[Chem. Pharm. Bull.
18(11)2151—2157(1970)]

UDC 547.546.04 : 547.97.02.04

Mechanism of the Color Reaction of Active Methylene Compounds with 1,3,5-Trinitrobenzene Derivatives. I. Crystalline Products of the Color Reaction of Acetone with 1,3,5-Trinitrobenzene (Organic Analysis. LXXI[1])

KAZUYA KOHASI, YOSUKE OHKURA and TSUTOMU MOMOSE

Faculty of Pharmaceutical Sciences, Kyushu University[2]

(Received January 16, 1970)

Two coloring matters produced in the color reaction of acetone with excessive 1,3,5-trinitrobenzene in an alkaline medium were separated in crystalline forms and one of them was determined as the Meisenheimer type complex of acetone (I). The other was a new type complex (II) and was characterized as a sodium salt of the anion group shown in Chart 1. Spectrophotometric studies of I, II and the color reaction showed that I formed in the early stage of the reaction and then changed to II with time in the alkaline medium in the presence of excessive trinitrobenzene. In addition, a reason for increase of the color intensity in the improved procedures of the detection and determination of acetone was clarified by studying spectrophotometrically some behaviors of I and II.

1,3,5-Trinitrobenzene (TNB) gave an intense purple red color when reacted with active methylene compounds in an alkaline medium. The reagent also showed a strong red color under the same conditions. When sodium dihydrogen phosphate solution was added to the reaction mixture, the blank color almost diminished and the developed color of active methylene compounds increased in its intensity with a few exceptions. This improved procedure was effectively used in the spot test detection of active methylene compounds[3] and successfully extended to the determinations of acetone bodies[4] and creatinine[5] in biological fluids.

On the other hand, the color reaction mechanism of acetone with TNB has been explained in general to form the Meisenheimer complex of acetone in the presence of a base.[6] However, spectrophotometric studies of the improved spot test detection showed that the developed color gave the Meisenheimer type spectrum with two maxima at 475 and 570 mμ only when a large excess of acetone was used, and gave a new type spectrum with a maximum at 480 mμ in the usual spot test in which a low concentration of sample was used in the presence of excessive TNB.

In the present paper, two main coloring matters, the Meisenheimer complex and a new one, were obtained in crystalline forms and the structure of the latter compound was investigated. And also, some behaviors of the Meisenheimer complex and the new coloring matter were spectrophotometrically investigated in relation to the improved procedure.[3,4]

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[1] A part of this work was presented at "Communications to the Editor" in *Chem. Pharm. Bvll.* (*Tokyo*) **17**, 858 (1969). Part LXX: T. Momose, Y. Ohkura and Ta. Momose, *Talanta*, **16**, 1451 (1969).

[2] Location: *Katakasu, Fukuoka.*

[3] T. Momose, Y. Ohkura and K. Kohashi, *Chem. Pharm. Bull.* (Tokyo), **11**, 301 (1963).

[4] T. Momose, Y. Ohkura, K. Kohashi and R. Nagata, *Chem. Pharm. Bull.* (Tokyo), **11**, 973 (1963); T. Momose, Y. Ohkura and K. Kohashi, *ibid.*, **13**, 534 (1965).

[5] T. Momose, Y. Ohkura, K. Kohashi, Y. Yano, K. Ohashi, R. Nagata and K. Ohta, *Yakugaku Zasshi*, **84**, 525 (1964); T. Momose, Y. Ohkura, K. Kohashi, Y. Yano, T. Tanaka and N. Itakura, *Rinshokensa*, **10**, 747 (1966).

[6] J. Meisenheimer, *Ann.*, **323**, 205 (1902); M. Kimura, *Yakugaku Zasshi*, **73**, 1219 (1953). For recent reviews, see T. Nambara, *Bunseki Kagaku*, **13**, 184 (1964); R. Foster and C.A. Fyfe, *Rev. Pure and Appl. Chem.*, **16**, 61 (1966).

Isolation of Coloring Matters from Reaction Mixture

The reaction between acetone and TNB in an alkaline medium was carried out under the conditions described in Experimental. The concentrated reaction mixture was spotted on a thin-layer of silica gel, developed with buthanol-ammonia, and separated into many colored fractions. Two main fractions were purified by repeating the thin-layer chromatography respectively. Other fractions were so small and could not be treated successfully.

