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Samarium diiodide promoted reactions of a diphenyl α-iminoketone, a new synthesis of some pyrrole derivatives

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Dedicated to Professor H. B. Kagan on the occasion of his 70th birthday

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Abstract—The reduction of a diphenyl α-iminoketone with samarium diiodide has been studied. A fast two-electron transfer gives a samarium (*Z*)-enamidolate, which is protonated to afford an α-aminoketone or reacted with a variety of ketones to furnish pyrrole derivatives. Possible mechanisms are proposed.

1. Introduction

During the past 10 years, some studies have been devoted to reactivity of samarium(II) compounds with α-diketones. Thus, it has been demonstrated that benzil is reduced into benzoin with 2 equiv. of samarium diiodide in the presence of a proton source.[1,2] Interestingly, with quinidine, (*R*)-benzoin can be obtained with enantiomeric excess up to 91%. A samarium (*Z*)-enediolate, generated by a two-electron transfer from 2 equiv. of SmI_2 to benzil is considered to be the intermediate of this reaction. Trapping of this species has been achieved with acetic anhydride (Scheme 1).[1]

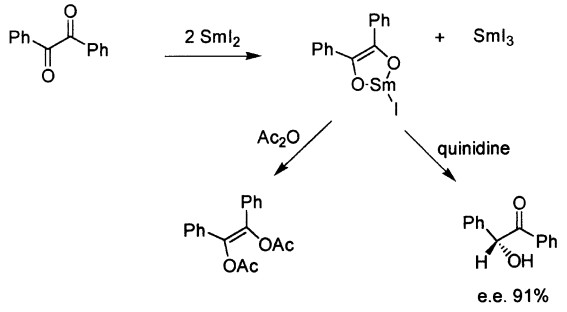
Besides, samarium diiodide-mediated coupling reactions between aliphatic α-diketones and aldehydes have been performed, affording 2,3-dihydroxyketones in good yields. This coupling probably proceeds through reaction of a samarium enediolate with an aldehyde (Scheme 2).[3]

In addition, we have recently reported a similar trapping of an enediolate, resulting of a samarium diiodide-mediated coupling reaction between an ester and an acid chloride.[4]

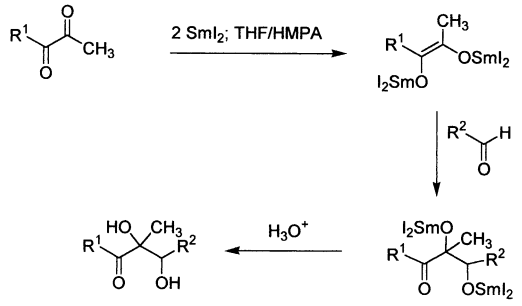
These findings prompt us to investigate the reactions of samarium(II) compounds with versatile substrates such as α-iminoketones which might give valuable compounds.

2. Results and discussion

Several routes for synthesis of α-iminoketones have been reported.[5–7] However, products are slowly obtained with moderate yields. In order to overcome this drawback, we tried to extend a previously reported preparation of imines,[8] to the synthesis of α-iminoketones. We were pleased to succeed in preparing 1,2-diphenyl-2-propylimino-ethanone **1** and 4-propylimino-hexan-3-one **2**, by the treatment of propyl amine with $LiAlH_4$, in THF followed by the addition



Scheme 1.



Scheme 2.

Keywords: samarium diiodide; imino ketones; amino ketones; pyrroles; coupling reactions; samarium enolates.

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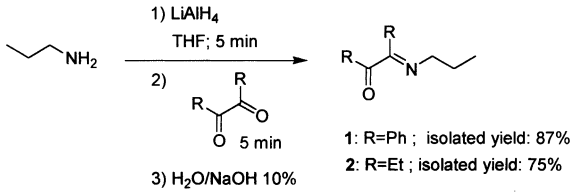
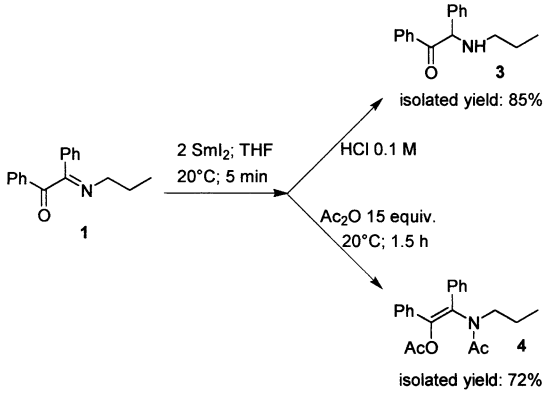


Scheme 3.

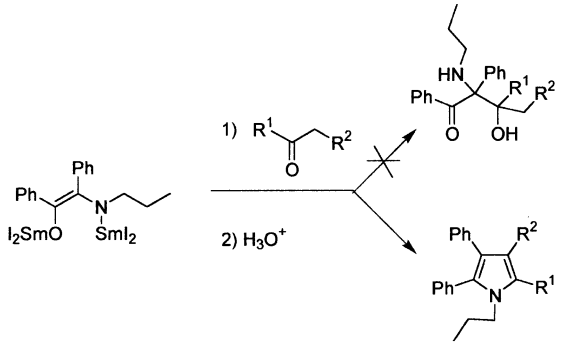


Scheme 4.

of benzil or 3,4-hexanedione. The products were obtained with excellent yields in a short reaction time (Scheme 3).

Reduction of α-iminoketones has been performed with a variety of reducing agents. Either α-aminoketones or aminoalcohols are obtained according to experimental conditions.[9–13] We found that samarium diiodide reacts instantaneously with α-iminoketone **1**, to give exclusively 1,2-diphenyl-2-propylamino-ethanone **3** after hydrolysis, with an excellent yield (Scheme 4).

