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

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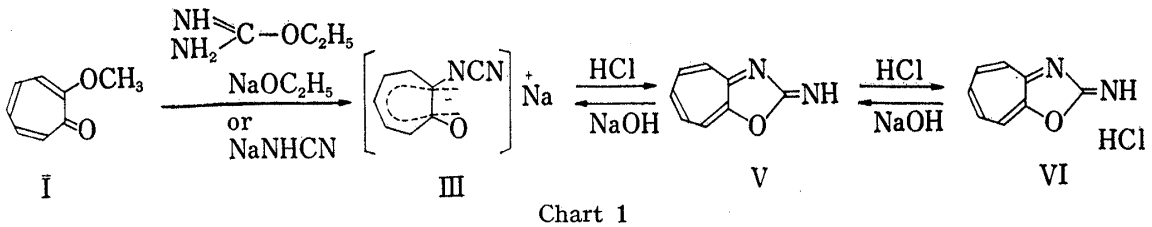
Formation and some electrophilic reactions of 2-imino-2*H*-cycloheptoxazole derivatives were described. Reaction of 2-methoxytropone (I) with O-ethylisourea or cyanamide in the presence of sodium ethoxide gave the sodium salt of 2-cyanaminotropone (III). Neutralization of III resulted in the cyclization to its ring-tautomer, 2-imino-2*H*-cycloheptoxazole. The sodium salts (VII—XIII) listed in Table I were obtained by the reaction of substituted 2-methoxytropones with sodium salt of cyanamide. 8-Isopropyl-(XIV), 6-chloro-(XV), and 8-chloro-2-imino-2*H*-cycloheptoxazole (XVI) were prepared by the neutralization of the sodium salts (XIII, VII, and VIII), and their ring-chain tautomerisms were discussed. The reaction of V with benzoyl, *p*-toluensulfonyl, and tropylium chloride in the presence of triethylamine gave 2-benzoyl-(XXV), 2-(*p*-toluensulfonyl)imino-(XXVIII), and 2-tropylimino-2*H*-cycloheptoxazole (XXX), respectively. The reaction of V with phenyl isocyanate gave 2-phenylcarbamoylimino-2*H*-cycloheptoxazole (XXIX). Heating of XXV in ethanol solution gave N-benzoylcarbamoyl-2-ethoxytroponeimine (XXVII). While the treatment of XXV with anhydrous hydrogen chloride gave its hydrochloride (XXVI), the similar acid treatment of XXX resulted in its decomposition to VI and a tropylium cation.

In a preceding paper,[1] it was demonstrated that the reaction of 2-methoxytropone (I) with O-ethylisourea gave 2-methoxycycloheptimidazole. To examine the limitation of this reaction, the same reaction was carried out in the presence of sodium ethoxide, and a new product, the sodium salt (III) of 2-cyanaminotropone (II), which cyclized, on neutralization, to its ring-tautomer, 2-imino-2*H*-cycloheptoxazole (V), was obtained. The details thereof and some reactions of V will be described in the present paper.

When 2-methoxytropone (I) and O-ethylisourea were refluxed in ethanol in the presence of sodium ethoxide, yellow crystals, $C_8H_5ON_2Na$, having no ethoxyl group, were obtained in a good yield, and the formation of 2-ethoxycycloheptimidazole, which had been reported for the reaction in the absence of sodium ethoxide, was not observed. At this point, in order to examine the effect of sodium ethoxide in this reaction and to determine the structure of the new product, the reaction between sodium ethoxide and O-ethylisourea was examined under the same conditions as above. White crystals were obtained in a good yield and these were proved to be sodium cyanamide by comparison with the authentic specimen. Consequently, sodium cyanamide was allowed to react with I and the formation of the same product obtained by the above-described reaction of I with O-ethylisourea and sodium ethoxide was confirmed. Hence, this new product was presumed to be the sodium salt (III) of 2-cyanaminotropone (II). The infrared (IR) spectrum of III displayed $\nu_{C\equiv N}$ at 2165 cm^{-1}, supporting the correctness of the structure of III.

Treatment of III with anhydrous hydrogen chloride afforded white crystals melting at 215°. The analytical values of this product agreed with the composition of the expected hydrochloride of 2-cyanaminotropone, $C_8H_7ON_2Cl$. However, its IR spectrum did not show $\nu_{C\equiv N}$ which was observed in III but did show $\nu_{C=N}$ at a 1686 cm^{-1}. Its UV spectrum was similar

1) Part XXVI: G. Sunagawa and M. Watatani, *Chem. Pharm. Bull.* (Tokyo), **16**, 1308 (1968).
2) Presented at the Kinki Local Meeting of the Pharmaceutical Society of Japan, Osaka, June 18, 1966.
3) Location: *Hiro-machi, Shinagawa-ku, Tokyo.*