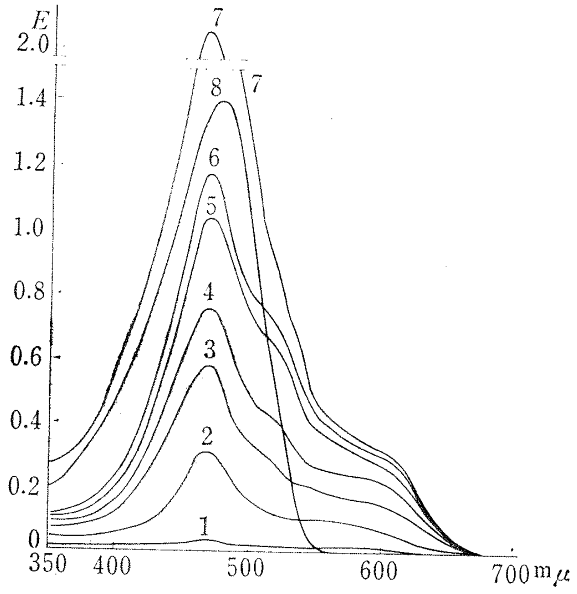

Fig. 1. Effect of the Reaction Time on the Absorption Curve of the Reaction Mixture of Acetone and TNB

To 2.0 ml of aq. acetone solution (1.72×10^{-2} M), 1.0 ml of 0.1% TNB (prepared by dissolving TNB in aq. 40% DMF[4]) and 1.0 ml of aq. 1.8% NaOH were successively added, kept for several periods (1—8) at 37° and then neutralized with 6.0 ml of aq. 3% $NaH_2PO_4 \cdot 2H_2O$. The spectra were measured against the reagent blank. The time (sec) is 1: immediately, 2: 30, 3: 60, 4: 90, 5: 120, 6: 150, 7: 180, 8: 3600 (60 min).

The coloring matter (I), separated from the fraction located at *Rf*=0.7, dark purple red needles, showed no melting point. It dissolved in water to give a purple red color, showing an absorption spectrum similar to that of the reaction mixture in the early stage (Fig. 1, 1—7).

The coloring matter (II), separated from the fraction located at *Rf*=0.4, deep red plates, also showed no melting point and exploded when ignited or heated rapidly. It was soluble in water, methanol, acetone, dimethylformamide (DMF), dimethylsulfoxide (DMSO) and pyridine, but insoluble in absolute ethanol, ethyl acetate, benzene, ethyl ether, chloroform and petroleum ether. The visible absorption spectrum of its aqueous solution (Fig. 2) resembled that of the reaction mixture at a prolonged reaction time (Fig. 1, 8). These spectral data indicated that both I and II were the main coloring matters in the color reaction of acetone with TNB.

Structure of Coloring Matters

I was identified as the Meisenheimer type complex of acetone by the comparison of its spectral data[7] with an authentic sample[6] and the elemental analysis.

II contained inevitably one molecule of benzene, when recrystallized from acetone and benzene, which was assigned by the signal in the nuclear magnetic resonance (NMR) spectrum (6H, a singletat 7.36 δ in acetone-d_6), and the decrease of weight on heating *in vacuo*. From the result of a spark ionized mass spectrum, II was characterized as a sodium salt of an anion group. The data of elemental analyses and the molecular weight (about 300) agreed with the formula $C_9HO_7N_3Na$ (293.18). The infrared (IR) spectrum indicated the presence of carbonyl, nitro and nitronium ion groups by their characteristic bands at 1725 (ν_{CO}), 1550, 1345 (ν_{NO_2}-) and 1320, 1220, 750 (ν_{NO_2}-) respectively. The NMR spectrum of II was shown in Fig. 3, a. The signal at 8.51 δ (a) was assigned to a ring proton in an original TNB ring system.[8] By the irradiation at 4.52 δ (c and c') (2H, a poorly-resolved quartet), a

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[7] NMR, IR, UV and visible spectra.

[8] R. Foster and C.A. Fyfe, *Tetrahedron*, **21**, 3363 (1965); K.L. Servis, *J. Am. Chem. Soc.*, **89**, 1508 (1967); R. Foster, C.A. Fyfe, P.H. Emslie and M.I. Foreman, *Tetrahedron*, **23**, 227 (1967).

