mg/kg of soil dry weight); (**i**) planted barley seeds, the 1st day.

The results obtained from the preliminary tests were confirmed by independently performed final tests. Increasing the concentration of ionic liquids **7** and **13** to 200, 400, and 800 mg per kilogram of the soil dry weight resulted in a systematic decrease in the crop fresh weight of total sprouts and the crop fresh weight per plant as well as a large increase in dry weight, both for spring barley and for common radish. The observed changes were greater when a higher concentration of the chemical compounds was applied (**Tables 5**−**8**). Moreover, in the case of the dicotyledonous plant, a constant drop in plant germinations was also found, which was much greater upon application of **7** (chloride). The ionic liquid **13** (nitrate) gave a slight decrease in germination of radish, whereas no differences in plant germination between the control and tested objects were observed for spring barley. Starting from the concentration equal to 200 mg of tested substance per kilogram of soil, a progressive inhibition of growth and permanent damage to the plants could be seen, which was particularly noticeable on radish plants (**Figures 4** and **5**).

On the basis of the obtained results one can state that both ionic liquids **7** and **13** are chemical compounds showing potential toxicity, with the toxic effect being dependent chiefly on the applied concentration. The highest concentration of the compounds tested, which did not cause a distinct reduction in the plant germination and growth (NOEC), was estimated at a level of 10 mg/kg of the soil dry weight, whereas the lowest concentration causing a reduction in plant growth/germination (LOEC) was 100 mg of the respective substance per kilogram of the soil dry weight. From an analysis of the variation in all phytotoxicity parameters, it can also be noted that common

barley is a more resistant plant which fairly well tolerates test ionic liquid concentrations of up to 200 mg/kg of soil, whereas, for radish, the growth and development inhibiting concentration is 100 mg/kg of the soil dry weight. The ionic liquid, applied in the form of nitrate salt, did not exhibit an inhibiting effect on the germination ability of seeds.

**Phytotoxicity Test for *N*-Methylimidazole 5.** It was interesting to compare the phytotoxicity of *N*-methylimidazole **5** used as a common substrate in syntheses of ionic liquids with the phytotoxicity of ionic liquids **7** and **13** as well as to evaluate the phytotoxicities of this compound itself and ionic liquids contaminated by the unreacted substrate.

In pot experiments carried out according to the phytotoxicity test based on the ISO-11269-2:1995 International Standard (*21*), it was found that *N*-methylimidazole **5** applied in high concentration (1000 mg/kg of soil dry weight) considerably inhibited the growth and germination of higher plants. Lower concentrations (1 and 10 mg/kg of soil dry weight) did not cause any changes in basic phytotoxicity test parameters and did not influence the appearance of tested plants (**Figures 6** and **7**; **Tables 9** and **10**).

In conclusion, the phytotoxicity of *N*-methylimidazole **5** is comparable with the phytotoxicity of tested ionic liquids **7** and **13**.

