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Studies on Seven-membered Ring Compounds. XXIX.[1] 2-Imino-2*H*-cycloheptoxazole Derivatives. (3)[2]

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Reactions of 2-imino-2*H*-cycloheptoxazoles with amines and hydrazines were examined. Reactions of 2-imino-2*H*-cycloheptoxazole derivatives with primary amines such as methylamine, benzylamine, and *p*-toluidine gave 1-substituted cycloheptimidazol-2(1*H*)-one derivatives (II: R=CH_3, R=$C_6H_5CH_2$, R=*p*-$CH_3C_6H_5$). In the reaction with benzylamine, a trace of 2-benzylaminocycloheptimidazole (IV) and 1-benzyl-2-imino-1,2-dihydrocycloheptimidazole (III) were obtained as by-products. Reaction of I with dimethylamine gave 2-dimethylaminocycloheptimidazole (XII) and cycloheptimidazol-2(1*H*)-one (XIII). Reaction with cyanamide gave 2-aminocycloheptimidazole (XIV). Hydrolyses of 4-bromo- (IIe) and 8-bromo-1-benzylcycloheptimidazol-2(1*H*)-one (IIg) gave 1-benzyl- (X) and 3-benzyl-cycloheptimidazole-2,4(1*H*,3*H*)-dione (XI), respectively. Reaciton of I with hydrazine hydrate, phenylhydrazine, *m*-nitrophenylhydrazine, and benzylhydrazine gave the corresponding 1-aminocycloheptimidazol-2(1*H*)-one derivatives (XV, XVIII—XX) shown in Table I. Reaction of I with benzoylhydrazine, isonicotinoylhydrazine, and acetylhydrazine gave 2-ureidotropone acylhydrazones (XXII—XXIV), which were easily converted to 1-acylaminocycloheptimidazol-2(1*H*)-ones (XXV—XXVII). Reaction of I with 2-hydrazinotropone gave 2-ureidotropone 2-troponylhydrazone (XXVIII).

The preceding paper described some nucleophilic reactions of 2-imino-2*H*-cycloheptoxazoles including their hydrolysis and their reactions with hydrogen sulfide, thiols, and active methylene compounds. The present paper is concerned with the reactions of 2-imino-2*H*-cycloheptoxazoles with various amines and hydrazines.

The reaction of 2-imino-2*H*-cycloheptoxazole (I) with methylamine gave 1-methylcycloheptimidazol-2(1*H*)-one (II: R=CH_3) in a good yield. Other primary amines such as benzylamine, 3-diethylaminopropylamine, *p*-toluidine, *p*-anisidine, *m*-chloroaniline, *o*-anthranilic acid, and 2-aminopyridine also gave the corresponding 1-substituted cycloheptimidazol-2(1*H*)-ones (II). Among these, reaction with benzylamine gave a trace of both 1-benzyl-2-imino-1,2-dihydrocycloheptimidazole (III) and 2-benzylaminocycloheptimidazole (IV), besides II (R=$C_6H_5CH_2$). The reaction of 2-imino-2*H*-cycloheptoxazoles having a halogen atom on the seven-membered ring with benzylamine similarly proceeded and gave substituted 1-benzylcycloheptimidazol-2(1*H*)-ones (IIe—IIh). Hitherto unreported 1-substituted cycloheptimidazol-2(1*H*)-one derivatives obtained are listed in Table I.

These reactions are available as a new procedure for the preparation of 1-substituted cycloheptimidazol-2(1*H*)-ones which have a strong analgesic and antiphlogistic activity.[4] The exceptional low yield of 8-bromo- (IIg) and 8-chloro-1-benzylcycloheptimidazol-2(1*H*)-one (IIh) from 8-bromo- (V) and 8-chloro-2-imino-2*H*-cycloheptoxazole (VI) was probably due to the steric interference of the halogen atom at C-8.

1) Part XXVIII: M. Watatani, *Chem. Pharm. Bull.* (Tokyo), **16**, 1503 (1968).
2) Presented at the Kinki Local Meeting of the Pharmaceutical Society of Japan, Osaka, June 18, 1966 (This paper comprises a part of the dissertation submitted by the author for the doctorate degree at the Kyoto University).
3) Location: *Hiromachi, Shinagawa-ku, Tokyo.*
4) H. Minakami, H, Takagi, and S. Kobayashi, *Life Sci.*, **3**, 305 (1964).

