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Sterically Hindered Ketiminium Salts: a New Generation of Phase-Transfer Catalysts

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Abstract—Sterically hindered hydrazone **2** undergoes an unpredicted N–N bond scission via a methiodination sequence leading to iminium salt **5**. This latter compound was found to be remarkably stable under basic and acidic conditions and it proved to be able to promote C-alkylation of the glycine derived imine **7** under classical catalytic liquid–liquid phase-transfer conditions. Both the reaction cleavage and the catalytic potential are discussed.

Introduction

Asymmetric phase-transfer catalysis (PTC) has attracted considerable attention as a convenient technique for the synthesis of chiral molecules.[1] The effectiveness of phase-transfer catalysts derived from cinchona alkaloids in different types of asymmetric reactions has triggered the development of a variety of modified quaternary ammonium salts either to improve the optical yields or to determine the geometrical factors that control the observed stereoselectivities.[2]

As part of an ongoing research programme aimed to develop new phase-transfer agents and to contribute to original ideas in the field, we recently suggested non-cinchona alkaloid catalysts based on benzophenone proline hydrazonium salts.[3] These species have been designed following a methodology of ion-pair structure control approach. Although they possess high catalytic properties in the alkylation of Schiff bases, their low resistance to hydrolysis resulted in erratic enantioselective alkylation reproducibility. In order to further explore the catalytic potency of such a system it appeared essential to strengthen the ketimine moiety by providing more steric hindrance as it has been shown that sterically crowded imines resist hydrolysis.[4]

Molecular models indicated that the introduction of two naphthyl groups in the ketimine part provides a structure which not only respects the required steric and electronic environment, but also might possess further stereoface differentiating ability. Unfortunately, the catalyst candidate could not be prepared because of an unpredicted methyl iodide-mediated N–N bond cleavage during the quaternisation step, leading to an iminium salt instead. This latter showed high stability and was found to possess a great deal of potential as a phase-transfer catalyst. Before disclosing these catalytic properties, we shall first focus on the hydrazone cleavage.

Results and Discussion

The preparation of sterically hindered 1-bisnaphthylmethylidenamino-2-(*S*)-hydroxymethylpyrrolidine **2** has been carried out following a modified transimination protocol between bisnaphthylmethylidenamine **1** and 1-amino-2-(*S*)-hydroxymethylpyrrolidine[5] (Scheme 1). The best result was obtained by slowly adding the hydrazine to a refluxing solution of imine **1** in 1,2-dichloroethane. This mode of addition results in the formation of a substantial amount of hydrazone during the first hours of the reaction and probably limits the side reactions that competed with transimination under standard conditions.[6]

The course of the quaternisation step proved to be highly solvent dependent since no reaction has been observed in benzene, benzene/ethanol mixture or in methyl iodide. Thus, heating hydrazone **2** with excess methyl iodide in acetonitrile for a period of 30 h led to a dark heterogeneous reaction medium. Filtration of the less soluble material and recrystallisation from acetonitrile surprisingly gave the *N*,*N*-dimethyl-bisnaphthylmethylidenammonium iodide **5** as a yellow solid. This compound was unambiguously characterised by comparison with an authentic sample prepared independently in 67% yield by methiodination of

