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An Anion Radical Precursor in the Nucleophilic Substitution of *o*-Dinitrobenzene

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By visible and ESR spectroscopies, the appearance of *o*-dinitrobenzene anion radical has been demonstrated for the replacement of one nitro group of *o*-dinitrobenzene by hydroxide ion in aqueous dimethyl sulfoxide. Kinetic studies have supported the suggestion that the anion radical is a precursor in the substitution reaction.

According to the electron transfer theory proposed by Nagakura and Tanaka,[1,2] nucleophilic aromatic substitution should proceed *via* the anion radical resulting from one-electron transfer from the highest occupied orbital of a nucleophilic reagent to the lowest vacant orbital of an aromatic molecule. Here the energy level of the highest occupied orbital must be higher than that of the lowest vacant orbital. Recently, some anion radicals observed during the course of nucleophilic substitution have been supposed to be precursors in the substitution mechanisms.[3-10] As described by Bernasconi,[10] there has been no evidence that the anion radicals are the precursors in the nucleophilic substitution rather than the products resulting from competing side reactions. We now present the experimental results strongly supporting that an *o*-dinitrobenzene anion radical is the precursor in the replacement of one nitro group of *o*-dinitrobenzene by hydroxide ion in aqueous dimethyl sulfoxide (DMSO).

Experimental

o-Dinitrobenzene was obtained commercially and purified by recrystallization. DMSO was kept in contact with barium oxide for a week and fractionated two times under reduced pressure. *N,N*-Dimethylformamide was treated with sodium hydroxide pellets and barium oxide, and distilled at 1 Torr. This solvent was kept with Molecular Sieves 4A after degassed.

Unless otherwise stated, all the mixings of degassed solutions of *o*-dinitrobenzene with degassed solutions of sodium hydroxide were carried out in sealed cells in order to obtain the electronic and ESR spectra. Electronic-spectral changes were recorded with a Cary 14 recording spectrophotometer equipped with a thermostated cell compartment. ESR spectra were recorded with a Varian E-4 EPR spectrometer.

Results and Discussion

When a DMSO solution of *o*-dinitrobenzene was mixed with an aqueous DMSO solution of sodium hydroxide, the resultant reaction system showed absorption spectral changes shown in Figs. 1 and 2. Curve e in Fig. 1 is obtained by correcting curve a for the absorption of DMSO, because DMSO absorbs above 700 nm as shown in Fig. 1. The reaction system, therefore, shows the absorption curve of e in the region 800—1200 nm. The bands at 325 and 800—1200 nm increased in intensity and gradually disappeared later on.

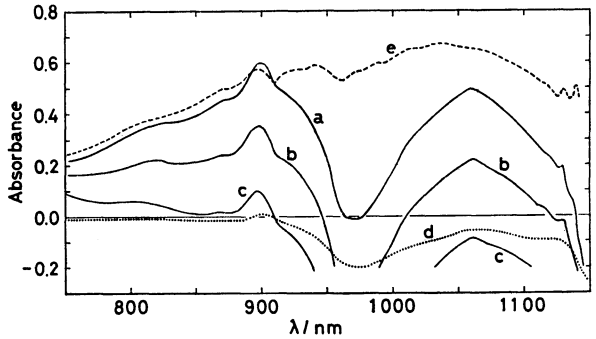


Fig. 1. Spectral change of the DMSO solution containing *o*-dinitrobenzene (3.30×10^{-4} M), sodium hydroxide (1.00×10^{-2} M) and 4% (v/v) water (25 °C). Time after mixing: a, 4.4 min; b, 15 min; c, 41 min. Curve e is obtained by correcting curve a for the absorption of DMSO (curve d). Path length was 2.87 cm except the case of d, whose path length was 1.00 cm.

