

AROMATIC NUCLEOPHILIC SUBSTITUTION BY HYDRIDE ELIMINATION

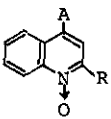
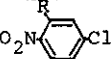
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In the course of studies of nucleophilic reactions of aromatic N-oxides, we happened to find that base-catalyzed reactions of 4-chloroquinoline N-oxide (**1**) with some active methylenes of rather lower acidity in $t\text{-BuNH}_2$ or liq NH_3 gave 2-alkylated quinoline N-oxides without any participation of the 4-chloro group. For instance, when **1** was slowly added at $-10\sim-15^\circ\text{C}$ to a suspension of pinacolone and $t\text{-BuOK}$ in $t\text{-BuNH}_2$, the reactants turned yellow, orange, orange-red and then dark brown, and afforded 4-chloro-2-pinacolylquinoline N-oxide in 79.5% yield after stirring for 40 min.

Among the various conditions, the use of 2 mol equiv of nucleophile and 2.5 mol equiv of bases gave the best results. Besides **1**, N-oxides of quinoline and 3-bromoquinoline, p-chloronitrobenzene and nitrobenzene were found to undergo this type of reaction. In reactions of nitrobenzenes the use of 3 mol nucleophiles and 4 mol bases were more preferable. Some representative example are listed below.

	A	Products, R, Reaction Conditions ¹⁾ , Yields(%)
	Cl	$-\text{CH}_2\text{COMe}$: (c) 2h, 34. $-\text{CH}_2\text{COCMe}_3$: (a) 40min, 79.5; (b) 30min, 54; (c) 2h, 90; (d) 2h, 70. $-\text{MeCHCOMe}$: (c) 1h, 65. $-\text{CH}_2\text{COPh}$: (a) 20min, 65; (c) 2h, 41.6.  : (c) 2h, 64.6; (d) 1h, 51.3. $-\text{CH}_2\text{COOEt}$: (a) 1h, 18.5. $-\text{CH}_2\text{COOCMe}_3$: (a) 40min, 62; (b) 1h, 67.
	H	$-\text{CH}_2\text{COMe}$: (c) 2h, 37.4. $-\text{CH}_2\text{COCMe}_3$: (a) 20min, 81; (b) 2h, 65; (c) 2h, 47.3. $-\text{CH}_2\text{COPh}$: (a) 1h, 65.  : (c) 2h, 46.7. $-\text{CH}_2\text{COOCMe}_3$: (b) 2h, 48. $-\text{CH}_2\text{CN}$: (a) 1h, 44.4.
		$-\text{CH}_2\text{COMe}$: (c) 8h, 56.3. $-\text{CH}_2\text{COCMe}_3$: (c) 2.5h, 62.4; (d) 4h, 44. $-\text{CH}_2\text{COPh}$: (c) 5h, 53.5. $-\text{CH}_2\text{COOCMe}_3$: (c) 3h, 21. $-\text{CH}_2\text{CN}$: 6h, 22.

1) (a): $t\text{-BuOK}-t\text{-BuNH}_2$, $-10\sim-15^\circ\text{C}$. (b): $n\text{-BuLi}-t\text{-BuNH}_2$, $-10\sim-15^\circ\text{C}$. (c): $t\text{-BuOK}-\text{liq NH}_3$, -70°C . (d): KNH_2 (or NaNH_2)-liq NH_3 , -70°C .

These reactions should be considered as aromatic nucleophilic substitutions by hydride elimination. However a few reactions conducted under nitrogen were found to give also the same products in somewhat lower yields; the combination of base and solvent seems to be a crucial factor for the reaction to proceed. Further studies are in progress to reveal the essential features of the reaction and extend its scope.