The Formation and Reactions of 3, 5, 7-Trinitrotropolone

By Tetsuo NOZOE, Minoru OYAMA* and Katsuo KIKUCHI**

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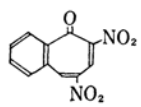
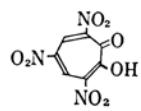
From the result of the molecular orbital calculation on tropone (I) it was predicted that the cationoid substitution reactions would occurr at 2 position of tropone nucleus[1], while the detailed studies of bromination[2] and Diels-Alder reactions[3] of I showed that it has a considerable degree of an unsaturated character compared with tropolone (II).

Recently Buchanan and others[4] obtained a dinitro derivative IV from the reaction of 2,3-benzotropone (III) with concentrated nitric acid, and they thought it must be produced through addition-elimination reaction of III and dinitrogen tetroxide, being produced by mutual oxidation-reduction of III and nitric acid. Doering[5], some years ago, stated in his lecture that the reaction of tropone (I) and nitric acid gave a complex (VI) of 3, 5, 7-trinitrotropolone (V) and I, but the details of which is not available yet. On the other hand, Nozoe, Kitahara and others[6] reported that the action of excess nitric acid on tropolone (II) or on ammonium salt of its 5-sulfonic acid afforded yellow needles (VII), m. p. 238°C (decomp.), and they thought it to be 3, 5, 7-trinitrotropolone, but because of its low yield, the detailed studies on its chemical behavior were not possible.

III



IV



V

As excellent methods for synthesizing tropone (I) from tropilidene were developed recently[7], we attempted to study the action of nitric acid on I as one of the wide range of examination on the properties of I. In this study, we ascertained the formation of 3, 5, 7-trinitrotropolone-tropone complex (VI) as stated by Doering[5], obtained 3, 5, 7-trinitrotropolone (V) therefrom and observed some interesting behaviors of them, and these results will be reported herein.

The reaction condition of tropone (I) and nitric acid to obtain VI is fairly sensitive. Under room temperature, the reaction does not occur practically, while once the reaction started it sometimes proceeds with explosive violence; such a case was already experienced by one[8] of us when hinokitiol was nitrated under variety of conditions. The following procedure is however found to be satisfactory; after the reaction is started by the preliminary addition of a small amount of I into a mixture of fuming nitric acid (4 mol. equiv.) and acetic acid, I (1 mol. equiv.) is added cautiously with stirring while the temperature is maintained at 60~70°C by which the yellow needles (VI), m. p. 228°C (decomp.), of the formula $C_{14}H_9O_9N_3$ are obtained in about a 55% yield.

The compound VI is sparingly soluble in non-polar solvents but very soluble in water and alcohol. With aqueous sodium bicarbonate it gives yellow sodium salt (VIII), $C_{14}H_8O_9N_3Na$, which regenerates original substance by hydrochloric acid. On being left stand at room temperature with aqueous sodium hydroxide or heated with aqueous sodium bicarbonate, VI is converted to colorless crystals (IX), m. p. 132°C (decomp.), which is identified as a 1 : 1-complex of 2, 4, 6-trinitrobenzoic acid (X) and I. VI is not affected with 4 N hydrochloric acid in acetone at refluxing temperature, but gives X when heated with concentrated hydrochloric or hydrobromic acid, and gives 1, 3, 5-trinitrobenzene (XI) when refluxed with aqueous acetic acid (50%). Heating of VI in methanol or ethanol affords methyl ester XII or ethyl ester XIII of X, with the liberation of tropone (I) which is identified as its picrate, m. p. 99~100°C. These facts indicate

* Present address: Research Institute, Toyo-Rayon, Inc., Kamakura, Kanagawa Prefecture.
** Present address: Department of Chemistry, Faculty of Liberal Arts and Science, Yamagata University, Yamagata.

