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TETRAHEDRON

A Novel Synthesis of Functionalized Aldehyde Equivalents Through Addition of Carbanions on Δ^2-Oxazolinium Cations[1].

Kamaljit Singh*, Jasbir Singh and Harjit Singh*

Department of Chemistry and Department of Applied Chemical Sciences and Technology,
Guru Nanak Dev University Amritsar, 143 005, India.

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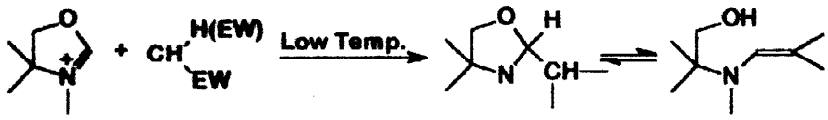
Abstract: Bis- and mono carbanions add at C-2 of Δ^2-oxazolinium cations to furnish novel oxazolidines existing mainly as their unprecedented enamine chain tautomers. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

2-Substituted oxazolidines represent one of the most versatile protecting groups for carbonyl substrates[2], and are most commonly obtained by reduction of corresponding 2-oxazolines[2e] obtained from the corresponding carboxylic acids[3] or nitriles[3] in modest to good yields. A plethora of reports[2a,3,4] are available on homologations through metalation of C-2 alkyl/aryl substituted oxazolines and their subsequent reduction to oxazolidines. In our efforts to develop a more general method for preparation of novel 2-substituted oxazolidines, we sought to employ, transformation of carboxylic acids to elaborated and functionalised carbonyl equivalents - an important methodology in organic synthesis through C-2 elaboration of the easily accessible 3,4,4-trimethyl-Δ^2-oxazolinium iodide by addition of functionalized carbanions – an operation beneficially used in procuring imidazolidines[5]. Such a straightforward procedure would be of pre-eminent interest both in view of the limitations of reported carbanion induced C-2 elaborations of **1c**[6] and its synthetic



Scheme 1

potential in making available vulnerable and variously functionalised aldehyde equivalents. We have found that additions of carbanions proceed at –40°C to –78°C and provide mainly unique functionalised aldehyde enamine chain tautomers (Scheme-1)[1].

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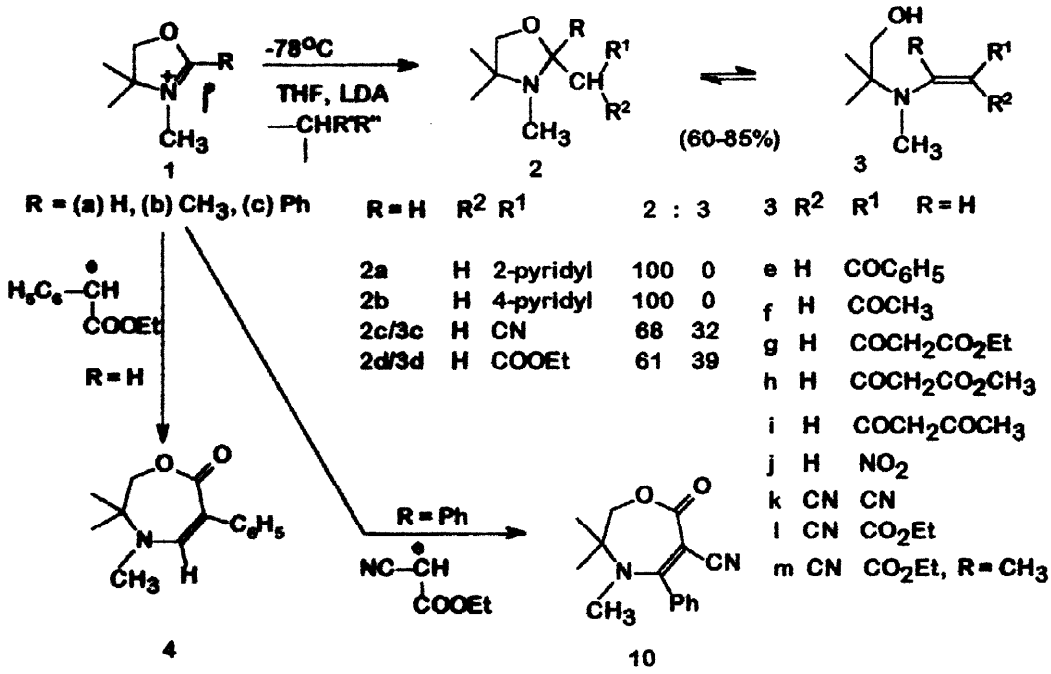
RESULTS AND DISCUSSION