The reaction can be also achieved with ethanol as an in situ proton source. However, small amounts of desoxybenzoin arising from a reductive cleavage of the carbon–nitrogen bond, according to a well-known process,[14] were detected under these conditions. In order to identify the samarium species whose hydrolysis gives the aminoketone, we allowed it to react with acetic anhydride in excess, α-acetoxy-α′-(*N*-propylacetylamino)stilbene **4** was then isolated as a single diastereomer. Comparison of its ^{1}H



Scheme 6.

NMR spectrum with those of the related products, (*Z*) and (*E*)-*O*,*O*′-diacetyl-1,2-diphenylethen-1,2-diol,[1] shows that the formation of the (*Z*) isomer is likely (Scheme 4).[15]

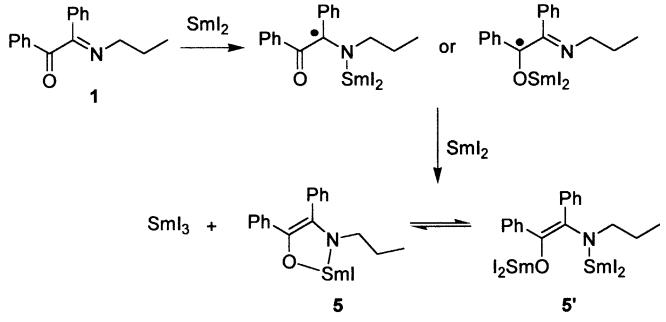
It can therefore, be presumed that the reduction of this α-iminoketone with 2 equiv. of SmI_2 gives a dianionic species **5** or **5**′ according to the process indicated in Scheme 5.

With the aim of preparing hydroxyaminoketones, **5** (or **5**′) was quenched with a carbonyl compound (ketone or aldehyde). We were surprised at isolating pyrrole derivatives instead, with good yields (Scheme 6).

Results with ketones having a single methylene group or 2 equiv. methylene groups linked to the carbonyl group are gathered in Table 1.

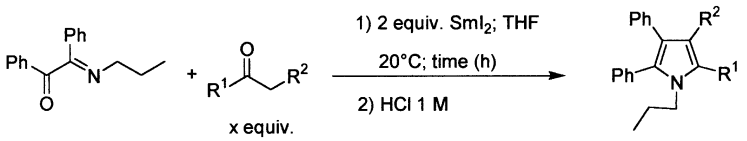
As reactions were slow at 20°C, 4–10 equiv. of ketone were used. However, ketone in excess was easily separated from pyrrole. Better results were obtained that way than performing reactions at 60°C with 1 equiv. ketone. Camphor and cyclobutanone did not give pyrrole derivatives (entries 3 and 4). The procedure II (Table 1, note b) must be used with aromatic ketones (entries 8–12), which are prone to pinacolic coupling. It can just as well be used with aliphatic ketones. With 4-propylimino-hexane-3-one **2** and acetone, under the same experimental conditions, a similar reaction occurred, giving the expected pyrrole (2,3-diethyl-5-methyl-1-propyl-1*H*-pyrrole **16**) but only in 20% yield (the main product is 4-propylamino-hexan-3-one).

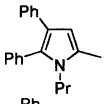
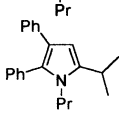
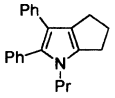
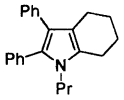
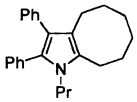
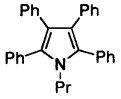
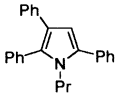
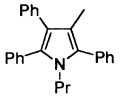
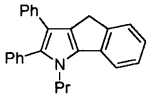
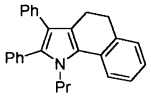
With ketones having two non-equivalent methylene groups



Scheme 5.

Table 1. Synthesis of pyrroles from ketones with a single type of methylene group



Entry	R^1; R^2	x	Time (h)	Products and isolated yields (%)
1[a]	CH_3; H	10	6	 **6**; 84
2[a]	*i*-Pr; H	10	12	 **7**; 76
3[a]	Camphor	5	12	–
4[a]	$-(CH_2)_2-$	10	48	–
5[a]	$-(CH_2)_3-$	6	12	 **8**; 96
6[a]	$-(CH_2)_4-$	6	12	 **9**; 73
7[a]	$-(CH_2)_6-$	5	12	 **10**; 78
8[b]	C_6H_5; C_6H_5	4	6	 **11**; 72
9[b]	C_6H_5; H	6	12	 **12**; 65
10[b]	C_6H_5, CH_3	6	12	 **13**; 68
11[b]	α-indanone	6	6	 **14**; 75
12[b]	α-tetralone	6	6	 **15**; 62

[a] Procedure I: samarium diiodide was added dropwise over 10 min to a mixture of α-iminoketone and *x* equiv. ketone (see Section 4).
[b] Procedure II: samarium diiodide was added dropwise over 10 min to α-iminoketone then *x* equiv. ketone were added (see Section 4).

a mixture of two pyrroles was obtained (Table 2), though 1-phenyl-2-propanone afforded a single product (entry 3).

Interestingly, β-tetralone gave large predominance of one of the two pyrroles (Scheme 7).