1) R. D. Brown, *J. Chem. Soc.*, **1951**, 2670.
2) T. Nozoe, T. Mukai, K. Takase and T. Nagase, *Proc. Japan Acad.*, **28**, 477 (1952); T. Nozoe, T. Mukai and K. Takase, *Sci. Repts. Tohoku Univ., Ser. I*, **39**, 164 (1956); T. Mukai, This Bulletin, **31**, 846 (1958).
3) T. Nozoe, T. Mukai, T. Nagase and Y. Toyooka, ibid., **33**, 1247 (1960).
4) G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, **1959**, 3586.
5) W. von E. Doering, *Abstracts of XIII, National Organic Symposium (Am. Chem. Soc.)*, p. 1 (1953).
6) T. Nozoe, Y. Kitahara, K. Doi and T. Arai, *Bull. Chem. Research Inst. of Non-Aqueous Solution, Tohoku Univ.*, **7**, 13 (1957).
7) T. Ikemi, T. Nozoe and H. Sugiyama, *Chem. & Ind.*, **1960**, 932; A. P. Ter. Borg, R. van Helden, A. F. Bickel, W. Renold and A. S. Dreiding, *Helv. Chim. Acta*, **43**, 457 (1960).
8) T. Nozoe, *Science of Drugs*, **3**, 174 (1949).

that VI is 1 : 1-complex of 3, 5, 7-trinitrotropolone (V) and tropone (I) and it is thought to be identical with what Doering stated to have obtained[5].

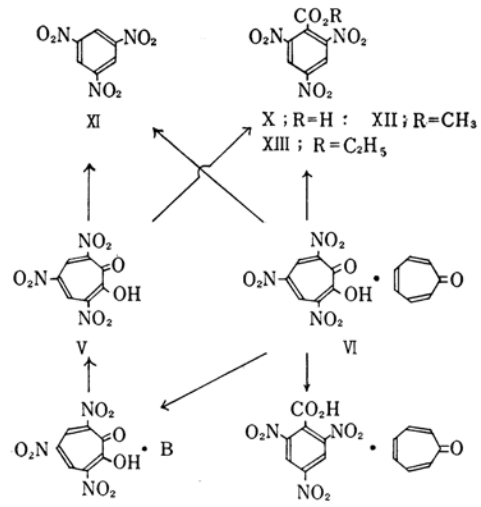
As mentioned above, the treatment of VI with sodium hydroxide or sodium bicarbonate did not yield V, and then the attempt was made to obtain salts of various amines through which V could be obtained as described below.

Treatment of the complex VI with ammonia gives red microcrystals which, when treated with dilute hydrochloric acid, is converted to yellow needles (XIV), m. p. 235°C (decomp.). Similarly, respective treatment of VI with methylamine and pyridine gives yellow needles (XV), m. p. 203°C (decomp.) and yellowish orange needles (XVI), m. p. 201°C (decomp.), respectively. From the fact that the ultraviolet spectra of XIV, XV and XVI resemble that of V (see below) and from the analytical values of them, these are showed to be 1 : 1-salts of V with ammonia, methylamine and pyridine respectively. By the reaction of VI with *p*-toluidine, there are obtained yellow needles (XVII), m. p. 123°C (decomp.) which is thought to be 1 : 1 : 1-complex of V, I and *p*-toluidine from the analytical value and ultraviolet spectrum.

Attempted removal of bases from XIV or from XV with dilute hydrochloric acid does not succeed and heating of XV at 160°C under reduced pressure (4 mmHg) also resulted in the recovery of original substance. But, when pyridinium salt XVI is treated with concentrated hydrochloric acid at room temperature, 3, 5, 7-trinitrotropolone (V) is obtained in about 80% yield with the addition of a small amout of the rearranged product X. Similar treatment of XIV or XV with concentrated hydrochloric acid also gives V but with rather poor yields. Treatment of V and I regenerates VI.

