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A Simple and Practical Method for the Preparation and Purity Determination of Halide-Free Imidazolium Ionic Liquids

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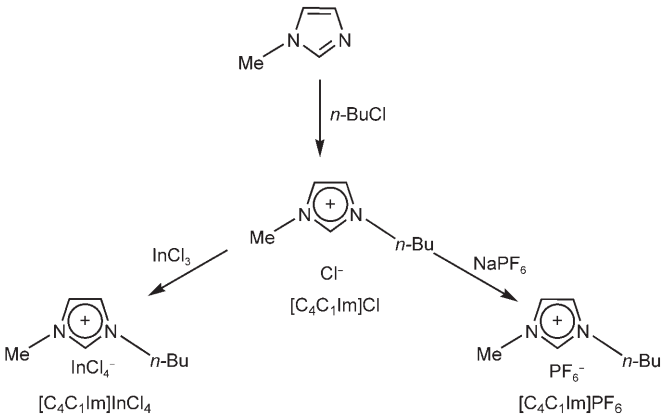
Abstract: The reaction of *N*-alkylimidazole with alkyl sulfonates at room temperature affords 1,3-dialkylimidazolium alkanesulfonates as crystalline solids in high yields. The alkanesulfonate anions can be easily substituted by a series of other anions [BF_4, PF_6, $PF_3(CF_2CF_3)_3$, CF_3SO_3 and $N(CF_3SO_2)_2$] by simple reaction of anions, salts, or acids in water at room temperature. Extraction with dichloromethane, filtration through a short basic alumina column and solvent evaporation affords the desired ionic liquids in 80–95% yield. The purity (>99.4%) of these ionic liquids can be determined by ^{1}H NMR spectra using the intensity of the ^{13}C satellites of the imidazolium *N*-methyl group as internal standard.

Keywords: imidazolium salts; ionic liquids; molten salt; NMR; synthetic methods



Scheme 1.

Introduction

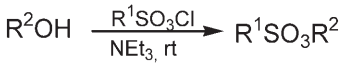
Without doubt, derivatives of the 1,3-dialkylimidazolium cation associated with various anions are amongst the most investigated class of ionic liquids (ILs).[1–7] This is most probably due to their ease of synthesis, stability and the possibility of fine-tuning their physical-chemical properties by the simple choice of the *N*-alkyl substituents and/or anions.[7] The vast majority of these ILs are usually prepared by simple *N*-alkylation of *N*-alkylimidazole, often employing alkyl halides as alkylating agents, followed by association with metal-halides[8–10] or anion metathesis[11–13] (Scheme 1).

The anion metathesis procedures generate a large variety of 1,3-dialkylimidazolium-based ILs of good quality. The determination of the purity of these ionic liquids is not a simple task. The main contaminant is usually residual chloride that can be detected by an $AgNO_3$ test (limit of 1.4 mg/L), ion chromatography (below 8 ppm)[14] or by cyclic voltametry (ppb).[15,16] The water content can be determined by Karl-Fischer titration or by cyclic voltametry.[17] The presence and quantification of these impurities is essential in many applications such as in catalysis[18–21] and spectroscopic investigations[22] since the physical-chemical properties of the ILs can vary significantly depending on their water and halide contents.[23] Alternatively, halide-free 1,3-dialkylimidazolium ILs can be prepared from the five-component reaction (glyoxal, formaldehyde, two different amines and acids)[24] and those containing alkyl sulfate or trifluoromethanesulfonate anions by simple alkylation of 1-alkylimidazole with the corresponding dialkyl sulfate[25] or alkyl trifluoromethanesulfonate ester,[26] respectively. Similar procedures, which use alkyl sulfonates and alkyl phosphates as alkylating agents, have been patented.[27,28] It is, however, quite surprising that no expeditious method is available for the preparation and purity determination of the halide-free 1,3-dialkylimidazolium cation associated with the most popular and used anions such as PF_6, BF_4 and $N(CF_3SO_2)_2$. In fact, ionic liquids

such as $[C_4C_1Im]PF_6$, $[C_4C_1Im]BF_4$ and $[C_4C_1Im]N(CF_3SO_2)_2$ are commercially available but with relatively high levels of chloride contaminants. It is evident that there is a need for more simple and practical methods for the preparation of such halide-free ionic liquids and also a more accessible, rapid and straightforward methodology for the determination of their purity. We disclose herein a simple method for the preparation of various halide-free 1,3-dialkylimidazolium and 1,2,3-trialkylimidazolium ionic liquids associated with PF_6, BF_4, $PF_3(CF_2CF_3)_3$, CF_3SO_3 and $N(CF_3SO_2)_2$ anions and their purity (>99.4%) can be determined by ^1H NMR using the ^{13}C satellites of the *N*-methyl group as internal standard.

