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A New Coupling Reaction Between β–Lactones and Electrophiles Mediated by a SmI_2/(NiI_2 catalytic) System.

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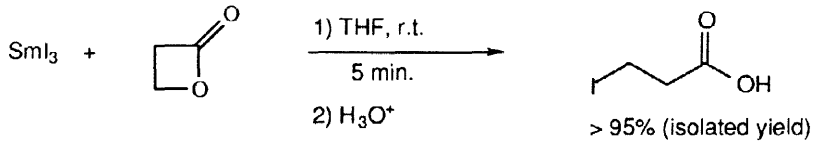
Abstract: β-lactones react with ketones aldehydes and imines in the presence of a SmI_2/(NiI_2 catalytic) system to afford substituted tetrahydrofuranones and pyrrolidinones.

INTRODUCTION.

In the course of studies concerning coupling reactions between acid chlorides and esters we observed that reactions with lactones failed[1]. In particular attempts to use β-propiolactone led to quantitative formation of 3-iodopropanoic acid. This product probably arises from the nucleophilic ring opening of the lactone; the complexation of samarium (II or III) with the lactone could facilitate this reaction.

We verified that SmI_3 readily react in THF with β-propiolactone to yield 3-iodopropanoic acid, after hydrolysis (scheme 1). It can be noticed that a similar ring opening of β-propiolactone by MgX_2 has also been reported.[2]



Scheme 1

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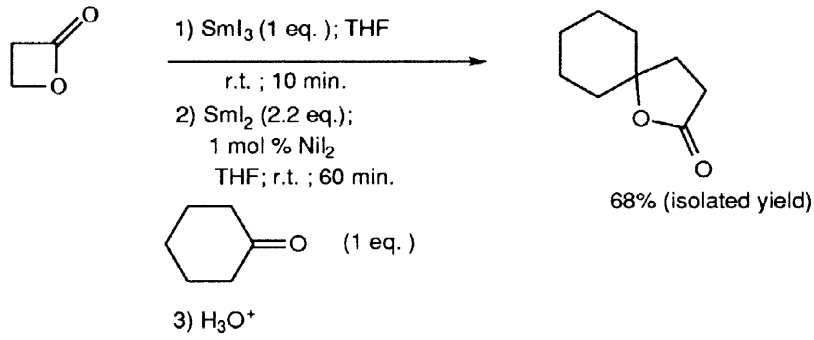
We postulated that it might be possible to take advantage of this transformation to transfer the propanoic acid moiety onto electrophilic substrates using Barbier-type reactions mediated by SmI_2.

RESULTS AND DISCUSSION.

Use of cyclohexanone as electrophile led to the formation of a spirolactone (Scheme 2).



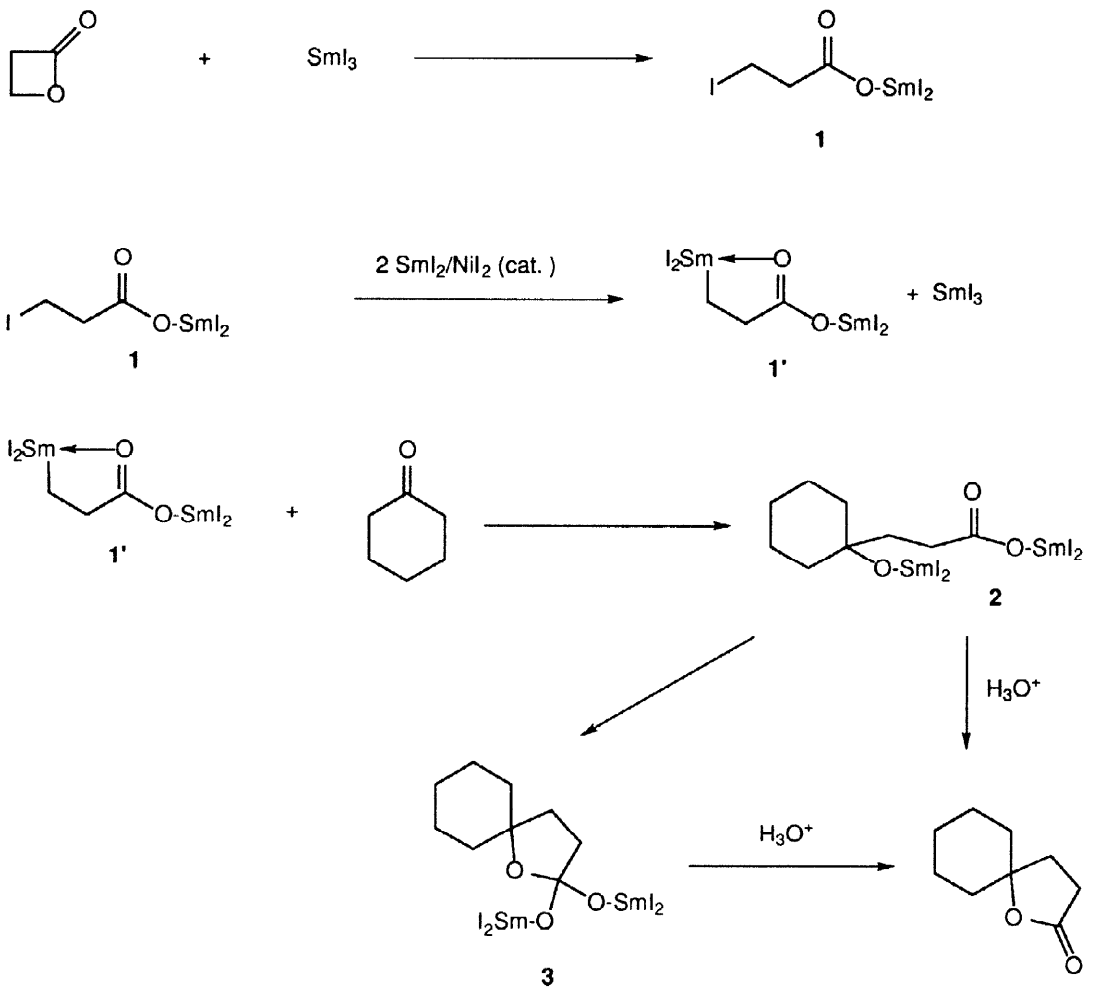
Scheme 2

This reaction needs a catalytic amount of nickel diiodide (1 mol% with respect to SmI_2). It is worthnoting that no coupling reaction occurs without this catalyst. The precise part of NiI_2 in this reaction has not been cleared up, however the beneficial effect of catalytic amounts of NiI_2 (and some other transition metal salts) on reactions mediated by SmI_2 has been previously reported and is again established here.[3]

