carried out. Ⅲ reacted with malononitrile to afford heptafulvene derivative, whereas Ⅲ reacted with cyanoacetamid, diethyl malonate and ethyl *p*-nitrophenylacetate to yield rearrangement products, coumarin derivatives. Ⅲ didn't react with ethyl carbamoylacetate, 2-cyanoacetophenone and cyanoacetone, which easily reacted with 2-chlorotropone.

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59. Genshun Sunagawa and Hideo Nakao: Studies on Seven-membered Ring Compounds. XIV.*1 Reactions of 2-Methoxytropone and 2-Halotropone with Hydrazides.

(*Research Laboratories, Sankyo Co., Ltd.**2)

Nozoe, *et al.*[1] reported that the reaction of 2-methoxytropone (I) or 2-chlorotropone (Ⅱ) with 2-cyanoacetamide afforded 3-cyanocyclohepta[*b*]pyrrol-2(1*H*)-one (Ⅲ). In order to examine the generality of this reaction some hydrazides were presently tested with I, Ⅱ and their analogues.

First, reaction of hydrazides with 2-methoxytropone (I) was attempted. Reaction of cyanoacetohydrazide with I, in the presence of sodium ethoxide, afforded pale yellow crystals, m.p. 201°, whose analytical values agreed with formula $C_{10}H_9O_2N_3$. The ultraviolet absorption spectrum was similar to that of 2-hydrazinotropone (Ⅳ) (Fig. 1) and the infrared spectrum exhibited absorption bands at 3340, 3160 cm^{-1} for either an amino or two imino groups, at 2260 cm^{-1} for a cyano group and 1725 cm^{-1} for carbonyl group. Thus, this compound was assumed to be 2-(2-cyanoacetylhydrazino)tropone (Ⅴ), and this was proved by comparison with Ⅴ prepared from Ⅳ and cyanoacetylchloride. Interestingly cyanoacetohydrazide didn't react with I to yield a cyclized compound in spite

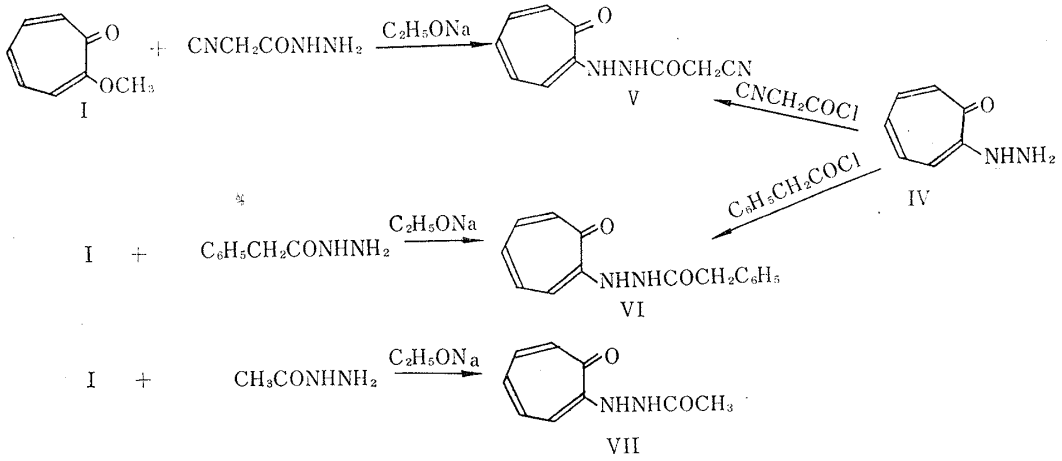

Chart 1.

*1 Part XIII. G. Sunagawa, H. Nakao: This Bulletin, **13**, 443 (1965).
*2 1-2-58 Hiromachi, Shinagawa-ku, Tokyo (砂川玄俊, 中尾英雄).
1) T. Nozoe, S. Seto, S. Nozoe: Proc. Japan Acad., **32**, 472 (1956).

of possessing an active methylene group. Nozoe, *et al.*[1] reported that in the reaction of I with cyanoacetamide, the carbanion and the amino group of cyanoacetamide attack at the 2- and 1-positions of I, respectively. However, in the reaction of I with cyanoacetohydrazide, the amino group of the hydrazide attacked the 2-position of I replacing the methoxy group.

Similarly phenylacetohydrazide or acetohydrazide and I afforded 2-(2-phenylacetylhydrazino)tropone (Ⅵ) and 2-(2-acetylhydrazino)tropone (Ⅶ), respectively. Consequently 2-methoxytropone (I) reacts with hydrazide to yield 2-(2-acylhydrazino)tropone, even when such a hydrazide possesses an active methylene group.

