

THE STABLE MEISENHEIMER-TYPE COMPLEX FORMED FROM 2-METHOXY-5-NITROTROPONE
AND METHOXIDE ION IN SOLUTION

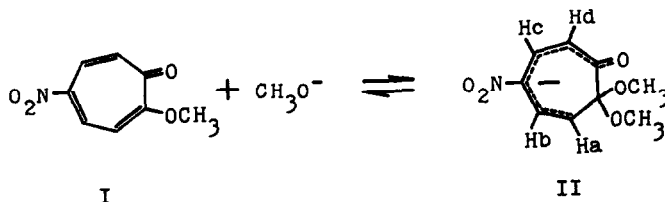
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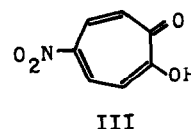
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A number of studies have been made on the Meisenheimer complexes formed from aromatic polynitro compounds and nucleophiles.¹⁾ The formations of the corresponding intermediates, however, have never been confirmed in the nucleophilic substitution reaction of the troponeid compounds,²⁾ although the intermediates have often been postulated in the reaction mechanisms²⁾ and the sole UV spectrum assigned to an intermediate in a nucleophilic substitution with rearrangement^{2e)} has been reported.

In the present communication, the evidence that 2-methoxy-5-nitrotropone (I)^{3,4)} forms the Meisenheimer-type complex (II) with methoxide ion will be given.



It is known from Fig. 1 that the interaction of I with methoxide ion in methanol reversibly produces the yellow species (the curve b) having an intense absorption peak at 451 nm, because the curve c closely resembles the curve a. Although it is known that 2,7-dimethoxytropone reacts with sodium methoxide to yield 3-methoxytropolone,⁵⁾ the yellow species is not the anion of 5-nitrotropolone (III) resulting from the hydrolysis, because the curve b apparently differs



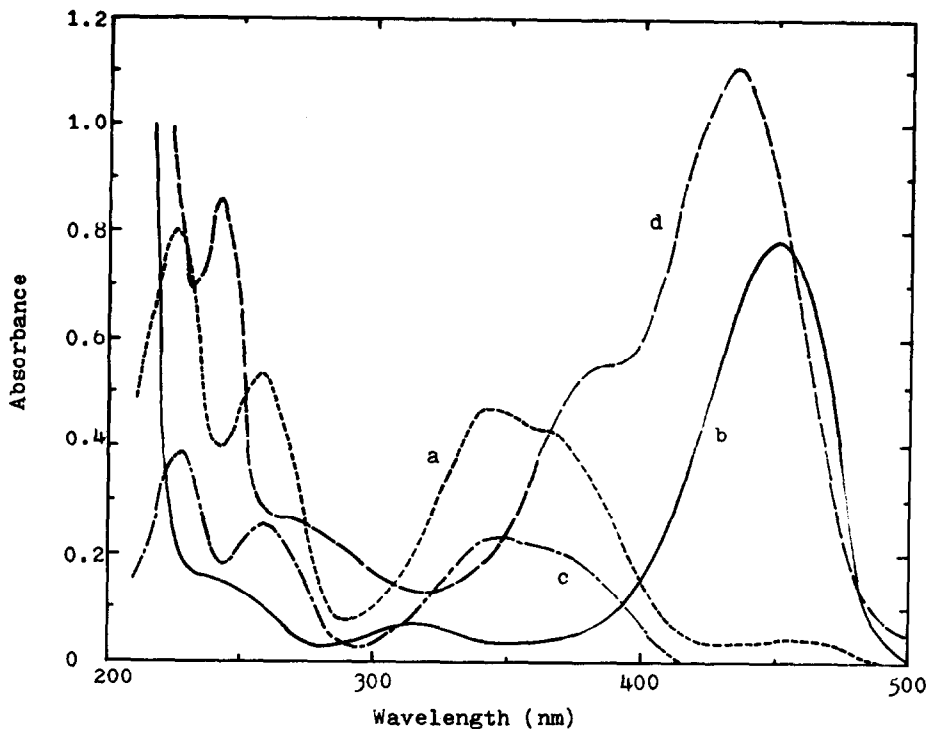


Fig. 1. UV spectra of the following solutions of 2-methoxy-5-nitrotropone (I) and 5-nitrotropolone (III): (a) A solution of I (4.4×10^{-5} M) in methanol; (b) a solution of I (2.5×10^{-5} M) in methanol containing sodium methoxide (4.7×10^{-2} M); (c) a solution obtained by adding a drop of a dilute aqueous solution of hydrochloric acid into the solution (b); (d) a solution of III (2.9×10^{-5} M) in methanol containing sodium methoxide (4.7×10^{-2} M).

from the curve d. Moreover, it has been reported that 2-methoxy-5-nitrotropone easily undergoes nucleophilic substitutions at the 2-position.^{2d,4,6)} Accordingly, by analogy with the cases of dinitro- and trinitro-anisoles,¹⁾ the yellow species of I may be assigned to the complex II. The solution of I in methanolic DMSO (dimethyl sulfoxide) in the presence of sodium methoxide similarly showed only an intense absorption peak at 453 nm in the wavelength region above 340 nm, although an absorption shoulder was observed at ca. 462 nm.

