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Studies on the Reaction between Polynitrobenzene Compounds and Active Methylene Groups. VIII.[1] On the Janovsky Reaction of Trinitroanisole in Acetone[2]

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Janovsky reaction of 2,4,6-trinitroanisole (TNA) and acetone in the presence of sodium methoxide was studied. By comparing the ratios of intensity of the peak at shorter wave length to that at longer one in the different solvents, the initial peaks at 418 and 488 mμ that observed three seconds after start of the reaction were assigned to be due to the Meisenheimer complex IVa and not to IIIa. That the final spectrum having maxima at 443 and 531 mμ in the reaction mixture coincides with the formation of Janovsky complex IVb, were clarified by NMR spectroscopy (Fig. 8) of IVb and by chemical way such as transferring it to 3-acetonyl-2,4,6-trinitroanisole. Contrary to the observation by Foster, *et al.* in the state of higher concentration, in the diluted acetone solution of IIIb extra sodium methoxide was necessary for transferring IIIb to IIIc. When TNA was added to the mixture prepared beforehand with acetone and sodium methoxide, the initial rate of increase in the absorbances at 443 and 531 mμ became higher than that in the simultaneous mixture of these three reactants. These would indicate that there was no solvolysis of IVa by acetone but the initial step was the deprotonation of solvent by the methoxide ion dissociated from IVa and the acetonate ion thus generated then attacked the dissociated TNA forming IVa. The rate of color development varied with the different interval between the addition of sodium methoxide and of TNA (Fig. 9); the reaction mixture of TNA, diacetone alcohol and sodium methoxide gave gradually the similar pattern having maxima at 445 and 526 mμ. The process of this reaction may thus be represented in Eq. (1), (3), (4), (5), and (6); Eq. (2) being excluded. The logarithmic equilibrium constant of the overall reaction was obtained as 5.4.

The color reactions of the active methylene compounds with polynitrobenzene derivatives in alkaline media have been employed widely in qualitative as well as quantitative analysis of these reactants and have been noted by the names of Janovsky-, Zimmermann-, Jaffé-, Baljet-, Raymond-, and Kedde-reaction *etc.* For a long while all of these had been thought to proceed under the same reaction mechanism, until it was pointed out in 1961 that in the Zimmermann reaction an oxidative step is involved and excess of the nitro compound plays a role as the dehydrogenating agent[4]; the similar results have been reported by other groups independently.[5] These reactions can be divided into two types depending on the relative quantities of the reactants: The one is the type containing excess active methylene compound (Janovsky's condition) and the other is in excess of nitro compound (Zimmermann's condition). In the reaction of *m*-dinitrobenzene with acetone, illustration of these colour reactions is shown as Chart 1. Such mode of the reactions is supported by the isolation of II and of the

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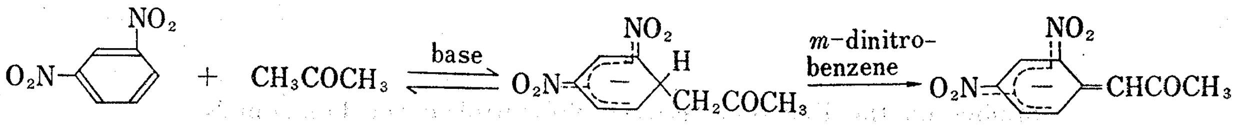
1) Part VII.: M. Kimura, M. Kawata, M. Nakadate. N. Obi and M. Kawazoi, *Chem. Pharm. Bull.* (Tokyo), **16**, 634 (1968).

2) A part of this paper was presented at the Meeting of Hokkaido Branch, Pharmaceutical Society of Japan, Sapporo, Feb. 1967.

3) Location: *Nishi-6-chome, Kita-12-jo, Sapporo.*

4) O. Neunhoffer, K. Thewalt and W. Zimmermann, *Z. physiol. Chem.*, **323**, 116 (1961).

5) T.J. King and C.E. Newall, *J. Chem. Soc.*, **1962**, 367; C.S. Corker, J.K. Norymberski and R. Thow, *Biochem. J.*, **83**, 583 (1962).