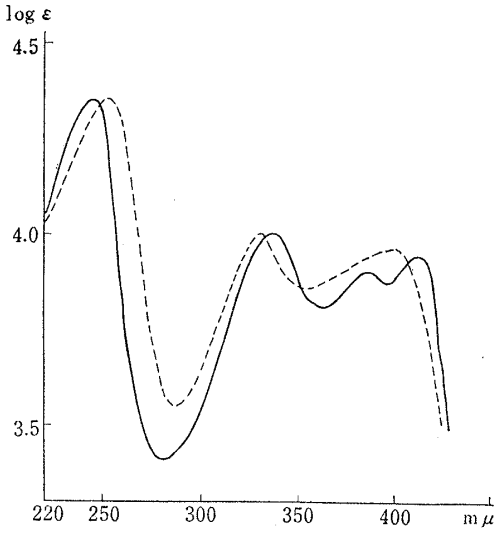

Fig. 1. Ultraviolet Absorption Spectra in Ethanol

——— Ⅳ ----- Ⅴ

Next, attempted was the reaction of hydrazides with 2-chlorotropone (Ⅱ), which has a similar reactivity to I. When Ⅱ was treated with acetohydrazide or phenylacetohydrazide, in the presence of sodium ethoxide, Ⅶ and Ⅵ were obtained, respectively. However, the reaction of Ⅱ with cyanoacetohydrazide afforded yellow crystals, m.p. 288° (decomp.), whose analytical values agreed with formula $C_{10}H_7ON_3$ were produced. The ultraviolet spectrum was similar to that of Ⅲ and infrared spectrum exhibited absorption bands at 3300, 3220 cm^{-1} for either an amino or two imino groups, at 2220 cm^{-1} for a cyano group and at 1670 cm^{-1} for carbonyl group. The spectral data implied that this compound was either 1-amino-3-cyanocyclohepta[*b*]pyrrol-2(1*H*)-one (Ⅷ) or 4-cyano-1,2-dihydro-3*H*-cyclohepta[*c*]pyridazin-3-one

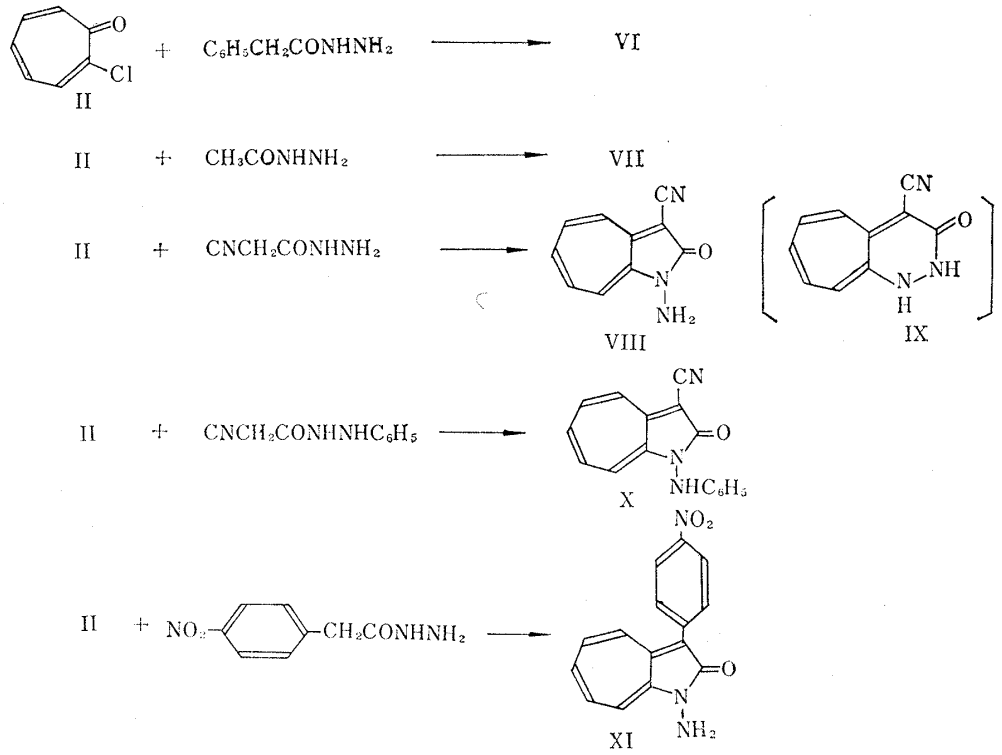

Chart 2.

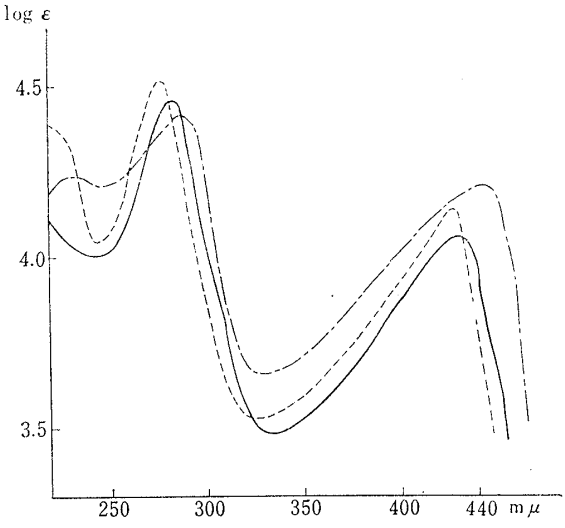

Fig. 2. Ultraviolet Absorption Spectra in Ethanol

——— Ⅷ ----- X —·—·— Ⅺ

(Ⅸ). Subsequently this compound was proved to be the former, since crystals of m.p. 160° obtained by hydrolysis followed by decarboxylation of this compound reacted with benzaldehyde to yield a condensation product. In addition this compound was identical with 1-amino-3-cyanocyclohepta[*b*]pyrrol-2(1*H*)-one (Ⅷ) synthesized by Kitahara, *et al.*[2] through another route. Consequently, the reaction of Ⅱ with cyanoacetohydrazide differed from that of I with cyanoacetohydrazide.

