2-Benzylaminotroponethione (XVI, X=H, R=$CH_2C_6H_5$) : m.p. 138°; *Anal.* Calcd. for $C_{14}H_{13}NS$: C, 73.96; H, 5.76; N, 6.16. Found : C, 73.61; H, 5.70; N, 6.11.

2-*p*-Toluidinotroponethione (XVI, X=H, R=*p*-$CH_3C_6H_4$) : m.p. 100°; *Anal.* Calcd. for $C_{14}H_{13}NS$: C, 73.96; H, 5.76; N, 6.16. Found : C, 73.69; H, 5.70; N, 6.18.

2-Ethylthiotroponeimine (XVII, R=X=H)——To an EtOH solution (50 ml.) of I prepared from 5.0 g. of 2-aminotropone, was added 10 g. of ethyl mercaptan. The pH of the mixture was adjusted to 10, and then the mixture was allowed to stand overnight. Ethanol and excess ethylmercaptan were removed under reduced pressure, and the residue was extracted with benzene, washed with water, dried over Na_2SO_4. Removal of benzene gave 1.1 g. of yellow oil. The picrate prepared by the usual method melted at 174°. *Anal.* Calcd. for $C_{15}H_{14}O_7N_4S$: C, 45.68; H, 3.58; N, 14.21; S, 8.13. Found : C, 45.34; H, 3.86; N, 14.21; S, 8.39.

The authors are indebted to Prof. T. Nozoe and Prof. Y. Kitahara of Tohoku University, Prof. S. Ueo of Kyoto University, and Mr. M. Matsui, Director of this Laboratory for guidance and encouragement. The authors are also indebted to the members of the Analytical and Physico-chemical Measurement Sections of this Laboratory for elemental analyses and absorption spectra, respectively.

Summary

Reactions of 2-methoxytroponeimines were examined. Reactions with amines afforded 2-aminotroponeimine derivatives, including N-nonsubstituted and N-substituted derivatives. The reactions of the former products with ethyl chloroformate gave 1-substituted cycloheptimidazol-2(1*H*)-ones (Ⅷ), whereas similar reaction on a latter gave 2-oxocycloheptimidazolium derivative (Ⅸ). Reactions of benzamidine, cyanamide, guanidine and their derivatives with 2-methoxytroponeimines afforded cycloheptimidazole derivatives (Ⅹ～ⅩⅢ). Reactions of 2-methoxytroponeimines with hydrogen sulfide afforded 2-aminotroponethiones (XVI) and the reaction with ethyl mercaptane afforded 2-ethylthiotroponeimine (XVII).

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108. Hideo Nakao, Nobuo Soma, and Genshun Sunagawa :

Studies on Seven-membered Ring Compounds. XX.[*1] Reactions of Troponeimine Derivatives. (2).

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In the previous paper of this series, Soma, *et al.*[*1] reported that the reaction of 2-methoxytroponeimine (I) with amines afforded 2-aminotroponeimine derivatives. The present paper deals with the reactions of I with active methylene compounds.

It has been previously reported1～4) that 2-chlorotropone or 2-methoxytropone reacts with active methylene compounds in the presence of sodium ethoxide to yield azulene, 1-azaazulene or 1-oxaazulene derivatives. According to these reactions, the reactions of I with active methylene compounds were carried out.

[*1] Part XIX : This Bulletin, 13, 819 (1965).

[*2] 1-2-58 Hiromachi, Shinagawa-ku, Tokyo (中尾英雄, 相馬信夫, 砂川玄俊).

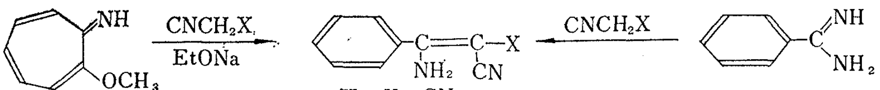
1) T. Nozoe, S. Seto, S. Matsumura, T. Asao : Proc. Japan Acad., 32, 339 (1956).

2) T. Nozoe, S. Seto, S. Nozoe : *Ibid.*, 32, 472 (1956).

3) S. Seto : Sci. Rept. Tohoku Univ., 37, 367 (1953).

4) S. Seto, S. Nozoe : Proc. Japan Acad., 32, 765 (1956).

The reaction of I with malononitrile in the presence of sodium ethoxide afforded a rearrangement product, (α-aminobenzylidene)malononitrile (II). The structure of this product was proved by its identity with an authentic sample, prepared from benzamidine and malononitrile according to the Kenner's method.[5] Similarly, the reactions of I with ethyl cyanoacetate, and cyanoacetamide gave ethyl 2-cyano-3-amino-3-phenylacrylate (III) and 2-cyano-3-amino-3-phenylacryl amide (IV), respectively. From these results, it became evident that the reaction of I with active methylene compounds in the presence of sodium ethoxide usually affords rearrangement products, that is phenylacrylonitrile derivatives.



I

II : X=CN
III : X=COOC₂H₅
IV : X=CONH₂

Chart 1.

These rearrangement products were thought to be probably produced through one of the following two paths : 1) I initially rearranges to benzimidoether with sodium ethoxide, and then condenses with active methylene compounds, 2) I reacts with active methylene compounds, thereafter the reaction product rearranges to benzene derivatives. In order to clarify the reaction path, the reaction of the benzimidoether with malononitrile in the presence of sodium ethoxide was attempted, and it was found that benzimidoether did not react with malononitrile under such condition. Consequently, the first reaction path was excluded and the latter was suggested to be the effective one. As regard the rearrangement reactions of tropone derivatives by the action of active methylene compounds, only few reports have appeared in the literature,[6,7] and it is still unknown that tropone derivatives except those having halogen atoms can undergo rearrangement with active methylene compound. However, the reaction mechanism is considered to be as follows :

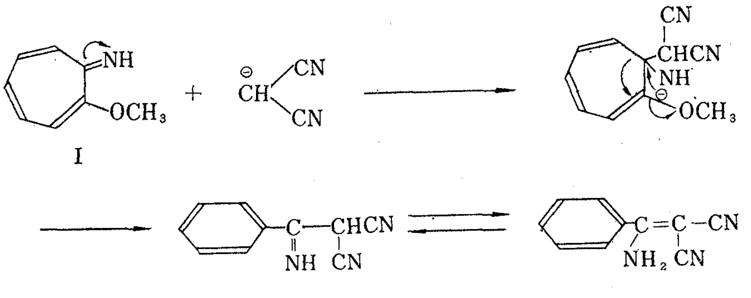


Chart 2.