I

II

Janovsky reaction

Zimmermann reaction

Chart 1

reduction products of *m*-dinitrobenzene from acidified reaction mixture. However, the direct demonstration had not been done until the authors isolated the compounds I and II.[6] The chemical structure of I has been given support by elemental analysis, ultraviolet (UV), infrared (IR) as well as nuclear magnetic resonance (NMR) spectroscopies and by some reactions[1] recoverying *m*-dinitrobenzene from I and transferring I to II. The present paper deals with the Janovsky reaction of 2,4,6-trinitroanisole (TNA) and acetone in the presence of sodium methoxide, particularly with the process of the reaction and the location of the attached acetonyl group.

Immediately after the addition of sodium methoxide to TNA in acetone, there appeared four maxima at 418,443,488 and 531 mμ in the visible region of absorption spectrum. While the peaks of 418 and 488 mμ gradually lowered, those of 443 and 531 mμ rised progressively and finally there remained the latter couple alone (Fig. 1). Although the color thus developed was stable for several weeks when the reaction mixture was kept in the dark, the spectrum altered complicatedly to the final pattern having a single maximum at 490 mμ in the visible region when large excess of sodium methoxide was present.

In general, the conjugate system of Meisenheimer type complexes, for instance III or IV, has two maxima in the visible absorption spectrum and one at shorter wave length has higher optical density than the other. These facts are supported theoretically by simple LCAO–MO

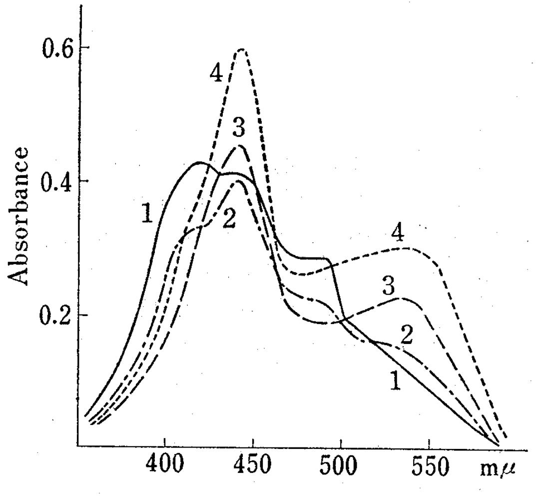


Fig. 1. Visible Absorption Spectra in the Reaction of TNA with Sodium Methoxide in Acetone

solvent system: acetone–methanol (98.4:1.6, v/v).
initial concentration of reactant: 2.46×10^{-5}M TNA, 6.42×10^{-5}M NaOMe
time after the start of reaction: 1) 1 min; 2) 3 min; 3) 15 min; 4) 90 hr

Curves are not corrected the error depending on the scanning time (1.5 min) of spectrophotometer; curves 3 and 4 are actually free from error.

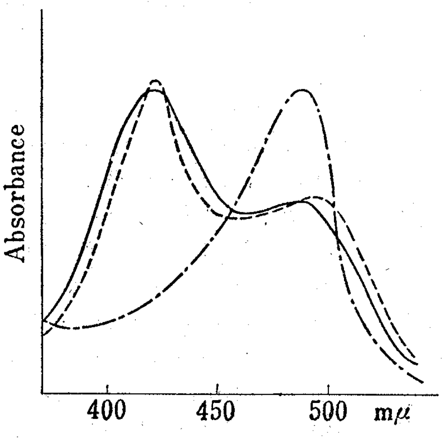


Fig. 2. Visible Absorption Spectra of IIIa

———: in MeOH
– – – –: in acetone
—— ——: in acetone at the presence of large quantities of NaOMe

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[6] M. Kimura, M. Kawata and M. Nakadate, *Chem. Ind.* (London), **1965**, 2065.

method[7] and by Pariser–Parr–Pople method[8]. The peaks at 418 and 488 mμ seemed to be due to the addition of methoxyl group to the benzene ring and the maximum absorptions of IIIa that was prepared by the procedure of Dyall[9] were shown at 417 and 487 mμ in methanol, and at 419 and 497 mμ in acetone. These peaks were, however, so steady in acetone that they did not alter to the maxima at 443 and 531 mμ even in the presence of small quantities of the methoxide; large quantities of the base turned the spectrum not to show these double maxima but a single one at 487 mμ (Fig. 2). Therefore, the maxima at 418 and 488 mμ can not be due to IIIa.