As all of hydrazides having an active methylene group might be expected to react with Ⅱ to yield 1-aminocyclohepta[*b*]pyrrol-2(1*H*)-one derivatives, the reaction of Ⅱ with other hydrazides having an active methylene group was investigated. Reaction of Ⅱ with cyanoacetophenylhydrazide afforded yellow crystals, m.p. 258° (decomp.), which were considered to be 1-anilino-3-cyanocyclohepta[*b*]pyrrol-2(1*H*)-one (X) since the analytical values agreed with formula of X, $C_{16}H_{11}ON_3$, furthermore the ultraviolet spectrum was similar to that of Ⅷ as shown in Fig. 2. Similarly the reaction of Ⅱ with *p*-nitrophenylacetohydrazide gave yellow crystals, m.p. 305° (decomp.) which was presumably 1-amino-3-(*p*-nitrophenyl)cyclohepta[*b*]pyrrol-2(1*H*)-one (Ⅺ) from the elemental analysis and ultraviolet spectrum. Cyanoacetohydrazide and 2-bromotropone (Ⅻ) also afforded Ⅷ in good yield. Thereafter, the reactions of 2-bromo-7-methoxytropone (XIII) with hydrazides were attempted. As reported in the previous paper*[1], 2-bromo-7-methoxytropone (XIII) usually reacts with active methylene compounds to yield rearranged products, benzene derivatives, not possessing a bromine atom. However, the reaction of XIII with cyanoacetohydrazide afforded a compound possessing a bromine atom. Ultraviolet spectrum of this compound was similar to that of 2-bromo-7-hydrazinotropone (XIV). These facts indicated this reaction product to be 2-bromo-7-(2-cyanoacetylhydrazino)tropone (XV), and it was identified as XV prepared from XIV and cyanoacetylchloride. Acetohydrazide and XIII furnished 2-bromo-7-(2-acetyl-hydrazino)tropone (XVI) by a similar reaction.

Nozoe, *et al.*[1] reported that in the reaction of 2-halotropone or 2-methoxytropone with cyanoacetamide, the former is usually attacked at the 7-position by the active methylene group of cyanoacetamide, whereas the latter is attacked at the 2-position. The former reaction is an abnormal substitution reaction. For example, the reaction of 2-chloro-4-methyltropone (XVII) with cyanoacetamide yielded 3-cyano-6-methylcyclohepta[*b*]pyrrol-2(1*H*)-one[3] (XVIII), whereas the reaction of 2-methoxy-4-methyltropone (XIX) with cyanoacetamide yielded 3-cyano-5-methylcyclohepta[*b*]pyrrol-2(1*H*)-one[1] (XX). In order to elucidate the reaction mechanism of 2-chlorotropone (Ⅱ) with cyanoacetohydrazide, the reaction of cyanoacetohydrazide with 2-chloro-5-methyltropone, in the presence of sodium ethoxide, was attempted. This afforded yellow crystals (A), m.p. 290°, which was considered the methyl derivative of Ⅷ from the elemental analysis and ultraviolet spectrum. The diazotization of this compound afforded 3-cyano-5-

2) Y. Kitahara, K. Doi : This work was presented at the 12th Annual Meeting of the Chemical Society of Japan, 1962.
3) S. Seto, S. Nozoe : Proc. Japan Acad., 32, 765 (1956).

methylcyclohepta[*b*]pyrrol-2(1*H*)-one, m.p. >300°. This structure was confirmed by comparison with a sample prepared from 2-chloro-5-methyltropone and cyanoacetamide by the abnormal substitution reaction. Consequently, compound A was confirmed to be 1-amino-3-cyano-5-methylcyclohepta[*b*]pyrrol-2(1*H*)-one(XXI). Therefore, in the reaction of 2-chlorotropone (II) with cyanoacetohydrazide, the carbanion of cyanoacetohydrazide initially attacked the 7-position of II, then the imino group attacked the 1-position of II with liberation of chloride and water.