A plausible mechanism is the following: after ring opening of the β-propiolactone, the samarium 3-iodocarboxylate **1** reacts with the SmI_2/(NiI_2 catalytic) system to give the samarium homoenolate **1'**. This compound adds to cyclohexanone to yield the samarium alkoxy carboxylate **2**. The hydrolysis of **2** leads to the spirolactone. Alternatively **2** could undergo cyclisation to **3** prior to hydrolysis (Scheme 3).

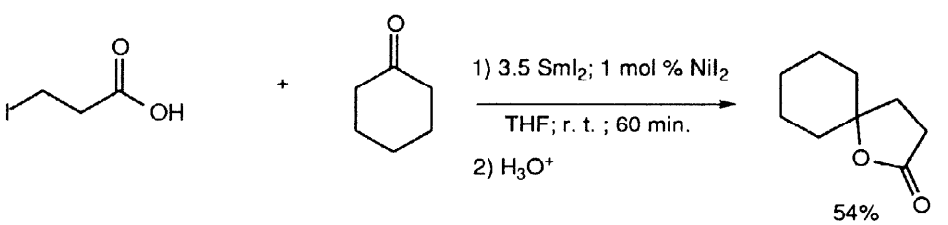
Metal homoenolates represent very useful nucleophilic species. Major efforts have been expended for exploration of their chemistry. Preparation of metal homoenolates and their addition to carbonyl compounds have been studied in the case of some metals (Zn, Ti, Li, Cu)[4]. In addition, reduction of 3-halopropionate by low valent lanthanides (Metals or divalent compounds) furnishes lanthanide homoenolates .[5-7]

The use of β-lactone and SmI_2/(NiI_2 catalytic) reported here, represents a convenient new entry to the homoenolate chemistry.



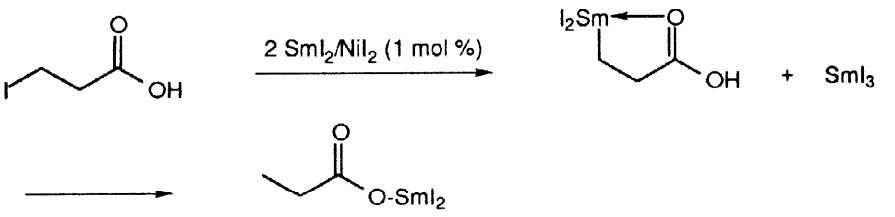
Scheme 3

Use of 3-iodopropanoic acid instead of β-propiolactone also leads to a spirolactone (scheme 4):



Scheme 4

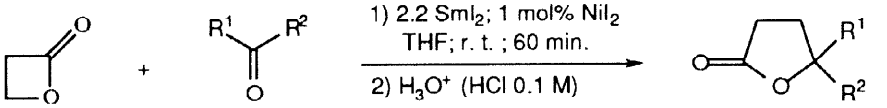
The yield however is lower probably because of a competitive reaction leading to samarium propanoate (scheme 5). The fact that sodium salts of 2-iodo- and 3-iodo-carboxylic acids readily react with ketones in the presence of the $SmI_2/(NiI_2$ catalytic) system supports this assumption.[8]



Scheme 5

In further experiments we have been able to obtain lactones in a similar fashion using a variety of ketones and aldehydes (fenchone and camphor do not react probably because of steric inhibition to carbonyl addition). It should be noticed that there is no need to perform the preliminary step of ring opening of β-propiolactone with samarium triiodide. The formation of the samarium iodocarboxylate presumably occurs from reaction of SmI_2[9] or a samarium(III) iodide (SmI_3 or an alkoxy samarium(III) iodide such as **2** and **3**) generated during Barbier reaction (Table 1).

Table 1: Coupling Reactions Between β-Propiolactone and Ketones or Aldehydes.

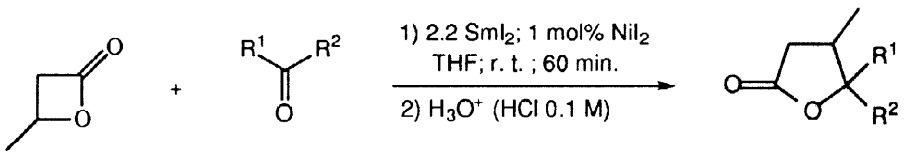


Entry	Ketone or Aldehyde	Products.and isolated yields (%)
1	cyclohexanone	**4**; 85
2	cyclopentanone	**5**; 80
3	cyclobutanone	**6**; 76
4	cycloheptanone	**7**; 81
5	2-octanone	**8**; 78
6	3-octanone	**9**; 83
7	2-butanone	**10**; 90
8	octanal	**11**; 83
9	hexanal	**12**; 75
10	2-phenyl propanal	**13**; 86 [a]
11	acetophenone	0 [b]
12	fenchone	0 [c]
13	camphor	0 [c]

a) ^{13}C NMR data indicate that a single diastereomer is generated.
b) Pinacols coupling products of acetophenone.
c) Unreacted ketone is recovered.

Use of other small ring lactones such as β-butyrolactone, also furnishes substituted tetrahydrofuranones (Table 2).

Table 2: Coupling Reactions Between β-Butyrolactone and Ketones or Aldehyde.