Recently Servis reported from the results of NMR spectroscopy that in dimethylsulfoxide (DMSO) TNA is converted by sodium methoxide initially to IVa and then to IIIa which in methanol can be formed directly.[10]

IIIa : R=OMe R'=OMe
IIIb : R=H R'=OMe
IIIc : R=H R'=CH_2COCH_3
IIId : R=OMe R'=CH_2COCH_3

IVa : R=OMe R'=OMe
IVb : R=OMe R'=CH_2COCH_3
IVc : R=OC_6H_5 R'=CH_2COCH_3

Chart 2

It is natural that these processes can also be detected by the absorption spectroscopy. When sodium methoxide was added to TNA in methanol, two peaks at 417 and 487 mμ grew steadily bearing the constant ratio (1.51) of the optical density at the former peak to that at the other one (Fig. 3). In DMSO, on the other hand, instantaneously after mixting the reactants the intensities of the peaks at 426 and 500 mμ were highly elevated showing the ratio of 1.26 that altered then to 1.31 after 20 minutes and finally after 48 hours to 1.48, nearly equal to that observed in methanol (Fig. 4). These facts are sure to correspond to the NMR study

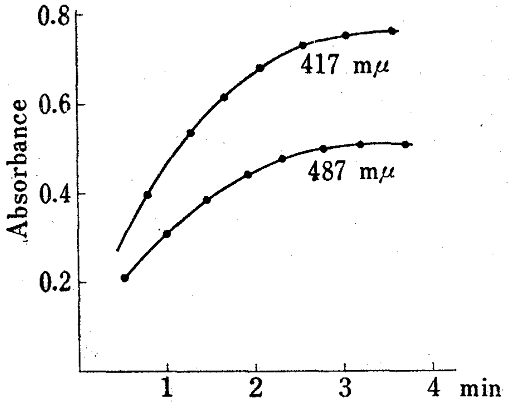

Fig. 3. Change of Absorbance at Maximum Wavelength in the Reaction of TNA with NaOMe in MeOH

[TNA]$_{t=0}$=3.05×10^{-5}M, [OMe$^-$]$_{t=0}$=6.89×10^{-4}M

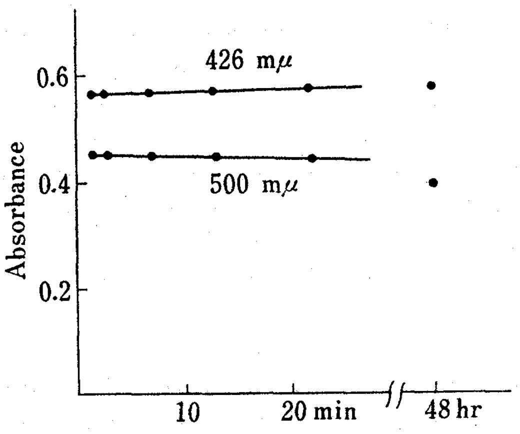

Fig. 4. Change of Absorbance at Maximum Wavelength in the Reaction of TNA with NaOMe in Dimethylsulfoxide

solvent system: DMSO–MeOH (98.2:1.8; v/v).
[TNA]$_{t=0}$=2.23×10^{-5}M [OMe$^-$]$_{t=0}$=4.43×10^{-4}M

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7) T. Abe, *Bull. Chem. Soc. Japan*, **37**, 508 (1964); S. Hoshino and S. Nagakura, The 19th Annual Meeting of Chemical Society of Japan, Tokyo, March, 1966; P. Caveng, P.B. Fischer, E. Heilbronner, A.L. Miller and H. Zollinger, *Helv. Chim. Acta*, **50**, 848 (1967).

8) H. Hosoya, S. Hosoya and S. Nagakura, The 21st Annual Meeting of Chemical Society of Japan, Osaka, April, 1968.