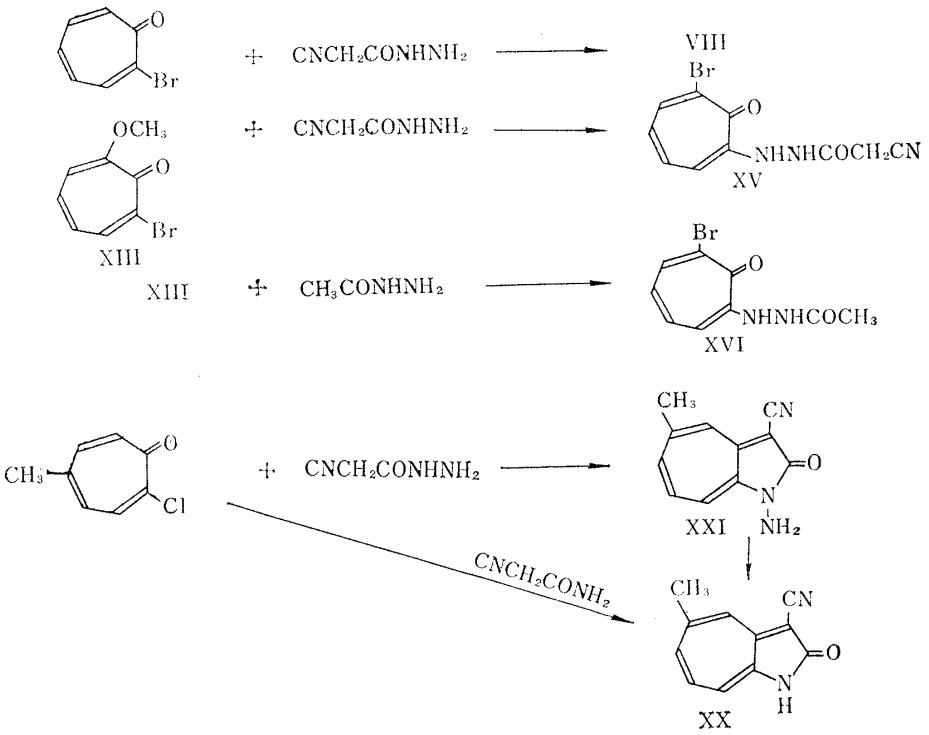

Chart 3.

Nosoe, *et al.*[4] reported that an electrophilic substitution such as bromination, nitration and nitrosation occurs at the 3-position in cyclohepta[*b*]pyrrol-2(1*H*)-one. In order to see whether or not 1-aminocyclohepta[*b*]pyrrol-2(1*H*)-one (XXII) also undergoes a similar reaction, XXII was prepared from VIII, and several reactions were attempted. Hydrolysis of VIII with acid afforded 1-amino-2-oxo-1,2-dihydro-cyclohepta[*b*]pyrrole-3-carboxamide (XXIII), whereas alkaline hydrolysis afforded 1-amino-2-oxo-1,2-dihydro-cyclohepta[*b*]pyrrole 3-carboxylic acid (XXIV). The latter was also obtained from XXIII by treatment with alkali. Heating XXIV with acid afforded XXII by decarboxylation melting at 160°. The ultraviolet spectrum of XXII was similar to that of cyclohepta[*b*]pyrrol-2(1*H*)-one as

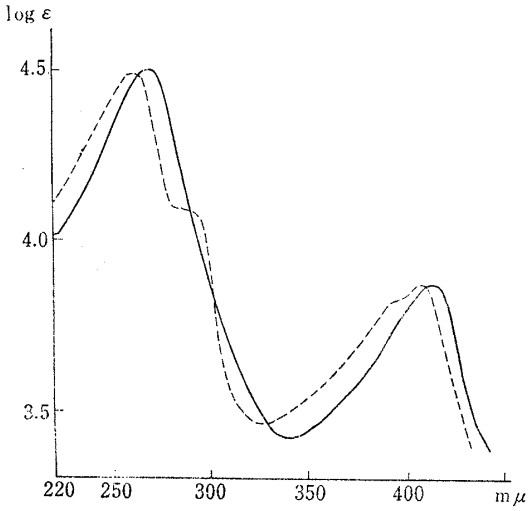

Fig. 3. Ultraviolet Absorption Spectra in Ethanol

——— 1-Aminocyclohepta[*b*]pyrrol-2(1*H*)-one
– – – – – Cyclohepta[*b*]pyrrol-2(1*H*)-one

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

shown in Fig. 3. Treatment of XXII with acetic anhydride yielded an acetyl derivative (XXV), m.p. 210°. Condensation of XXII with benzaldehde furnished 1-benzilideneamino-cyclohepta[*b*]pyrrol-2(1*H*)-one (XXVI), m.p. 134° as described above. Moreover, bromination of XXII in chloroform afforded a monobromocompound (XXVII), m.p. 203° (debomp.). Sulfonation of XXII with fuming sulfuric acid followed by neutralization gave a sodium salt (XXVIII), m.p. 267° (decomp.), of the corresponding sulfonic acid. Azo coupling of XXII with *p*-toluidine afforded corresponding *p*-tolylazo compound (XXIX). Thus, XXII undergoes electrophilic substitution reactions. Presumably the substituted position was the same 3-position as that of cyclohepta[*b*]pyrrol-2(1*H*)-one.