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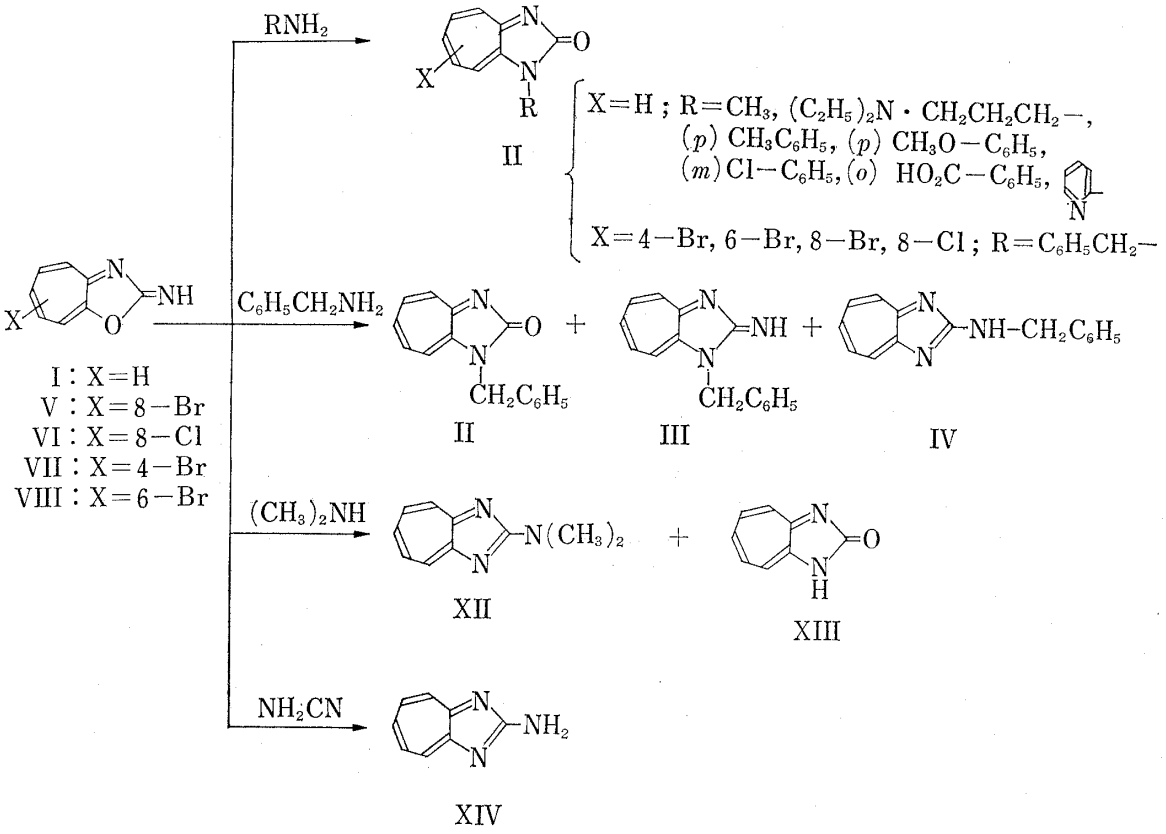

Chart 1

Nakao, *et al.*[5] previously reported that the benzylation of 4–hydroxycycloheptimidazol–2(1*H*)–one (IX) gave 1,3–dibenzylcycloheptimidazole–2,4(1*H*,3*H*)–dione and a monobenzyl derivative of mp 234°, which was assumed to be either 1–benzyl– (X) or 3–benzyl–cycloheptimidazole–2,4(1*H*,3*H*)–dione (XI). Furthermore, the same monobenzyl derivative was obtained as a metabolite of 1–benzylcycloheptimidazol–2(1*H*)–one (II: R=$C_6H_5CH_2$) by a rat.[6] An attempt was made to establish the structure of this monobenzyl derivative. Heating of the above obtained 4–bromo– (IIe) and 8–bromo–1–benzylcycloheptimidazol–2(1*H*)–one (IIg) with concentrated hydrobromic acid gave the authentic specimens of X and XI. Thus, identification of the above monobenzyl derivative by Nakao, *et al.* with X was recognized

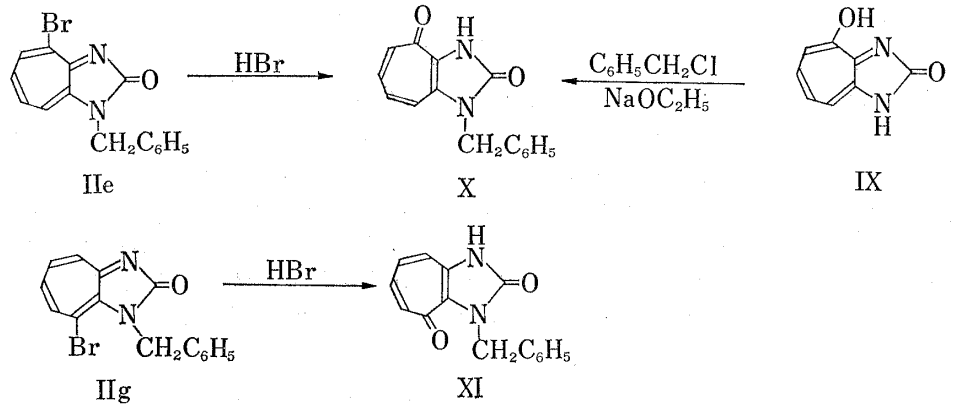

Chart 2

5) H. Nakao, N. Soma, Y. Sato, and G. Sunagawa, *Chem. Pharm. Bull.* (Tokyo), **13**, 473 (1965).
6) H. Murata and A. Yasumura, *Seikagaku*, **37**, 461 (1965).