9) L.K. Dyall, *J. Chem. Soc.*, **1960**, 5160.

by Servis[10] and the ratios 1.5 and 1.26 may correspond to IIIa and IVa, respectively. In acetone the reaction profile at the very early stage of the attack by the methoxide could successfully be observed by the rapid scan spectrophotometer equipped with memoryscope using mixing cell (Fig. 5). From the spectrum three seconds after the start of reaction the methoxide alone seems to affect TNA as shown in Fig. 6; the ratio of the intensity of two maxima was 1.24 that was almost equally estimated at the beginning of the same reaction in DMSO. The peaks at 418 and 488 mμ given in acetone, therefore, are best interpreted to be due to IVa, not to IIIa and this is very probable, for acetone is similar in quality to DMSO as dipolar aprotic solvent.[11]

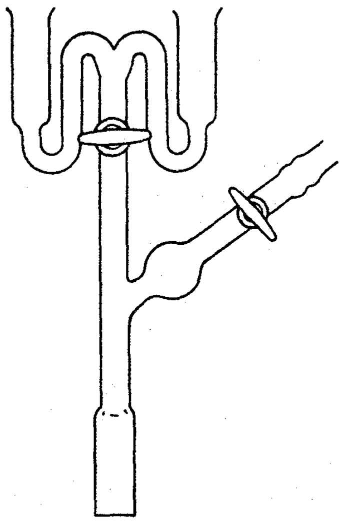

Fig. 5. Mixing Cell

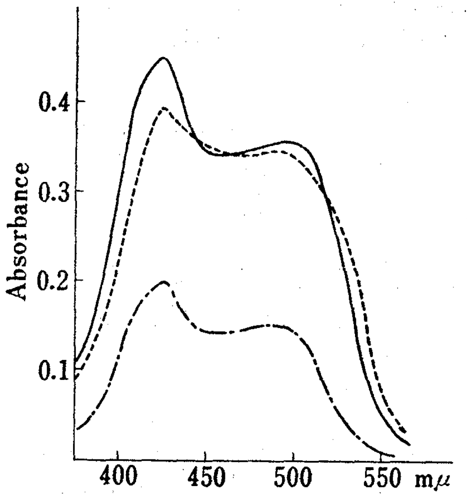

Fig. 6. Absorption Spectra at the Early Stage in the Reaction of TNA with Sodium Methoxide in Acetone

------: at 3 sec after the start of reaction
————: at 10 sec
-·-·-·-: at 40 sec

The final spectrum having maxima at 443 and 531 mμ (Fig. 1) may reasonably be due to the addition of acetonyl group to the benzene ring, for the Meisenheimer complex IIIb in acetone transfers easily to the Janovsky compound IIIc.[12] This may be corresponded to the fact that IIIb has far smaller formation constant than IIIa[13] and may be meant—seemingly, owing to the reason described later—that methoxyl group attched to the sp^3 hybridized ring carbon carring hydrogen in the Meisenheimer complex can easily be substituted by acetonyl group. The problem is then the position attacked by acetonyl group and the possiblility is C–1 addition (IIId) or C–3 (IVb) or the mixture of the two. In the case of *m*-dinitrobenzene derivatives Pollitt, *et al.* showed from the visible absorption spectroscopy that the position of attack is the unoccupied position by some functional groups.[14] In the case of 2-or 4- chloro-3,5-dinitrobenzoic acid, however, the addition occurs at the carbon carrying chlorine atom as well as at the unsubstituted position.[15] On trinitrobenzene derivatives Foster, *et al.* studied recently by NMR spectroscopic method that addition occurs at unoccupied position alone.[16]

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10) K.L. Servis, *J. Am. Chem. Soc.*, **89**, 1508 (1967).
11) A.J. Parker, "Advances in Organic Chemistry: Methods and Results," Vol. 5, ed. by R.A. Raphael, E.C. Taylor and H. Wynberg, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1965, pp. 1—46; Also see A.J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).
12) R. Foster and C.A. Fyfe, *Tetrahedron*, **21**, 3363 (1965).
13) V. Gold and C.H. Rochester, *J. Chem. Soc.*, **1964**, 1692; T. Abe, T. Kumai and H. Arai, *Bull. Chem. Soc. Japan*, **38**, 1526 (1965).
14) R.J. Pollitt and B.C. Saunders, *J. Chem. Soc.*, **1965**, 4615.
15) M. Akatsuka, *Yakugaku Zasshi*, **80**, 389 (1960).
16) R. Foster, C.A. Fyfe and (in part) P.H. Emslie and M.I. Foreman, *Tetrahedron*, **23**, 227 (1967).

