Tetrahedron Vol. 42, No. 5, pp. 1449 to 1460, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00
© 1986 Pergamon Press Ltd.

CARBON TRANSFER REACTIONS OF Δ^2-OXAZOLINIUM AND THIAZOLINIUM CATIONS[1]

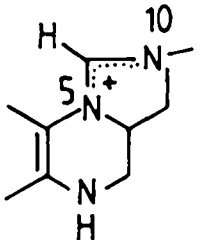
HARJIT SINGH* and RAKESH SARIN

Department of Chemistry, Guru Nanak Dev University,
Amritsar - 143 005, India

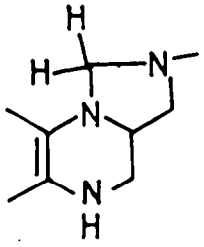
(*Received in UK 17 December 1985*)

Abstract - Δ^2-Oxazolinium and thiazolinium cations with or without an appendage at any of the heteroatoms transfer their C(2) units at the carboxylic acid oxidation level to binucleophiles and provide the corresponding heterocycles, thus mimicking carbon transfer reactions exhibited by THF models, N-methyl N'-tosyl/acetyl imidazolinium cations. However, these azolinium cations react with phenethylamine and tryptamine to furnish their N-acyl derivatives.

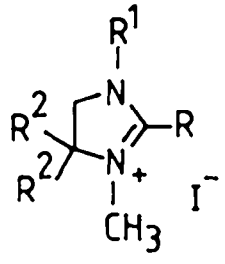
The imidazolinium moiety in the coenzyme N^5,N^{10}-methenyltetrahydrofolate 1 is responsible for the biochemical transfer of its carbon unit flanked by two nitrogens, at the carboxylic acid oxidation level.[2] Since the ease and regioselectivity of ring opening of imidazolidine in N^5,N^{10}-methylenetetrahydrofolate 2 are attributed to the difference in the basicity of both the nitrogen atoms[3-5], a similar factor could be playing a dominant role in the corresponding reactions of imidazolinium moiety of 1. Consequently, such transfer of carbon units at the COOH oxidation level have been performed with the imidazolinium cation 3a possessing an electron donating group (CH_3) at one nitrogen and an electron



1



2

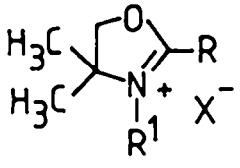


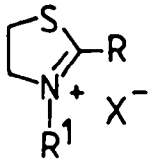
	R	R^1	R^2
3a	H	tosyl	CH_3
3b	CH_3	CH_3	H

withdrawing group (tosyl) at the other, to create the requisite difference in their basicity.[6] We envisaged that, because of the inherent difference[7] in the basic character of O and N as well as N and S, the oxazolinium and thiazolinium cations[8], even in the absence of any appendage at either of the heteroatoms, might perform carbon transfer of their C-2 units at the carboxylic acid oxidation level. Here we report the reactions of Δ^2-oxazolinium and thiazolinium cations with a variety of binucleophiles. It has been found that C(2) unit of these cations is transferred in a facile manner to form both aromatic and nonaromatic heterocycles.

3,4,4-Trimethyl-Δ^2-oxazolinium iodide 4a and o-phenylenediamine in refluxing dimethylformamide as well as in acetonitrile furnish benzimidazole 6a (85-90%). 4,4-Dimethyl-Δ^2-oxazolinium chloride 4b, which does not possess the electron donating methyl group at nitrogen, performs the same reaction on refluxing in dimethylformamide to give 6a in 85% yield.[9] Likewise, Δ^2-thiazolinium bromide 5a with o-phenylenediamine forms benzimidazole in 35% yield. Other azolinium cations, viz., 2,3,4,4-tetramethyl-Δ^2-oxazolinium iodide 4c, 3,4,4-trimethyl-2-phenyl-Δ^2-oxazolinium iodide 4d, 2,3-dimethyl-Δ^2-thiazolinium iodide 5b and 3-methyl-2-phenyl-Δ^2-thiazolinium iodide 5c in refluxing acetonitrile or dimethylformamide transfer their C(2)-CH_3 and C(2)-C_6H_5 moieties to o-phenylenediamine to form 2-methyl/phenylbenzimidazoles 6b/6c (Table I).

Evidently in case of Δ^2-oxazolinium/thiazolinium cations, even in the absence of any substituents at the heteroatoms, the inbuilt difference in their basicity is enough for effecting their C(2) carbon transfer reactions at the carboxylic acid oxidation level. In the case of Δ^2-imidazolinium cations, the presence of an electron withdrawing group at one nitrogen and electron donating substituent at the second nitrogen is essential as 1,2,3-trimethyl-Δ^2-imidazolinium iodide 3b having equivalent electron density on both nitrogen atoms with o-phenylenediamine in refluxing dimethylformamide does not furnish 2-methylbenzimidazole but decomposes to a multitude of products.