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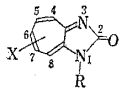
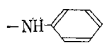
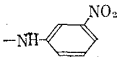
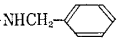
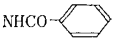
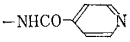
Table I. 1-Substituted-cycloheptimidazol-2(1*H*)-one Derivatives



Compound No.	X	R	mp (°C)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
IIa	H	$(C_2H_5)_2N\cdot(CH_2)_3$ [a]	115—118	$C_{23}H_{29}O_9N_3$	56.20	5.95	8.55	56.14	6.02	9.04
IIb	H		224	$C_{14}H_9ON_2Cl$	65.50	3.53	10.91	65.46	3.54	11.05
IIc	H		>300	$C_{15}H_{10}O_3N_2$	67.66	3.79	10.52	67.39	3.76	10.67
IId	H		172.5	$C_{13}H_9ON_3$	69.94	4.06	18.83	69.91	4.30	19.06
IIe	4-Br		212	$C_{15}H_{11}ON_2Br$	57.15	3.51	8.89	57.86	3.64	9.20
IIf	6-Br		225 (decomp.)	$C_{15}H_{11}ON_2Br$	57.15	3.51	8.89	56.97	3.57	8.85
IIg	8-Br		184.5	$C_{15}H_{11}ON_2Br$	57.15	3.51	8.89	57.31	3.68	8.91
IIh	8-Cl		178	$C_{15}H_{11}ON_2Cl$	66.55	4.10	10.35	66.30	4.24	10.45
XV	H	$-NH_2$	236	$C_8H_7ON_3$	59.62	4.38	26.07	59.51	4.41	26.14
XVIII	H		241 (decomp.)	$C_{14}H_{11}ON_3$	70.87	4.67	17.71	70.64	4.72	17.67
XIX	H		265 (decomp.)	$C_{14}H_{10}O_3N_4$	59.57	3.57	19.85	59.38	3.56	19.73
XX	H		130	$C_{15}H_{13}ON_3$	71.69	5.21	16.72	71.56	5.24	16.87
XXV	H		229	$C_{15}H_{11}O_2N_3$	67.91	4.18	15.84	67.77	4.20	15.67
XXVI	H		280 (decomp.)	$C_{14}H_{10}O_2N_4$	63.15	3.79	21.04	62.93	3.47	21.02
XXVII	H	$-NHCOCH_3$	182	$C_{10}H_9O_2N_3\cdot\frac{1}{2}H_2O$	56.60	4.75	19.80	56.51	4.69	19.67

a) dimaleate

by mixed mp determination and comparison of their ultraviolet (UV) and infrared (IR) spectra.

The reaction of I with dimethylamine gave 2-dimethylaminocycloheptimidazole (XII) and cycloheptimidazol-2(1*H*)-one (XIII) in approximately 1: 2 ratio. Furthermore, reaction of I with cyanamide gave 2-aminocycloheptimidazole (XIV). The following mechanisms may be presumed for the above-described reactions of I with various amines.

The reaction with primary amines to give II probably proceeds through the course shown in Chart 3 (a), which involves the attack of the amine on C-8a of I results in the ring cleavage of the oxazole, the successive ring closure to intermediate (B), and liberation of ammonia. Although another course of the formation of II via 1-substituted 2-imino-1,2-dihydrocycloheptimidazole (III), which is assumed to be produced by the dehydration of intermediate (B) is possible, this path was excluded from the fact that III ($R=C_6H_5CH_2$) was not converted into II ($R=C_6H_5CH_2$) under the above reaction condition.

Furthermore, with regard to the reaction with cyanamide, the intermediate (A') shown in Chart 3(a) underwent cyclization between the cyano group and the nitrogen of troponeimine,