As TNA was not taken by Foster and the physical method might hardly be able to detect trace components, the authors studied on the reactions of this compound by using chemical method as follows. In the visible absorption spectra of TNA in acetone containing sodium methoxide, the wave lengths of the two maxima and the ratio of their extinctions became fixed after 15 minutes (Fig. 1). This means that if the final spectrum is due to the mixture of IIId and IVb, the composition of the two should be constant at least after 15 minutes. This is, however, unprobable, for there must be equilibrium between TNA and Meisenheimer type complexes and be difference between the rates of formation of IIId and IVb, if the both would be formed. While it is unfortunate that the isolated TNA–acetone Janovsky complex was not obtained in a crystalline state, it gave a coloured spot (*Rf* 0.35) alone on thin–layer chromatogram (solvent: benzene–EtOH (2:1); plate: silicagel) and gave the absorption spectrum consistent with the final one shown by the reaction mixture. This also supports the presence of a single complex, IIId or IVb, and not the mixture of them. The Janovsky complex thus formed was decomposed in acidic condition and thin–layer chromatogram of the diethyl ether extract from acidified solution is shown in Fig. 7. If the spot having the color as well as *Rf* value analogus to those of picrylacetone is really due to the very ketone, the parent Janovsky complex must be IIId. However, NMR spectrum gave a proof of IVb (Fig. 8).

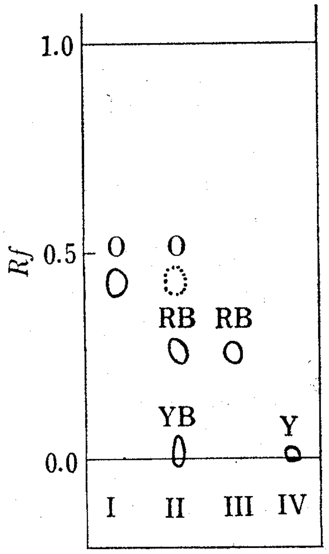

Fig. 7. Thin–Layer Chromatogram of the Extract from Decomposed Product of Janovsky Complex

plate: Wakogel B-5; solvent system: $CHCl_3$–benzene (3:1); detection: 2N NaOH
I: TNA, II: decomposed product, III: picrylacetone, IV: picric acid; O: orange, RB: reddish brown, YB: yellowish brown, Y: yellow

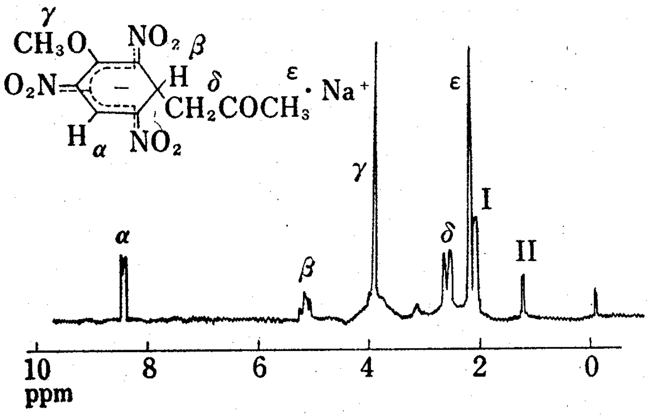

Fig. 8. NMR Spectrum of Janovsky Complex in CD_3COCD_3

I and II may be ascribed to acetone and diacetone alcohol, respectively; being contaminated by Janovsky complex in preparative process.

To solve this discrepancy, the questionable compound was isolated from the extract by silica gel column chromatography. The melting point and IR spectrum of the purified substance were different from those of picrylacetone, and NMR spectrum and elemental analysis proved it to be 3-acetonyl-2,4,6-trinitroanisole; the yield was about 8% from the parent Janovsky complex. Thus, the structure of this complex was decided as IVb. Despite of the careful experiment, picrylacetone could not be detected and the possibility of the existence of IIId might be eliminated.