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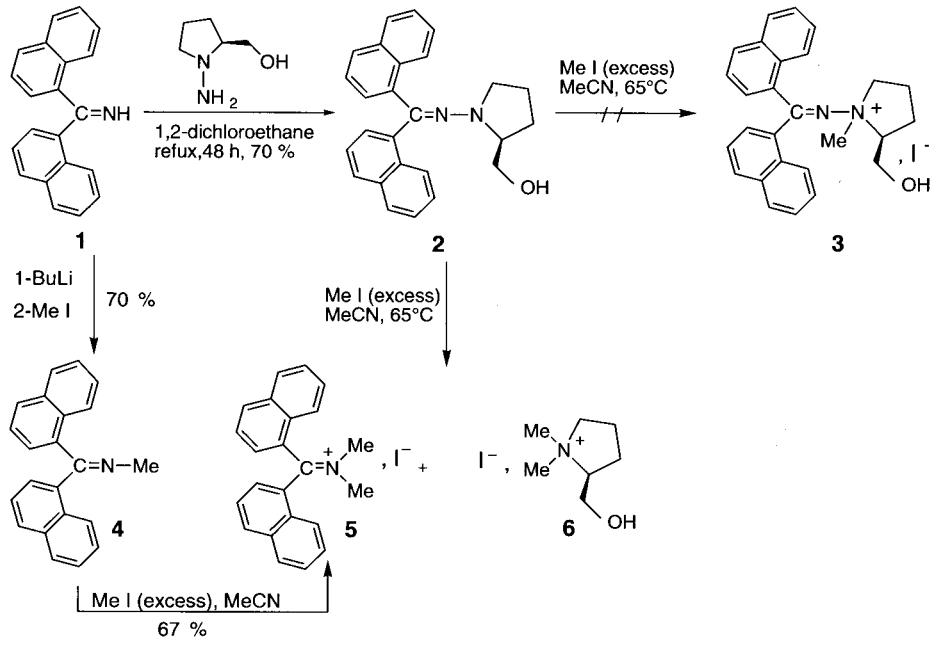
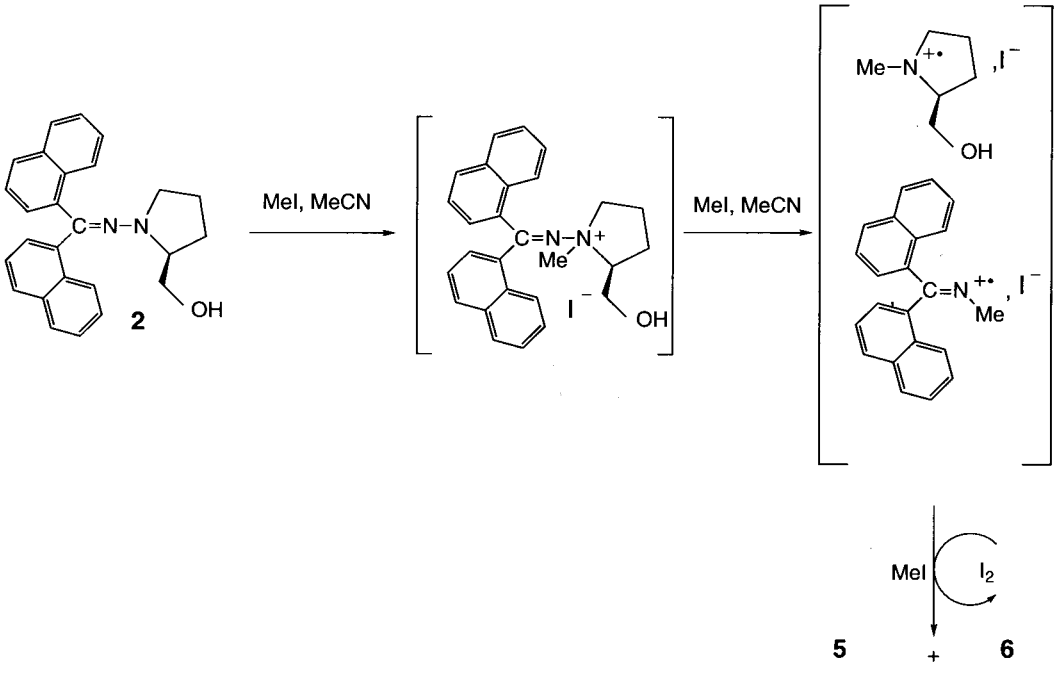


Scheme 1.