In the context of a limited literature concerning the synthesis and application of chiral ionic liquids, we synthesized new ionic liquids with chiral anion and/or chiral cation incorporating the (−)-(1*R*)-nopyl moiety from the chiral pool. A combination of the solution NMR studies with X-ray analysis allowed a full NMR resolution of this rigid bicyclic structure. A nonreacting
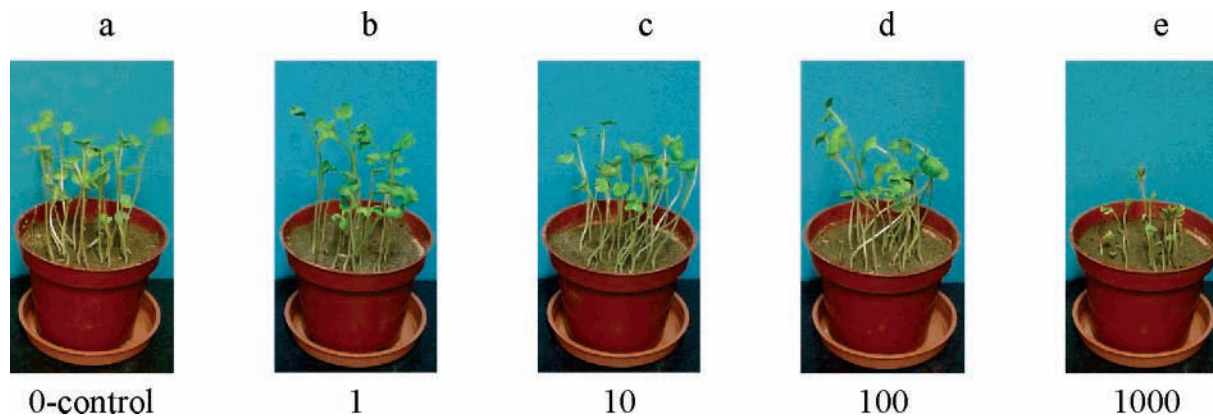
**Figure 6.** Digital photographs of common radish seedlings on the 14th day (**a**–**e**) after introducing to the soil specific amounts of *N*-methylimidazole (in mg/kg of soil dry weight).
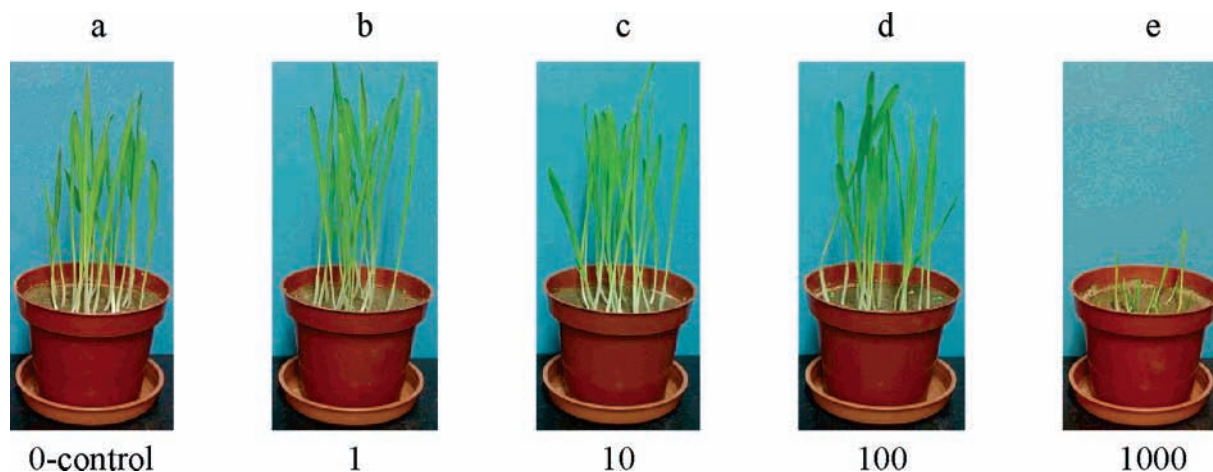


**Figure 7.** Digital photographs of spring barley seedlings on the 14th day (**a**–**e**) after introducing to the soil specific amounts of *N*-methylimidazole (in mg/kg of soil dry weight).

**Table 9.** Changes in Basic Parameters of the Phytotoxicity Preliminary Test for Spring Barley Following the Introduction of *N*-Methylimidazole (in Milligrams per Kilogram of Soil Dry Weight) to the Soil

| sample | no. of seeds planted | no. of plants | % germination relative to control | crop fresh wt (g/pot) | % crop relative to control | mean wt of single plant (g) | % of single plant wt relative to control | dry wt (mg/g of fresh wt) | % dry wt relative to control |
|---|---|---|---|---|---|---|---|---|---|
| 0, control | 20 | 19 | 100 | 1.956 | 100 | 0.103 | 100 | 0.0804 | 100 |
| 1 | 20 | 18 | 95 | 1.789 | 91 | 0.099 | 97 | 0.0763 | 94 |
| 10 | 20 | 20 | 105 | 1.993 | 102 | 0.100 | 97 | 0.0791 | 98 |
| 100 | 20 | 19 | 100 | 1.886 | 96 | 0.102 | 99 | 0.0803 | 100 |
| 1000 | 20 | 18 | 95 | 0.160 | 8 | 0.009 | 9 | 0.1287 | 160 |
| | | $LSD_{0.95} = 1$ | | $LSD_{0.95} = 0.078$ | | $LSD_{0.95} = 0.004$ | | $LSD_{0.95} = 0.0073$ | |

