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STRUCTURE EFFECT OF IMIDAZOLIUM-BASED DICATIONIC IONIC LIQUIDS ON CLAISEN REARRANGEMENT

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GRAPHICAL ABSTRACT



Abstract A large group of imidazolium-based dicationic ionic liquids (DILs) has been prepared in good yields. Thermal stability of all DILs has been determined. The effects of the reaction time, cation, imidazolium C_2 –H acidity, and anion on the Claisen rearrangement of allyl phenyl ether have been investigated. Type of anion and the presence of the acidic C_2 –H bond in the imidazolium moieties have proven to be essential for this reaction. The simple procedure and the possibility of avoiding the use catalysts and volatile organic solvents make this synthetic method environmentally benign and adaptable for large-scale applications.

Keywords Allyl phenyl ether; Claisen rearrangement; dicationic ionic liquid; thermal stability

INTRODUCTION

Ionic liquids (ILs) have acquired a remarkable status in organic synthesis because of their advantageous properties.^[1,2] Many *task-specific* ILs have been synthesized and successfully applied in organic chemistry to improve yields and decrease reaction times.^[3] Recently, dicationic ionic liquids (DILs) have also attracted

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increasing interest. The possible combinations of cations and anions in DILs provide a broader variability of their properties than is the case for monocationic ILs.^[4–9] Various organic transformations have been performed by using monocationic and dicationic ILs as solvents or catalysts.^[2,10,11]

The Claisen rearrangement is a powerful carbon-carbon bond-forming reaction that may be applied in the synthesis of heterocyclic compounds, condensed aromatic structures, carboxylic acid derivatives, etc. Conventional conditions for the Claisen rearrangement usually include the use of high temperature, high pressure, and/or microwave irradiation, or different catalysts (ammonium chloride, transition metal complexes, Lewis acids, Brønsted acids, bases, water, etc.). However, these methods require the use of chemically and thermally stable solvents that provide convenient conditions of the reaction.^[12,13] Only a few groups have reported the Claisen rearrangement in dicationic ILs. Armstrong and coworkers have performed the thermal Claisen rearrangement of allyl aryl ethers in imidazolium- and pyrrolidinium-based DILs $C_9(bim)_2$ -NTf₂, $C_9(mim)_2$ -NTf₂, and $C_9(mpy)_{2-}$ NTf₂.^[10] To the best of our knowledge, the results of this rearrangement in other imidazolium-based DILs with shorter alkyl chains and different substituents on the aromatic moieties have not been reported. In this communication, an examination of the use of imidazolium-based DILs (the same or similar to the DILs reported in literature)^[7] as solvents for the Claisen rearrangement of allyl phenyl ether is reported. The effects of the reaction time, cation, imidazolium C_2 -H acidity, and anion have been investigated. The simple procedure and the possibility of avoiding the use of catalysts and volatile organic solvents make this approach environmentally benign and adaptable for large-scale applications.

RESULTS AND DISCUSSION

Imidazolium-based DILs for this research were prepared by reacting substituted imidazoles with α, ω -dihaloalkanes. Halide anion exchange of DILs with NTf₂⁻ and PF₆⁻ anions was performed according to the procedure reported in the literature^[7] with LiNTf₂ and KPF₆, respectively. To the best of our knowledge, the preparation, properties, and application of DILs **5b**, **5c**, **9c**, **9d** (see the Supplementary Material), **1a**, **1c** (Fig. 1), **4a**, **4c**, and **4d** (Fig. 2) have not been previously reported. Therefore, we present here an advanced synthesis of these DILs and their application in the Claisen rearrangement.

The application of DILs in the Claisen rearrangement has not yet been sufficiently widely investigated; hence we have examined in more detail the role they might play in facilitating this transformation. The main advantage of DILs in comparison to their monocationic analogs is their increased thermal stability.^[4] Our measurements have shown that DILs with bis(trifluoromethylsulfonyl)imide anions are more thermally stable than other DILs; the thermal stability of DILs with various anions increases in the following sequence: $Br^- \approx Cl^- < PF_6^- < NTf_2^-$ (see the Supplementary Material). Stability at high temperatures was one of the key advantages considered in the selection of these DILs for use in thermal Claisen rearrangements.

