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A NEW ALKYLAMIDATION REACTION

REGIOSPECIFIC CONDENSATION OF CARBANIONS ON CYCLO 1,3-OXOIMMINIUM SALTS

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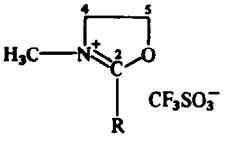
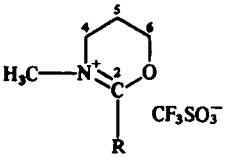
Abstract—Cyclo 1,3-oxoimminium salts are found to react regiospecifically with functional carbanions. Steric effects induced at the C-2 site on salts or at the carbanionic centers promote the condensation at the C-5 or C-6 opposite sites. A bulky substituent such as 2-mesityl group is a powerful auxiliary which not only modifies the steric environment at the reactive C-2 site but also contributes to enhance the reactivity of the cyclo oxoimminium ring.

Résumé—Les sels de cyclo-oxoimminium-1,3 réagissent régiospécifiquement avec les carbanions porteurs de groupes fonctionnels. Les condensations sur les sites C-5 et C-6 des sels sont obtenues par encombrements soit du site C-2 (le plus réactif) des sels III, IV, V, soit des carbanions. Le substituant mesityle introduit en position C-2 inhibe stériquement l'attaque sur ce site et contribue à accroître la réactivité des carbones C-5 et C-6 des sels d'iminoethers cycliques.

Amide groups are introduced by well known reactions which usually involve C—N bond formation.[1] We recently observed that alkylamidation can be easily performed by reaction of cyclo 1,3-oxoimminium salts with functional carbanions. In fact, these salts are known to display good electrophilic properties towards various heteronucleophiles.[2-7] Such condensations can be oriented at different sites on the salts depending on the nature of the nucleophiles, the structural parameters and the reaction conditions. Since the electrophilicity at the C-2 site on salts is higher, the condensation with carbanions needs to be forced at the less reactive C-5 and C-6 sites in order to promote the alkylamidation reaction.





I R=Phenyl
III R= Isopropyl
IV R= Mesityl

II R=Phenyl
V R= Mesityl

We have reported earlier that functional carbanions are able to condense either at C-2 or C-5 sites on cyclo 1,3-oxoimminium salts.[8,9]

This fact illustrates the ambident character of salt I towards carbanions. Among the factors which are likely to be efficient in controlling the nucleophilic attack is the inhibiting action of bulky groups placed either at the C-2 site on salts or at the nucleophilic centre. We are considering here these two aspects as tools to improve the regiospecific control of these condensations.

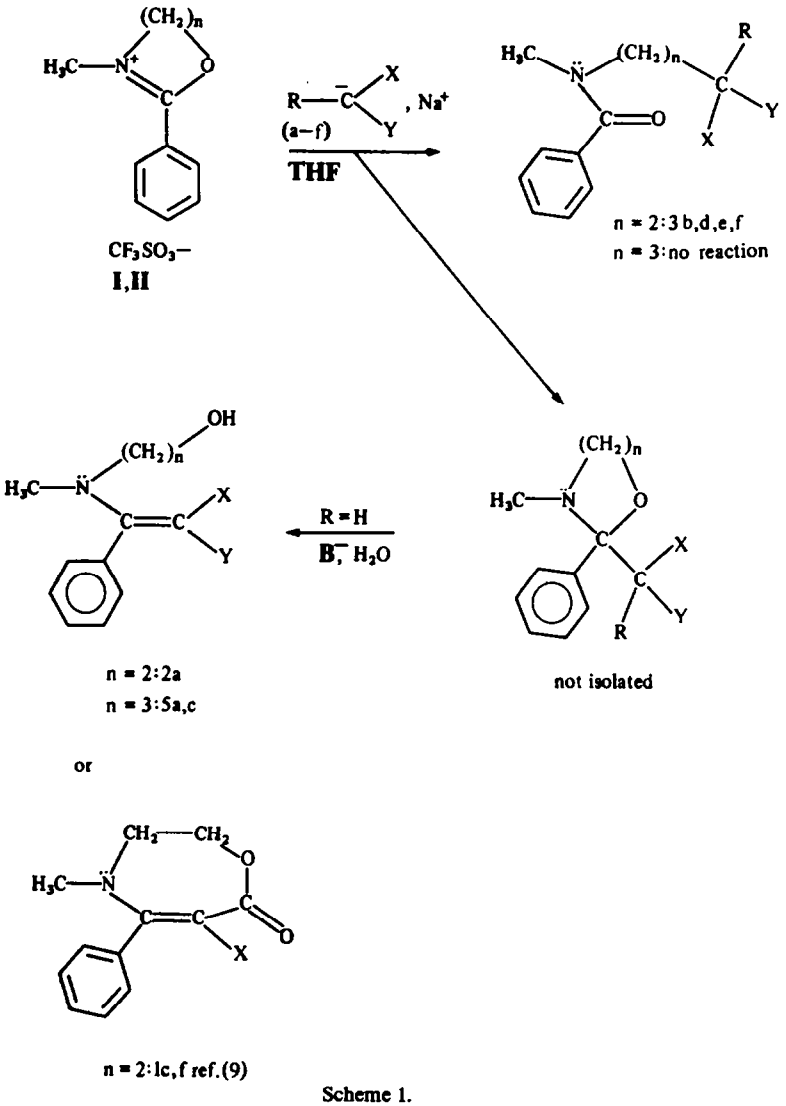
Reactions of hindered functional carbanionic nucleophiles on cyclo 1,3-*oxoimminium triflates* I *and* II