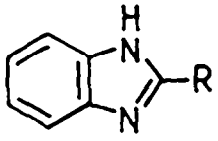


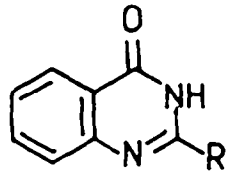


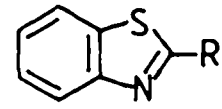
	R	R^1	X
4a	H	CH_3	I
4b	H	H	Cl
4c	CH_3	CH_3	I
4d	C_6H_5	CH_3	I
4e	C_6H_5	H	Cl

	R	R^1	X
5a	H	H	Br
5b	CH_3	CH_3	I
5c	C_6H_5	CH_3	I

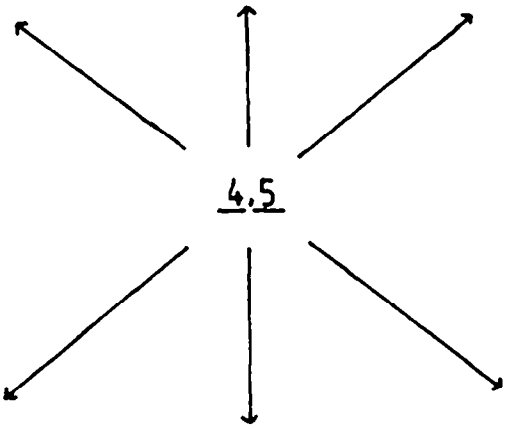
Similar reactions of 4a, 4b, 4c, 4d, 5a, 5b and 5c with o-aminobenzamide and o-aminothiophenol give the corresponding quinazolone 7 and benzothiazole 8 derivatives (Table I). With o-aminophenol, C(2)-H and C(2)-CH_3 derivatives of azolinium cations, i.e. 4a, 4b, 4c, 5a and 5b, furnish N-formyl/acetyl derivatives of o-aminophenol 9, whereas 4d and 5c yield 2-phenylbenzoxazole (Table I, Scheme I). Evidently the benzoxazole and 2-methylbenzoxazole, it formed in these reactions, are hydrolysed during aqueous work-up and form 2-formamidophenol and 2-acetamidophenol respectively. Similar results have been reported in case of the reactions of the imidazolinium cation.[6]

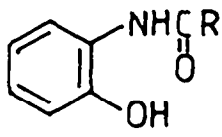


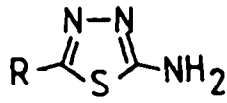


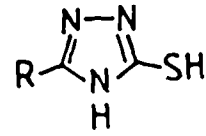


6a	R = H	7a	R = H	8a	R = H
6b	R = CH_3	7b	R = CH_3	8b	R = CH_3
6c	R = C_6H_5	7c	R = C_6H_5	8c	R = C_6H_5









9a	R = H	10b	R = CH_3	11a	R = H
9b	R = CH_3	10c	R = C_6H_5	11b	R = CH_3

Scheme I

Table I Benzimidazole, Quinazolone, Benzothiazole and o-Acylaminophenol derivatives

Reagent	Product 6/7/8/9 R	Time (h) 6	7	8	9	Yield (%) 6	7	8	9
4a	H	10[a]	12	9	100[a]	90	60	35	65
4b	H	1	1	2	15	85	90	50	55
4c	CH_3	7	16	6	15	70	65	30	45
4d	C_6H_5	7	9	12	10	60	35	20	b
5a	H	2	3	3	3	35	60	60	50
5b	CH_3	4	10	2.5	4	65	50	70	50
5c	C_6H_5	70[a]	8	70[a]	3	75	55	35	b

a - Reactions run in refluxing acetonitrile. All other reactions have been run in refluxing dimethylformamide, b - From a complex product mixture, only 2-phenylbenzoxazole could be isolated in 5-10% yield.

In the reactions of azolinium cations with thiosemicarbazide, possessing three nucleophilic sites, the formation of the corresponding 2-amino-1,3,4-thiadiazole 10 as well as 3-mercapto-1,2,4-triazole 11 derivatives is possible. In case of 3,4,4-trimethyl-2-phenyl-Δ^2-oxazolinium iodide 4d and 3-methyl-2-phenyl-Δ^2-thiazolinium iodide 5c, the only product formed is 2-amino-5-phenyl-1,3,4-thiadiazole 10c which is identical with an authentic sample prepared by acid catalysed cyclodehydration of benzoylthiosemicarbazide.[10] 3-Mercapto-5-phenyl-1,2,4-triazole 11c, an authentic sample of which has been obtained by base catalysed cyclization of benzoylthiosemicarbazide[10] as well as from 3-hydroxy-5-phenyl-1,2,4-triazole[11] and phosphorus pentasulphide could not be detected (tlc) in the product mixture. However 2,3,4,4-tetramethyl-Δ^2-oxazolinium iodide 4c and 2,3-dimethyl-Δ^2-thiazolinium iodide 5b react with thiosemicarbazide to yield 2-amino-5-methyl-1,3,4-thiadiazole 10b[12] as the major product and 3-mercapto-5-methyl-1,2,4-triazole 11b[13] as the minor product. In the reaction of thiosemicarbazide with 3,4,4-trimethyl-Δ^2-oxazolinium iodide 4a, 4,4-dimethyl-Δ^2-oxazolinium chloride 4b and Δ^2-thiazolinium bromide 5a, only 3-mercapto-1,2,4-triazole 11a[13] is formed and 2-amino-1,3,4-thiadiazole 10a[14] is not detected (tlc) in the product mixture (Table II).

