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STERIC INFLUENCE ON THE REACTIVITY OF AMINO RADICAL IONS.
NEW TYPE OF BENZYLIC CHLORINATION.

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RECENTLY we[1] have postulated that the amine radical ions, generated by protonated N-chloroamines and reducing metal salts, simultaneously attack aromatic rings and benzylic positions of the alkylbenzenes. A strong steric effect has been observed in the ortho positions in nuclear amination.

Here we report that these two competitive reactions are strongly affected by the steric nature of the alkyl groups in N-chloroamines. Results with several N-chloroamines and toluene are listed in table 1; yields are based on N-chloroamines and have been determined by gas-liquid chromatography.

Table 1

			benzyl chloride	toluidines
N-chlorodimethylamine	sulphate	and Fe^{++}	23%	52%
"	"	and Ti^{+++}	13%	65%
N-chloropiperidine	"	and Fe^{++}	20%	41%
N-chlorodiethylamine	"	"	35%	7%
N-chlorodi-n-butylamine	"	"	12%	-
N-chlorodiisobutylamine	"	"	61%	-

All the reactions have been carried out under the same conditions, at room temperature (20-30°C) in 30 minutes, by adding solid ferrous sulphate or titanous chloride to the mixture of N-chloroamine, toluene, sulphuric and acetic acid (ratio 3/1).

The increasing bulk of the alkyl groups in N-chloroamines determines a decrease of nuclear attack and an increase of benzylic chlorination, which is exclusive with N-chlorodiisobutylamine and N-chlorodi-n-butylamine.

Yield of benzyl chloride is low with N-chlorodi-n-butylamine owing to the competition with intramolecular reaction (Hofmann-Löffler reaction).

Also a competitive reduction of the amine radicals always occurs to some extent:

$$R_{2}\overset{+}{N}H^{\bullet} + Fe^{++} \longrightarrow R_{2}NH + Fe^{+++}$$

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REFERENCES

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