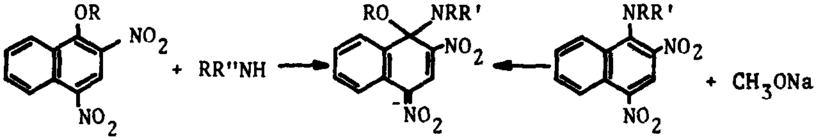
Tetrahedron Letters No. 19, pp 1745 - 1748, 1974. Pergamon Press. Printed in Great Britain.

AROMATIC NUCLEOPHILIC SUBSTITUTION IV.[1] EXISTENCE OF 1,3- AND 1,1-DISUBSTITUTED MEISENHEIMER COMPLEXES IN THE REACTIONS OF 1-SEC-AMINO-2,4-DINITRO-NAPHTHALANES WITH SODIUM ETHOXIDE

S.Sekiguchi, K.Shinozaki, T.Hirose, K.Matsui, and T.Itagaki
Department of Synthetic Chemistry, Gunma University, Kiryu, Gunma 376, JAPAN

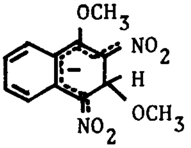
(Received in Japan 20 March 1974; received in UK for publication 1 April 1974)

We found in previous work[1,2] that same 1,1-disubstituted Meisenheimer complexes (hereinafter referred to as σ complex) could be formed in the reactions of 1-sec-amino-2,4-dinitronaphthalenes with sodium methoxide or in the reactions of 1-alkoxy-2,4-dinitronaphthalenes with secondary amines. In these works, however, no 1,3-disubstituted σ complex could be found. Regarding 1,3-disubstituted 2,4-dinitronaphthalene σ complexes,[3] Millot and Terrier[4] reported the existence of I by use of visible spectra [λ_{max} 505, 550-600(sh) nm]. There has, however, been no NMR evidence for I as a transient species, although NMR measurement would be a more conclusive means for confirming σ complexes.

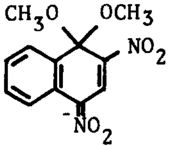


R,R': alkyl, piperidyl

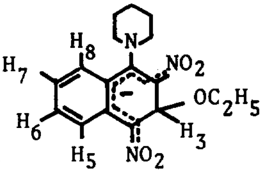
In addition, we found in previous work[5] that the spiro σ complexes (III and IV) could be isolated at room temperature in the reaction of 1-[N-methyl-(2'-hydroxy) ethylamino]-2,4,6-trinitrobenzene or 1-[N-methyl-(2'-hydroxy) ethyl-amino]-2,4-dinitronaphthalene with MeONa; these results are the same as those of Bernasconi et al.[6] The NO_2 group ortho to C-1 is nearly copolanar with the ring, whereas the dihedral angles have been observed to be up to 62° between the ring and NO_2 group ortho to the ethoxyl one in trinitrophenetole, presumably owing to the steric compression between these groups.[7] Release of this compression in the complex may correspond to one of the principal reasons for greater thermodynamic stability of 1,1-disubstituted complexes such as II, relative to 1,3-disubstituted ones such as I.



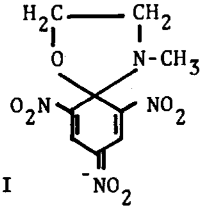
I



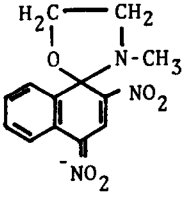
II



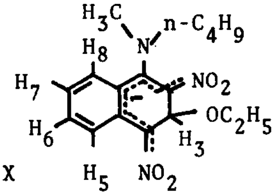
VI



III



IV



IX

On the basis of the above-described results we have recently carried out the title reactions and found that at first a 1,3-disubstituted σ complex was formed, and then, changed to the 1,1-disubstituted one.

When ethanolic C_2H_5ONa was added to a solution of 1-N-piperidyl-2,4-dinitronaphthalene (V) in DMSO (V 2.06×10^{-4} mol, C_2H_5ONa 2.06×10^{-4} mol, DMSO/C_2H_5OH 0.5 ml/0.076 ml), the solution immediately colored red, indicating the formation of a complex. The time-dependent NMR spectra of the reaction system are shown in Fig. 1. Immediately after mixing, the sharp singlets appeared at δ 9.24 and 6.29, attributable to the H_3 protons of VII and VI, respectively,[1,2] and the $H_{5,8}$ and $H_{6,7}$ peaks of V disappeared, and, instead, the H_8 peak was shifted to δ 8.91 (downfield) and the H_5 and $H_{6,7}$ peaks to δ 7.77 and 7.27 (upfield), respectively. In 1 hr after mixing, the H_3 peak of VI disappeared (Fig. 1C). As clearly shown by a comparison of the spectrum in Fig. 1A with that in Fig. 1C, almost V changed to the 1,1-disubstituted σ complex (VII) in 1 hr after mixing. From these results the following