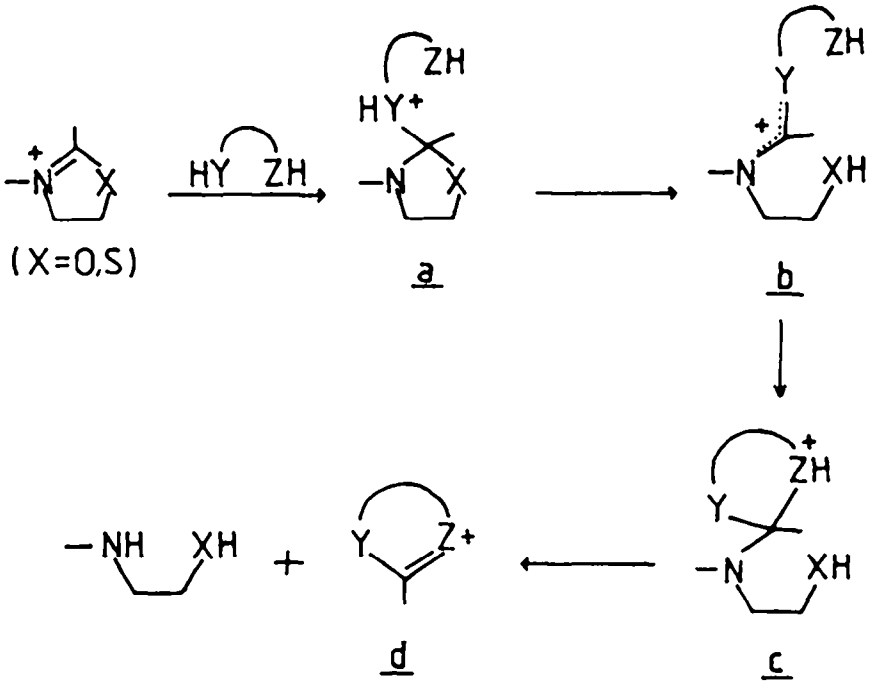
The above results clearly depict that Δ^2-oxazolinium and thiazolinium cations even in the absence of any substituents at any of the heteroatoms react with nucleophiles in a manner comparable with or even faster than azolinium cations having electron donating methyl group at nitrogen. Thus, as envisaged, Δ^2-oxazolinium and thiazolinium cations lacking any appendage at any of the heteroatoms exhibit a facile carbon transfer character. It has been noted that when using acetonitrile as solvent, reactions take a longer time for completion, but the work-up of the reaction mixture is easier than when dimethylformamide is used.

Table II - 2-Amino-1,3,4-thiadiazole and 3-Mercapto-1,2,4-triazole Derivatives

Reagent	Product	Time (h)	Yield (%)
4a	11a	75[a]	50
4b	11a	2	50
4c	10b 11b	6	30 05
4d	10c	5	15
5a	11a	3	50
5b	10b 11b	2	50 10
5c	10c	3	40

a - Reaction run in acetonitrile. Other reactions run in dimethylformamide

These carbon transfer reactions may be visualised to proceed as in the case of imidazolinium cations[6] by the attack of the nucleophile at C(2) of thiazolinium and oxazolinium cations to form the adduct a which can tautomerise to b. Subsequently, an intramolecular reaction between the electrophilic and nucleophilic centers would result in the formation of c. Fragmentation of the latter intermediate involving loss of $-NHCH_2CH_2OH/SH$ leads to heterocycle d incorporating the carbon unit transferred from the model (Scheme II).

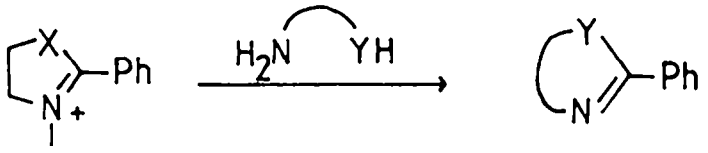


Scheme II

The successful demonstration of carbon transfer character by the oxazolinium and thiazolinium cations towards appropriate binucleophiles to furnish aromatic heterocycles and multifarious advantages of interchange of heterocyclic rings such as the transformation of dithiolanes to dioxolanes,[15,16] thiazolidines to oxazolidines[17] prompted us to study the reactions of azolinium cations with various aliphatic binucleophiles which would form nonaromatic heterocycles and thus accomplish a heterocyclic ring interchange (Table III).