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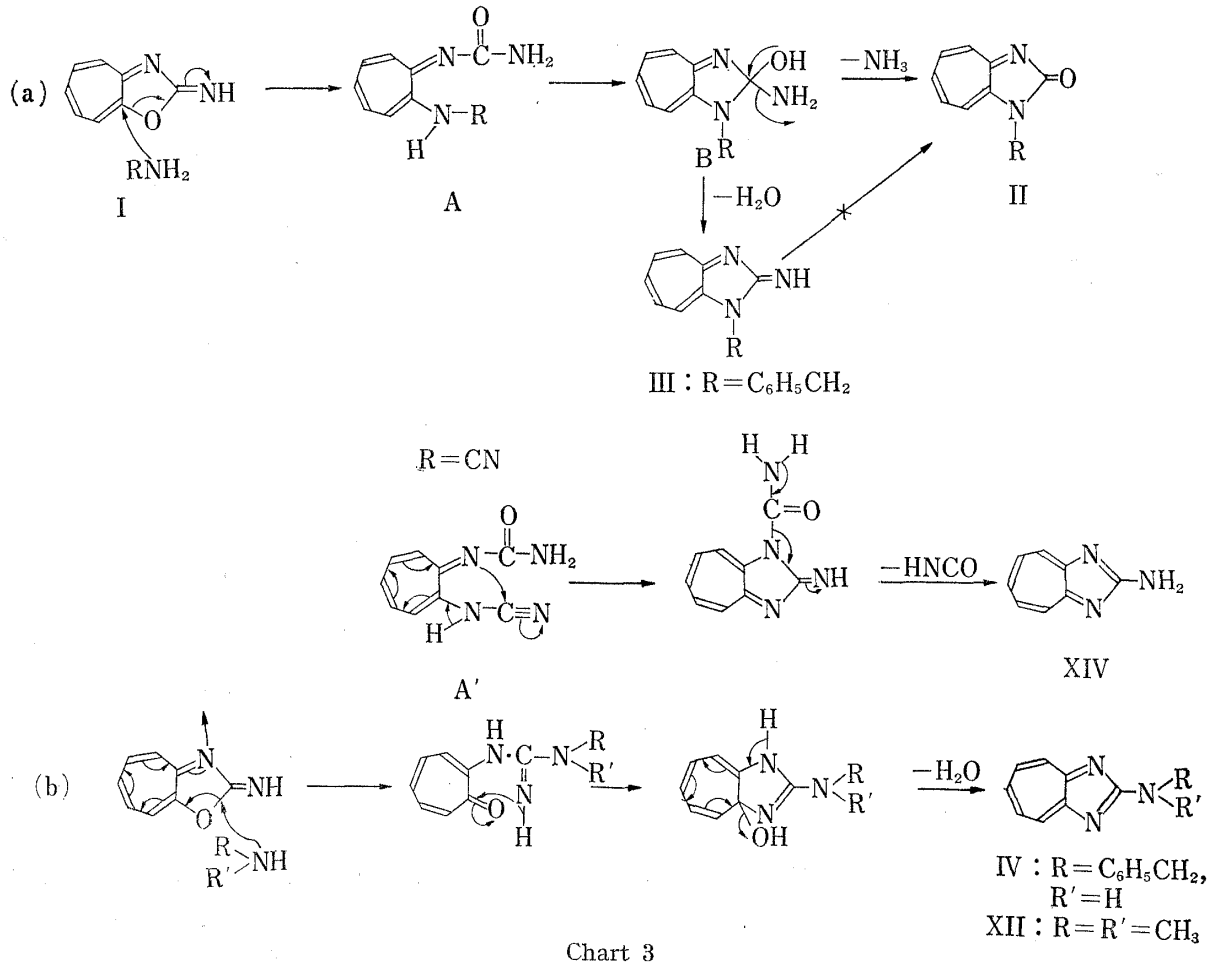

Chart 3

and a cyclization between carbonyl group and nitrogen of cyanamino group as observed in the reaction with methylamine did not occur. This is probably due to the stronger electrophilic property of the cyano group than that of carbonyl group. In contrast with the above attack of amines at C–8a of I, formation of IV by the reaction with benzylamine indicates that the attack of this amine also occurred at C–2 of I, besides that at C–8a to form II. The reaction proceeds through the course shown in Chart 3(b), which involves the attack of the amine on C–2 of I results in the cleavage of the oxazole ring, a successive ring closure to imidazole, and a dehydration to form IV. A plenty of such an attack of the amine on C–2 of I was observed in the reaction with dimethylamine and resulted in an increased yield of XII. This is perhaps due to the bulkiness of dimethylamine and a less selectivity of this amine for the attack owing to its increased basicity.

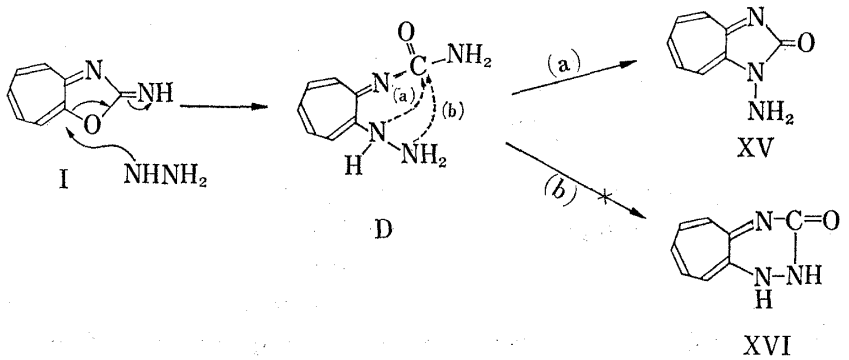

Chart 4

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Next, the reaction of I with hydrazines was examined. If the reaction is initiated by an attack of hydrazines on C–8a of I, similar to the reaction with the above–described primary amines, two directions are possible for the ring closure of the resultant intermediate (D) shown in Chart 4 and either 1–aminocycloheptimidazol–2(1*H*)–one (XV) or 1,2–dihydro–3*H*–cyclohepta[*c*]–1,2,4–triazin–3–one (XVI) will be obtained through the path (a) or (b).