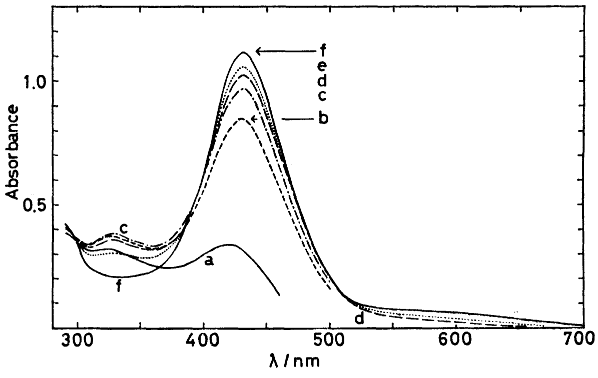


Fig. 2. Spectral change of the same solution as in Fig. 1 (25 °C). Time after mixing: a, 15 s; b, 1.3 min; c, 4.6 min; d, 11 min; e, 30 min; f, 100 min. Path length was 0.390 cm.

The initial 420 nm band (curve a in Fig. 2) differs from the final 430 nm band (curve f) in peak position. In the case of the similar reaction system open to the air, it was distinctly observed with a Hitachi rapid scan spectrophotometer RSP-2 that at the initial stage the 420 nm band increased in intensity in the same way as the 325 nm band. The time courses of absorption-coefficient changes at 900 and 430 nm are shown in Fig. 3. Curve b in Fig. 3 indicates that the whole course of increasing absorption coefficient at 430 nm is not due to one species, since the increase in the coefficient is abruptly slow down at *ca.* 5 min after mixing. Accordingly, the initial 420 nm band is assigned to the labile

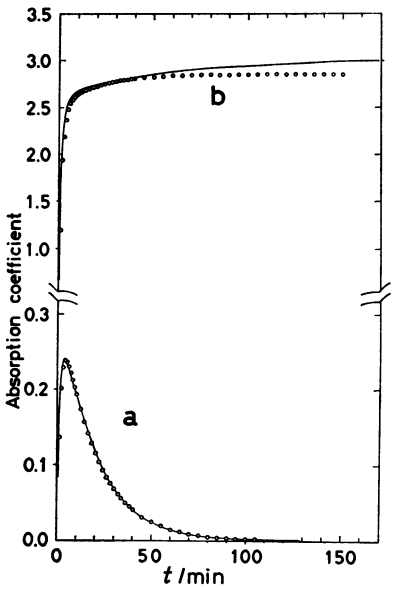


Fig. 3. Time course (full lines) of absorption coefficient of the same solution as in Fig. 1 (25.0 °C). a, 900 nm; b, 430 nm. Circles show the values calculated according to Eqs. 1 and 2 or to Eqs. 3 and 4.

species showing the bands at 325 and 800—1200 nm.

The bands at 325 and 420 nm do not correspond to the 430 and 455 nm bands, respectively, of the π-electronic structure (*i.e.*, 1-nitropentadienate) of 1-amino-1-methoxy-2-nitrocyclohexadienate formed from *o*-nitroaniline and methoxide ion in dichloromethane.[11] The bands at 325, 420, and 800—1200 nm correspond to those at 350, 440, and 1090 nm, respectively, assigned to the *o*-dinitrobenzene anion radical in a γ-irradiated rigid solution in 2-methyltetrahydrofuran at 77 K.[12] We, therefore, assign the labile species showing these bands to the anion radical.