The carbanion of active methylene compound attacks I at position 1, and this is followed by ring contraction and liberation of methanol.

Furthermore, taking consideration that since I has strong basicity, the reaction of I with active methylene compounds probably proceed even in the absence of base such as sodium ethoxide, several reactions were attempted. The reaction of I with malononitrile afforded 2-methoxy-8,8-heptafulvenedicarbonitrile[8] (V) besides a main

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[5] G. W. Kenner, B. Lythgoe, A. R. Todd, A. Topham : J. Chem. Soc., **1943**, 388.

[6] S. Matsumura : Bull. Chem. Soc. Japan, 35, 672 (1962).

[7] N. Soma : Yakugaku Zasshi, 82, 892 (1962).

[8] Y. Kitahara, K. Doi : Presented at the General Meeting of Tohoku District of the Chemical Society of Japan, Akita, October, 1959.

product, m.p. 238° as yellow needles, but no rearrangement product was obtained. The ultraviolet spectrum of this yellow compound was similar to that of 3-cyanocyclohepta-[*b*]pyrrol-2-(1*H*)-one (VI).[2] Heating this compound with sulfuric acid afforded cyclohepta[*b*]pyrrol-2(1*H*)-one.[9] From these facts, this compound is considered to be 2-imino-3-cyano-1,2-dihydrocyclohepta[*b*]pyrrole (VII). Further, the reaction of I with ethyl cyanoacetate afforded two kinds of crystals, $C_{12}H_{12}O_2N_2$, m.p. 150° and $C_{13}H_{13}O_3N$. m.p. 78° besides VI. The former is considered to be ethyl 2-imino-1,2-dihydrocyclohepta[*b*]-pyrrole-3-carboxylate (VIII) because its ultraviolet spectrum is similar to that of VII. The latter was proved to be ethyl 2-methoxy-8-cyano-8-heptafulvenecarboxylate[8] (IX) by its identity with an authentic sample of IX, prepared from 2-methoxytropone and ethyl cyanoacetate. The reaction of I with cyanoacetamide afforded 2-imino-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxamide (X). Heating X with sulfuric acid gave a mixture of cyclohepta[*b*]pyrrol-2(1*H*)-one and a compound, $C_9H_8N_2$, which is assumed to be 2-imino-1,2-dihydrocyclohepta[*b*]pyrrole (XI) from its ultraviolet spectrum.

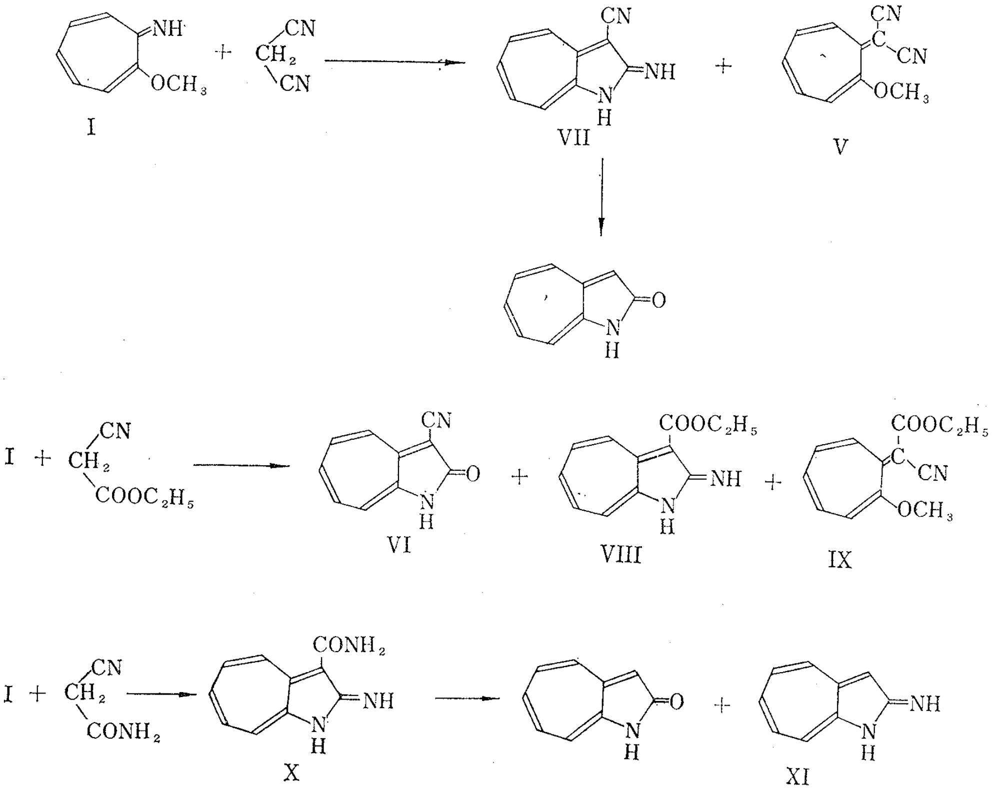

Chart 3.

Moreover, the reaction of I with diethyl malonate did not give the anticipated ethyl 2-oxo-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate, but gave instead yellow crystals (A), $C_{13}H_{13}O_4N$. Heating A with ethanolic potassium hydroxide afforded ethyl 2,8-dioxo-1,2,3,8-tetrahydrocyclohepta[*b*]pyrrole-3-carboxylate[10] (XII) and yellow crystals (B), $C_{11}H_{11}O_2N$, m.p. 184°. Heating B with hydrobromic acid gave 8-hydroxycyclohepta[*b*]pyrrol-2-(1*H*)-one[10] (XIII). The nuclear magnetic resonance spectrum of B showed the presence of an ethxy group and the protons of 1- and 3-position of cyclohepra[*b*]pyrrol-2-(1*H*)-one (Fig. 1). On the basis of these facts, B is considered to be 8-ethoxycyclohepta[*b*]-pyrrol-2(1*H*)-one (XIV). Consequently, A is apparently ethyl 2-oxo-8-methoxy-1,2-

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[9] T. Nozoe, S. Seto, S. Matsumura, T. Terasawa : Chem. & Ind. (London), **1954**, 1356.

[10] N. Soma, G. Sunagawa : Yakugaku Zasshi, 82, 418 (1962).