When I was allowed to react with hydrazine hydrate, a crystalline product of mp 235—236° was obtained. Its UV spectrum was closely similar to that of II, suggesting the presence of a cycloheptimidazol–2(1*H*)–one ring and its IR spectrum showed two νNH at 3268 and 3125 cm^{-1}, and a $\nu_{C=O}$ in a five–membered ring lactam at 1684 cm^{-1}. The reaction of this product with nitrous acid resulted in deamination giving XIII, and the condensation with benzaldehyde gave 1–benzylideneaminocycloheptimidazol–2(1*H*)–one (XVII). From these results, the above reaction product was proved to be not XVI, but XV. Thus, the intermediate (D) underwent ring closure to the five–membered ring system through the path (a) shown in Chart 4. On the contrary, it has been shown that cyclization between the hydrozino and β–carbonyl group of *o*–hydrazinomandelic acid, whose structure resembles that of the intermediate (D), takes place to the six–membered ring system forming 3–hydroxycinnoline.[7]

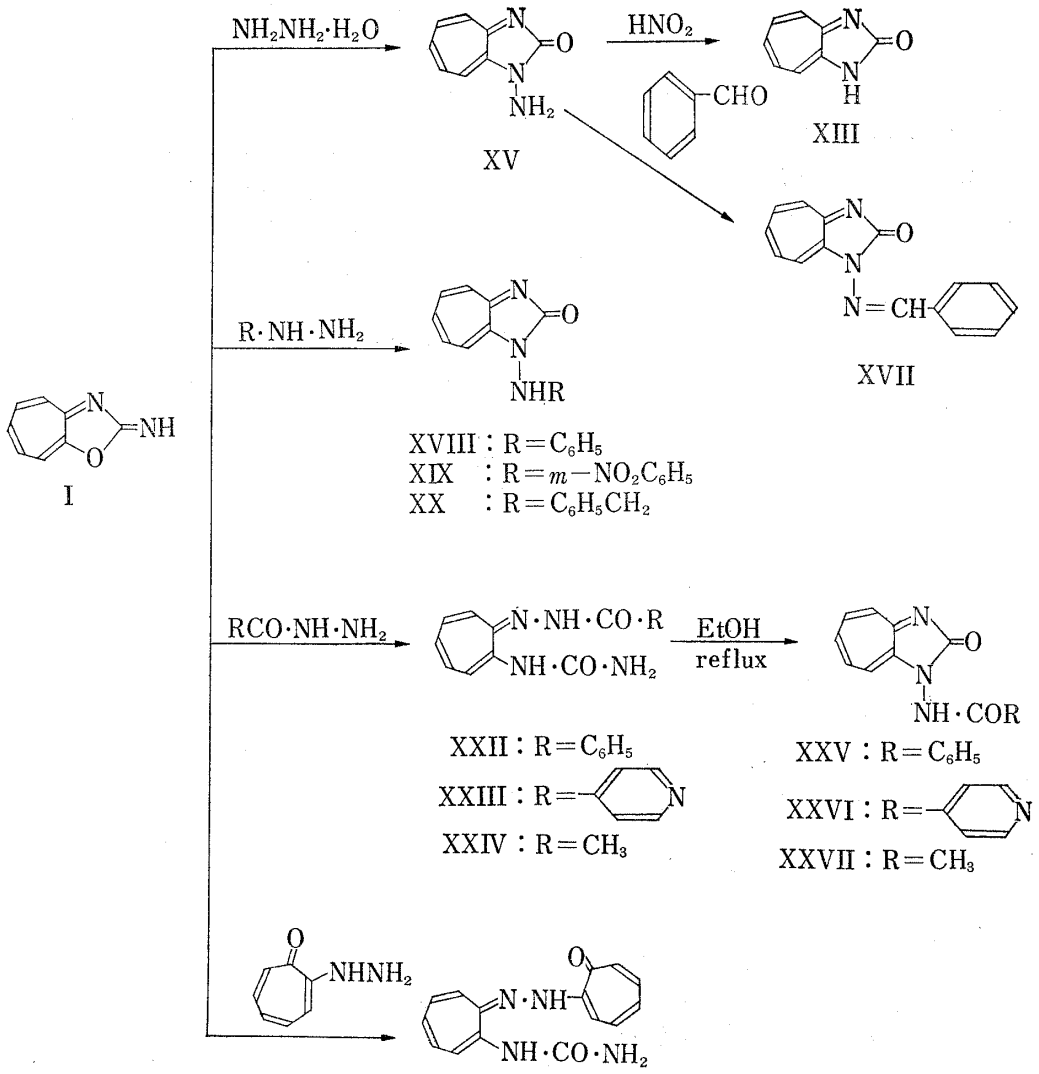

Chart 6

7) E. J. Alford and K. Shofield, *J. Chem. Soc.*, **1952**, 2102.

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Furthermore, the reactions of I with phenylhydrazine, *m*-nitrophenylhydrazine, and benzylhydrazine also gave the corresponding 1-substituted aminocycloheptimidazol-2(1*H*)-one derivatives (XVIII—XX). Among these, in the reaction with benzylhydrazine, a small amount of XIII and 2-benzylhydrazinocycloheptimidazole (XXI), which was identical with the product obtained from 2-chlorocycloheptimidazole and benzylhydrazine, were obtained as the by-products.

Finally, reactions of I with acylhydrazines were examined. When I was allowed to react with benzoylhydrazine, 2-ureidotropone benzoylhydrazone (XXII) was obtained. The UV spectrum of XXII was not similar to that of XV but resembled that of 2-methylaminotropone benzoylhydrazone[8] as shown in Fig. 1. Similar reactions with isonicotinoylhydrazine and acetylhydrazine gave 2-ureidotropone isonicotinoylhydrazone (XXIII) and 2-ureidotropone acetylhydrazone (XXIV), respectively. These products, XXII to XXIV, correspond to the intermediate (D) of XV shown in Chart 4 and underwent the expected ring closure on heating in EtOH solution to give 1-acylaminocycloheptimidazol-2(1*H*)-ones (XXV—XXVII) listed in Table I. The lower electron density on the hydrazino groups of XXII to XXIV owing to their acyl groups probably caused the difficulty of the ring closure, favoring the isolation of these compounds. The reaction of I with 2-hydrazinotropone also resulted in the isolation of 2-ureidotropone 2-troponylhydrazone (XXVIII) and its cyclized product was not obtained. This indicates that the tropone ring has an electronwithdrawing character similar to that of the acyl groups in XXII to XXIV.

