Aromatic Nucleophilic Substitution. XVII.[1] Formation and Decomposition of Anionic σ Complexes in Reactions of 2-Acetylaminoethyl 2,6-Dinitrophenyl Ether and *N*-Acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline with Potassium *t*-Butoxide

Shizen Sekiguchi,* Ohtomo Hoshino, Motohiko Hirai, Keiji Okada, and Noboru Tomoto
Department of Synthetic Chemistry, Gunma Uuiversity, Kiryu, Gunma 376

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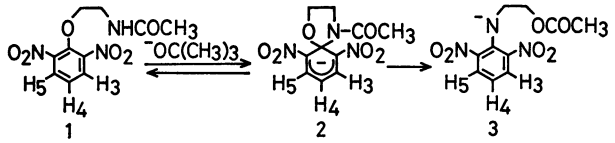
Synopsis. Reactions of 2-acetylaminoethyl 2,6-dinitrophenyl ether and *N*-acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline with *t*-butyl alcoholic $KOC(CH_3)_3$ in DMSO were followed by UV-VIS and NMR spectroscopies. In both reactions the same spiro anionic σ complex was formed.

Previously we reported the kinetics of the base-catalyzed Smiles rearrangement of 2-acetylaminoethyl 2-X-4-nitrophenyl ether (X: NO_2, Br, and CN) giving *N*-(2-acetoxyethyl)-2-X-4-nitroaniline in aqueous DMSO.[2] We have been successful in preparing 2-acetylaminoethyl 2,6-dinitrophenyl ether (**1**) and *N*-acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline (**8**).

This paper reports the formation and decomposition of the same anionic σ complexes in the reactions of **1** and **8** with $KOC(CH_3)_3$ in DMSO–*t*-BuOH mixtures by UV-VIS and NMR spectroscopies.

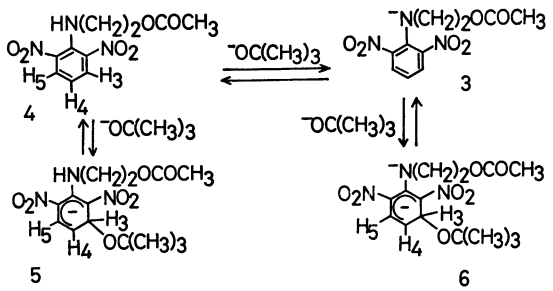
Results and Discussion

*Absorption Spectra. Reaction of 2-Acetylaminoethyl 2,6-Dinitrophenyl Ether (**1**) with $KOC(CH_3)_3$*: Upon addition of *t*-butyl alcoholic $KOC(CH_3)_3$ [1.10×10^{-2} M (1 M=1 mol dm^{-3})] to **1** (2.68×10^{-5} M) in DMSO, the solution was colored purple instantly [λ_{max} 340 (m) and 585 nm (s)], which could be attributed to the formation of **2** (Scheme 1),[3] and then the color slowly faded away. The absorption spectrum after 4 h [λ_{max} 368 nm (m)] could be attributed to the anionic species **5** (Scheme 2).[4] These results show that the respective O→N and N→O migrations of 2,6-dinitrophenyl and acetyl groups take place concurrently, and would be compatible with Scheme 1.



Scheme 1.

Reaction of N-*(2-Acetoxyethyl)-2,6-dinitroaniline (**4**) with $KOC(CH_3)_3$*: In order to elucidate further the final species in the reaction of **1** with $KOC(CH_3)_3$, the reaction of **4** with $KOC(CH_3)_3$ was carried out. Upon addition of *t*-butyl alcoholic $KOC(CH_3)_3$ (1.10×10^{-2} M) to **4** (4.71×10^{-5} M) in DMSO, the solution was colored purple instantly [λ_{max} 320 (m), 368 (m), and 585 nm (w)], and then the color slowly faded away. From a consideration of the results of Crampton *et al.*[3,4] Pollitt and Saunders,[3] and ours[2] together with the NMR spectral evidence, these bands could be attributed to a mixture of **3** (585 nm), **5** (368 nm), and **6** (320 nm). After 2 h the absorption peak at 368 nm (**5**) increased at the expense of that at 320 nm (**6**). Therefore Scheme 2 would be compatible with the results.



Scheme 2.

Reaction of N-*Acetyl*-N-*(2-hydroxyethyl)-2,6-dinitroaniline (**8**) with $KOC(CH_3)_3$*: In order to elucidate the processes described above in detail the reaction of **8** with $KOC(CH_3)_3$ was carried out.