Various nucleophiles of type Na^+C^- (X, Y, R) [(a) X = Y = CN, R = H; (b) X = Y = CN, R = CH_3; (c) X = CN, Y = COOEt, R = H; (d) X = CN, Y = COOEt, R = CH_3; (e) X = Y = SO_2Ph, R = H; (f) X = Y = COOEt, R = H] were added to 2-alkyl or 2-aryl oxazolinium and 5,6-dihydro oxazinium triflates easily prepared from methyl triflate and cyclo 1,3-iminoethers.[9] The condensations of carbanions are readily obtained between room temperature and 50° in THF, and the resulting products are isolated by liquid chromatography. The products are those expected on the basis of the induced steric effects at the carbanionic centre (Scheme 1).

For example it was observed that secondary carbanions (a and c) react specifically at the C-2 site on 2-phenyl oxazolinium salt while the tertiary ones (b and d) condense at the C-5 site. Other examples are illustrated by carbanions (e) (100% of C-5 site condensation) and (f) which gives a C-5 : C-2 selectivity of 90 : 10.

Attempts to modify the sites of condensation by varying factors such as concentration of reactants and temperature and also by an inversion of the sense of the addition do not significantly affect the results. For the carbanions (f) and (c), it was clearly established that the reactions do not occur below + 10°, contrasting with the report of Kaloustian who has obtained a reversible addition below − 60° with heterosulfur nucleophiles.[6] Increasing the concentration of carbanions up to two equivalents decreases the global yield due to the sensitivity of the intermediates to the basic conditions of the medium but do not affect the selectivity.

With N-methyl 2-phenyl 5,6-dihydro oxazinium salt II, the C-2 addition is again observed exclusively with secondary functional carbanions (a and c), while the



Scheme 1.

carbanions (d, e and f) are found to be unreactive towards II whatever are the experimental conditions.

Such results might be explained by a weak electrophilic reactivity of the C-6 site and to a large activation energy demand to cleave the C—O bond in the oxazinium series.[2]

Reactions of functional carbanionic nucleophiles on hindered C-2 *cyclo* 1,3-*oxoimminium triflates* III, IV, V

The bulky (2-alkyl or 2-aryl) substituents have been introduced on cyclo 1,3-iminoethers as inhibiting auxiliar to allow the condensation of unsubstituted difunctional carbanions at the less electrophilic C-5 and C-6 positions.

With the N-*methyl* 2-*isopropyl oxazolinium triflate* III carbanions (c and f) give products in a 1 : 1 ratio from C- and O-alkylation in 30% yield. The products are isolated (**6c**, **7c**, **8f**, **9f**) by LC and are identified by IR, NMR and mass spectrum analysis as C-5-condensed products (Scheme 2). These results are in sharp contrast with other examples (2-nonyl and 2-methyl oxazolinium salts) where an exclusive C-2 addition is obtained.[9]

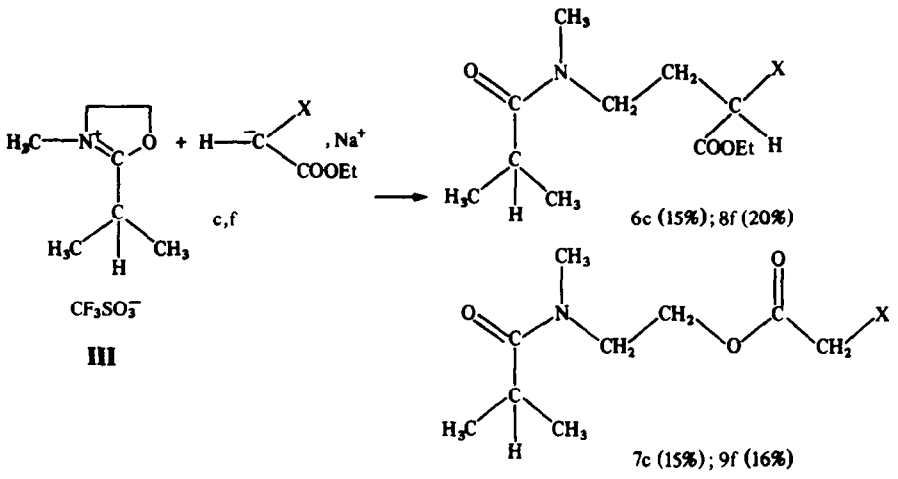
The observed reactivity of III towards carbanions (c and f) is unexpectedly low as compared to salt I. Since both C- and O-alkylation products are formed, the low reaction yield might be, in part, attributed to an hydrolytic cleavage of the ring-opened intermediates.

N-*methyl* 2-*mesityl cyclo* 1,3-*oxoimminium triflates* are then studied in the same way. They are prepared in good yields by cyclization of β-chloroethyl- (or γ-chloropropyl-) benzamides under basic conditions and efficiently transformed into the corresponding triflates IV ($n = 2$) and V ($n = 3$).