N-methyl-bisnaphthylmethylidenamine **4** under the above reaction conditions. The filtrate consisted of a complex mixture of polar compounds (TLC) among which (*S*)-*N*,*N*-dimethyl-2-hydroxymethylpyrrolidinium iodide **6** was present in substantial amounts.[7]

When irradiated with a 750 W tungsten lamp in the same conditions, the medium became heterogeneous within 30 min and after only 4 h the iminium salt **5** was isolated in 90% yield. Additionally, the use of 5-mol% of hydroquinone inhibited the reaction and only 25% of the iminium salt was formed even after a prolonged time with the help of radiant energy. These two observations as well as the formation of iodine, noticed at an early stage of the reaction, and probably responsible for the dark coloration of the reaction medium, gave support to a radical mechanism as a feasible process. Such a single-electron transfer mechanism has been postulated to explain the N–N bond cleavage in the reaction of Grignard reagents with benzophenone dialkylhydrazonium salt.[8] Moreover, during the course of this work, Singh et al.[9] reported isoxazolidines N–O bond cleavage mediated with methyl iodide in refluxing THF leading to quaternary ammonium iodide and α,β-unsaturated aldehyde.



Scheme 2.

Thus, we can envisage that the formation of the *N*-methylpyrrolidinium salt is followed by the homolytic cleavage of the weak N–N bond facilitated by inductive and steric effects. Subsequent reaction of the two radicals with methyl iodide led to the formation of iminium **5** and ammonium **6** (Scheme 2).

On the other hand, the possibility for the formation of iminium **5** from imine **4** was rejected considering the fact that the imine was not detected at any time of the quaternisation sequence. Moreover, methiodination has been shown to require a prolonged time with respect to 2-(*S*)-hydroxymethyl-1-methylpyrrolidine.

Iminium salt 5 as phase-transfer catalyst

The iminium salt resulting from the unexpected cleavage reaction proved to be remarkably stable toward hydrolysis even in strong acidic medium. Owing to this property, we wondered if this species might behave as a catalyst in phase-transfer alkylation reactions. This idea was particularly attractive since the structure could be easily modified through the incorporation of variety of substituents, especially in designing chiral catalysts.

Iminium salt chemistry is well documented as these compounds give rise to useful synthetic applications. They have been used extensively as precursors for the synthesis of cyclic amines,[10a–c] aminoalcohols,[10d] indoles[10e] and lactams.[10f] They also have been found versatile intermediates in intramolecular cycloadditions,[11a] 1,2 and 1,3 dipolar cyclisations,[11b–e] and asymmetric Diels–Alder reactions.[11f] Moreover, they recently proved to be useful catalysts for the epoxidation of alkene pioneered by Lusinchi et al.[12–15] It has been demonstrated that the oxaziridinium salt generated in situ serves as an oxidant relay in the catalytic cycle. However, to our knowledge the use of iminium salts as catalysts in alkylation reactions under phase-transfer catalysis conditions has never been reported probably due to their reactivity under strongly basic conditions.

We studied the phase-transfer catalytic ability of iminium salt **5**, taking the well-documented alkylation of glycine derived imine **7** [2] as a model (Scheme 3).

It was clearly established, from control experiments, that no hydrolysis of the C–N double bond occurred when a mixture of catalyst **5** and 50% aqueous sodium (or potassium) hydroxide was stirred 24 h in dichloromethane (standard liquid–liquid phase-transfer conditions). Moreover, in the same experiment, less than 30% of N-demethylation occurred providing the imine precursor **4**.

Under solid–liquid phase-transfer conditions, iminium salt **5** showed a remarkable stability when a mixture of K_2CO_3/KOH (1/1) was used as a base, since neither N-demethylation nor hydrolysis were detected even after a prolonged period of time.

On the other hand, the use of monohydrated caesium hydroxide in the same conditions resulted in complete N-demethylation within fifteen minutes as judged from the full recovery of molar equivalent of the corresponding imine **4**. However, in the same conditions, iminium **5** was stable for more than 24 h at −60°C.

