

Δ^2 -OXAZOLINIUM AND THIAZOLINIUM CATIONS AS ONE CARBON UNIT
TRANSFER AGENTS

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Abstract - N-Methyl- Δ^2 -oxazolinium and thiazolinium cations transfer their C_2 units to binucleophiles in refluxing DMF or CH_3CN and provide the corresponding heterocycles.

Imidazolidines¹ and imidazolinium cations² bearing an electron-withdrawing group at one and an electron-donating substituent at the other nitrogen exhibit a facile transfer of one carbon units at carbonyl and carboxylic acid oxidation levels respectively to nucleophiles in a synthetically useful manner and serve as N^5N^{10} -methylene and N^5N^{10} -methenyl tetrahydrofolate models. Thioiminium^{3,4} and imidate cations^{4,5} possessing heteroatoms of different electronegativity perform such one carbon unit transfers under conditions milder than those needed in the case of amidinium cations⁵. We envisaged that Δ^2 -oxazolinium and thiazolinium cations might also perform the above reactions given by Δ^2 -imidazolinium cations. In the first instance, we have studied the reactions of such cations with binucleophiles which by the transfer of one carbon unit form aromatic heterocyclic compounds.

3,4,4-Trimethyl- Δ^2 -oxazolinium iodide 2a and o-phenylenediamine in refluxing DMF and CH_3CN react to furnish benzimidazole in 85% and 90% yields respectively. Even with 4,4-dimethyl- Δ^2 -oxazolinium chloride 2c⁶, the same reaction run in DMF gives the product in 70% yield. However, with 4,4-dimethyl- Δ^2 -oxazoline, the product is formed in very poor yield. Likewise, Δ^2 -thiazolinium bromide 1a⁷ with o-phenylenediamine in refluxing DMF forms benzimidazole in 35% yield. As Δ^2 -thiazolinium bromide⁷ decomposes on neutralisation, the reactions with Δ^2 -thiazoline and 3-methyl- Δ^2 -thiazolinium iodide could not be performed. However, 2-methyl- Δ^2 -thiazoline and o-phenylenediamine in refluxing DMF furnish 2-methylbenzimidazole in poor yield and the decomposition of the thiazoline prevails. Thus like 1-tosyl-3,4,4-trimethyl- Δ^2 -imidazolinium iodide 4a², 3,4,4-trimethyl- Δ^2 -oxazolinium iodide and Δ^2 -thiazolinium bromide even in the absence of an electron-withdrawing group at any of the

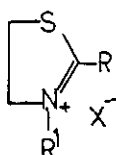
TABLE

Reagent	Substrate	Isolated product ^g	Time (h)			Yield (%)		
			a	b	c	a	b	c
<u>1a/2a/3a</u>	2-H ₂ NC ₆ H ₄ NH ₂	Benzimidazole	2	10 ^d	10	35	90 ^d	55
<u>1a/2a/3a</u>	2-H ₂ NC ₆ H ₄ SH	Benzo thiazole	3	9	2	60	35	55
<u>1a/2a/3a</u>	2-H ₂ NC ₆ H ₄ OH	2-HOC ₆ H ₄ NHCHO ^e	3	100 ^d	8	50	65 ^d	55
<u>1a/2a/3a</u>	2-H ₂ NC ₆ H ₄ CONH ₂	Quinazoline-4(3H)-one	3	12	10	60	60	60
<u>1a/2a/3a</u>	H ₂ NCSNHNH ₂	3-Mercap to-1, 2, 4- triazole	3	75 ^d	3	50	50 ^d	55
<u>1b/2b/3b</u>	2-H ₂ NC ₆ H ₄ NH ₂	2-Methyl benzimidazole	4	7	4	65	70	70
<u>1b/2b/3b</u>	2-H ₂ NC ₆ H ₄ SH	2-Methyl benzo thiazole	2.5	6	2.5	70	30	65
<u>1b/2b/3b</u>	2-H ₂ NC ₆ H ₄ OH	2-HOC ₆ H ₄ NHCOCH ₃ ^e	4	15	3	50	45	50
<u>1b/2b/3b</u>	2-H ₂ NC ₆ H ₄ CONH ₂	2-Methyl quinazoline-4(3H)-one	10	16	8	50	65	50
<u>1b/2b/3b</u>	H ₂ NCSNHNH ₂	2-Amino-5-methyl-1, 3, 4- thiadiazole and 3-Mercap to-5-methyl-1, 2, 4- triazole	2	6	3	50	30	40
						10	5	15
<u>1c</u>	2-H ₂ NC ₆ H ₄ NH ₂	2-Phenyl benzimidazole	70 ^d			75 ^d		
<u>1c</u>	2-H ₂ NC ₆ H ₄ SH	2-Phenyl benzo thiazole	70 ^d			35 ^d		
<u>1c</u>	2-H ₂ NC ₆ H ₄ OH	2-Phenyl benzoxazole	3			10 ^f		
<u>1c</u>	2-H ₂ NC ₆ H ₄ CONH ₂	2-Phenyl quinazoline-4(3H)-one	8			55		
<u>1c</u>	H ₂ NCSNHNH ₂	2-Amino-5-phenyl-1, 3, 4- thiadiazole	3			40		

