

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

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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).

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.

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. = 3.3×10^{-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

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	—
Hexanal ^c ..	0.4	76	—
	0.1	67	2
	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.

aldehydes (5—12 h). The product yield can be increased by using a larger amount of catalyst as shown in the case of butanal.

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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.