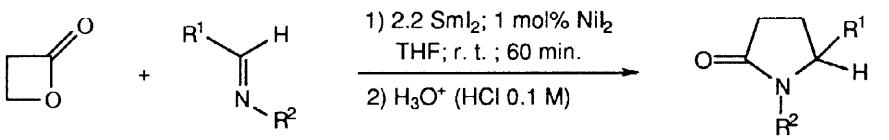


Entry	Ketone or Aldehyde	Products.and isolated yields (%)
1	cyclohexanone	**14**; 79
2	4-*t* -butylcyclohexanone	**15**; 74 [a]
3	octanal	**16**; 86
4	butanone	**17**; 98

a) Mixture of diastereomers: 83/17

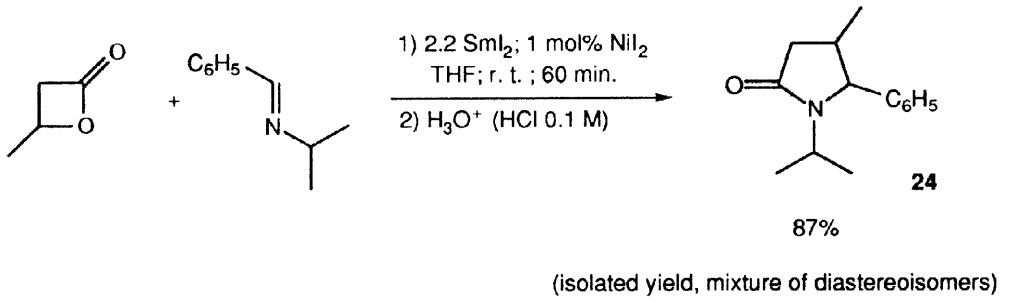
Coupling reactions of β-propiolactone with aldimines instead of ketones or aldehydes allows preparation of lactams in good yields (Table 3).

Table 3: Coupling Reactions Between β-Propiolactone and Imines.



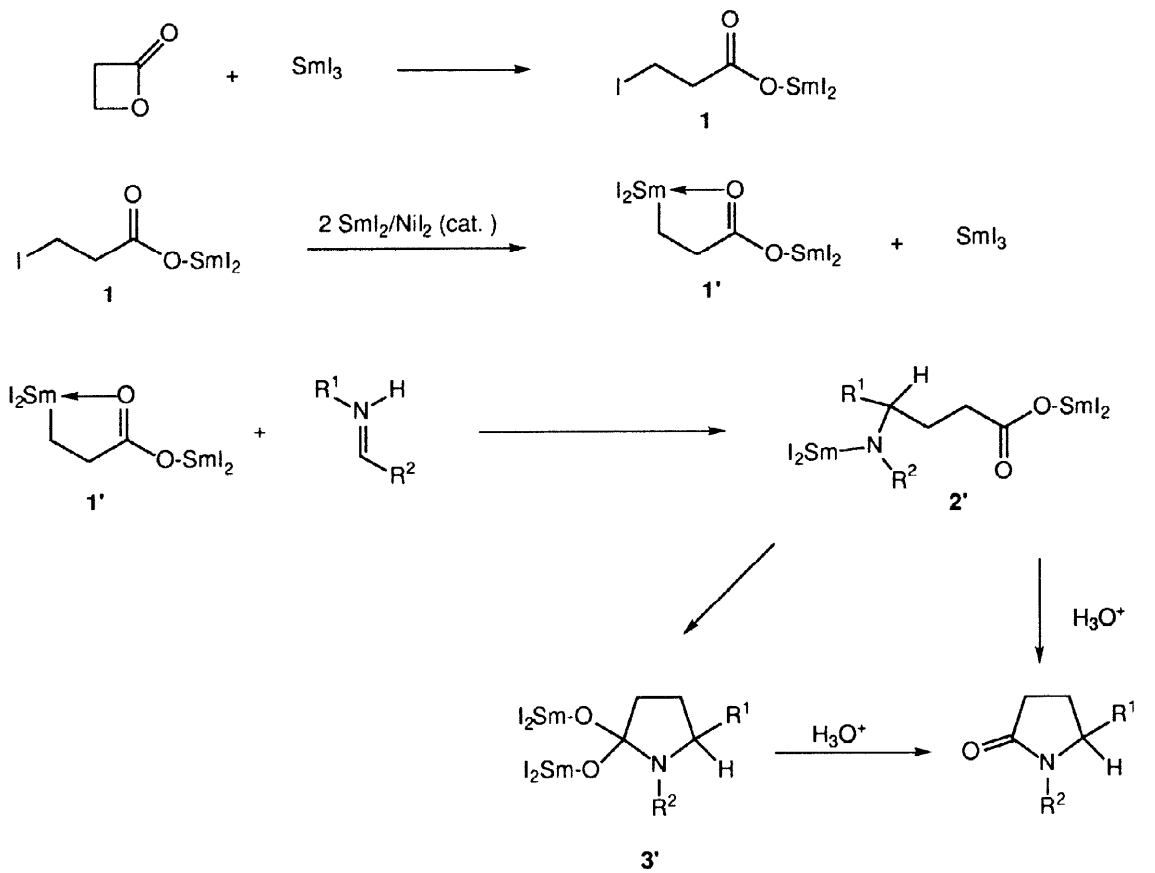
Entry	R^1, R^2	Products.and isolated yields (%)
1	C_6H_5, C_2H_5	**18**; 90
2	C_6H_5, *i*-propyl	**19**; 80
3	C_6H_5, cyclopentyl	**20**; 83
4	C_6H_5, cycloheptyl	**21**; 70
5	C_6H_5, pentyl	**22**; 77
6	1-naphthyl, C_6H_5	**23**; 93

Coupling between β-butyrolactone and a Schiff's base is also effective for the formation of a lactam (Scheme 6).



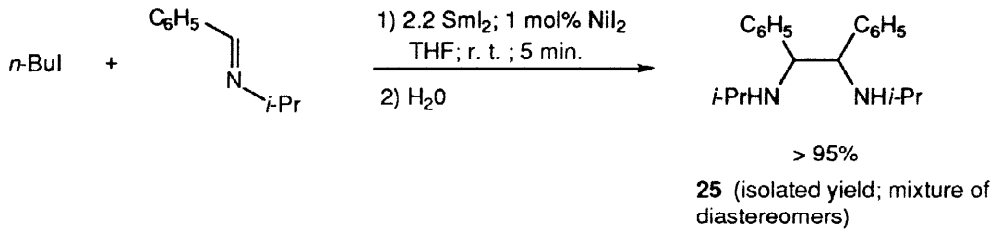
Scheme 6

The following mechanistic scheme accounts for the formation of lactams (Scheme 7). It is very similar to the one proposed above in the case of cyclohexanone (see Scheme 3).