The condensations of functional carbanions (c, e, f) on IV and V are observed exclusively at the C-5 and C-6 sites as expected (Scheme 3).

Sodio ethylmalonate (f) and sodio ethylcyanoacetate (c) undergo fast and specific addition giving in good yields the compounds **11** and **12** as two stereoisomers in each case. For example the addition of sodio ethylcyanoacetate on V ($n = 3$) give **12c** as a mixture of two rotamers (i, ii) after purification by liquid chromatography.

Compound **12c** crystallizes in di-isopropylether as a single compound ($F_c = 90°$) as shown by ^{1}H-NMR which is the pure *syn*-rotamer having the N–Me group as a singlet at δ 2.76 (mesityl and N–Me are in *syn* position; see spectrum a). This compound slowly isomerizes at room temperature in various solvents



III

Scheme 2.

(CH_2Cl_2, $CHCl_3$, DMF, EtOAc) giving a mixture of the two rotamers (i and ii) as shown by ^{1}H-NMR: the N–Me group splits at 2.76 and 3.11 ppm while the CH_2 group to αN is pointed at 3.65 (i) and 3.13 ppm (ii) (see spectrum b).

The temperature of coalescence was determined in hexachlorobutadiene ($T_c = 160°$) and is in good agreement with the results described earlier by Mannschreck.[13]

Interestingly the 2-mesityl group induces a greater reactivity towards functional carbanions in contrast to the 2-phenyl group in the oxazinium series. For example, sodio *bis* (diphenyl sulfone) methane reacts efficiently with V, giving **12e** (as two rotamers i, ii in 3 : 1 ratio), but not with II.

No evident reason appears which can take into account the increase of reactivity of the C-5 and C-6 sites in IV and V, however a decrease in the C—O bond energy is probably implicated due to a deformation of the ring related to the steric hindrance of mesityl group.

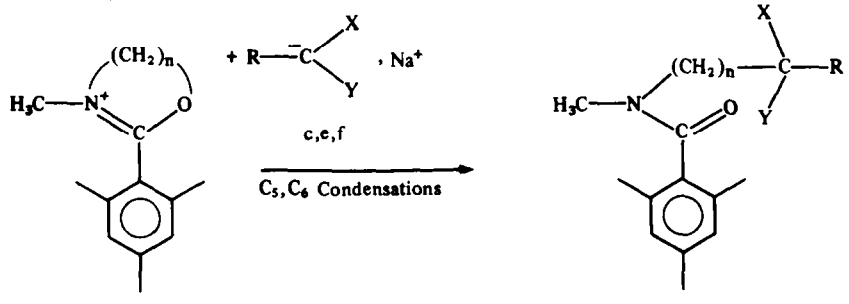
This analysis is supported by the striking differences between the ^{13}C-NMR chemical shifts of the neutral 2-aryl cyclo 1,3-iminoethers and the ones of their corresponding salts (Table 1). Particularly large deshielding effects are found in IV at C-4 and C-5 while the C-2 carbon is weakly affected, however such differences are not observed between II and V.

Although there is uncertainty about the correlation in literature between chemical shift displacements ($\Delta\delta$ ppm) and the charge density localization, a direct substituent effect on the magnetic susceptibility anisotropy is commonly observed with substituted benzenes.[12]

Since the C-2 position (α to benzene ring) is profoundly affected in IV but not in V, different spatial arrangements can be likely proposed as a source of this effect. Particularly in IV an orthogonal conformation of the oxazolinium ring with the 2-mesityl nucleus will minimize the steric effect but will inhibit the mesomeric charge stabilisation by the aromatic ring. Consequently the cationic character will be strongly increased at C-4 and C-5 in IV and at a lesser extent at C-4 and C-6 in V.

CONCLUSION

Specific alkylamidation reactions of functional carbanions are described by condensing the car-