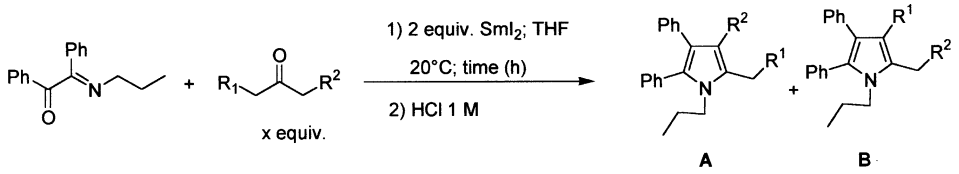
Besides, diisopropyl ketone was unreactive under the same experimental conditions as well as 3,4-hexanedione. Aliphatic aldehydes (pentanal and hexanal) furnished a complex mixture of products. The main ones (detected by GC–MS), were 2,4,6-trialkyl-1,3,5-trioxacyclohexane (mixture of stereomers) arising from a trimerization of aldehydes, esters resulting of a Tishchenko-type reaction, and homo-aldol reaction products. It is known that these reactions are efficiently catalyzed by lanthanide (III) salts.[16–18]

Finally, an attempt at synthesis of a furane from benzil was a failure, and benzoin was obtained instead after hydrolysis (Scheme 8).

Syntheses of pyrroles derivatives have been recently reviewed.[19] In particular, the condensation of carbonyl compounds with α-aminoketones gives pyrroles. It is known as the Knorr pyrrole synthesis. The reaction proceeds by initial enamine formation. However, in most examples the carbonyl compounds are β-ketoesters or β-diketones and the experimental conditions are very different from ours. A plausible mechanistic pathway to pyrrole is illustrated in Scheme 9, though the details are unclear as yet.

The species **5** that is generated by a two-electron transfer

Table 2. Synthesis of pyrroles from ketones with two non-equivalent methylene groups



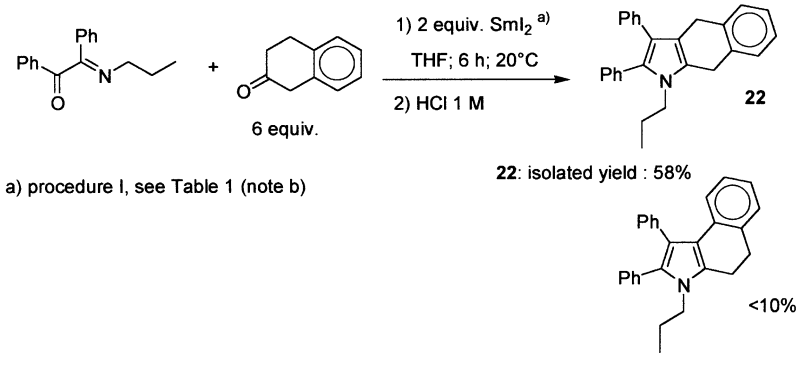
Entry	R^1; R^2	*x*	Time (h)	Products (A+B) and isolated yields (%)	A/B
1[a]	CH_3; H	10	12	**17** + **71** **18**;	60/40
2[a]	*n*-C_5H_{11}; H	6	6	**19** + **82** **20**;	62/38
3[a]	C_6H_5; H	6	6	**21**; 85	100/0

[a] Procedure I: samarium diiodide was added dropwise over 10 min to a mixture of α-iminoketone and *x* equiv. ketone.

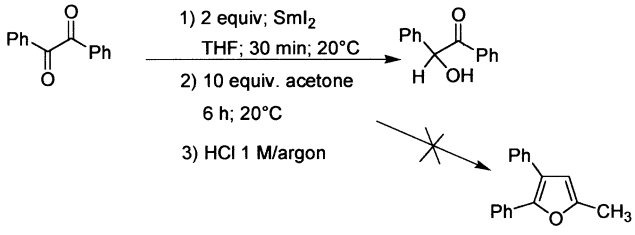
from 2 equiv. of SmI_2 to the α-iminoketone, reacts with ketone to give an enolate **C** and the species **2′**. A subsequent reaction furnishes adduct **D** which upon cyclization gives product **E** whose hydrolysis leads to **F**, and then a fast dehydration occurs that gives rise to a pyrrole. Such a mechanism is in agreement with the lack of reactivity of cyclobutanone, which is not prone to enolization, and diisopropyl ketone, which has no methylene groups. Assuming this mechanism is true, it appears also that enolization involving the less hindered methylene group is the predominant pathway (see Table 2 and Scheme 7). All these transformations might be facilitated by the presence of samarium(III) salts.

3. Conclusion

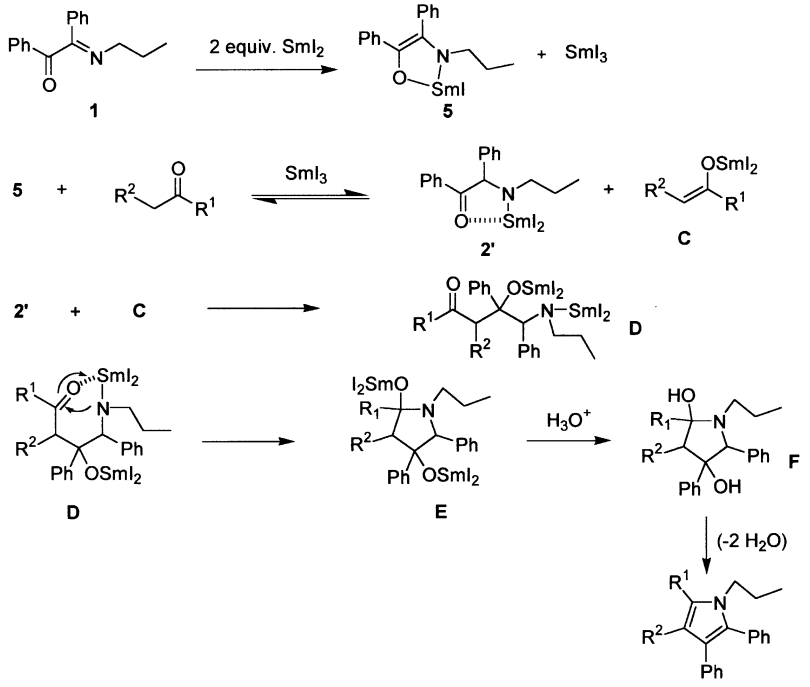
In conclusion, two α-iminoketones have been readily prepared from benzil or 3,4-ethanedione and a primary amine. The diphenyl α-iminoketones undergoes a two-electron transfer from 2 equiv. of SmI_2 to give a dianionic species **5** (or **5′**) which can be trapped by acetic anhydride in excess to give the corresponding diacetylated compound **4** having the (*Z*) configuration. Protonation of the dianionic species furnishes the α-aminoketone **3**, whereas reactions with a variety of ketones give pyrrole derivatives with good yields. With the aliphatic α-iminoketone, a pyrrole is also obtained, though in modest yield (20%). Mechanistic schemes have



