Aromatic Nucleophilic Substitution. III.[1] Meisenheimer Complexes in the Reactions of 1-(*N*,*N*-Dialkylamino)-2,4-dinitronaphthalenes with Sodium Methoxide

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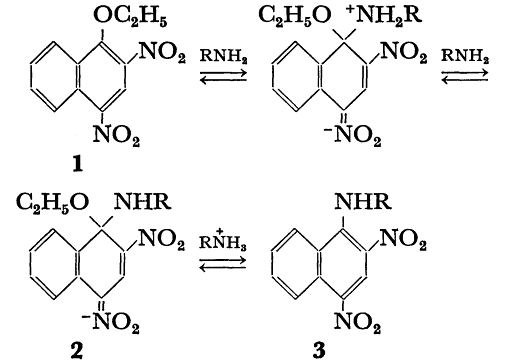
The intermediates in the reaction of 1-(*N*,*N*-dimethylamino)-2,4-dinitronaphthalene (**9**) with sodium methoxide have been studied in the mixtures of DMSO and CH_3OH. The NMR spectra of the equimolar mixture of **9** and sodium methoxide indicate that **9** and a 1,1-disubstituted Meisenheimer complex coexist immediately after mixing, and that nearly all **9** changed into the Meisenheimer complex 15 min after mixing. The addition of 2 mol of sodium methoxide to 1 mol of **9** gave no 1,1,3,3-tetrasubstituted 2,4-dinitronaphthalene Meisenheimer complex. 1-Piperidino- or 1-(*N*-methyl-*N*-*n*-butylamino)-2,4-dinitronaphthalene reacted with sodium methoxide to give a similar Meisenheimer complex.

Many Meisenheimer complexes have been prepared by nucleophilic attack on polynitroaromatic compounds, the reactions being extensively studied and the results reviewed in detail.[2]

In the nucleophilic substitution reaction of 1-ethoxy-2,4-dinitronaphthalene (**1**) with primary amines, Orvik and Bunnett[3] confirmed the presence of the Meisenheimer complex (**2**, hereinafter referred to as σ complex) during the course of reaction by means of the kinetics and visible spectra as shown in Eq. (1). We reported on the presence of σ complexes (**4**) in the reactions of **1** or 1-ethoxy-2,4,5-trinitronaphthalene (**5**) with secondary amines by NMR measurement:[1] Only a few papers have appeared on the reactions of amino-substituted polynitromaromatic compounds with sodium or potassium alkoxides.



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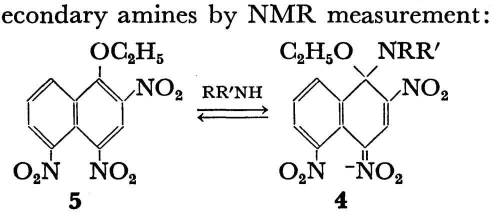
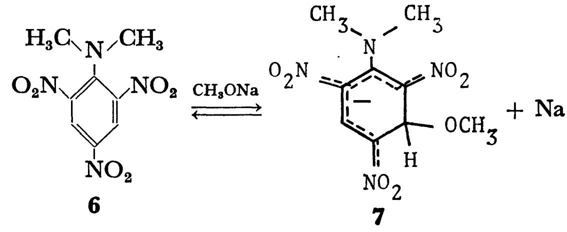


(2)

Crampton and Gold[4] reported that 1-(*N*,*N*-dimethylamino)-2,4,6-trinitrobenzene (**6**) reacted with CH_3ONa to give a 1,3-disubstituted Meisenheimer complex (**7**) and that addition of excess CH_3ONa produced dianion (**8**).



