Stereo-ordered Macromolecular Matrices Bearing Ammonium Groups as Catalysts in Alkylation and Carbenation Reactions

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Summary Selective alkylation of benzyl cyanide and dichlorocarbenation of styrene and benzaldehyde are promoted by macromolecular ammonium salts under polyphase conditions.

TETRA-ALKYLAMMONIUM salts are known to catalyse many reactions under 'phase transfer' conditions.[1,2] The mechanism of these reactions is claimed to be similar to that of reactions occurring at cell membranes.[3]

In connection with our interest in the preparation of functional stereo-ordered and conformationally homogeneous chiral polymers,[4] to be employed as catalysts in asymmetric synthesis,[5] macromolecular ammonium salts have been tested as possible polymer reagents under conditions similar to those reported for low molecular weight salts. It would be interesting to correlate the chemical and stereochemical requirements of the macromolecular matrix with the activity and selectivity in chemical transformations

TABLE. Ethylation[a] and dichlorocarbenation[b] reactions catalysed under polyphase conditions by macromolecular ammonium salts of tertiary amines with poly(4-chloromethyl)styrene (PCS).

Substrate (mmol)	PCS catalyst[d] ($DP_n \times 10^{-2}$)	Amine (mmol)	Yield[c] /%
$\mathrm{PhCH_2CN}$ (34)[f]	Cationic (0·5)	$\mathrm{Me_3N}$ (0·3)	59
,,	,,	$\mathrm{Et_3N}$ (0·3)	78
,,	Ziegler-Natta (125)	$\mathrm{(HOCH_2CH_2)_3N}$ (0·3)	90
,,	,,	$\mathrm{Bu^n{}_3N}$ (0·3)	100
,,	Cationic (0·5)	*N*-Methylephedrine (0·4)	76[e]
,,	Anionic (4·8)	(*R*)-$\mathrm{MeCH(Ph)NMe_2}$ (0·4)	49[e]
Styrene (48)[g]	Cationic (0·5)	$\mathrm{Me_3N}$ (0·4)	8
,,	,,	$\mathrm{Et_3N}$ (0·4)	18
,,	Radical (1·8)	$\mathrm{(HOCH_2CH_2)_3N}$ (0·4)	2
,,	Cationic (0·5)	$\mathrm{Bu^n{}_3N}$ (0·4)	32
,,	,,	,,	96[e]
,,	,,	*N*-Methylephedrine (0·4)	6
PhCHO (36)[h]	Anionic (0·4)	*N*-Methylephedrine (0·7)	69[e]
,,	Anionic (4·8)	(*R*)-$\mathrm{MeCH(Ph)NMe_2}$ (0·7)	71[e]

[a] Of benzyl cyanide, molar ratio benzyl cyanide: ethyl bromide 1 : 1·2. [b] Of styrene to 1,1-dichloro-2-phenylcyclopropane, molar ratio chloroform : styrene 1·1 : 1, and benzaldehyde to mandelic acid, molar ratio chloroform : benzaldehyde 2·1 : 1. [c] Evaluated for runs carried out in sealed vials under mechanical shaking (30 c.p.m.). [d] Obtained by chloromethylation with monochlorodimethyl ether–$\mathrm{ZnCl_2}$ system (ref. 6, and A. D. Jones, *Ind. Eng. Chem.*, 1952, **44**, 2686) of polystyrene prepared by $\mathrm{EtAlCl_2}$ (cationic), $\mathrm{VCl_4{-}AlBu^i{}_3}$ (Ziegler-Natta), sodium naphthalene (anionic), and azobisisobutyronitrile (radical). [e] For runs carried out in round bottomed flasks under magnetic stirring (>200 r.p.m.). [f] 320 mmol 50% aq. NaOH, 70 °C, 7 h. [g] 195 mmol 50% aq. NaOH, 40 °C, 5 h. [h] 195 mmol aq. NaOH, 56 °C, 2 h.

of suitable substrates. Therefore macromolecular ammonium salts, obtained by quaternization of tertiary amines with poly(4-chloromethyl)styrene (PCS)[6] having different DP_n and stereoregularity degree, were used in the ethylation of benzyl cyanide[1] and in dichlorocarbenation of styrene[1] and benzaldehyde[7] (Table). In all cases these salts were capable of promoting, under polyphase conditions (highly swollen charged polymer, organic substrate, and 50% aq. NaOH), catalytic transformations (molar ratio of substrate : ammonium salt, 50—120 : 1) of the employed substrates with good yield and high selectivity ($> 90\%$). Blank runs, without the ammonium salt, resulted in either no reaction or reaction whose extent was at the best one order of magnitude lower than that observed in catalysed runs.

In runs where ammonium salts of optically active amines were used, the final chiral products display low but definite optical rotation (stereoselectivity $\leqslant 10\%$).

Asymmetric induction is also observed when ammonium salts of achiral amines and copolymers of 4-chloromethylstyrene with optically active α-olefins[4] were used which shows that the charged macromolecular systems participate in the transition state of the reported reactions.

In contrast to their structurally analogous low molecular weight ammonium salts, these polymeric catalysts are insoluble in water which makes the separation of the catalyst from the reaction mixture easier.

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