Scheme 7.



Scheme 8.



Scheme 9.

been proposed. We are currently studying preparation of some others aromatic and aliphatic α-iminoketones and reactions of these compounds, especially trapping of the dianionic or radical–anionic species generated by electron transfer from samarium(II) derivatives, with a variety of substrates.

4. Experimental

4.1. General

^{1}H- and ^{13}C NMR spectra were recorded at 250 and 63 MHz, respectively on a Bruker AM 250 instrument (unless otherwise stated). Chemical shifts are reported in part per million (δ) downfield from TMS. Infrared (IR) spectra were recorded neat on a FTIR IFS 66 Bruker and are reported in cm^{-1}.

Mass spectra (MS) were determined on a GC–MS Ribermag R10-10 instrument. Electronic impact was performed at 70 eV. High Resolution Mass Spectra were performed on a GC–MS Finningan-MAT-95-S. Flash chromatography was performed on silica gel (Merck 230–240 mesh; 0.0040–0.0630 mm).

All commercially available organic compounds were distilled before use. Samarium was purchased from the Acros Company. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl. Samarium diiodide was prepared as previously described.[20]

All reactions were carried out under argon in Schlenk tubes using standard vacuum line techniques.

4.2. Preparation and reduction of iminoketones

4.2.1. 1,2-Diphenyl-2-propylimino-ethanone, 1. Propylamine (40 mmol, 0.329 mL) was added dropwise, with stirring to $LiAlH_4$ (10 mmol) in THF (40 mL), at room temperature. Stirring was maintained for 5 min, and then benzil (40 mmol) in THF (10 mL) was added dropwise. The mixture was stirred for 10 min. The work-up was done by successive addition of H_2O (2 mL), and 10% NaOH (0.5 mL). After filtration and evaporation of the solvent, 875 mg of crude product were obtained which from ^{1}H and ^{13}C NMR spectra contained only the desired α-ketoimine (yield 87%). Attempt at purification of the product by flash chromatography on silica gel results in partial transformation (~15%) into benzil, distillation under reduced pressure leads to degradation of the product.

Yellow powder, yield: 87%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.90 (3H, t, J=7.3 Hz); 1.70 (2H, sext, J=6.8 Hz); 3.39 (2H, t, J=6.8 Hz); 7.3–8.0 (10H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.8 (CH_3); 24.2 (CH_2) 55.6 (CH_2N); 127.1; 128.6; 129.1; 130.7; 134.5; 134.6; 135.3; 166.2 (C=N); 199.1 (C=O). GC–MS *m/z* (% base peak): 43 (17); 51 (18); 77 (47); 104 (100); 146 (55); 251 (1). HRMS calcd for $C_{17}H_{17}NO$: 251.1310, found: 251.1308.

4.2.2. 4-Propylimino-hexan-3-one, 2. The compound is prepared by the experimental procedure described above for **1**, it is purified by distillation under reduced pressure.

Yellow oil, yield: 75%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.90 (3H, t, J=7.6 Hz); 0.91 (3H, t, J=7.3 Hz); 1.02 (3H, t, J=7.3 Hz); 1.67 (2H, sext, J=7.3 Hz); 2.44 (2H, q, J=7.6 Hz); 2.82 (2H, q, J=7.3 Hz); 3.43 (2H, t, J=6.8 Hz). ^{13}C NMR

($CDCl_3$) δ (ppm): 7.9 (CH_3); 10.8 (CH_3); 11.9 (CH_3); 18.7 (CH_2); 23.8 (CH_2); 29.8 (CH_2); 53.4 (CH_2N); 169.7 (CN); 203.0 (CO). GC–MS *m/z* (% base peak): 41(16); 43(17); 55(30); 56(100); 98(24); 155(1); 156(4). HRMS calcd for $C_9H_{17}NO$: 155.1310, found: 155.1308.

4.2.3. 1,2-Diphenyl-2-propylamino-ethanone, 3. In a Schlenk tube under argon, to 1 mmol of α-iminoketone in 10 mL of THF, were added dropwise in 10 min, 20 mL of a 0.1 M solution of SmI_2 in THF, at 20°C. The blue-green color of SmI_2 turned immediately yellow. Stirring was maintained for 10 min. The mixture was then quenched with HCl (0.1 M) and stirred for 30 min to obtain a clear solution and then extracted with ether. The combined extracts were washed with sodium thiosulfate and brine. The organic layer was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude material was recrystallized from ether.

White crystals, yield: 85%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.81 (3H, t, *J*=7.3 Hz); 1.96 (2H, sext, *J*=7.3 Hz); 2.92 (2H, t, *J*=8.3 Hz); 6.40 (1H, s); 7.2–8.0 (10H, m); 9.1 (1H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.2 (CH_3); 19.9 (CH_2); 47.6 (CH_2N); 66.2 (CH); 128.1; 128.9; 129.5; 130.0; 130.3; 130.7; 132.9; 134.5; 192.4 (CO). HRMS calcd for $C_{17}H_{19}NO$: 253.1467, found: 253.1464.