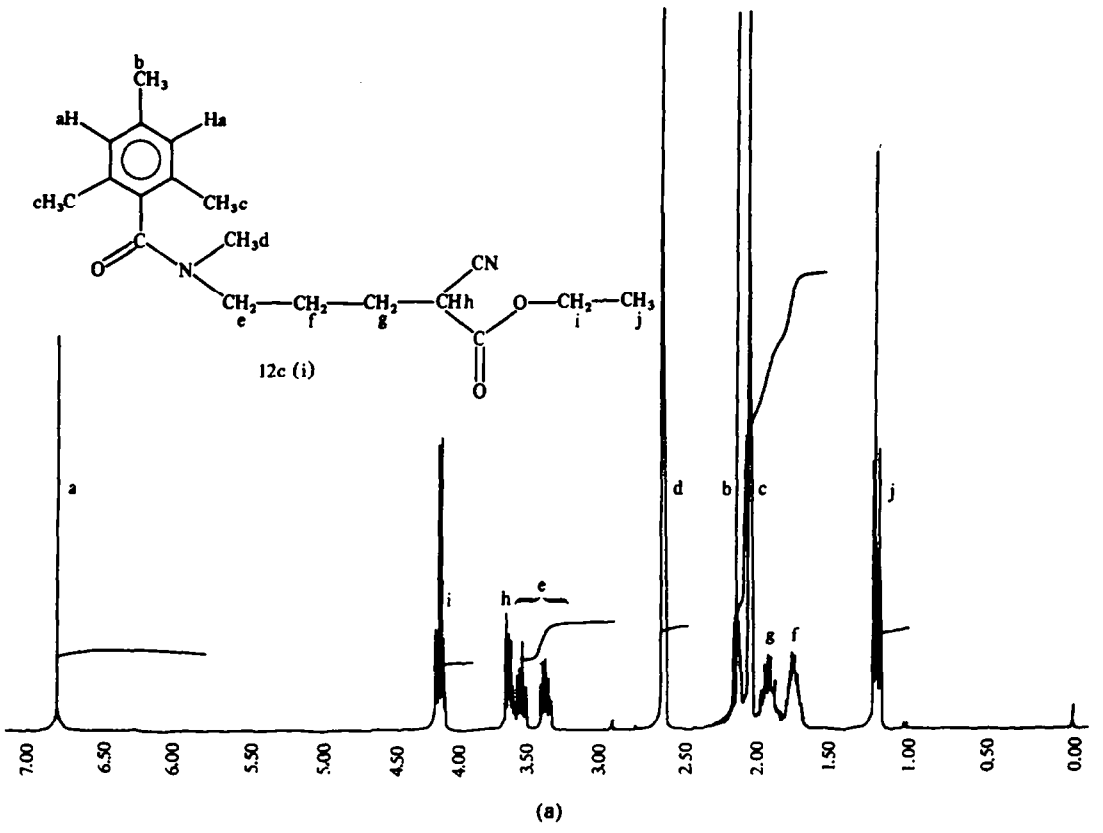


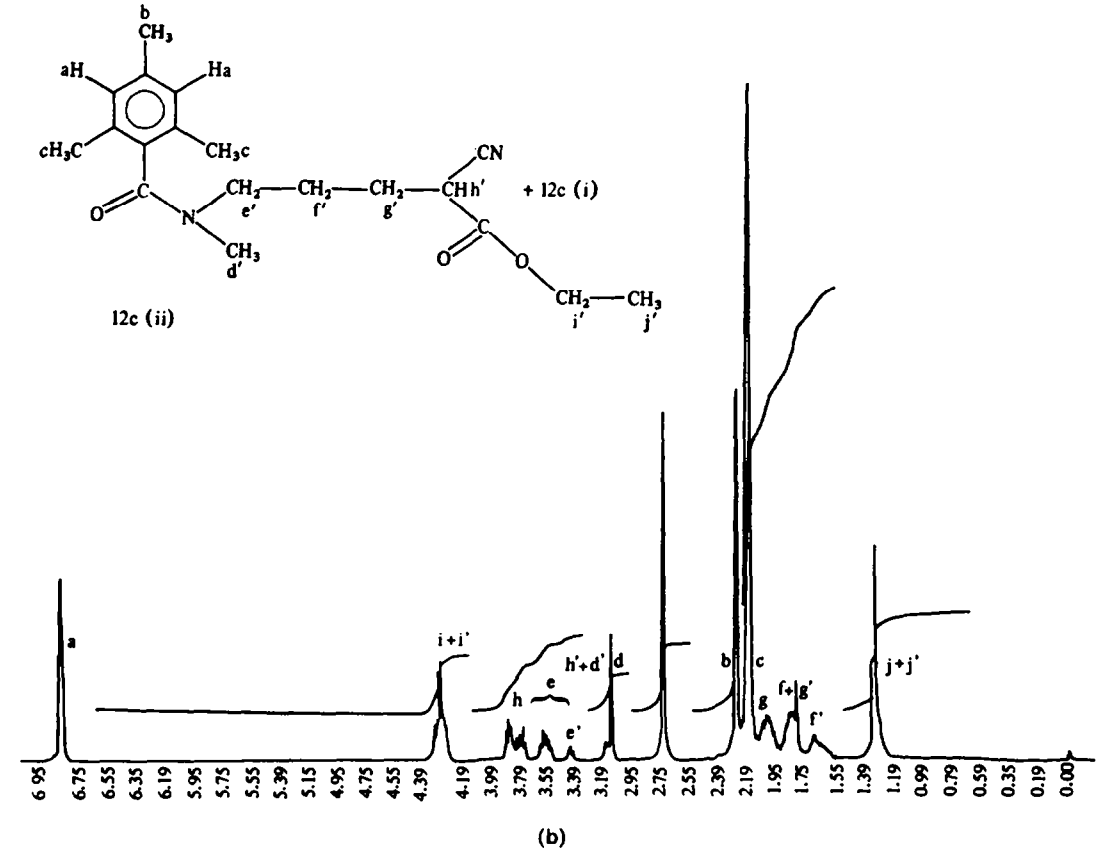
$CF_3SO_3^-$

IV (n = 2)
V (n = 3)

yield (%)	
11c	90
11f	80
12c	60
12f	91
12e	87

Scheme 3.





Spectrum 1.

Table 1. Deshielding effects on carbon atoms in cyclo 1,3-iminoethers and their salts (^{13}C-NMR)

Products	Δδ C-2	Δδ C-4	Δδ C-5 or C-6
2-Phenyl oxazoline; I	+8.3	−1	+3.8
2-Mesityl oxazoline; IV	*+4.5*	*+11.2*	*+29.3*
2-Phenyl oxazine; II	+16.4	+6.2	+4.9
2-Mesityl oxazine; V	+16.3	+5.85	+5.4

$\Delta\delta\ C_{(ppm)} = \delta C_{(salt)} - \delta C_{(neutral)}$; solvent CD_3CN.

banionic species onto cyclo 1,3-oxoimminium triflates. Regiospecific condensations at the less reactive sites are obtained by inducing steric effects either with bulky substituents at the C-2 position on salts or by the use of sterically hindered carbanions.