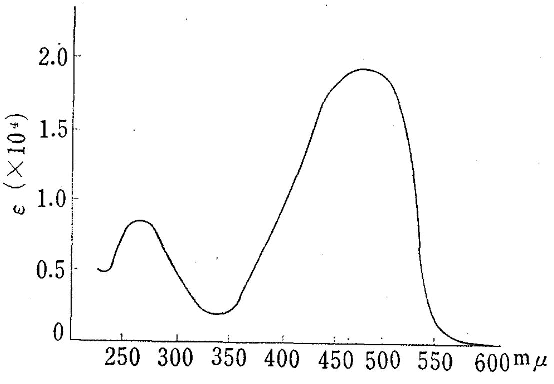

Fig. 2. Absorption Spectrum of II in Water

14.84 mg of II was dissolved in 1000 ml of H_2O.

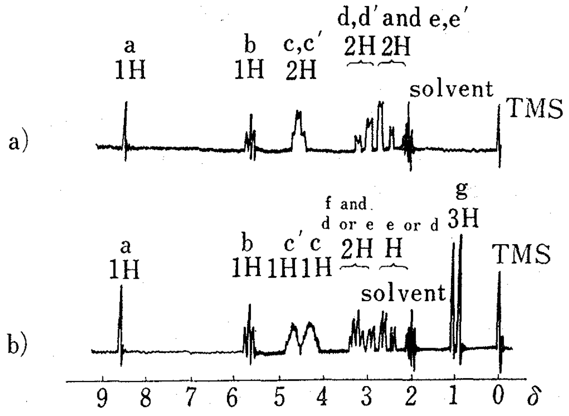

Fig. 3. The NMR Spectra of II and III in Acetone-d_6

a) II, b) III

triplet at 5.72 δ (b) (1H, J=3.0 cps) became a singlet, and two quartets (two double doublets) at 3.10 δ (d, d′ or e, e′) (2H, J=4.0 and 13.1 cps) and 2.56 δ (e, e′ or d, d′) (2H, J=1.6 and 13.1 cps) turned to sharp two doublets (both 2H, J=13.1 cps) respectively. These doublets might be explained as two groups of geminal protons on carbon atoms adjacent to a carbonyl group in a partially rigid cyclohexanone system. On the basis of the above results, the structure of anion group ($C_9H_8O_7N_3^-$, II^-) of II was assumed as shown in Chart 1.

It is important to note that II^- was also obtained from the reaction mixture of acetone, TNB and piperidine or diethylamine as its salts, indicating that II^- was easily formed not only in an aqueous alkali hydroxide medium, but also in a medium of organic bases.[9] The data of elemental analyses of the piperidinium and diethylammonium salts thus obtained agreed well with their calculated values, and the ultraviolet (UV) and visible absorption spectra were identical with those of II. The NMR spectra were the seam as that of II except the signals caused by the cation groups. Furthermore, these salts were easily converted to sodium salt by treating them with sodium hydroxide.

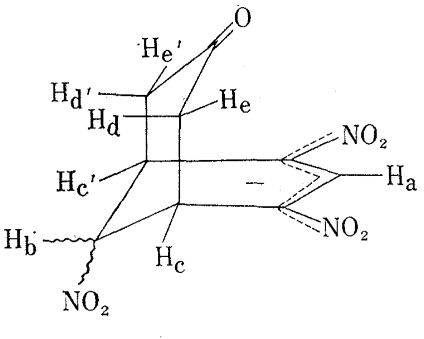

Chart 1

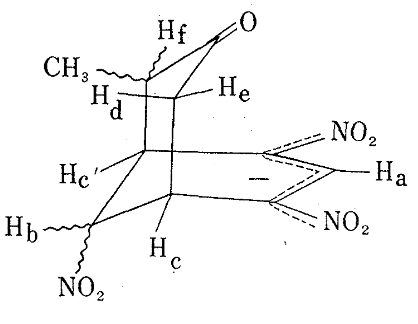

Chart 2

Another evidence to confirm the structure of II^- was given by the analytical data of another piperidinium or diethylammonium salt, separated from the reaction mixture of methyl ethyl ketone and TNB in piperidine or diethylamine in crystalline forms. These salts had the formula of anion group of $C_{10}H_{10}O_7N_3^-$, III^-, and were easily converted to