I III V VI

Chart 1

to that of 3-cyano-2-imino-2*H*-cyclohepta[*b*]-furane (IV)[4] as shown in Fig. 1. Therefore, this hydrochloride was considered to be 2-imino-2*H*-cycloheptoxazole hydrochloride (VI). On the above treatment with hydrochloric acid, III underwent a ring closure and was converted to its ring-tautomer, VI. Reversely, treatment of VI with alkali resulted in the ring cleavage and afforded III. Such isolation of both the ring and chain tautomers as above has been previously reported in the seven-membered ring compounds such as 3-cyano-2-imino-2*H*-cyclohepta[*b*]furane derivatives[4,5] and 2-(ω,ω-diethoxycarbonyl-methyl)-2,3-dihydro-8*H*-cycloheptoxazol-8-one.[6] A solution of III neutralized with one molar equivalent of acetic acid displayed $\nu_{C\equiv N}$ at 1672 cm^{-1} in its IR spectrum and UV absorption spectrum similar to that of VI. These facts indicate that, in the neutral circumstances, 2-cyanaminotropone (II) exists in its ring tautomeric form, 2-imino-2*H*-cycloheptoxazole (V). The electron-attracting effect of the cyano group and the higher electron density on the oxygen of 2-cyanaminotropone, induced by the

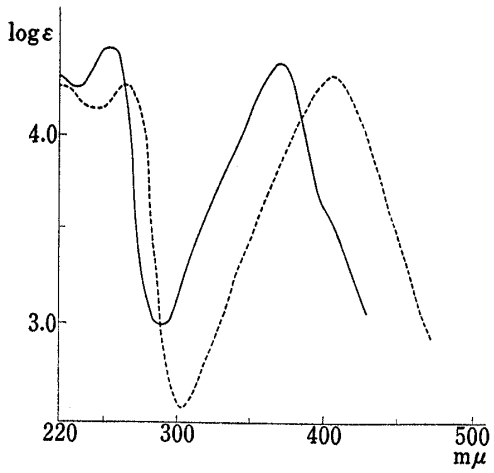
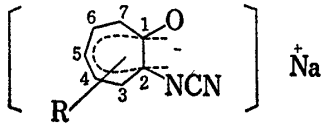


Fig. 1. Ultraviolet Absorption Spectra in EtOH

——— VI
- - - - - - 3-Cyano-2-imino-2*H*-cyclohepta[*b*]furane hydrochloride

Table I. Sodium Salt of 2-Cyanaminotropone Derivatives



Compound No.	R	mp (°C)	IR $\nu_{C\equiv N}$ cm^{-1}	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
III	H	>300	2165	$C_8H_5ON_2Na$	57.15	3.00	16.66	56.82	3.02	16.76
VII	5-Cl	>300	2155	$C_8H_4ON_2ClNa$	47.43	1.99	13.83	47.24	1.92	13.51
VIII	7-Cl	257(d)	2193 2160	$C_8H_4ON_2ClNa$	47.43	1.99	13.83	47.18	2.16	13.59
IX	5-Br	>300	2146	$C_8H_4ON_2BrNa$	38.89	1.63	11.34	38.48	1.56	11.27
X	7-Br	268(d)	2193(s) 2151(m)	$C_8H_4ON_2BrNa$	38.89	1.63	11.34	38.89	1.75	11.24
XI	5-NO_2	>300	2212 2174	$C_8H_4O_3N_3Na\cdot H_2O$	41.57	2.62	18.18	41.56	2.69	18.02
XIII	7-iso-C_3H_7	220(d)	2151	$C_{11}H_{11}ON_2Na$	*) Unstable					

4) T. Nozoe, T. Mukai, and T. Suzuki, *Bull. Chem. Soc. Japan*, **36**, 38 (1963).
5) G. Sunagawa and H. Nakao, *Chem. Pharm. Bull.* (Tokyo), **13**, 443 (1965).
6) T. Nozoe, K. Doi, and K. Kitahara, *Bull. Chem. Soc. Japan*, **34**, 611 (1961).

strong electron-releasing character of the cycloheptatriene ring, seem to facilitate the ring closure of II to its ring tautomer, V. Although the concentration of the solution of V resulted in a polymerisation to a resinous product, V is stable in a dilute solution and no change was observed after standing of the solution for a few days.

The above-described reaction of I with sodium cyanamide was applied to the substituted 2-methoxytropones and sodium salts of 2-cyanaminotropones listed in Table I were obtained.

Next, 8-isopropyl-(XIV), 6-chloro-(XV), and 8-chrolo-2-imino-2*H*-cycloheptoxazole (XVI) were respectively prepared by the neutralization of the sodium salts (XIII, VII, and VIII) and their properties were compared with each other.

