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SPECIFIC CHLORINATION WITH N-CHLOROPOLYMALEIMIDE

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We wish to report specific chlorinations of alkylaromatic compounds by the polymeric chlorinating agent, N-chloropolymaleimide (PNCS). Polymaleimide was prepared by free radical polymerization of maleimide, in the presence of divinylbenzene (5%) or N,N'-methylenebisacrylamide (5-10%) as cross-linking agents. It was chlorinated by addition of a solution of chlorine in carbon tetrachloride to a suspension of the polymer in aqueous sodium hydroxide solution. The average extent of chlorination amounted to 78%. Several alkylaromatic compounds were reacted with PNCS and the products obtained were compared with those produced by reactions of alkylaromatic compounds with the low molecular weight analogue, N-chlorosuccinimide (NCS).

Substrate [a]	PNCS			NCS					
	Total yield (%)	Product distribution (%)		Total yield (%)	Product distribution (%)				
		Aromatic substitution[b]	Aliphatic substitution		Aromatic substitution	Aliphatic substitution			
						α	β	α,α	α,β
t-Butylbenzene[c]	70	100	-	23	86		14		
Cumene[d]	80	100	-		mixture of products				
Ethylbenzene [e]	88	100	-	68	traces	66	17		17
Toluene[f]	85	100	-	100	16	66		17	

a All reactions were carried out with a 1:1 molar ratio of substrate to reagent,
b Essentially 100% of monochlorinated products. Di-ar-chloro compounds were obtained in less than 1%.
c The reactions were carried out at 140°C for 16 hr.
d The reactions were carried out at 138°C for 18 hr.
e The reactions were carried out at 120°C for 18 hr.
f The reactions were carried out at 110°C for 16 hr.

The reactions between alkylaromatic compounds and PNCS or NCS (see Table) were carried out in the absence of solvents and free radical initiators, at 100-140°C, for 16-20 hr. Under these conditions, the alkylaromatic compounds studied were found to react specifically with the polymeric chlorinating agent to yield the corresponding aryl-chlorosubstituted products. In contrast, reaction of the low molecular weight analogue, NCS, with the alkyl aromatic compounds yielded a mixture of products, consisting of side-chain and aryl-chlorinated compounds.

The products were identified by their nuclear magnetic resonance spectra, vapor phase chromatography and mass spectra. Chlorobenzene reacted with PNCS, in 1:1 molar ratio, at 130°C for 20 hr, to yield dichlorobenzenes in 37% yield. The mixture consisted of o- and p-chlorobenzenes in a ratio of 1:3, respectively. The polymeric reagent, being insoluble, is conveniently isolated from the reaction mixture and can be rechlorinated and reused.

The difference in specificity of the polymeric reagent and the low molecular weight analogue is most probably due to the influence of the polymeric backbone on the chemical reactivity of its functional groups. Each N-chlorosuccinimide residue on the polymer is situated in a polar environment provided by adjacent succinimide residues. We have already pointed out (2) the difference in the products obtained from some alkylaromatic compounds upon reaction with N-bromopolymaleimide and N-bromosuccinimide in apolar media and in the presence of free radical initiators. We attributed these differences to the local polar environment of the N-bromosuccinimide residues provided by two adjacent succinimide residues on the polymeric backbone. Indeed, when N-bromosuccinimide reacted with alkylaromatic compounds in polar solvents, it yielded the same products as those obtained by employing the polymeric brominating agent in non-polar solvents, such as carbon tetrachloride.

It was expected, then, that N-chlorosuccinimide, in the presence of succinimide, and in the absence of solvent, should react similarly to the polymeric reagent with alkylaromatic compounds. As expected, marked changes occurred in the distribution of products when t-butylbenzene and toluene reacted with N-chlorosuccinimide in the presence of succinimide. Thus, when a mixture of N-chlorosuccinimide, succinimide and t-butylbenzene, in 1: 1.8 :1 molar ratio, was heated to 140°C for 18 hr, the yield of chlorination amounted to 70% (23% in the absence of succinimide, 70% upon reaction with the polymeric reagent) and almost 100% of the chlorinated products were ar-chloro-t-butylbenzene. The amount of β-chloro-t-butylbenzene was less than 1% (14% in the absence of succinimide, 0% upon treatment with the polymeric reagent). When a mixture of N-chlorosuccinimide, toluene and succinimide, in a molar ratio of 1:3:1, was reacted at 132°C for 18 hr, the extent of chlorination amounted to 77% (100% in the absence of succinimide, counting dichlorination, and 85% upon reaction with the polymeric reagent). The distribution of products was 91% ar-chlorotoluene (16% in the absence of succinimide, 100% upon treatment with the polymeric reagent), 9% of benzylchloride (66% in the absence of succinimide) and traces of dichlorinated products (17% in the absence of succinimide).

The above findings show that the specificity and reactivity of a functional group incorporated into a polymeric backbone may change because of the microenvironment caused by the polymeric chain.

References

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