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[9] Piperidinium and diethylammonium salts of II^- had already been obtained in the forms of precipitates by R. Foster and C.A. Fyfe (*Tetrahedron*, **22**, 1831 (1966)), and their structures were not resolved. Recently, the structure of diethylammonium salt of II^- was characterized by M.J. Strauss and H. Schran (*J. Am. Chem. Soc.*, **91**, 3974 (1969)).

sodium salts by sodium hydroxide. The NMR spectrum of sodium salt of III$^-$ (III) was shown in Fig. 3, b. The spectrum closely resembled that of II (Fig. 3,a) except the signals due to $\rangle$CH–CH$_3$ group, supporting that the structure of III$^-$ was analogous to that of II$^-$. The anion III$^-$ was also characterized as shown in Chart 2 from the results of spin decoupling in the NMR measurements and other analytical data described in Experimental.

The analogous bridged compounds have been isolated from the reaction mixture of TNB and phloroglucinol,[10] acetylacetone or dibenzylketone[11] in an alkaline medium.

Some Behaviors of I and II in Alkaline Medium

When an aqueous solution of the Meisenheimer complex (I) was made alkaline with sodium hydroxide and then neutralized with sodium dihydrogen phosphate, the absorption spectrum gradually changed to the spectrum of II with increasing time of standing the complex in the alkaline medium as shown in Fig. 4.

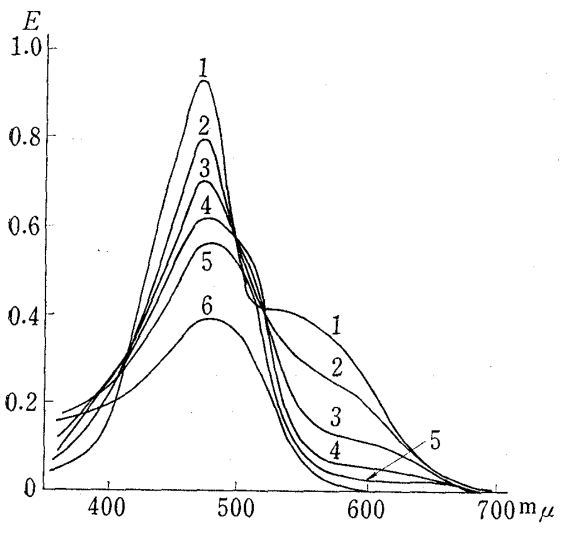

Fig. 4. Conversion of the Meisenheimer Type Spectrum (1) into the New Type Spectrum (6) in the Absence of TNB

To 2.0 ml of aq. solution of I (1.0×10^{-4}M), 1.0 ml of aq. 40% DMF and 1.0 ml of aq. 0.18% NaOH were successively added, kept for several periods (1—6) at room temperature (23°) and then neutralized with 1.0 ml of aq. 1.8% $NaH_2PO_4 \cdot 2H_2O$. The spectra were measured against H_2O. The time (min) is 1: immediately, 2: 5, 3: 30, 4: 60, 5: 90, 6: 180.

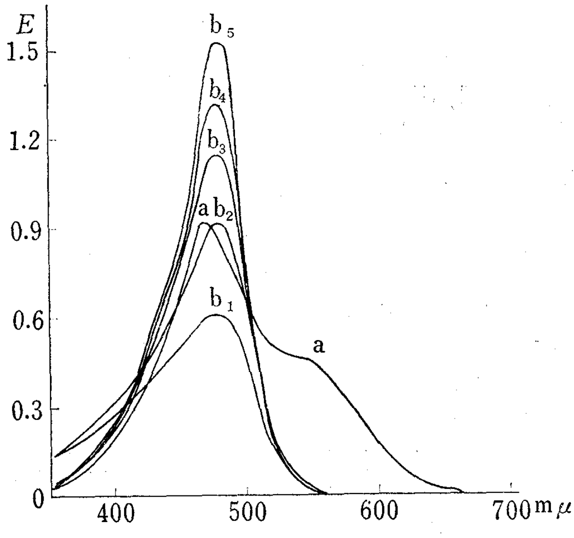

Fig. 5. Conversion of the Meisenheimer Type Spectrum (a) into the New Type Spectrum (b$_1$—b$_5$) in the Presence of TNB

a: 2.0 ml of aq. solution of I (1.0×10^{-4}M) was diluted with 3.0 ml of H_2O.