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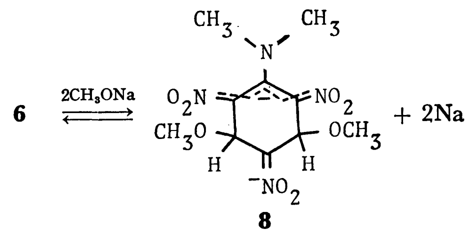

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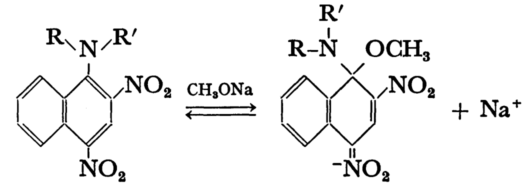
We have carried out the reactions of 1-(*N*,*N*-dialkylamino)-2,4-dinitronaphthalenes with CH_3ONa in DMSO–CH_3OH mixture and found that 1,1-disubstituted σ complexes were formed but no 1,3-disubstituted σ complex, and that the reactions give an easy method for the preparation of 1,1-disubstituted naphthalene σ complexes containing both an alkoxyl- and a dialkylamino groups at C-1:



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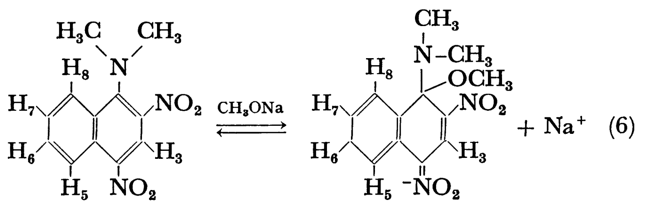
This paper reports on the presence of σ complexes in the reactions of 1-(*N*,*N*-dialkylamino)-2,4-dinitronaphthalenes with CH_3ONa.

Results and Discussion

*Reaction of 1-(*N,N*-Dimethylamino)-2,4-dinitronaphthalene (9) with Sodium Methoxide.* The addition of methanolic CH_3ONa to a solution of **9** in DMSO (**9** 2.19×10^{-5} mol/l, CH_3ONa 2.05×10^{-1} mol/l) gave a red species (λ_{max} 351, 264, and 518 nm). Not only the shape but also the positions and intensities of these bands are similar to those of 1,1-disubstituted polynitronaphthalene σ complexes.[1,2]

The NMR spectra of the reaction system are shown in Fig. 1. Immediately after methanolic CH_3ONa was added to **9** in DMSO (0.20 ml) (CH_3ONa 1.68×10^{-4}



9 **10**

mol, **9** 1.68×10^{-4} mol), to which a small amount of CH_3OH had been added so that the volume ratio ($DMSO/CH_3OH$) was 1.5, the H_3 band intensity of **9** (δ 8.61, Fig. 1A, 1B) decreased, and, at the same time, its band position was shifted to δ 9.32, attributed to H_3 of **10**.[1,4] A new multiplet appeared at δ 7.33, attributed to H_6 and H_7 of **10** (Fig. 1B).[1,4] The calculation of band intensity indicates the presence of the H_3 band of **9**, which overlaps the H_8 band (d, δ 8.79) of **10**. Thus, the spectrum (Fig. 1B) indicates that compounds **9** and **10** coexist in this reaction system. The bands at δ 8.45 (Table 1) disappeared 15 min after mixing (Figs. 1B and 1C). Even 1 hr after mixing, the spectrum of the system was the same as that in Fig. 1C. After 24 hr a part of **10** decomposed to **9** since bands attributed to **9** appeared (Fig. 1D).[5]

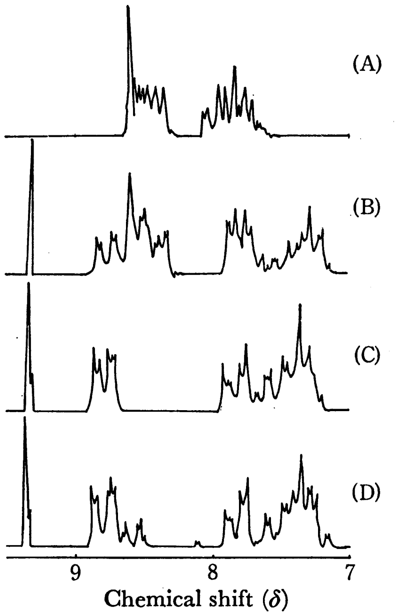
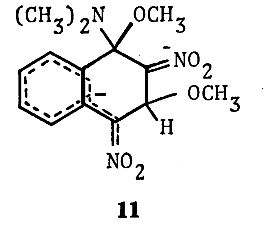