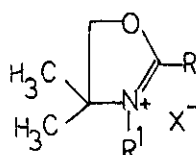
a, b & c refer to reactions of 1, 2 & 3 performed in DMF. d - reactions run in acetonitrile. e - upon hydrolysis
 f - other products could not be isolated. g - for all the compounds satisfactory spectral data and comparison
 with authentic samples have been obtained.

heteroatoms exhibit a carbon transfer character. However 1,2,3-trimethyl- Δ^2 -imidazolinium iodide 4b having equivalent electron density on both nitrogen atoms, with o-phenylenediamine in refluxing DMF does not furnish 2-methylbenzimidazole and provides a multitude of products. The results of the reactions of Δ^2 -thiazolinium bromide 1a, 2,3-dimethyl- Δ^2 -thiazolinium iodide 1b, 2-phenyl-3-methyl- Δ^2 -thiazolinium iodide 1c, 3,4,4-trimethyl- Δ^2 -oxazolinium iodide 2a, 2,3,4,4-tetramethyl- Δ^2 -oxazolinium iodide 2b, N-methyl-N[[(phenylmethyl)thio]methylene]methanaminium chloride 3a and benzyl ethanimidothiolate hydrochloride 3b with various binucleophiles, viz, o-phenylenediamine, o-aminothiophenol, o-aminophenol, o-aminobenzamide and thiosemicarbazide are tabulated.

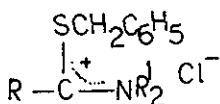
It has been noticed that in the reactions of o-aminophenol with 1, 2, & 3 to procure benzoxazole derivatives, the hydrolysed products are obtained during work up. In the reactions with thiosemicarbazide, there is the possibility of the formation of the corresponding 2-amino-1,3,4-thiadiazole/3-mercapto-1,2,4-triazole derivatives.



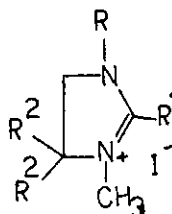
	R	R ¹	X
<u>1a</u>	H	H	Br
<u>1b</u>	CH ₃	CH ₃	I
<u>1c</u>	C ₆ H ₅	CH ₃	I



	R	R ¹	X
<u>2a</u>	H	CH ₃	I
<u>2b</u>	CH ₃	CH ₃	I
<u>2c</u>	H	H	Cl



	R	R ¹
<u>3a</u>	H	CH ₃
<u>3b</u>	CH ₃	H



	R	R ¹	R ²
<u>4a</u>	tosyl	H	CH ₃
<u>4b</u>	CH ₃	CH ₃	H

It has been found that in the case of 1a, 2a and 3a, the 3-mercapto-1,2,4-triazole is the sole product formed and with 1b, 2b and 3b, the 2-amino-5-methyl-1,3,4-thiadiazole is formed as the major product and 3-mercapto-5-methyl-1,2,4-triazole constitutes a minor product, whereas with 1c, only 2-amino-5-phenyl-1,3,4-thiadiazole is formed⁸. The reactions could be visualised to proceed through a mechanism similar to the one proposed for the reactions of Δ^2 -imidazolinium cations². The behaviour of the oxazolidines and thiazolidines in the transfer of C₂ units at a carbonyl group oxidation level is being investigated.

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- 6 The hygroscopic 4,4-dimethyl- Δ^2 -oxazolinium chloride procured by treatment of a solution of 4,4-dimethyl- Δ^2 -oxazoline in anhydrous ether with anhydrous HCl.
- 7 An extremely hygroscopic material obtained by refluxing thioformamide in an excess of 1,2-dibromoethane.
- 8 The reaction mixture (tlc) does not show the presence of 3-mercapto-5-phenyl-1,2,4-triazole, an authentic sample of which has been obtained from 3-hydroxy-5-phenyl-1,2,4-triazole and phosphorus pentasulfide.

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