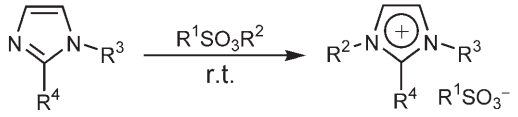
Results and Discussion

As alkylating agents we have chosen alkyl sulfonate esters due to their ease, simple accessibility and possibility to use different R^1 and R^2 groups and thus generate a large variety of 1,3-dialkylimidazolium alkanesulfonate salts (Scheme 2). The simple treatment of alcohols with alkanesulfonyl chlorides in the presence of a base such as triethylamine affords the pure (>99.4%) alkylsulfonate esters in high yields (>90%) after a simple distillation.



Scheme 2.

The alkylation of *N*-alkylimidazoles such as *N*-methylimidazole with the alkyl sulfonate can be performed in solventless conditions at room temperature affording after 48–72 h the corresponding 1,3-dialkylimidazolium alkanesulfonate salts as crystalline solids in almost quantitative yield (Scheme 3).



Scheme 3.

These salts can be further purified by simple re-crystallization in acetone leading to crystalline samples (purity > 99.4% by NMR, see below) in most of the cases and in high yields (Table 1).

This procedure can be applied from small-scale (10 g) to 500-g scale for the preparation of the dialkylimidazolium salts. These salts have been characterized by DSC, ^1H, ^{13}C NMR and C,H,N analysis. This alkylation method has several advantages such as: it is performed at room temperature without the use of solvents; the products are crystalline solids and can be purified by simple recrystallization in acetone. In opposition to the classical procedure that employs alkyl halides and must be performed at reflux temperature using generally acetonitrile solutions, 1,3-dialkylimidazolium chlorides are sometimes difficult to crystallize and the recrystallization necessitates the use of large amounts of acetonitrile and ethyl acetate.[29] Note that primary, secondary and functionalized alkanesulfonates can be employed.

Table 1. Yield and mp of the imidazolium alkanesulfonate salts.

Entry	R^1	R^2	R^3	R^4	Yield [%]	mp [°C]
1	Me	Me	*n*-Bu	H	96	77.1
2	2-Bu	Me	*n*-Bu	H	80	76.1
3	n-Bu	Me	*n*-Bu	H	83	63.0
4	Me	Me	Me	H	85	93.2
5	Me	Me	*n*-Bu	Me	94	109.0
6	Et	Me	*n*-Bu	H	78	57.0
7	*n*-Bu	Me	Me	H	75	52.0
8	Me	*n*-Bu	*n*-Bu	H	82	−56.0
9	Et	*n*-Bu	*n*-Bu	H	76	−68.0
10	Et	$(CH_2)_2OMe$	Me	H	91	−86.1[a]

[a] Transition glass temperature.

The alkanesulfonate anions can be easily substituted by a series of other anions [BF_4, PF_6, $PF_3(CF_2CF_3)_3$, CF_3SO_3 and $N(CF_3SO_2)_2$] by simple reaction of anion salts or acids (Scheme 4) in water at room temperature. Extraction with dichloromethane, filtration through a short basic alumina column and solvent evaporation affords the desired ionic liquids in 80–95% yield. These yields are similar to those obtained from the methathesis using 1,3-dialkylimidazolium halides.[13,13,30]

Scheme 4.