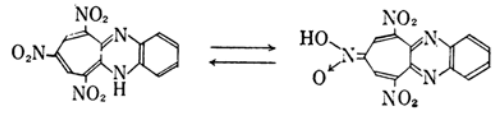
The compound V, yellow needles of m. p. 175°C (decomp.), shows red coloration with ferric chloride in ethanol or dioxane though not colored in water, benzene or chloroform, and gives yellowish orange sodium salt and a yellowish green copper complex. No liberation of nitrogen is observed when treated of V with diazomethane and only a small amount of yellow crystals of unknown structure is obtained. Heating of V with concentrated hydrochloric acid or with sodium hydroxide gives X, and refluxing of V with aqueous acetic acid (50%) gives XI. Treatment of V with methanol or ethanol gives XII or XIII respectively ; these properties are quite similar to those of VI.

The reaction of *o*-phenylenediamine with the compound V or with VI gives dark red crystals (XIX), m. p. over 240°C, soluble in alkaline solution, which is thought to be 6, 8,-



XIV B = NH_3
XV B = CH_3NH_2
XVI B = Pyridine
XVII B = Tropone·*p*-Toluidine
XX B = Guanidine

10-trinitrocyclohepta[b]quinoxaline from its analytical value and ultraviolet spectrum[9]. Attempted synthesis of 1, 3-diazaazulene derivative through the reaction of V or VI with guanidine gives only guanidinium salt (XX) of V, yellowish brown needles of m. p. 258°C (decomp.). Heating of V with aniline on a water bath gives colorless scales (XXI), m. p. 245.5°C, the structure of which is not clarified yet.



XIX

It seems of interest to note that the compound V, while it is easily rearranged into aromatic compounds on treatment with acid or alkali and on mere heating with alcohols, forms stable salts with various amines.

Ultraviolet spectra of V in methanol and alkaline solution are shown in Fig. 1 ; the absorption curve in methanol resembles those of 5-nitro-[5] and 3, 5-dinitrotropolones[6]. The ultraviolet absorption curve of VI (shown in Fig. 1) corresponds to a superposition of those of V and I. The infrared spectrum of V in Nujol is given in Fig. 2.

Now, the compound VII[6], previously obtained by the nitration of tropolone (II) is considered not to be true 3, 5, 7-trinitrotropolone. We reexamined these experiments and found that

9) S. Ito, *Sci. Repts. Tohoku Univ., Ser. I*, 43. 216 (1959).

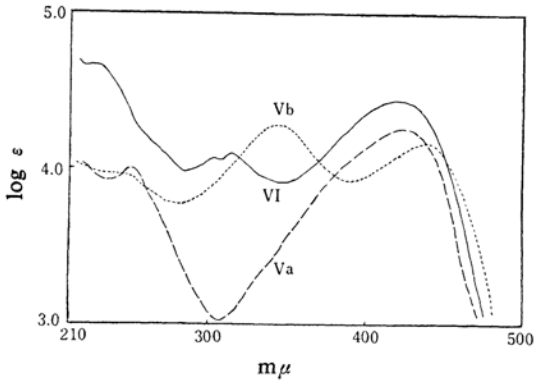


Fig. 1. UV spectra of V in methanol (Va) and in methanolic 0.1 N NaOH (Vb) and of VI in methanol.

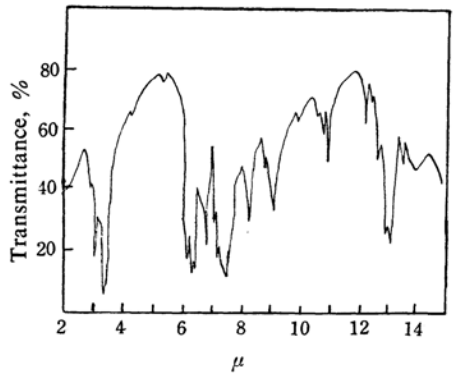
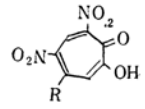


Fig. 2. IR spectrum of V in Nujol.

