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Chiral Ionic Liquids Based on Abietane

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Abstract—A number of chiral ionic liquids were synthesized by reaction of 12-chloromethylabieta-8,11,13-trien-18-oic acid methyl ester with *N*-alkylimidazoles.

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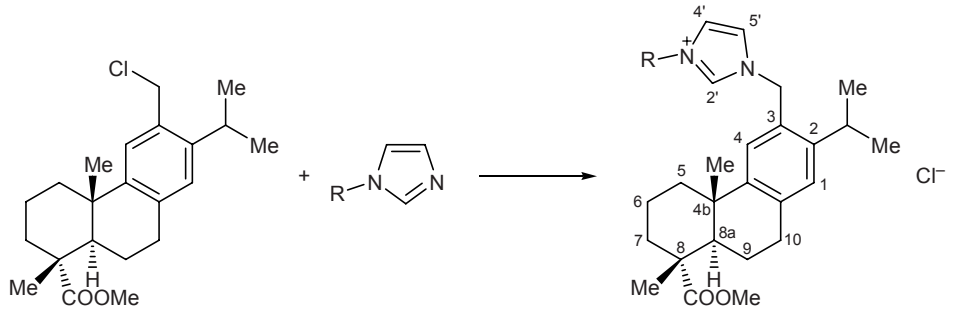
Ionic liquids are increasingly used in organic synthesis and catalysis [1–3]. Among these, *N*,*N*′-disubstituted imidazolium salts have been studied most thoroughly [4]. Imidazolium salts containing chiral functional groups are used for generation of N-heterocyclic carbenes as catalysts and reagents in asymmetric syntheses [5–7]. Chiral imidazole derivatives having pinane fragments have been reported [8, 9]. Pernak et al. [10] recently synthesized optically active ionic liquids on the basis of menthol [10]. However, ionic liquids based on di- and triterpenes remain so far unknown.

The goal of the present work was to synthesize new chiral imidazolium salts (ionic liquids) on the basis of abietane. For this purpose, we examined reactions of imidazole (**Ia**) and *N*-alkylimidazoles **Ib**–**Ie** (R = Me, CH_2=CH, *i*-Pr, *t*-Bu) with 12-chloromethylabieta-8,11,13-trien-18-oic acid methyl ester [**II**, methyl (1*R*,4a*R*,4b*R*,10a*R*)-3-chloromethyl-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene-1-carboxylate]. As a result, we isolated imidazolium salts **IIIa**–**IIIe** (Scheme 1), whose structure was confirmed by elemental analysis and IR and ^{1}H NMR spectroscopy.

The IR spectra of **IIIa**–**IIIe** contained strong absorption bands at 1720–1724 cm^{-1}, corresponding to stretching vibrations of the ester carbonyl group, and broad bands with their maxima at 3384–3412 cm^{-1}. The latter did not disappear even after drying under reduced pressure (5 mm, 80°C, 1 h), indicating the presence of crystallization water. Nevertheless, the elemental compositions of compounds **IIIa**, **IIIc**, and **IIIe** were consistent with the assumed structure; only the data for imidazolium salts **IIIb** and **IIId** having methyl and isopropyl groups, respectively, on the nitrogen atom indicated that these compounds were

Scheme 1.



II **Ia–Ie** **IIIa–IIIe**

R = H (**a**), Me (**b**), CH_2=CH (**c**), *i*-Pr (**d**), *t*-Bu (**e**).

isolated as hydrate (**IIIb**) and hemihydrate (**IIId**) (see Experimental).