Scheme 7

It is noteworthy that samarium iodocarboxylate **1** is much more reactive in Barbier-type reactions with imines than 1-iodobutane. In this latter case the only product of the reaction is the diamine which results from the reductive coupling of the imine (Scheme 8).



Scheme 8

Finally it was established that β-propiolactone does not react with electrophiles such as benzonitrile, succinic anhydride, ethyl octanoate, 1,2 epoxydecane, phenyl isocyanate or propyl isocyanate.

CONCLUSION.

To conclude, a new coupling reaction mediated by the SmI_2/NiI_2 (cat.) system, using β-lactones as reactants has been established. With ketones or aldehydes, disubstituted and monosubstituted tetrahydrofuranones are obtained in high yields. This procedure gives an alternative for the SmI_2 promoted synthesis of lactones. In fact, the same type of lactone products has been obtained from reactions of aldehydes and ketones with acrylate esters.[10] Nevertheless, the mechanisms are probably quite different and the experimental conditions are not the same. Using β-lactones, reactions can be readily carried out in the absence of HMPA and proton donors; consequently, the stereoselectivities could be different. In addition, reactions can be performed with imines, which allows the preparation of a variety of pyrrolidinones. We are currently trying to extend the scope of these reactions towards polyfunctionalized substrates.

EXPERIMENTAL.

General:

^1H and ^{13}C NMR spectra were recorded at 250 MHz 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. Coupling constants are reported in Hz. Infrared (IR) spectra were recorded neat on a FT-IR IFS 66 Bruker and are reported in cm^{-1}.

Mass spectra (MS) were determined on a GC/MS Ribermag R10-10 instrument. Chemical ionisation (CI) was carried out using NH_3 as the reactant gas and electronic impact was performed at 70eV. High Resolution Mass Spectra were performed on a GC/MS Finningan-MAT-95-S. Flash chromotography was performed on silica gel (Merck 230-240 mesh; 0.0040-0.0630 mm).

All commercially available organic compounds were distilled before use. Samarium powder (40 mesh) was purchased from the Labelcomat Company. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl. Samarium diiodide was prepared as previously described.[5]

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

Procedure for reactions of β-propiolactone (and β-butyrolactone):

To a solution of SmI_2 (2.2×10^{-3} mol) in THF (22 mL) is added a solution of NiI_2 (2.2×10^{-5} mol) in THF (2.2 mL); β-propiolactone (10^{-3} mol) and ketone, aldehyde or imine (10^{-3} mol) are mixed in THF (4 mL) and added to the SmI_2 solution.

The initially deep blue-green solution turns brown within 10 min. The mixture is stirred during an additional period of 50 min. The mixture is 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 are washed with sodium thiosulfate and brine. The organic layer is dried over $MgSO_4$, and the solvents are removed under reduced pressure. The crude material is purified by flash chromatography on silica gel.

Identification of products:

1-oxaspiro[4.5]decan-2-one (4): purification : pentane/ether : 80/20, yellow oil, yield : 85%. ^1H NMR: δ = 1.20-1.93 (m, 10H), 2.09 (t, J = 7.8 Hz, 2H), 2.31 (t, J = 7.8 Hz, 2H) ; ^{13}C NMR: δ = 22.5, 24.4, 25.3, 27.7, 30.6, 67.8, 177.9,; IR ($CHCl_3$) : ν= 2930, 2860, 1775, 1685, 1215, 1163 ; MS (70eV, EI) : m/z (%) = 154 (16) [M^+], 111 (100) [$C_7H_{11}O^+$], 99 (16) [$C_6H_{11}O^+$], 83 (14) [$C_6H_{11}O^+$], 85 (5) [$C_6H_{10}^+$], 43 (5) [$C_3H_7^+$], 41 (15) [$C_3H_5^+$] ; CI/NH_3 : m/z (%) = 155 (100) [MH^+], 172 (98) [MNH_4^+] ; HRMS calcd for $C_9H_{14}O_2$ [M^+] : 154.0990, found : 154.0990.

1-oxaspiro[4.4]nonan-2-one (5): purification : pentane/ether : 80/20, yellow oil, yield : 80%. ^1H NMR: δ= 1.56-2.01 (m, 8H), 3.01 (t, J = 7.8 Hz, 2H), 3.28 (t, J = 7.8 Hz, 2H) ; ^{13}C NMR: δ = 22.2, 22.7, 27.7, 37.9, 69.4, 179.2 ; IR ($CHCl_3$) : ν = 2941, 2850, 1780, 1684, 1230, 1205 ; MS (70eV, EI): m/z (%) = 140 (21) [M^+], 112 (17) [$C_7H_{12}O^+$], 111 (75) [$C_7H_{11}O^+$], 84 (7) [$C_5H_8O^+$], 68 (24) [$C_4H_4^+$], 56 (58) [$C_4H_8^+$], 55 (100 [$C_3H_3O^+$], 41 (52) [$C_3H_5O^+$] ; CI/NH_3 : m/z (%) = 141 (100) [MH^+], 158 (98) [MNH_4^+] ; HRMS calcd for $C_8H_{12}O_2$ [M^+] : 140.0834, found : 140.0836.

1-oxaspiro[3.4]octan-2-one (6): purification : pentane/ether : 90/10, yellow oil, yield : 76%. ^1H NMR: δ= 1.86-1.95 (m, 6H), 3.97 (t, J = 7.8 Hz, 2H), 4.16 (t, J = 7.8 Hz, 2H) ; ^{13}C NMR: δ = 22.5, 27.8, 29.9, 47.8, 72.6, 184.9 ; IR ($CHCl_3$) : ν = 2952, 2863, 1781, 1660, 1180, 905 ; MS (70 eV, EI): m/z (%) = 126 (18) [M^+], 98 (35) [$C_6H_{10}O^+$], 70 (23) [$C_4H_6O^+$], 56 (100) [$C_3H_4O^+$], 54 (84) [$C_4H_6^+$], 42 (72) [$C_2H_2^+$] ; CI/NH_3 : m/z (%) = 271 (100) [MH^+], 144 (100) [MNH_4^+] ; HRMS calcd for $C_7H_{10}O_2$ [M^+] : 126.0678, found : 126.0678.