Controlled addition of solid 3,4,4-trimethyl-Δ^2-oxazolinium iodide **1a** under a blanket of dry nitrogen at



-78°C to a pregenerated anion of α–picoline in anhydrous THF followed by stirring for 0.5 hr. (-40°C) and at room temperature for 2 hr. upon workup furnishes oxazolidine **2a**. Similar reaction of **1a** with the anion of γ-picoline generated at -78°C with LDA furnishes oxazolidine **2b**[7]. Reaction of anion of acetonitrile (generated with LDA at -78°C) with **1a** run at -78°C to -40°C (0.5 hr.) followed by stirring at ambient temperature for 2 hr. furnishes a product which is a liquid mixture of two components as visualized by TLC [Rf = 0.2 and 0.8 (ethyl acetate : hexane :: 8 : 1)]. These components could not be separated by flash chromatography or even by preparative TLC and were charaterized as **2c** and **3c** in the ratio 68:32[8]. When the ^{1}H NMR spectrum of the **2c/3c** mixture was recorded in $(CD_3)_2SO$ (ambient temperature or at 70°C) complete transformation of **2c** to **3c** was observed. This conversion could be induced by stabilisation of **3c** by hydrogen bonding between the electronegative O of $(CD_3)_2SO$ and the OH of the acyclic enamine form and/or by the acidity of methylene proton at C-2 which could get deprotonated by DMSO and the anion is stabilized as **3c**[9]. The reaction of anion of ethyl acetate (LDA, -78°C) with **1a** performed at -78°C, after workup, gives a product mixture (TLC). On flash chromatography one fraction [Rf = 0.2, (ethyl acetate : hexane :: 8 : 1)], was isolated as pure **3d**. Another fraction [Rf = 0.8 (ethyl acetate : hexane :: 8:1)] depicts two fused non-separable components and its ^{1}H NMR spectrum (vide experimental) signals correspond to both the ring and chain tautomeric forms (**2d** : **3d** :: 61 : 39). Presumably, the cyclic structure **2d** in solution equilibrates to the stable acyclic isomer **3d**.

Thus, whereas the adducts of oxazolinium cation **1a** and carbanions derived from picolines exist entirely

as oxazolidines, the analogous adducts of **1a** and carbanions of acetonitrile/ethyl acetate constitute a mixture of ring - chain tautomers. It may be argued that a combination of extended conjugation and planar structures of the enamine tautomers in the latter cases possessing carbethoxy and nitrile groups may be responsible for their existence as open chain enamines. Further, the presence of strong electron withdrawing groups at α-carbon of 2-substituted oxazolidine viz. CN and COOEt, enhances the acidic character of the hydrogen attached to the α-carbon. Thus, ease of deprotonation of α-CH may induce ring opening and formation of enamine - chain tautomer in the mixture. In compounds **2a** and **2b**, steric hindrance to deprotonation and possible non-planarity of the carbanion system due to orthogonal disposition of pyridine ring, might not be invoking enamine formation and hence **2a** and **2b** exist entirely in oxazolidine form.

In order to determine the effect of the similarly placed carbonyl group, on ring - chain tautomerism in oxazolidines, we have performed addition reactions of mono - carbanions derived from acetophenone and acetone and of bis - carbanions derived from ethyl acetoacetate, methyl acetoacetate and 2,4-pentanedione with **1a**. In the latter cases, the enamine structures of the products would be further conjugated through enolic structures in the appendages and these compounds should exist solely as enamine - chain tautomers.