It is well-known that the reaction of *o*-dinitrobenzene with hydroxide ion yields *o*-nitrophenol and nitrite ion.[13] Sodium nitrite (4.5×10^{-4} M) in DMSO containing 4% (v/v) water and sodium hydroxide (1.00×10^{-2} M) absorbed very weakly in the region above 400 nm. The final 430 nm band of the reaction system (curve f in Fig. 2) differed in peak position from the 450 nm band of the similar solution of *o*-nitrophenol, while the similar DMSO solution of *p*-dinitrobenzene finally showed the band identical with that of the similar solution of *p*-nitrophenol in the peak position and shape.[8] When the reaction system containing *o*-dinitrobenzene (0.3 M) and sodium hydroxide (0.7 M) in aqueous DMSO-d_6 was stood for 4 h in the dark at room temperature, the system showed the ^{1}H NMR spectrum of *o*-nitrophenoxide ion at the range δ 5—8 ppm.[14] The reaction of *o*-dinitrobenzene (0.745 g, 0.12 M) with sodium hydroxide (0.26 M) in DMSO containing 19% (v/v) water at room temperature afforded a yellowish-orange crude substance (0.485 g) after dilution with water, neutralization, and extraction with diethyl ether. The IR spectrum of the crude substance exhibited the absorption bands corresponding to *o*-nitrophenol. The results of thin-layer chromatography for the aqueous DMSO solution of *o*-dinitrobenzene (7.2×10^{-2} M) and sodium hydroxide (1.8×10^{-1} M), allowed to stand overnight in the dark at room temperature, showed the major product of *o*-nitrophenol and the absence of unaltered *o*-dinitrobenzene, though there was the small spot which could not be eluted with benzene containing a small amount of methanol. From the above results, the final species showing the 430 nm band was identified as *o*-nitrophenoxide ion. The production of nitrite ion was confirmed by the brown ring test.

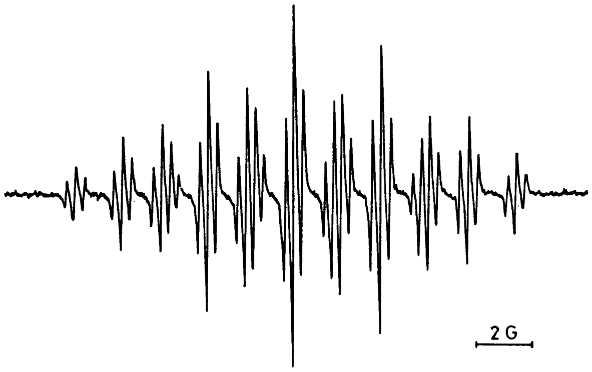


Fig. 4. ESR Spectrum of the same solution as in Fig. 1 (*ca.* 21 °C).

The formation of the labile *o*-dinitrobenzene anion radical in the reaction system was confirmed by ESR spectroscopy. The reaction system showed a strong ESR signal. Hyperfine structure of the ESR spectrum (Fig. 4) is consistent with that of the *o*-dinitrobenzene anion radical having the two equivalent nitrogen atoms. The splitting constants, $a_N = 3.02$, $a_H(3,6) = 0.30$, and $a_H(4,5) = 1.64$ gauss, agreed well with the reference values.[15] The time course of relative ESR-signal intensity of the anion radical in the reaction system at *ca.* 21 °C resembled that of the absorption coefficient change at 900 nm in Fig. 3.

No other radical species was found in the ESR spectrum of the reaction system, even if the system kept at 19 °C for 3 min after mixing was suddenly cooled to −130 °C and then warmed gradually over recording the spectrum. This result indicates that any long-lived radical other than the *o*-dinitrobenzene anion radical was not present in the reaction system, and eliminates any mechanism including persisting radicals other than the *o*-dinitrobenzene anion radical. Thus, the result eliminates the following schemes in which the hydroxyl radical produced reversibly should long live together with the anion radical.

$$\begin{tikzcd}[row sep=large]
o\text{-Dinitrobenzene} \arrow[d, shift left, "\mathrm{OH^-}"] & \\
\text{A Meisenheimer-type intermediate} \arrow[u, shift left] \arrow[r] \arrow[d, shift left] & o\text{-Nitrophenol} \\
{[o\text{-Dinitrobenzene anion radical} \cdots \dot{\mathrm{O}}\mathrm{H}]} \arrow[u, shift left] &
\end{tikzcd}$$