In the above–mentioned column chromatography TNA was isolated in the yield of only 4%. It is very interesting that picric acid was also obtained in the yield of 66%; generally, acid degradation of the Meisenheimer type complexes regenerates the parent nitro–compound[9,17] and in this condition TNA can not be expected to give picric acid. Even if the degradation was done in non–aqueous condition, the results was the same. The initial step of the degradation may reasonably be the protonation to ether oxygen and not the attack of hydroxyl anion at the carbon carrying methoxyl group. Phenolic *t*-butyl ether having very high basicity cleaves rapidly to phenol in 18% sulfuric acid at 0° and the reason was discussed to be due to the steric inhibition of resonance.[18] In Meisenheimer type complex, three nitro groups tend to exist in a plane of the conjugated ring system as has been confirmed through X–ray diffraction analysis[19] and thus the methoxyl group in IVb suffers highly steric inhibition of the resonance. It may, therefore, be reasonable that picric acid was formed from IVb in moderately weak acidic condition. In degradation of IVc the product was not picric acid but phenyl picrate[17b]. This fact may be in no discrepancy, for the steric interaction in IVc is much higher than in IVb but the electron density at ether oxygen is lowered by phenyl group.

From these results and the transformation of Meisenheimer complex to the Janovsky one studied by Foster,[12] the color reaction of TNA in acetone with sodium methoxide might be represented in equations (1) and (2).

$$\mathrm{TNA} + \mathrm{OMe}^- \rightleftarrows \mathrm{IVa} \qquad (1)$$

$$\mathrm{IVa} + \mathrm{CH_3COCH_3} \rightleftarrows \mathrm{IVb} + \mathrm{MeOH} \qquad (2)$$

However, it is to be noted that in the highly concentrated acetone solution the transfer of synthetic IIIb to IIIc could be observed as reported by Foster, *et al.*[12] whereas in the diluted solution of IIIb sodium methoxide should be necessarily added for the transfer. This would indicate that there was no solvolysis of IIIb by acetone and the initial step was the deprotonation of solvent by the methoxide ion dissociated from IIIb and the acetonate ion thus generated then attacked the dissociated trinitrobenzene forming IIIc. When the concentration of IIIb is fairly reduced, on the contrary, the methoxide ion must be generated so small in quantity that it may be abolished by carbon dioxide present in acetone. Thus, equations (3) and (4) are reasonable also in the TNA series and (2) may rather be excluded. When sodium methoxide was present in acetone beforehand and then after one or two minutes TNA in acetone was added to this, the initial rate of increase in the absorbances at 443 and 531 mμ became higher than that obtained in the case where the methoxide was added directly to the mixture of acetone and TNA. This would also stand for the process of reaction described below; the equilibrium in equation (3) being rather inclined to the right.

$$\mathrm{CH_3COCH_3} + \mathrm{OMe}^- \rightleftarrows \mathrm{CH_3COCH_2}^- + \mathrm{MeOH} \qquad (3)$$

$$\mathrm{TNA} + \mathrm{CH_3COCH_2}^- \rightleftarrows \mathrm{IVb} \qquad (4)$$

When the interval between the additions of sodium methoxide and of TNA was made variable, the rate of the color development changed as shown in Fig. 9. Along with the alteration of the time interval the rate became larger initially and then became smaller than the standard. It means that according to equation (3) the concentration of acetonate ion became higher initially but the ion thus formed then turned out to something. On the other hand, the optical density at equilibrium condition did not alter in all cases, if the alkaline concentration was kept constant. This would indicate the regeneration of acetonate ion during the elapse of time. The condensation of acetone to diacetone alcohol has been known as the base cata-

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17) *a*) M. Kimura, *Yakugaku Zasshi*, **73**, 1219 (1953); *b*) M. Kimura, *Pharm. Bull.*, **3**, 75 (1955); c) M. R. Crampton and V. Gold, *J. Chem. Soc.* (*B*), **1967**, 23.

18) E.M. Arnett and C.Y. Wu, *J. Am. Chem. Soc.*, **82**, 5660 (1960).

19) R. Destro, C.M. Gramaccioli and M. Simonetta, *Nature*, **215**, 389 (1967); H. Ueda, N. Sakabe, J. Tanaka and A. Furusaki, *ibid.*, **215**, 956 (1967).