Upon addition of *t*-butyl alcoholic $KOC(CH_3)_3$, almost similar absorption spectra to that obtained at the initial stage in the reaction of **1** with $KOC(CH_3)_3$ appeared [λ_{max} 340 (m) and 585 nm (s)] indicating the presence of the complex **2**. In course of time the absorption peak at 368 nm increased at the expense of the peak at 585 nm, indicating that after the complex **2** had been formed, the anionic species **5** was produced *via* **3** (Scheme 2).

*NMR Spectra. Reaction of 2-Acetylaminoethyl 2,6-Dinitrophenyl Ether (**1**) with $KOC(CH_3)_3$*: Upon addition of 1 equiv. of *t*-butyl alcoholic $KOC(CH_3)_3$ amide proton signal (δ=8.00) of **1** disappeared instantly, and $H_{3,5}$ and H_4 signals shifted upfield respectively (δ=8.33→7.77; 7.57→5.15) (Fig. 1). Such shifts are quite the same as the results observed in the reaction of 2-acetylaminoethyl 2,4-dinitrophenyl ether with $NaOCH_3$ in DMSO,[5] indicating the proton abstraction by $^-OC(CH_3)_3$ followed by the intramolecular nucleophilic attack of amide ion on C-1 position (Scheme 3).

Reaction of N-*(2-Acetoxyethyl)-2,6-dinitroaniline (**4**) with $KOC(CH_3)_3$*: Upon addition of 1 equiv. of *t*-butyl alcoholic $KOC(CH_3)_3$ amide proton signal (δ=8.10) of **4** disappeared instantly, and $H_{3,5}$ and H_4 signals shifted upfield instantly (δ=8.27→8.00; 6.93→6.43), which are due to the formation of **3** (Fig. 2b). After 2 h, collapsed doublets appeared at δ=*ca.* 7.87 and 5.30, attributed to H_5 and H_3 protons of **6**, respectively (Fig. 2c). Further, $H_{3,5}$ doublet (δ=8.27) of **4** reappeared, indicating the reversion of **6**⇄**3**⇄**4** (Scheme 2). This is also strongly evidenced by the presence of amino proton signal at δ=*ca.* 8.10, although it partly overlapped $H_{3,5}$ doublet (δ=8.27) of **4** (Fig. 2c). Collapsed triplet at δ=6.93 could be attributed to H_4 proton of **4**. The weak signals at δ=*ca.* 5.45 would be a part of the doublet due to H_3 proton of **5**. H_3 doublet (δ=*ca.* 5.20) of **5** partly overlapped collapsed H_3 doublet (δ=*ca.* 5.40) of **6**.

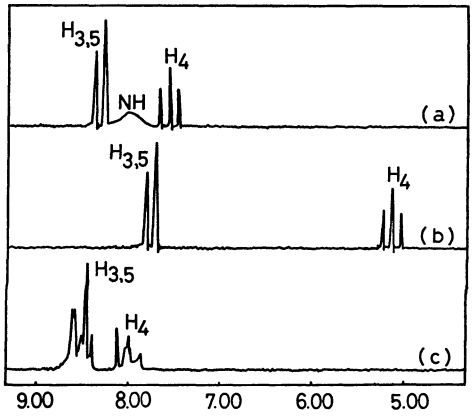


Fig. 1. NMR spectral change relevant to the reactions of 2-acetylaminoethyl 2,6-dinitrophenyl ether (**1**) and *N*-acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline (**8**) with $KOC(CH_3)_3$ in DMSO. a: **1**, b: just after addition of 1 equiv. of *t*-butyl alcoholic $KOC(CH_3)_3$, c: **8**.

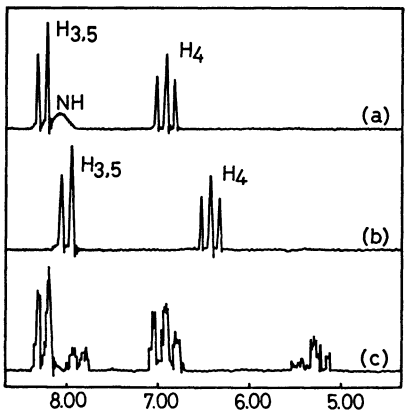
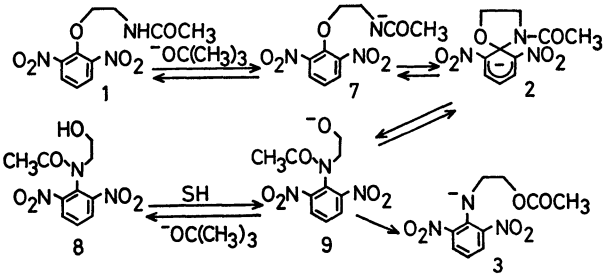


Fig. 2. NMR spectral change relevant to the reaction of *N*-(2-acetoxyethyl)-2,6-dinitroaniline (**4**) with $KOC(CH_3)_3$ in DMSO. a: **4**, b: just after addition of 1 equiv. of *t*-butyl alcoholic $KOC(CH_3)_3$, c: 6 h after addition.