The formation of the *o*-dinitrobenzene anion radical in DMSO is not due to electron transfer from methylsulfinyl methanide[16] to *o*-dinitrobenzene, because the

$$\begin{tikzcd}
 & \text{o-Nitrophenol} \\
\text{o-Dinitrobenzene} \arrow[r, shift left, "\text{OH}^-"] \arrow[d, shift left, "\text{OH}^-"] & \text{A Meisenheimer-type intermediate} \arrow[u] \arrow[l, shift left] \\
\text{A Meisenheimer-type complex} \arrow[u, shift left] \arrow[d, shift left] & \\
{[\text{o-Dinitrobenzene anion radical} \cdots \dot{\text{O}}\text{H}]} \arrow[u, shift left] &
\end{tikzcd}$$

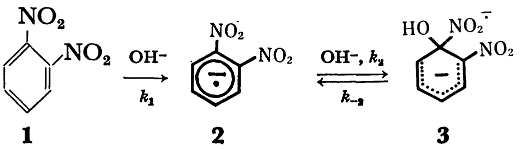
mixture obtained by mixing two drops of aqueous solution of sodium hydroxide (5 M) with an *N*,*N*-dimethylformamide solution of *o*-dinitrobenzene (1×10^{-2} M) also showed the ESR spectrum of the *o*-dinitrobenzene anion radical with $a_N=3.25$, $a_{H3}=0.40$, and $a_{H4}=1.68$ gauss.

The mixture of *o*-dinitrobenzene (1.00×10^{-2} M) and sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienate (9.21×10^{-3} M)[17] in DMSO did not show any ESR signal at the temperatures of 0° and 25 °C. This fact suggests that an electron transfer does not occur between *o*-dinitrobenzene and the Meisenheimer-type intermediate in the reaction system under study. Since the Meisenheimer intermediate has the stable π-electronic structure of pentadienate, the highest-occupied energy level of the intermediate would be lower than the lowest-vacant energy level of *o*-dinitrobenzene, so that the electron transfer can not occur.[1,2]

Thus, the formation of *o*-dinitrobenzene anion radical is probably due to the direct electron transfer from hydroxide ion to *o*-dinitrobenzene. The lowest-vacant energy level of *o*-dinitrobenzene can be estimated to be −5.84 eV from the values[18] of the lowest π-π^* transition energy (4.43 eV) and ionization potential (10.27 eV) of *o*-dinitrobenzene. The energy level is sufficiently lower than the occupied energy level of OH^- (−2.1 eV[1]). According to Nagakura and Tanaka's theory, therefore, the anion radical can be formed as a result of the direct electron transfer from hydroxide ion to *o*-dinitrobenzene. In the case of the aqueous DMSO solution of *p*-dinitrobenzene and hydroxide ion, the production of the short-lived hydroxyl radical has been confirmed by spin-trapping with 2-nitroso-2-methylpropane.[9]

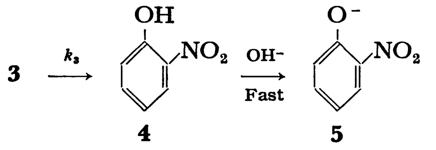
Here we denote the initial concentrations of *o*-dinitrobenzene and sodium hydroxide by $[o\text{-DNB}]_0$ and $[\text{NaOH}]_0$, respectively. The rate of decrease in the 900 nm absorption coefficient of the DMSO solution containing 4% (v/v) water, $[o\text{-DNB}]_0=3.31 \times 10^{-4}$ M, and $[\text{NaOH}]_0=1.00 \times 10^{-2}$ M was faster than that for the same solution except for $[\text{NaOH}]_0=5.0 \times 10^{-3}$ M at 25 °C. When $3 \times [o\text{-DNB}]_0<[\text{NaOH}]_0=1.00 \times 10^{-2}$ M, the decrease in the 900 nm absorption coefficient obeyed the pseudo-first order kinetics and was relatively fast. In the case of $[o\text{-DNB}]_0 : [\text{NaOH}]_0=1:2$ where $[\text{NaOH}]_0=1.00 \times 10^{-2}$ M, the decrease in the 900 nm absorption coefficient was extremely slow. The radical species in this solution lived for a few days at room temperature after mixing. The thin-layer chromatography of the reaction system, stood overnight in the dark at room temperature, distinctly showed the presence of unaltered *o*-dinitrobenzene for the case of $2.5 \times [o\text{-DNB}]_0>[\text{NaOH}]_0$. All these facts mean that the relatively fast decomposition of the anion radical requires hydroxide ion. The further reaction of the anion radical with hydroxide ion is possibly the formation of a dianion radical such as proposed by Shein *et al.*[4,10] The question, however, remains, since the formation of the dianion radical is unfamiliar. Hydroxide ion will be further consumed for ionizing *o*-nitrophenol, because *o*-nitrophenol in the DMSO solution containing 4% (v/v) water in the absence of sodium hydroxide did not show any absorption band above 400 nm.

