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SPECIFIC HALOGENATION OF ALKYLAROMATIC COMPOUNDS IN THE PRESENCE OF SILICA

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We wish to report a simple method of halogenating alkylaromatic compounds specifically in the aromatic nucleus. The method consists of mixing the alkylaromatic substrate, adsorbed on silica, with free halogens at ambient temperature. After reaction is complete, the mixture is extracted with a non-polar solvent, and, after evaporation of the solvent, high yields of halogenated products are obtained, in which the aromatic nucleus is substituted. The silica, after washing with polar solvents, may be reused for further halogenations. Thus, 4.2 ml of ethylbenzene (34 mmoles), adsorbed on 10.5 g silicic acid (Mallinckrodt, 100 mesh, powder) was added to a homogeneous mixture of 1.55 ml of bromine (29 mmoles) in 9.8 g silicic acid. The reaction mixture was stirred for 22 hr at ambient temperature, then extracted with petroleum ether, and the solvent removed by evaporation. The products, obtained in quantitative yield, consisted of aryl-substituted bromoethylbenzenes in which the isomer ratio of _p_:_o_ bromoethylbenzene was 2.8:1, while dibromination occurred to an extent of less than 1%. In a similar manner, reaction with toluene yielded 90% of aryl-substituted bromotoluenes, and no side chain brominated products were obtained. Cumene reacted, under the same conditions, to yield 88% of brominated products with substitution in the aromatic nucleus; the isomer ratio of _p_:_o_-bromocumene was 8:1.

Chlorination was carried out using a solution of chlorine in carbon tetrachloride, adsorbed on silicic acid, as chlorinating agent. Thus, 8.4 ml of ethylbenzene (68.5 mmoles) in 24.6 g silicic acid, were added to 53 ml of a solution of 1.44 N chlorine in carbon tetrachloride (38.11 meq) mixed with 34.5 g silicic acid. The reaction mixture was stirred for 30 hr at room temperature and extracted with pentane to yield 74% of aryl-chlorinated ethylbenzenes in the extract, of which 48% consisted of the _p_-isomer and 52% of the _o_-isomer.

It is worthwhile to note, that practically no reaction took place when ethylbenzene was allowed to react with a carbon tetrachloride solution of chlorine in the absence of silica.

In order to rule out the possibility that traces of metal salts were serving as catalysts for the aromatic halogenation, silicic acid was treated with disodium ethylenediaminetetraacetate, the complexing agent removed by aqueous washing and the residual silicic acid employed in halogenation; no reduction in specificity or yields were found.

When evolution of hydrogen-halide is undesirable, N-haloamides or N-haloimides, in the presence of silica, may be employed; the reaction is performed at 60-110°C. Thus, 2.2 ml of ethylbenzene (17.9 mmoles), adsorbed on 10 g of silicic acid, was added to 2.26 g of N-chlorosuccinimide (17 mmoles) in 5 g silicic acid. The mixture was kept at 60°C for 12 hr and then extracted with petroleum ether. Aryl-chlorinated chloroethylbenzenes were obtained in 50% yield. No side-chain chlorinated products were obtained.

The alkylaromatic compounds, as well as the halogenating agents, being adsorbed on the silica, are situated in a polar environment provided by the silica. This environment promotes the aromatic substitution, rather than the side-chain halogenation, which is a free radical reaction. We have already demonstrated the differences in specificity of halogenating alkylaromatic compounds employing polymeric N-halo-amides and imides and their low molecular weight analogs[1,2,3] as halogenating agents. In the absence of solvents and free radical initiators, both N-bromopolymaleimide[3] and N-chloropolymaleimide[2] reacted specifically with alkylaromatic compounds to yield arylhalogenated alkylaromatic products. In contrast, N-bromosuccinimide, the low molecular weight analog, reacted with alkylaromatic compounds under the same conditions to yield side-chain brominated alkylaromatic products. N-Chlorosuccinimide, upon reaction with alkylaromatic compounds, yielded a mixture of products, consisting of side-chain and aryl-chlorinated products. The differences in specificity of the polymeric reagent and the low molecular weight analog were attributed to the influence of the polymeric backbone on the chemical reactivity of its functional groups: each N-halosuccinimide residue is situated on the polymer in a polar environment provided by adjacent succinimide residues. Indeed, upon reaction of alkylaromatic compounds with N-chlorosuccinimide in the presence of succinimide, the predominant product was aryl-substituted chloroalkylaromatic compound, rather than the side-chain substituted product, prevailing in the absence of succinimide. Silicic acid acts in the same manner as succinimide, providing polar media for the halogenation reaction. It is interesting to note that both of these weak acids have pKa of the same order of magnitude (9.5 for succinimide and 9.7 for silicic acid).

In contrast to halogenation in silicic acid media, the usual aromatic halogenations, which are performed by free halogens in the presence of halides of aluminium and iron as catalysts, have the following shortcomings:
(1) Strict anhydrous conditions are required; (2) Absence of light is necessary; (3) Strong electrophiles, like ferric and aluminium halide, cause alkyl-isomerization and transalkylation; (4) Certain alkyl substituents tend to undergo halogenolysis, i.e., to be displaced by halogens, an effect accentuated by increase in the temperature, the degree of substitution on the adjacent carbon atom and the electrophilicity of the catalyst.

The products were characterized by their NMR spectra and by vapor phase chromatography techniques. Acknowledgement is due to Mr. M. Geda for performing the NMR measurements.

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