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Aromatic Nucleophilic Substitution. VI.[1] ^{1}H Nuclear Magnetic Resonance Evidence for the Rearrangement of 1,3- to 1,1-Anionic σ Complex in the Reactions of 1-Dialkylamino-2,4-dinitronaphthalenes with Potassium Alkoxides

Shizen SEKIGUCHI, Shigeru FUJISAWA, and Yumiko ANDO

Synthetic Chemistry Department, Gunma University, Tenjincho, Kiryu, Gunma 376

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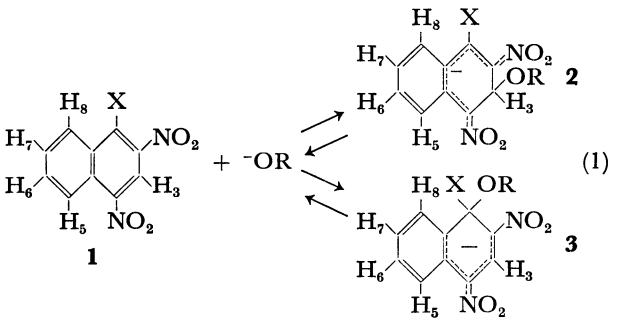
Synopsis. By use of NMR spectroscopy the rearrangement of 1,3- to 1,1-anionic σ complex (Meisenheimer complex) in the reactions of 1-dialkylamino-2,4-dinitronaphthalenes (dimethylamino-, diethylamino-, and *N*-methyl-*N*-butylamino, piperidyl) with potassium alkoxides in DMSO has been studied. The alkoxides used are potassium methoxide, ethoxide, isopropoxide, and *t*-butoxide. In the reactions of 1-dialkylamino-2,4-dinitronaphthalenes with the alkoxides the rearrangement could be spectrometrically analyzed. However, in the reaction of 1-dimethylamino-2,4-dinitro naphthalene with potassium *t*-butoxide the rearrangement was too fast to be clearly analyzed.

Regarding the 1,3-anionic σ complex (hereinafter referred to as 1,3-adduct) in the reaction of 1-methoxy-2,4-dinitronaphthalene with sodium methoxide, Millot and Terrier[2] reported the existence of the 1,3-adduct by use of visible spectra [λ_{max} 505, 550—600 (sh) nm], but showed no NMR evidence for it although NMR measurement would be a more conclusive means for confirming adducts. Fendler *et al.*, however, found no NMR evidence for the 1,3-adduct in the same reaction.[3] Although we carried out the reaction of 1-dialkylamino-2,4-dinitronaphthalenes with sodium methoxide in DMSO, no 1,3-adducts could be found.[4] Crampton and Gold reported that *N*,*N*-dimethylamino-2,4,6-trinitrobenzene with sodium methoxide gave the 1,3-adduct only[5] in MeOH, while Fyfe *et al.* found the rearrangement of the 1,3- to 1,1-adduct in the reaction of 3,5-dinitrocyanobenzene with sodium methoxide in DMSO.

Following our preliminary work[6] we now report that in the reactions of 1-dialkylamino-2,4-dinitronaphthaleneswith potassium alkoxides in DMSO the rearrangement could be followed by use of NMR spectroscopy as follows:



(1)

Replacing of sodium alkoxides by potassium ones is found to make possible measurement of NMR spectra on 1,3-adducts, which may be ascribed to the larger nucleophilicity of alkoxide ion in potassium alkoxides than in sodium ones. This greater nucleophilicity is considered to be caused by the increasing solvation of the cation (K^+) with alcohols.[7]