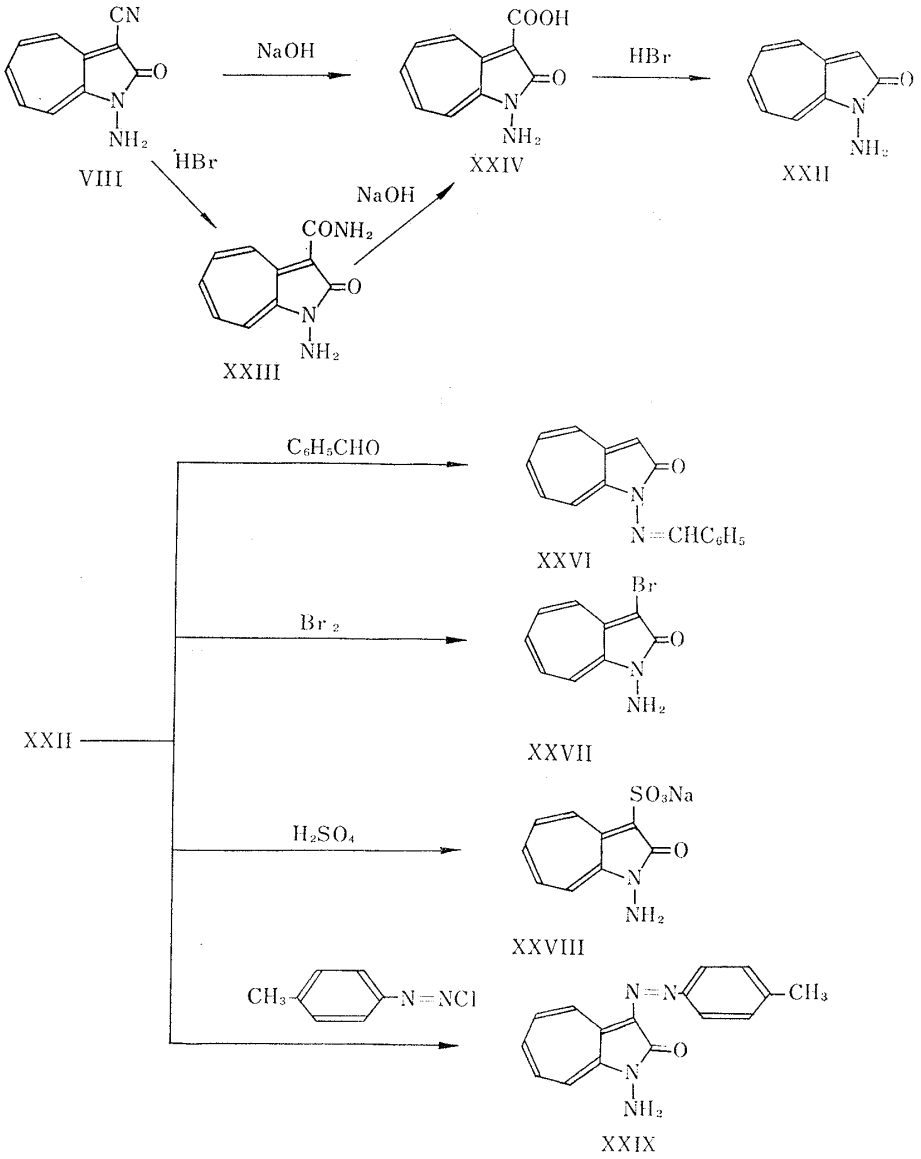

Chart 4.

Experimental

1-Amino-3-cyanocyclohepta[*b*]pyrrol-2(1*H*)-one (VIII)——To a solution of Na (320 mg.) and cyanoacetohydrazide (1.4 g.) in 120 ml. of EtOH was added a solution of 2-chlorotropone (1 g.) in 10 ml. of EtOH. The mixture was allowed to stand at room temperature for 2 hr. and separated crystals were collected, washed with H_2O and recrystallized from EtOH to give 0.7 g. of yellow needles, m.p. 288° (decomp.). *Anal.*

Calcd. for $C_{10}H_7ON_3$: C, 64.86; H, 3.81; N, 22.69. Found : C, 64.79; H, 4.04; N, 22.75. UV λ_{max}^{EtOH} mμ (log ε) : 282 (4.45), 425 (4.06). IR ν_{max}^{Nujol} cm^{-1} : 3300, 3220, 2220, 1670.

1-Anilino-3-cyanocyclohepta[*b*]pyrrol-2(1*H*)-one (X)——To a solution of Na (92 mg.) and cyanoacetophenylhydrazide (700 mg.) in 20 ml. of EtOH was added a solution of 2-chlorotropone (280 mg.) in 5 ml. of EtOH. The mixture was allowed to stand at room temperature for 2 hr., and separated crystals were collected, washed with H_2O and recrystallized from EtOH to give 300 mg. of yellow needles, m.p. 258° (decomp.). *Anal.* Calcd. for $C_{16}H_{11}ON_3$: C, 73.55; H, 4.24; N, 16.08. Found : C, 73.92; H, 4.19; N, 16.07. UV λ_{max}^{EtOH} mμ (log ε) : 230 (4.40), 275 (4.51), 423 (4.14). IR ν_{max}^{Nujol} cm^{-1} : 3300, 2220, 1670.

1-Amino-3-(*p*-nitrophenyl)cyclohepta[*b*]pyrrol-2(1*H*)-one (XI) ——To a solution of Na (29 mg.) and *p*-nitrophenylacetohydrazide (250 mg.) in 40 ml. of EtOH was added a solution of 2-chlorotropone (90 mg.) in 5 ml. of EtOH. The mixture was allowed to stand at room temperature for 3 hr., and separated crystals were collected, washed with H_2O and recrystallized from AcOH to give 100 mg. of orange-red crystals, m.p. 305° (decomp.). *Anal.* Calcd. for $C_{15}H_{11}O_3N_3$: C, 63.60; H, 3.91; N, 14.84. Found : C, 63.40; H, 4.15; N, 14.61. UV λ_{max}^{EtOH} mμ (log ε) : 235 (4.26), 287 (4.41), 440 (4.21). IR ν_{max}^{Nujol} cm^{-1} : 3400, 3230, 1650.