1-oxaspiro[4.6]undecan-2-one (7): purification : pentane/ether : 80/20, yellow oil, yield : 81%. ^1H NMR: δ= 1.14-1.86 (m, 12H), 2.11 (t, J = 7.8 Hz, 2H), 2.43 (t, J = 7.8 Hz, 2H) ; ^{13}C NMR: δ = 22.3, 24.4, 27.9, 30.6, 43.9, 69.5, 177.0 ; IR ($CHCl_3$) : ν = 2938, 2850, 1768, 1684, 1230, 1205, 910; MS (70 eV, EI): m/z (%) = 168 (14) [M^+], 96 (14) [$C_7H_{12}^+$], 83 (21) [$C_6H_{11}^+$], 72 (11) [$C_4H_4O^+$], 56 (18) [$C_3H_4^+$], 42 (31) [$C_2H_2O^+$] CI/NH_3 : m/z (%) = 169 (70) [MH^+], 186 (100) [MNH_4^+] ; HRMS calcd for $C_{10}H_{16}O_2$ [M^+] : 168.1146, found : 168.1147.

5-hexyl-5-methyl-2-tetrahydrofuranone (8): purification : pentane/ether : 80/20, yellow oil, yield : 78%. ^1H NMR: δ = 1.10 (t, J =7.8 Hz, 3H), 1.16-1.51 (m, 13H), 1.71 (t, J = 7.8 Hz, 2H), 1.93 (t, J = 7.8 Hz, 2H) ; ^{13}C

NMR: δ = 14.6, 15.2, 23.6, 31.4, 32.1, 34.2, 40.7, 91.2, 180.2 ; IR ($CHCl_3$) : IR ($CHCl_3$) : ν = 2941, 2850, 1780, 1684, 1230, 1205 ;MS (70 eV, EI) : m/z (%) = 184 (10) [M^+], 169 (41) [$C_{10}H_{17}O_2^+$], 155 (5) [$C_9H_{15}O_2^+$], 99 (100) [$C_5H_7O_2^+$], 85 (9) [$C_6H_{13}^+$], 71 (4) [$C_5H_{11}^+$], 57 (9) [$C_4H_9^+$], 43 (12) [$C_3H_4^+$] ; CI/NH_3 : m/z (%) = 185 (62) [MH^+], 202 (100) [MNH_4^+] ; HRMS calcd for $C_{11}H_{20}O_2$ [M^+]: 184.1458, found : 184.1458.

5-ethyl-5-pentyl-2-tetrahydrofuranone (9): purification : pentane/ether : 80/20, yellow oil, yield : 83%. ^1H NMR: δ = 0.98-1.11 (m, 6H), 2.23-2.38 (m, 10H), 1.68 (t, J = 7.8 Hz, 2H), 1.79 (t, J = 7.8 Hz, 2H) ; ^{13}C NMR: δ = 13.5, 13.9, 14.2, 15.7, 22.8, 25.2, 25.7, 26.4, 28.3, 69.2, 168.1; IR ($CHCl_3$) : ν = 2939, 2850, 1768, 1664, 1230, 1205, 914; MS (70 eV, EI) : m/z (%) = 184 (12) [M^+], 155 (16) [$C_9H_{12}O_2^+$], 113 (100) [$C_6H_9O_2^+$], 71 (8) [$C_5H_{11}^+$], 57 (13) [$C_4H_9^+$], 56 (5) [$C_3H_4O_2^+$], 43 (12) [$C_3H_7^+$] ; CI/NH_3 : m/z (%) = 185 (78) [MH^+], 202 (100) [MNH_4^+] ; HRMS calcd for $C_{11}H_{20}O_2$ [M^+]: 184.1458, found : 184.1458.

5-ethyl-5-methyl-2-tetrahydrofuranone (10): purification : pentane/ether : 80/20, yellow oil, yield : 90%. H NMR: δ = 1.10 (t, J = 7.8Hz, 3H), 1.21-1.42 (m, 5H), 1.67 (t, J = 7.8 Hz, 2H), 1.82 (t, J = 7.8 Hz, 2H) ; ^{13}C NMR: δ = 13.8, 14.5, 22.2, 27.4, 25.8, 69.5, 168.3; IR ($CHCl_3$) : ν = 2933, 2850, 1760, 1661, 1218, 1205, 947; MS (70 eV, EI) : m/z (%) = 128 (11) [M^+], 113 (13) [$C_6H_9O_2^+$], 99 (100) [$C_6H_7O_2^+$], 84 (14) [$C_4H_4O_2^+$], 56 (18) [$C_3H_4O_2^+$], 43 (33) [$C_3H_7^+$] ; CI/NH_3 : m/z (%) = 129 (76) [MH^+], 146 (100) [MNH_4^+] ; HRMS calcd for $C_7H_{12}O_2$ [M^+] : 128.0834, found : 128.0836.

5-heptyl-2-tetrahydrofuranone (11): purification : pentane/ether : 80/20, yellow oil, yield : 83%. ^1H NMR: δ = 0.98 (t, J = 7.8 Hz, 3H), 1.20-1.63 (m, 13H), 1.90 (m, 2H), 2.41 (t, J = 7.8 Hz, 2H) ; ^{13}C NMR: δ = 14.6, 23.8, 24.7, 30.0, 30.6, 31.2, 33.1, 39.7, 70.9, 179.6; IR ($CHCl_3$) : ν = 2952, 2863, 1781, 1660, 1180, 905; MS (70 eV, EI): m/z (%) = 184 (13) [M^+], 169 (31) [$C_{10}H_{17}O_2^+$], 141 (40) [$C_8H_{13}O_2^+$], 127 (36) [$C_7H_{11}O_2^+$], 99 (100) [$C_7H_{15}^+$], 85 (25) [C_4H5O^+], 57 (26) [$C_4H_9^+$] 43 (21) [$C_3H_7^+$] ; CI/NH_3 : m/z (%) = 185 (68) [MH^+], 202 (100) [MNH_4^+] ; HRMS calcd for $C_{11}H_{20}O_2$ [M^+] : 184.1458, found : 184.1458