4.2.4. (*Z*)-α-Acetoxy-α′-(*N*-propylacetylamino)stilbene, 4. In a Schlenk tube under argon, to 1 mmol of α-iminoketone in 10 mL of THF, were added dropwise in 10 min, 20 mL of a 0.1 M solution of SmI_2 in THF, at 20°C. The blue-green color of SmI_2 turned immediately yellow. Stirring was maintained for 10 min, 15 mmol of acetic anhydride were then added and the mixture was stirred during an additional period of 1.5 h. The mixture was then quenched with HCl (0.1 M) and stirred for 30 min to obtain a clear solution and then extracted with ether. The combined extracts were washed with sodium thiosulfate and brine. The organic layer was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel.

Purification: eluent AcOEt/pentane (1/2), colorless oil, yield: 72%. FTIR (film): 2967, 1768, 1653, 1493, 1446, 1391, 1368, 1296, 1276, 1242, 1198, 1128, 1068, 1023 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.79 (3H, t, *J*=7.3 Hz); 1.4–1.7 (2H, m); 2.17 (3H, s); 2.19 (3H, s); 3.04–3.16 (1H, m, NCH_2); 3.39–3.51 (1H, m, CH_2N); 7.12–7.23 (10H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.4 (CH_3); 20.8 (CH_3); 21.4 (CH_2); 21.8 (CH_3); 48.5 (CH_2N); 128.2; 128.5; 128.8; 129.0; 129.6; 131.5; 134.3; 144.6; 168.7 (CO amide); 171.2 (CO ester). GC–MS *m/z* (% base peak): 43 (41); 78 (34); 105 (63); 132 (10); 222 (13); 236 (4); 278 (100); 337 (1). HRMS calcd for $C_{21}H_{23}NO_3$: 337.1678, found: 337.1676.

4.3. General procedures for samarium diiodide promoted synthesis of pyrroles

Procedure I. In a Schlenk tube under argon, to a mixture of 1 mmol of α-iminoketone and 4–10 mmol of ketone, in 10 mL of THF, were added dropwise in 10 min, 20 mL of a 0.1 M solution of SmI_2 in THF, at 20°C. The blue-green color of SmI_2 turned immediately yellow. Stirring was continued for 3–12 h, The mixture was then quenched with 20 mL of HCl (1 M) and stirred for 30 min to obtain a clear solution and then extracted with ether. The combined extracts were washed with sodium thiosulfate and brine. The organic layer was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel.

Procedure II. In a Schlenk tube under argon, to 1 mmol of α-iminoketone in 10 mL of THF, were added dropwise in 10 min, 20 mL of a 0.1 M solution of SmI_2 in THF, at 20°C. The blue-green color of SmI_2 turned immediately yellow. Stirring was maintained for 10 min, 4–10 mmol of ketone were then added and stirring was continued for 3–12 h. Work-up was performed as described above in procedure I.

4.3.1. 5-Methyl-2,3-diphenyl-1-propyl-1*H*-pyrrole, 6. Purification: eluent CH_2Cl_2/pentane (1/1), yellow oil, yield: 84%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.80 (3H, t, *J*=7.8 Hz); 1.59 (2H, sext, *J*=7.8 Hz); 2.40 (3H, s); 3.74 (2H, t, *J*=7.8 Hz); 6.26 (1H, s); 7.04–7.47 (10H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.11 (CH_3); 12.4 (CH_3); 24.3 (CH_2); 45.6 (CH_2N); 106.7 (C4); 121.4; 124.6; 127.3; 127.5; 127.9; 128.4; 128.5; 129.6; 131.3; 133.8; 136.6. GC–MS *m/z* (% base peak): 217 (13); 232 (18); 246 (64); 260 (5); 275 (100). HRMS calcd for $C_{20}H_{21}N$: 275.1674, found: 275.1673.

4.3.2. 5-Isopropyl-2,3-diphenyl-1-propyl-1*H*-pyrrole, 7. Purification: eluent CH_2Cl_2/pentane (1/1), yellow oil, yield: 76%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.78 (3H, t, *J*=7.3 Hz); 1.46 (6H, d, *J*=6.8 Hz); 1.55 (2H, sext, *J*=7.3 Hz); 3.05 (1H, sept, *J*=6.8 Hz); 3.81 (2H, t, *J*=7.8 Hz); 6.31 (1H, s); 7.05–7.5 (10H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.1 (CH_3); 23.7 (CH_3); 24.8 (CH_2); 25.8 (CH); 45.4 (CH_2N); 103.2 (C4); 121.5; 124.5; 127.3; 127.4; 127.8; 128.4; 129.2; 131.3; 133.9; 136.7; 140.0. GC–MS: *m/z* (% base peak): 246 (10); 288 (100); 303 (52). HRMS: calcd for $C_{22}H_{25}N$: 303.1987, found: 303.1986.