3,4,4-Trimethyl-2-phenyl-Δ^2-oxazolinium iodide 4d and 1,2-diaminoethane in acetonitrile solution, on stirring (2 hrs) and subsequent refluxing (2 hrs) furnishes 2-phenyl-Δ^2-imidazoline. Similar reactions of 3,4,4-trimethyl-2-phenyl-Δ^2-oxazolinium iodide 4d, 4,4-dimethyl-2-phenyl-Δ^2-oxazolinium chloride 4e and 3-methyl-2-phenyl-Δ^2-thiazolinium iodide 5c with 1,2-diaminoethane, 1,2-diaminopropane and 1,3-diaminopropane give 2-phenyl-Δ^2-imidazoline, 4-methyl-2-phenyl-Δ^2-imidazoline and 2-phenyl-1,4,5,6-tetrahydropyrimidine respectively.

Table III Heterocyclic Ring Interchange Reactions



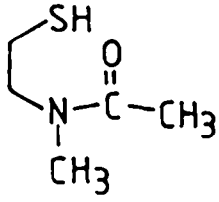
Reagent	Substrate	Product	Time(h) a	b	c	Yield(%) a	b	c
4d/4e/5c	1,2-Diaminoethane	2-Phenyl-Δ^2-imidazoline	4	4	4	96	80	90
4d/4e/5c	1,2-Diaminopropane	4-Methyl-2-phenyl-Δ^2-imidazoline	4	4	4	95	80	88
4d/4e/5c	1,3-Diaminopropane	2-Phenyl-1,4,5,6-tetrahydropyrimidine	4	6	4	90	50	85
4d/4e	2-Aminoethanethiol hydrochloride[d]	2-Phenyl-Δ^2-thiazoline	10	10	-	15	10	-
5c	2-Aminoethanol	2-Phenyl-Δ^2-oxazoline	-	-	6	-	-	70
5c	2-Amino-2-methyl-1-propanol	4,4-Dimethyl-2-phenyl-Δ^2-oxazoline	-	-	8	-	-	40

a, b and c refer to reactions of 4d, 4e and 5c respectively. d - An equivalent amount of triethylamine was used

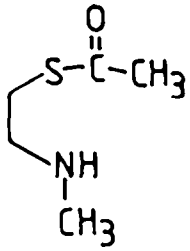
3,4,4-Trimethyl-2-phenyl-Δ^2-oxazolinium iodide 4d as well as 4,4-dimethyl-2-phenyl-Δ^2-oxazolinium iodide 4e with 2-aminoethanethiol furnish 2-phenyl-Δ^2-thiazoline. 3-Methyl-2-phenyl-Δ^2-thiazolinium iodide with ethanolamine and 2-amino-2-methyl-1-propanol furnishes 2-phenyl-Δ^2-oxazoline and 4,4-dimethyl-2-phenyl-Δ^2-oxazoline respectively. However, the reactions of all these binucleophiles with 2,3-dimethyl-Δ^2-thiazolinium iodide/3,4,4-trimethyl-Δ^2-

oxazolinium iodide/2,3,4,4-tetramethyl-Δ^2-oxazolinium iodide do not proceed smoothly and result in the formation of a multitude of products.

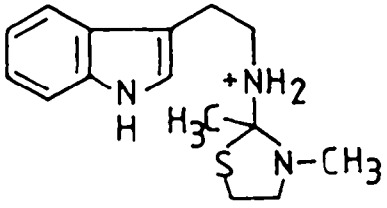
From these results (Table III) it may be pointed out that 2-phenyl derivatives of Δ^2-thiazoline/oxazoline ring systems as their N-quaternary salts react with 1,2 & 1,3-binucleophiles to form a variety of 2-phenyl derivatives of 1,3-heterocycles but 2-alkyl substituted as well as unsubstituted oxazoline/thiazoline derivatives do not perform similar heterocyclic ring interchange reactions.