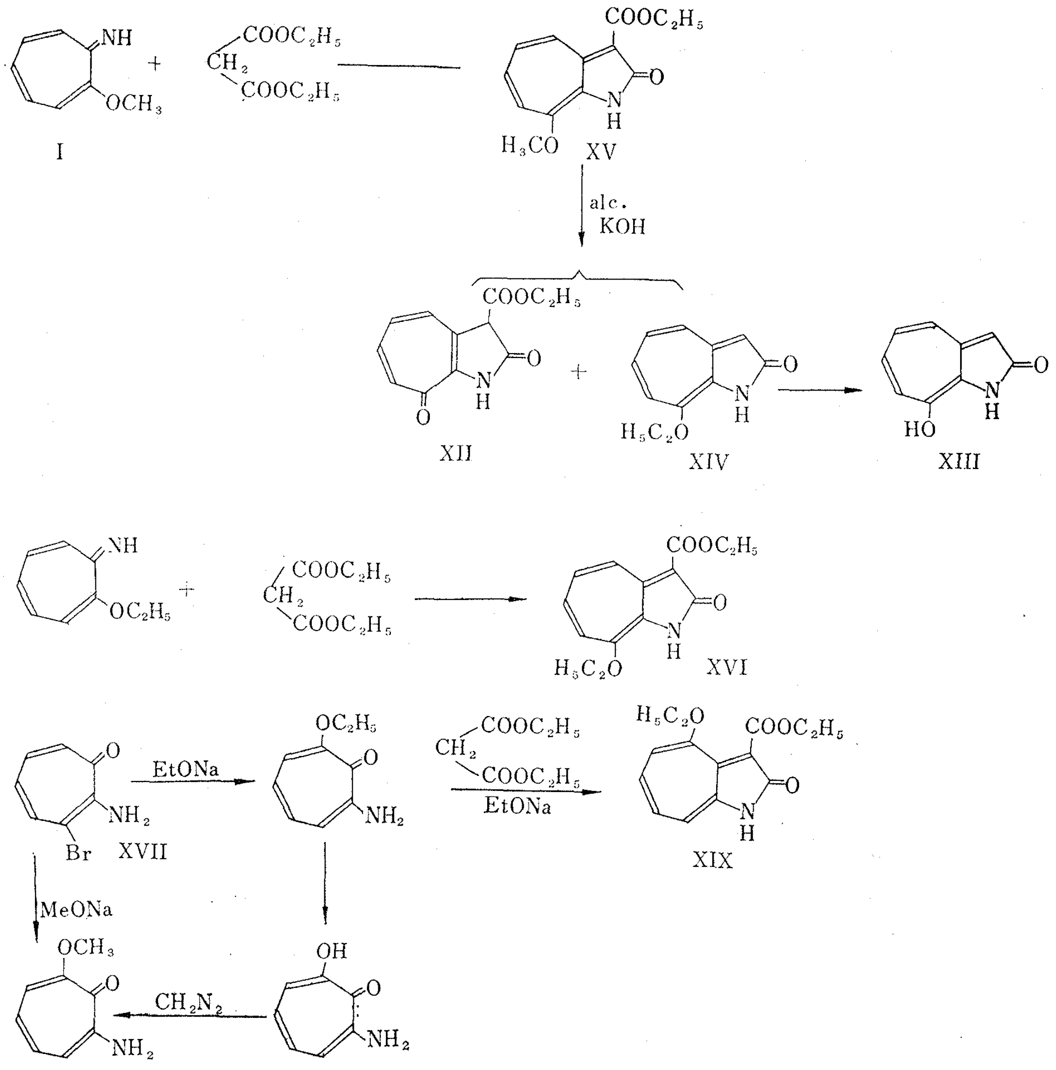

Chart 4.

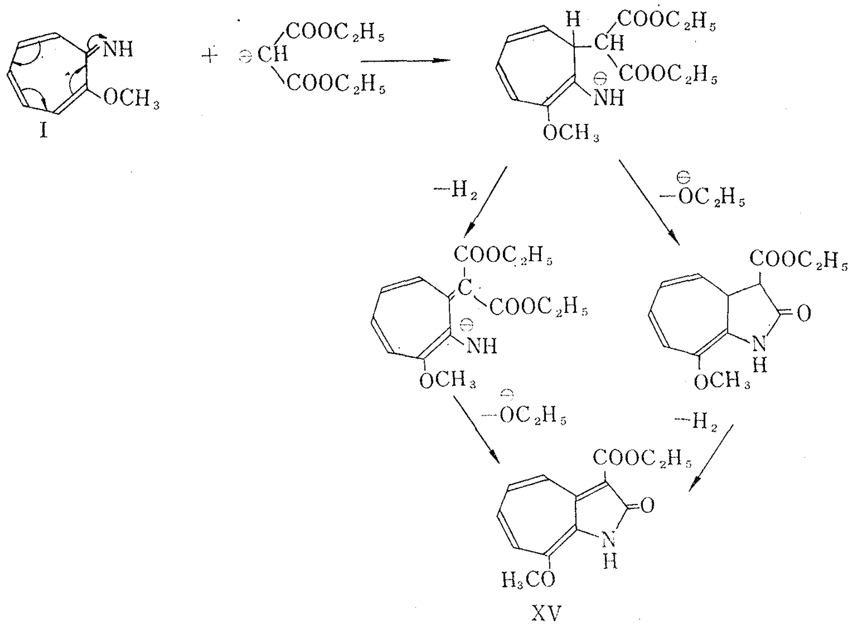

Chart 5.

dihydrocyclohepta[*b*]pyrrole-3-carboxylate (XV). Similarly, the reaction of I with diethyl malonate in the presence of sodium ethoxide afforded also XV. Further, the reaction of 2-ethoxytroponeimine instead of I with diethyl malonate gave yellow crystals, which is considered to be ethyl 2-oxo-8-ethoxy-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate (XVI) from the results of its elementary analysis and ultraviolet spectrum. Previously, Soma[11] reported that XVI was obtained by the reaction of diethylmalonate with 2-amino-3-ethoxytropone (XVIII), prepared from 2-amino-3-bromotropone (XVII) and sodium ethoxide. However, the compound which was obtained from 2-ethoxytroponeimine was not identical with the sample prepared from XVII according to the Soma's method. In order to elucidate this fact, the structure of the compound which was considered to be XVIII was investigated, and it became clear that this compound is 2-amino-7-ethoxytropone because it gave 3-aminotropolone on acid hydrolysis. Such abnormal reaction which afforded 2-amino-7-ethoxytropone from XVII and sodium ethoxide was also observed in the case of reaction of XVII and sodium methoxide. On the basis of these results, the compound derived from XVII is not XVI, but apparently ethyl 2-oxo-4-ethoxy-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate (XIX).