2-(2-Phenylacetylhydrazino)tropone (VI)——a) To a solution of Na (46 mg.) and phenylacetohydrazide (300 mg.) in 20 ml. of EtOH was added a solution of 2-chlorotropone (140 mg.) in 5 ml. of EtOH. The mixture was allowed to stand at room temperature for 3 days and concentrated under reduced pressure. The resulting residue was poured into 10 ml. of H_2O and neutralized with 10% hydrochloric acid. The precipitate was collected, washed with H_2O and recrystallized from MeOH to give 50 mg. of pale yellow crystals, m.p. 178°. *Anal.* Calcd. for $C_{15}H_{14}O_2N_2$: C, 70.85; H, 5.55; N, 11.02. Found : C, 71.02; H, 5.53; N, 11.12. UV λ_{max}^{EtOH} mμ (log ε) : 240 (4.31), 282 (3.74), 333 (4.00), 387 (4.09).

b) VI was obtained from Na (60 mg.), phenylacetohydrazide (400 mg.) and 2-methoxytropone (400 mg.) by the same procedure described above, yield 400 mg.

c) To a soltion of 2-hydrazinotropone (500 mg.) in 20 ml. of dioxane was added dropwise 600 mg. of phenylacetyl chloride. The separated crystals were collected, washed with H_2O and recrystallized from MeOH to give 400 mg. of pale yellow crystals, m.p. 178°. This substance was identical with the product, prepared by methods a) or b).

2-(2-Acetylhydrazino)tropone (VII)——a) To a solution of Na (46 mg.) and acetohydrazide (148 mg.) in 20 ml. of EtOH was added 140 mg. of 2-chlorotropone. After standing overnight, the mixture was concentrated under reduced pressure. To the resulting residue was added 5 ml. of H_2O, then precipitate was collected, dried and recrystallized from benzene to yield 30 mg. of yellow needles, m.p. 177°. This compound was identical with 2-(2-acetylhydrazino)tropone in all respects.

b) To a solution of Na (60 mg.) and acetohydrazide (200 mg.) in 20 ml. of EtOH was added 400 mg. of 2-methoxytropone. The mixture was allowed to stand at room temperature for 2 days, and concentrated *in vacuo*. To the resulting residue was added 7 ml. of H_2O and the mixture was neutralized with 10% HCl, then extracted with chloroform. After concentrating the chloroform solution, the residue was recrystallized from EtOH to yield 10 mg. of yellow needles, m.p. 178°. This substance was identical with 2-acetylhydrazinotropone.

1-Amino-3-cyano-5-methylcyclohepta[*b*]pyrrol-2(1*H*)-one (XXI)——XXI was prepared by the reaction of 2-chloro-5-methyltropone (500 mg.) with cyanoacetohydrazide (500 mg.) by the same procedure dercribed for VIII, yield 400 mg. *Anal.* Calcd. for $C_{11}H_9ON_3$: C, 66.32; H, 4.55; N, 21.10. Found : C, 66.22; H, 4.38; N, 21.06.

3-Cyano-5-methylcyclohepta[*b*]pyrrol-2(1*H*)-one (XX)——a) To a suspension of XXI (300 mg.) in 7 ml. of 50% sulfuric acid was added a solution of sodium nitrate (220 mg.) in 1.5 ml. of H_2O with heating on a steam bath. After cooling, 5 ml. of H_2O was added to the reaction mixture and reaction product was coollected, washed with H_2O and dissolved in 7 ml. of 5% sodium hydroxide. After decolorizing the solution with charcoal, neutralization with 10% hydrochloric acid gave yellow crystals, which was recrystallized from EtOH to yield 150 mg. of yellow crystals, m.p. 303° (decomp.). *Anal.* Calcd. for $C_{11}H_8ON_2$: C, 71.72; H, 4.38; N, 15.21. Found : C, 71.39; H, 4.36; N, 15.11. UV λ_{max}^{EtOH} mμ (log ε) : 276 (4.59), 420 (4.21).

b) To a solution of Na (60 mg.) and cyanoacetamide (220 mg.) in 20 ml. of EtOH was added a solution of 2-chloro-5-methyltropone (250 mg.) in 2 ml. of EtOH. The mixture was allowed to stand at room temperature for 3 hr., and the separated orange-red crystals were filtered off and after concentrating the filtrate, 7 ml. of H_2O was added to the residue. The mixture was neutralized with 10% hydrochloric acid, then extracted with $CHCl_3$. After concentrating the $CHCl_3$ solution, the resulting residue was dissolved in 1% sodium hydroxide. Decolorizing the solution with charcoal and neutralization with 10% hydrochloric acid gave a precipitate, which was recrystallized from EtOH to yield 20 mg. of yellow crystals, m.p. 303° (decomp.). This substane was identical with the product, prepared by the method a).