4.3.3. 2,3-Diphenyl-1-propyl-1,4,5,6-tetrahydrocyclopenta[*b*]pyrrole, 8. Purification: eluent CH_2Cl_2/pentane (1/1), yellow crystals, yield: 69%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.81 (3H, t, *J*=7.3 Hz); 1.6 (2H, sext, *J*=7.3 Hz); 2.53 (2H, q, *J*=6.8 Hz); 2.83 (2H, t, *J*=6.8 Hz); 2.91 (2H, t, *J*=6.8 Hz); 3.71 (2H, t, *J*=7.3 Hz); 7.01–7.42 (10H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.2 (CH_3); 24.4 (CH_2); 25.1 (CH_2); 26.2 (CH_2); 28.6 (CH_2); 47.2 (CH_2N); 117.4 (C4); 124.4; 124.9; 127.2; 127.8; 128.4; 131.3; 132.7; 133.8; 136.7; 138.3. GC–MS: *m/z* (% base peak): 244 (12); 258 (21); 272 (46); 301 (100). HRMS calcd for $C_{22}H_{23}N$: 301.1830, found: 301.1828.

4.3.4. 2,3-Diphenyl-1-propyl-4,5,6,7-tetrahydro-1*H*-indole, 9. Purification: eluent CH_2Cl_2/pentane (1/1), yellow crystals, yield: 73%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.77 (3H, t, *J*=7.3 Hz); 1.48–1.64 (2H, m); 1.68–1.86 (2H, m); 1.88–2.05 (2H, m); 2.55–2.75 (4H, m); 3.69 (2H, t, *J*=7.8 Hz); 7.05–7.4 (10H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.2 (CH_3); 22.5 (CH_2); 23.0 (CH_2); 23.4 (CH_2); 23.8 (CH_2); 24.6 (CH_2); 45.5 (CH_2N); 116.1 (C2, C4); 120.6; 124.7; 126.8; 127.6; 128.2; 129.6; 131.2; 133.4; 136.3. GC–MS *m/z* (% base

peak): 244 (11); 286 (34); 315 (100). HRMS calcd for $C_{23}H_{25}N$: 315.1987, found: 315.1984.

4.3.5. 2,3-Diphenyl-1-propyl-4,5,6,7,8,9-hexahydro-1*H*-cycloocta[*b*]pyrrole, 10. Purification: eluent CH_2Cl_2/pentane (1/1), white crystals, yield: 78%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.72 (3H, t, J=7.3 Hz); 1.4–1.8 (10H, m); 2.58 (2H, t, J=5.8 Hz); 2.8 (2H, t, J=5.8 Hz); 3.74 (2H, t, J=7.3 Hz); 7.0–7.3 (10H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.2 (CH_3); 23.4 (CH_2); 23.6 (CH_2); 25.1 (CH_2); 26.0 (CH_2); 26.2 (CH_2); 29.5 (CH_2); 31.6 (CH_2); 45.6 (CH_2); 118.9 (C4); 122.2 (C2); 124.8; 126.4; 127.5; 127.9; 129.4; 130.5; 131.1; 133.8; 136.8. GC–MS *m*/*z* (% base peak): 202 (12); 230 (12); 244 (23); 258 (14); 274 (20); 288 (34); 314 (100); 343 (80). HRMS calcd for $C_{25}H_{29}N$: 343.2300, found: 343.2296.

4.3.6. 2,3,4,5-Tetraphenyl-1-propyl-1*H*-pyrrole, 11. Purification: eluent CH_2Cl_2/pentane (1/1), yellow crystals, yield: 72%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.58 (3H, t, J=7.3 Hz); 1.39 (2H, sext, J=7.3 Hz); 3.77 (2H, t, J=7.8 Hz); 6.91–7.05 (10H, m); 7.27–7.38 (10H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.1 (CH_3); 24.5 (CH_2); 46.3 (CH_2N); 122.0; 124.9; 127.3; 127.3; 128.1; 130.9; 131.2; 131.4; 133.2; 135.6. GC–MS *m*/*z* (% base peak): 265 (23); 293 (16); 308 (19); 384 (32); 413 (100). HRMS calcd for $C_{31}H_{27}N$: 413.2143, found: 413.2145.

4.3.7. 2,3,5-Triphenyl-1-propyl-1*H*-pyrrole, 12. Purification: eluent CH_2Cl_2/pentane (1/1), white crystals, yield: 65%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.52 (3H, t, J=7.3 Hz); 1.29 (2H, sext, J=7.3 Hz); 3.93 (2H, t, J=7.3 Hz); 6.51 (1H, s); 7.1–7.6 (15H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 10.8 (CH_3); 24.0 (CH_2); 46.5 (CH_2); 109.4 (C4); 122.8; 125.0; 127.0; 127.3; 127.5; 127.6; 128.0; 128.4; 128.5; 129.0; 131.2; 133.5; 134.0; 135.1; 136.4. GC–MS *m*/*z* (% base peak): 165 (13); 189 (37); 202 (11); 216 (11); 232 (18); 294 (28); 308 (58); 337 (100). HRMS calcd for $C_{25}H_{23}N$: 337.1830, found: 337.1822.

4.3.8. 3-Methyl-2,4,5-triphenyl-1-propyl-1*H*-pyrrole, 13. Purification: eluent CH_2Cl_2/pentane (1/1), yellow crystals, yield: 68%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.43 (3H, t, J=7.3 Hz); 1.17 (2H, sext, J=7.3 Hz); 2.07 (3H, s); 3.84 (2H, t, J=7.3 Hz); 7.10–7.5 (15H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 10.9 (CH_3); 11.1 (CH_3); 24.0 (CH_2); 46.6 (CH_2N); 115.9 (C3); 123.4; 125.0; 126.8; 126.9; 127.6; 128.2; 128.3; 130.3; 130.6; 131.1; 131.8; 132.2; 133.4; 133.5; 136.3. GC–MS *m*/*z* (% base peak): 308 (10); 322 (36); 351 (100). HRMS calcd for $C_{26}H_{25}N$: 351.1987, found: 351.1975.

