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Acyloin Condensation of Aldehydes Catalysed by *N*-Laurylthiazolium Bromide

By Waichiro Tagaki* and Heihachi Hara

(*Department of Chemistry, Faculty of Technology, Gunma University, Kiryu, Gunma, Japan*)

Summary Acyloins were obtained in high yields, by stirring a heterogeneous mixture of an aldehyde and *N*-laurylthiazolium bromide in aqueous phosphate buffer (pH 8).

It is well known that *N*-alkylthiazolium salts catalyse the acyloin condensation of aldehyde in the model reaction of thiamine coenzyme.[1] However, the yields of acyloins are generally low, especially when the substrate is an aliphatic aldehyde. The catalyst used had a relatively small *N*-substituent. Thiazolium ion-containing polymers, however, have been reported to give high yields of benzoin and furoin.[2] We now report that *N*-laurylthiazolium bromide which forms a micelle appears to be a much better catalyst than those so far reported.

The condensation reactions were carried out under the conditions given in the Table. A micelle-forming *N*-laurylthiazolium bromide ($n = 12$) (c.m.c. = $3{\cdot}3 \times 10^{-3}$M in water) is a far better catalyst than a non-micelle-forming *N*-butyl substituted salt ($n = 4$).[3] The reaction of aromatic aldehydes is extremely fast; oily benzaldehyde turned to solid benzoin within a few minutes stirring. A much longer reaction time was necessary for aliphatic aldehydes (5—12 h). The product yield can be increased by using a larger amount of catalyst as shown in the case of butanal.

Table. Yield (%) of products in reaction of aldehyde in aqueous phosphate buffer (5 ml, 0·5 M, pH 8) in the presence of *N*-alkyl(C_nH_{2n+1})thiazolium bromide after 12 h stirring at room temperature, under nitrogen.

RCHO (1·39 mmol)	Catalyst mmol	Yield of RCH(OH)COR[a] $n = 12$	$n = 4$
Propanal[b] . .	0·1	16	0
Butanal[c] . .	0·05	20	—
	0·1	39	Trace
	0·2	61	—
	0·4	76	—
Hexanal[c] . .	0·1	67	2
Octanal[c] . .	0·1	63	2
Benzaldehyde[c]	0·1	95	0
Furfural[c] . .	0·1	80	0

[a] Determined by g.l.c. for aliphatic aldehydes, other possible products, such as aldols, were not detected. Yields for aromatic aldehydes are isolated yields. [b] Homogeneous. [c] Heterogeneous.

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[1] T. C. Bruice and S. J. Benkovic, 'Bioorganic Mechanism,' Benjamin, New York, 1966, vol. 2, ch. 8.

[2] C. L. Schilling and J. E. Mulvaney, *Macromolecules*, 1968, **1**, 452; K. Arai, Y. Ueno, and M. Okawara, Report on the 28th Annual Meeting of Japan Chemical Society, **1973**, Vol. III, p. 2156.

[3] See, E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, 1970, **8**, 271; Y. Yano, T. Okonogi, M. Sunaga, and W. Tagaki, *J.C.S. Chem. Comm.*, **1973**, 527.