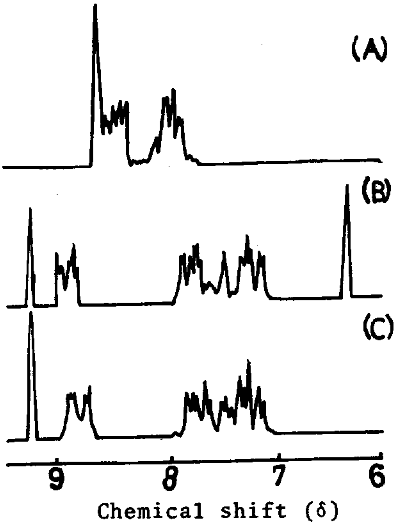


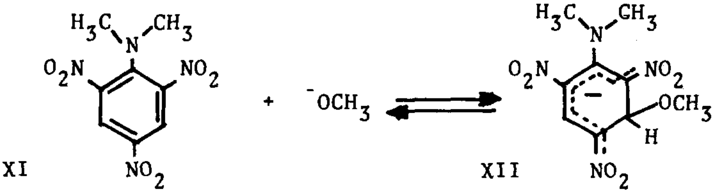
Fig. 1 NMR spectra of the reaction of V with C_2H_5ONa (25 °C): (A) V before addition of C_2H_5ONa: (B), (C) immediately, 1 hr after addition of C_2H_5ONa.

formula is indicated on the basis of the work of Millot and Terrier:[3,8]

$$\mathrm{V} \quad + \quad \mathrm{C_2H_5ONa} \quad \begin{array}{l} \rightleftharpoons \ \mathrm{VI\ (unstable)} \\ \rightleftharpoons \ \mathrm{VII\ (stable)} \end{array}$$

In the reaction of 1-(N-methyl-n-butylamino)-2,4-dinitronaphthalene (VIII) with C_2H_5ONa, the similar results were also obtained. Our present work is the first case, in which the existence of 1,3-disubstituted 2,4-dinitronaphthalene σ complexes could be confirmed by NMR measurement.

Crampton and Gold reported that N,N-dimethylamino-2,4,6-trinitrobenzene (XI) reacted with sodium methoxide to give a 1,3-disubstituted σ complex (XII) only:[9]



However, our results are much different from their ones. The relevant NMR data are summarized in Table 1.

References

1 Part III, S.Sekiguchi, K.Shinozaki, T.Hirose, K.Matsui, and K.Sekine, Bull.Chem.Soc.Japan, submitted for.

2 S.Sekiguchi, T.Itageki, T.Hirose, K.Matsui, and K.Sekine, Tetrahedron, 29, 3527(1973).

3 M.J.Strauss, Chem.Rev., 70, 667(1970).

4 F.Millot and F.Terrier, Bull.Soc.Chim.Fr., 2692(1969).

5 S.Sekiguchi and T.Shiojima, Bull.Chem.Soc.Japan, 46, 693(1973).

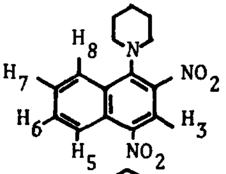
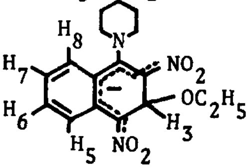
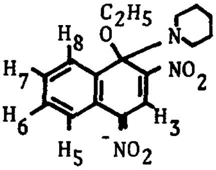
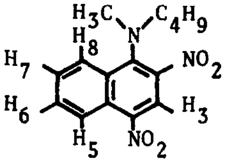
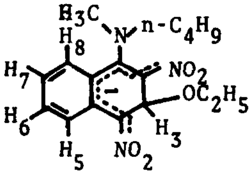
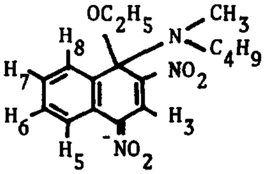
6 C.F.Bernasconi, R.H.deRossi, and C.L.Gehriger, J.Org.Chem., 38, 2838(1973).

7 C.M.Gramaccioli, R.Destro, and M.Simmonetta, Acta Crystallogr., 24, 129(1968)

8 F.Millot and F.Terrier, Bull.Soc.Chim.Fr., 3897(1971).

9 M.R.Crampton and V.Gold, J.Chem.Soc.(B), 893(1966).

Table 1 NMR spectral data for relevant compounds (δ).[a]

Compound		H_3	H_8	H_5	$H_{6,7}$
V		8.60	8.47		7.92
VI		9.24	8.81[b]	7.72[b]	7.20[b]
VII		6.29	8.81[b]	7.72[b]	7.20[b]
VIII		8.65	8.50		7.94
IX		9.28	8.79[b]	7.71[b]	7.19[b]
X		6.42	8.79[b]	7.71[b]	7.19[b]

[a] Chemical shifts relative to internal TMS.

[b] The H_8, H_5, and $H_{6,7}$ peaks of 1,3-disubstituted σ complexes (VI, IX) are not distinguishable from those of 1,1-disubstituted ones.