2-mesityl group onto cyclo 1,3-oxoimminium triflates is particularly efficient in controlling both the orientation of the condensation of the carbanions and the enhancement of reactivity at the C-5 and C-6 sites of the corresponding salts.

The chemical consequences attached to this substituent are: (i) an efficient reactivity of salt IV with all functional carbanionic species (a, c, e, f) giving rise to the corresponding alkylamides in good yields; (ii) a clear enhancement of reactivity of salt V which allows the condensations of functional carbanions at the C-6 site on V.

This new way to introduce alkylamide functionality (both ethyl- and propyl-alkylamides are obtained) might found various applications in synthesis since the reaction occurs by C—C bond process with two or three C units homologation. Extension of this type of reaction using other organometallic derivatives are under development.

EXPERIMENTAL

Products were purified by liquid column chromatography (Silica Gel Woelm TSC) and the yields calculated from the isolated fractions.

^{1}H-NMR spectra were recorded on Hitachi Perkin–Elmer R24 and Bruker WP80 CW usually in $CDCl_3$ with TMS as internal reference, and ^{13}C-NMR spectra on Bruker WP80 FT. Chemical shifts are given in ppm. IR spectra were recorded on Perkin–Elmer 297 (wave number in cm^{-1}). Mass spectra were obtained on a VG micromass 70–70. All melting points are given uncorrected. Elemental analyses were made at the Service Central d'Analyses (69390 Vernaison, France).

(A) *Preparation of oxazolines and 5,6-dihydro oxazines*

2-Phenyloxazoline and *2-phenyl-5,6-dihydro oxazine* have been previously described (ref. 9).

2-Isopropyl oxazoline is prepared by the conventional method.[9,14] Yield 65% (oil); Eb_{50} = 64° IR (neat): 1668 (N=C—O). ^{1}H-NMR: 1.2 (d, J = 6.5 Hz, 6H), 2.55 (sept., J = 6.5 Hz, 2H), 3.5–4.5 (m, 4H).

2-Mesityl oxazoline and 2-mesityl-5,6-dihydro oxazine. The synthesis is performed starting from β-chloro ethylamine and γ-chloropropylamine and mesitoyl chloride.

To a mixture of 10.4 g (0.057 mol) of mesitoyl chloride in 150 ml of anhyd benzene and 0.057 mol of the chlorhydrate of the amines was added cautiously 17.3 g (0.17 mol) of Et_3N in 50 ml benzene, in order to avoid temp change. After this the mixture was refluxed for 24 h then poured into cold water and extracted with benzene. The organic layers were washed with water and dried over Na_2SO_4, then concentrated. The crude oil (a mixture of 1,3-iminoethers and the corresponding uncyclized chloroamides) is dissolved in 100 ml of EtOH with 4 g of KOH dissolved in the minimum of water. This mixture is refluxed for 18 h then diluted with water. EtOH was stripped off in a rotary evaporator and the residue extracted twice with CH_2Cl_2. After washing with water the mixture was dried and concentrated.

2-Mesityloxazoline was crystallized from nonane (93% yield). F = 95° IR (KBr): 1660 (N=C—O), 1610–1575 (aryl); ^{1}H-NMR: 2.25 (s, 3H), 2.28 (s, 6H), 3.8–4.45 (m, 4H), 6.8 (s, 2H).

2-Mesityl-5,6-dihydro oxazine. Oil. Yield 80%. $Eb_{0.1}$ = 102°; IR (neat): 1670 (N=C—O), 1610–1575 (aryl); ^{1}H-NMR: 1.94 (q, J = 5.5 Hz, 2H), 2.25 (s, 3H), 2.28 (s, 6H), 3.5 (t, J = 5.5 Hz, 2H), 4.48 (t, J = 5.5 Hz, 2H), 6.75 (s, 2H).

(B) *Preparation of oxazolinium* (I, III, IV) *and 5,6-dihydro-oxazinium* (II, V) *triflate salts*

The general procedure has been reported.[9] Reacting 0.047 mol of methyl triflate and 0.05 mol of the cyclo 1,3-iminoethers in CH_2Cl_2 gave I–V. I and II are described (see ref. 9).

III (*2-Isopropyloxazolinium triflate*) is a deliquescent solid. IR (CCl_4): 1670 (N=C—O); 1030, 1270 (SO_3^-); ^{1}H-NMR: 1.2 (d, J = 7.5 Hz, 6H), 3.15 (hept, J = 7.5 Hz, 1H), 3.4 (s, 3H), 4–4.5 (m, 2H), 4.8–5.2 (m, 2H). $C_8H_{14}F_3NO_4S$ (277.26) [% calc (found): C, 34.66 (34.35); H, 5.09 (5.20); N, 5.05 (5.09); S, 11.56 (11.31); F, 20.56 (20.61)].