b: To 2.0 ml of aq. solution of I (1.0×10^{-4}M), 1.0 ml of various concentrations (1—5) of TNB in aq. 40% DMF and 1.0 ml of aq. 1.8% NaOH were successvely added, kept for 60 min at 37° and neutralized with 1.0 ml of aq. 18% $NaH_2PO_4 \cdot 2H_2O$. The spectra were measured against the blank. The concentration of TNB ($\times 10^{-4}$M) is 1: 0, 2: 2.0, 3: 4.0, 4: 8.0, 5: 46.9.

It is of interest to note that, when the conversion of I to II was carried out in the presence of TNB, the absorption intensity at 480 mμ greatly increased with increasing concentration of TNB as shown in Fig. 5.

This spectral change was also observed when an aqueous solution of acetone was treated with TNB in an alkaline medium as described in the legend of Fig. 1. These facts indicate that, in the color reaction of acetone with TNB, I forms in the early stage of the reaction, and then is converted to II in an alkaline medium with an influence of the excessive reagent as shown in Chart 3.

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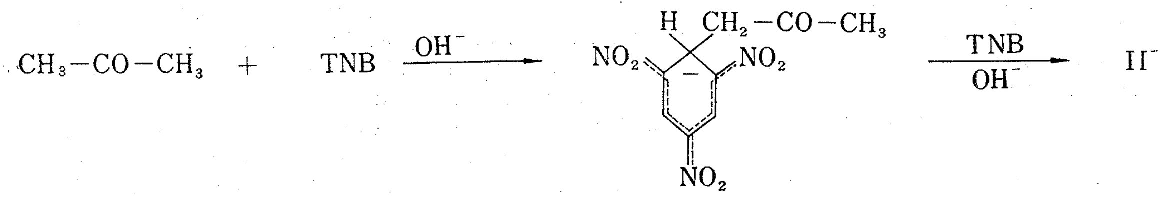
10) T. Severin, *Chem. Ber.*, **90**, 2898 (1957); T. Sevein, *ibid.*, **92**, 1517 (1959).

11) R. Foster, M.I. Foreman and M.J. Strauss, *Tetrahedron Letters*, **1968**, 4949.



purple red
(the Meisenheimer complex, I)

orange red
(a new type complex, II)

Chart 3

Fig. 6 showed the absorption spectra of II in variously concentrated sodium hydroxide solutions. In the UV region of spectra, the maximum at 262 mμ (Fig. 6, a) shifted to 252 mμ with a higher absorption intensity with increasing sodium hydroxide concentration (Fig. 6, b_5 and b_4) and finally was transferred to a new absorption band with a maximum at 282 mμ (Fig. 6, b_3—b_1). In the visible region, the absorption intensity at 480 mμ steadily decreased with a higher concentration of the alkali, leading finally to zero. (Fig. 6, b_5—b_1). These spectra showed isosbestic points at 242, 264 and 306 mμ.

On the other hand, when these alkaline solutions of II were neutralized with sodium dihydrogen phosphate, they recovered the initial spectrum of II dissolved in water (Fig. 6, c_1—c_5). These facts might indicate that some equilibria between II^- and other structures might exist in the solutions, which might be analogized with di- or tri-sodium salt of some structural anion.[12] This recovery of absorption intensity in the visible region well coincides with the fact that the alkaline color of acetone and TNB is intensified by neutralizing the alkali with sodium dihydrogen phosphate as mentioned before.