The anion of acetophenone, generated at -78°C with LDA, upon reaction with **1a** resulted in the formation of **3e**. This adduct exists only as open chain enamine tautomer (^{1}H NMR). The anion derived from acetone under similar conditions furnished the adduct **3f**. Addition of **1a** to the pre-generated bis-anion of ethyl acetoacetate or methyl acetoacetate (i NaH, 0°C; ii n-BuLi, 0°C)[10] at -78°C resulted in the formation of enamine chain tautomers **3g** and **3h** respectively. The bis-anion of 2,4-pentanedione generated under similar set of conditions with **1a** at -78°C furnished open chain tautomer **3i**[11]. Similarly addition of **1a** to the anion derived from nitromethane (-78°C, LDA) at -78°C furnished **3j**.

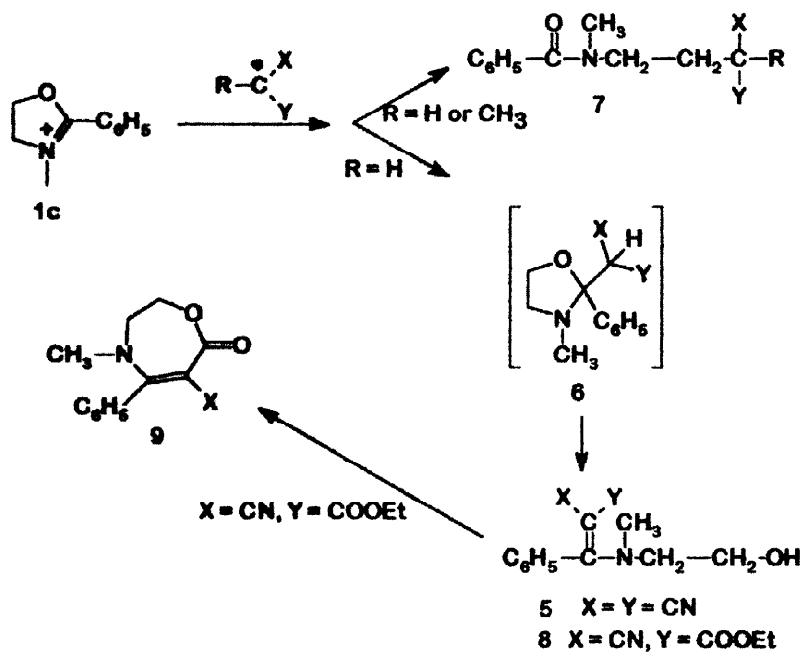
The anion of active methylene compounds viz. malononitrile (-78°C/LDA or 10°C/NaH) and ethyl cyanoacetate (10°C/NaH) reacted with **1a** to furnish **3k** and **3l** respectively. The reaction of carbanion derived from carbon acids such as toluene, o-toulic acid methyl ester, 2,4,4-trimethyl oxazoline and 2,4,4,6-tetramethyl-5,6-dihydro-(4H)-1,3-oxazine with **1a** under variety of reaction conditions[12] met with failure.

The reactivity pattern of the carbanions of these carbon acids with 3,4,4-trimethyl-Δ^2-oxazolinium cation can be correlated with the pK_a values[13] of precursor carbon acids. Thus, methyl acetoacetate (pK_a = 10.0), ethyl acetoacetate (pK_a = 10.6), 2,4-pentanedione (pK_a = 9.0), acetophenone (pK_a = 24.7), acetone (pK_a = 20.0), malononitrile (pK_a = 31.3), ethyl acetate (pK_a = 24.5), nitromethane (pK_a = 17.2), 2-methyl pyridine (pK_a = 29.5), ethyl cynoacetate ($pK_a \leq 9.0$) and acetonitrile (pK_a = 11.1) form carbanions which behave as nucleophiles and add smoothly at C-2 of oxazolinium cation to provide corresponding oxazolidine derivatives or acyclic tautomers. Whereas, mono-anions/bis - anions derived from weak acids i.e. toluene (pK_a = 41), 2-methyl oxazine, 2-methyl oxazoline and o-toluic acid/methyl ester behave as bases and induce

reactions other than nucleophilic addition at C-2 of **1**.