5-pentyl-2-tetrahydrofuranone (12): purification : pentane/ether : 80/20, yellow oil, yield : 75%. ^1H NMR: δ = 1.10 (t, J = 7.8 Hz, 3H), 1.18-1.58 (m, 9H), 1.79 (m, 2H), 2.43 (t, J = 7.8 Hz, 2H) ; ^{13}C NMR: δ = 14.6, 22.2, 22.8, 24.6, 27.4, 29.6, 70.7, 179.4; IR ($CHCl_3$) : ν = 2958, 2863, 1761, 1660, 1160, 1148, 908; MS (70 eV, EI) : m/z (%) = 156 (15) [M^+], 141 (9) [$C_8H_{13}O_2^+$], 127 (7) [$C_7H_{11}O_2^+$], 85 (100) [$C_4H_5O_2^+$], 71 (11) [$C_5H_{11}^+$], 57 (8) [$C_4H_9^+$],43 (31) [$C_3H_7^+$] ; CI/NH_3 : m/z (%) = 157 (68) [MH^+], 147 (100) [MNH_4^+] ; HRMS calcd for $C_9H_{16}O_2$ [M^+] : 156.1146, found : 156.1149.

5-(1-phenylethyl)-2-tetrahydrofuranone (13): purification : pentane/ether : 80/20, yellow oil, yield : 86%. ^1H NMR: δ = 1.45 (q, J = 7.8 Hz, 3H), 2.10 (q, J = 7.8 Hz, 2H), 2.28 (t, J = 7.8 Hz, 2H), 3.63 (m, 1H), 5.1 (q, J = 7.9 Hz, 1H), 7.25 (m, 5H) ; ^{13}C NMR: δ = 23.2, 28.7, 29.1, 34.1, 98.9, 114.1, 120.5, 129.5, 159.9, 186.7 ; IR ($CHCl_3$) : ν = 3090, 2965, 2875, 1765, 1605, 1495, 1215, 1160, 741, 438 ; MS (70 eV, EI) : m/z (%) = 190 (21) [M^+], 105 (57) [$C_8H_9^+$], 85 (100) [$C_4H_5O_2^+$], 77 (17) [$C_6H_5^+$], 56 (7) [$C_3H_4^+$] ; CI/NH_3 : m/z (%) = 191 (58) [MH^+], 208 (100) [MNH_4^+] ; HRMS calcd for $C_{12}H_{14}O_2$ [M^+] : 190.099, found : 190.099.

4-methyl-5-cyclohexyl-2-tetrahydrofuranone (14): purification : pentane/ether : 80/20, yellow oil, yield : 79%. ^{1}H NMR: δ = 1.14 (d, J = 7.8 Hz, 3H), 1.18-1.86 (m, 12H), 2.05 (q, J = 7.8 Hz, 1H), 2.36 (d, J = 7.8 Hz, 2H) ; 13C NMR: δ = 17.2, 23.2, 24.6, 27.7, 41.8, 68.6, 178.2; IR ($CHCl_3$) : ν = 2950, 2813, 1778, 1678, 1215, 1163 ; MS (70 eV, EI) : m/z (%) = 168 (28) [M^+], 153 (8) [$C_9H_{13}O_2^+$], 125 (70) [$C_8H_{13}O^+$], 82 (69) [$C_6H_{10}^+$], 70 (41) [$C_4H_6O^+$], 69 (45) [$C_4H_5O^+$], 57 (5) [$C_4H_9^+$], 55 (100) [$C_3H_3O^+$], 43 (11) [$C_3H_7^+$], 41 (67) [C_2HO^+] ; CI/NH_3 : m/z (%) = 169 (78) [MH^+], 186 (100) [MNH_4^+] ; HRMS calcd for $C_{10}H_{16}O_2$ [M^+] : 168.1146, found : 168.1148.

8-*t*-butyl-1-oxaspiro[4.5]decan-2-one (15): purification : pentane/ether : 80/20, yellow oil, yield : 74%. ^{1}H NMR: δ = 1.06 (d, J = 7.8 Hz, 3H), 1.14 (m, 9H), 1.20-1.80 (m, 9H), 2.20-2.35 (m, 2H), 2.58-2.78 (m, 1H) ; ^{13}C NMR: δ = 14.0, 15.6, 21.4, 22.2, 25.0, 30.4, 35.7, 36.3, 39.0, 40.3, 87.7, 177.5 ; IR($CHCl_3$) : ν = 2951, 2870, 1778, 1650, 1210, 1156 ; MS (70 eV, EI) : m/z (%) = 224 (1) [M^+], 165 (100) [$C_{12}H_{21}^+$], 96 (19) [$C_5H_4O_2^+$], 57 (15) [$C_4H_9^+$], 43 (5) [$C_3H_7^+$] ; CI/NH_3 : m/z (%) = 225 (82) [MH^+], 242 (100) [MNH_4^+] ; HRMS calcd for $C_{14}H_{24}O_2$ [M^+] : 224.1770, found : 224.1772.

5-heptyl-4-methyl-2-tetrahydrofuranone (16): purification : pentane/ether : 80/20, yellow oil, yield : 86%. ^{1}H NMR: δ = 1.10 (t, J = 7.8 Hz, 3H), 1.18-1.58 (m, 16H), 2.10 (m, 1H), 2.39 (d, J = 7.8 Hz, 2H); ^{13}C NMR: δ = 13.8, 14.6, 24.5, 24.7, 30.2, 30.8, 32.0, 33.1, 38.5, 39.7, 89.9, 179.4; IR ($CHCl_3$) : ν = 2965, 2875, 1765, 1605, 1495, 1215, 1160, 741, 438; MS (70 eV, EI) : m/z (%) = 198 (21) [M^+], 183 (31) [$C_{11}H_{19}O_2^+$], 155 (10) [$C_9H_{15}O_2^+$], 141 (22) [$C_8H_{13}O_2^+$], 99 (100) [$C_7H_{15}^+$], 84 (16) [$C_4H_4O_2$], 57 (20) [$C_4H_9^+$] , 43 (21) [$C_3H_7^+$] CI/NH_3 : m/z (%) = 191 (71) [MH^+], 216 (100) [MNH_4^+] ; HRMS calcd for $C_{12}H_{22}O_2$ [M^+] : 198.1614, found : 198.1614.