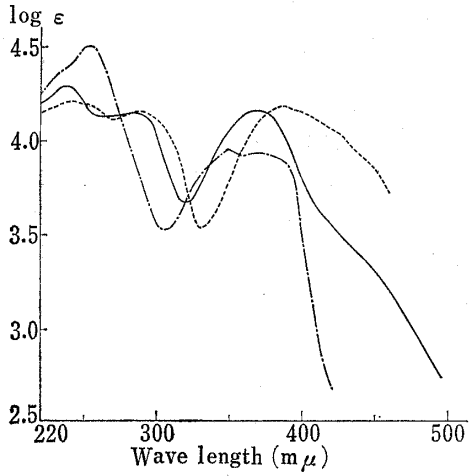

Fig. 1. Ultraviolet Spectra

——— 2-ureidotropone benzoylhydrazone (XXII)
- - - - - - 2-methylaminotopone benzoylhydrazone
—·—·— 1-benzamidocycloheptimidazol-2-(1*H*)-one (XXV) (in EtOH)

Experimental[9]

Reactions of 2-Imino-2*H*-cycloheptoxazole (I) with Primary Amines——An example is cited for 1-methylcycloheptimidazol-2(1*H*)-one (II: R=CH_3, X=H). To an aqueous solution (30 ml) of I, prepared from 1.7 g of Na salt of 2-cyanaminotropone, 0.85 g of 40% aqueous $MeNH_2$ was added and the mixture was stirred at room temperature for 1 hr. The reaction mixture was extracted with $CHCl_3$ and the extract was evaporated to dryness. Recrystallization of the residue from benzene gave 0.74 g of yellow needles, mp 191—192°, which were identified with an authentic sample of 1-methylcycloheptimidazol-2(1*H*)-one by mixed mp determination and comparison of their IR spectra.

The reactions of I with 3-diethylaminopropylamine, *p*-toluidine, *p*-anisidine, *m*-chloroaniline, anthranilic acid, and 2-aminopyridine were carried out in the same manner as above and gave the corresponding 1-substituted cycloheptimidazol-2(1*H*)-ones (II: R=CH_3, Et_2N-$(CH_2)_3$, *p*-$CH_3C_6H_4$, *p*-CH_3O-C_6H_4, *m*-ClC_6H_4, *o*-$HO_2C \cdot C_6H_4$, and 2-C_5H_4N). In a similar manner, substituted 2-imino-2*H*-cycloheptoxazoles (V—VIII) were reacted with benzylamine and the corresponding substituted 1-benzylcycloheptimidazol-2(1*H*)-ones (IIe—IIh) listed in Table I were obtained. The mp and the analytical data of hitherto unreported derivatives among the products are listed in Table I.

By the same procedure as described for the reaction of I with $MeNH_2$, I prepared from 1.7 g of Na salt of 2-cyanaminotropone was allowed to react with benzylamine and 43 mg of 2-benzylaminocycloheptimidazole (IV) and 65 mg of 1-benzyl-2-imino-1,2-dihydrocycloheptimidazole (III) were obtained, besides 1.7 g of 1-benzylcycloheptimidazol-2(1*H*)-one (II: R=$C_6H_5CH_2$), by the following procedure. The mother liquor from the recrystallization of crude II (R=$C_6H_5CH_2$) was concentrated and submitted to alumina chromato-

8) Y. Sato and G. Sunagawa, *Chem. Pharm. Bull.*(Tokyo), **15**, 634 (1967).
9) All melting points are uncorrected.

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graphy. The benzene eluate gave IV as orange needles, mp 175°, which was identified with an authentic sample by mixed mp determination and comparison of their UV and IR spectra. The AcOEt eluate gave III as yellow crystals, mp 201° (decomp.), which was identified with an authentic sample by comparison of their IR spectra.

Reaction of I with Me_2NH——An aqueous solution containing 0.5 g of Me_2NH and I, prepared from 1.7 g of Na salt of 2–cyanaminotropone, was allowed to stand overnight at room temperatures. The reaction mixture was extracted with $CHCl_3$, the extract was dried over Na_2SO_4, and evaporated to dryness. Recrystallization of the residue from cyclohexane gave yellow crystals, mp 133—134°, which were identified with an authentic sample of 2–dimethylaminocycloheptimidazole (XII) by mp determination and comparison of their IR spectra. Yield, 275 mg.

The aqueous layer from the above extraction was pH 10, which was adjusted to pH 4—5. The separated crystals were collected by filtration. Recrystallization from water gave 643 mg of pale yellow needles, mp 245°, which were identified with an authentic sample of cycloheptimidazol–2(1*H*)–one (XIII) by mixed mp determination and comparison of their UV and IR spectra.