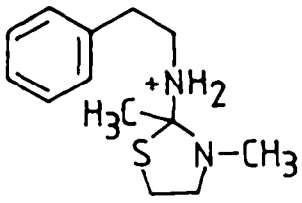
12



13



14



15

Conceptually, C(2) units of azolinium cations could be transferred to C,N nucleophilic sites in β-arylethylamines, providing an alternate mode of Pictet-Spengler synthesis. 2,3-Dimethyl-Δ^2-thiazolinium iodide 5b with tryptamine and β-phenethylamine in refluxing acetonitrile followed by aqueous treatment and extractive work-up gave back the amine and N-(2-mercaptoethyl)-N-methyl acetamide 12[18] which could also be obtained from 5b and aqueous sodium bicarbonate. However, on performing these reactions in refluxing dimethylformamide, N-acetyltryptamine and N-acetylphenethylamine could be isolated. Thus at a higher temperature, the adducts 14 and 15 are formed but fail to undergo further sequence of reactions depicted in Scheme II, and during aqueous work-up the thiazolidine ring cleaves to provide N-acetyl derivatives of the amines. Such a mode of reaction may be ascribed to the weaker nucleophilicity of the aromatic carbon and its failure to perform C-C bond formation at the electrophilic carbon generated from C(2) of the thiazolidine moiety of the adduct 14/15. The formation of

N-acetyl derivatives of amines does depict the carbon transfer of the C(2) unit of the thiazoline ring at the carboxylic acid oxidation level but an *in situ* Bischler-Napieralski type cyclization could not be accomplished even on performing the reactions in the presence of TFA. Similarly 2,3,4,4-tetramethyl-Δ^2-oxazolinium iodide 4c reacts with β-phenethylamine and tryptamine in refluxing dimethylformamide to furnish the corresponding N-acetyl derivatives, but 4c with β-arylethylamines in refluxing acetonitrile gives a mixture of products.

EXPERIMENTAL

M.ps were determined in capillaries and are uncorrected. ^{1}H NMR spectra were recorded on TESLA BS 487C 80 MHz and Perkin Elmer R-32 90 MHz instruments using TMS as an internal standard. Infra-red spectra were recorded on Hungarian Spectromom 2000 instrument. Mass spectra were run on Hitachi Perkin Elmer RMU-6OD and Varian MAT CH-7 instruments. For TLC, plates coated with silicagel G were run in chloroform, ethylacetate or benzene or their mixtures and the spots were developed in an iodine chamber.

Azolinium cations 3/4/5

3,4,4-Trimethyl-Δ^2-oxazolinium iodide 4b,[19] 2,3,4,4-tetramethyl-Δ^2-oxazolinium iodide 4c[20], 3,4,4-trimethyl-2-phenyl-Δ^2-oxazolinium iodide 4d[20], 2,3-dimethyl-Δ^2-thiazolinium iodide 5b[21] and 1,2,3-trimethyl-Δ^2-imidazolinium iodide 3b[22], were procured by methods reported in literature.

4,4-Dimethyl-Δ^2-oxazolinium chloride 4a[23]

Dry HCl gas was passed through a cooled etheral solution of 4,4-dimethyl-Δ^2-oxazoline[19] for ten minutes. The solid separated was immediately filtered, washed with dry ether and stored in a vacuum desiccator as it was very hygroscopic.

4,4-Dimethyl-2-phenyl-Δ^2-oxazolinium chloride 4e[23]

was prepared from 4,4-dimethyl-2-phenyl-Δ^2-oxazoline and dry HCl as above.

Thiazolinium hydrobromide 5a[23]

A mixture of thioformamide (0.1 mol) and 1,2-dibromoethane (1 mol) was refluxed for four hrs. On cooling, 5a, separated. It was filtered, washed with dry ether and used as such for further reactions.

2-Phenyl-Δ^2-thiazoline

A mixture of thiobenzamide (0.1 mol) and 1,2-dibromoethane (1 mol) was refluxed for four hrs and was cooled to give 2-phenyl-Δ^2-thiazolinium hydrobromide which was separated. Its aqueous solution was basified (pH 8) with sodium bicarbonate. After extractive work-up, 2-phenyl-Δ^2-thiazoline (65%) was obtained as a thick liquid which gave the i.r. spectrum identical with the one reported in literature.[24]

^{1}H NMR ($CDCl_3$): δ 3.29 (t, J=7Hz, 2H, $-S-CH_2$), 4.36 (t, J = 7Hz, 2H, $N-CH_2$), 7.28 - 8.00 (m, 5H, Ar-H).

3-Methyl-2-phenyl-Δ^2-thiazolinium iodide 5c

A solution of 2-phenyl-Δ^2-thiazoline (0.1 mol) and methyl iodide (0.2 mol) in nitromethane (5 ml) was heated at a bath temperature of 60-70° for 12 hrs. To the cooled reaction mixture, dry ether was added and separated solid was filtered to furnish 5c (60%). It was crystallized from acetonitrile, m.p. 168-9° (lit. 168-9°)[25].

Reactions of azolinium cations with binucleophiles:

General Procedure:

A solution of binucleophile (0.01 mol) and azolinium cation (0.01 mol) in dry acetonitrile or dimethylformamide was refluxed till the reaction was completed (tlc). The solvent was distilled off, at reduced pressure in case of dimethylformamide. The residue was taken in water. After extractive work-up, the product obtained was purified by chromatography.