In view of the above results, the reaction scheme for the present reaction may be written below under the condition of $3 \times [o\text{-DNB}]_0<[\text{NaOH}]_0$.

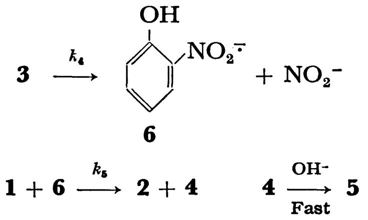


Scheme 1.

Here k_i denotes the rate constant for the *i*th step. The first-order rate constants of k_1 and k_2 contain $[\text{NaOH}]_0$. The authors propose Scheme 2 or 3 for the further reactions of **3**.

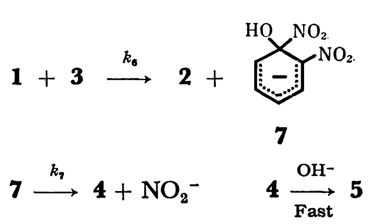


Scheme 2.



Scheme 3.

According to one of the mechanisms proposed by Schein *et al.*,[4,10] **3** should undergo the reaction indicated in Scheme 4.



Scheme 4.

Dianion radical **3** seems very labile, because any Meisenheimer-type complex, in which the nucleophilic reagent attacks the carbon atom carrying a nitro group, has never been observed. Dianion radical **3** is, therefore, likely to decompose rather than to exchange an electron with *o*-dinitrobenzene. Moreover, Scheme 4 would give the concentration changes different from those for Schemes 2 and 3, which can explain the experimental data shown in Fig. 3, as described below. Accordingly, Scheme 4 is ignored here.

Since no band other than those of **2** and **5** is found in Fig. 2, we can assume the restrictions of $k_2 \ll k_3$ and $k_2 \ll k_4$ or k_5 in Schemes 2 and 3, respectively. Then, the steady state treatment was applied for the concentrations of **3** and **6**. The absorption-coefficient changes for 900 and 430 nm with time *t* are expressed below. For Schemes 1 and 2,

$$a(900\,\mathrm{nm}) = \frac{k_1}{k_1-k_2'}\varepsilon_{\mathrm{R}}[o\text{-DNB}]_0\{\exp(-k_2't)-\exp(-k_1t)\} \tag{1}$$

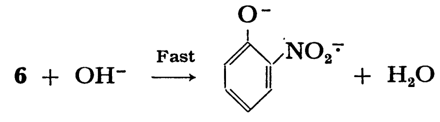
$$a(430\,\mathrm{nm}) = \varepsilon_{\mathrm{NP}}[o\text{-DNB}]_0-\frac{k_1}{k_1-k_2'}(\varepsilon_{\mathrm{NP}}-\varepsilon_{\mathrm{R}}')[o\text{-DNB}]_0 \times\exp(-k_2't)-\frac{k_1\varepsilon_{\mathrm{R}}'-k_2'\varepsilon_{\mathrm{NP}}}{k_1-k_2'}[o\text{-DNB}]_0\exp(-k_1t) \tag{2}$$

