Chem. Pharm. Bull.
15(5) 619~626 (1967)

UDC 547.517.07

76. Nobuo Soma, Jun-ichi Nakazawa, Taiichiro Watanabe, Yoshio Sato, and Genshun Sunagawa: Studies on Seven-membered Ring Compounds. XXII.*1 Preparation of Tropylium Ions Having Fused Heterocyclic Systems.

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

The preparation of tropylium ions having a fused oxazole, imidazole or thiazole nucleus is described.

The heating of 2-benzoylaminotropone (I) and dimethyl sulfate produced 2-phenyloxazolotropylium ion (IIIa). The disproportionation reaction of IIIa with aqueous alkali gave 2-phenyl-6*H*-cycloheptoxazole (V) and 2-phenyl-6*H*-cycloheptoxazol-6-one (IV), the structures of which were proved by the reactions shown in Chart 1 and by examination of the spectra.

2-Phenylthiazolotropylium ion (XVIIb) and 1-*p*-tolyl-2-phenylimidazolotropylium ion (XXI) were prepared, respectively, by the simple dissolution of 2-benzoylaminotroponthion (XVI) and 2-benzoylamino-N-*p*-tolyltroponeimine (XX) in dilute hydrochloric acid. Treatment of both ions XVIIb and XXI with aqueous alkali resulted in the disproportionation reaction in which the former gave XVIII and XIX and the latter XXII and XXIII.

The NMR spectra of the ions, XVII and XXI, showed the significant contribution of the tropylium ion structure of these compounds.

(Received March 29, 1966)

In recent years, the tropylium cation has been extensively studied by many investigators because of its unusual ring system. However, little attention has been paid to the tropylium ion having a fused heterocyclic system. This paper deals with the preparation of tropylium ions fused with the oxazole, thiazole or imidazole nucleus.

In a previous paper of this series,1) it was shown that the reaction of 2-aminotropone with dimethylsulfate resulted in O-methylation, giving 2-methoxytroponeimine. To extend the study, the reaction of 2-benzoylaminotropone (I) and its analogues with dimethyl sulfate were examined. The results are reported in this paper.

When I was heated in excess dimethyl sulfate, a crystalline product, m.p. 160° (decomp.), was obtained together with methyl alcohol. The infrared spectrum of this product exhibits no carbonyl absorption band. Therefore, this product, apparently, is not 2-methoxy-N-benzoyltroponeimine (II) as would be expected from the information obtained in the previous investigation.1) The analysis of this product agreed with the composition $C_{14}H_{10}ON \cdot CH_3SO_4$; furthermore, the analytical results of the chloroplatinate derived from the above product were in good agreement with the formula $C_{14}H_{10}ON \cdot (PtCl_6)_{1/2}$. From these results, the product was assumed to be 2-phenyloxazolotropylium monomethylsulfate (IIIa). To prove this assumption, the reaction of IIIa with aqueous alkali was examined, anticipating a similar disproportionaion reaction to that observed in the case of the simple tropylium ion.2) When IIIa was treated with aqueous sodium hydroxide, two kinds of crystals, $C_{14}H_9O_2N$ and $C_{14}H_{11}ON$, were obtained, and their structures were, respectively, assigned as 2-phenyl-6*H*-cycloheptoxazol-6-one (IV) and 2-phenyl-6*H*-cycloheptoxazole (V) by the following evidences. The structure of (V) was confirmed by (i) its infrared spectrum which exhibited no ν_{OH} or ν_{NH}, (ii) the isolation of 2-phenyloxazole-4,5-dicarboxylic acid (VIII) on permanganate oxidation

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[*1] Part XXI: Y. Matsumoto: Ann. Sankyo Res. Lab., **16**, 33 (1964).

[*2] 1-2-58 Hiromachi, Shinagawa-ku, Tokyo (相馬信夫, 中沢準一, 渡辺泰一郎, 佐藤良雄, 砂川玄俊).

1) N. Soma, J. Nakazawa, T. Watanabe, Y. Sato, G. Sunagawa: This Bulletin, **13**, 457 (1965).

2) T. Ikeme, T. Nozoe, H. Sugiyama: Chem. Ind., **1960**, 932; A.P. Ter Borg, R. van Helden, A.F. Bickel, W. Renold, A.S. Dreiding: Helv. Chim. Acta, **43**, 457 (1960).