The purity of these ionic liquids can be assessed by ^1H NMR spectra using the intensity of ^{13}C satellites of the imidazolium *N*-methyl group. Note that the natural abundance of ^{13}C is 1.11% therefore the intensity of each satellite peak corresponds to 0.555% in the case of the *N*-methyl singlet. For example, the purity of the $[C_4C_1Im]PF_6$ is > 99.4% since no signals relative to other hydrogen-containing compounds are present except the residual water peak at 2.97 ppm in the ^1H NMR spectra (Figure 1) of the ionic liquid $[C_4C_1Im]PF_6$ isolated from the reaction of $[C_4C_1Im]CH_3SO_3$ with KPF_6 in water. The purity of this liquid was also checked by cyclic vol-

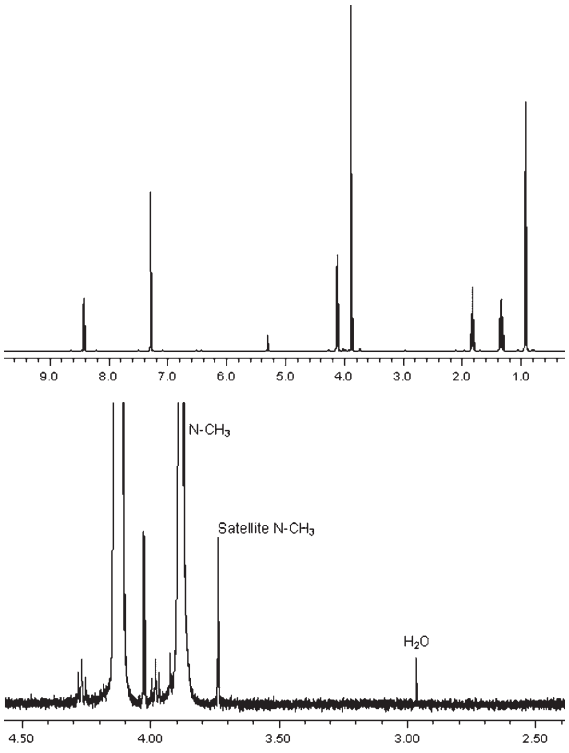


Figure 1. ^{1}H NMR spectra (500 MHz, 25 °C) of $[C_4C_1Im]PF_6$ in CD_2Cl_2 (*top*) and expansion between 2.3 and 4.5 ppm (*bottom*) showing the signal of the *N*-methyl ^{13}C satellites and residual water. (Relative intensities: one ^{13}C satellite = 5.73 and water = 1.54).

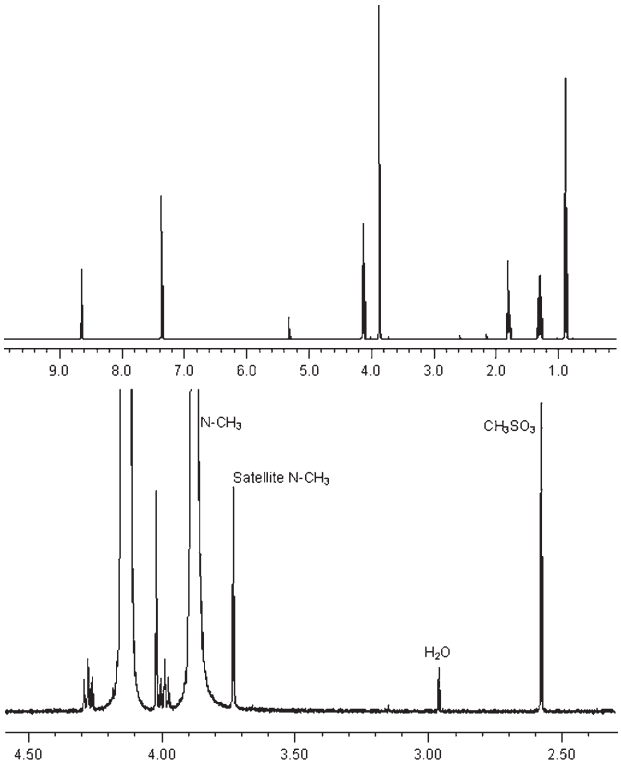


Figure 2. ^{1}H NMR spectra (500 MHz, 25 °C) of $[C_4C_1Im]BF_4$ in CD_2Cl_2 (*top*) and expansion between 2.4 and 4.6 ppm (*bottom*) showing the signals of the *N*-methyl ^{13}C satellites, residual water and of the CH_3SO_3 anion pertinent to the starting material $[C_4C_1Im]CH_3SO_3$. (Relative intensities: one ^{13}C satellite = 9.25, CH_3SO_3 =23.44 and water = 1.53).

tametry and only water was detected. In opposition, in the ^{1}H NMR spectra of $[C_4C_1Im]BF_4$ (Figure 2) the peak of the CH_3SO_3 anion (2.58 ppm) due to the starting $[C_4C_1Im]CH_3SO_3$ salt, clearly appears at 2.58 ppm with an intensity greater than one of the ^{13}C *N*-methyl satellites. The purity of this ionic liquid can be estimated as > 98.5%.