IV (*2-Mesityl oxazolinium triflate*) is a white solid crystallized from EtOAC. F = 134°; IR (KBr): 1668 (N=C—O), 1612–1580 (aryl), 1280–1260 and 1030. ^{1}H-NMR: 2.30 (s, 6H), 2.35 (s, 3H), 3.30 (s, 3H), 4.5–5.5 (m, 4H), 6.98 (s, 2H). $C_{14}H_{18}NO_4SF_3$ (353) [% calc (found): C, 47.59 (47.39); H, 5.10 (5.13); N, 3.97 (4.06); F, 16.15 (16.16); S, 9.06 (9.19).]

V (*2-Mesityl-5,6-dihydrooxazinium triflate*) is a white, low melting solid. IR (KBr): 1670 (N=C—O), 1610–1575 (aryl), 1270–1030 (SO_3^-). ^{1}H-NMR: 2.28 (s, 6H), 2.32 (s, 3H), 2.52 (m, 2H), 3.3 (s, 3H), 4.18 (t, J = 4.1 Hz, 2H), 4.90 (t, J = 4.7 Hz, 2H), 6.98 (s, 2H). $C_{15}H_{20}F_3NO_4S$ (367.4) [% calc (found): C, 49.04 (49.29); H, 5.49 (5.51); N, 3.81 (3.87); S, 8.73 (8.34); F, 15.51 (15.26)].

(C) *Condensation of 2-phenyl N-methyl oxazolinium triflate* I *with carbanions* a–f

3.1 g (0.01 mol) of I was dissolved in 30 ml of anhydrous THF and the soln was added to 1.3 equivalent of sodio carbanion generated *in situ*.[9]

After 24 hr under agitation, THF was slowly evaporated and the product extracted with diethyl ether, washed with water, dried over Na_2SO_4 and concentrated. It was then purified by liquid column chromatography on Silica Gel using an ether–pentane mixture as eluent.

Product identifications were achieved by IR, NMR and mass spectra. In some cases, microdistillations under reduced pressure were used to purify further viscous compounds.

Compound **2a**: *3-Methyl-3-aza-1,1-dicyano-2-phenyl-1-penten-5-ol.* Sodio malonotrile *a* reacts with I and leads to alcohol **2a** as a low melting solid. Compound **2a** turned out to be difficult to purify and is therefore converted into stable urethane with *p*-chlorophenyl isocyanate: yield 85% (white needles). F = 150°; IR (KBr): 3770 (NH), 2200–2190 (C=N), 1738 (COOR), 1583 (Ar). ^{1}H-NMR (acetone-d_6): 2.87 (s, 3H), 3.5 (m, 2H), 4.3 (m, 2H), 7.43 (m, 9H), 9.0 (m, 1H). MS: M^+ 380

and 382; 153 (100%). $C_{20}H_{17}N_4O_2Cl$ (380.83) [% calc (found): C, 63.08 (62.44); H, 4.50 (4.50); N, 14.71 (14.44)].

Compound **3b**: N-*Methyl*, N-(3,3-*dicyanobutyl*) *benzamide*. Yield 75%. Oil from microdistillation. $Eb_{0.05} = 150°$. IR (neat): 2250 (CN), 2200 (CN), 1634 (R—CON). ^{1}H-NMR: 1.8 (s, 3H), 2.27 (t, J = 7.5 Hz, 2H), 2.97 (s, 3H), 3.75 (t, J = 7.5 Hz, 2H), 7.35 (s, 5H). MS: M^+ 241; 105 (100%) for $C_{14}H_{15}N_3O$ = 241.3 g.

Compound **1c**: See ref. 9.

Compound **3d**: N-*Methyl*, N-(3-*carboethoxy*,3-*cyanobutyl*) *benzamide*. Yield 50%. Oil from liquid column chromatography. IR (neat: 2238 (CN), 1740 (COOR), 1635 (RNCO). ^{1}H-NMR: 1.23 (t, J = 7.5 Hz, 3H), 1.6 (s, 3H), 2.17 (m, 2H), 2.97 (s, 3H), 3.57 (m, 2H), 4.23 (q, J = 7.5 Hz, 2H), 7.40 (s, 5H). MS: M^+ 288; 105 (100%). $C_{16}H_{20}N_2O_3$ (288.35) [% calc (found): C, 66.65 (65.92); H, 6.99 (6.97); N, 9.71 (9.70); O, 16.65 (16.63)].

Compound **3e**: N-*Methyl* N-(3,3-*diphenylsulfone propyl*) *benzamide*. Yield 85%; yellow crystals from EtOH. F = 154°; IR (KBr): 1632 (RNCO), 1322, 1163–1148 (SO_2). ^{1}H NMR: 2.57 (m, 2H), 2.87 (s, 3H), 3.73 (t, J = 6 Hz, 2H); 5.33 (m, 1H), 7.40 (s, 5H), 7.47–8.03 (m, 10H). MS: M^+ 457; 105 (100%). $C_{23}H_{23}NO_5S_2$ (457.56) [% calc (found): C, 60.37 (60.34); H, 5.07 (4.95); N, 3.06 (3.04); O, 17.48 (17.58); S, 14.01 (13.53).

Compound **1f**: See refs 8, 9.