The ^{1}H NMR spectra of **IIIa**–**IIIe** contained signals from diastereotopic protons in the NCH_2 group as two doublets at δ 5.5–5.6 ppm with a coupling constant of 14–15 Hz, which is typical of geminal protons. The 2-H proton in the imidazole ring resonated at δ 9.64–11.11 ppm. Compound **IIIa** displayed two signals from 2-H at δ 8.56 and 10.25 ppm with an intensity ratio of 1:1, indicating the presence of two tautomers. Signals from the 4-H and 5-H protons in the imidazole ring of compounds **IIIa**, **IIIb**, **IIId**, and **IIIe** were located in the regions δ 6.98–7.03 and 7.27–7.38 ppm, while the corresponding signals of **IIIc** were displaced downfield (δ 7.82 and 8.31 ppm), presumably due to effect of the *N*-vinyl group. Signals from protons in the aromatic ring of the hydrogenated phenanthrene fragment appeared at δ 7.14–7.31 (4-H) and 6.88–7.03 ppm (1-H). The NMe group in **IIIb** gave rise to a signal at δ 4.12 ppm; its relatively downfield position is consistent with the presence of positive charge on the corresponding nitrogen atom. Presumably, analogous quaternization of the imidazole nitrogen atom is typical of compounds **IIIc**–**IIIe**. The optical rotations of chiral imidazolium salts **IIIa**–**IIIe** smoothly decrease in the R series H > CH_2=CH > Me > *t*-Bu > *i*-Pr.

Formalistically, compounds **IIIa**–**IIIe** are ionic liquids. Only imidazolium salt **IIId** has an anomalously low melting point (82–88°C), so that it could be used as chiral solvent. In any case, all compounds **IIIa**–**IIIe** attract interest as novel ligands for the synthesis of metal complexes based on N-heterocyclic carbenes.

EXPERIMENTAL

The IR spectra were measured on a Specord M80 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were recorded on a Varian Mercury Plus instrument at 300 MHz using $CDCl_3$ or DMSO-d_6 (compound **IIIc**) as solvent and hexamethyldisiloxane as internal reference. Signals in the ^{1}H NMR spectra were assigned taking into account the data of [11]. The optical rotations (deg cm^2 g^{-1}) were measured on a Perkin–Elmer 341 polarimeter in chloroform of analytical grade, stabilized by addition of 0.6–1% of ethanol. TLC analysis was performed on Sorbfil plates using hexane–ethyl acetate as eluent (10:1); spots were visualized by treatment with a 10% solution of phosphomolybdic acid in ethanol, followed by heating at 120–130°C. The elemental compositions were determined on a Leco CHNS analyzer.

Imidazole and 1-methyl-1*H*-imidazole were commercial products (from Lancaster). 1-Isopropyl- and 1-*tert*-butyl-1*H*-imidazoles were synthesized according to the procedure described in [12]. Dehydroabietic (abieta-8,11,13-trien-18-oic) acid was prepared by desulfurization of 12-sulfodehydroabietic acid as reported in [13]; the subsequent methylation with methyl iodide in acetone in the presence of potassium carbonate gave dehydroabietic acid methyl ester [14] which was subjected to chloromethylation according to the procedure described in [15]. Yield of 12-chloromethylabieta-8,11,13-trien-18-oic acid methyl ester (**II**) 45%, mp 117–119°C (from methanol). ^{1}H NMR spectrum, δ, ppm (abietane atom numbering is assumed): 1.15 d (3H, CH_3, J = 6 Hz), 1.17 d (3H, CH_3, J = 6 Hz), 1.18 s (6H, CH_3), 1.37–1.83 m (7H, 1α-H, 2-H, 3-H, 6-H), 2.15 m (1H, 1β-H), 2.24 m (1H, 5-H), 2.81 m (2H, 7-H), 3.15 m (1H, 13-CH), 3.66 s (3H, OCH_3), 4.56 s (2H, CH_2Cl), 6.90 s (1H, 14-H), 7.08 s (1H, 11-H).

Compounds IIIa–IIIe (*general procedure*). A mixture of 10 mmol of compound **II** and 11 mmol of imidazole **IIIa**–**IIIe** in 50 ml of benzene was heated for 8–12 h under reflux until a solid separated. The colorless product was filtered off, washed with benzene, and dried under reduced pressure. In the synthesis of compounds **IIId** and **IIIe**, the solvent was distilled off, the precipitate was ground with diethyl ether, and the liquid phase was separated by decanting (this procedure was repeated three times). The undissolved imidazolium salt was filtered off and dried under reduced pressure.