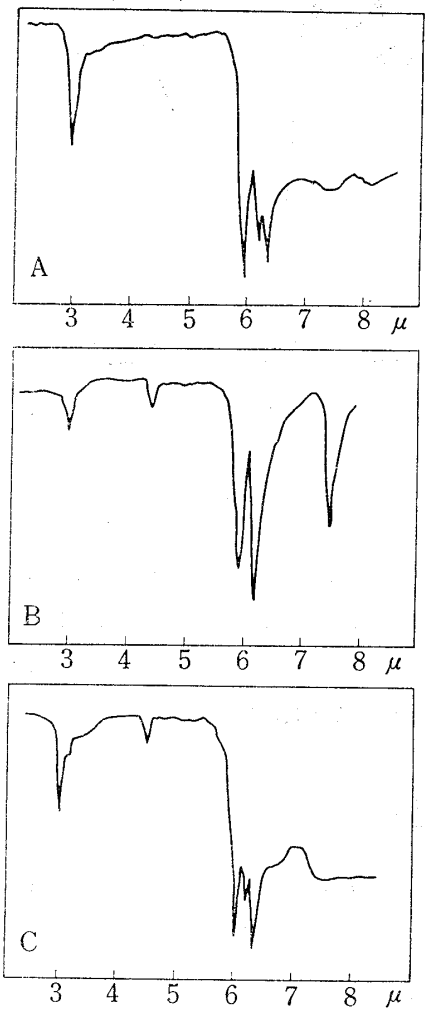


Fig. 2. Infrared Spectra of A (XIV), B (XV), and C (XVI)
(0.02M $CHCl_3$ solution)

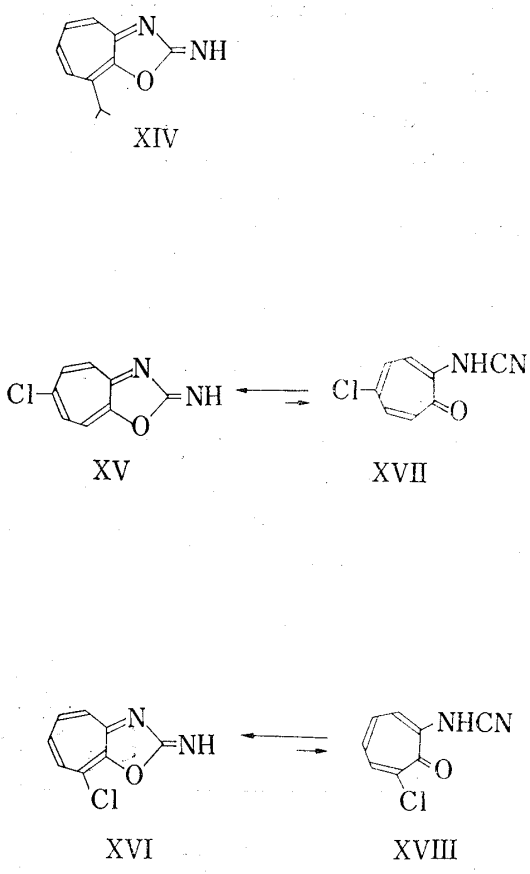


Chart 2

In their IR spectra, XV and XVI showed $\nu_{C\equiv N}$ at 2262 cm^{-1} besides $\nu_{C=N}$ at 1672 cm^{-1} as shown in Fig. 2, while XIV did not show any absorption around 2200 cm^{-1}. This indicates that XV and XVI exist, in the solution, in an equilibrium with their chain-tautomers, 5-chloro-(XVII) and 7-chloro-2-cyanaminotropone (XVIII), respectively, and that no chain-tautomer is present in the solution of XIV. The examination of the UV spectra was also consistent with this inference; the UV spectra of XVII and XVIII showed a shoulder at around 450 mμ as shown in Fig. 3 and these shoulders were presumed to be the absorption due to their chain isomers, since VII and VIII showed an absorption at 440 and 436 mμ, respectively, in an alkaline soultion. The above contribution of the chain isomer in XV and XVI is probably due to the electron-attracting character of the chlorine atom which induced lower electron density

on the oxygen atom and, consequently, difficulty in their ring closure to their ring-isomers.

In connection with the above-described prepartion of the sodium salts of 2-cyanaminotropones, some rearrangement reactions to benzene derivatives were observed. When 2-cyano-7-methoxytropone (XIX) was allowed to react with O-ethylisourea in the presence of sodium ethoxide, 2-cyano-3-iminophthalimidine (XX) was obtained. The IR spectrum of XX showed the presence of cyano, imino, and carbonyl groups, and its ultraviolet (UV) spectrum displayed maximum absorptions at 222, 267, and 306 mμ supporting its structure as a benzene derivative. Alkaline hydrolysis of XX gave phthalic acid, while acid hydrolysis yielded phthalimide and phthalic acid. 3-Cyano-2-methoxytropone (XXII) also gave XX by the reaction with sodium ethoxide and O-ethylisourea.