The data for various compounds obtained by reactions depicted in tables I and II are given below:

Benzimidazole (6a) : m.p. 166-8° (lit. 170°)[26]; IR (KBr): 3250 cm^{-1}; ^1H NMR (TFA): δ 7.60-8.00 (m, 4H, Ar-H), 9.00 (s, 1H, C(2)-H).

2-Methylbenzimidazole (6b) : m.p. 173-4° (lit. 175-6°)[26]; IR (KBr): 3350 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.68 (s, 3H, CH_3), 7.10-7.70 (m, 4H, Ar-H), 10.01 (br, 1H, D_2O exchangeable, NH).

2-Phenylbenzimidazole (6c) : m.p. 291-3° (lit. 294-5°)[27]; IR (KBr): 3300 cm^{-1}; ^1H NMR (TFA): δ 7.50-8.10 (m, Ar-H).

Benzothiazole (8a)[28]: Liquid; IR (neat): 3250, 3000, 1600 cm^{-1}; ^1H NMR (CCl_4): δ 7.00 - 8.50 (m, Ar-H).

2-Methylbenzothiazole (8b)[28]: Liquid; IR (neat): 3200, 2880, 1580 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.72 (s, 3H, CH_3), 7.00-7.80 (m, 4H, Ar-H); Mass: $M^{+\cdot}$ m/e 149.

2-Phenylbenzothiazole (8c) : m.p. 110-2° (lit. 112-3°)[27]; IR (KBr): 3200, 2900, 1600 cm^{-1}; ^1H NMR (CCl_4): δ 7.00 - 8.10 (m, Ar-H).

N-Formyl-o-aminophenol (9a) : m.p. 128-9° (lit. 123-6°)[6]; IR ($CHCl_3$): 3200, 3000, 1650 cm^{-1}; ^1H NMR (DMSO): δ 3.43 (br, 1H, D_2O exchangeable, NH), 6.50-6.80 (m, 4H, Ar-H), 9.43 (br, 1H, D_2O exchangeable, OH), 8.29 (s, 1H, -CHO).

N-Acetyl-o-aminophenol (9b) : m.p. 203-5° (lit. 207-8°)[29]; IR ($CHCl_3$): 3200, 2800, 1675 cm^{-1}; ^1H NMR (TFA): δ 2.50 (s, 3H, CH_3), 6.80 - 8.00 (m, 4H, Ar-H).

2-Phenylbenzoxazole (10) : m.p. 101-3° (lit. 102-3°)[27]; IR (KBr): 3200, 2950, 1620 cm^{-1}; ^1H NMR (CCl_4): δ 7.00-8.25 (m, Ar-H).

Quinazolin-4(3H)-one (7a) : m.p. 210-2° (lit. 211-2°)[30]; IR (KBr): 3060, 2800, 1700, 1660 cm^{-1}; ^1H NMR (DMSO): δ 7.40-8.20 (m, Ar-H).

2-Methylquinazolin-4(3H)-one (7b): m.p. 229-30° (lit. 234°)[31]; IR (KBr); 3350, 3040, 1665 cm^{-1}; ^1H NMR (DMSO): δ 3.33 (s, 3H, CH_3) 7.00 - 8.00 (m, 4H, Ar-H).

2-Phenylquinazolin-4(3H)-one (7c) : m.p. 226-9° (lit. 231-2°)[32]; IR (KBr): 3200, 3000, 1690, 1640 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.65 (br, 1H, D_2O exchangeable, NH), 7.50 - 8.50 (m, Ar-H).

3-Mercapto-1,2,4-triazole (12a) : m.p. 214-6° (lit. 215-6°)[13]; IR (KBr): 3000, 1640, 1560 cm^{-1}; ^1H NMR (DMSO): δ 8.10 (s, C(5)-H).

3-Mercapto-5-methyl-1,2,4-triazole (12b) : m.p. 252-4° (lit. 255-6°)[13]; IR (KBr): 3300, 3100, 2900, 1635, 1600 cm^{-1}; ^1H NMR (TFA): δ 3.15 (s, 3H, CH_3); Mass : $M^{+\cdot}$ m/e 115.

2-Amino-5-methyl-1,3,4-thiadiazole (11b) : m.p. 216-8° (lit. 223°)[12]; IR (KBr): 3200, 3050, 1640 cm^{-1}; ^1H NMR (TFA): δ 2.65 (s, 3H, CH_3).

2-Amino-5-phenyl-1,3,4-thiadiazole (11c) : m.p. 221-2° (lit. 224°)[10]; IR (KBr): 3100, 2900, 1630 cm^{-1}; ^1H NMR (TFA): δ 7.50-8.00 (m, Ar-H).