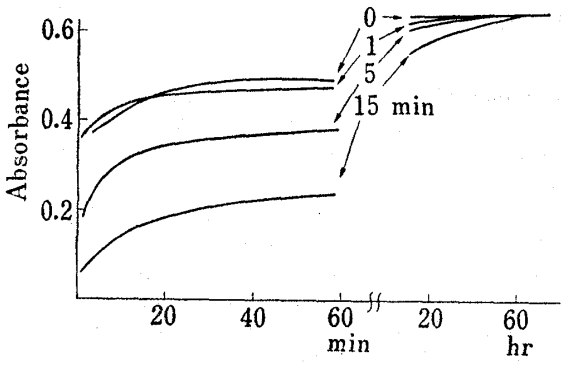

Fig. 9. The Rate of Colour Development at 443 mμ

After different intervals shown in the Fig., TNA was added to the mixture of NaOMe and acetone. Time 0 min means that TNA was added at first and then NaOMe was added. solvent system: acetone–methanol (98.4:1.6; v/v).
$[\text{TNA}]_{t=0}=2.46\times10^{-5}\text{M}$, $[\text{OMe}^-]_{t=0}=6.42\times10^{-5}\text{M}$

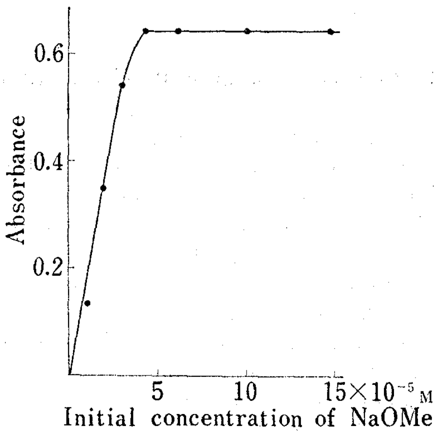

Fig. 10 Absorbance at Equilibrium in Various Concentrations of NaOMe

solvent system: acetone–methanol (98.4: 1.6; v/v) $[\text{TNA}]_{t=0}=2.46\times10^{-5}\text{M}$

lized reversible reaction[20] and actually the alcohol was detected in the mixture of acetone and sodium methoxide through gas chromatography. The equations (5) and (6) must, therefore, be added too.

$$CH_3COCH_2^- + CH_3COCH_3 \rightleftarrows CH_3COCH_2C(CH_3)_2O^- \qquad (5)$$

$$CH_3COCH_2C(CH_3)_2O^- + MeOH \rightleftarrows CH_3COCH_2C(CH_3)_2OH + MeO^- \qquad (6)$$

When sodium methoxide was added to the mixture of TNA and diacetone alcohol, the colour developed very slowly showing the maxima at 445 and 526 mμ, presumably along the processes presented by the equations (6), (5) and (4); methoxyl anion disappeared so quickly that IVa or IIIa could not be formed and anion of diacetone alcohol decomposed very slowly to acetonate ion which finally attacked TNA forming IVb as usual. Although the absorption maxima appeared at slightly different wavelenghts from those in acetone solution, this can not be due to the Meisenheimer complex of diacetone alcohol with TNA, for despite of the presence of anion of the alcohol no color was observed at the very early stage of reaction and synthetic IVb gave maxima also at 445 and 526 mμ in this alcohol. Anion of diacetone alcohol may probably be unable to form the Meisenheimer complex. Through these investigations, the process of the Janovsky reaction of TNA and sodium methoxide in acetone can be explained by equations (1), (3), (4) (5), and (6) under complicated relations with each other.

The absorbance of the reaction mixture at equilibrium was measured at various sodium methoxide concentrations as illustrated in Fig. 10. As the concentration of IVa is negligible at equilibrium, the absorbance at 443 mμ is due to IVb alone. The molar absorptivity of IVb at 443 mμ is estimated as about 26200 from the results shown in Fig. 10 and the equilibrium constant of the overall reaction is given as follows:

$$K=\frac{K_4}{1/K_3+1+K_5}=\frac{[\text{IVb}]}{(A-[\text{IVb}])(B-[\text{IVb}])}$$

Where K_3,K_4 and K_5 are equilibrium constants of equations (3), (4) and (5), respectively and A and B are the initial concentrations of TNA and the base, respectively. Log K calculated from the experimental results, was 5.4. Since K_3 and K_5 are unknown, K_4 can not be obtained. As K_4, however, is larger than K, equation (4) inclined extremely to the right hand.

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20) A.A. Frost and R.G. Pearson, "Kinetics and Mechanism," 2nd ed., John Wiley & Sons, Inc., New York, 1961, pp. 335—350.

21) internal standard: tetramethylsilane.