**Table 10.** Changes in Basic Parameters of the Phytotoxicity Preliminary Test for Common Radish Following the Introduction of *N*-Methylimidazole (in Milligrams per Kilogram of Soil Dry Weight) to the Soil

| sample | no. of seeds planted | no. of plants | % germination relative to control | crop fresh wt (g/pot) | % crop relative to control | mean wt of single plant (g) | % of single plant wt relative to control | dry wt (mg/g of fresh wt) | % dry wt relative to control |
|---|---|---|---|---|---|---|---|---|---|
| 0, control | 20 | 18 | 100 | 2.369 | 100 | 0.136 | 100 | 0.0816 | 100 |
| 1 | 20 | 18 | 100 | 2.584 | 109 | 0.140 | 103 | 0.0818 | 100 |
| 10 | 20 | 19 | 105 | 2.260 | 95 | 0.119 | 87 | 0.0825 | 101 |
| 100 | 20 | 18 | 100 | 1.996 | 84 | 0.111 | 82 | 0.0862 | 106 |
| 1000 | 20 | 11 | 61 | 0.537 | 23 | 0.049 | 35 | 0.2286 | 280 |
| | | $LSD_{0.95} = 2$ | | $LSD_{0.95} = 0.171$ | $LSD_{0.95} = 0.007$ | | | $LSD_{0.95} = 0.0046$ | |

double bond of the nopyl moiety in a sense of the Diels−Alder reaction was introduced to structures of ionic liquids in order to check the sandwich electron acceptor−donor model of this reaction including electron-rich and electron-deficient double bonds and chiral environment of the ionic liquid. To our knowledge, this is the first such reaction performed in both diastereomeric ionic liquids including *R*- and *S*-mandelate anions.

**1892** *J. Agric. Food Chem.,* Vol. 55, No. 5, 2007

Bałczewski et al.

In light of the introduction for the first time to industrial processes of bulky amounts of ionic liquids, we noted a necessity to check the phyto(eco)toxicity of not only the obtained chiral ionic liquids but also *N*-methylimidazole, which was a common starting material in the syntheses of all imidazole-based ionic liquids. We revealed their substantial toxicity to plants and soil depending on the applied concentrations and type of plant (monocotyledonous, >200 mg; and dicotyledonous, >100 mg/ kg of the soil dry weight), which should be seriously taken into account by industry and environmenta; protection agencies in case of possible environment pollution. Our results call attention to the necessity for further investigations on the influence of the ionic liquids, the starting materials used in their syntheses, and the biodegradation products on various elements of eco-systems.

**Supporting Information Available:** Digital photographs showing results of the phytotoxicity tests involving spring barley and ionic liquid **7** as well as common radish and ionic liquid **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

### LITERATURE CITED

(1) Welton, T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071−2083.

(2) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. Ionic liquid (molten salt) phase organometallic catalysis. *Chem. Rev.* **2002**, *102*, 3667−3692.

(3) Wasserscheid, P.; Keim, W. Ionic liquids−new solutions for transition metal catalysis. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772−3789.

(4) Jastorff, B.; Mölter, K.; Behrend, P.; Bottin-Weber, V.; Filser, J.; Heimers, A.; Ondruschka, B.; Ranke, J.; Schaefer, M.; Schröder, H.; Stark, A.; Stepnowski, P.; Stock, F.; Störmann, R.; Stolte, S.; Welz-Biermann, V.; Ziegert, S.; Thöming, J. Progress in evaluation of risk potential of ionic liquids-basis for an eco-design of sustainable products. *Green Chem.* **2005**, *7*, 362−372.

(5) Sheldon, R. A. Green solvents for sustainable organic synthesis: state of the art. *Green Chem.* **2005**, *7*, 267−278.

(6) Gathergood, N.; Scammells, P.; Garcia, T. Biodegradable ionic liquids. Part III. The first readily biodegradable ionic liquids. *Green Chem.* **2006**, *8*, 156−160.

(7) Jain, N.; Kumar, N. A.; Chauhan, S.; Chauhan, S. M. S. Chemical and biochemical transformations in ionic liquids. *Tetrahedron* **2005**, *61*, 1015−1060.

(8) Ding, J.; Armstrong, D. W. Chiral ionic liquids: synthesis and applications. *Chirality* **2005**, *17*, 281−292.