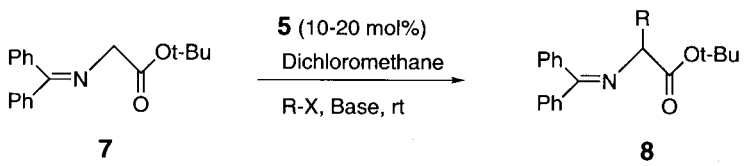
Phase-transfer alkylation of 7

With the above results in hand, solid liquid catalytic alkylation of **7** was investigated. Although the stability of **5** and the reactivity of such systems have been previously established,[16] no alkylation occurred at room temperature with a variety of alkylating agents under a large set of conditions.

Without carrying out any further investigations, efforts were oriented toward the L/L system as we reasoned that the low percentage of N-demethylation noticed in these conditions probably occurs only in the absence of the substrate. Indeed, it has been confirmed that in the case of quaternary ammonium salts the ion pairs with lipophilic anions decompose very slowly.[17] We therefore studied the catalytic alkylation of Schiff base **7** at room temperature using 50% aqueous potassium hydroxide (20 equiv.) and iminium salt **5** as catalyst in different organic solvents (Table 1).

It appears from the data gathered in Table 1 that iminium **5** displayed comparable catalytic properties with respect to previously described phase-transfer catalysts such as onium salts and metal complexes. Its stability in the basic L/L system in the presence of substrate **7** was confirmed since no decomposition was noticed during the reaction process in all the studied cases. It should be noted that in the case of methyl iodide, 48 h is a reasonable stopping point in terms of time to reach a maximum of 50% transformation (entries 5–6). The yields and reaction times could not be significantly improved when 20 mol% of catalyst was used (entries 3–6). With a more active alkylating agent, only 5 mol% of catalyst was required to reach 85% yield within a relatively shorter reaction time (entry 1). However, chemical yields were lower in non-polar solvents such as benzene and toluene. This result was predictable as the solubility of catalyst **5** was found to be limited in both solvents compared to dichloromethane.

On the other hand, recovery of the catalyst was accomplished in the case of allyl and benzyl bromides by simply removing dichloromethane in vacuo and treating the crude reaction residue with diethylether. Although substantial amounts of solid could be collected, the yield determination



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Scheme 3.

Table 1. Liquid–liquid PTC alkylation of Schiff base **7** catalysed by iminium salt **5**

Entry	R–X	Solvent	**5** (mol%)	Reaction time (h)	Yield (%)[a]
1	CH_2═$CHCH_2$–Br	Dichloromethane	5	10	85
2	$PhCH_2$–Br		10	20	78
3			20	20	80
4	CH_3CH_2–Br		10	18	65
5	CH_3–I		10	48	35
6			20	48	40
7	$CH_3(CH_2)_3$–Br		20	28	45
8	CH_2═$CHCH_2$–Br	Toluene	10	18	49
9	$PhCH_2$–Br		10	21	53
10	CH_2═$CHCH_2$–Br	Benzene	10	20	59
11	$PhCH_2$–Br		10	20	67

[a] After flash chromatography purification of the corresponding alkylated imine product **8**.

was not convenient because of anion exchange. It can be therefore assumed that good recovery of the catalyst is possible in all cases

In conclusion, a sterically hindered and, therefore, stable iminium salt which resulted from an unexpected cleavage reaction of hydrazone mediated with methyl iodide, was found to be an active phase-transfer catalyst for the *C*-alkylation of glycine derived imine **7**. Its limited solubility in organic solvents did not inhibit the transfer rate and was an advantageous parameter for the recycling. Moreover, convinced that iodide is far from being the anion of choice, an investigation on the nature of the counter ion together with the substituents, should have a positive impact on the transfer rate. The increased catalytic potency would consequently be helpful to carry out the alkylation with fewer active alkylating agents and work in non-polar solvents to limit the interfacial reactions. Last but not least, as stated previously, the potential to introduce a wide range of substituents should help in the design of a new generation of effective chiral phase-transfer catalysts, especially those with restricted conformations. Our work is currently oriented toward both directions.