Reaction of I with Cyanamide——By the same manner as described for the reaction with Me_2NH, the reaction of I with cyanamide was carried out giving 2–aminocycloheptimidazole (XIV) as yellow crystals, mp 295° (decomp.), in 76% yield.

1-Benzylcycloheptimidazole-2,4(1*H*,3*H*)-dione (X)——A mixture of 6.5 g of 1–benzyl–4–bromocycloheptimidazol–2(1*H*)–one (IIe) and 60 ml of conc. HBr was refluxed for 43 hr. The reaction mixture was evaporated to dryness *in vacuo* and the residue was dissolved in water. The aqueous solution was made alkaline with dil. NaOH. After filtration the filtrate was made slightly acid with dil. HCl. The separated crystals were collected and recrystallized from EtOH to 3.4 g of pale yellow needles, mp 234°. The product was identified with the monobenzyl derivative obtained by the benzylation of 4–hydroxycycloheptimidazol–2(1*H*)–one (IX) according to the direction of Nakao, *et al.*,[5] by mixed mp determination and comparison of their UV and IR specra. *Anal.* Calcd. for $C_{15}H_{12}O_2N_2$: C, 71.41; H, 4.80; N, 11.11. Found: C, 70.87; H, 4.82; N, 11.20.

3-Benzylcycloheptimidazole-2,4(1*H*,3*H*)-dione (XI)——By the same procedure as for the preparation of X, 0.4 g of 1–benzyl–8–bromocycloheptimidazol–2(1*H*)–one (IIg) gave 35 mg of pale yellow needles, mp 231°. *Anal.* Calcd. for $C_{15}H_{12}O_2N_2$: C, 71.41; H, 4.80; N, 11.11. Found: C, 71.17; H, 5.00; N, 10.96.

1-Aminocycloheptimidazol-2(1*H*)-ones (XV, XVIII, XIX)——An example is cited for 1–aminocycloheptimidazol–2(1*H*)–one (XV). To an aqueous solution (40 ml) of I, prepared from 1.7 g of Na salt of 2–cyanaminotropone, 0.63 g of 80% hydrazine hydrate was added and the mixture was allowed to stand at room temperatures for 5 hr. The separated crystals (1.1 g) were collected and recrystallized from EtOH to 0.8 g of XV as pale yellow crystals, mp 235—236°. UV λ_{max}^{EtOH} mμ (log ε): 254.5 (4.42), 345 (3.98), 390 (shoulder). IR ν_{max}^{Nujol} cm^{-1}: 3268, 3125, 1684 (broad).

1–Anilinocycloheptimidazol–2(1*H*)–one (XVIII) and 1–(*m*–nitroanilino)cycloheptimidazol–2(1*H*)–one (XIX) were obtained by silmiar reactoins of I with phenylhydrazine and *m*–nitropheynlhydrazine. The analytical data of these products are given in Table I.

Deamination of XV——To a solution of 1 g of XV in 10 ml of 50% H_2SO_4, was added an aqueous solution (5 ml) of 0.86 g of $NaNO_2$, while heating on a water bath. After additional 5 min of heating, the reaction mixture was cooled, made alkaline, and then filtered. The filtrate was adjusted to pH 5—6 giving 0.98 g of pale yellow needles, mp 245°, which were identified with an authentic sample of XIII by mixed mp determination and comparison of their IR spectra.

1-Benzylidenaminocycloheptimidazol-2(1*H*)-one (XVII)——To a solution of 100 mg of XV in 20 ml of EtOH, 100 mg of benzaldehyde was added and the mixture was heated on a water bath for 2 hr. After removal of EtOH, the residue was washed with ether and recrystallization from AcOEt gave yellow scales, mp 166—167°. Yield, 113 mg. *Anal.* Calcd. for $C_{15}H_{11}ON_3$: C, 72.27; H, 4.45; N, 16.86. Found: C, 72.33; H, 4.29; N, 16.98. IR ν_{max}^{Nujol} cm^{-1}: 1724, 1695 (broad), 1603.

Reaction of I with Benzylhydrazine——By the same procedure as for the preparation of XV, I, prepared from 1.7 g of Na salt of 2–cyanaminotropone, was allowed to react with 1.3 g of benzylhydrazine. The separated crystals were collected by filtration and recrystallization from cyclohexane—benzene gave 0.11 g of 2–benzylhydrazinocycloheptimidazole (XXI) as pale yellow crystals, mp 120°, which was identified with the product obtained by the reaction of 2–chlorocycloheptimidazole with benzylhydrazine by mixed mp determination and comparison of IR spectra. *Anal.* Calcd. for $C_{15}H_{14}N_4$: C, 71.97; H, 5.64; N, 22.39. Found: C, 71.82; H, 5.61; N, 22.48. UV λ_{max}^{EtOH} mμ (log ε): 242 (4.41), 263 (4.40), 295 (3.80), 368 (4.27).