Compound **3f**: N-*Methyl*, N-(3,3 *dicarboethoxypropyl*) *benzamide*. Yield 63%. Oil from column liquid chromatography. IR (neat): 1745–1738 (COOR), 1635 (RNCO). ^{1}H-NMR: 1.20 (t, J = 7.5 Hz, 6H), 2.2 (m, 2H), 3.05 (s, 3H), 3.5 (m, 3H), 4.22 (q, J = 7.5 Hz, 4H), 7.52 (s, 5H). MS: M^+ 321; 105 (100%). $C_{17}H_{23}NO_5$ (321.37) [% calc (found): C, 63.55 (63.81); H, 7.16 (7.18); N, 4.36 (4.24); O, 24.92 (24.86)].

Besides **3f** and **1f**, 30% of the dialkylated product, *bis*[2-(methylbenzamido)ethyl] diethyl malonate is isolated. $Eb_{0.001} = 190°$. ^{1}H-NMR: 1.2 (t, J = 7.5 Hz, 6H), 2.2 (m, 4H), 3.05 (s, 6H), 3.47 (m, 4H), 4.13 (m, 4H), 7.40 (s, 10H). MS: M^+ 482; 105 (100%).

(D) *Condensation of* 2-*phenyl*-N-*methyl*-5,6-*dihydrooxazinium triflate* II *with carbanions* a, c–f

Standard conditions are described as in case of salt I. Sodio ethylcyanoacetate reacts with II and gives **5c**.[9] Sodio malonoitrile reacts with II and gives exclusively **5a**.

Compound **5a**: 3-*Methyl*-3-*aza*-1,1-*dicyano*-2-*phenyl*-1-*hexene*-6-*ol*. Yellow oil from liquid column chromatography. Yield 90% IR (neat): 3475 (OH), 2198–2205 (CN), 1560 (C=C). ^{1}H-NMR: 1.5–2.2 (m, 2H), 2.55 (s, 1H), 2.7–4.2 (m, 7H), 7.4–7.9 (m, 5H).

This alcohol is further reacted with *p*-chlorophenyl isocyanate and gives the corresponding urethane: F = 178°; MS: M^+ 394; 153 (100%).

Carbanions d, e, f are unreactive towards II: starting materials are recovered and salt II gives the hydrolytic cleavage product N-methyl-N-3-(hydroxypropyl) benzamide and the corresponding amino-ester isomer.

(E) *Condensation of* 2-*isopropyl*-N-*methyloxazolinium triflate* III *with carbanions* c *and* f

Standard conditions are as described in case of salt I. Sodio ethyl cyanacetate *c* reacts with III giving rise to a mixture of products which are obtained by liquid column chromatography.

Two main products are isolated and characterized:

Compound **6c**: N-*Methyl*, N-(3-*cyano*,3-*carboethoxypropyl*) *isobutyramide*. Yield 15%. Oil from liquid column chromatography. IR (neat): 2255 (CN), 1745 (COOEt), 1640 (RNCO). ^{1}H-NMR: 1.25 (d, J = 7 Hz, 6H), 1.47 (t, J = 5 Hz, 3H), 2.37 (q, J = 7 Hz, 2H), 3.2 (m, 1H), 3.37 (s, 3H), 3.73–4.13 (m, 3H), 4.63 (q, J = 5 Hz, 2H). MS: M^+ 240; 43 (100%) ($C_{12}H_{20}N_2O_3$ = 240.3 g).

Compound **7c**: N-*Methyl*, N-(2-*cyanacetato ethyl*) *isobutyramide*. Yield 15%. Oil from liquid column chromatography. IR (neat): 2255 (CN), 1735 ($OCOCH_2$), 1645 (RNCO). ^{1}H-NMR: 1.2 (d, J = 7 Hz, 6H), 3.15 (sept, J = 7 Hz, 1H), 3.37 (s, 3H), 3.83 (s, 2H), 3.93 (t, J = 5 Hz, 2H), 4.67 (t, J = 5 Hz). MS: M^+ 212.9; 44 (100%) ($C_{12}H_{16}N_2O_3$ = 212.25).

Sodio diethylmalonate *f* reacts with III and gives two isolated products.

Compound **8f**: N-*Methyl*, N-(3,3-*dicarboethoxypropyl*) *isobutyramide*. Yield 20%. Oil from liquid column chromatography. IR (neat): 1750, 1733 (COOR), 1648 (RNCO). ^{1}H-NMR: 1.04–1.37 (m, 12H), 2.08 (q, J = 7 Hz, 2H), 2.9 (sept, J = 7 Hz, 1H), 3.00 (s, 3H), 3.2–3.5 (m, 3H), 4.2 (q, J = 7 Hz, 4H). MS: M^+ 287; 43 (100%) ($C_{14}H_{25}NO_5$ = 287.35 g).

Compound **9f**: N-*Methyl*,N-(2-*carboethoxyacetatoethyl*) *isobutyramide*. Yield 16%. Oil from liquid column chromatography. IR (neat): 1754, 1739 (RCOO), 1647 (RNCO). ^{1}H-NMR: 1.05–1.4 (m, 9H), 2.93 (sept, J = 7 Hz, 1H), 3.07 (s, 3H), 3.33 (s, 2H), 3.6 (t, J = 5.5 Hz, 2H), 4.17 (q, J = 7 Hz, 2H), 4.27 (t, J = 5 Hz, 2H). MS: M^+ 259; 43 (100%) ($C_{12}H_{21}NO_5$ = 259.3 g).