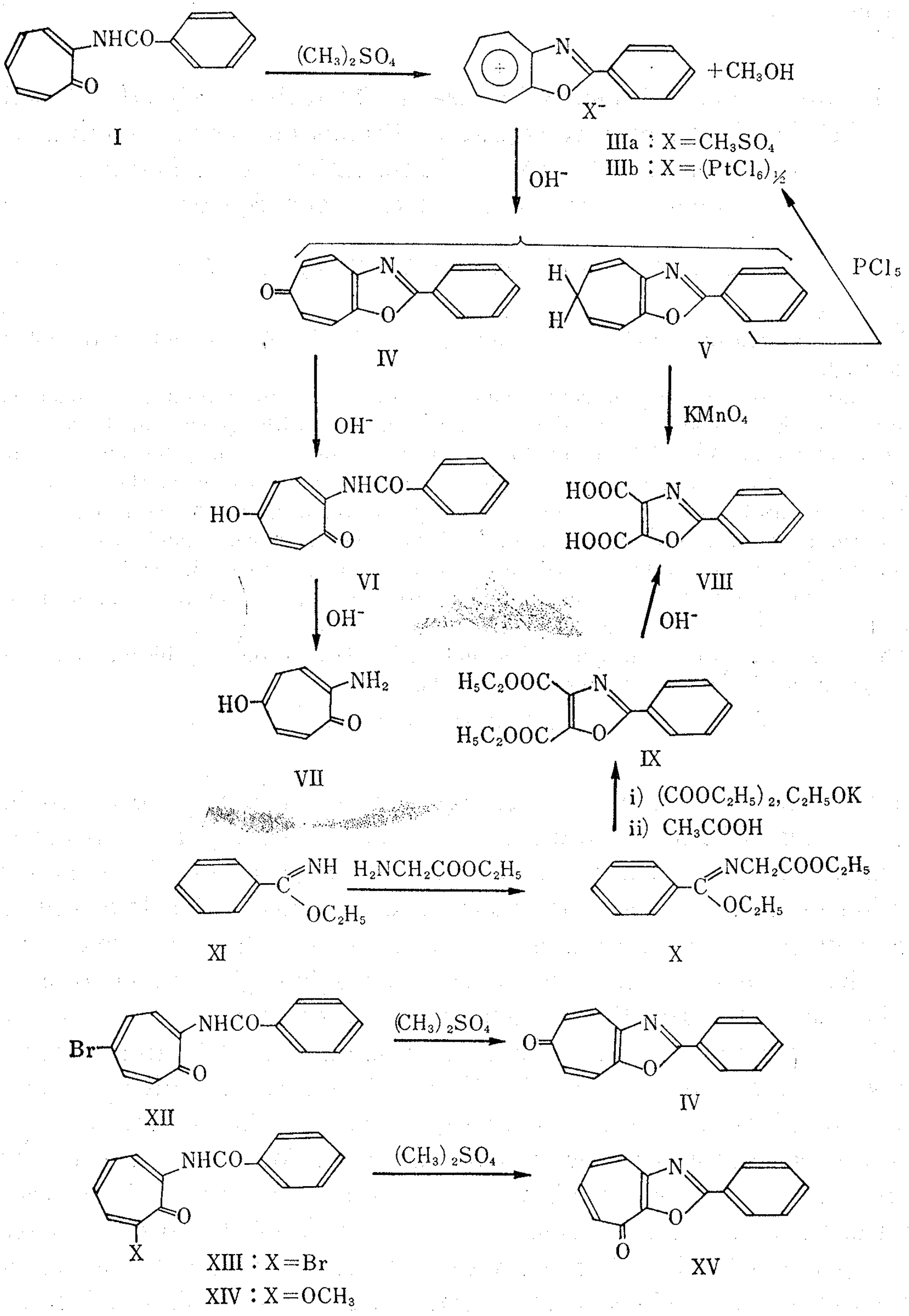

Chart 1.

(Preparation of the authentic sample of VIII is shown in Chart 1.), and (iii) the agreement of the NMR (nuclear magnetic resonance) spectrum with the proposed structure. (The assignment is shown in Fig. 1.) The structure of IV was demonstrated by (i) its infrared spectrum which showed no ν_{OH} or ν_{NH} and (ii) identification of IV with the product derived from 2-benzoylamino-5-bromotropone (XII) which will be described later. The alkaline hydrolysis of IV gave 2-amino-5-hydroxytropone (VII) via 2-benzoylamino-5-hydroxytropone (VI). The above formation of IV and V from IIIa indicates the occurrence of the expected disproportionation reaction. Furthermore, the treatment of V with phosphorus pentachloride resulted in the hydride abstraction, giving the same cation as that of IIIa. This result is analogous to the formation of the tropylium cation from 1,3,5-cycloheptatriene.3) From these results, the structure of IIIa is confirmed.