2-(2-Cyanoacetylhydrazino)tropone (V)——a) To a solution of Na (850 mg.) and cyanoacetohydrazide (3.6 g.) in 150 ml. of EtOH was added 2.5 g. of 2-methoxytropone. The mixture was allowed to stand overnight at room temperature, then concentrated *in vacuo*. After 20 ml. of H_2O was added to the residue, neutralization of the mixture with 10% hydrochloric acid gave a precipitate, which was recrystallized

from EtOH to give 1 g. of pale yellow crystals, m.p. 201° (decomp.). *Anal.* Calcd. for $C_{10}H_9O_2N_3$: C, 59.10; H, 4.46; N, 20.68. Found: C, 59.22; H, 4.49; N, 20.58.

b) To a solution of 2-hydrazinotropone (1.7 g.) in 70 ml. of dioxane was added 1.2 g. of cyanoacetylchloride dropwise. The precipitated product was collected, washed with 2% sodium hydroxide followed by H_2O. Recrystallization from EtOH yielded 0.6 g. of pale yellow needles, m.p. 199° (decomp.). This compound was identical with the product, prepared by the method a).

2-Bromo-7-(2-Cyanoacetylhydrazino)tropone (XV)——a) To a hot solution of 2-bromo-7-hydrazinotropone (0.5 g.) in 60 ml. of dioxane was added 0.3 g. of cyanoacetyl chloride dropwise. The precipitated crystals were collected, washed with H_2O and recrystallized to give 0.2 g. of pale yellow crystals, m.p. 239° (decomp.). *Anal.* Calcd. for $C_{10}H_8O_2N_3Br$: C, 42.57; H, 2.86; N, 14.90. Found: C, 42.58; H, 2.90; N, 14.34. UV λ_{max}^{EtOH} mμ (log ε): 259 (4.36), 340 (4.03), 405 (4.09).

b) To a solution of Na (46 mg.) and cyanoacetohydrazide (198 mg.) in 35 ml. of EtOH was added a solution of 2-bromo-7-methoxytropone (215 mg.) in 10 ml. of EtOH. The mixture was allowed to stand overnight at room temperature, then concentrated. To the residue was added 5 ml. of chloroform and the precipitated product collected and dissolved in 3 ml. of H_2O. Neutralization of this solution afforded a precipitate, which was recrystallized from EtOH to give pale yellow crystals, m.p. 240° (decomp.). This compound was identical with the product, prepared by the method a).

2-Bromo-7-(2-Acetylhydrazino)tropone (XVI)——XVI was prepared by the reaction of acetohydrazide (148 mg.) with 2-bromo-7-methoxytropane (215 mg.) according to method b) for Ⅶ, yield 100 mg. *Anal.* Calcd. for $C_9H_9O_2N_2Br$: C, 42.04; H, 3.53; N, 10.87. Found: C, 42.09; H, 3.62; N, 11.17. This compound was identical with authentic sample, prepared by the Nozoe's method.

1-Amino-2-oxo-1,2-dihydrocyclohepta[*b*]pyrrole-3-carboxamide (XXIII)——A mixture of Ⅷ (250 mg.) and 5 ml. of conc. hydrobromide was refluxed for 1 hr. After cooling, separated crystals were collected, washed with H_2O and recrystallized from AcOH to yield 100 mg. of yellow crystals, m.p. 301° (decomp.). *Anal.* Calcd. for $C_{10}H_9O_2N_3$: C, 59.10; H, 4.46; N, 20.68. Found: C, 59.21; H, 4.71; N, 20.46.

1-Amino-2-oxo-1,2-hydrocyclohepta[*b*]pyrrole-3-carboxylic Acid (XXIV)——a) A mixture of Ⅷ (200 mg.) and 6 ml. of 10% sodium hydroxide was refluxed 4 hr. After cooling, separated crystals were collected and dissolved in 20 ml. of hot water. Neutralization of the solution gave a precipitate, which was recrystallized from EtOH to give 100 mg. of yellow crystals, m.p. 235° (decomp.). *Anal.* Calcd. for $C_{10}H_8O_3N_2$: C, 58.82; H, 3.95; N, 13.72. Found: C, 58.95; H, 4.11; N, 13.50. UV λ_{max}^{EtOH} mμ (log ε): 230 (4.23), 283 (4.44), 421 (4.09).

b) XXIV was also prepared from XXⅢ by the same procedure described above.

1-Aminocyclohepta[*b*]pyrrol-2(1*H*)-one (XXII)——A mixture of XXIV (300 mg.) and 4 ml. of 15% hydrobromic acid was heated at 90° for 20 min. After cooling, the reaction mixture was poured into 20 ml. of H_2O and filtered off to remove a small amount of insoluble substance. The filtrate was neutralized with solid sodium carbonate and then extracted with chloroform. After concentrating the chloroform solution, the resulting residue was recrystallized from benzene to give 150 mg. of orange needles, m.p. 160°. *Anal.* Calcd. for $C_7H_8ON_2$: C, 67.48; H, 5.03; N, 17.49. Found: C, 67.77; H, 5.08; N, 17.25. UV λ_{max}^{EtOH} mμ (log ε): 267 (4.50), 410 (3.86). IR ν_{max}^{Nujol} cm^{-1}: 3340, 3220, 3140, 1715.