4.3.9. 1,2-Diphenyl-3-propyl-3,8-dihydro-3-aza-cyclopenta[*a*]indene, 14. Purification: eluent CH_2Cl_2/pentane (1/1), yellow crystals, yield: 75%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.90 (3H, t, J=7.3 Hz); 1.85 (2H, sext, J=7.3 Hz); 3.82 (2H, s); 4.11 (2H, t, J=7.3 Hz); 7.1–7.6 (14H, m). ^{13}C NMR (50.3 MHz-$CDCl_3$) δ (ppm): 11.1 (CH_3); 24.7 (CH_2); 31.5 (CH_2); 46.9 (CH_2N); 116.3; 118.1; 123.0; 124.9; 125.3; 126.5; 127.7; 128.0; 128.5; 131.4; 133.1; 134.5; 135.6; 136.2; 137.9; 146.7. GC–MS *m*/*z* (% base peak): 304 (11); 320 (19); 349 (100). HRMS calcd for $C_{26}H_{23}N$: 349.1830, found: 349.1825.

4.3.10. 2,3-Diphenyl-1-propyl-4,5-dihydro-1*H*-benzo[*g*]-indole, 15. Purification: eluent CH_2Cl_2/pentane: (1/1), yellow crystals, yield: 62%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.81 (3H, t, J=7.8 Hz); 1.73 (2H, sext, J=7.8 Hz); 2.77–2.98 (4H, m); 4.19 (2H, t, J=7.8 Hz); 7.12–7.53 (14H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 10.9 (CH_3); 21.3 (CH_2); 24.3 (CH_2); 31.3 (CH_2); 47.2 (CH_2N); 120.5; 120.9; 121.5; 124.6; 125.1; 126.5; 127.3; 127.7; 127.9; 128.2; 128.4; 129.7; 130.3; 131.5; 132.9; 133.5; 135.5; 136.9. GC–MS *m*/*z* (% base peak): 320 (19); 334 (12); 363 (100). HRMS calcd for $C_{27}H_{25}N$: 363.1987, found: 363.1987.

4.3.11. 2,3-Diethyl-5-methyl-1-propyl-1*H*-pyrrole, 16. Purification: eluent CH_2Cl_2/pentane: (1/1), yellow oil, yield: 20%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.94 (3H, t, J=7.3 Hz); 1.07–1.18 (6H, m); 1.54–1.74 (2H, m); 2.19 (3H, s); 2.39 (2H, q, J=7.3 Hz); 2.53 (2H, q, J=7.3 Hz); 3.64 (2H, t, J=7.8 Hz); 5.71 (1H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.4 (CH_3); 12.3 (CH_3); 15.7 (CH_2); 16.0 (CH_3); 17.7 (CH_3); 19.1 (CH_2); 24.8 (CH_2); 45.2 (CH_2N); 105.3 (C4). GC–MS *m*/*z* (% base peak): 41(19); 53(5); 65(5); 77(7); 91(3); 107(7); 120(7); 122(11); 134(6); 136(4); 150(6); 164(100); 179(37). HRMS calcd for $C_{12}H_{21}N$: 179.1674, found: 179.1669.

4.3.12. 5-Ethyl-2,3-diphenyl-1-propyl-1*H*-pyrrole, 17 and 2,3-dimethyl-4,5-diphenyl-1-propyl-1*H*-pyrrole, 18. Purification: eluent CH_2Cl_2/pentane (1/1), yellow oil, yield 84%, (mixture 60/40). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.6–0.9 (3H, m); 1.20–1.70 (3.8H, m); 2.11 (1.2H, s, CH_3(**16**)); 2.31 (1.2H, s, CH_3(**16**)); 2.70 (1.2H, q, J=7.3 Hz, CH_2(**15**)); 3.65–3.80 (2H, m, CH_2N); 6.24 (0.6H, s, CH(**15**)); 7.00–7.5 (10H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 10.2; 11.2; 12.7; 19.8; 24.4; 24.6; 45.5; 45.9; 104.7 (C4, **15**); 113.3 (C3, **16**); 122.4; 124.6; 124.9; 125.1; 126.7; 127.3; 127.5; 127.6; 127.9; 128.0; 128.4; 129.6; 130.2; 130.6; 131.2; 131.4; 133.4; 133.8; 134.9; 136.5; 136.7. GC–MS *m*/*z* (% base peak): 230 (12); 246 (20); 260 (58); 289 (100) (**15**), *m*/*z* (% base peak): 232 (27); 260 (14); 274 (100); 289 (93) (**16**). HRMS calcd for $C_{21}H_{23}N$: 289.1830, found: 289.1833 (**15**), found: 289.1829 (**16**).

4.3.13. 5-Hexyl-2,3-diphenyl-1-propyl-1*H*-pyrrole, 19 and 2-methyl-3-pentyl-4,5-diphenyl-1-propyl-1*H*-pyrrole, 20. Purification: eluent CH_2Cl_2/pentane (1/1), yellow oil, yield: 82%, (mixture 62/38). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.7–1.1 (6H, m, CH_3); 1.15–2.05 (9.24H, m, CH_2); 2.34 (1.14H, s, CH_3(**18**)); 2.51 (0.76H, t, J=7.8 Hz, CH_2(**18**)); 2.68 (1.24H, t, J=7.8 Hz, CH_2(**17**)); 3.60–3.90 (2H, m, CH_2N); 6.26 (0.62H, s, CH(**17**)); 7.0–7.5 (10H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 10.3; 11.2; 14.1; 22.4; 22.6; 24.5; 24.7; 26.7; 28.6; 29.4; 31.4; 31.8; 31.9; 45.5; 45.8; 105.3 (C4, **17**); 119.1; 121.4; 124.6; 124.9; 126.4; 127.3; 127.5; 127.9; 128.4; 129.4; 130.4; 131.1; 131.3; 133.6; 133.8; 136.7; 136.9. GC–MS *m*/*z* (% base peak): 274 (100); 345 (34) (**17**), *m*/*z* (% base peak): 288 (100); 345 (50) (**18**). HRMS calcd for $C_{25}H_{31}N$: 345.2456, found: 345.2450 (**17**), found: 345.2441 (**18**).