where $k_{2'}=k_2\{1-k_{-2}/(k_3+k_{-2})\}$. Here ε_{R} and $\varepsilon_{\mathrm{NP}}$ are molar absorption coefficients of **2** and **5**, respectively. For Schemes 1 and 3,

$$a(900\,\mathrm{nm}) = \frac{k_1}{r_1-r_2}\varepsilon_{\mathrm{R}}[o\text{-DNB}]_0\{\exp(-r_2t)-\exp(-r_1t)\} \tag{3}$$

$$a(430\,\mathrm{nm}) = \varepsilon_{\mathrm{NP}}[o\text{-DNB}]_0-\frac{r_1\varepsilon_{\mathrm{NP}}-k_1\varepsilon_{\mathrm{R}}'}{r_1-r_2}[o\text{-DNB}]_0\exp(-r_2t) -\frac{k_1\varepsilon_{\mathrm{R}}'-r_2\varepsilon_{\mathrm{NP}}}{r_1-r_2}[o\text{-DNB}]_0\exp(-r_1t) \tag{4}$$

where $r_1=k_1/2+\{(k_1/2)^2-k_1k_2k_3/(k_{-2}+k_3)\}^{1/2}$ and $r_2=k_1/2-\{(k_{1/2})^2-k_1k_2k_3/(k_{-2}+k_3)\}^{1/2}$. Instead of the last two steps in Scheme 3, the following steps are also possible and give the same results.



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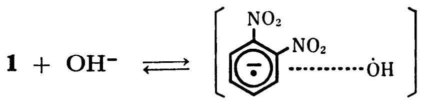
$$\mathbf{1}+\mathbf{8}\xrightarrow{k_8}\mathbf{2}+\mathbf{5}$$

The values calculated for the absorption coefficients according to Eqs. 1 and 2, are plotted in Fig. 3 by assuming the following values: $k_1=0.638\,\mathrm{min}^{-1}$, $k_2'=0.0519\,\mathrm{min}^{-1}$, $\varepsilon_{\mathrm{R}}(900\,\mathrm{nm})=9.05\times10^2$, $\varepsilon_{\mathrm{R}'}(430\,\mathrm{nm})=7.63\times10^3$, and $\varepsilon_{\mathrm{NP}}(430\,\mathrm{nm})=8.62\times10^3$. Equations 3 and 4 also give the identical plot by assuming the following values: $k_1=0.690\,\mathrm{min}^{-1}$, $r_1=0.638\,\mathrm{min}^{-1}$, $r_2=0.0519\,\mathrm{min}^{-1}$, $\varepsilon_{\mathrm{R}}(900\,\mathrm{nm})=8.37\times10^2$, $\varepsilon_{\mathrm{R}'}(430\,\mathrm{nm})=7.05\times10^3$, and $\varepsilon_{\mathrm{NP}}(430\,\mathrm{nm})=8.62\times10^3$.

The calculated values of absorption coefficients for 430 nm are somewhat lower than the found ones after 50 min. The values finally found may be made up by the small superposition of absorption coefficients of nitrite ion and a minor by-product upon that of *o*-nitrophenoxide ion at 430 nm. The molar absorption coefficients of 440 and 1090 nm bands of the anion radical in the rigid solution at 77 K are 6×10^3 and 4×10^3, respectively.[12] The values of $\varepsilon_{\mathrm{R}}'(430\,\mathrm{nm})$ are comparable to 6×10^3, while the values of $\varepsilon_{\mathrm{R}}(900\,\mathrm{nm})$ are considerably smaller than 4×10^3.

Now we can not select one of Schemes 2 and 3. In Scheme 2, the decomposition of **3** should yield the dianion radical $NO_2\cdot^{2-}$. The formation $NO_2\cdot^{2-}$ is unfamiliar, though it has been identified by ESR spectroscopy in KCl crystals dropped with KNO_2.[19] As shown in Fig. 3, the two sets of Eqs. 1 and 2 and of Eqs. 3 and 4 can well reproduce the experimental data to the same extent. In conclusion, the kinetic results strongly support that the *o*-dinitrobenzene anion radical is the precursor in the reaction under study, though the further reaction of the anion radical is not established.