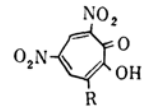
the fraction, considered to be polynitrotropolone, gave a small amount of the compound VI on adding tropone (I), but the compound VII could not be isolated; in this reaction condition trinitrotropolone once formed must have suffered from further destructive oxidation or rearrangement. On the other hand, the present synthetic procedure for V starting from I is excellent because it is easily isolated as a stable and sparingly soluble complex VI with tropone.

As to the formation of the complex VI from I, two main routes may be considered; one in which VI is formed through the addition-elimination reaction on tropone nucleus and the other in which VI is formed by the preliminary oxidation of I to tropolone (II) followed by the nitration. If the latter is the case, a distinct increasing in the yield of VI may be expected when the mixture of I and II is nitrated under similar conditions, but only slight increasing is actually realized, while the intermediate addition product that might be expected to be formed in the former case is not actually isolated, and the mechanism of its formation remains to be examined.

It is well known from the previous examination that 4-alkyl-5, 7-dinitrotropolones (XXII: R; CH_3[10], C_2H_5[11], *iso*-C_3H_7[12]) are easily rearranged into 3-alkyl-4, 6-dinitrobenzoic acids or their esters by mere warming with various alcohols or with aqueous acetic acid, while 5, 7-dinitrotropolones having substituent at 3 position (XXIII: R; H[6], Br[6], *iso*-C_3H_7[13]) are not rearranged in these conditions as above though they do in alkaline media, and it has been considered that in such rearrangement reactions steric interference between an alkyl group in 4 position and a nitro group in 5 position plays an important role. It seems noteworthy to say that 3, 5, 7-trinitrotropolone (V), having no such substituents at 4 position as to cause steric interaction, is now shown to undergo such a specific rearrangement.



XXII



XXIII

Experimental

Reaction of Tropone (I) with Nitric Acid.—After the reaction was induced at 60~70°C by adding several drops of I to a mixture of 14 g. of 94% fuming nitric acid and 15 ml. of acetic acid, a solution of 5 g. of I dissolved in 5 ml. of acetic acid was carefully added to this mixture with stirring while the reaction temperature was maintained at 60~70°C by external cooling. After a violent evolution of nitrogen dioxide ceased, the crystals that formed were collected by filtration to obtain 3.2 g. of yellow crystals, m. p. 218°C (decomp.). Recrystallization from dioxane containing a small amount of water gave yellow needles (VI), m. p. 228°C (decomp.). These crystals showed red coloration in ethanol or dioxane with ferric chloride solution. λ_{max}^{MeOH} mμ (log ε): 225 (4.66), 302 (4.08), 310 (4.09), 420 (4.42); $\lambda_{max}^{H_2O}$ mλ (log ε): 228 (4.49), 313 (3.98), 422 (4.27).

Found: C, 46.22; H, 2.33; N, 11.69. Calcd. for $C_{14}H_9O_9N_3$: C, 46.29; H, 2.50; N, 11.57%.

The filtrate was evaporated under reduced pressure at room temperature and 0.6 g. of colorless crystals, m. p. 97~98°C, was obtained. These crystals were reacted with ethereal diazomethane solution to give colorless crystals, m. p. 54°C., which showed no depression on admixture with dimethyl oxalate.

Nitration of a Mixture of Tropone (I) and Tropolone (II) with Nitric Acid.—To a solution

10) T. Nozoe, T. Mukai, M. Kunori, T. Muroi and K. Matsui, ibid., 35, 242 (1952); T. Muroi, *Bull. Yamagata Univ. Natural Science*, 3, 155 (1954).

11) T. Nozoe, K. Takase and K. Umino, to be published soon.

12) T. Nozoe, Y. Kitahara, K. Yamane and Y. Yamaki, *Proc. Japan Acad.*, 26, (8) 14 (1950).