This purity determination method is much more simple and straightforward than the others employed to date ($AgNO_3$ test, ion chromatography[14] and cyclic voltametry[15,16]) and can be used in any laboratory in possession of an NMR apparatus.

Conclusion

In summary, we have described a simple straightforward procedure for the preparation of halide-free imidazolium based ionic liquids. Moreover, the purity of these ionic liquids is easily verified through simple ^{1}H NMR experiments.

Experimental Section

General Remarks

Solvents were dried with suitable drying agents and distilled under argon prior to use. The alkanesulfonates were prepared using a slightly modified procedure (see below).[31] All other chemicals were purchased from commercial sources (Acros or Aldrich) and used without further purification. Elemental analyses were performed by the Analytical Central Service of IQ-USP (Brazil). NMR spectra were recorded on a Varian Inova 300 or a Bruker ARX500 spectrometers. Infrared spectra were performed on a Bomem B-102 spectrometer. The calorimetric experiments were carried out on a 12000 PL-DSC equipment with a heating rate of 10 °C/min. The spectroscopic data of the new imidazolium salts are described in the Supporting Information.

Butyl Methanesulfonate

Methanesulfonyl chloride (183.2 g, 1.60 mol) was added (over 45 min), with vigorous stirring, to a solution of *n*-butanol (118.4 g, 1.60 mol) and triethylamine (161.6 g, 1.60 mol) in dichloromethane (1.5 L). An external water-ice bath was used to control the reaction mixture temperature between 10–

20 °C. After addition, stirring was continued for further 2 h. at room temperature. Water (300 mL) was added, the aqueous layer containing the triethylammonium chloride by-product was separated; the organic layer was washed with water (200 mL) and dried with sodium carbonate. Solvent evaporation followed by reduced pressure distillation of the residue afforded the desired butyl methanesulfonate, as a colorless liquid; yield: 227.0 g (93%); bp 81–83 °C/4 mmHg.

1-Butyl-3-methylimidazolium Methanesulfonate

Butyl methanesulfonate (241.9 g, 1.59 mol) was mixed with 1-methylimidazole (130.5 g, 1.59 mol) and the reaction mixture was kept at room temperature by means of an external water bath. After 24 h, one crystal of 1-butyl-3-methyl imidazolium methanesulfonate was added and the resulting crystalline reaction mass was kept at room temperature for a further 72 h. Recrystallization was performed twice using acetone as solvent (350 mL; from reflux temperature to freezer temperature overnight). After vacuum drying, colorless and very hygroscopic crystals of 1-butyl-3-methylimidazolium methanesulfonate were obtained; yield: 357.1 g (96%); mp 77.1 °C.

1-Butyl-3-methylimidazolium 2-Butanesulfonate

Butyl 2-butanesulfonate (29.10 g, 150 mmol) was mixed with 1-methylimidazole (12.30 g, 150 mmol) and the reaction mixture was kept at room temperature for 72 h. The resulting crystalline mass was washed twice with ethyl acetate (20 mL) and, after vacuum drying, colorless and very hygroscopic crystals of 1-butyl-3-methylimidazolium 2-butanesulfonate were obtained; yield: 33.10 g (80%); mp 76.1 °C.

1-Butyl-3-methylimidazolium *n*-Butanesulfonate

Butyl *n*-butanesulfonate (6.51 g, 33.5 mmol) was mixed with 1-methylimidazole (2.75 g, 33.5 mmol) and the reaction mixture was kept at room temperature for 72 h. The resulting crystalline mass was washed twice with ethyl acetate (10 mL) and, after vacuum drying, colorless and very hygroscopic crystals of 1-butyl-3-methylimidazolium *n*-butanesulfonate were obtained; yield: 7.68 g (83%); mp 63.0 °C.