Experimental

Matearials and Standard Procedure of Color Development——Acetone was treated with potassium permanganate, then dried with anhydrous potassium carbonate and distilled, bp 56.5°. Methanol was distilled without any other purification, bp 65°. Diacetone alcohol and DMSO were distilled under reduced pressure and middle fraction was used. DMSO was kept under molecular sieve. TNA was prepared *via* picryl chloride from picric acid and was recrystalized from methanol, mp 67°. A stock solution of sodium methoxide was prepared by mixing fresh piecies of metallic sodium in methanol which was refluxed under protecting by soda–lime. The concentration was established by titration of samples diluted with water against sulfamic acid as standard reagent. When the concentration of sodium methoxide was meaningful, the solvent that was refluxed with soda-lime tube was used and all the procedures were took with care to avoid the disturbance by carbon dioxide in air. Standard procedure of colour development was as follows: 0.1 ml of sodium methoxide in methanol was added to 6 ml of TNA in acetone.

Instruments——Absorption spectra were measured on Hitachi recording spectrophotometer type EPS-2U or EPS-3T. In the experiment shown in Fig. 6, Hitachi rapid scan spectrophotometer type RSP-2 was used; scanning time was about 0.15 sec. NMR spectra were measured on Hitachi H-60 spectrometer. IR spectrum was obtained through Koken-DS-301. Gas chromatogram was taken with Shimadzu GC-4APF.

Janovsky Complex (IVb)——A mixture of 2N NaOMe (0.5 ml) and acetone (30 ml) was added dropwise to TNA (250 mg) in acetone (300 ml) with vigorous stirring. After 1 hr the solution was concentrated to about 2 ml under reduced pressure. Then benzene was added to precipitate Janovsky complex, which was filtrated, dissolved in acetone, and precipitated again by adding benzene; this procedure was repeated several times for purification. Distillation of the final acetone solution under reduced pressure left 300 mg of gummy dark red Janovsky complex, having trace amount of impurities that might mainly be diacetone alcohol. As the contamination disturbed the interpretation of NMR spectrum the gummy substance was once dissolved in acetone-d_6 and then solvent was distilled off giving the residue which was dissolved again in acetone-d_6 for the measurement. NMR (in acetone-d_6) ppm:[21] 8.40 (1H, doublet, $J=1$ cps, sp^2 ring H), 5.18 (1H, sextet (doublet, triplet), $J_1=1$ cps $J_2=6$ cps, sp^3 ring H), 3.94 (3H, singlet, OCH_3), 2.65 (2H, doublet, $J=6$ cps, CH_2), 2.25 (3H, singlet, $COCH_3$). On the preparation of IVb the composition of solvents was meaningful; when the volume of methanol was larger than that mentioned above, some compound, probably IIIa, contaminated.

Degradation of IVb by Acid——To the dark red aqueous solution (50 ml) of IVb (462 mg) 0.1N HCl (13.7 ml) was added little by little for 30 min with stirring at room temperature. The mixture was stirred for another 30 min, which became brownish yellow and muddy, and then was extracted by ether. The extract was chromatographed using silicagel (10 g) giving TNA (15 mg), 3-acetonyl-2,4,6-trinitroanisole (36 mg) and picric acid (176 mg). From the aqueous layer in the ether-extraction picric acid (49 mg) was also obtained.

3-Acetonyl-2,4,6-trinitroanisole——Colorless needles, mp 131.5° (corr.) and IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1732 (C=O), 1535 (asym. NO_2), 1350 (sym. NO_2), 1251 (asym. =C–O–C), 1076 (sym. =C–O–C). *Anal.* Calcd. for $C_{10}H_9O_8N_3$: C, 40.14; H, 3.03; N, 14.05. Found: C, 40.14; H, 3.19; N, 13.76. NMR (in acetone-d_6) ppm[21]: 8.96 (1H, singlet, ring H), 4.35 (2H, singlet, CH_2), 4.16 (3H, singlet, OCH_3), 2.37 (3H, singlet, $COCH_3$).

Gas Chromatography of Diacetone Alcohol——Retention time of diacetone alcohol was 5.7 min using the column 3% OV-1 on Gas-Chrom Q 3 mm × 3 m at 50°. From the sample of acetone containing sodium methoxide, the peak at t_R 5.7 was detected.

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