13) K. Yamane and S. Morosawa, This Bulletin, 27, 18 (1954).

of 4.0 g. of 94% nitric acid (6 mol. equiv. for II) dissolved in 5 ml. of acetic acid was added a mixture of 1.0 g. of I and 1.2 g. of II in 5 ml. of acetic acid in drops under stirring at 30~40°C, and the reaction mixture was allowed to stand for 3 hr. and the yellow crystals were collected by filtration to afford 1.49 g. of VI, m. p. 224°C (decomp.), which showed no depression on admixture with the sample obtained above and the infrared spectra were also identical.

Reaction conditions and the yields of VI were shown in Table I.

Table I. Nitration of mixture of tropone (I) and tropolone (II) with 94% nitric acid

I g.	II g.	Nitric acid g.	React. temp. °C	Yield of VI g.
5.0	0	14	60~70	3.2
1.0	1.2	2.7	40~50	0.63
1.0	1.2	2.7	60~70	0.41
1.0	1.2	4.0	30~40	1.49
1.0	1.2	5.4	30~40	1.27

Reaction of the Compound VI and Aqueous Sodium Bicarbonate or Sodium Hydroxide.—a) Addition of 300 mg. of VI in 2 ml. of saturated aqueous sodium bicarbonate gave deep red solution, and the crystals that precipitated after sometime were collected by filtration and washed with a small amount of water to give 200 mg. of yellow prisms (VIII), m. p. 185°C (decomp.). $\lambda_{max}^{H_2O}$ mμ (log ε): 228 (4.56), 313 (4.08), 420 (4.24), 500 (inf.). $\lambda_{max}^{0.1N\text{-}NaOH}$ mμ (log ε): 224 (4.56), 304 (4.25), 442 (4.27).

Found: C, 43.65; H, 2.35; N, 10.70; Na, 5.54. Calcd. for $C_{14}H_8O_9N_3Na$: C, 43.65; H, 2.09; N, 10.91; Na, 5.97%.

Acidification of an aqueous solution of 50 mg. of VIII with 2 N hydrochloric acid gave 30 mg. of yellow crystals, m. p. 220°C (decomp.). Recrystallization from dioxane containing a small amount of water gave yellow needles, m. p. 228°C (decomp.), which were shown to be identical, by a mixed melting point and the infrared spectra, with VI.

b) A mixture of 200 mg. of VI and 6 ml. of saturated sodium bicarbonate solution was heated for 10 min. on a water bath, and the reaction mixture was acidified with 2 N hydrochloric acid and extracted with ether. The solvent was evaporated from the extract, and 150 mg. of a brown residue thereby obtained was recrystallized from benzene to give 1:1-complex IX of 2, 4, 6-trinitrobenzoic acid and tropone (I) as colorless microneedles, m. p. 132°C (decomp.). The mixed melting point with an authentic sample which was obtained by mixing these two components was not depressed and the infrared spectra were identical. λ_{max}^{MeOH} mμ (log ε): 225 (4.63), 301 (4.10).

Found: C, 46.31; H, 2.43; N, 12.17. Calcd. for $C_{14}H_9O_9N_3$: C, 46.29; H, 2.50; N, 11.57%.

c) A mixture of 200 mg. of VI and 4 ml. of aqueous sodium hydroxide solution was allowed to stand at room temperature for 30 min. The reaction mixture was acidified with 2 N hydrochloric acid, extracted with benzene and the solvent was removed from the extract to give 150 mg. of colorless crystals, m. p. 130°C (decomp.). Recrystallization from a mixture of acetone and benzene gave colorless microneedles, m. p. 132°C (decomp.), identical with IX obtained above.