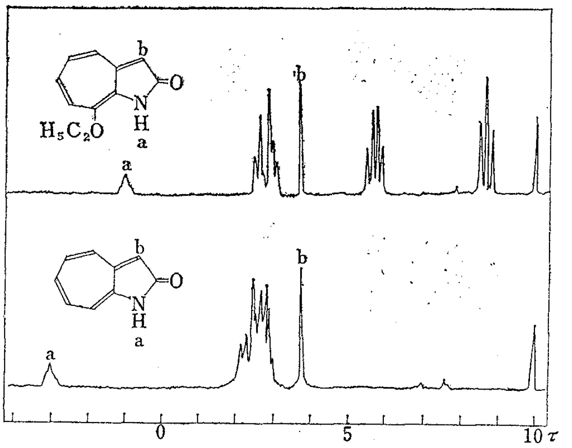

Fig. 1. Nuclear Maganetic Resonance Spectra at 60 Mc. in Deuterochloroform

Based on the assumption that diethylmalonate could not attack the 2-position of I because diethyl malonate is bulky, the formation of XV can be explained by the mechanism shown in chart 5.

Furthermore, the previous observation that I undergoes abnormal reaction has led the present authors to confirm that the 2-position of I was attacked during the reaction with malononitrile by the following experiments. The reaction of malononitrile

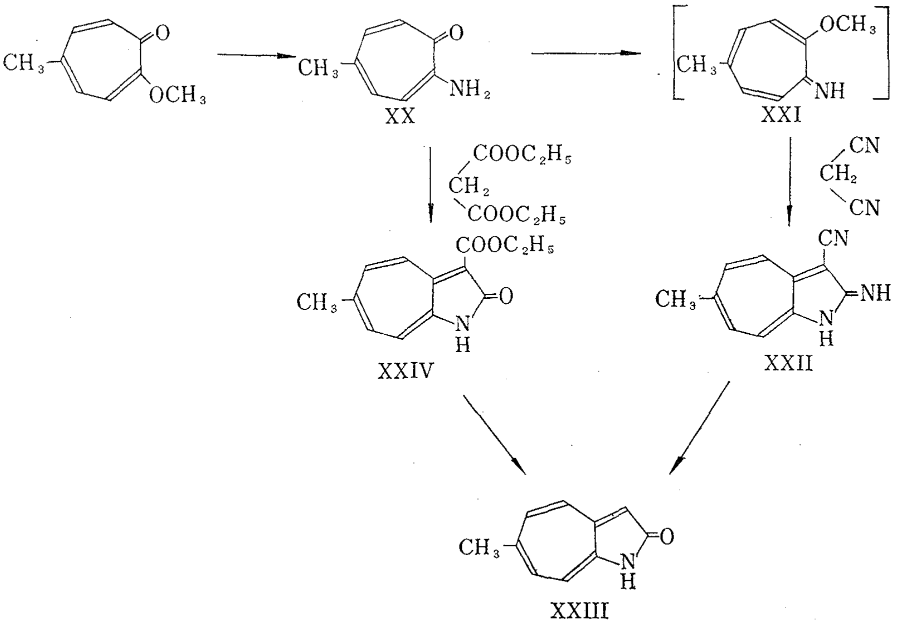

Chart 6.

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[11] N. Soma: His Doctor Report.

with 2-methoxy-5-methyltroponeimine (XXI), prepared from 2-amino-5-methyltropone (XX) and dimethyl sulfate afforded methyl derivative (XXII) of VI. Treatment of XXII with sulfuric acid gave the corresponding methyl derivative (XXIII) of cyclohepta[*b*]-pyrrol-2(1*H*)-one. XXIII was identical with 6-methylcyclohepta[*b*]pyrrol-2(1*H*)-one which was obtained by hydrolysis followed by decarboxylation of ethyl 2-oxo-6-methyl-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate (XXIV), prepared from XX and diethyl malonate. Therefore, it became evident that the methyl group of XXII is located at the 6-position and malononitrile attacks XXI at position 2.

Next, reactions of N-methyl-2-methoxytroponeimine (XXV) instead of I with active methylene compounds were carried out. Reaction of XXV with malononitrile in the