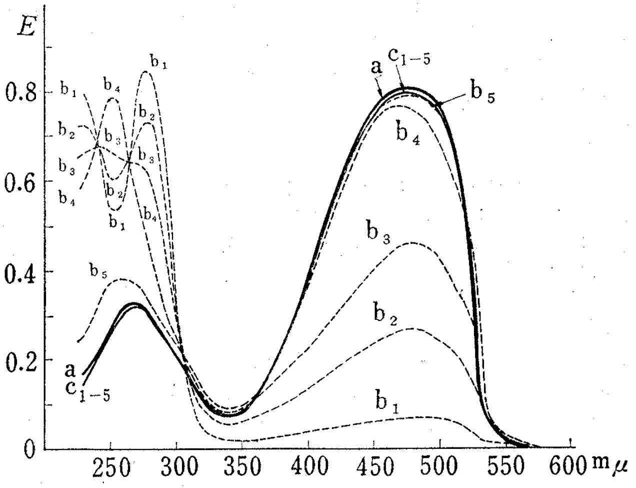


Fig. 6. Absorption Spectra of II in Various Concentrations of Sodium Hydroxide

a ——: 2.0 ml of aq. solution of II (1.0×10^{-4}M) was diluted with 3.0 ml of H_2O.

b ------: To 2.0 ml of aq. solution of II (1.0×10^{-4}), 1.0 ml of H_2O and 1.0 ml of variously concentrated NaOH (1—5) were successively added, kept for 60 min at 37°, and diluted with 1.0 ml of H_2O. NaOH concentration (%) is 1: 5.0, 2: 2.4, 3: 1.6, 4: 0.4, 5: 0.012.

c ——: The reactions were carried out under the same procedure as b, and after keeping for 60 min at 37°, each alkaline reaction mixtures was neutralized with 1.0 ml of variously concentrated $NaH_2PO_4 \cdot 2H_2O$ (1—5). $NaH_2PO_4 \cdot 2H_2O$ concentration (%) is 1: 25, 2: 12, 3: 8, 4: 2, 5: 0.06.

The spectra were measured against the blank.

The kinetic study on the equilibria and an attempt to isolate the new substances are now going on.

Experimental

Isolation of the Coloring Matters——To a solution of 0.7 g of acetone in 150 ml of H_2O, a solution of 3.5 g of TNB in 150 ml of DMF and 100 ml of aq. 1.8% NaOH were successively added with stirring and

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12) Ya. Kaminskii and S.S. Gitis suggested the structures of di- or tri-potassium salt of the Meisenheimer type complex formed in the reaction of TNB with acetone in alkaline medium from their spectral data (*J. Org. Chem. U.S.S.R.*, 2, 1780 (1961)).

warmed in a water-bath of 37° for 60 min. The reaction mixture was neutralized with 100 ml of aq. 18% $NaH_2PO_4 \cdot 2H_2O$ and allowed to stand overnight. After removing oily precipitate, the mixture was concentrated to about 50 ml under reduced pressure and spotted on layers of silica gel (250 μ thickness, Wakogel B-5) and developed by *n*-BuOH saturated with aq. 3% NH_4OH. After drying the chromatogram in the air at room temperature, two fractions ($Rf=0.7$ and 0.4) were scraped and extracted with acetone respectively. The extracts remained on evaporating the solvent gave a purple red or a deep red residue respectively. Each of them was dissolved in a small amount of acetone and separately rechromatographed in the same way as described above. These procedures were repeated several times to give finally a single fraction on the chromatogram respectively. The residues from each single fraction were separately dissolved in dry acetone and filtrated. When an appropriate amount of benzene was added to the acetone filtrates, crystals began to separate gradually, which were recrystallized from acetone and benzene (1:3) respectively.

I, eluted from the Fraction located at $Rf=0.7$——Dark purple red needles. *Anal.* Calcd. for $C_9H_8O_7N_3Na$: C, 36.89; H, 2.73; N, 14.34; Na, 7.84. Found: C, 36.90; H, 2.91; N, 14.20; Na, 8.00. The IR, NMR, UV and visible spectra of this crystal were identical with those of the authentic sample.[6]

II, eluted from the Fraction located at $Rf=0.4$——Deep red plates. The elemental analyses were carried out after heating at 100—110° for 6 hr *in vacuo* to remove the crystal benzene. *Anal.* Calcd. for $C_9H_8O_7N_3Na$: C, 36.89; H, 2.73; N, 14.34; Na, 7.84; mol. wt., 293.18. Found: C, 36.77; H, 2.76; N, 14.37; Na, 8.00; mol. wt. (Barger–Rast[13]), 300. UV and visible $\lambda_{max}^{H_2O}$ mμ (log ε): 262 (3.91), 480 (4.26).