(F) *Condensation of* 2-*mesityl*-N-*methyl*-1,3-*oxazolinium triflate* IV *with carbanions* c *and* f

Standard conditions are used as described for salt I. Sodio ethylcyanoacetate *c* reacts with IV and gives exclusively **11c**.

Compound **11c**: N-*Methyl*, N-(3-*cyano*,3-*carboethoxypropyl*) *mesityl amide*. Yield 80%. Oil. $Eb_{0.05}$: 150°; IR (neat): 2242 (CN), 1745 (COOR), 1630 (RNCO). ^{1}H-NMR: 1.25 (t, J = 7 Hz, 3H), 1.8–2.05 (m, 2H), 2.05 (s, 6H), 2.17 (s, 3H), 2.65 and 2.95 (2s, 3H), 2.80–3.70 (m, 3H), 4.13 (q, J = 7 Hz, 2H), 6.70 (s, 2H). MS: M^+ 316; 147 (100%). $C_{18}H_{24}N_2O_3$ (316.4) [% calc (found): C, 68.33 (68.23); H, 7.65 (7.68); N, 8.85 (8.90).

Socio diethylmalonate *f* reacts with IV and gives:

Compound **11f**: N-*Methyl*, N-(3,3-*dicarboethoxypropyl*) *mesityl amide*. Yield 90%. Oil from column liquid chromatography. IR (neat): 1735–1750 (COOR), 1640 (RNCO), 1580–1615 (aryl). ^{1}H-NMR: 1.26 (t, J = 7 Hz, 6H), 1.5–2.2 (m, 4H), 2.2 (s, 6H), 2.26 (s, 3H), 2.75 and 3.20 (2s, 3H), 3–3.75 (m, 3H), 4.20 (q, J = 7 Hz, 4H), 6.8 (s, 2H). MS: M^+ 363; 147 (100%). $C_{20}H_{29}NO_5$ (363.45) [calc (found): C, 66.09 (65.90); H, 8.04 (8.34); N, 3.85 (3.78); O, 22.01 (22.34)].

(G) *Condensation of* 2-*mesityl*-N-*methyl*-5,6-*dihydro* 1,3-*oxazinium triflate* V *with carbanions* c, e, *and* f

Sodio ethylcyanoacetate *c* reacts with V and gives **12c**.

Compound **12c**: N-*Methyl*,N-(4-*cyano*,4-*carboethoxybutyl*) *mesityl amide* (*pure isomer*). Yield 60%. White crystals from di-isopropyl ether. F = 90°; IR (KBr): 2240 (CN), 1745 (COOR), 1630 (RNCO), 1575–1610 (aryl). ^{1}H-NMR (350 (MHz-CAMECA): 1.32 (t, J = 7.3 Hz, 3H), 1.84–1.95 (m, 2H), 2.03–2.15 (m, 2H), 2.19 (s, 6H), 2.27 (s, 3H), 2.76 (s, 3H), 3.69–3.77 and 3.52–3.60 (2m, 2H), 3.78–3.83 (m, 1H), 4.27 (q, J = 7.3 Hz, 2H), 6.84 (s, 2H). MS: M^+ 330; 147 (100%). $C_{19}H_{26}N_2O_3$ (330.4) [calc % (found): C, 69.06 (69.00); H, 7.93 (7.95); N, 8.48 (8.45); O, 14.53 (14.83).

Sodio diethylmalonate reacts with V and gives **12f**.

Compound **12f**: N-*Methyl*,N-(4,4-*dicarboethoxybutyl*) *mesityl amide*. Yield 91%. Oil from liquid column chromatography. IR (neat): 1730 (COOR), 1635 (RNCO), 1612–1578 (aryl). ^{1}H-NMR: 1.25 (t, J = 7 Hz, 6H), 2–2.2 (m, 4H), 2.2 (s, 6H), 2.3 (s, 3H), 2.75 and 3.05 (2s, 3H), 3.05–3.75 (m, 3H), 4.22 (q, J = 7 Hz, 4H), 6.80 (s, 2H). MS: M^+ 377; 147 (100%). $C_{21}H_{31}NO_5$ (377.48) [% calc (found): C, 66.82 (66.23); H, 8.28 (8.23); N, 3.71 (3.75); O, 21.19 (20.92).

Sodio *bis* (diphenylsulfone) methane *e* reacts with V and gives **12e**.

Compound **12e**: N-*Methyl*, N-(4,4-*diphenylsulfonebutyl*) *mesityl amide*. Yield 87%. Low melting solid from liquid column chromatography. IR (neat): 1630 (RNCO), 1615–1585 (aryl), 1330–1150 (SO_2). ^{1}H-NMR: 1.8–2.2 (m, 2H), 2.2 (s, 6H), 2.27 (s, 3H), 2.75 and 3.05 (2s, 3H), 3.0 and 3.55 (2t, J = 6 Hz, 2H), 4.27 and 4.95 (2t, J = 5.5 Hz, 1H), 6.85 (s, 2H), 7.4–8 (m, 10H). MS: M^+ 513; 147 (100%) ($C_{27}H_{31}NO_5S_2$ = 513.66).

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