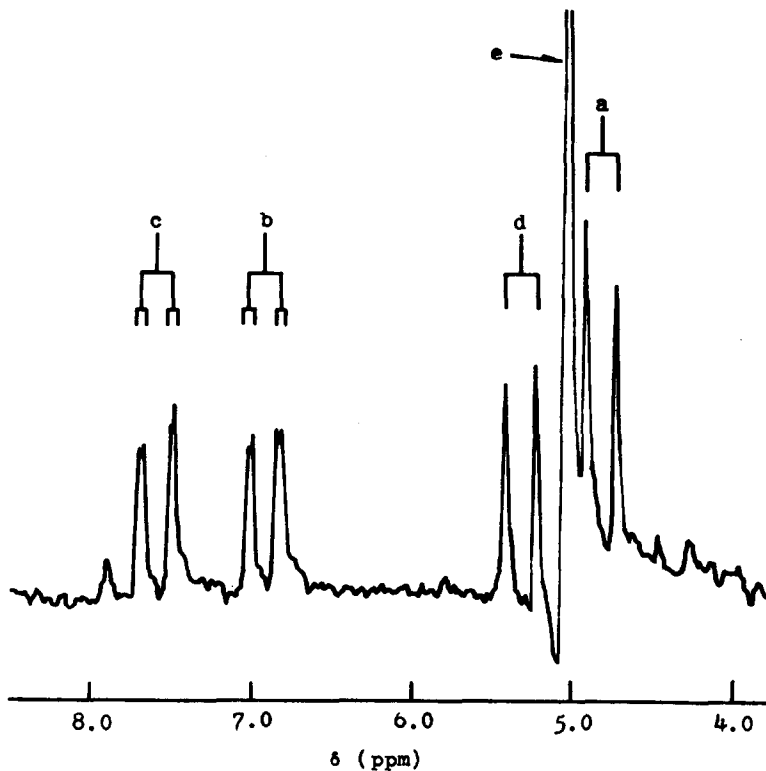


Fig. 2. ^1H Nmr spectrum produced on the addition of CD_3ONa in CD_3OD to I in CD_3OD . The signals labelled as a, b, c and d are assigned to the ring protons of Ha, Hb, Hc and Hd, respectively, in II.

The structure of II can be confirmed by the ^1H nmr spectrum⁷⁾ shown in Fig. 2. In Fig. 2, the intense singlet labelled as e is probably due to the hydroxy protons of water or methanol in the solvent of CD_3OD , since the solution of CD_3ONa in CD_3OD in the absence of I similarly showed an intense singlet at δ 5.20 ppm. The nmr pattern consisting of two double-doublets (b and c) and two doublets (a and d) is consistent with the structure of II. The chemical shifts (δ in ppm) and coupling constants are obtained as follows: 4.79 (Ha), 6.88 (Hb), 7.54 (Hc), 5.28 (Hd), 2.81 (methoxy protons); $J_{ab} = 11.0$ Hz, $J_{bc} = 1.4$ Hz and $J_{cd} = 11.8$ Hz. When the solution initially showing the nmr spectrum indicated in Fig. 2 was kept at room temperature, all the signals labelled as a, b, c and d slowly decreased in intensity and new two singlets at δ 7.75 and

7.86 ppm increased in intensity. The former signals completely disappeared in 12 days. The nmr pattern of the ring protons, observed with the solution of I in methanolic DMSO- d_6 containing CH_3ONa was the same as that in Fig. 2 but quite differed from those of III and p-nitrobenzoic acid in the same media,⁷⁾ although p-nitrobenzoic acid arises from the reaction of I with sodium methoxide or sodium hydroxide in refluxing methanol.^{3,4)} It was found that the complex II produced by the addition of CD_3ONa in CD_3OD to I in DMSO- d_6 was so stable that the solution stood for two weeks at room temperature showed no change in the nmr spectrum.⁸⁾

The reaction of I with sodium ethoxide in ethanol afforded a small amount of I and the major product of 2-ethoxy-5-nitropropone as yellow microneedles (from dioxane), m.p. 145-146°C (Found: C, 54.97; H, 4.55; N, 7.23. Calcd. for $C_9H_9O_4N$: C, 55.38; H, 4.65; N, 7.18%). This strongly supports the direct addition of methoxide ion at the 2-position in I, as shown in II.

References

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- 7) Nmr spectra were recorded with a Hitachi R-24 spectrometer (60 MHz) by the use of tetramethylsilane as an external reference.
- 8) The remarkable stability may be due to the solvent effect of DMSO.