5-ethyl-4,5-dimethyl-2-tetrahydrofuranone (17): purification : pentane/ether : 80/20, yellow oil, yield : 98%. ^{1}H NMR: δ = 1.10 (t, J = 7.8 Hz, 3H), 1.20-1.47 (m, 8H) 2.12 (m, 1H), 2.43 (d, J = 7.9 Hz, 2H) ; ^{13}C NMR: δ = 13.8, 14.7, 22.2, 22.6, 23.5, 27.9, 69.4, 179.1; IR ($CHCl_3$) : ν = 2945, 2875, 1758, 1662, 1495, 1218, 1160, 938; MS (70 eV, EI) : m/z (%) = 142 (10) [M^+], 127 (48) [$C_7H_{11}O_2^+$], 113 (100) [$C_6H_9O_2^+$], 83 (26) [$C_4H_3O_2^+$]; CI/NH_3 : m/z (%) = 143 (68) [MH^+], 160 (100) [MNH_4^+] ; HRMS calcd for $C_8H_{14}O_2$ [M^+] : 142.099, found : 142.099.

1-ethyl-5-phenyl-2-pyrrolidinone (18): purification : pentane/ether : 80/20, yellow oil, yield : 90%. ^{1}H NMR: δ = 2.05 (t, J = 7.8 Hz, 3H), 2.35 (q, J = 7.8 Hz, 2H), 2.51 (m, 2H), 2.60 (m, 2H), 2.80 (t, J = 7.8 Hz, 1H), 7.24 (m, 5H) ; ^{13}C NMR: δ = 13.9, 18.1, 31.5, 36.7, 48.2, 114.1, 120.8, 129.5, 146.9, 178.7; IR ($CHCl_3$) : ν = 3008, 2965, 2940, 1680, 1605, 1495, 1466, 741, 438 ; MS (70 eV, EI) : m/z (%) = 165 (13) [M^+] , 150 (8) [$C_9H_{12}NO^+$] ,88 (100) [$C_6H_{10}NO^+$] , 77 (69) [$C_6H_5^+$] , 71 (20) [$C_4H_5NO^+$] , 56 (13) [$C_3H_4O^+$] , 51 (43) [$C_4H_3^+$] ; CI/NH_3 : m/z (%) = 166 (78) [MH^+], 183 (100) [MNH_4^+] ; HRMS calcd for $C_{10}H_{15}NO$ [M^+] : 165.1150, found : 165.1152.

1-isopropyl-5-phenyl-2-pyrrolidinone (19): purification : pentane/ether : 80/20, yellow oil, yield : 80%. ^{1}H NMR: δ = 1.20 (d, J = 7.8 Hz, 6H), 2.31-2.37 (sextuplet, J = 7.8 Hz, 1H), 2.49 (m, 2H), 2.62 (m, 2H), 2.82 (t, J = 7.8 Hz, 1H), 7.31 (m, 5H) ; ^{13}C NMR: δ = 14.0, 19.4, 31.5, 36.7, 48.7, 114.8, 120.8, 129.9, 148.2, 178.6; IR

($CHCl_3$) : ν = 3010, 2960, 2940, 1678, 1615, 1495, 1466, 740, 430 ; MS (70 eV, EI) : m/z (%) = 203 (10) [M^+] , 160 (56) [$C_{10}H_{10}NO^+$] , 126 (100) [$C_7H_{12}NO^+$] ,77 (41) [$C_6H_5^+$], 71 (15) [$C_4H_5NO^+$] , 56 (8) [$C_3H_4O^+$] , 43 (47) [$C_3H_7^+$] ; CI/NH_3 : m/z (%) = 204 (56) [MH^+], 221 (100) [MNH_4^+] ; HRMS calcd for $C_{13}H_{17}NO$ [M^+] : 203.1306, found : 203.1306.

1-cyclopentyl-5-phenyl-2-pyrrolidinone (20): purification : pentane/ether : 80/20, yellow oil, yield : 83%. ^1H NMR: δ = 0.98-1.90 (m, 8H), 2.38 (m, 2H), 2.54 (m, 2H), 2.80 (t, J = 7.8 Hz, 1H), 3.95 (quintuplet J = 7.8 Hz, 1H), 7.28 (m, 5H) ; ^{13}C NMR: δ = 25.0, 30.4, 32.1, 32.4, 36.4, 48.7, 115.1, 120.9, 130.2, 150.3, 176.7; IR ($CHCl_3$) : ν= 3015, 2960, 1685, 1600, 1467, 750, 428 ; MS (70 eV, EI) : m/z (%) = 229 (21) [M^+] , 160 (41) [$C_{10}H_{10}NO^+$] , 152 (100) [$C_9H_{14}NO^+$] ,77 (63) [$C_6H_5^+$], 69 (58) [$C_5H_9^+$] , 56 (10) [$C_3H_4O^+$] , 43 (12) [$C_3H_7^+$] ; CI/NH_3 : m/z (%) = 230 (51) [MH^+], 247 (100) [MNH_4^+] ; HRMS calcd for $C_{15}H_{19}NO$ [M^+] : 229.1462, found : 229.1464.

1-cycloheptyl-5-phenyl-2-pyrrolidinone (21): purification : pentane/ether : 80/20, yellow oil, yield : 70%. ^1H NMR: δ = 1.10-1.92 (m, 12H), 2.40 (m, 2H), 2.51 (m, 2H), 2.83 (t, J = 7.8 Hz, 1H), 4.01 (quintuplet, J = 7.8 Hz, 1H) , 7.24 (m, 5H) ; ^{13}C NMR: δ = 18.2, 24.6, 30.1, 32.4, 32.6, 36.8, 48.9, 115.0, 121.0, 130.1, 150.5, 177.0; IR ($CHCl_3$) : ν = 3008, 2960, 1681, 1605, 1467, 768, 421 ; MS (70 eV, EI) : m/z (%) = 257 (15) [M^+] , 160 (51) [$C_{10}H_{10}NO^+$] , 180 (100) [$C_{11}H_{18}NO^+$] ,93 (36) [$C_7H_{13}^+$], 77 (34) [$C_6H_5^+$] , 57 (15) [$C_4H_9^+$] , 43 (15) [$C_3H_7^+$] ; CI/NH_3 : m/z (%) = 258 (78) [MH^+], 275 (100) [MNH_4^+] ; HRMS calcd for $C_{17}H_{23}NO$ [M^+] : 257.1774, found : 257.1774.