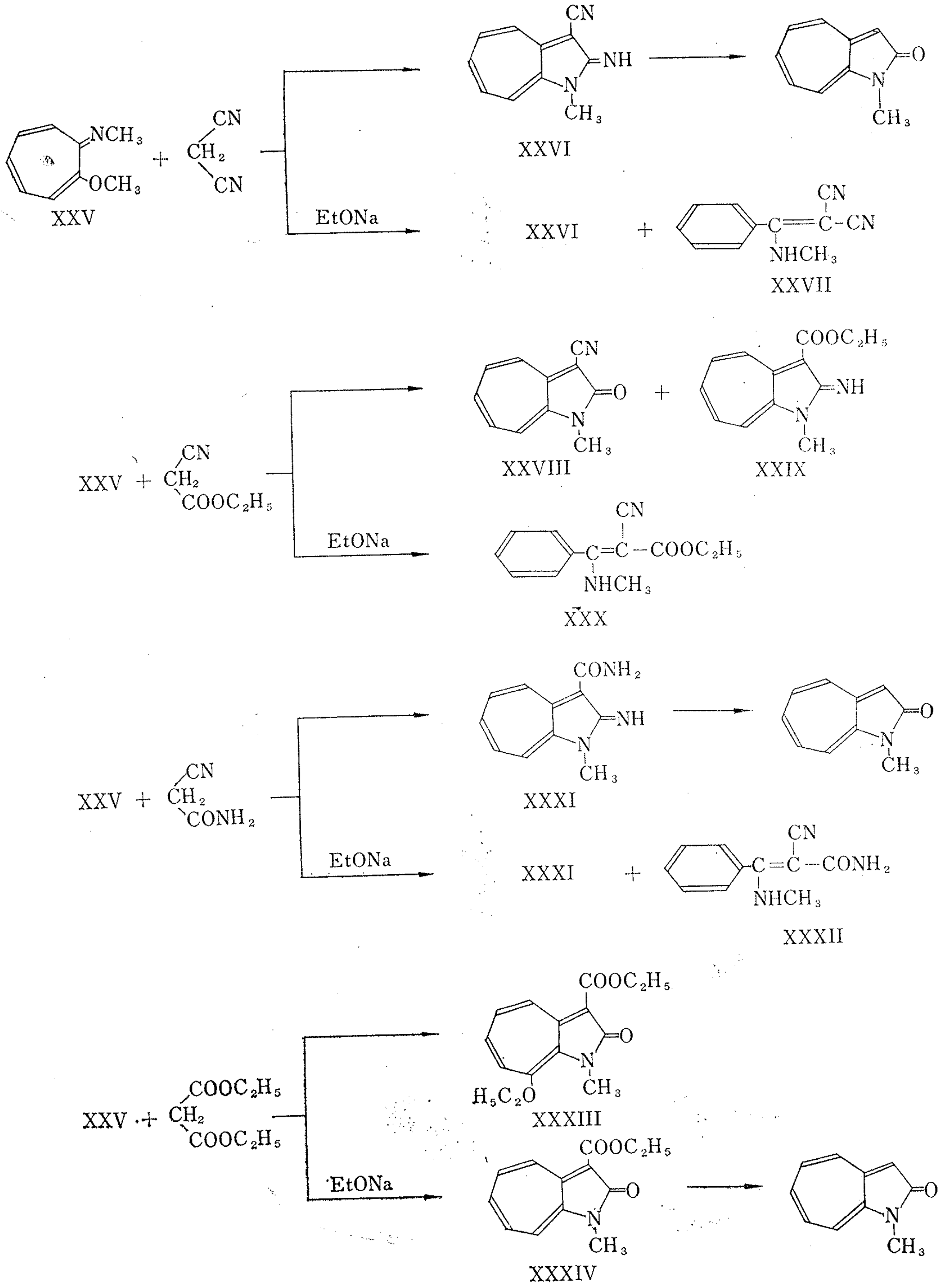

Chart 7.

absence of base afforded 1-methyl-2-imino-3-cyano-1,2-dihydrocyclohepta[*b*]pyrrole (XXVI), which was converted to 1-methylcyclohepta[*b*]pyrrol-2(1*H*)-one by treament with sulfuric acid. On the other hand, the same reaction in the presence of sodium ethoxide gave XXVI and a small amount of (α-methylaminobenzylidene)malononitrile (XXVII). Reaction of XXV with ethyl cyanoacetate afforded 1-methyl-3-cyanocyclohepta-[*b*]pyrrol-2(1*H*)-one (XXVIII) and ethyl 1-methyl-2-imino-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate (XXIX). The same reaction in the presence of sodium ethoxide gave only a small amount of ethyl 2-cyano-3-methylamino-3-phenylacrylate (XXX). Similaly, XXV and 2-cyanoacetamide afforded 1-methyl-2-imino-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxamide (XXXI), which was converted to 1-methylcyclohepta[*b*]pyrrol-2(1*H*)-one by treatment with sulfuric acid. The same reaction in the presence of sodium ethoxide gave XXXI and 2-cyano-3-methylamino-3-phenylacrylamide (XXXII). Furthermore, reaction of XXV with diethyl malonate gave yellow crystals, $C_{15}H_{17}O_4N$, which is assumed to be ethyl 1-methyl-2-oxo-8-ethoxy-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate (XXXIII) because its ultraviolet spectrum is similar to that of XV. The same reaction in the presence of sodium afforded ethyl 1-methyl-2-oxo-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate (XXXIV), which was converted to 1-methylcyclohepta[*b*]pyrrol-2(1*H*)-one by treatment with sulfuric acid.

From the above experimental results, XXV was found to exhibit some different reactivity from I. Namely, XXV did not afford 2-methoxyheptafulvene derivatives in the absence of sodium ethoxide, and XXV gave cyclohepta[*b*]pyrrol-2(1*H*)-one derivatives besides rearrangement products in the presence of sodium ethoxide. These facts can be explained by assuming that the 1-position of XXV is attacked by active methylene compound with more difficulty than in case of I due to attribution of sterric and electron donating effects of N-methyl group.

Experimental

Reaction of 2-Methoxytroponeimine*1 (I) with Malononitrile——a) To a solution of 1 g. of malononitrile and 350 mg. of Na in 30 ml. of EtOH was added a solution of I, prepared from 2 g. of 2-aminotropone, in 30 ml. of EtOH. The mixture was allowed to stand at room temperature for 4 days. After removal of EtOH under reduced pressure, 70 ml. of water was added, and separated crystals were collected and recrystallized from EtOH to give 0.5 g. of (α-aminobenzylidene)malononitrile as colorless prisms, m.p. 183°. *Anal.* Calcd. for $C_{10}H_7N_3$: C, 70.99; H, 4.17; N, 24.84. Found: C, 70.85; H, 4.29; N, 25.02. UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (log ε): 230 (3.98), 290 (4.20).

b) To a solution of 1.6 g, of malononitrile in 30 ml. of EtOH was added a solution of 3 g. of I in 25 ml. of EtOH. After standing for 1 hr., separated crystals were collected and poured into 20 ml. of 10% HCl. Insoluble crystals were collected, washed with water and recrystallized from EtOH to give 0.2 g. of 2-methoxy-8,8-heptafulvenedicarbonitrile, m.p. 206°.

On the other hand, HCl solution was neutralized with 10% NaOH, and separated crystals were recrystallized from EtOH to give 1.5 g. of 2-imino-1,2-dihydrocyclohepta[*b*]pyrrole-3-carbonitrile (VII) as yellow needles, m.p. 238°. *Anal.* Calcd. for $C_{12}H_7N_3$: C, 70.99; H, 4.17; N, 24.84. Found: C, 70.62; H, 4.18; N, 24.73.

(α-Aminobenzylidene)malononitrile——To a solution of 460 mg. of Na in 50 ml. of EtOH was added 3.5 g. of benzamidine hydrochloride. After stirring under reflux for 30 min., 1.3 g. of malononitrile was added, and the mixture was stirred under reflux for 8 hr. After cooling, the reaction mixture was filtered off to remove insoluble matter, and the filtrate was concentrated to small volume under reduced pressure. To the resulting residue was added 100 ml. of water. The separated crystals were recrystallized from water to give 0.5 g. of colorless prisms, m.p. 183°, which were identical with the sample of m.p. 183°, obtained by (a) method of reaction of I with malononitrile.

Hydrolysis of VII——A mixture of 300 mg. of VII and 4 ml. of 50% H_2SO_4 was heated under reflux for 2.5 hr. After cooling, 10 ml. of water was added, and the mixture was treated with charcoal, then neutralized with 10% NaOH, and extracted with $CHCl_3$. Concentration of the extract gave crude product, which was recrystallized from benzene to give 100 mg. of cyclohepta[*b*]pyrrol-2(1*H*)-one, m.p. 165°.