Reaction of VI and Hydrochloric or Hydrobromic Acid.—a) A mixture of 90 mg. of VI and 2 ml. of concentrated hydrochloric acid was heated at 60~70°C for 30 min., cooled and 40 mg. of colorless crystals, m. p. 195°C (decomp.), that obtained was recrystallized from water to give colorless microneedles (X), m. p. 198°C (decomp.). The mixed melting point with an authentic sample of 2, 4, 6-trinitrobenzoic acid was not depressed and the infrared spectra were identical.

b) Heating of VI and 47% hydrobromic acid at the refluxing temperature for 2 hr. also gave X.

Reaction of VI and Aqueous Acetic Acid.—A mixture of 150 mg. of VI and 2 ml. of 50% aqueous acetic acid was refluxed for 5 hr., cooled and 70 mg. of colorless crystals, m. p. 120°C that obtained was recrystallized from the same solvent to afford colorless microneedles (XI), m. p. 120~121°C. These crystals showed no depression of the melting point on admixture with 1, 3, 5-trinitrobenzene and the infrared spectra were identical.

Reaction of VI and Methanol or Ethanol.—a) A mixture of 50 mg. of VI and 2 ml. of methanol was refluxed for 1 hr., the solution was concentrated and the crystals thereby obtained were collected by filtration to give colorless scales (XII), m. p. 157°C. These crystals showed no depression of the melting point on admixture with methyl 2, 4, 6-trinitrobenzoate and the infrared spectra were also identical.

b) Similar treatment of 30 mg. of VI and 2 ml. of ethanol as in the reaction of VI and methanol gave 15 mg. of colorless scales (XIII), m. p. 154°C, which showed no depression of the melting point on admixture with ethyl 2, 4, 6-trinitrobenzoate and the infrared spectra were identical.

Separation of Tropone (I) from the Complex VI.—A solution of 300 mg. of VI in ethanol was passed through an alumina column and the solvent was evaporated from the elute. The residue was dissolved in a mixture of ether and benzene and the solution was washed with 6 N hydrochloric acid. The aqueous layer was neutralized with sodium bicarbonate, extracted with chloroform and the solvent was removed from the extract to give 45 mg. of pale yellow oil (λ_{max}^{MeOH}: 225, 302 mμ) which afforded a picrate as yellow needles, m. p. 99~100°C. These crystals showed no depression of the melting point on admixture with an authentic sample of tropone picrate.

The solvent was removed from the original benzene-ether solution and the pale yellow crystals that were obtained were recrystallized from ethanol to afford 120 mg. of colorless scales, m. p. 154°C, undepressed on admixture with the authentic sample of XIII.

Reaction of VI and Aqueous Ammonia.—To the suspension of 100 mg. of VI in 1 ml. of ethanol was added 0.2 ml. of 28% aqueous ammonia and the precipitate thereby formed was collected by

filtration and washed with ethanol to give 70 mg. of red crystals which did not show a clear melting point.

The solution of 70 mg. of these red crystals in 1 ml. of water was acidified with concentrated hydrochloric acid and 50 mg. of yellow needles, m. p. 228°C (decomp.), that were obtained was recrystallized from a mixture of acetone and benzene to give 20 mg. of yellow needles (XIV), m. p. 235°C (decomp.). These crystals showed red coloration with ferric chloride in ethanol. λ_{max}^{MeOH} mμ (log ε) : 245 (4.18), 420 (4.40).

Found : C, 30.46 ; H, 2.25 ; N, 20.06. Calcd. for $C_7H_6O_8N_4$: C, 30.67 ; H, 2.21 ; N, 20.44%.

Reaction of VI and Methylamine Hydrochloride.—A mixture of 40 mg. of methylamine hydrochloride, 200 mg. of VI, 2 ml. of ethanol and 1 ml. of water was refluxed for 30 min., the solution was concentrated and 140 mg. of yellow crystals, m. p. 191°C (decomp.), was obtained. Recrystallization from a mixture of ethanol and benzene gave yellow needles (XV), m. p. 205°C (decomp.). λ_{max}^{MeOM} mμ (log ε) : 243 (4.25), 420 (4.40).

