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

Harjit Singh* and Rakesh Sarin
Department of Chemistry, Guru Nanak Dev University
Amritsar - 143 005, India

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.

Imidazolidines[1] and imidazolinium cations[2] 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}-methenyltetrahydrofolate 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 cations[5]. 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 2c[6], 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 1a[7] with o-phenylenediamine in refluxing DMF forms benzimidazole in 35% yield. As Δ^2-thiazolinium bromide[7] 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 4a[2], 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

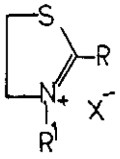
TABLE

Reagent	Substrate	Isolated product[g]	Time (h)			Yield (%)		
			a	b	c	a	b	c
1a/2a/3a	2-$H_2NC_6H_4NH_2$	Benzimidazole	2	10[d]	10	35	90[d]	55
1a/2a/3a	2-$H_2NC_6H_4SH$	Benzothiazole	3	9	2	60	35	55
1a/2a/3a	2-$H_2NC_6H_4OH$	2-HOC_6H_4NHCHO[e]	3	100[d]	8	50	65[d]	55
1a/2a/3a	2-$H_2NC_6H_4CONH_2$	Quinazoline-4(3H)-one	3	12	10	60	60	60
1a/2a/3a	$H_2NCSNHNH_2$	3-Mercapto-1,2,4-triazole	3	75[d]	3	50	50[d]	55
1b/2b/3b	2-$H_2NC_6H_4NH_2$	2-Methylbenzimidazole	4	7	4	65	70	70
1b/2b/3b	2-$H_2NC_6H_4SH$	2-Methylbenzothiazole	2.5	6	2.5	70	30	65
1b/2b/3b	2-$H_2NC_6H_4OH$	2-$HOC_6H_4NHCOCH_3$[e]	4	15	3	50	45	50
1b/2b/3b	2-$H_2NC_6H_4CONH_2$	2-Methylquinazoline-4(3H)-one	10	16	8	50	65	50
1b/2b/3b	$H_2NCSNHNH_2$	2-Amino-5-methyl-1,3,4-thiadiazole and	2	6	3	50	30	40
		3-Mercapto-5-methyl-1,2,4-triazole				10	5	15
1c	2-$H_2NC_6H_4NH_2$	2-Phenylbenzimidazole	70[d]			75[d]		
1c	2-$H_2NC_6H_4SH$	2-Phenylbenzothiazole	70[d]			35[d]		
1c	2-$H_2NC_6H_4OH$	2-Phenylbenzoxazole	3			10[f]		
1c	2-$H_2NC_6H_4CONH_2$	2-Phenylquinazoline-4(3H)-one	8			55		
1c	$H_2NCSNHNH_2$	2-Amino-5-phenyl-1,3,4-thiadiazole	3			40		

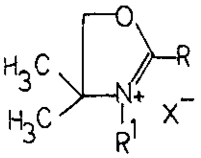
a, b & c refer to reactions of 1, 2 & 3 performed in DMF. d - reactions run in acetonitrile. e - upon hydrolysis f - other products could not be isolated. g - for all the compounds satisfactory spectral data and comparison with authentic samples have been obtained.

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.

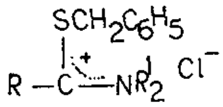
It has been noticed that in the reactions of o-aminophenol with 1, 2, & 3 to procure benzoxazole derivatives, the hydrolysed products are obtained during work up. In the reactions with thiosemicarbazide, there is the possibility of the formation of the corresponding 2-amino-1,3,4-thiadiazole/3-mercapto-1,2,4-triazole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



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

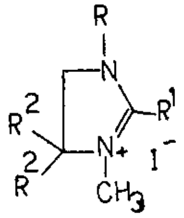


	R	R^1	X
2a	H	CH_3	I
2b	CH_3	CH_3	I
2c	H	H	Cl



$R-\overset{SCH_2C_6H_5}{\overset{|}{C}}\overset{+}{=}NR^1_2\ Cl^-$

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



	R	R^1	R^2
4a	tosyl	H	CH_3
4b	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 formed[8]. The reactions could be visualised to proceed through a mechanism similar to the one proposed for the reactions of Δ^2-imidazolinium cations[2]. The behaviour of the oxazolidines and thiazolidines in the transfer of C_2 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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