Preparation of the Piperidinium and Diethylammonium Salts of the Anion Group of II——To a solution of 3.0 g of TNB in 20 ml of acetone, 3.5 g of piperidine or diethylamine was slowly added with stirring. After standing for 3 hr at room temperature, 50—60 ml of ether was added, and allowed to stand at room temperature to give dark purple crystals. Yield 3.0 g for the piperidinium salt and 2.5 g for the diethylammonium salt.

Piperidinium Salt——Deep purple red plates, mp 174—176° (uncorr.) (from MeOH). *Anal.* Calcd. for $C_9H_8O_7N_3 \cdot C_5H_{12}N$: C, 47.18; H, 5.65; N, 15.72. Found: C, 47.31; H, 5.68; N, 15.65. UV and visible $\lambda_{max}^{H_2O}$ mμ (log ε): 262 (3.69), 480 (4.18). IR ν_{max}^{KBr} cm^{-1}: 1725 (CO), 1550, 1340 (NO_2). NMR (in DMSO-d_6) δ ppm: 8.35 (1H, singlet, sp^2 ring H), 5.75 (1H, triplet, $J=3.0$ cps, sp^3 ring H), 4.30 (2H, poorly resolved quartet, sp^3 ring H). Three signals at 8.0 (2H), 3.0 (4H) and 1.6 (6H) δ were due to the piperidinium group. Other signals overlapped with those of protons in DMSO and H_2O in DMSO-d_6.

Diethylammonium Salt——Deep red needles, mp 152—154° (uncorr.) (from acetone and ether). *Anal.* Calcd. for $C_9H_8O_7N_3 \cdot C_4H_{12}N$: C, 45.34; H, 5.85; N, 16.27. Found: C, 45.40; H, 5.90; N, 16.15. UV and visible $\lambda_{max}^{H_2O}$ mμ (log ε): 262 (3.51), 480 (4.21). IR ν_{max}^{KBr} cm^{-1}: 1725 (CO), 1550, 1335 (NO_2). NMR (in acetone-d_6) δ ppm: 8.51 (1H, singlet, sp^2 ring H), 5.71 (1H, triplet, $J=3.0$ cps, sp^3 ring H), 4.5 (2H, poorly resolved quartet, sp^3 ring H). Three singals at 6.81 (2H, broad), 3.23 (4H, quartet, $J=7.5$ cps), 1.35 (6H, triplet, $J=7.5$ cps) δ resulted from the diethylammonium group. Other signals at 2.90 (doublet, $J=4.0$ cps), 2.65 (doublet, $J=1.6$ cps), 2.40 (doublet, $J=1.6$ cps) δ were due to the geminal protons adjacent to the carbonyl group.

II, derived from the Piperidinium or Diethylammonium Salts——To a MeOH solution of the piperidinium or diethylammonium salt, a calculated amount of NaOH dissolved in aq. 50% MeOH, was added with stirring and allowed to stand overnight at room temperature. After removing the solvent under reduced pressure, the oily residue was washed with benzene, then diluted with a small amount of acetone and filtered. From the filtrate, deep red plates were separated when a mixture of ether and benzene (2:1) was added and recrystallized from acetone and benzene (1:3). The IR, NMR, UV and visible spectra and elemental analyses were identical with those of II.

Preparation of the Color Products from the Reaction of Methyl Ethyl Ketone and TNB in Piperidine or Diethylamine——The reaction was carried out in the same way as in the case of acetone using 3.0 g of TNB, 20 ml of methyl ethyl ketone and 5 ml of piperidine or diethylamine. The piperidinium or diethylammonium salts were recrystallized from MeOH.

III$^-$-Piperidinium Cation——Deep red crystals, mp 172—174° (uncorr.). *Anal.* Calcd. for $C_{10}H_{10}O_7N_3 \cdot C_5H_{12}N$: C, 48.64; H, 5.99; N, 15.12. Found: C, 48.50; H, 6.00; N, 15.10. UV and visible $\lambda_{max}^{H_2O}$ mμ (log ε): 263 (3.82), 485 (4.22).

III$^-$-Diethylammonium Cation——Deep red crystals, mp 160—162° (uncorr.). *Anal.* Calcd. for $C_{10}H_{10}O_7N_3 \cdot C_4H_{12}N$: C, 46.92; H, 6.18; N, 15.63. Found: C, 46.76; H, 5.98; N, 15.28. UV and visible $\lambda_{max}^{H_2O}$ mμ (log ε): 263 (3.78), 485 (4.20).