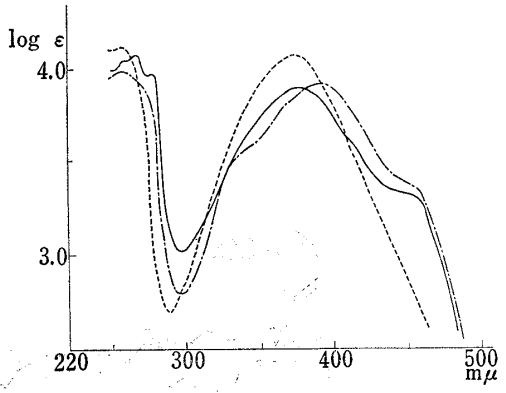
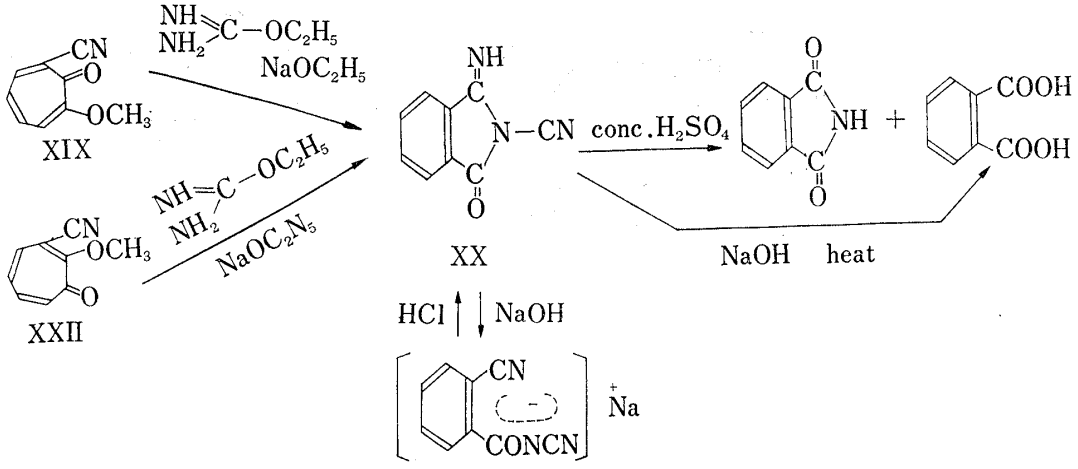


Fig. 3. Ultraviolet Absorption Spectra in $CHCl_3$

——— XVI ····· V
—·—·— XV



XXI

Chart 3

Treatment of XX with cold aqueous alkali gave a sodium salt, whose IR spectrum showed the presence of two cyano groups and the absence of imino group. Therefore, the sodium salt of XX is presumed to exist in the form of its chain-tautomer, the sodium salt of *o*-cyanobenzoylcyanamide (XXI). Treatment of XXI with acid resulted in the recovery of XX. It has been reported that the alkaline treatment of 3-iminophthalimidine, which is the skeletal compound of XX, resulted in a decomposition to phthalimide and ammonia, and no chain-tautomer is isolated.[7]

Benzoylation of V in the presence of triethylamine yielded 2-benzoylimino-2*H*-cycloheptoxazole (XXV). The UV spectrum of XXV was similar to that of V and its IR spectrum showed $\nu_{C=N}$ and $\nu_{C=O}$ at 1645 and 1610 cm^{-1}. Chemical proof for the structure of XXV was given by its acid hydrolysis to 2-(3-benzoylureido)tropone (XXIII). Further hydrolysis of XXIII with dilute hydrochloric acid gave 2-aminotropone and benzoic acid. Similarly, reactions of V with *p*-toluenesulfonyl chloride and phenylisocyanate afforded 2-(*p*-toluenesulfon-

7) T. Posner, *Chem. Ber.*, **30**, 1693 (1897) [Beilstein, "Handbuch der organischen Chemie," **21**, p. 460 (Springer-verlag, Berlin)].

