

195. The Benzylolation of Aromatic Amines. Part V. The Reactions between *o*-, *m*-, and *p*-Cyanobenzyl Chlorides and Aniline, Ethylaniline, and Dimethylaniline.

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WITH aromatic amines *m*-nitrobenzyl chloride reacts faster than does the *p*-compound (Peacock, J., 1925, 127, 2177; *J. Physical Chem.*, 1927, 31, 535; Baker, J., 1933, 1128). With pyridine (Baker, J., 1936, 1448) and trimethylamine (Norrish and Smith, J., 1928, 129) the order is reversed. It seemed of interest to examine the rates of reaction of the cyanobenzyl chlorides with some aromatic amines, as the cyano-group, like the nitro-group, is a meta-directing substituent. Methyl alcohol was used as solvent.

TABLE I.

[Base] = 0.4M; [halide] = 0.1M.

Base.	Halide.	$k \times 10^3$ (35°).	$k \times 10^3$ (45°).
Aniline	Benzyl chloride	4.63	10.25
	<i>o</i> -Cyano- "	2.25	5.41
	<i>m</i> - " "	1.98	4.81
Ethyl- aniline	<i>p</i> - " "	1.67	4.08
	Benzyl chloride	5.76	12.90
	<i>o</i> -Cyano- "	2.03	4.56
Dimethyl- aniline	<i>m</i> - " "	2.13	4.77
	<i>p</i> - " "	1.82	4.12
	Benzyl chloride	3.50	7.92
	<i>o</i> -Cyano- "	0.63	1.47
	<i>m</i> - " "	0.88	1.90
	<i>p</i> - " "	0.75	1.73

TABLE II.

[Base] = 0.2M; [halide] = 0.05M.

Base.	Halide.	$k \times 10^3$ (30°).	$k \times 10^3$ (50°).
Aniline	Benzyl chloride	2.39	13.2
	<i>o</i> -Cyano- "	1.32	6.98
	<i>m</i> - " "	1.21	6.68
Ethyl- aniline	<i>p</i> - " "	1.00	5.29
	Benzyl chloride	3.40	17.7
	<i>o</i> -Cyano- "	1.13	5.71
Dimethyl- aniline	<i>m</i> - " "	1.25	6.65
	<i>p</i> - " "	0.98	5.11
	Benzyl chloride	2.25	11.2
	<i>o</i> -Cyano- "	0.32	1.69
	<i>m</i> - " "	0.49	2.69
	<i>p</i> - " "	0.36	2.02

With the three aromatic bases examined, *m*-cyanobenzyl chloride reacted faster than did the *p*-compound; the cyano-group thus resembles the nitro-group in this respect. The introduction of the cyano-group in any position lowers the rate of reaction. With the three bases examined, the factor governing the effect of the substituent seems to be its electron-attracting character; the greater this is, the slower is the rate of reaction.

The behaviour of *o*-cyanobenzyl chloride is interesting. Its rate of reaction is lower than that of benzyl chloride; with aniline, it is the fastest of the three cyano-compounds, with ethylaniline the second fastest, and with dimethylaniline the slowest. There is here the emergence of a steric effect not shown with aniline.

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