1-Acetamidocyclohepta[*b*]pyrrol-2(1*H*)-one (XXV)——A mixture of XXII (100 mg.) and 2 ml. of acetic anhydride was heated on a steam bath for 15 min., then concentrated *in vacuo*. To the resulting residue was added 5 ml. of benzene and separated crystals were collected, washed with benzene to give 70 mg. of yellow crystals, m.p. 210°. *Anal.* Calcd. for $C_{11}H_{10}O_2N_2$: C, 65.33; H, 4.98; N, 13.86. Found: C, 65.28; H, 5.01; N, 13.49.

1-Benzylideneaminocyclohepta[*b*]pyrrol-2(1*H*)-one (XXVI)——A mixture of XXII (100 mg.), benzaldehyde (70 mg.) and 3 ml. of EtOH was refluxed 4 hr., then concentrated *in vacuo*. The residue was purified by chromatogrphy over alumina with chloroform. Recrystallization of the residue afforded 40 mg. of orange needles, m.p. 134°. *Anal.* Calcd. for $C_{16}H_{12}ON_2$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.37; H, 4.98; N, 11.00. UV λ_{max}^{EtOH} mμ (log ε): 251 (4.37), 310 (4.60), 415 (3.84). IR ν_{max}^{Nujol} cm^{-1}: 1670.

1-Amino-3-bromocyclohepta[*b*]pyrrol-2(1*H*)-one (XXVII)——To a solution of XXII (160 mg.) in 5 ml. of chloroform was added dropwise a solution of bromine (160 mg.) in 1 ml. of chloroform with stirring. The mixture was stirred at room temperature for 3 hr., then separated crystals were collected, washed with H_2O and recrystallized from EtOH to yield 100 mg. of yellow brown crystals, m.p. 203° (decomp.). *Anal.* Calcd. for $C_9H_7ON_2Br$: C, 45.21; H, 2.95; N, 11.72. Found: C, 45.03; H, 3.00; N, 11.34. UV λ_{max}^{EtOH} mμ (log ε): 278 (4.49), 420 (3.92).

Sodium Salt of 1-Amino-2-oxo-1,2-hydrocyclohepta[*b*]pyrrole-3-sulfonic Acid (XXVIII)——XXII (110 mg.) was added to a mixture of 50% fumed sulfuric acid (0.5 ml.) and conc. sulfuric acid (0.5 ml.). The reaction mixture was stirred at room temperature for 1 hr., then poured into 10 ml. of ice water. Addition of sodium carbonate to the solution gave a precipitate, which was recrystallized from 80% EtOH to give 50 mg. of yellow needles, m.p. 267° (decomp.). *Anal.* Calcd. for $C_9H_7O_4N_2NaS$: C, 41.23; H, 2.69; N, 10.69. Found: C, 41.24; H, 2.82; N, 10.42.

1-Amino-3-(*p*-tolylazo)cyclohepta[*b*]pyrrol-2(1*H*)-one (XXIX)——A solution of XXII (160 mg.) in 8 ml. of 7% hydrochloride was added dropwise to a solution of *p*-tolyldiazonium chloride obtained from 107 mg. of *p*-toluidine and 69 mg. of sodium nitrite by the usual method. The mixture was stirred at 0° to 4° for 1 hr., allowed to stand overnight at room temperature, neutralized with sodium carbonate and extracted with benzene. After concentrating the benzene solution, the resulting residue was purified by chromatography on alumina. The crude crystals, obtained from the elution were recrystallized from MeOH to give 40 mg. of yellow crystals, m.p. 220°. *Anal.* Calcd. for $C_{16}H_{14}ON_4$: C, 69.05; H, 5.07; N, 20.13. Found: C, 69.00; H, 5.11; N, 19.61.

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Summary

Reactions of 2-methoxytropone and 2-halotropone with hydrazides were carried out. Hydrazide reacted with 2-methoxytropone to yield 2-(2-acylhydrazino)tropones. With hydrazides having an active methylene group, 2-halotropones gave 1-aminocyclohepta-[*b*]pyrrol-2(1*H*)-one derivatives and with other hydrazides, 2-(2-acylhydrazino)tropones were obtained.

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60. Nobuo Soma, Jun-ichi Nakazawa, Taiichiro Watanabe, Yoshio Sato, and Genshun Sunagawa: Studies on Seven-membered Ring Compounds. XV.*1 Preparations of Troponeimine Derivatives.*2

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Some years ago, N,N-dimethylcolchiceinamide was prepared by methylation of colchiceinamide in this laboratory as part of the total synthesis of colchiceine.[1] To explore this preparative route, we examined the methylation of 2-aminotropone (I) as a model compound for colchiceinamide. The results obtained in those experiments are now reported in this paper.

It has been reported that 2-aminotropone exists in an amino-type structure (I) forming a hydrogen bonding between amino hydrogen and carbonyl group, despite the possibility of another, tautomeric imino-type structure.[2] Acylation of I afforded an N-acyl but not an O-acyl derivative.[3] Recently, however, Ikegami suggested the

*1 Part XIV. G. Sunagawa, H. Nakao: This Bulletin, **13**, 450 (1965).

*2 This work was presented at the 84th Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, April 4, 1964.

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1) G. Sunagawa, T. Nakamura, J. Nakazawa: This Bulletin, **10**, 291 (1962); T. Nakamura: *Ibid.*, **10**, 299 (1962).

2) T. Nozoe, *et al.*: Proc. Japan Acad., **27**, 558 (1951).

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