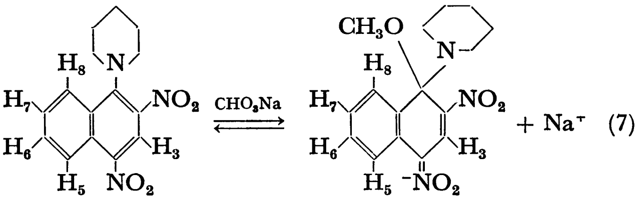
Fig. 1. NMR spectra relevant to the reaction of **9** with CH_3ONa: (A) **9** before addition of CH_3ONa; (B), (C), and (D) immediately, *ca.* 15 min, and 24 hr, respectively, after addition of CH_3ONa.



11

When two mol of CH_3ONa had been added to one mol of **9** under similar conditions, the same spectrum as that in Fig. 1C was obtained. In the case of **9**, therefore, no dianion such as **11**, which is similar in structure to **8**, was produced. When the solvent ratio was varied, the chemical shift of each proton band of **10** was substantially the same in both cases (Table 1). The results and the large shift of each proton band position in the conversion of **9** into **10** indicate that the intermediate in the reaction of **9** with CH_3ONa is not a charge transfer complex, but a σ one.[6-8]

*Reaction of 1-Piperidino-2,4-dinitronaphthalene (**12**) with Sodium Methoxide.* The addition of methanolic CH_3ONa to a solution of **12** in DMSO (**12** 2.39×10^{-5} mol/l, CH_3ONa 2.39×10^{-2} mol/l) gave a red species (λ_{max} 352, 361, and 517 nm). The spectrum was similar in shape, position and intensity to that of the complex in the reaction of **9** with CH_3ONa.



12 **13**

The NMR spectra of the reaction system are shown in Fig. 2[9] [**12** 1.83×10^{-4} mol, CH_3ONa 1.83×10^{-4} mol, $DMSO/CH_3OH$ 0.62 ml (4.2/1)].

The time-dependent change of the spectrum of the reaction system differs from that in the reaction of **9** with CH_3ONa. Immediately after mixing, the H_3 bands of **12** and **13** appeared at δ 8.65 and 9.31, respectively (Figs. 2A and 2B). The H_8, H_5, and $H_{6,7}$ bands of **12** appeared at δ 8.78, 7.71, and 7.29, respectively, besides the bands of the aromatic protons of **12** (Fig. 2B). These results indicate that **12** and **13** coexist immediately after mixing. Twenty-four hours after mixing, nearly all **12** changed into **13** (Fig. 2C). Calculation of band intensity indicates that 43 hr after mixing a part of **13** decomposes to **12**.[5]

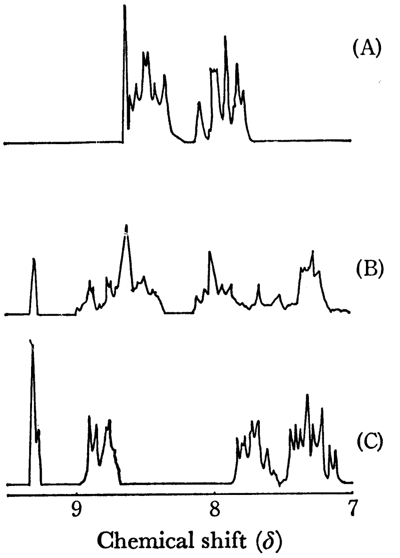


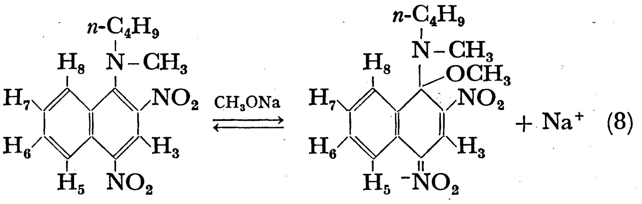
Fig. 2. NMR spectra relevant to the reaction of **12** with CH_3ONa: (A) **12** before addition of CH_3ONa; (B) and (C) immediately and 24 hr, respectively, after addition of CH_3ONa.