(9) Wasserscheid, P.; Bösmann, A.; Bolm, C. Synthesis and properties of ionic liquids derived from the chiral pool. *Chem. Commun.* **2002**, 200−201.

(10) Baudequin, C.; Brégeon, D.; Levillain, J.; Guillen, F.; Plaquevent, J.-C.; Gaumont, A.-C. Chiral ionic liquids, a renewal for the chemistry of chiral solvents? Design, synthesis and applications for chiral recognition and asymmetric synthesis. *Tetrahedron: Asymmetry* **2005**, *16*, 3921−3945.

(11) Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A.-C.; Plaquevent, J.-C. Ionic liquids and chirality: opportunities and challenges. *Tetrahedron: Asymmetry* **2003**, *14*, 3081−3093 and refs cited therein.

(12) Génisson, Y.; Lauth-de, V. N.; Andre, C.; Baltas, M.; Gorrichon, L. New chiral imidazolinic derivatives. *Tetrahedron: Asymmetry* **2005**, *16*, 1017−1023.

(13) Clavier, H.; Coutable, L.; Guillemin, J.-C.; Mauduit, M. New bidentate alkoxy-NHC ligands for enantioselective copper-catalysed conjugate addition. *Tetrahedron: Asymmetry* **2005**, *16*, 921−924.

(14) Abraham, R. J.; Jones-Parry, R.; Giddings, R. M.; Guy, J.; Whittaker, D. 3-Acetoxy-6,6-dimethylbicyclo[3.1.1]heptane-2-spiro-1-cyclopropane from nopylamine deamination. *J. Chem. Soc., Perkin Trans. 1* **1998**, 643−646.

(15) Baranyai, K. J.; Deacon, G. B.; MacFarlane, D. R.; Pringle, J. M.; Scott, J. L. Thermal degradation of ionic liquids at elevated temperatures. *Aust. J. Chem.* **2004**, *57*, 145−147.

(16) Begley, M. J.; Gill, G. B.; Wallace, B. X-Ray structure analysis of the tosylate ester of (1*S*,5*S*)-6,6-dimethyl-2-[(2*S*)-3,3,3-trichloro-2-hydroxypropyl]bicyclo[3.1.1]hept-2-ene, the major product of the iron(III) chloride-catalysed ene addition of chloral to (−)-(1*S*,5*S*)-pin-2(10)-ene. *J. Chem. Soc., Perkin Trans. 1* **1978**, 93−97.

(17) Manivannan, V.; Vembu, N.; Nallu, M.; Sivakumar, K.; Linden, A. Phenyl 4-toluenesulfonate: supramolecular aggregation through weak C-H...O and C-H..$_\pi$ interactions *Acta Crystallogr.* **2005**, *E61*, o690−o692.

(18) Clapham, G.; Shipman, M. Selective Lewis acid complexation of 2-hydroxyethyl esters using competitive Diels−Alder reactions as a mechanistic probe. *Tetrahedron* **2000**, *56*, 1127−1134.

(19) Diego-Castro, M. J.; Hailes, H. C. Studies on the use of surfactants in aqueous Diels−Alder reactions. *Tetrahedron Lett.* **1998**, *39*, 2211−2214.

(20) Kumar, A.; Pawar, S. S. Rate acceleration and subsequent retardation of Diels−Alder reactions in $LiClO_4$−diethyl ether: an experimental investigation. *J. Org. Chem.* **2001**, *66*, 7646−7652.

(21) ISO 11269-2: Soil quality−determination of the effect of pollutants on soil flora−Part 2: effect of chemicals on the emergence and growth of higher plants; International Organisation for Standarization: Geneva, Switzerland, 1995.

(22) Flack, H. D. On enantiomorph-polarity estimation. *Acta Crystallogr. A* **1983**, *39*, 876−881.

(23) Oxford Diffraction. *Data Collection Program, CrysAlisCCD*, version 1.171; Oxford Diffraction Poland: Wrocław, Poland, 2003.

(24) Oxford Diffraction. *Data Reduction Program, CrysAlisRED*, version 1.171; Oxford Diffraction Poland: Wrocław, Poland, 2003.

(25) Sheldrick, G. M. *SHELXS97*; University of Göttingen, Germany, 1997.

(26) Sheldrick, G. M. *SHELXL97*; University of Göttingen, Germany, 1997.