It was envisaged that the presence of an electron withdrawing group in the CH_3 of toluene might induce nucleophilicity in the derived anion. Thus, a reaction of the anion of ethyl phenyl acetate with **1a** at -78°C proceeded smoothly to provide a product which could be assigned structure **4**. The formation of **4** may be envisaged by addition of anion of ethyl phenyl acetate at C-2 of **1a** to furnish the intermediate adduct **3** (R = H, R^1 = COOEt, R^2 = C_6H_5) which could undergo the subsequent cyclization to furnish the lactone ring.

In contrast to reactions of **1a** which is unsubstituted at C-2, the reaction of carbanion of malononitrile with 2-phenyl-3-methyl-Δ^2-oxazolinium cation **1c** performed at room temperature to +50°C, provides[6] 3-methyl-3-aza-1,1-dicyano-2-phenyl-1-penten-5-ol (**5**; X = Y = CN) by the attack at C-2 followed by ring opening of the intermediate oxazolidine (**6**; X = Y = CN). However, similar reaction of 1,1-dicyanoethane furnishes N-methyl-N-(3,3-dicyanobutyl)benzamide (7; R = Me, X = Y = CN) by its attack at C-5 of **1c**. The



carbanion of ethyl cyanoacetate has been added on **1c** at room temperature to furnish 5-phenyl-6-cyano-2,3-dihydro-1,4-oxazepine-7-one **9** (X = CN), evidently through the cyclization of initially formed intermediate **8**. The addition of carbanion of ethyl 2-cyanopropionate on **1c** gives **7** (R = Me, X = CN, Y = COOEt). These reactions of **1c** do not take place at temperature below +10°C.

In view of these reports on indiscriminate mode of reactions in case of **1c**, we have studied reactions of C-2 substituted oxazolinium cations. The reaction of anion of ethyl cyanoacetate with **1b** (R=CH_3) at room temperature resulted in the formation of **3m**. In contrast to the reactions of anion of ethyl cyanoacetate with

1a and 1b, the reaction with **1c** at 50°C leads to the formation of oxazepine **10**. Here too probably the initially formed **3** (R = C_6H_5, R^1 = COOEt, R^2 = CN) undergoes cyclization at ester moiety to form **10**. The formation of **10** only in the latter case points to the role of bulky C-2 phenyl group in effecting cyclization of **3** (R = Ph) to **10**. However, at low temperature both **1b** and **1c** fail to react with the anions of ethyl cyanoacetate, acetophenone, ethyl acetate and acetonitrile.

Thus, we find that anions of carbon acids which have pK_a values higher than 40 behave as bases and do not undergo nucleophilic additions at C-2 of **1**. The substituents at C-2 of oxazolinium cation play a dominant role in determining the regio-specificity of the reaction and thus the nature of the product.

Acknowledgements The authors thank CSIR, New Delhi for financial assistance.

EXPERIMENTAL

General experimental details are given in reference 14.

Oxazolinium salts, **1a-c** were prepared from corresponding oxazolines as reported in literature[15,16]. All solvents CH_3CN (P_2O_5), THF (sodium benzophenone ketyl), acetone (P_2O_5), hexane (sodium wire), ethyl acetate (acetic anhydride/H_2SO_4) were dried and distilled before use. All reactions were run under an atmosphere of nitrogen which was purified over BASF catalyst and dried by passing over fused calcium chloride, potassium hydroxide and molecular sieves (4Å) respectively. Commercial NaH (50% in mineral oil) was adequately washed with anhydrous hexane prior to use. n-BuLi was prepared in anhydrous hexane and was standardized volumetrically.

(A) Generation of dianions[10]: In a typical procedure dry THF (25 ml) was distilled directly from sodium-benzophenone ketyl into a round bottomed flask (100 ml capacity), containing sodium hydride (50% in mineral oil, 0.2g, 0.92 mol) pre - washed with anhydrous hexane and dried. The flask was stoppered with a septum cap (Aldrich), flushed with nitrogen and cooled in ice. Methyl acetoacetate (0.51ml, 0.52g ,4.42 mmol) was added dropwise and the colorless solution was stirred (10 min.) at 0°C. To this solution, n-BuLi (1.85 ml, 2.2 M solution in hexane) was added drop wise and the yellow to orange colored solution of the bis-anion was stirred for additional time (10 min.) at 0°C before use. Following the same procedure bis - anions of ethyl acetoacetate and 2,4-pentanedione were also prepared.