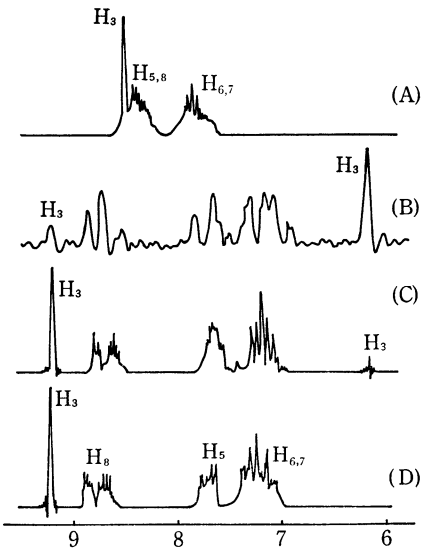


Fig. 1. NMR spectra relevant to the reaction of 1-piperidino-2,4-dinitronaphthalene (**1**, X=piperidino, 1.43×10^{-4} mol) with methanolic potassium methoxide (1.43×10^{-4} mol) in DMSO-d_6 (0.5 ml): A **1** before addition of potassium methoxide; B immediately after addition of potassium methoxide (500 Hz/50 s); C and D 2.5 min and 4 h after addition of potassium methoxide.

Immediately after addition of methanolic potassium methoxide (1.43×10^{-4} mol) to a DMSO solution (0.5 ml) of 1-piperidino-2,4-dinitronaphthalene (**1**, X=piperidino, 1.43×10^{-4} mol) at room temperature, the red solution gave the spectrum of Fig. 1B;[5,6,8] the poor resolution was due to the fast sweep time (500 Hz/150 s). The sharp singlet, attributable to H_3 of **2** (X=piperidino, R=CH_3), appeared at δ 6.21 with the resonance peak at δ 9.27, attributable to H_3 of **3** (X=piperidino, R=CH_3).[5,8] In 4 h after addition of potassium methoxide the 1,3-adduct (**2**) entirely rearranged to the 1,1-adduct (**3**). In addition, comparison of Fig. 1B with 1D shows that H_5, H_6, H_7, and H_8 resonance peaks of the 1,3- and 1,1-adducts do not substantially differ in position from each other. Similar results were obtained in other reactions of 1-dialkyl-

Table 1. H_3 Chemical shift (δ, ppm)[a]

Substrate[b]	$KOCH_3$		KOC_2H_5		$KOCH(CH_3)_2$		$KOC(CH_3)_3$	
	1,3-	1,1-	1,3-	1,1-	1,3-	1,1-	1,3-	1,1-
$CH_3\backslash N/CH_3$	6.33	9.31	6.39	9.27	6.52	9.31	—[c]	9.27
$C_2H_5\backslash N/C_2H_5$	6.37	9.27	6.26	9.23	6.51	9.27	6.58	9.27
$CH_3\backslash N/C_4H_9$	6.35	9.30	6.23	9.28	6.55	9.28	6.64	9.30
	6.21	9.27	6.25	9.20	6.35	9.24	6.28	9.23

a) In dimethyl sulfoxide with TMS as an internal standard. b) Only the substituents at C_1 of 2,4-dinitronaphthalene are indicated. c) Not clearly observed, perhaps owing to fast rearrangement.

amino-2,4-dinitronaphthalenes with potassium alkoxides studied. The fact that Fendler *et al.* could not find the existence of a 1,3-adduct is considered to be due to the fast rearrangement which is caused by the higher thermodynamic stability of **3** (X, OR; OCH_3) than **2** (X, OR; OCH_3).[3]

In the present case, therefore, both low reactivity of the 1-position of **2** and larger steric crowding at the 1-position of **3**, due to dialkylamino groups, would make the difference in stability between **2** and **3** smaller, and accordingly the rearrangement becomes so slow that the 1,3-adducts can be detected by use of NMR spectroscopy. Only the chemical shifts of H_3 of the adducts are summarized in Table 1.

In the reaction of 1-dimethylamino-2,4-dinitronaphthalene with potassium *t*-butoxide the low thermodynamic stability of **3** caused by addition of a bulky *t*-butoxide ion should make the difference in free energy between **2** and **3** larger, and accordingly make the rearrangement so fast that **2** can not clearly be observed.

Experimental

NMR spectra were recorded on a Varian A-60D spectrometer. 1-Dialkylamino-2,4-dinitronaphthalenes are prepared according to the method described in previous paper.[4]

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