1-pentyl-5-phenyl-2-pyrrolidinone (22): purification : pentane/ether : 80/20, yellow oil, yield : 77%. ^1H NMR: δ = 0.95 (t, J = 7.8 Hz, 3H), 1.30 (m, 6H), 2.30 (m, 2H), 2.31 (m, 2H), 2.79 (t, J = 7.8 Hz, 1H), 3.41 (t, J = 7.8 Hz, 2H) , 7.28 (m, 5H) ; ^{13}C NMR: δ = 18.1, 22.2, 26.3, 26.5, 28.5, 30.1, 32.0, 42.1, 46.5, 114.3, 120.5, 129.6, 146.8, 176.6; IR ($CHCl_3$) : ν = 3008, 2930, 1683, 1610, 1450, 741, 436 ; MS (70 eV, EI) : m/z (%) = 231 (11) [M^+] , 218 (21) [$C_{14}H_{18}NO^+$] , 190 (15) [$C_{12}H_{12}NO^+$] , 160 (48) [$C_{10}H_{10}NO^+$] , 154 (100) [$C_9H_{16}NO^+$] , 77 (31) [$C_6H_5^+$] , 57 (11) [$C_4H_9^+$] , 43 (8) [$C_3H_7^+$] ; CI/NH_3 : m/z (%) = 232 (62) [MH^+], 249 (100) [MNH_4^+] ; HRMS calcd for $C_{15}H_{21}NO$ [M^+] : 231.1618, found : 231.1618.

1-(1-naphthyl)-5-phenyl-2-pyrrolidinone (23): purification : pentane/ether : 80/20, yellow oil, yield : 93%. ^1H NMR: δ = 2.33 (m, 2H), 2.36 (d, J = 7.9 Hz, 2H), 2.81 (t, J = 7.8 Hz, 1H), 6.90-7.70 (m, 12H) ; ^{13}C NMR: δ = 20.9, 46.5, 52.4, 109.2, 117.4, 119.9, 120.1, 122.6, 125.9, 126.0, 127.2, 128.1,128.6, 128.9, 134.4, 141.4, 143.0, 174.7; IR ($CHCl_3$) : ν = 3015, 2980, 1685, 1595, 1461, 750, 426 ; MS (70 eV, EI) : m/z (%) = 287 (12) [M^+] , 210 (68) [$C_{13}H_{12}NO^+$] , 160 (100) [$C_{10}H_{10}NO^+$] , 127 (38) [$C_{10}H_7^+$] , 77 (28) [$C_7H_5^+$] , 71 (11) [$C_4H_5NO^+$] , 51 (28) [$C_4H_3^+$] ; CI/NH_3 : m/z (%) = 288 (65) [MH^+], 305 (100) [MNH_4^+] ; HRMS calcd for $C_{20}H_{17}NO$ [M^+] : 287.1306, found : 287.1306.

1-isopropyl-4-methyl-5-phenyl-2-pyrrolidinone (24): purification : pentane/ether : 80/20, yellow oil, yield : 87%. ^1H NMR: δ = 1.12 (d, J = 7.8 Hz, 3H) , 1.20 (d, J = 7.8 Hz, 6H) , 2.36 (sextuplet, J = 7.8 Hz, 1H) , 2.49 (m, 2H) , 2.61 (m, 1H) , 2.78 (m, 1H) , 7.28 (m, 5H) ; ^{13}C NMR: δ = 14.2, 15.1, 19.7, 33.8, 36.8, 49.4, 114.6, 121.0, 129.6, 146.1, 180.0; IR ($CHCl_3$) : ν= 3009, 2985, 1680, 1610, 1495, 760, 428 ; MS (70 eV, EI) : m/z

(%) = 217 (14) [M^+] , 202 (18) [$C_{13}H_{16}NO^+$] , 174 (41) [$C_{11}H_{12}NO^+$] , 140 (100) [$C_7H_{14}NO^+$] , 77 (51) [$C_7H_5^+$] , 56 (10) [$C_3H_4NO^+$] ; CI/NH_3 : m/z (%) = 218 (65) [MH^+], 235 (100) [MNH_4^+] ; HRMS calcd for $C_{14}H_{19}NO$ [M^+] : 217.1462, found : 217.1462.

***N, N'*-diisopropyl-1,2-diphenyl-1,2-ethanediamine (25):** purification : pentane/ether : 70/30, white crystals, yield : 95%. ^1H NMR: δ = 0.76-0.92 (m, 12H), 1.61 (s, 2H) , 2.44 (q, J = 7.8 Hz, 2H) , 3.65 (s, 1H) , 3.84 (s, 1H) , 6.95-7.21 (m, 10H) ; ^{13}C NMR: δ = 22.2, 22.3, 24.6, 24.8, 45.7, 46.4, 65.7, 126.9, 127.5, 128.1, 128.3, 128.4, 128.7, 141.6, 142.4; IR ($CHCl_3$) : ν = 3372, 3008, 2965, 2940, 1667, 1605, 1466, 1073, 1057, 1022, 741, 438 ; MS (70 eV, EI) : m/z (%) = 296 (23) [M^+] , 253 (41) [$C_{17}H_{11}N_2^+$] , 219 (28) [$C_{14}H_{23}N_2^+$] , 148 (100) [$C_{10}H_{14}N^+$] , 77 (58) [$C_6H_5^+$] , 43 (34) [$C_3H_7^+$] ; CI/NH_3 : m/z (%) = 297 (99) [MH^+], 314 (100) [MNH_4^+] ; HRMS calcd for $C_{20}H_{28}N_2$ [M^+] : 296.2246, found : 296.2246.

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