The filtrate of XXI was extracted with $CHCl_3$ and the $CHCl_3$ extract was submitted to alumina chromatography. The $CHCl_3$ eluate gave 0.3 g of 1–benzylaminocycloheptimidazol–2(1*H*)–one (XX) as yellow crystals (from AcOEt), mp 129—130°. *Anal.* Calcd. for $C_{15}H_{13}ON_3$: C, 71.69; H, 5.21; N, 16.72. Found: C, 71.56; H, 5.24; N, 16.87. UV λ_{max}^{EtOH} mμ (log ε): 254 (4.36), 346 (3.90), IR ν_{max}^{Nujol} cm^{-1}: 3195, 1695 (broad).

The aqueous layer from the above extraction was adjusted to pH 5—6 and the separated crystals were collected to 1 g of pale yellow crystals, mp 245°, which were identified with an authentic sample of XIII by mixed mp determination and comparison of their IR spectra.

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Reaction of 2-Chlorocycloheptimidazole with Benzylhydrazine——A mixture of 1 g of 2-chlorocycloheptimidazole, 1.48 g of benzylhydrazine, and 40 ml of EtOH was refluxed for 4 hr. After filtration, the reaction mixture was evaporated to dryness and the residue was taken up in $CHCl_3$. The $CHCl_3$ solution was submitted to alumina chromatography. The AcOEt eluate was evaporated to dryness and the residue was recrystallized from cyclohexane—benzene to 1.1 g of XXI, mp 120°. *Anal.* Calcd. for $C_{15}H_{14}N_4$: C, 71.97; H, 5.64; N, 22.39. Fond: C, 72.14; H, 5.60; N, 21.93.

2-Ureidotropone Benzoylhydrazone (XXII)——To an aqueous solution (100 ml) of I, prepared from 5.1 g of Na salt of 2-cyanaminotropone, a solution of 4.5 g benzoylhydrazine in 20 ml of EtOH was added and the mixture was stirred at room temperatures for 15 min. After filtration, the separated crystals were recrystallized from $CHCl_3$ to reddish orange scales, mp 124—125° (decomp.). Yield, 7.6 g. *Anal.* Calcd. for $C_{15}H_{14}O_2N_4 \cdot H_2O$: C, 59.99; H, 5.37; N, 18.66. Found: C, 59.67; H, 5.32; N, 18.49. The UV spectrum of XXII is shown in Fig. 1. IR ν_{max}^{Nujol} cm^{-1}: 3500—3190 (broad), 1712, 1629 (broad).

2-Ureidotropone Isonicotinoylhydrazone (XXIII)——By the same manner as for the preparation of XXII, the reaction of I with isonicotinoylhydrazine gave reddish orange crystals of mp 151° (decomp.) in 81% yield. *Anal.* Calcd. for $C_{14}H_{13}O_2N_5 \cdot H_2O$: C, 55.81; H, 5.02; N, 23.25. Found: C, 55.31; H, 4.51; N, 22.93.

1-Acetamidocycloheptimidazol-2(1*H*)-one (XXVII) and 2-Ureidotropone Acetylhydrazone (XXIV)——By the same procedure as for the preparation of XXII, I from 1.7 g of Na salt of 2-cyanaminotropone was allowed to react with 0.74 g of acetylhydrazine and gave 0.761 g of orange crystals, decomposing at 128° [2-ureidotropone acetylhydrazone (XXIV); UV λ_{max}^{EtOH}: 250 (shoulder), 282, 350, 428. IR ν_{max}^{Nujol} cm^{-1}: 3360—3200 (broad), 1678, 1645]. Recrystallization of the above crystals from EtOH gave 1-acetamidocycloheptimidazol-2(1*H*)-one (XXVII) as yellow needles, mp 170°. The analytical data are given in Table I. UV λ_{max}^{EtOH} mμ (log ε): 252 (4.45), 343 (3.93), 371 (3.91). IR ν_{max}^{Nujol} cm^{-1}: 3333 (broad), 1715—1678 (broad).

1-Benzamidocycloheptimidazol-2(1*H*)-one (XXV)——An EtOH solution of 1.5 g of XXII was refluxed for 1 hr and then concentrated. The separated crystals were collected and recrystallized from AcOEt—EtOH to 1.36 g of yellow crystals, mp 228—229°. The analytical data are given in Table I. UV λ_{max}^{EtOH} mμ (log ε): 252 (4.51), 345 (3.96), 370 (3.94).

1-Isonicotinoylaminocycloheptimidazol-2(1*H*)-one (XXVI)——By the same manner as for the preparation of XXV, heating of the EtOH solution of XXIII gave XXVI as yellow cubic crystals of mp 280° (decomp.). The analytical data are given in Table I. UV λ_{max}^{EtOH} mμ (log ε): 253 (4.49), 343 (3.96), 370 (3.95).

2-Ureidotropone 2-Troponylhydrazone (XXVIII)——By the same procedure as for the preparation of XXII, I prepared from 1.7 g of Na salt of 2-cyanaminotropone was allowed to react with 1.49 g of 2-hydrazinotropone and 1.56 g of XXVIII was obtained as reddish brown needles, mp 205° (decomp.). *Anal.* Calcd. for $C_{15}H_{14}O_2N_4$: C, 63.82; H, 5.00; N, 19.85. Found: C, 63.85; H, 4.97; N, 20.31. UV λ_{max}^{EtOH} mμ (log ε): 244.5 (4.41), 282 (4.24), 460 (4.48).

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