1-[(4b*S*,8*R*)-2-Isopropyl-8-methoxycarbonyl-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-ylmethyl]-1*H*-imidazol-3-ium chloride (Ia). Yield 54%, mp 214–217°C, $[\alpha]_D^{24}$ = +58.4° (*c* = 1.07, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3404 br (NH), 1720 (C=O), 1580 (C=C), 1562 (C=N), 1504 (C=C), 1248, 1176, 1132, 1114, 1048, 958, 896. ^{1}H NMR spectrum, δ, ppm: 1.05 d (3H, CH_3, J = 6.6 Hz), 1.08 d (3H, CH_3, J = 6.6 Hz), 1.15 s (3H, CH_3), 1.25 s (3H, CH_3), 1.42 m (2H, 5α-H, 6α-H), 1.60–1.83 m (5H, 6β-H, 7-H, 9-H), 2.15 m (1H, 5β-H), 2.24 m (1H, 8b-H), 2.88 m (3H, 10-H, 2-CH), 3.66 s (3H, OCH_3), 5.52 m (2H, NCH_2), 6.98 s (1H, 1-H), 7.03 s (1H, 4′-H or 5′-H), 7.14 s (1H, 4-H), 7.31 s (1H, 5′-H or 4′-H), 8.57 s and 10.25 s (0.5H each, 2′-H); the HN^+ signal was not observed due to fast exchange. Found, %:

C 69.76; H 8.14; N 6.17. $C_{25}H_{35}ClN_2O_2$. Calculated, %: C 69.67; H 8.18; N 6.50.

1-[(4b*S*,8*R*)-2-Izopropyl-8-methoxycarbonyl-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-ylmethyl]-3-methyl-1*H*-imidazol-3-ium chloride hydrate (Ib). Yield 62%, mp 233–234°C, $[\alpha]_D^{24}$ = +49.5° (*c* = 0.3, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3384 br (OH), 1720 (C=O), 1576, 1504, 1250, 1178, 1132, 1114, 1048, 992, 958, 876. ^{1}H NMR spectrum, δ, ppm: 1.07 d (3H, CH_3, *J* = 7 Hz), 1.12 d (3H, CH_3, *J* = 7 Hz), 1.18 s (3H, CH_3), 1.26 s (3H, CH_3), 1.42 m (2H, 5α-H, 6α-H), 1.63–1.85 m (5H, 6β-H, 7-H, 9-H), 2.15 m (1H, 5β-H), 2.27 m (1H, 8b-H), 2.88 m (2H, 10-H), 2.94 m (1H, 2-CH), 3.66 s (3H, OCH_3), 4.12 s (3H, 3-CH_3), 5.47 d and 5.53 d (1H each, NCH_2, *J* = 14 Hz), 6.86 s (1H, 1-H), 6.99 s (1H, 4′-H or 5′-H), 7.15 s (1H, 4-H), 7.29 s (1H, 5′-H or 4′-H), 10.73 s (1H, 2′-H). Found, %: C 67.13; H 8.30; N 5.86. $C_{26}H_{37}ClN_2O_2\cdot H_2O$. Calculated, %: C 67.43; H 8.48; N 6.05.

1-[(4b*S*,8*R*)-2-Isopropyl-8-methoxycarbonyl-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-ylmethyl]-3-vinyl-1*H*-imidazol-3-ium chloride (Ic). Yield 55%, mp 183–186°C, $[\alpha]_D^{24}$ = +53.4° (*c* = 1.07, $CDCl_3$). IR spectrum, ν, cm^{-1}: 3412 br (OH), 1722 (C=O), 1658 (C=C), 1568 (C=N), 1548, 1506 (C=C), 1250, 1176, 1134, 1112, 1046, 964. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.02 d (3H, CH_3, *J* = 6.6 Hz), 1.07 d (3H, CH_3, *J* = 6.6 Hz), 1.15 s (3H, CH_3), 1.20 s (3H, CH_3), 1.32 m (2H, 5α-H, 6α-H), 1.57–1.82 m (5H, 6β-H, 7-H, 9-H), 2.03 m (1H, 8b-H), 2.33 m (1H, 5β-H), 2.81 m (2H, 10-H), 3.07 m (1H, 2-CH), 3.66 s (3H, OCH_3), 5.40 d.d (1H, CH_2=C**H**, *J* = 8.7, *J* 2.1 Hz), 5.45 d and 5.52 d (1H each, NCH_2, *J* = 14.4 Hz), 6.03 d.d (1H, =CH_2, *J* = 15.6, 2.1 Hz), 7.03 s (1H, 1-H), 7.31 s (1H, 4-H), 7.38 d.d (1H, =CH_2, *J* = 15.6, 8.7 Hz), 7.82 s and 8.31 s (1H each, 4′-H, 5′-H), 9.64 s (1H, 2′-H). Found, %: C 69.24; H 8.34; N 5.87. $C_{25}H_{35}ClN_2O_2$. Calculated, %: C 69.67; H 8.19; N 6.65.