It is unlikely that the primary step of formation of **2** in Scheme 1 is an elementary reaction. The step may be accounted for below. In the case of photosubstitution reaction of 3,5-dinitroanisole with hydroxide ion to produce 3,5-dinitrophenol, a primary reaction step is the formation of intermediate [3,5-dinitroanisole···ȮH] owing to an electron transfer from hydroxide ion to the *π-π** triplet state of 3,5-dinitroanisole.[20,21] The half-lifetime of the intermediate is *ca.* 5×10^{-7} s.[20] Therefore, the corresponding intermediate (**9**) is reasonably supposed to be formed in the present reaction. On the other hand, the rate constant for the reaction of hydroxyl radical with DMSO in aqueous DMSO ($HO\cdot+CH_3SOCH_3\rightarrow CH_3\cdot+CH_3SO\cdot OH$) is $5\times10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ (25 °C).[22] The reaction between DMSO and hydroxyl radical in **9** is probably faster than that of **9**. Thus, the persisting *o*-dinitrobenzene anion radical in the present reaction system may be generated as follows:



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$$\mathbf{9}+CH_3SOCH_3\longrightarrow\mathbf{2}+CH_3\cdot+CH_3SO\cdot OH$$

The methyl radical will undergo a rapid reaction.

References

1) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 563 (1954); *Bull. Chem. Soc. Jpn.*, **32**, 734 (1959).
2) S. Nagakura, *Tetrahedron*, **19**, Suppl. 2, 361 (1963).
3) K. A. Bilevitch, N. N. Pubnov, and O. Yu. Okhlobystin, *Tetrahedron Lett.*, **1968**, 3465.
4) S. M. Shein, L. V. Bryukhovetskaya, V. F. Starichenko, and T. M. Ivanova, "Organic Reactivity," Vol. 6, Tartua (SSSR) (1969), p. 1087.
5) L. A. Blyumenfeld, L. V. Bryukhovetskaya, G. V. Fomin, and S. M. Shein, *Zh. Phys. Khim*, **44**, 931 (1970).
6) S. M. Shein, L. V. Bryukhovetskaya, and T. M. Ivanova, *Izv. Acad. Nauk SSSR, Ser. Khim*, **1973**, 1596.
7) L. V. Bryukhovetskaya, L. V. Mironova, and S. M. Shein, *Izv. Acad. Nauk SSSR, Ser. Khim*, **1973**, 1601.
8) T. Abe, *Chem. Lett.*, **1973**, 1339.
9) I. I. Bilkis and S. M. Shein, *Tetrahedron*, **31**, 969 (1975).
10) C. F. Bernasconi, "Aromatic Compounds," H. Zollinger, ed., Butterworths, London (1973), p. 33.
11) S. Ohsawa, *Nippon Kagaku Kaishi*, **1973**, 1486.
12) T. Shida and S. Iwata, *J. Phys. Chem.*, **75**, 2591 (1971).

13) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold, New York, N. Y. (1961), p. 678.

14) The authors wish to thank Professor Toyonobu Asao of Tohoku University for the NMR measurement, which was carried out with a Hitachi high-resolution NMR spectrometer, Model R-22 (90 MHz).

15) D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Am. Chem. Soc.*, **86**, 987 (1964).

16) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

17) The Meisenheimer complex was crystallized from the methanolic solution of 2,4,6-trinitroanisole and sodium methoxide.

18) M. D. Gordon and J. F. Neumer, *J. Phys. Chem.*, **78**, 1868 (1974).

19) J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

20) G. P. de Gunst and E. Havinga, *Tetrahedron*, **29**, 2167 (1973).

21) W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975).

22) B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J. Chem. Soc., Perkin Trans.* 2, **1975**, 303.