Chlorination of Organic Compounds by Means of Polymer-supported Chlorine

By Alessandro Bongini, Gianfranco Cainelli, Michele Contento, and Francesco Manescalchi*
(*Istituto Chimico 'G. Ciamician' dell'Università, Via Selmi* 2, 40126 *Bologna, Italy*)

Summary. Chlorination of organic compounds is achieved, under mild conditions, using chlorine incorporated into an anion-exchange resin.

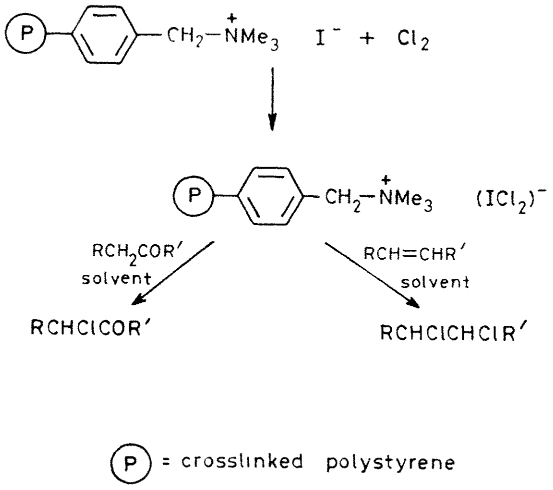
Commercially available anion-exchange resins have been recently used as halogen carriers in the bromination[1,2] of various organic substrates and in the chlorobromination[2] of alkenes and alkynes. As a development of our previous work,[2] we have found that the macroreticular anion-exchange resin Amberlyst A-26 (Rohm e Haas Co.), in the iodide form,[3] can readily incorporate chlorine, when the polymer is shaken overnight in a dichloromethane solution of the halogen.

TABLE Chlorination by Amberlyst A-26[$(ICl_2)^-$ form]

Compound	Reaction conditions (solv /temp /time)	Product	% Yield[a]	^1H and ^{13}C n m r data δ/p p m
Hexanal	CCl_4/reflux/15 min	2-chlorohexanal	84	9 45 (d, C*H*O)
Nonanal	CCl_4/reflux/20 min	2-chloronananal	88	9 45 (d, C*H*O)
Decanal	CCl_4/reflux/30 min	2-chlorodecanal	80	9 50 (d, C*H*O)
Cyclohexanone	CCl_4/reflux/20 min	2 chlorocyclohexanone	45	4 30 (t, C*H*Cl)
Acetophenone	CH_2Cl_2/room temp /20 h	ω-chloroacetophenone	66	4 75 (s, CH_2Cl)
Cyclohexene	CH_2Cl_2/room temp /2 h	1,2-dichlorocyclohexane[b]	75	62 9 (d, *C*HCl) 4 0 (m, C*H*Cl)
Oct-2-ene	CH_2Cl_2/room temp /2 h	2,3-dichloro-octane[c]	82	60 2, 60 0 [d, *C*(2)] 67 4, 66 2 [d, *C*(3)]

[a] Yields are for purified isolated products [b] Determined by ^1H n m r spectroscopy to be *trans* (H M Van Dort and T J Sekuur *Tetrahedron Lett* , 1963 1301) A similar result has been obtained (M L Hallensleben *Angew Makromol Chem* 1972, **27** 223) with chlorine supported on poly *p* iodostyrene Our polymeric reagent however, is much easier to prepare and has a wider applicability [c] *Erythro* and *threo* forms

The yellow–greenish beads, probably carrying, as counter-ions of the benzyltrimethylammonium groups, anions[4] of the type $(ICl_2)^-$, proved to be efficient in the chlorination of carbonyl and unsaturated compounds (Scheme and Table)



SCHEME

The content of the halogenating species was determined by iodometry to be 2·5 mmol/g (average value) and the reagent is stable at room temperature without appreciable loss of efficiency when stored in a tightly stoppered flask

In a typical experiment nonanal (1·42 g) was added to a slurry of resin (8 0 g) in CCl_4 (10 ml) and the mixture was stirred at reflux for 20 min, with the reaction being monitored by g l c and ^1H n m r spectroscopy The resin was filtered off, the solvent removed under reduced pressure, and the product isolated by distillation (1 56 g, 88%) b p 39—42 °C/6 × 10^{-2} Torr

The most interesting property of our reagent is the direct chlorination of saturated aldehydes, the reaction occurs very quickly under mild conditions and the ease and simplicity of our method seem to provide an improvement over other existing routes to 2-chloroaldehydes [5]

Ketones also are α-chlorinated to give monochloro-derivatives in moderate yields In this case, indeed, polychlorinated products have been obtained as by-products

Alkenes are converted into vicinal dichloroalkanes when a fourfold excess of polymeric reagent is used and the reaction is started in an ice bath Equimolar amounts of reagent and substrate lead to a 50:50 mixture of dichloro- and chloroiodo-compounds The latter result was the exclusive one in the case of the reaction with alkynes

The products were identified by means of i r , ^1H and ^{13}C n m r , and mass spectra

Regeneration of the resin was accomplished by washing the exhausted reagent with aqueous NaOH followed by neutralization with HI and suspension in a CH_2Cl_2 solution of chlorine

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[2] A Bongini, G Cainelli, M Contento, and F Manescalchi, *Synthesis*, 1980, 143

[3] G Cainelli, F Manescalchi, and M Panunzio, *Synthesis*, 1976, 472.

[4] H McCombie and T H Reade, *J Chem Soc* , 1923, 141

[5] L Lorenzini and C Walling, *J Org Chem* , 1967, **32**, 4008, R H Reuss and A Hassner, *ibid* , 1974, **39**, 1785.