1,3-Dimethylimidazolium Methanesulfonate

A mixture of 1-methylimidazole (4.10 g, 50 mmol) and methyl methanesulfonate (5.50 g, 50 mmol) was kept at room temperature for 72 h. The resulting crystalline mass was recrystallized with acetone/methanol, yielding hygroscopic colorless crystals of 1,3-dimethylimidazolium methanesulfonate; yield: 8.15 g (85%): mp 93.1 °C.

1,2-Dimethyl-3-butylimidazolium Methanesulfonate

A mixture of 1,2-dimethylimidazole (164.2 g, 1.71 mol) and butyl methanesulfonate (260.0 g, 1.71 mol) was kept at room temperature for 96 h. The resulting crystalline mass was recrystallized twice with acetone (3.5 L), yielding hygroscopic colorless crystals of 1,2-dimethyl-3-butylimidazolium methanesulfonate; yield: 399.0 g (94%); mp 109.0 °C.

1-Butyl-3-methylimidazolium Ethanesulfonate

Butyl ethanesulfonate (10.46 g, 63.0 mmol) was mixed with 1-methylimidazole (5.17 g, 63.0 mmol) and the reaction mixture was kept at room temperature for 96 h. The resulting crystalline mass was washed twice with ethyl acetate (20 mL) and, after vacuum drying, colorless and very hygroscopic crystals of 1-butyl-3-methylimidazolium ethanesulfonate were obtained; yield: 7.68 g (78%); mp 57.0 °C.

1-(2-Methoxyethyl)-3-methylimidazolium Ethanesulfonate.

2-Methoxyethyl ethanesulfonate (5.38 g, 32.0 mmol) was mixed with 1-methylimidazole (2.62 g, 32.0 mmol) and the reaction mixture was kept at 60 °C for 30 h. The resulting liquid was washed twice with ethyl acetate (5 mL) and, after vacuum drying, 1-(2-methoxyethyl)-3-methylimidazolium ethanesulfonate was obtained as colorless and very hygroscopic liquid; yield: 7.28 g (91%); Tg −86.1 °C

1,3-Dimethylimidazolium *n*-Butanesulfonate

Methyl *n*-butanesulfonate (7.10 g, 50.0 mmol) was mixed with 1-methylimidazole (4.10 g, 50.0 mmol) and the reaction mixture was kept at room temperature for 96 h. The resulting crystalline mass was washed twice with ethyl acetate (10 mL) and, after vacuum drying, colorless and very hygroscopic crystals of 1,3-dimethylimidazolium *n*-butanesulfonate were obtained; yield: 8.40 g (75%); mp 52.0 °C.

1,3-Dibutylimidazolium Methanesulfonate

Butyl methanesulfonate (8.58 g, 56.5 mmol) was mixed with 1-butylimidazole (7.00 g, 56.5 mmol) and the reaction mixture was kept at room temperature for 96 h. The resulting liquid was washed twice with ethyl acetate (10 mL) and, after vacuum drying, 1,3-dibutylimidazolium methanesulfonate was obtained as an amber-colored liquid; yield: 12.77 g (82%); mp −56.0 °C.

1,3-Dibutylimidazolium Ethanesulfonate

Butyl ethanesulfonate (11.53 g, 69.4 mmol) was mixed with 1-butylimidazole (8.70 g, 69.5 mmol) and the reaction mixture was kept at room temperature for 96 h. The resulting liquid was washed twice with ethyl acetate (15 mL) and, after vacuum drying, 1,3-dibutylimidazolium ethanesulfonate was obtained as an amber-colored liquid; yield: 15.42 g (76%); mp −68.0 °C.

1-Butyl-3-methylimidazolium Tetrafluoroborate[12]

A mixture of 1-butyl-3-methylimidazolium methanesulfonate (82.0 g, 350 mmol), sodium tetrafluoroborate (42.5 g,

387 mmol) and distilled water (75 mL) was vigorously stirred for 30 min. The lower aqueous phase was separated and discarded and, to the remaining liquid, sodium tetrafluoroborate (3.0 g, 27.3 mmol) and distilled water (5 mL) were added. Stirring was continued for 15 min and dichloromethane (200 mL) was added. The organic phase was separated, dried with sodium carbonate and filtered through a short (3 cm) basic alumina column. Solvent evaporation afforded the desired 1-butyl-3-methylimidazolium tetrafluoroborate as a pale amber liquid; yield: 61.3 g (79%).