(B) Generation of monoanions: To a solution of diisopropylamine (0.58 ml, 0.42g, 4.42 mmol) in THF (2ml) was added n- BuLi (1.85 ml, 2.2 M) dropwise at -78°C, under nitrogen atmosphere. The solution was allowed to warm to (0°C) and stirred for additional time (10 min.). The solution was cooled (-78°C) and addition of pre - cooled THF (25 ml) was made with stirring. The appropriate carbon acid e.g. acetonitrile, acetone, acetophenone, nitromethane, malononitrile, ethyl cyanoacetate, ethyl phenyl acetate (4.42 mmol)

was then added with the help of a hypodermic glass syringe through the septum cap (Aldrich). The solution was stirred for additional time (10 min.) at the same temperature before use.

(C) Generation of anions of active methylene compounds with sodium hydride : Anhydrous THF (35 ml) was distilled in a round bottomed flask containing sodium hydride (50% in mineral oil, 0.2g, (0.92 mmol) previously washed with anhydrous hexane and dried. It was cooled to 10°C and a solution of active methylene compound (4.42 mmol) in dry THF (15 ml) was added to it dropwise. The solution was warmed slowly to 50°C and stirred for additional time (30 min.) at the same temperature before use.

(D) Reactions of oxazolinium cations with bis-anions/ mono- anions : Appropriate oxazolinium cation (1g, 4.42 mmol) was weighed rapidly and placed in a L shaped solid addition glass assembly which was rapidly fitted to one neck of the flask to be used for generating mono - anion or bis - anion (4.42 mmol) by the above procedures (A, B or C) and the oxazolinium salt was added to the stirred solution slowly in portions. After the reaction was completed, the reaction mixture was treated with saturated aqueous solution of ammonium chloride (25 ml). and was extracted with ethyl acetate (2x50ml). The extract was dried (anhydrous sodium sulphate). Solvent was removed and the residue was chromatographed using hexane, chloroform, ethyl acetate and their mixtures as eluents.

Using the procedure "D" the following compounds were synthesized.

Adduct (2a) : Yield 78%; Yellow liquid[17], IR ($CHCl_3$) ν : 2974, 1620, 1593, 1084 cm^{-1}; ^1H NMR ($CDCl_3$) δ : 0.95 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 2.35 (s, 3H, N-CH_3), 2.68 and 2.86 (ABX splitting, J_{AB} = 13 Hz, J_{AX} = 7 Hz, J_{BX} = 2 Hz, 2H, CH_2), 3.56 and 3.58 (deformed AB quartet, 2H, OCH_2), 4.39-4.45 (dd, J = 7 Hz, 2 Hz, 1H, CH), 7.06-7.61 (m, 3H, ArH), 8.50-8.53 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$) δ : 16.86, 23.52, 29.80, 43.51, 77.41, 94.83, 118.72, 120.77, 124.07, 135.42, 148.61, 158.08; MS *m/z* : 206 (M^+).

Adduct (2b) : Yield 82%; Yellow liquid[17]; IR ($CHCl_3$) ν : 3013, 1620, 1590, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ : 0.98 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.22 (s, 3H, NCH_3), 2.78 and 2.94 (ABX splitting, J_{AB} = 13 Hz, J_{AX} = 8 Hz, J_{BX} = 2 Hz, 2H, CH_2), 3.33-3.55 (AB quartet, J = 7 Hz, 2H, OCH_2), 4.25 (m, 1H, CH), 7.17 (m, 2H, ArH), 8.45 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ : 16.65, 23.14, 29.62, 39.71, 58.99, 77.33, 94.42, 124.90, 146.22, 148.48; MS *m/z* : 206 (M^+).