Reaction of I with Ethyl Cyanoacetate——a) By the same procedure as (a) method for the reaction of I with malononitrile, 2 g. of I, 1.7 g. of ethyl cyanoacetate and 350 mg. of Na gave 1 g. of ethyl 2-

cyano-3-amino-3-phenylacrylate (III) as colorless needles, m.p. 127°. *Anal.* Calcd. for $C_{12}H_{12}O_2N_2$: C, 66.65; H, 5.59; N, 12.96. Found : C, 66.56; H, 5.47; N, 12.86.

b) A mixture of 10 g. of I, 8.3 g. of ethyl cyanoacetate and 70 ml. of EtOH was allowed to stand overnight at room temperature. The reaction mixture was concentrated to small volume under reduced pressure, and to the residue were added 50 ml. of $CHCl_3$ and 30 ml. of 5% HCl. The mixture was shakened, and then filtered off to remove insolnble matter, which was identified as 3-cyanocyclohepta[*b*]pyrrol-2(1*H*)-one by comparison of its IR spectrum with that of an authentic sample.

The acid layer of the filtrate was made alkaline with 10% NaOH, and extracted with $CHCl_3$. The extract was concentrated, and the residue was chromatographed on alumina with benzene. The benzene eluate gave orange crystals, which were recrystallized from benzene to give 110 mg. of ethyl 2-imino-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate (VIII) as orange-yellow needles, m.p. 150°. *Anal.* Calcd. for $C_{12}H_{12}O_2N_2$: C, 66.65; H, 5.59; H, 12.96. Found : C, 66.55; H, 5.55; N, 12.85.

On the other hand, the organic layer of the filtrate was concentrated to dryness under reduced pressure, and the residue was purified by alumina chromatography with benzene. The benzene eluate gave crude product, which was recrystallized from cyclohexane to give 0.1 g. of ethyl 2-methoxy-8-cyano-8-heptafulvenecarboxylate (IX) as orange crystals, m.p. 78°. *Anal.* Calcd. for $C_{13}H_{13}O_3N$: C, 67.52; H, 5.67; N, 6.06. Found : C, 67.82; H, 5.62; N, 6.20.

Reaction of I with Cyanoacetamide——a) By the same procedure as (a) method for the reaction of I with malononitrile, 5 g. of I, 3.1 g. of cyanoacetamide and 850 mg. of Na gave 1.5 g. of 2-cyano-3-amino-3-phenylacrylamide (IV) as colorless needless, m.p. 194°. *Anal.* Calcd. for $C_{10}H_9ON_3$: C, 64.16; H, 4.85; N, 22.45. Found : C, 64.19; H, 4.86; N, 22.64.

b) To a solution of 3.1 g. of cyanoacetamide in 150 ml. of EtOH was added 5 g. of I. The mixture was allowed to stand at room temperatuure for 4 hr., and separated crystals were collected, washed with water and then dissolved in 10 ml. of 10% HCl. After treating with charcoal, the HCl solution was neutralized with 10% NaOH, and the separated crystals were recrystallized from EtOH to give 300 mg. of 2-imino-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxamide (X) as yellow crystals, m.p. 275° (decomp.). *Anal.* Calcd. for $C_{10}H_9ON_3$: C, 64.16; H, 4.85. Found : C, 63.77; H, 5.17.

Hydrolysis of X——A mixture of 300 mg. of X and 4 ml. of 50% H_2SO_4 was heated at 150° for 2.5 hr. After cooling, 10 ml. of water was added, and the mixture was treated with charcoal, then made alkaline with 10% NaOH. The separated crystals were collected by filtration, and purified by alumina chromatography. The $CHCl_3$ eluate gave crude product, which was recrystallized from benzene to give 50 mg. of 2-imino-1,2-dihydrocyclohepta[*b*]pyrrole (XI) as orange-yellow crystals, m.p. 176°. *Anal.* Calcd. for $C_9H_8N_2$: C, 74.97; H, 5.59; N, 19.43. Found : C, 74.82; H, 5.72; N, 19.65.

On the other hand, the alkaline filtrate was adjusted to pH 3 with 10% HCl, and extracted with $CHCl_3$. The extract was concentrated to small volume and chromatographed on alumina. The $CHCl_3$ eluate gave crude product, which was recrystallized from benzene to give 80 mg. of cyclohepta[*b*]pyrrol-2(1*H*)-one.

Reaction of I with Diethyl Malonate——To a solution of 12 g. of diethyl malonate and 1.7 g. of Na in 200 ml. of EtOH was added a solution of 10 g. of I in 30 ml. of EtOH. The mixture was allowed to stand at room temperature for 2 days, and separated crystals were collected and poured into 50 ml. of water. After. neutralizing with 10% HCl, the mixture was extracted with $CHCl_3$. The extract was concentrated, and the residue was chromatographed on alumina. The $CHCl_3$ eluate gave crude product, which was recrystallized from EtOH to give 1 g. of ethyl 2-oxo-8-methoxy-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate (XV) as yellow crystals, m.p. 241°. *Anal.* Calcd. for $C_{13}H_{13}O_4N$: C, 63.15; H, 5.30; N, 5.67. Found : C, 63.61; H, 5.34; N, 5.84. UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (log ε) : 237 (4.31), 280 (4.07), 314 (4.29), 408 (4.10).

Hydrolysis of XV——a) A mixture of 500 mg. of XV, 100 ml. of EtOH and 10 ml. of 10% KOH was heated under reflux for 7 hr. After cooling, separated crystals were collected by filtration and then poured into 30 ml. of hot water. The mixture was filtered off to remove insoluble matter, and the filtrate was neutralized with 10% HCl to separate crude product, which was recrystallized from EtOH to give 50 mg. of yellow crystals, m.p. 226°. This compound was identified as ethyl 2,8-dioxo-1,2,3,8-tetrahydrocyclohepta[*b*]pyrrole-3-carboxylate (XII).

On the other hand, the filtrate of reaction mixture was concentrated to small volume, and 20 ml. of water was added. After neutralizing with 10% HCl, the mixture was extracted with $CHCl_3$. The extract was concentrated, and the residue was purified by alumina chromatography. The $CHCl_3$ eluate gave crude product, which was recrystallized from benzene to give 100 mg. of 8-ethoxycyclohepta[*b*]pyrrol-2(1*H*)-one (XIV), m.p. 184°. *Anal.* Calcd. for $C_{11}H_{11}O_2N$: C, 69.82; H, 5.86; N, 7.40. Found : C, 69.62; H, 6.04; N, 7.46.

b) A mixture of 1 g. of XV and 5 ml. of 48% HBr was heated at 135° for 3 hr. The reaction mixture was diluted with 10 ml. of water and made alkaline with 20% NaOH. After treating with charcoal, the mixture was adjusted to pH 4 to separate yellow crystals, which were recrystallized from AcOH to give 500 mg. of yellow crystals, m.p. 278° (decomp.). This compound was identified as 8-hydroxycyclohepta[*b*]pyrrol-2(1*H*)-one.