III$^-$-Sodium, III——This was obtained from the piperidinium or diethylammonium salts of III$^-$ by treating with NaOH in the same way as II, showed no melting point and exploded when ignited or heated.

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13) G. Barger, *Chem. Ber.*, 37, 1745 (1910); K. Rast, *ibid.*, **54**, 1979 (1921); S. Akiya, *Yakugaku Zasshi*, 57, 967 (1937); E. Müller (Hg.), "Methoden der organischen Chemie (Houben-Weyl)," Bd. III (1), Georg Thieme Verlag, Stuttgart, 1955, p. 355. The estimation of molecular weight of II was carried out by using acetone as a solvent and azobenzene as a reference with capillary tubes of 0.5—1.0 mm diameter at room temperature (23°).

rapidly. UV and visible $\lambda_{max}^{H_2O}$ mμ (log ε): 262 (3.76), 480 (4.15). *Anal.* Calcd. for $C_{10}H_{10}O_7N_3Na$: C, 39.08; H, 3.28; N, 13.67; Na, 7.48. Found: C, 39.10; H, 3.48; N, 13.50; Na, 7.62. IR ν_{max}^{KBr} cm^{-1}: 2835 (CH_3), 1725 (CO), 1545, 1340 (NO_2). NMR (10% acetone-d_6 solution): The multiplet centered at about 4.75 δ (c′, 1H) was supposed to be caused by the CH proton adjacent to $\rangle$CH–CH_3 group, which was deshielded by the introduction of a CH_3 group. The doublet at 0.98 δ (g, 3H, *J*=6.0 cps) might be due to a CH_3 group because this produced a quartet (f, *J*=6.0 cps) in down field region (3.20 δ) ascribed to the CH proton. By the irradiation of the multiplet centered at about 4.40 δ (c, 1H), a triplet at 5.72 δ (b, 1H, *J*=3.0 cps) turned to a doublet (1H, *J*=3.0 cps) and three doublets at 2.85 (d or e, *J*=4.5 cps), 2.65 (e or d, *J*=3.0 cps) and 2.40 (e or d, *J*=3.0 cps) δ became singlet respectively. By the irradiation of the multiplet centered at about 4.72 δ (c′, 1H), the triplet at 5.72 δ (b, 1H) turned to a doublet (*J*=3.0 cps). By the irradiation at 4.72 and 4.40 δ (triple resonance), the triplet at 5.72 δ which was assigned to H–C–NO_2 proton in cyclohexane or cyclohexene ring,[14] Hb in Chart 2, became a singlet. Three doublets at 2.85, 2.65 and 2.40 δ and a doublet which overlapped with a quartet centered at 3.20 δ were assigned to $\rangle$CH–C$\underline{H}_2$–CO– protons (d and e, geminal *J*=15.0 cps) in a partially rigid 6 membered ring.[15] A singlet at 8.53 δ (a, 1H) was assigned to a sp^2 ring proton.[8] These results and the presence of the CH group supported the formation of bridged structure as shown in Chart 2.

Absorption spectra were measured by a Shimadzu Recording Spectrometer SV-50A in a cell of 10 mm optical length. IR spectra were measured by a Koken DS-301 Infrared Spectrometer in KBr pellets. NMR spectra were measured by a JEOL C-60H NMR Spectrometer using TMS as an internal standard. Spark ionized mass spectra were measured by a JEOL JMS-01BM Mass Spectrometer using graphite electrodes. Samples were packed between the electrodes.

Acknowledgement The authors express their gratitude to Miss. K. Egami, Mrs. R. Ogata and I. Kawai for their cooperation in the experiment. Their thanks are also due to Mr. H. Matsui and Miss. Y. Soeda for the absorption spectral measurements, Messes. M. Shido, M. Abe, K. Ishimura and Y. Inoue for the elemental analyses, Mr. Y. Tanaka for the NMR spectral measurements and the staffs of Nihondenshi Co., Ltd. for the spark ionized mass and NMR spectral measurements.

This work was partly supported by a grant from Yakuri Kenkyukai (President: Prof. Y. Asahina).

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