3-Isopropyl-1-[(4b*S*,8*R*)-2-isopropyl-8-methoxycarbonyl-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-ylmethyl]-1*H*-imidazol-3-ium chloride hemihydrate (Id). Yield 47%, mp 82–88°C, $[\alpha]_D^{24}$ = +45.6° (*c* = 1.05, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3392 br (OH), 1720 (C=O), 1556 (C=N), 1504 (C=C), 1250, 1178, 1152, 1132, 1112, 1046, 1028, 992, 958. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.05 d (3H, CH_3, *J* = 7 Hz), 1.10 d (3H, CH_3, *J* = 7 Hz), 1.18 s (3H, CH_3), 1.26 s (3H, CH_3), 1.43 m (1H, 5α-H), 1.49 m (1H, 6α-H), 1.61 d (6H, 3-CH**Me**$_2$, *J* = 6.6 Hz), 1.69–1.88 m (5H, 6β-H, 7-H, 9-H), 2.17 m (1H, 5β-H), 2.28 m (1H, 8b-H), 2.88 m (2H, 10-H), 3.00 m (1H, 2-CH), 3.66 s (3H, OCH_3), 4.93 sept (1H, 3-CH), 5.51 d and 5.60 d (1H, NCH_2, *J* = 14.7 Hz), 6.87 s (1H, 1-H), 6.99 s (1H, 4′-H or 5′-H), 7.15 s (1H, 4-H), 7.38 s (1H, 5′-H or 4′-H), 11.01 br.s (1H, 2′-H). Found, %: C 67.95; H 8.75; N 6.04. $C_{26}H_{40}ClN_2O_2\cdot 0.5H_2O$. Calculated, %: C 68.02; H 8.78; N 6.18.

3-*tert*-Butyl-1-{[(4b*S*,8*R*)-2-isopropyl-4b,8-dimethyl-8-(methoxycarbonyl)-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-ylmethyl]-1*H*-imidazol-3-ium chloride (Ie). Yield 44%, mp 219–221°C. $[\alpha]_D^{21}$ = +48.5° (*c* = 1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3384 (OH), 1724 (C=O), 1652 (C=N), 1548 (C=C), 1294, 1248, 1202, 1134, 1116, 1096, 1044, 966, 908. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.07 d (3H, CH_3, *J* = 6 Hz), 1.09 d (3H, CH_3, *J* = 6 Hz), 1.18 s (3H, CH_3), 1.26 s (3H, CH_3), 1.41 m (2H, 5α-H, 6α-H), 1.73 s (9H, *t*-Bu), 1.63–1.88 m (5H, 6β-H, 7-H, 9-H), 2.17 m (1H, 5β-H), 2.27 m (1H, 8b-H), 2.87 m (2H, 10-H), 3.07 m (1H, 2-CH), 3.66 s (3H, OCH_3), 5.62 d and 5.69 d (1H each, NCH_2, *J* = 15 Hz), 6.87 s (1H, 1-H), 6.99 s (1H, 4′-H or 5′-H), 7.17 s (1H, 4-H), 7.38 s (1H, 5′-H or 4′-H), 11.11 br.s (1H, 2′-H). Found, %: C 70.08; H 8.85; N 6.01. $C_{27}H_{42}ClN_2O_2$. Calculated, %: C 71.50; H 8.90; N 5.75.

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