Although the Claisen rearrangement in DILs has been reported previously,^[10] no attempts were made to clarify the impact of the structures of the media on the product yields. In this communication, we report for the first time the use of the most



Figure 1. Yield of 2-allylphenol (3) obtained in DILs at different reaction times. (a) Determined by GC-FID (internal standard method).

thermally stable DILs with the bis(trifluoromethylsulfonyl)imide anion as solvents for the thermal Claisen rearrangement of allyl phenyl ether (2). The greatest yield of the product, 2-allylphenol (3), was reached after 30 min (Fig. 1) and remained at this level or slightly increased when the reaction time was extended to 60 min. Only in some DILs was a decrease in the yield of 2-allylphenol (3) observed after 60 min, due to side reactions of the product. Stirring the pure product 3 under the same conditions as used for the Claisen rearrangement in the relevant DILs confirmed that after 60 min 28% and 44% of the product had been converted into unidentified side products. The results depicted in Fig. 1 also revealed that the distance (spacer length) between the imidazolium moieties and the alkyl chain length at the imidazolium N atom had only negligible effect on the yield of the rearrangement product 3.

Additionally, the effect of the C_2 -H acidity of the imidazolium cation on the outcome of the Claisen rearrangement was investigated by comparing the products in four DILs bearing methyl groups at their imidazolium C_2 atoms with those in the analogous DILs with C_2 -H bonds. This comparison [Fig. 2(I)] showed that, on the contrary, the presence of the acidic C_2 -H bond in the imidazolium moieties was beneficial for the Claisen rearrangement of allyl phenyl ether (**2**). This implies that, according to the literature,^[14,15] the C_2 -H bond of the imidazolium cation may be involved in additional hydrogen bonding with the oxygen atom of the ether and therefore may be responsible



Figure 2. (I) Yield of 2-allylphenol (3) after 30 min in DILs bearing methyl groups at their imidazolium C_2 atoms and in the analogous DILs with C_2 -H bonds. (II) Impact of the anions of DILs on the yield of 2-allylphenol (3) after 30 min. (a) Determined by GC-FID (internal standard method). (b) The reaction was performed under Ar atmosphere.

for the solute–solvent interaction in the investigated reaction systems in DILs. This would also be in accordance with reported mechanistic insights into the Claisen rearrangement.^[16,17] Besides the diminished yields of the product **3**, the lack of a hydrogen at the imidazolium C_2 atom also led to increased formation of side products. The most significant C_2 –H bond effects on clean Claisen rearrangement after 30 min were observed for DILs **1e** and **1h**. For the selection of convenient DILs for the Claisen rearrangement, the effect of the anions was also investigated.

A significant impact of the anions of the DILs on the Claisen rearrangement was observed. A comparison of DILs with NTf_2^- , PF_6^- , and Br^- anions, having a common 1,3-bis(3-butylimidazolium-1-yl)propane cation, revealed that the yield of the product decreased significantly in the DIL with PF_6^- (**1b**) as the anion and that no product was detected in the DIL with Br^- (**5a**) as the anion [Fig. 2(II)]. This might be attributed to the influence of the anions on the polarity of the DILs, with **1a** ($E_T^N = 0.574$) and **1b** ($E_T^N = 0.571$) being more polar than **5a** ($E_T^N = 0.538$). (The normalized polarity parameter E_T^N was determined for binary mixtures of DILs with dimethylsulfoxide according to a known procedure.^[18,19]) This assumption is consistent with the reported polar solvent effect on acceleration of the Claisen rearrangement.^[20] However, some of the examined DILs with NTf₂⁻ anions are even less polar than 5a, yet still provided reasonable yields of the product 3. This prompted us to speculate that the cation-anion interaction in DILs could affect the capability of DILs to interact with the transition state during the Claisen rearrangement of allyl phenyl ether (2). To substantiate this assumption, the electrospray ionization (ESI) mass spectra acquired in negative-ion mode of the different investigated DILs were analyzed. The results, based on the relative abundances and peak distribution of naked anions (A⁻) and singly charged anionic aggregates $[(C+3A)^{-}, (2C+5A)^{-}, (3C+7A)^{-}, \text{ etc.}]$, have allowed us to propose the qualitative order of bond strengths of the different anions to α, ω -bis(3-alkylimidazolium-1yl)alkane cations as follows: $Br^- > PF_6^- > NTf_2^-$. This trend is in accordance with the previously reported abilities of the anions to coordinate to the cation moiety in monocationic ILs^[21] and correlates with the results depicted in Fig. 2(II). In addition to the aforementioned, the thermal stability of DILs 1a, 1b, and 5a was considered as a possible reason for the observed results of the reaction. The relatively lower thermal stability of DIL 5a than of DILs 1a and 1b (see the Supplementary Material, Table S1), which is in accordance with the information in the literature,^[7] may also be crucial for this reaction. Partial decomposition (determined by ¹H NMR; see the Supplementary Material) of this solvent under the conditions of the thermal Claisen rearrangement may lead to the loss of its functions and thereby reduce the expected yield of the product 3.

