

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 University, Kiryu, Gunma 376

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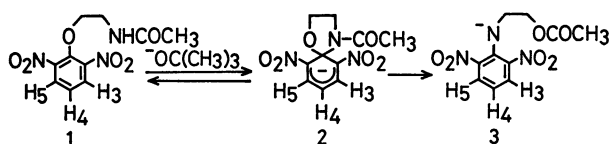
Synopsis. Reactions of 2-acetylaminoethyl 2,6-dinitrophenyl ether and *N*-acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline with *t*-butyl alcoholic $\text{KOC}(\text{CH}_3)_3$ in DMSO were followed by UV-VIS and NMR spectroscopies. In both reactions the same spiro anionic σ complex was formed.

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 $\text{KOC}(\text{CH}_3)_3$ in DMSO-*t*-BuOH mixtures by UV-VIS and NMR spectroscopies.

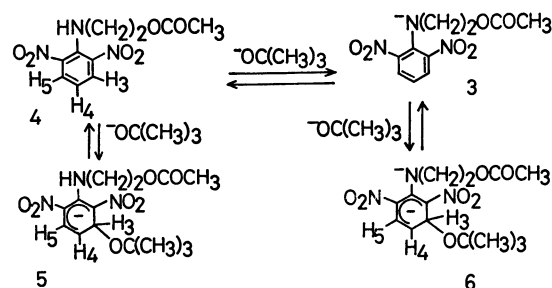
Results and Discussion

Absorption Spectra. *Reaction of 2-Acetylaminoethyl 2,6-Dinitrophenyl Ether (1) with $\text{KOC}(\text{CH}_3)_3$:* Upon addition of *t*-butyl alcoholic $\text{KOC}(\text{CH}_3)_3$ [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 $\rightarrow$ N and N $\rightarrow$ 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 $\text{KOC}(\text{CH}_3)_3$: In order to elucidate further the final species in the reaction of **1** with $\text{KOC}(\text{CH}_3)_3$, the reaction of **4** with $\text{KOC}(\text{CH}_3)_3$ was carried out. Upon addition of *t*-butyl alcoholic $\text{KOC}(\text{CH}_3)_3$ (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 ours²⁾ 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 $\text{KOC}(\text{CH}_3)_3$: In order to elucidate the processes described above in detail the reaction of **8** with $\text{KOC}(\text{CH}_3)_3$ was carried out.

Upon addition of *t*-butyl alcoholic $\text{KOC}(\text{CH}_3)_3$, almost similar absorption spectra to that obtained at the initial stage in the reaction of **1** with $\text{KOC}(\text{CH}_3)_3$ 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 $\text{KOC}(\text{CH}_3)_3$:* Upon addition of 1 equiv. of *t*-butyl alcoholic $\text{KOC}(\text{CH}_3)_3$ amide proton signal ($\delta=8.00$) of **1** disappeared instantly, and $\text{H}_{3,5}$ and H_4 signals shifted upfield respectively ($\delta=8.33 \rightarrow 7.77$; $7.57 \rightarrow 5.15$) (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 $-\text{OC}(\text{CH}_3)_3$ 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 $\text{KOC}(\text{CH}_3)_3$: Upon addition of 1 equiv. of *t*-butyl alcoholic $\text{KOC}(\text{CH}_3)_3$ amide proton signal ($\delta=8.10$) of **4** disappeared instantly, and $\text{H}_{3,5}$ and H_4 signals shifted upfield instantly ($\delta=8.27 \rightarrow 8.00$; $6.93 \rightarrow 6.43$), which are due to the formation of **3** (Fig. 2b). After 2 h, collapsed doublets appeared at $\delta \approx 7.87$ and 5.30 , attributed to H_5 and H_3 protons of **6**, respectively (Fig. 2c). Further, $\text{H}_{3,5}$ doublet ($\delta=8.27$) of **4** reappeared, indicating the reversion of $6 \rightleftharpoons 3 \rightleftharpoons 4$ (Scheme 2). This is also strongly evidenced by the presence of amino proton signal at $\delta \approx 8.10$, although it partly overlapped $\text{H}_{3,5}$ doublet ($\delta=8.27$) of **4** (Fig. 2c). Collapsed triplet at $\delta=6.93$ could be attributed to H_4 proton of **4**. The weak signals at $\delta \approx 5.45$ would be a part of the doublet due to H_3 proton of **5**. H_3 doublet ($\delta \approx 5.20$) of **5** partly overlapped collapsed H_3 doublet ($\delta \approx 5.40$) of **6**.