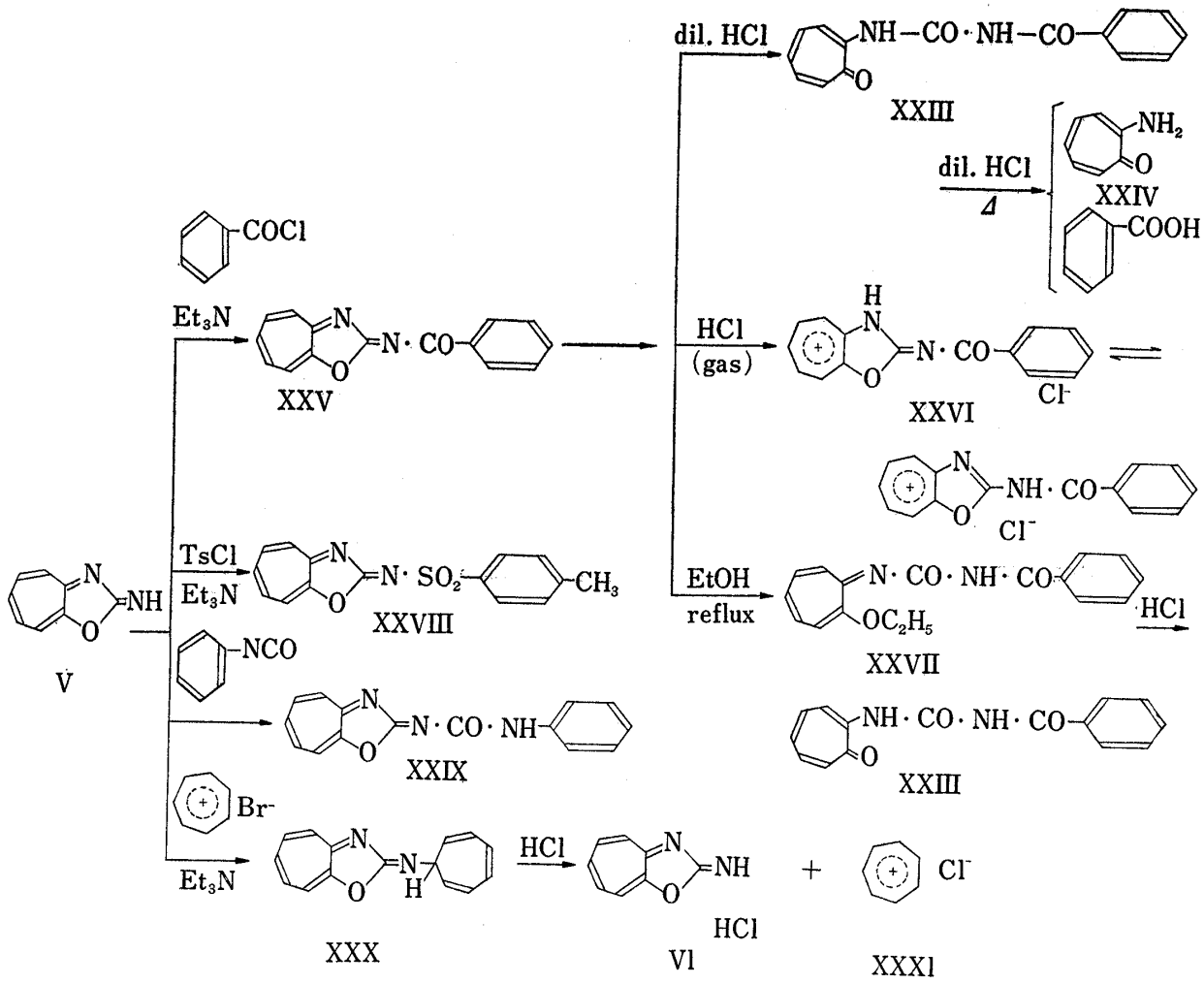


Chart 4

yl)imino–2*H*–cycloheptoxazole (XXVIII) and 2–(phenylcarbamoyl)imino–2*H*–cycloheptoxazole (XXIX), respectively. Moreover, the reaction of V with tropylium bromide gave 2–tropylimino–2*H*–cycloheptoxazole (XXX). The structure of XXX was confirmed by its satisfactory elemental analysis, the similarity of its UV spectrum to that of V, and the nuclear magnetic resonance (NMR) spectrum which showed a triplet corresponding to one proton at 6.15 τ characteristic to the methyne proton at C_7 of the cycloheptatriene ring.

Further investigation was made to compare the properties of XXV and XXX. Heating of XXV in ethanol resulted in a facile cleavage of its oxazole ring to afford N–benzoylcarbamoyl-2–ethoxytroponeimine (XXVII), whereas XXX did not suffer any change on refluxing in ethanol. This easy attack of the ethoxide anion towards XXV is probably due to the lower electron density on its seven–membered ring owing by the electron–attracting benzoyl group. The structure of XXVII was proved by its hydrolysis to XXIII.

Treatment of XXV with anhydrous hydrogen chloride in chloroform solution afforded the expected hydrochloride which showed NMR spectrum of its seven–membered ring protons at around 0.6 τ, indicative of the significant contribution of the tropylium ion structure, XXXVI. On the other hand, the same acid treatment of XXX resulted in its decomposition to VI and tropylium cation. This was recognized by the examination of the NMR spectrum of XXX in trifluoroacetic acid which showed the summation of the absorption of tropylium cation and that of the conjugate acid of V. Moreover, the actual isolation of tropylium chloride and VI was achieved from the solution of XXX after its treatment with anhydrous hydrochloric acid. This C–N bond fission of XXX by the acid is probably due to the preferable formation of the

cycloheptatriene ring to a tropylium cation, that is, 6π–electron system. Compound V obtained above is a new active troponoid, and further work is in progress on its reactions and will be reported in the proceeding paper.

Experimental[8)]

Sodium Salt of 2-Cyanaminotropone (III)——i) To an EtOH solution of NaOEt, prepared from 0.506 g of Na and 20 ml of EtOH, a solution of 1.94 g of O–ethylisourea in 10 ml of EtOH and then 2.7 g of 2–methoxytropone (I) were added and the mixture was refluxed for 3 hr. The separated crystals were collected by filtration and recrystallized from EtOH to 3.13 g of yellow needles, mp above 300°. *Anal.* Calcd. for $C_8H_5ON_2Na$: C, 57.15; H, 3.00; N, 16.66; Na, 13.68. Found: C, 56.82; H, 3.02; N, 16.76; Na, 13.60. UV λ_{max}^{EtOH} mμ (log ε): 226 (4.32), 250 (shoulder), 256 (4.23), 370 (4.15). $\lambda_{max}^{0.1N\ HCl\text{-}EtOH}$ mμ (log ε): 220 (4.27), 252.5 (4.47), 366 (4.36). $\lambda_{max}^{0.1\ NKOH\text{-}EtOH}$ mμ (log ε): 255 (4.29), 358 (4.14), 416 (4.24). IR ν_{max}^{Nujol} cm^{-1}: 2165, 1600.

ii) A mixture of 1.65 g of I, 0.78 g of sodium cyanamide, and 50 ml of EtOH was refluxed for 2 hr. By the same treatment as described in i), there were obtained 1.8 g of yellow needles, which were identified with the product obtained in i) by comparison of their IR spectra.