Further studies on the structure effect of imidazolium-based DILs with OMs, OTs, and $OP(O)(OCH_3)_2$ anions and their monocationic analogs on the thermal Claisen rearrangement are in progress. Different cation and anion combinations provide the broad range of properties seen for DILs. This new information on the effects of the cations and anions of imidazolium-based DILs on the Claisen rearrangement should greatly expedite the design of new, advanced ILs for this reaction.

In conclusion, a large group of dicationic ionic liquids (DILs), nine of them being new compounds, have been successfully applied as media for the thermal Claisen rearrangement of allyl phenyl ether. The greatest yields of the product were obtained in DILs with bis(trifluoromethylsulfonyl)imide as the anion and hydrogen at the imidazolium C_2 atom. The distance between the two imidazolium cations in the DILs was found to have no significant impact on the yields of the Claisen rearrangement product.

EXPERIMENTAL

Instruments and Reagents

All chemicals (except 1-butyl-2-methylimidazole, which was synthesized according to a procedure reported in the literature^[22]) were of analytical grade from Alfa Aesar or Sigma-Aldrich and were used as received without any further purification. ¹H NMR spectra were recorded on a Varian 400 MR spectrometer. For more information about the instruments and their parameters, see the Supplementary Material.

General Procedure for the Synthesis of Dicationic Ionic Liquids

The requisite substituted imidazole (30 mmol) and acetonitrile (25 mL), unless mentioned otherwise, were placed in a 100-mL flask equipped with a reflux condenser and a drying tube. The alkylating agent (15 mmol) was added at room temperature and the resulting mixture was heated under reflux for 24 h. After cooling to room temperature, the reaction mixture was filtered and the product was washed with cold acetonitrile (2×5 mL) and then diethyl ether (2×10 mL). Any remaining solvent was removed by means of a rotary evaporator and the product was dried under vacuum (2 Torr) at 60 °C for 2 h. For slight modifications of this procedure, see the Supplementary Material.

DILs 1a, 1c, 1d, 1e, 1g, 1h, and 4a–d were synthesized according to the procedure reported in the literature,^[7] except that the reaction mixture was stirred for 24 h. The reported procedure^[7] for the preparation of DILs 1b and 1f was modified by using KPF₆ instead of hexafluorophosphoric acid and by stirring the reaction mixture for 24 h. DILs formed by anion-exchange reactions were tested with AgNO₃ to verify that no halide impurities remained.

General Procedure for the Claisen Rearrangement in Imidazolium-Based Dicationic Ionic Liquids

The rearrangement of allyl phenyl ether (2) was performed according to the literature^[10] and the molar ratio of substrate to DIL was 1:1. Unless mentioned otherwise, the reaction was carried out under an air atmosphere. For kinetic studies and quantitative analysis, 0.2 equiv. of an internal standard (biphenyl) was added to the reaction mixture and five samples (taken after 5, 10, 20, 30, and 60 min, respectively) in diethyl ether were prepared and analyzed by gas chromatography–flame ionization (GC-FID). The yield of the product **3** varied according to the reaction conditions.