3-Mercapto-5-phenyl-1,2,4-triazole:

An equimolar mixture of 3-hydroxy-5-phenyl-1,2,4-triazole[11] and phosphorus pentasulfide was heated at an oil bath temperature of 130-40° for six hrs. After completion of the reaction (tlc), the residue was treated with aq. sodium carbonate and extracted with chloroform. The extracts were washed with water, dried (Na_2SO_4) and filtered. Chloroform was distilled off to furnish 3-mercapto-5-phenyl-1,2,4-triazole 13c (70%). m.p. 274-5° (lit. 274-6°)[10].

Reactions of aliphatic binucleophiles with azolinium cations :

General Procedure

Binucleophile (0.1/0.2 mol) was added dropwise to a solution of Δ^2-azolinium cation (0.1 mol) in acetonitrile. The addition was accompanied by decolorisation of the solution. After stirring for two hrs at ambient temperature, the reaction mixture was refluxed for 2-8 hrs[33] (Table III). The solvent was removed and the residue was taken in water. After extractive work-up, the product was isolated, which was purified by chromatography/crystallisation.

Imidazoline/pyrimidine derivatives isolated after extractive work-up were sufficiently pure but oxazolines and thiazolines were purified by chromatography.

The data for various compounds obtained by reactions depicted in Table III are given below:

2-Phenyl-Δ^2-imidazoline: m.p. 101-2° (lit. 102-3°)[34].

4-Methyl-2-phenyl-Δ^2-imidazoline[35] : Liquid; IR ($CHCl_3$): 3250, 2950, 1620 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.20 (d, J = 7Hz, 3H, CH_3), 3.00 - 4.20 (m, 3H, CH and CH_2), 4.70 (s, 1H, D_2O exchangeable, NH), 7.20 - 8.00 (m, 5H, Ar-H).

2-Phenyl-1,4,5,6-tetrahydropyrimidine : m.p. 155°; IR (KBr): 3100, 2950, 1635 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.89 (quintet, J = 6 Hz, 2H, CH_2), 3.50 (t, J = 6Hz, 4H, 2 x CH_2), 7.30-8.10 (m, 5H, Ar-H); Mass: $M^{+\cdot}$ m/e 160.

2-Phenyl-Δ^2-thiazoline[24] : Liquid; IR (neat): 2950, 2850, 1600 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.29 (t, J=7Hz, 2H, S-CH_2), 4.36 (t, J=7Hz, 2H, N-CH_2), 7.28 - 8.00 (m, 5H, Ar-H).

2-Phenyl-Δ^2-oxazoline[36] : Liquid; IR (neat): 3075, 2980, 1650, 1605 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.08 (t, J=7Hz, 2H, N-CH_2), 4.41 (t, J=7Hz, 2H, O-CH_2), 7.20-8.20 (m, 5H, Ar-H).

4,4-Dimethyl-2-phenyl-Δ^2-oxazoline[20] : Liquid; IR (neat): 2970, 1645, 1600 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.40 (s, 6H, 2xCH_3), 4.10 (s, 2H, CH_2), 7.30-8.10 (m,5H, Ar-H).

Reactions of β-arylethylamines with Δ^2-azolinium cations:

General Procedure

A solution of β-arylethylamine (0.01 mol) and an Δ^2-azolinium cation (0.01 mol) in dimethylformamide was stirred at ambient temperature for two hours

and subsequently refluxed for ten hours. The solvent was distilled off at reduced pressure. The residue was taken in water. After extractive work-up, the product was purified by chromatography.

N-Acetyltryptamine from tryptamine and 2,3-dimethyl-Δ^2-thiazolinium iodide/ 2,3,4,4-tetramethyl-Δ^2-oxazolinium iodide; Yield: 15-20%, m.p. 76-7°(lit.77°).[37]

N-Acetylphenethylamine from β-phenethylamine and 2,3-dimethyl-Δ^2-thiazolinium iodide/2,3,4,4-tetramethyl-Δ^2-oxazolinium iodide; Yield: 15-18%, m.p. 50° (lit. 45°).[38]

N-(2-Mercaptoethyl)-N-methylacetamide (12)

2,3-dimethyl-Δ^2-thiazolinium iodide (0.01 mol) was refluxed in aq. sodium bicarbonate (10%, 25 ml) solution for one hour. On extractive work-up, 12 was isolated and purified by chromatography. Yield: 50%

IR ($CHCl_3$): 1640 cm^{-1}; ^1H NMR (CCl_4)[39]: δ 2.03/2.08 (s, 3H, $-C(O)CH_3$), 2.15-2.75 (m, 2H, $-SCH_2$), 2.85/3.09 (s, 3H, $N-CH_3$), 3.12-3.75 (m, 2H, $N-CH_2$); Mass: $M^{+\cdot}$ m/e 133.

Acknowledgement : We thank the CSIR, New Delhi, for financial assistance.