Reaction of O-Ethylisourea with Sodium Ethoxide——To an EtOH solution of NaOEt, prepared from 0.7 g of Na and 20 ml of EtOH, a solution of 2.64 g of O–ethylisourea in 10 ml of EtOH was added and the mixture was refluxed for 2 hr. The reaction mixture was concentrated and yielded 1.3 g of colorless crystals (sodium cyanamide: IR ν_{max}^{Nujol} cm^{-1}: 3310, 2130, 1560). This sodium salt was characterized as the Cu salt obtained by the treatment with $CuSO_4$ solution. This Cu salt was identified with an authentic cupric cyanamide by comparison of their IR spectra.

2-Imino-2*H*-cycloheptoxazole (V)——To a suspension of 1.7 g of III in 500 ml of $CHCl_3$, 0.6 g of AcOH was added and the mixture was shaken vigorously for 10 min. The separated crystals were collected and washed with $CHCl_3$. The filtrate and washings were combined, giving a $CHCl_3$ solution of V. Its UV spectrum is shown in Fig. 3. The spectrum did not vary after standing for 2 days. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1672, 1603 (0.02 M solution). The solution was diluted with $CHCl_3$ to 525 ml in total volume and used for the following experiments. Treatment of 230 ml of the above solution of V with 20% NaOH gave 0.7 g of III. The passage of anhyd. HCl into 150 ml of the above solution of V gave 0.5 g of pale yellow needles, which changed to black from around 215°. *Anal.* Calcd. for $C_8H_7ON_2Cl$ [2–imino–2*H*–cycloheptoxazole hydrochloride (VI)]: C, 52.62; H, 3.86; N, 15.34; Cl, 19.42. Found: C, 52.31; H, 4.04; N, 15.33; Cl, 19.21. The UV spectrum is shown in Fig. 1. IR ν_{max}^{Nujol} cm^{-1}: 3077, 1686. NMR (in D_2O): 1.47 τ (multiplet); (in CF COOH): 1.14 τ (multiplet).

The passage of anhyd. HCl into the suspension of III also gave VI in 78% yield. Treatment of the aqueous solution (3 ml) of 300 mg of the hydrochloride (VI) with 40% NaOH gave 200 mg of III. Hydrobromide of V: Pale yellow needles, changing to black from around 270°. *Anal.* Calcd. for $C_8H_7ON_2Br$: C, 42.31; H, 3.11; N, 12.34; Br, 35.19. Found: C, 42.26; H, 3.19; N, 12.71; Br, 35.56. Hydriodide of V: Orange–yellow needles, mp 205° (decomp.). *Anal.* Calcd. for $C_8H_7ON_2I$: C, 35.06; H, 2.57; N, 10.22. Found: C, 34.88; H, 2.82; N, 10.14.

Sodium Salts of Substituted 2-Cyanaminotropones (VII—XIII)——The sodium salts listed in Table I were prepared from the corresponding substituted 2–methoxytropones or 2–ethoxytropone and sodium cyanamide by the same procedure as described for the preparation of III.

Substituted 2-Imino-2*H*-cycloheptoxazole (XIV—XVI)——The sodium salts of substituted 2–cyanaminotropones (XIII, VII, VIII) were treated with AcOH by the same procedure as described for V. The IR spectra of XIV, XV, and XVI are shown in Fig. 2, and the UV spectra of XV and XVI in Fig. 3.

2-Cyano-3-iminophthalimidine (XX)——i) To an EtOH solution of NaOEt, prepared from 0.13 g of Na and 20 ml of EtOH, 0.41 g of O–ethylisourea hydrochloride and 0.483 g of 2–cyano–7–methoxytropone (XIX) were added. The mixture was refluxed for 5 hr and filtered. The filtrate was evaporated and the residue was taken up in water. The aqueous solution was neutralized with dil. HCl, the separated crystals were collected, and recrystallized from EtOH to 0.12 g of white scales, mp 229—230°. *Anal.* Calcd. for $C_9H_5ON_3$: C, 63.16; H, 2.94; N, 24.55. Found: C, 62.94; H, 2.97; N, 24.34. UV λ_{max}^{EtOH} mμ (log ε): 222 (4.57), 267 (4.31), 280 (shoulder), 306 (3.96). IR ν_{max}^{Nujol} cm^{-1}: 3106, 2212, 1761, 1661.

ii) By the same procedure as described in i), 0.16 g of XX was obtained from 0.3 g of 3–cyano–2–methoxytropone (XXII).

Acid Hydrolysis of XX——A solution of 0.52 g of XX in 2 ml of conc. H_2SO_4 was heated on a water bath for 3 hr. When cooled, the reaction mixture was poured into ice water and filtered. The separated crystals were recrystallized from EtOH to white crystals of mp 233—235°, which were identified with an authentic sample of phthalimide by mixed mp determination and comparison of their IR spectra. Yield, 0.26 g. *Anal.* Calcd. for $C_8H_5O_2N$: C, 65.30; H, 3.43; N, 9.52. Found: C, 65.28; H, 3.53; N, 9.42.