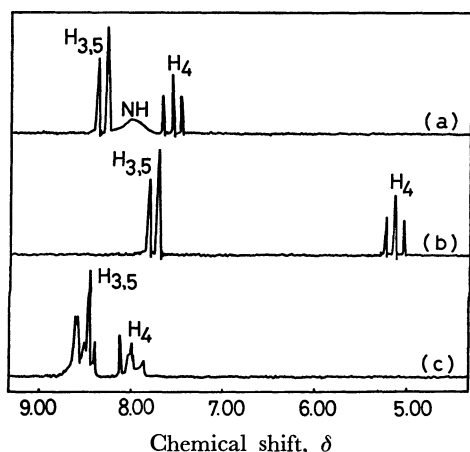


Fig. 1. NMR spectral change relevant to the reactions of 2-acetylaminophenyl ether (**1**) and *N*-acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline (**8**) with $\text{KOC}(\text{CH}_3)_3$ in DMSO. a: **1**, b: just after addition of 1 equiv. of *t*-butyl alcoholic $\text{KOC}(\text{CH}_3)_3$, c: **8**.

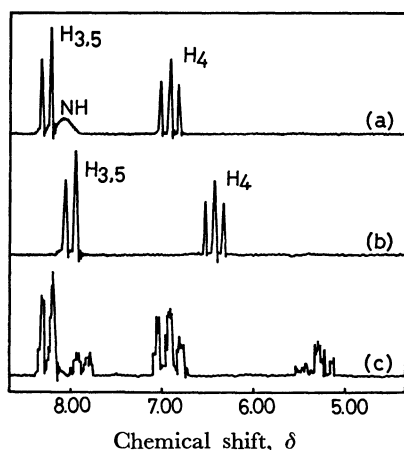
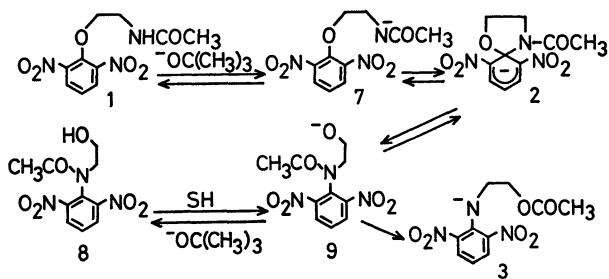


Fig. 2. NMR spectral change relevant to the reaction of *N*-(2-acetoxyethyl)-2,6-dinitroaniline (**4**) with $\text{KOC}(\text{CH}_3)_3$ in DMSO. a: **4**, b: just after addition of 1 equiv. of *t*-butyl alcoholic $\text{KOC}(\text{CH}_3)_3$, c: 6 h after addition.



Scheme 3.

These results show that just after addition of $\text{KOC}(\text{CH}_3)_3$ **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 $\text{KOC}(\text{CH}_3)_3$:** Upon addition of 1 equiv. of *t*-butyl alcoholic $\text{KOC}(\text{CH}_3)_3$ to **8** in DMSO (Fig. 1c), the same signal pattern as Fig. 1b appeared, indicating the formation of the complex **2**. Complicated $\text{H}_{3,5}$ 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-Acetylaminophenyl 2,6-Dinitrophenyl Ether (1**).** According to the method described in the literature⁶⁾ 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-acetylaminophenol 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 ($\epsilon=1970$).

***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 ($\epsilon=6.05 \times 10^3$).

***N*-Acetyl-*N*-(2-hydroxyethyl)-2,6-dinitroaniline (**8**).** A 50 ml dioxane solution of 5.5 g (0.053 mol) of 2-acetylaminophenol, 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 ($\epsilon=4.13 \times 10^3$).

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