Scheme 3.

These results show that just after addition of $KOC(CH_3)_3$ **4** is transformed to **3**, which partly reverts to **4**, producing **5**, and partly changes into **6** (Scheme 2).

Reaction of N-*Acetyl*-N-*2-(hydroxyethyl)-2,6-dinitroaniline (8) with* $KOC(CH_3)_3$: Upon addition of 1 equiv. of *t*-butyl alcoholic $KOC(CH_3)_3$ to **8** in DMSO (Fig. 1c), the same signal pattern as Fig. 1b appeared, indicating the formation of the complex **2**. Complicated $H_{3,5}$ and H_4 signals (Fig. 1c) are considered to be due to the coexistence of (*E*) and (*Z*) isomers of **8**.

In conclusion, it is confirmed that **1** undergoes the base-catalyzed Smiles rearrangement, producing **4** *via* the spiro anionic σ complex **2**, producing **4** *via* **9** and **3**, and that **8** is base-catalyzed to at first produce **2**, which reverts to **9**, producing **4** *via* **3**.[2]

Experimental

Mps were uncorrected. Compounds **1**, **4**, and **8** were identified by NMR, IR, and MS. Their results of the elementary analysis were in good agreement with those calculated ones within the experimental errors.

2-Acetylaminoethyl 2,6-Dinitrophenyl Ether (1). According to the method described in the literature[6] was prepared 2,6-dinitroaniline (DNA) from chlorobenzene (yield 20%), and 2,6-dinitrochlorobenzene (DNC) prepared from DNA (yield 69%).

After a nitrobenzene (10 g) solution of KF (6 g, 0.103 mol) and DNC (14 g, 0.0069 mol) was stirred at 190 °C for 5 h and, then, the nitrobenzene distilled off under reduced pressure, the residue was further distilled at 145—150 °C/6 mmHg to produce 8.4 g of 2,6-dinitrofluorobenzene (DNF) (yield 61%), mp 60—62 °C (lit, 60—63 °C).[10]

From DNF and 2-acetylaminoethanol was prepared **1** according to the method described previously.[5] Recrystallization from ligroin gave pure **1** crystals (yield 13%); mp 92—93 °C; UV_{max} (DMSO) 305 nm (ε=1970).

N-(2-Acetoxyethyl)-2,6-dinitroaniline (4). A 30 ml DMSO solution of 2.4 g (0.0039 mol) of 2-aminoethanol was added dropwise to a 60 ml DMSO stirred solution of 4 g (0.020 mol) of DNC for 3 h at room temperature, and then the mixture poured into an ice–water. The precipitate formed was filtered and recrystallization from ethanol gave 2 g of pure *N*-(2-hydroxyethyl)-2,6-dinitroaniline (HDNA) (yield 44.5%). After a 100 ml dioxane solution of 2 g (0.0088 mol) of HDNA and 1.4 g (0.018 mol) of acetyl chloride was stirred at 80 °C for 1 h, the mixture was poured into an ice–water and extracted with benzene. The benzene layer was dried over anhydrous Na_2SO_4 overnight, filtered and evaporated. The residue was chromatographed over silica gel (benzene) and recrystallized from methanol to give 1.7 g of **4** (yield 75.5%); mp 55—56 °C; UV_{max} (DMSO): 428 nm ($\varepsilon=6.05\times10^3$).

N-Acetyl-N-(2-hydroxyethyl)-2,6-dinitroaniline (8). A 50 ml dioxane solution of 5.5 g (0.053 mol) of 2-acetylaminoethanol, and 1.0 g (0.027 g-atom) of potassium was refluxed until potassium was dissolved. To this solution was rapidly added a 50 ml dioxane solution of 5.0 g (0.027 mol) of DNF, and the mixture swirled for *ca.* 3 min (short reaction time should be necessary). Then, the mixture was poured into an ice–water, neutralized with dilute HCl (10%), and extracted with chloroform. The chloroform layer was dried over anhydrous Na_2SO_4 overnight, filtered, evaporated, and chromatographed over silica gel (benzene:acetone 5:1 v/v), and recrystallized from ligroin to give 0.09 g (yield 1.3%) of **1** and 0.32 g (yield 4.4%) of **8**; mp 118—119 °C; UV_{max} (DMSO) 320 nm ($\varepsilon=4.13\times10^3$).

References

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