Hydrolysis of XIV——By the same procedure as above mentioned (b) method, 100 mg. of XIV and 1 ml. of 48% HBr gave 40 mg. of 8-hydroxycyclohepta[*b*]pyrrol-2(1*H*)-one.

Ethyl 2-Oxo-8-ethoxy-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate (XVI)——A mixture of 23.6 g. of diethyl malonate, 2-ethoxytroponeimine, prepared from 20 g. of 2-aminotropone and 40 g. of diethyl sulfate, aud 240 ml. of EtOH was allowed to stand at room temperature for 2 days. After concentrating the reaction mixture under reduced pressure, separated crystals were collected and poured into 100 ml. of water. The mixture was extradted with $CHCl_3$. Concentration of the extract gave crude product, which was recrystallized from EtOH to give 1 g. of yellow crystals, m.p. 241°. *Anal.* Calcd. for $C_{14}H_{15}O_4N$: C, 64.36; H, 5.79; N, 5.36. Found : C, 64.15; H, 5.79; N, 5.44. Picrate, m.p. 178°.

2-Imino-6-methyl-1,2-dihydrocyclohepta[*b*]pyrrole-3-carbonitrile (XXII)——To a solution of 2-methoxy-5-methyltroponeimine, prepared from 1 g. of 2-amino-5-methyltropone (XX) and 3 ml. of dimethylsulfate, in 20 ml. of benzene was added a solution of 500 mg. of malononitrile in 15 ml. of benzene. The mixture was allowed to stand at room temperature for 3 hr. The separated crystals were collected, washed with benzene and then dissolved in 5% HCl. After treating with charcoal, the solution was neutralized with 10% NaOH to separate yellow crystals, which were recrystallized from EtOH to give 400 mg. of yellow needles, m.p. above 280°. *Anal.* Calcd. for $C_{11}H_9N_3$: C, 72.11; H, 4.95; N, 22.94. Found : C, 72.19; H, 5.03; N, 23.01.

Ethyl 2-Oxo-6-methyl-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate (XXIV)——To a solution of 280 mg. of Na in 15 ml. of EtOH were added 2 g. of diethyl malonate and 1 g. of 2-amino-5-methyltropone. The mixture was heated at 140° for 4 hr. in a sealed tube. After cooling, 40 ml. of water was added, and the mixture was acidified with 10% HCl. The separated crystals were collected, washed with water and recrystallized from MeOH to give 0.6 g. of yellow needles, m.p. 229°. *Anal.* Calcd. for $C_{13}H_{13}O_3N$: C, 67.52; H, 5.67; N, 6.06. Found : C. 67.50; H, 5.70; N, 6.24.

6-Methylcyclohepta[*b*]pyrrol-2(1*H*)-one (XXIII)——a) A mixture of 350 mg. of XXIV and 4 ml. of 50% H_2SO_4 was heated at 150° for 5 hr. After cooling, 5 ml. of water was added and the mixture was neutralized with 10% NaOH to separate crystals, which were recrystallized from EtOH to give 50 mg. of orange-yellow needles, m.p. 246°. *Anal.* Calcd. for $C_{10}H_9ON$: C, 75.45; H, 5.70; N, 8.80. Found : C, 75.45; H, 5.90; N, 9.11.

b) By the same procedure as above mentioned method, XXIII was obtained from 400 mg. of XXII and 50% H_2SO_4. Yield, 50 mg.

Reaction of N-Methyl-2-methoxytroponeimine (XXV) **with Malononitrile**——a) To a solution of 760 mg. of Na and 2.2 g. of malononitrile in 50 ml. of EtOH was added a solution of XXV, prepared from 5 g. of 2-methylaminotropone and 10 g. of dimethyl sulfate, in 20 ml. of EtOH. The mixture was allowed to stand overnight at room temperature. The reaction mixture was concentrated to about 20 ml. under reduced pressure, and 100 ml. of $CHCl_3$ was added. The mixture was extracted with 10% HCl. The acid layer was neutralized with 10% NaOH to separate crystals which were recrystallized from EtOH to give 1 g. of 1-methyl-2-imino-1,2-dihydrocyclohepta[*b*]pyrrole-3-carbonitrile (XXVI) as orange crystals, m.p. 185°. *Anal.* Calcd. for $C_{11}H_9N_3$: C, 72.11; H, 4.95; N, 22.94. Found : C, 72.26; H, 5.04; N, 22.65. UV λ_{max}^{EtOH} mμ (log ε) : 228 (4.16), 281 (4.45), 433 (4.17).

On the other hand, the $CHCl_3$ layer was purified by alumina chromatography. The eluate gave crude crystals which were recrystallized from benzene to afford 100 mg. of (α-methylaminobenzylidene)malononitrile (XXVII) as colorless prisms, m.p. 189°. *Anal.* Calcd. for $C_{11}H_9N_3$: C, 72.11; H, 4.95; N, 22.94. Found : C, 72.20; H, 4.93; N, 22.52. UV λ_{max}^{EtOH} mμ (log ε) : 229 (3.96), 290 (4.14).

b) To a solution of 2.2 g. of malononitrile in 50 ml. of EtOH was added an ethanolic solution of XXV, prepared from 5 g. of 2-methylaminotropone. The mixture was allowed to stand at room temperature for 5 hr., and separated crystals were collected, washed with water and poured into 50 ml. of 10% HCl. The mixture was fiiltered off and the filtrate was neutralized with 20% NaOH to separate crystals, which were recrystallized, from EtOH to give 1.8 g. of orange crystals, m.p. 185°. This compound was proved to be identical with XXVI by mixed fussion.