TABLE 1. RELEVANT NMR DATA

Compound	H_3	H_8	H_5	$H_{6,7}$	Solvent ratio $\frac{DMSO}{CH_3OH}$ (vol.)
9	8.61 (s)	8.45 (m)		7.85 (m)	DMSO[b]
10	9.32 (d) 9.31 (d)	8.79 (d) 8.80 (d)	7.79 (d) 7.65 (d)	7.33 (m) 7.23 (m)	1.5 4.4
12	8.60 (s)	8.47 (d)		7.92 (m)	DMSO[b]
13	9.23 (s)	8.78 (d)	7.71 (m)	7.29 (m)	4.3
14	8.65 (s)	8.50 (m)		7.94 (m)	DMSO[b]
15	9.31 (s)	8.83 (m)	7.61 (m)[c]	7.21 (m)	4.5

a) Chemical shifts were described in δ values relative to TMS. b) NMR spectra were measured in DMSO only. c) The doublets were split into multiplets by long range coupling.

*Reaction of 1-(*N*-Methyl-*N*-n-butylamino)-2,4-dinitronaphthalene (14) with Sodium Methoxide.* As in the reaction of **9** or **12** with CH_3ONa, the addition of methanolic CH_3ONa to a solution of **14** in DMSO (**14**, 2.47×10^{-5} mol/l; CH_3ONa, 2.47×10^{-1} mol/l) gave a red species (λ_{max} 349, 364, and 516 nm). The spectrum was also similar to that obtained in the reaction of **9** or **12** with CH_3ONa.



14 **15**

The NMR spectra of the reaction system are shown in Fig. 3[9] [**14** 1.79×10^{-4} mol, CH_3ONa 1.79×10^{-4} mol, $DMSO/CH_3OH$ 0.24 ml (4.5/1)]. Only the bands attributed to the aromatic protons of **15** appeared immediately after mixing (Figs. 3A and 3B). The spectrum did not substantially change 24 hr after mixing, but a part of **15** decomposed to **14** 43 hr after mixing (Fig. 3C).[5]

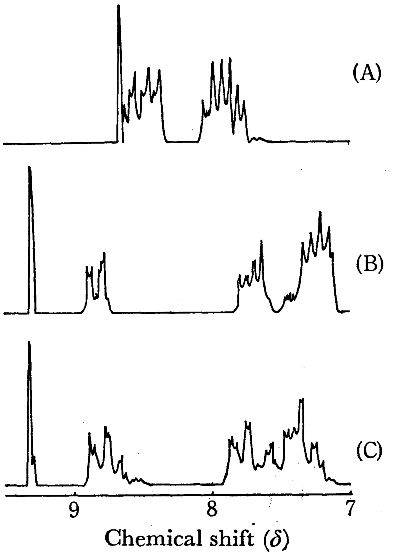


Fig. 3. NMR spectra relevant to the reaction of **14** with CH_3ONa: (A) **14** before addition of CH_3ONa; (B) and (C) immediately and 43 hr, respectively, after addition of CH_3ONa.

It is thus concluded that a 1,1-disubstituted naphthalene σ complex is formed in the reaction of 1-(*N*,*N*-dialkylamino)-2,4-dinitronaphthalene with CH_3ONa. Bunnett and Zahler[10] stated that the formation of an anion by the dissociation of a complex depends upon the stability of the anion: the ease of anion separation decreases in the order alkoxide ions>amide ions.

The fact that no nucleophilic substitution by methoxide ion took place confirms the interpretation of Bunnett and Zahler. For the sake of confirmation relevant NMR spectral data are included in Table 1.

Experimental

NMR spectra were recorded on a Varian A-60D spectrometer. Visible spectra were measured on a Hitachi-124 UV-VIS spectrophotometer. Compounds **9**, **12**, and **14** were prepared according to the method given previously.[1]

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5) The decomposition might be caused by a trace of water remaining almost invariably in dried DMSO.

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10) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).