Experimental

General

Uncorrected melting points were determined on a Büchi 510 instrument. Optical rotations were determined at 25°C on Perkin–Elmer 341 polarimeter using the sodium D line, concentrations are given in g/100 ml. IR spectra were recorded on Perkin–Elmer 16 PC FT instrument (in cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AC 300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts are in ppm referenced to TMS in $CDCl_3$. Mass spectra were determined on ATI Unicom automass spectrometer. High resolution mass spectrum was recorded on a Jeol GCmate. Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} glass plates (0.25 mm), compounds were visualised by UV light (254 nm) or phosphomolybdic acid–ethanol (22.1 g–180 ml) spray. Column chromatography was carried out on Merck Kieselgel 60H. Solvents were distilled according to known procedures.

Bisnaphthylmethylidenamine 1. Imine **1** was prepared in 80% yield according to the procedure described in reference 6 using 1-bromonaphthalene and 1-cyanonaphthalene. Data for imine **1**: R_f, 0.62 (40:60 EtOAc:Heptane); mp 92°C; FTIR (KBr) 3242, 3053, 1620, 1583, 1506, 1360, 1325, 1260, 1220. ^1H NMR: δ10.67 (br s, 1H), 8.63 (m, 2H), 8.18–8.16 (m, 4H), 7.80–7.67 (m, 8H); ^{13}C NMR: δ 178.5, 138.4, 133.5, 132.09, 130.1, 129.7, 128.1, 127.4, 127.09, 126.7, 126.1, 125.7, 125.5, 125.2, 124.5, 123.9; EIMS 281 [M^+]; Anal. Calcd for $C_{21}H_{15}N$: C, 89.67; H, 5.33; N, 4.98. Found: C, 89.61; H, 5.32; N, 4.81.

1-Bisnaphthylmethylidenamino-2-(*S*)-hydroxymethylpyrrolidine 2. To a refluxing solution of imine **1** (1 g, 3.5 mmol) in 1,2-dichloroethane (5 ml) was added under stirring a solution of 1-amino-2-(*S*)-hydroxymethylpyrrolidine (619 mg, 1.5 equiv.) in 1,2-dichloroethane (4 ml) over a period of 1 h, after which time the resulting brown solution was left under reflux for 48 h. After cooling, the dark gum was eliminated by washing with water (3×5 ml), the organic layer dried over $MgSO_4$, filtered, and concentrated in vacuo. Column chromatography on silica gel using 40:60 EtOAc: Hexane (R_f, 0.25) afforded hydrazone **2** (947 mg, 70%) as a yellow powder. Data for compound **2**: mp 170°C; $[\alpha]_D^{20}$=+355.6 (*c* 1.02, $CHCl_3$); FTIR (KBr) 3450, 3050, 1580, 1500, 1420, 1375, 1350, 1175; ^1H NMR: δ 8.86–8.42 (m, 1H), 7.91–7.15(m, 13H), 3.79–3.63 (m, 3H), 3.18(br s, 1H), 2.56–253(m, 1H), 1.98–1,95(m, 1H), 1.74–1.35(m, 4H); ^{13}C NMR: δ 148.04, 138.65, 138.02, 137.73, 134.34, 133.24, 131.91, 129.6, 128.91, 128.78, 128.43, 127.68, 126.92, 126.47, 126.18, 125.81, 125.49, 125.27, 125.03, 67.49, 67.1, 66.74, 66.22, 54.33, 25.61, 25.32, 23.68, 23.43; EIMS 380 [M^+]; Anal. Calcd for $C_{26}H_{24}N_2O$: C, 82.10; H, 6.31; N, 7.36. Found: C, 82.01; H, 6.76; N, 7.22.