Found : C, 32.64 ; H, 2.75 ; N, 18.66. Calcd. for $C_8H_8O_8N_4$: C, 33.34 ; H, 2.80 ; N, 19.44%.

Reaction of VI and Pyridine.—A mixture of 50 mg. of VI and 0.2 ml. of pyridine was heated for several minutes on a boiling water bath and benzene was added to the mixture to precipitate orange crystals, m. p. 197~198°C (decomp.). Yield 40 mg. Recrystallization from a mixture of ethanol and pyridine gave yellowish orange needles (XVI), m. p. 201°C (decomp.). λ_{max}^{MeOH} mμ (log ε) : 245 (4.16), 422 (4.36).

Found : C, 43.23 ; H, 2.36 ; N, 16.62. Calcd. for $C_{12}H_8O_8N_4$: C, 42.86 ; H, 2.40 ; N, 16.67%.

Reaction of VI and *p*-Toluidine.—A mixture of 200 mg. of VI, 60 mg. of *p*-toluidine and 3 ml. of ethanol was refluxed for 30 min., the solvent was removed and a reddish brown oily residue that was obtained was extracted with hot benzene. The benzene extract gave 120 mg. of yellow crystals, m. p. 119~120°C, which was recrystallized from benzene to give yellow needles (XVII), m. p. 123°C. λ_{max}^{MeOH} mμ (log ε) : 232 (4.62), 300 (4.63), 420 (4.40).

Found : C, 53.97 ; H, 3.97 ; N, 11.18. Calcd. for $C_{21}H_{18}O_9N_4$: C, 53.62 ; H, 3.86 ; N, 11.91%.

Separation of 3, 5, 7-Trinitrotropolone (V) from Amine Salts of V.—a) Trituration of 1.3 g. of pyridinium salt XVI with 20 ml. of concentrated hydrochloric acid at room temperature gave a clear solution from which yellow crystals were reprecipitated. After the mixture was allowed to stand for one hour the crystals were collected by filtration to obtain 0.82 g. of yellow microneedles (V), m. p. 178°C (decomp.). Recrystallization was carried out from benzene but with some difficulty. These crystals showed red coloration in ethanol or dioxane with ferric chloride, but not colored in water, benzene or chloroform. λ_{max}^{MeOH} mμ (log. ε) : 245 (4.20), 420 (4.40).

Found : C, 32.66 ; H, 1.29 ; N, 15.63. Calcd. for $C_7H_3O_8N_3$: C, 32.70 ; H, 1.18 ; N, 16.34%.

Na Salt.—Yellow microprisms, m. p. 133°C (decomp.).

Cu Complex.—Yellowish green crystals, m. p. over 300°C.

The original filtrate was extracted with ether and the solvent was removed from the extract to give 110 mg. of yellow crystals, m. p. 203~206°C (decomp.). Addition of a solution of 50 mg. of tropone in ether to these crystals, extraction with hot benzene followed by the removal of the solvent gave 80 mg. of IX, m. p. 132°C, and 20 mg. of VI, m. p. 221°C (decomp.).

b) Similar treatment of 30 mg. of ammonium salt XIV with 0.3 ml. of concentrated hydrochloric acid as in the case of a) gave 10 mg. of yellow needles (V), m. p. 178°C (decomp.).

c) Similar treatment of 150 mg. of salt (XV) with 1 ml. of concentrated hydrochloric acid gave 95 mg. of yellow needles (V), m. p. 178°C (decomp.).

Reaction of V and I.—To a solution of 50 mg. of V dissolved in 5 ml. of ether was added 30 mg. of I, and the yellow crystals thereby precipitated were collected by filtration and washed with benzene to give 68 mg. of yellow needles, m. p. 227°C (decomp.). The mixed melting point with authentic sample of VI was not depressed and the infrared spectra were identical.