For the characterization of the product **3**, the reaction mixture obtained in DIL **1a** was extracted and purified according to the literature^[10] by flash chromatography (gradient CH₃OH/CH₂Cl₂) to give 2-allylphenol (**3**) as a colorless liquid, 53% yield. ¹H NMR (CDCl₃) δ 3.43 (2H, d, J = 6.4 Hz, ArCH₂CH), 4.95 (1H, s, ArOH), 5.21–5.14 (2H, m, CH₂CHCH₂), 6.10–5.97 (1H, m, ArCH₂CHCH₂), 6.82 (1H, dd, J = 7.9, 1.1 Hz, <u>Ar</u>), 6.90 (1H, td, J = 7.4, 1.2 Hz, <u>Ar</u>), 7.17–7.09 (2H, m, <u>Ar</u>). R_f(0.5% CH₃OH/CH₂Cl₂) 0.47. m/z (EI, %) 134 (100, M⁺), 119 (41), 115 (39), 91 (49), 77 (36).

SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher's website.

REFERENCES

- Sowmiah, S.; Srinivasadesikan, V.; Tseng, M.-C.; Chu, Y.-H. Molecules 2009, 14, 3780–3813.
- 2. Hallett, J. P.; Welton, T. Chem. Rev. 2011, 111, 3508-3576.

- Sawant, A. D.; Raut, D. G.; Darvatkar, N. B.; Salunkhe, M. M. Green Chem. Lett. Rev. 2011, 44, 1–54.
- 4. Shirota, H.; Mandai, T.; Fukazawa, H.; Kato, T. J. Chem. Eng. Data 2011, 56, 2453-2459.
- 5. Ito, K.; Nishina, N.; Ohno, H. Electrochim. Acta 2000, 45, 1295–1298.
- 6. Wang, R.; Jin, C.-M.; Twamley, B.; Shreeve, J. M. Inorg. Chem. 2006, 45, 6396–6403.
- Anderson, J. L.; Ding, R.; Ellern, A.; Armstrong, D. W. J. Am. Chem. Soc. 2005, 127, 593–604.
- Payagala, T.; Huang, J.; Breitbach, Z. S.; Sharma, P. S.; Armstrong, D. W. Chem. Mater. 2007, 19, 5848–5850.
- 9. Breitbach, Z. S.; Armstrong, D. W. Anal. Bioanal. Chem. 2008, 390, 1605-1617.
- 10. Han, X.; Armstrong, D. W. Org. Lett. 2005, 7, 4205-4208.
- 11. Jawale, D. V.; Pratap, U. R.; Mulay, A. A.; Mali, J. R.; Mane, R. A. J. Chem. Sci. 2011, 123, 645–655.
- 12. Castro, A. M. M. Chem. Rev. 2004, 104, 2939-3002.
- 13. Majumdar, K. C.; Alam, S.; Chattopadhyay, B. Tetrahedron 2008, 64, 597-643.
- 14. Inoue, T.; Misono, T. J. Colloid Interface Sci. 2008, 326, 483-489.
- 15. Inoue, T.; Misono, T. J. Colloid Interface Sci. 2009, 337, 247-253.
- 16. Gajewski, J. J. Acc. Chem. Res. 1997, 30, 219-225.
- 17. Acevedo, O.; Armacost, K. J. Am. Chem. Soc. 2010, 132, 1966-1975.
- Salari, H.; Khodadadi-Moghaddam, M.; Harifi-Mood, A. R.; Gholami, M. R. J. Phys. Chem. B 2010, 114, 9586–9593.
- Garcia, B.; Aparicio, S.; Alcalde, R.; Ruiz, R.; Dávila, M. J.; Leal, J. M. J. Phys. Chem. B 2004, 108, 3024–3029.
- Hu, H.; Kobrak, M. N.; Xu, C.; Hammes-Schiffer, S. J. Phys. Chem. A 2000, 104, 8058–8066.
- Bini, R.; Bortolini, O.; Chiappe, C.; Pieraccini, D.; Siciliano, T. J. Phys. Chem. B 2007, 111, 598–604.
- Serpell, C. J.; Kilah, N. L.; Costa, P. J.; Felix, V.; Beer, P. D. Angew. Chem., Int. Ed. 2010, 49, 5322–5326.