8) All melting points are uncorrected.

The filtrate was extracted with ether, the extract was dried over Na_2SO_4 and evaporated to dryness. Recrystallization of the residue from water gave 0.16 g of white needles, mp 195—197° (decomp.), which were identified with an authentic sample of phthalic acid by mixed mp determination and comparison of their IR spectra. *Anal.* Calcd. for $C_8H_6O_4$: C, 57.83; H, 3.64: Found: C, 57.92; H, 3.64.

Treatment of XX with Alkali——i) A mixture of 0.2 g of XX and 5 ml of 10% NaOH was heated on a water bath for 2 hr. When cooled, the reaction mixture was made slightly acid with dil. HCl and extracted with ether. Evaporation of the solvent and recrystallization of the residue from ether gave 175 mg of white crystals, mp 195—197° (decomp.), which were identified with an authentic sample of phthalic acid by mixed mp determination and comparison of their IR spectra. *Anal.* Calcd. for $C_8H_6O_4$: C, 57.83; H, 3.64. Found: C, 57.67; H, 3.68.

ii) To 0.5 g of XX, 5 ml of 10% NaOH was added at room temperature. The separated crystals were collected and washed with EtOH to 0.3 g of white crystals, mp above 280° (Na salt of *o*-cyanobenzoylcyanamide). IR ν_{max}^{Nujol} cm^{-1}: 2212, 2183, 1698.

Neutralization of the aqueous solution of this Na salt gave the starting material, XX.

2-Benzoylimino-2*H*-cycloheptoxazole (XXV)——By the same procedure as the preparation of $CHCl_3$ solution of V, the benzene solution (400 ml) was prepared from 3.5 g of III and 1.2 g of AcOH. To this solution, 2.2 g of triethylamine and then 3.0 g of BzCl were added and the reaction mixture was stirred at room temperatures for 4 hr. The separated crystals were collected and dissolved in $CHCl_3$. The $CHCl_3$ solution was washed with water, dried over Na_2SO_4, and evaporated to dryness. Recrystallization of the residue from dioxane gave 3.15 g of cubic orange crystals, mp 172—174° (decomp.). *Anal.* Calcd. for $C_{15}H_{10}O_2N_2$: C, 71.99; H, 4.03; N, 11.20. Found: C, 71.74; H, 4.22; N, 11.23. UV λ_{max}^{EtOH} mμ (log ε): 225 (4.44), 254 (4.30), 396 (4.33). IR ν_{max}^{Nujol} cm^{-1}: 1645, 1610.

The hydrochloride (XXVI) was obtained by passing anhyd. HCl into the $CHCl_3$ solution of XXV as hygroscopic pale yellow needles, mp 166—168° (decomp.). IR ν_{max}^{Nujol} cm^{-1}: 3322, 2717, 1715, 1631, 1603.

The chloroplatinate was prepared from XXVI by the usual method. mp 224—226° (decomp.). *Anal.* Calcd. for $C_{30}H_{22}O_4N_4Cl_6Pt \cdot H_2O$: C, 38.85; H, 2.61; N, 6.04; Cl, 22.94. Found: C, 38.53; H, 2.75; N, 5.97; Cl, 23.18. IR ν_{max}^{Nujol} cm^{-1}: 3571, 3484, 1718, 1631, 1608.

N-Benzoylcarbamoyl-2-ethoxytroponeimine (XXVII)——An EtOH solution (30 ml) of 1 g of XXV was refluxed for 1 hr. The solution was concentrated and the separated crystals were collected to 0.7 g of yellow needles, mp 152—153° (decomp.). *Anal.* Calcd. for $C_{17}H_{16}O_3N_2$: C, 68.90; H, 5.44; N, 9.45. Found: C, 68.62; H, 5.43; N, 9.75. UV λ_{max}^{EtOH} mμ (log ε): 232 (4.26), 273 (4.37), 326 (shoulder), 339 (4.16), 356.5 (4.15), 372 (4.21), 391 (4.04). IR ν_{max}^{Nujol} cm^{-1}: 3086, 1631, 1618.

Deuteration of XXVII resulted in the appearance of the absorption at 2252 cm^{-1} and the disappearance of the absorption at 3086 cm^{-1} in the IR spectra. NMR (in $CDCl_3$) τ: −2.96 (1H, singlet), 1.5—1.9 (3H, multiplet), 2.5—3 (7H, multiplet), 5.32 (2H, quartet, J=7 cps), 8.52 (3H, triplet, J=7 cps).