4.3.14. 5-Benzyl-2,3-diphenyl-1-propyl-1*H*-pyrrole, 21. Purification: eluent CH_2Cl_2/pentane (1/1), yellow crystals, yield: 85%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.70 (3H, t, J=7.3 Hz); 1.45 (2H, sext, J=7.8 Hz); 3.69 (2H, t, J=7.8 Hz);

4.08 (2H, s); 6.17 (1H, s); 7.05–7.50 (15H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.1 (CH_3); 24.4 (CH_2); 33.4 (CH_2); 45.7 (CH_2N); 107.9 (C4); 121.5; 124.6; 126.3; 127.4; 127.9; 128.0; 128.4; 128.8; 130.2; 131.3; 131.5; 133.7; 136.5; 139.2. GC–MS *m/z* (% base peak): 91 (16); 232 (17); 274 (20); 322 (13); 351 (100). HRMS calcd for $C_{26}H_{25}N$: 351.1987, found: 351.1977.

4.3.15. 2,3-Diphenyl-1-propyl-4,9-dihydro-1*H*-benzo[*f*]-indole, 22. Purification: eluent CH_2Cl_2/pentane (1/1), yellow crystals, yield: 58%. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.84 (3H, t, J=7.3 Hz); 1.65 (2H, sext, J=7.3 Hz); 3.90 (2H, t, J=7.3 Hz); 4.12 (4H, s); 7.16–7.5 (14H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 11.2 (CH_3); 24.6 (CH_2); 27.5 (CH_2); 28.5 (CH_2); 45.7 (CH_2N); 113.6 (C4); 120.2; 122.9; 123.8; 124.9; 125.6; 126.0; 127.1; 127.8; 128.2; 129.2; 129.4; 129.6; 130.7; 131.2; 133.2; 135.6; 136.2. GC–MS *m/z* (% base peak): 286 (19); 363 (100). HRMS calcd for $C_{27}H_{25}N$: 363.1987, found: 363.1978.

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References

1. Takeuchi, S.; Miyoshi, N.; Hirata, K.; Hayashida, H.; Ohgo, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2001–2003.
2. Bao, W.; Zhang, Y.; Qi, S. *Synth. Commun.* **1994**, *24*, 2437–2440.
3. Miyoshi, N.; Takeuchi, S.; Ohgo, Y. *Chem. Lett.* **1993**, 2129–2132.
4. Machrouhi, F.; Namy, J.-L.; Kagan, H. B. *Tetrahedron Lett.* **1997**, *38*, 7183–7186.
5. Wheatley, W. B.; Fitzgibbon, W. E.; Cheney, L. C. *J. Org. Chem.* **1953**, *18*, 1564–1571.
6. Jousseaume, B.; Vilcot, N.; Ricci, A.; Tiekink, E. R. T. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2283–2287.
7. Barluenga, J.; Aznar, F.; Liz, R. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1093–1098.
8. Solladié-Cavallo, A.; Bencheqroun, M.; Bonne, F. *Synth. Commun.* **1993**, *23*, 1683–1687.
9. Alcaide, B.; Arjona, O.; De la Pradilla, R. F.; Plumet, J.; Rodriguez-Campos, I. M.; Santesmases *J. Chem. Res. Miniprint* **1988**, *3*, 932–957.
10. Alcaide, B.; Escobar, G.; Gonzales-Simo, J. L.; Lopez-Mardomingo, C.; Perez-Ossorio, R.; Plumet, J. *Tetrahedron Lett.* **1982**, *23*, 2033–2036.
11. Alper, H.; Amaratunga, S. *Tetrahedron Lett.* **1981**, *22*, 3811–3812.
12. Alcaide, B.; Lopez-Mardomingo, C.; Perez-Ossorio, R.; Plumet, J. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1649–1653.
13. Shibata, I.; Moriuchi-Kawakami, T.; Tanizawa, D.; Suwa, T.; Sugiyama, E.; Matsuda, H.; Baba, A. *J. Org Chem.* **1998**, *63*, 383–385.
14. Molander, G. A.; Stengel, P. J. *Tetrahedron* **1997**, *53*, 8887–8912.
15. ^{1}H NMR spectrum of product **4**: 2.17 (3H, s, CH_3CO); 2.19 (3H, s, CH_3CO); 7.12–7.23 (10H, bs, aromatic) is very similar to that of (*Z*)-*O,O′*-diacetyl-1,2-diphenylethen-1,2-diol: 2.20 (6H, s, CH_3CO); 7.24 (10H, bs, aromatic) but different from that of the (*E*) isomer: 2.08 (6H, s, CH_3CO); 7.36 and 7.54 (10H, m, aromatic).
16. Namy, J.-L.; Souppe, J.; Collin, J.; Kagan, H. B. *J. Org. Chem.* **1984**, *49*, 2045–2049.
17. Mascarenhas, C. M.; Duffey, M. O.; Liu, S.-Y.; Morken, J. P. *Org. Lett.* **1999**, *1*, 1427–1429.
18. Lu, L.; Chang, H.-Y.; Fang, J.-M. *J. Org. Chem.* **1999**, *64*, 853 and references quoted therein.
19. Sundberg, R. J. *Comprehensive Heterocyclic Chemistry II*, Pergamon: Oxford, 1996; Vol. 2, pp 119–200.
20. Girard, P.; Namy, J.-L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693–2698.