Adduct (2c)/(3c) : Yield 75%; Yellow liquid[17], IR ($CHCl_3$) ν : 2190 cm^{-1}; ^1H NMR[18] ($CDCl_3$) δ : 1.03* (s, 3H, CH_3), 1.16* (s, 3H, CH_3), 1.28 (s, 6H, 2xCH_3), 2.27* (s, 3H, NCH_3), 2.52* and 2.67* (ABX splitting, J_{AB} = 16 Hz, J_{AX} = 3 Hz, J_{BX} = 3 Hz, 2H, CH_2CN), 2.68 (s, 3H, NCH_3), 3.32 (brs, 1H, exchanges with D_2O, OH), 3.48* (s, 2H, OCH_2), 3.70 (s, 2H, OCH_2), 3.75 (d, J = 13 Hz, 1H, CH), 4.29* (t, J = 3 Hz, 1H, CH), 7.30 (d, J = 13 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ : 23.23, 23.57, 24.08, 24.46, 29.64, 29.91, 60.14, 61.16, 67.83, 76.503, 90.98, 117.00, 123.22, 151.30, MS *m/z* : 154 (M^+). ^1H NMR ($\{CD_3\}_2SO$) δ : 1.18 (s, 6H, 2xCH_3), 2.61 (s, 3H, NCH_3), 3.30 (brs, 1H, OH), 3.42 (s, 2H, CH_2), 3.78 (d, J = 8 Hz, 1H, CH), 7.25 (d, J = 8 Hz, 1H, CH).

Adduct (2d)/(3d) : Yield 34%; Yellow liquid[17]; IR ($CHCl_3$) ν : 1720, 1670 cm^{-1} ; ^1H NMR[18] ($CDCl_3$) δ : 1.02* (s, 3H, CH_3), 1.12* (s, 3H, CH_3), 1.25* (two diffused triplets, J = 7 Hz, 2xCH_3), 1.28 (s, 6H, 2xCH_3), 2.19* (s, 3H, NCH_3), 2.42* and 2.61* (ABX splitting, J_{AB} = 13 Hz, J_{AX} =3 Hz, J_{BX} = 3 Hz, 2H, CH_2), 2.73 (s, 3H, NCH_3), 3.16 (brs, 1H, exchanges with D_2O, OH), 3.53* (s, 2H, OCH_2), 3.63 (s, 2H, OCH_2), 4.10* (q, J = 7 Hz, 2H, CH_2), 4.17 (q, J = 7 Hz, 2H, CH_2), 4.47* (dd, J = 3 Hz, 7 Hz, 1H, CH), 4.54 (d, J = 12 Hz, 1H,

CH), 7.81 (d, J = 12 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ : 14.22, 14.65, 23.63, 23.70, 26.15, 29.99, 40.66, 59.18, 60.15, 60.40, 60.96, 67.52, 67.58, 77.90, 84.63, 92.10, 149.37, 161.67, 170.27, 170.80, MS *m/z* : 201 (M^+).

Adduct (3d) : Yield 55%; Yellow liquid[17]; IR ($CHCl_3$) ν : 1720, 1640 cm^{-1} ; ^{1}H NMR ($CDCl_3$) δ : 1.28 (t, J = 7 Hz, 3H, CH_3), 1.30 (s, 6H, 2xCH_3), 2.80 (s, 3H, NCH_3), 3.33 (s, 1H, OH), 3.53 (s, 2H, CH_2), 4.17 (q, J = 7 Hz, 2H, CH_2), 4.67 (d, J = 12 Hz, 1H, CH), 7.90 (d, J = 12 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ : 14.20, 23.64, 31.93, 48.41, 60.98, 66.98, 151.32, 162.98, 186.92, MS *m/z* : 201 (M^+).

Adduct (3e) : Yield 67%; m. p. 102°C ($CHCl_3$/hexane); IR (KBr) ν : 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ : 1.34, (s, 6H, 2xCH_3), 2.82 (s, 3H, NCH_3), 3.60 (s, 2H, CH_2), 5.34 (brs, exchanges with D_2O, 1H, OH), 5.59 (d, J = 12 Hz, 1H, CH), 7.29-7.46 (m, 3H, ArH), 7.76-7.80 (m, 2H, ArH), 8.09 (d, J = 12 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ: 23.73, 31.92, 62.70, 67.62, 92.15, 127.54, 127.83, 130.80, 140.60, 151.92, 188.57; MS *m/z* : 233 (M^+); (Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.10; H, 8.15; N 6.01 Found C, 71.89; H 7.94; N 6.24).