Reaction of V and Diazomethane.—To a solution of 100 mg. of V in 15 ml. of ether was added an equivalent amount of ethereal diazomethane. No evolution of nitrogen gas occurred though transient red coloration was observed on mixing both solutions. Yellow crystals which precipitated were collected by filtration to give 30 mg. of yellow needles which sintered at about 80°C and decomposed at 170°C, but the purification was not possible.

Reactions of V with Acids, Alkali and Alcohols.—*a) Hydrochloric Acid.*—A mixture of 50 mg. of V and 2 ml. of concentrated hydrochloric acid was refluxed for one hour to give 40 mg. of colorless needles (X), m. p. 204~205°C (decomp.).

b) Aqueous Acetic Acid.—Similar treatment of 50 mg. of V and 2 ml. of 50% aqueous acetic acid as in the reaction of VI and the same acid gave colorless needles (XI), m. p. 120~121°C.

c) *Sodium Hydroxide Solution.*—A mixture of 100 mg. of V and 1 ml. of 2 N sodium hydroxide solution was heated for 2 min. on a water bath and acidified with 2 N hydrochloric acid to obtain 90 mg. of orange crystals, m. p. 188°C (decomp.). Recrystallization from a mixture of benzene and ethanol gave colorless crystals (X), m. p. 194°C (decomp.).

d) Methanol.—Similar treatment of 50 mg. of V with 2 ml. of methanol as in the case of VI gave 25 mg. of colorless scales (XII), m. p. 157°C.

e) Ethanol.—Similar treatment of 30 mg. of V with 2 ml. of ethanol as in the case of VI afforded 25 mg. of colorless scales (XIII), m. p. 154°C.

Reaction of V and VI with *o*-Phenylenediamine.—a) A mixture of 200 mg. of VI, 60 mg. of *o*-phenylenediamine and 2 ml. of ethanol was refluxed for 10 min. and the precipitates thereby formed were collected by filtration and washed with ethanol to afford 140 mg. of a dark reddish violet amorphous solid (XIX), m. p. over 240°C. These

crystals were sparingly soluble in usual organic solvents, but soluble in aqueous sodium hydroxide solution. λ_{max}^{MeOH} mμ (log ε) : 236 (4.54), 321 (3.92), 480 (4.35).

Found : C, 47.73 ; H, 2.35. Calcd. for $C_{13}H_7O_6N_5$: C, 47.42 ; H, 2.14%.

b) Similar treatment of 100 mg. of V as in the case of a) gave 100 mg. of XIX, m. p. over 240°C.

Reaction of V and VI with Guanidine Sulfate.—a) To a mixture of 65 mg. of guanidine sulfate and 50 mg. of sodium methoxide in 2 ml. of methanol was added 200 mg. of VI. The mixture was refluxed for one hour, diluted with 10 ml. of water and 150 mg. of yellow crystals, m. p. 253°C (decomp.), that was obtained, was recrystallized from methanol to give 120 mg. of yellowish brown needles (XX), m. p. 258°C (decomp.). λ_{max}^{MeOH} mμ (log ε) : 245 (4.18), 423 (4.43).

Found : C, 30.73 ; H, 2.41 ; N, 26.51. Calcd. for $C_8H_8O_8N_6$: C, 30.39 ; H, 2.55 ; N, 26.58%.

b) Similar treatment of 100 mg. of V as in the case of a) afforded 110 mg. of XX, m. p. 258°C (decomp.).

Reaction of V and Aniline.—A mixture of 100 mg. of V and 0.5 ml. of aniline was heated for one hour on a water bath and the crystals that precipitated were collected by filtration to afford 55 mg. of pale yellow scales, m. p. 244°C. Recrystallization from acetone gave colorless scales, m. p. 245.5°C. λ_{max}^{MeOH} 275 mμ.

Found : C, 70.29 ; H, 4.69 ; N, 11.31%.

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Department of Chemistry
Faculty of Science
Tohoku University
Katahira-cho, Sendai