2-(3-Benzoylureido)tropone (XXIII)——i) To 0.5 g of XXV, 5 ml of 10% HCl was added. The separated crystals were collected, washed with water, and recrystallized from EtOH to 0.4 g of white fibrous crystals, mp 206—208° (decomp.). *Anal.* Calcd. for $C_{15}H_{12}O_3N_2$: C, 67.15; H, 4.51; N, 10.44. Found: C, 67.15; H, 4.40; N, 10.55. UV λ_{max}^{EtOH} mμ (log ε): 237 (4.41), 253.5 (4.45), 331 (4.06), 346 (3.91), 363 (4.02), 380 (3.87). IR ν_{max}^{Nujol} cm^{-1}: 3226, 3106, 1706, 1695, 1631.

ii) To 50 ml of water, 200 mg of XXVI was added. The separated crystals were treated as described in i) giving 80 mg of white fibrous crystals, mp 206—208° (decomp.), undepressed on admixture with the sample obtained in i).

iii) In 5 ml of 10% HCl, 200 mg of XXVII was dissolved and the solution was allowed to stand for a few minutes. The separated crystals were treated as described in i) to give 106 mg of white fibrous crystals, mp 206—208° (decomp.), undepressed on admixture with the sample obtained in i).

Hydrolysis of XXIII——A mixture of 0.2 g of XXIII, 10 ml of 10% HCl, and 30 ml of EtOH was heated on a water bath for 2 hr. The reaction mixture was neutralized with dil. NaOH and extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated to dryness. Sublimation of the residue gave 70 mg of yellow crystals, mp 106—107°, which were identified with an authentic sample of 2-aminotropone (XXIV) by mixed mp determination and comparison of their UV and IR spectra. The aqueous layer separated from the $CHCl_3$ layer was acidified with dil. HCl and extracted with ether. The extract was dried over Na_2SO_4 and ether was evaporated to 60 mg of white crystals of mp 120—121°, which were identified with an authentic sample of BzH by mixed mp determination and comparison of their IR spectra.

2-(*p*-Toluenesulfonylimino)-2*H*-cycloheptoxazole (XXVIII)——This compound was obtained by the reaction of V prepared from 3.4 g of III and 1.2 g of AcOH with 4.2 g of *p*-toluenesulfonyl chloride in the similar procedure as described for the preparation of XXV, except that the reaction was carried out by refluxing for 7 hr. Yield, 0.28 g of yellow crystals, mp 229—230° (decomp.). *Anal.* Calcd. for $C_{15}H_{12}O_3N_2S$: C, 60.00; H, 4.03; N, 9.33. Found: C, 59.51; H, 4.01; N, 9.27. UV λ_{max}^{EtOH} mμ (log ε): 224 (4.35), 255 (4.39), 380 (4.19). IR ν_{max}^{Nujol} cm^{-1}: 1631, 1321, 1149.

2-Phenylcarbamoylimino-2*H*-cycloheptoxazole (XXIX)——To a $CHCl_3$ solution of V prepared from 3.6 g of III and 1.2 g of AcOH and 500 ml of $CHCl_3$, a solution of 2.6 g of phenyl isocyanate in 26 ml of $CHCl_3$ was

added and the reaction mixture was stirred at room temperatures for 2 hr. After concentration, the separated crystals were collected and recrystallized from dioxane to 1.6 g of orange crystals, mp 169—170° (decomp.). *Anal.* Calcd. for $C_{15}H_{11}O_2N_3$: C, 67.91; H, 4.18; N, 15.84. Found: C, 67.76: H, 4.24; N, 16.01. UV λ_{max}^{EtOH} mμ (log ε): 227.5 (4.45), 252 (4.50), 390 (4.33). IR ν_{max}^{Nujol} cm^{-1}: 3247, 1672, 1639, 1590.

2-Tropylimino-2*H*-cycloheptoxazole (XXX)——A mixture of 1.7 g of tropylium bromide, 1.1 g of triethylamine, and a $CHCl_3$ solution (300 ml) of V, prepared from 1.7 g of III and 0.6 g of AcOH, was stirred at room temperature for 1 hr. The reaction mixture was washed with water, dried over Na_2SO_4, and evaporated to dryness. Recrystallization of the residue from AcOEt gave 2.0 g of orange needles, mp 142—143°. *Anal.* Calcd. for $C_{15}H_{12}ON_2$: C, 76.25; H, 5.12; N, 11.86. Found: C, 75.91; H, 5.10; N, 11.88. UV λ_{max}^{EtOH} mμ (log ε): 228 (4.40), 252 (4.31), 380 (4.23). IR ν_{max}^{Nujol} cm^{-1}: 1675, 1603. NMR (in $CDCl_3$) τ: 2.6—3.1 (5H, multiplet), 3.25 (2H, triplet, $J=3$ cps), 3.78 (2H, multiplet), 4.55 (2H, doublet-doublet, $J=9$ cps, $J=4$ cps), 6.15 (1H, broad triplet). (in CF_3COOH): 0.6 (7H, singlet), 1.2 (6H, multiplet).

Treatment of XXX with HCl——Anhyd. HCl gas was passed through the solution of 200 mg of XXX in 20 ml of $CHCl_3$. The separated crystals were collected and washed with $CHCl_3$ containing a small amount of EtOH to 100 mg of white crystals, which were identical with VI by comparison of their IR spectra. The filtrate and washings were combined, evaporated, and the residue which was dissolved in water. To this aqueous solution, chloroplatinic acid was added and the separated crystals were collected. The crystals were identified with an authentic sample of tropylium chloroplatinate by comparison of their IR spectra.

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