Adduct (3f) : Yield 68%; Yellow liquid[17]; IR ($CHCl_3$) ν : 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ :1.31 (s, 6H, 2xCH_3), 2.02 (s, 3H, CH_3), 2.78 (s, 3H, NCH_3), 3.50 (s, 2H, CH_2), 5.04 (d, J = 12 Hz, 1H, CH), 7.80 (d, J = 12 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ : 23.88, 29.82, 31.75, 62.04, 64.04, 67.58, 150.28, 195.48; MS *m/z* : 171 (M^+).

Adduct (3g) : Yield 79%; Yellow liquid[17]; IR ($CHCl_3$) ν : 1720, 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ : 1.26 (t, J = 6 Hz, 3H, CH_3), 1.27 (s, 6H, 2xCH_3), 2.80 (s, 3H, NCH_3), 3.29 (s, 2H, CH_2), 3.52 (s, 2H, CH_2), 4.16 (q, J = 6 Hz, 2H, CH_2), 4.86 (brs, exchanges with D_2O, 1H, OH), 5.06 (d, J = 12 Hz, 1H, CH), 7.84 (d, J = 12 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ : 14.14, 23.56, 31.88, 48.28, 60.66, 62.47, 67.32, 151.36, 162.93, 169.10, 188.77; MS *m/z* : 243 (M^+).

Adduct (3h) : Yield 75%; Yellow liquid[17]; IR ($CHCl_3$) ν : 1735, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ : 1.32 (s, 6H, 2xCH_3), 2.83 (s, 3H, NCH_3), 3.36 (s, 2H, CH_2), 3.56 (s, 2H, CH_2), 3.71 (s, 3H, CH_3), 5.09 (d, J = 12 Hz, 1H, CH), 7.94 (d, J = 12 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ : 23.60, 31.92, 48.10, 52.11, 62.57, 67.44, 151.49, 156.57, 169.61, 188.78; MS *m/z* : 229 (M^+).

Adduct (3i) : Yield 72%; m. p. 92°C ($CHCl_3$/hexane); IR (KBr) ν : 3220, 1620 cm^{-1}; ^{1}H NMR[18] ($CDCl_3$) δ : 1.32 (s, 6H, 2xCH_3), 1.95 (s, 1.84H, $COCH_3$), 2.23* (s, 1.15H, $COCH_3$), 2.82 (s, 3H, NCH_3), 3.46 (s, 1.10H, CH_2), 3.64 (s, 2H, CH_2), 4.74* (d, J = 12 Hz, 0.53H, CH), 5.03 (d, J = 12 Hz, 0.47 H, CH), 5.29* (s, 0.9H, CH), 7.90 (d, J = 12 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ : 23.24, 23.61, 23.66, 30.27, 31.67, 31.88, 62.05, 62.43, 67.57, 67.76, 92.94, 146.57, 151.31, 161.67, 167.92, 169.54, 204.63; MS *m/z* 213 (M^+); (Anal. Calcd. for $C_{11}H_{19}NO_3$: C, 61.97; H, 8.92; N, 6.57 Found C, 61.75; H, 8.72; N, 6.69).

Adduct (3j) : Yield 67%; Yellow oil[17]; IR ($CHCl_3$) ν :1614, 1323 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ : 1.37 (s, 6H, 2xCH_3), 2.83 (s, 3H, NCH_3), 3.48 (s, 2H, CH_2), 6.54 (d, J = 10 Hz, 1H, CH), 8.35 (d, J = 10 Hz, 1H, CH); ^{13}C NMR ($CDCl_3$) δ : 23.90, 29.82, 32.61. 67.69, 112.74, 146.45; MS *m/z* : 174 (M^+).

Adduct (3k) : Yield 69%; Reaction time 8 hr. (r.t.); m. p. 111°C ($CHCl_3$/hexane/diethyl ether); IR (KBr) ν : 3414, 2190, 2195, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ : 1.35 (s, 6H, 2xCH_3), 3.28 (s, 3H, NCH_3), 3.55 (s, 2H, CH_2), 7.29 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ : 23.34, 33.15, 48.72, 65.07, 66.63, 116.49, 118.42, 155.95; (Anal. Cald. for $C_9H_{13}N_3O$, C 60.34, H 7.26, N 23.46; Found C 60.60, H 6.99, N 23.22).