Attempt preparation of hydrazonium salt 3. A solution of hydrazone **2** (700 mg, 1.84 mmol) and methyl iodide (1.5 ml, 24.09 mmol) in dry acetonitrile (2.5 ml) was heated under reflux for a period of 30 h. The product which crystallised out was filtered off and washed with cold acetonitrile. Additional material could be collected from the filtrate after cooling. The iminium salt **5** was isolated as a yellow solid (568 mg) and characterised by comparison with an authentic sample (see below). After evaporation of the filtrate under vacuo, the residue was dissolved in dichloromethane (5 ml) and extracted with water (3×3 ml). Low

pressure evaporation of the combined aqueous phases yielded a brown gum from which ^{1}H NMR analysis proved ammonium **6**[7] to be the major product.

***N*-methyl-bisnaphthylmethylidenamine 4.** To a solution of imine **1** (150 mg, 0.508 mmol) in anhydrous THF (1.5 ml) was added *n*-BuLi (1.1 equiv.) at −78°C under N_2 atmosphere. The deep red solution was left stirring for 30 min after which time a solution of methyl iodide (1.1 equiv.) in THF (0.5 ml) was added. The temperature was allowed to rise to 20°C and stirring was continued for 1 h. To the crude mixture, water (3 ml) and diethylether (5 ml) were added. The aqueous phase was separated and washed with ether (2×5 ml). The organic phases were combined, washed with brine (5 ml), dried over $MgSO_4$ and evaporated. Flash chromatography (35:65 EtOAc:Heptane) afforded imine **4** (70%) as a colourless oil. R_f, 0,72; FTIR (film) 3050, 2900, 2850, 1630, 1520, 1300, 1260, 1250, 1190; ^{1}H NMR: δ 8.97–8.94(m, 2H), 7.85–7.7(m, 4H), 7.54–7.42(m, 8H), 3.25(s, 3H); ^{13}C NMR: δ 185.07, 166.69, 135.18, 134.49, 131.88, 130.97, 129.85, 129.30, 128.21, 127.09, 126.30, 125.39, 26.15; EIMS 295 $[M^+]$, 294$[M-H]^+$, 265 $[M-NCH_3]^+$, 168 $[M-Naph]^+$, 127, 77; HRMS calc. For $C_{22}H_{17}N$: 295.1361. Found 295.1295.

***N*,*N*-dimethyl bisnaphthylmethylidenammonium iodide 5.** A mixture of imine **4** (147.5 mg, 0.5 mmol) and methyl iodide(3 equiv.) in acetonitrile (1.5 ml) was stirred at 65°C overnight. After cooling, the solid was collected by filtration and washed with cold acetonitrile to yield compound **5** (146.4 mg, 67%); mp 273°C; FTIR (KBr) 3444, 3038, 2996, 1640, 1588, 1508, 1450, 1382, 1346, 1256, 1240, 1190; ^{1}H NMR: δ 8.34–8.28(m, 2H), 8.15–7.98(m, 4H), 7.78–7.51(m, 8H), 4.058(s, 3H), 4.045(s, 3H); ^{13}C NMR: δ 135.27, 134.67, 134.15, 133.92, 132.21, 131.43, 130.7, 130.3, 130.09, 129.43, 128.76, 128.12, 126.27, 125.83, 124.97, 124.18, 50.46, 50.08; CIMS 311 $[M+H-I]^+$, 296 $[M+H-CH_3-I]^+$; Anal. Calcd For $C_{23}H_{20}IN$: C, 63.15; H, 4.57; I, 29.06; N, 3.2. Found: C, 62.94; H, 4.66; I, 29.63; N, 3.18.

PTC alkylation procedure

Schiff base **7** (0.5 mmol) and catalyst **5** (0.05 mmol) were dissolved in the organic solvent (5 ml) and to this solution was added the alkylating agent (0.7 mmol) and 50% aqueous potassium hydroxide (1.2 ml). The mixture was then vigorously stirred at room temperature until the reaction was complete (TLC, 10:90 EtOAc:Hexane). Aqueous work-up and extraction with ethyl acetate provided the crude imine products **8** which were then purified by flash chromatography using 10:90 EtOAc:Hexane as eluent. Data of the alkylated products are given in Ref. 2e.

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