Electron-transfer Reductions by Active Aldehydes catalysed by Thiazolium Salt in the Presence of Triethylamine

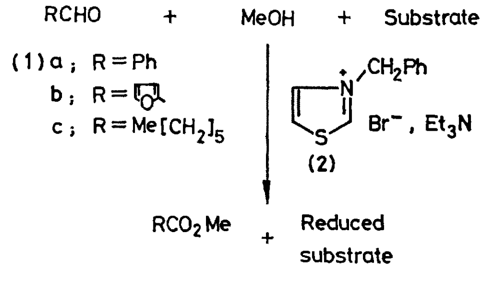
By HIROO INOUE* and KUNIHIKO HIGASHIURA

(Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan)

Summary 3-Benzylthiazolium salts, in methanol containing triethylamine, catalyse the redox reaction in which aldehydes are oxidized to methyl esters concurrently with the reduction of several organic compounds.

THE redox reactions with electron acceptors of the active aldehydes derived from thiazolium salts and aldehydes in the presence of bases have not been explored. As the active aldehydes are related to the carbanion of 2-(1-hydroxyethyl)thiamine pyrophosphate, they may be expected to exhibit interesting activity as reducing reagents. We have studied the reducing behaviour of the active aldehydes produced from the aldehydes (**1**) and 3-benzylthiazolium bromide (**2**) in the presence of triethylamine in methanol and now report novel examples of the electron-transfer reduction of organic substrates coupled with the oxidation of the aldehydes to methyl esters, in which the thiazolium salt acts as a catalyst.

The reactions were carried out by one of the following two methods. (A) Triethylamine and the substrate were added to a frozen solution of a mixture of (**1**) and (**2**) in degassed methanol. The solution, after melting, was stirred under argon at room temperature for 20 h. (B) A solution of a mixture of (**1**), (**2**), and triethylamine in degassed methanol was stirred under argon for 20 min, the substrate was added to the resulting solution, and the mixture was stirred under argon at room temperature for 20 h. To increase the yield in the reduction, an excess of (**1**) was added. The reactions were stopped by adding dilute hydrochloric acid and the reduction products were isolated in the usual manner. The methyl esters were analysed by g.l.c. and the results are summarized in the Table. The reaction of 10-methylacridinium chloride was carried out by method (B), since method (A) resulted in considerably lower yields of 10,10′-dimethyl-9, 9′-biacridan and methyl esters because of the formation of unidentified by-products.



TABLE

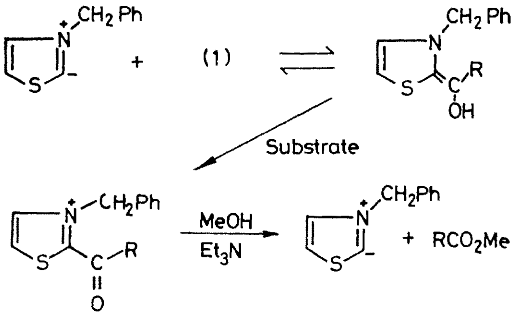
Substrate	RCHO	Method	Molar ratio (**1**) : substr. : (**2**)[a]	Product (% Yield)		% Yield of RCO_2Me
Acridine	(**1a**)	(A)	6:4:1	9,9′-Biacridan[b]	(93)	87
	(**1a**)	(A)	20:20:1		(75)	59
	(**1b**)	(A)	6:4:1		(40)	30
	(**1c**)	(A)	6:4:1		(72)	67
10-Methyl acridinium chloride	(**1a**)	(B)	1:1:1	10,10′-Dimethyl-9,9′-biacridan	(88)[b]	87
	(**1b**)	(B)	1:1:1		(83)[b]	74
Phenazine	(**1a**)	(A)	6:4:1	5,10-Dihydrophenazine	(83)[c]	84[c]
Azobenzene	(**1a**)	(A)	6:4:1	Benzidine	(66)[c]	65[d]
				Aniline	(6)[e]	
Nitrobenzene	(**1a**)	(A)	6:4:1	Aniline	(25)[c]	60[d]
				N-Benzoyl-N-phenylhydroxylamine	(22)[c]	

[a] The amount of (**2**) was 0.5 mmol in 5 ml of MeOH. The molar ratio (**2**):Et_3N was 1:5. [b] Yield of acridans or ester: [acridans or ester (mmol)] × 200/substrate (mmol). [c] [Product or ester (mmol)] × 100/substrate (mmol). [d] [Ester (mmol) × 100]/(**1a**) (mmol). [e] [Aniline (mmol) × 100]/[2 × azobenzene (mmol)].

Acridine, 10-methylacridinium chloride, phenazine, and azobenzene were reduced by the (**1**)–(**2**)–triethylamine system to the corresponding reduction products in high yields. Hydrazobenzene, produced in the reduction of azobenzene, was converted into benzidine on treatment with hydrochloric acid after the reaction. The reduction of nitrobenzene gave *N*-benzoyl-*N*-phenylhydroxylamine and aniline as the products. In these reactions, (**1**) was oxidised to methyl esters. The excess of (**1**) was converted into α-hydroxy-ketones by benzoin condensation.[1]

The formation of biacridans, 5,10-dihydrophenazine, and hydrazobenzene with methyl esters constitutes evidence for the transfer of electrons from the active aldehydes to the substrates. The yields of the products and methyl esters indicate that a molecule of the active aldehydes can furnish two electrons. Furthermore, the (**2**)–triethylamine system was found to exert a catalytic effect on reductions of substrates other than 10-methylacridinium chloride.

The mechanism of formation of the methyl esters may be explained by assuming that methanol reacts with an intermediate (**3**)[2] which is formed from the oxidation of the active aldehydes by the substrates.



(3)

The above results provide evidence for the electron-transferring function of thiazolium salt-derived active aldehydes and these studies may be useful in other oxidation–reduction reactions.

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