Reaction of XXV with Ethyl Cyanoacetate——a) By the same procedure as above mentioned (a) method, the reaction of XXV with ethyl cyanoacetate afforded colorless crystals, m.p. 116° from $CHCl_3$ soluble part. This compound was considered to be ethyl 2-cyano-3-methylamino-3-phenylacrylate. *Anal.* Calcd. for $C_{13}H_{14}O_2N_2$: C, 67.81; H, 6.13; N, 12.17. Found : C, 67.85; H, 5.90; N, 12.00. UV λ_{max}^{EtOH} mμ (log ε) : 230 (3.86), 293 (4.25).

b) A mixture of 3.7 g. of ethyl cyanoacetate, 5 g. of XXV and 50 ml. of EtOH was allowed to stand overnight at room temperature. After removal of EtOH under reduced pressure, 100 ml. of $CHCl_3$ was added, and the mixture was extracted with 10% HCl. The acid layer was neutralized with 10% NaOH, and extracted with $CHCl_3$. The extract was purified by alumina chromatography. The eluate gave a crude product, which was recrystallized from cyclohexane to give 100 mg. of ethyl 1-methyl-2-imino-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate as orange-red crystals, m.p. 105°. *Anal.* Calcd. for $C_{12}H_{14}O_2N_2$: C, 67.81; H, 6.13; N, 12.17. Found : C, 67.70; H, 6.16; N, 12.05. UV λ_{max}^{EtOH} mμ (log ε) : 240 (4.18), 283 (4.47), 425 (4.10). Picrate, m.p. 248° (decomp.).

On the other hand, the $CHCl_3$ layer was concentrated under reduced pressure, and the residue was purified by alumina chromatography. The resulting crude crystals were recrystallized from EtOH to give 110 mg. of yellow needles, m.p. 227°. This compound was proved to be identical with 1-methyl-3-cyanocyclohepta[*b*]pyrrol-2(1*H*)-one by mixed fussion.

Reaction of XXV with Cyanoacetamide——a) To a solution of 760 mg. of Na in 30 ml. of EtOH was added a solution of 2.8 g. of cyanoacetamide in 50 ml. of EtOH followed by an ethanolic solution of XXV, prepared from 5 g. of 2-methylaminotropone. The mixture was allowed to stand at room temperature for 2 days, and separated crystals were collected by filtration, washed with water and recrystallized from EtOH to give 1.7 g. of 1-methyl-2-imino-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxamide (XXXI), m.p. 200°. *Anal.* Calcd. for $C_{11}H_{11}ON_3$: C, 65.67; H, 5.51; N, 20.88. Found : C, 65.38; H, 5.57; N, 20.03. Picrate, m.p. 261° (decomp.).

On the other hand, the filtrate was concentrated to about 30 ml. under reduced pressure, and 100 ml. of $CHCl_3$ was added to the residue. The mixture was washed with 10% HCl, and concentrated to small volume. The residue was purified by alumina chromatography, and the resulting crude crystals were recrystallized from benzene to give 170 mg. of 2-cyano-3-methylamino-3-phenylacrylamide as colorless prisms, m.p. 224°. *Anal.* Calcd. for $C_{11}H_{11}ON_3$: C, 65.67; H, 5.51; N, 20.88. Found : C, 65.33; H, 5.45; N, 21.16. UV λ_{max}^{EtOH} mμ (log ε) : 220 (4.01), 291 (4.25).

b) To a solution of 2.8 g. of cyanoacetamide in 50 ml. of EtOH was added an ethanolic solution of 5 g. of XXV. The mixture was allowed to stand overnight at room temperature, and separated crystals were collected and recrystallized from EtOH to give 1 g. of orange crystals, m.p. 200°, which were proved to be identical with XXXI by mixed fussion.

Hydrolysis of XXVI——A mixture of 1 g. of XXVI and 12 ml. of 50% H_2SO_4 was heated at 150° for 7.5 hr. After cooling, 20 ml. of water was added, and the mixture was neutralized with 10% NaOH and extracted with $CHCl_3$. After concentrating the extract, the residte was purified by alumina chromatography. The resulting crude product was recrystallized from benzene to give 200 mg. of yellow crystals, m.p. 75°, which were identified as 1-methylcyclohepta[*b*]pyrrol-2(1*H*)-one.

Hydrolysis of XXXI——By the same procedure as described above, hydrolysis of XXXI afforded 1-methylcyclohepta[*b*]pyrrol-2(1*H*)-one.

Reaction of XXV with Diethyl Malonate——a) To a solution of 3.16 g. of Na in 200 ml. of EtOH was added 22 g. of diethyl malonate, followed by an ethanolic solution of XXV, prepared from 20 g. of 2-methylaminotropone. The mixture was allowed to stand overnight at room temperature. After removal of EtOH, 150 ml. of $CHCl_3$ was added, and the mixture was washed with 10% HCl, then concentrated *in vacuo*. The residue (5.2 g.) was purified by alumina chromatography and recrystallization from cyclohexane-benzene to give ethyl 1-methyl-2-oxo-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate as yellow prisms, m.p. 103°. *Anal.* Calcd. for $C_{13}H_{13}O_3N$: C, 67.52; H, 5.67; N, 6.06. Found : C, 67.44; H, 5.43; N, 6.04. UV λ_{max}^{EtOH} mμ (log ε) : 230 (4.22), 280 (4.56), 428 (4.27).

b) A mixture of 5 g. of XXV, 5.3 g. of diethyl malonate and 50 ml. of EtOH was allowed to stand for 2 weeks. After removal of EtOH under reduced pressure, 100 ml. of $CHCl_3$ was added, and the mixture was washed with 10% HCl, then concentrated to dryness under reduced pressure. The resulting residue (2.0 g.) was purified by alumina chromatography and recrystallization from benzene to give yellow crystals, m.p. 132°. This compound is considered to be ethyl 1-methyl-8-ethoxy-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate. *Anal.* Calcd. for $C_{15}H_{17}O_4N$: C, 65.44; H, 6.22; N, 5.09. Found : C, 65.31; H, 6.25; N, 4.97.

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Summary

The reaction of 2-methoxytroponeimine (I) and its N-methyl derivative (II) with active methylene compounds were carried out. The reaction of I with malononitrile, ethyl cyanoacetate or cyanoacetamide in the presence of sodium ethoxide afforded rearrangemet products, that is 3-phenylacrylic acid derivatives. The same reaction in the absence of sodium ethoxide gave mainly 2-imino-1,2-dihydrocyclohepta[*b*]pyrrole derivatives. However, the reaction of I with diethyl malonate afforded ethyl 2-oxo-8-methoxy-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxylate. II showed some different reactivity from I. Namely, the reaction of II with active methylene compounds in the presence of sodium ethoxide afforded 2-imino-1,2-dihydrocyclohepta[*b*]pyrrole derivatives besides rearrangement products.

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