References and Notes :

1 H. Singh and R. Sarin, Heterocycles, 22, 1101 (1984), a preliminary report.
2 S.J. Benkovic and W.P. Bullard, Progress in Bioorganic Chemistry (Edited by E.T. Kaiser and F.J. Kezdy), Vol. 2, Wiley-Interscience, New York, 133 (1973).
3 T.H. Barrows, P.R. Farina, R.L. Chrzanowski, P.A. Benkovic and S.J. Benkovic, J. Am. Chem. Soc., 98, 3678 (1976).
4 T.H. Fife and A.M. Pellino, J. Am. Chem. Soc., 102, 3062 (1980).
5 T.H. Fife and A.M. Pellino, J. Am. Chem. Soc., 103, 1201 (1981).
6 H. Bieraugel, R. Plemp, H.C. Hiemstra and U.K. Pandit, Tetrahedron, 39, 3971 (1983).
7 T - L. Ho, Tetrahedron, 41, 3 (1985)
8 From the scattered literature reports, it is noticed that imidate $\left[R-\overset{O}{\overset{\|}{C}}-\overset{\oplus}{N}< \right]$ and thioiminium $\left[R-\overset{S}{\overset{\|}{C}}-\overset{\oplus}{N}< \right]$ cations perform carbon transfer to nucleophiles in a more facile manner than amidinium $\left[R-\overset{N}{\overset{\|}{C}}-\overset{\oplus}{N}< \right]$ cations. W. Kantlehner, Iminium salts in organic chemistry (Edited by H. Bohme and H.G. Viehe) Part 2, Wiley-Interscience, New York, 181-392 (1979).
9 Since with 4,4-dimethyl-Δ^2-oxazoline, the product is formed in very poor yield, the presence of an iminium moiety in azolines becomes an essential structural element for such carbon transfer reactions.
10 E. Hoggarth, J. Chem. Soc., 1163 (1949).
11 H. Weidinger and J. Kranz, Chem. Ber., 96, 1064 (1963).
12 G. Fumatsukuri and M. Ueda, Japan, 20944 (1966), C.A., 66, 46430f (1967).
13 J. Goerdeler and J. Gölinke, Chem. Ber., 90, 202 (1957).
14 R.F. Lauer and G. Zenchoff, J. Heterocycl. Chem., 13, 291 (1976).
15 E.J. Corey and T. Hase, Tetrahedron Lett., 3267 (1976).
16 R.M. Manavu and H.H. Szmant, Tetrahedron Lett., 4543 (1975).
17 W. Ando, T. Takata, L. Haung and Y. Tamura, Tetrahedron Lett., 26, 869 (1985).
18 The alternative structure 13 is ruled out because the IR absorption band for $-S-\overset{O}{\overset{\|}{C}}-$ expected at 1675 cm^{-1} is absent.
19 A.I. Meyers and E.W. Collington, J. Am. Chem. Soc., 92, 6676 (1970).
20 P. Allen and J. Ginos, J. Org. Chem., 28, 2759 (1963).
21 L.G.S. Brooker, J. Am. Chem. Soc., 58, 662 (1936).
22 J.A. King and F.H. McMillan, J. Am. Chem. Soc., 68, 1774 (1946).
23 The product was very hygroscopic and its m.p. and spectral data could not be obtained.
24 W. Otting and F. Drawert, Chem. Ber., 88, 1469 (1955)

25 A.D. Clark and P. Sykes, J. Chem. Soc. C, 103 (1971)
26 M.A. Phillips, J. Chem. Soc., 2393 (1928).
27 D.W. Hein, R.J. Alheim and J.J. Leavitt, J. Am. Chem. Soc., 79, 427 (1957).
28 G.L. Jenkins, A.M. Knevel and C.S. Davis, J. Org. Chem., 26, 274 (1961).
29 N.N. Crounse and L.C. Raiford, J. Org. Chem., 10, 419 (1945).
30 V.S. Patel and S.R. Patel, J. Ind. Chem. Soc., 42, 531 (1965).
31 A. Duzas and C. Hoffmann, Bull. Soc. Chim. Fr., 1889 (1959).
32 Y. Hagiwara, M. Kurihara and N. Yoda, Tetrahedron, 25, 783 (1969).
33 Refluxing of the reaction mixture immediately after mixing of reactants results in decomposition products.
34 R. Forsyth, V.K. Nimkar and F.L. Pyman, J. Chem. Soc., 800 (1926).
35 Ajinomoto Co., Fr. 2121106 (1972). C.A., 78, 97656q (1973).
36 H. Witte and W. Seeliger, Angew Chem., Int. Ed. Engl, 11, 287 (1972).
37 E. Spath and E. Lederer, Ber., 63, 120 (1930).
38 J.L.E. Erickson, Ber. 59, 2665 (1926).
39 Due to hindered rotation around the C-N bond of the amide functionality of 12, extra signals appear in the PMR spectrum.