Adduct (3l) : Yield 80%; Reaction time 6 hr. (r.t.); m. p. 105 °C ($CHCl_3$/hexane/diethyl ether); IR (KBr) ν: 2180, 1720, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ : 1.30 (t, J = 7 Hz, 3H, CH_3), 1.37 (s, 6H, 2xCH_3), 2.70 (brs, 1H, exchanges with D_2O, OH), 3.36 (s, 3H, NCH_3), 3.60 (s, 2H, OCH_2), 4.22 (q, J = 7 Hz, 2H, CH_2), 8.03 (s, 1H, CH); ^{13}C NMR ($CDCl_3$) δ : 14.38, 23.39, 33.24, 60.78, 64.57, 66.73, 69.59, 119.28, 155.15, 167.57; MS *m/z* : 226 (M^+); (Anal. Calcd. for $C_{11}H_{18}N_2O_3$: C, 58.40; H, 7.96; N, 12.38 Found C, 58.65; H 7.80, N, 12.17).

Adduct (3m) : Yield 55% ; Reaction time 12 hr. (r.t.); m. p. 114°C ($CHCl_3$/hexane); IR (KBr) ν : 2185, 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ : 1.27-1.33 (m, 9H, 3xCH_3), 2.48 (s, 3H, CH_3), 2.87 (s, 3H, NCH_3), 4.14-4.25 (m, 4H, 2xCH_2); ^{13}C NMR ($CDCl_3$) δ : 13.90, 22.18, 23.27, 27.04, 59.62, 60.99, 78.90, 79.30, 121.47, 165.00, 166.34; (Anal. Calcd. for $C_{12}H_{20}N_2O_3$ C 60.00, H 8.33, N 11.67; Found C 59.87, H 8.03, N 11.41).

Oxazepine (4) : Yield 41%; m.p. 136°C ($CHCl_3$/diethyl ether); IR (KBr) ν : 1604, 1664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ : 1.36 (s, 6H, 2xCH_3), 3.03 (s, 3H, NCH_3), 4.23 (s, 2H, CH_2), 6.62 (s, 1H, CH), 7.19-7.35 (m, 5H,

ArH); ^{13}C NMR ($CDCl_3$) δ : 22.41, 39.41, 59.40, 72.57, 98.68, 125.73, 127.86, 129.62, 140.85, 148.11, 168.78, MS *m/z* : 231 (M^+); (Anal. Calcd. for $C_{14}H_{17}NO_2$ C 72.72, H 7.36, N 6.06; Found C 72.47, H 7.03, N 5.98).

Oxazepine (10) : Yield 54%; Solid, m.p. 260°C (ethyl alcohol/ diethyl ether); IR (KBr) ν : 2199, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$+{CD_3}$_2$SO) δ : 1.40 (s, 6H, 2xCH_3), 2.65 (s, 3H, CH_3), 4.44 (s, 2H, CH_2), 7.39-7.50 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$+{CD_3}$_2$SO) δ : 20.36, 36.41, 61.57, 69.64, 105.08, 117.83, 125.54, 127.17, 127.93, 135.43, 162.18, 172.06; MS *m/z* : 256 (M^+); (Anal. Calcd. for $C_{15}H_{16}N_2O_2$ C 70.31, H 6.25, N 10.93; Found C 70.42, H 5.93, N 10.71).

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11. The adduct **3i** shows considerable enol form (61.5%) in its ^{1}H NMR recorded in $CDCl_3$.
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17. For these compounds satisfactory micro analytical analyses could not be obtained since these decomposed during attempted distillation. However, their use and micro analytical data of the products obtained in their reactions have been recorded elsewhere[14b].
18. Since oxazolidines are known to exist as ring-enamine chain tautomers, the ^{1}H NMR data depicts the products to be a mixture of two tautomeric isomers. From the multiplicities and the integral ratios, the signals marked asterisk seem to belong to one isomer.