1-Butyl-3-methylimidazolium Hexafluorophosphate[12]

A mixture of 1-butyl-3-methylimidazolium methanesulfonate (109.9 g, 470 mmol), potassium hexafluorophosphate (90.7 g, 493 mmol) and distilled water (250 mL) was vigorously stirred for 30 min. The upper aqueous phase was separated and discarded and, to the remaining liquid, potassium hexafluorophosphate (4.3 g; 23 mmol) and distilled water (40 mL) were added. Stirring was continued for 15 min and dichloromethane (250 mL) was added. The organic phase was separated, dried with sodium carbonate and filtered through a short (3 cm) basic alumina column. Solvent evaporation afforded the desired 1-butyl-3-methylimidazolium hexafluorophosphate as a colorless liquid; yield: 126.9 g (95%).

1-Butyl-3-methylimidazolium Trifluoromethanesulfonate[32]

An aqueous sodium trifluoromethanesulfonate solution was prepared by slow trifluoromethanesulfonic acid addition (34.5 g, 230 mmol) to a cold aqueous sodium hydroxide solution (9.2 g, 230 mmol; dissolved in 28 mL of water). The pH of the solution was adjusted to 6–7 with trifluoromethanesulfonic acid or sodium hydroxide, 1-butyl-3-methylimidazolium methanesulfonate (47.0 g; 200 mmol) was added and the resulting mixture was vigorously stirred for 30 min. The water was evaporated under reduced pressure (70 °C, 40 mmHg) and dichloromethane (200 mL) was added to the semi-solid residue. The organic phase was separated, dried with sodium carbonate and filtered through a short (3 cm) basic alumina column. Solvent evaporation afforded the desired 1-butyl-3-methylimidazolium trifluoromethanesulfonate as a pale amber liquid; yield: 53.0 g (92%).

1-Butyl-3-methylimidazolium Trifluoromethanesulfonimidate.[30]

N-Lithium trifluoromethanesulfonimidate (50.0 g, 174 mmol) was dissolved in water (25 mL) and 1-butyl-3-methylimidazolium methanesulfonate (38.6 g, 165 mmol) was also dissolved in water (65 mL). Both solutions were mixed, vigorously stirred for 30 min and dichloromethane (200 mL) was added. The organic phase was separated, washed with water (30 mL) and dried with sodium carbonate. Solvent evaporation afforded the desired 1-butyl-3-methylimidazolium trifluoromethanesulfonimidate as a colorless liquid; yield: 67.6 g (98%).

1,2-Dimethyl-3-butylimidazolium Hexafluorophosphate[33,34]

A mixture of 1,2-dimethyl-3-butylimidazolium methanesulfonate (389.0 g, 1.57 mol), potassium hexafluorophosphate (304.0 g, 1.65 mol) and distilled water (840 mL) was vigorously stirred for 30 min. The upper aqueous phase was separated and discarded and, to the remaining liquid, potassium hexafluorophosphate (9.0 g, 0.05 mol) and distilled water (130 mL) were added. Stirring was continued for 15 min and dichloromethane (1 L) was added. The organic phase was separated, dried with sodium carbonate and filtered through a short (4 cm) basic alumina column. Solvent evaporation afforded the desired 1,2-dimethyl-3-butylimidazolium hexafluorophosphate as a colorless solid; yield: 445.0 g (95%); mp 44.0 °C.

1-Butyl-3-methylimidazolium Tris(pentafluoroethyl)trifluorophosphate[35]

1-Butyl-3-methylimidazolium methanesulfonate (39.5 g, 169 mmol) was dissolved in water (50 mL) and, with stirring and temperature control ($10\,^{\circ}C < T < 20\,^{\circ}C$), tris(pentafluoroethyl)trifluorophosphoric acid (99.0 g, 177.5 mmol) was added. Stirring was continued for further 30 min. The upper aqueous layer was removed and the remaining liquid was washed ($5\times$) with small portions (10 mL) of water. Dichloromethane (250 mL) was added and the solution was dried with sodium carbonate. Solvent evaporation afforded the 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, as a pale amber liquid; yield: 96.80 g (98%).

Acknowledgements

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