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3) D. N. Kursanov, M. E. Vol'pin: Doklady Akad. Nauk. S. S. S. R., **113**, 339 (1957)(C. A., **51**, 1457e (1957)).

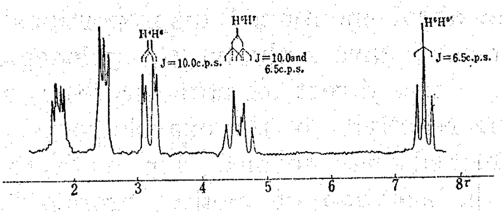


Fig. 1. NMR Spectrum of 2-Phenyl-6*H*-cycloheptoxazole (V)*[3]

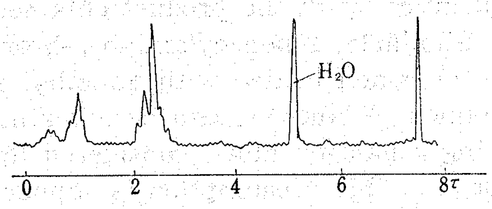


Fig. 2. NMR Spectrum of 2-Phenyl-6-*p*-tolylimidazolotropylium Chloride (XXI)

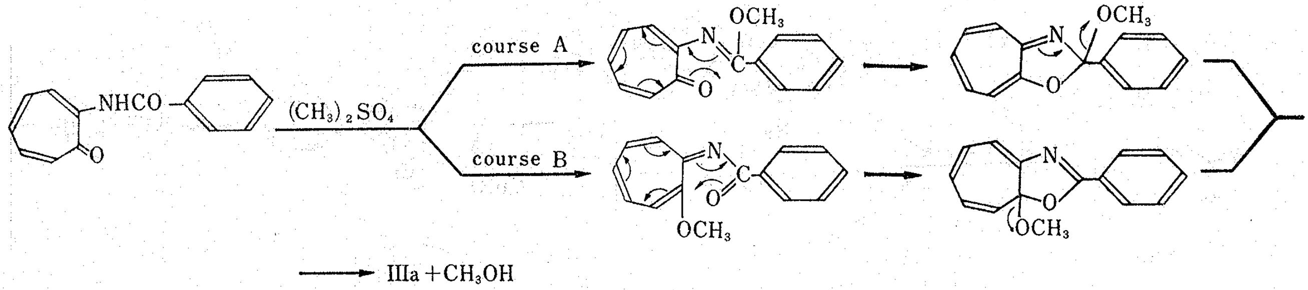
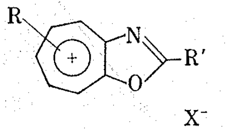


Chart 2.

Two possible courses for the formation of IIIa from I are shown in Chart 2. One arises from the methylation of the oxygen of the benzoyl carbonyl (course A in Chart 2); the other arises from that of the tropone oxygen (course B). However, the former course appears to be preferable on the basis of the formation of thiazolotropylium ion (XVIIa) from 2-benzoylaminotroponethione (XVI) by a similar reaction which will be described later.

This preparative method of oxazolotropylium ion was applied to substituted 2-benzoylaminotropones and resulted in the expected tropylium ions shown in Table I. However, in the case of the 2-benzoylaminotropones carrying a halogen atom or alkoxy group on its seven-membered ring, a different mode of reaction was observed. Namely, 2-benzoylamino-5-bromotropone (XII) did not give the expected 2-phenyl-6-bromo-oxazolotropylium monomethylsulfate but 2-phenyl-6*H*-cycloheptoxazol-6-one (IV), which

Table I. Oxazolotropylium ions



No.	R	R′	X	m.p. (°C)
1	H	C_6H_5	CH_3SO_4	160 (dec.)
2	〃	〃	$(PtCl_6)_{1/2}$	280
3	〃	*p*-C_6H_4Cl	CH_3SO_4	165 (dec.)
4	〃	*p*-$C_6H_4CH_3$	〃	160 (〃)
5	〃	*p*-$C_6H_4OCH_3$	〃	155 (〃)
6	〃	*m*-$C_6H_4CF_3$	〃	145 (〃)
7	〃	*p*-$C_6H_4NO_2$	〃	172 (〃)
8	6-C_6H_5	C_6H_5	〃	217 (〃)
9	H	β-$C_{10}H_7$	〃	161 (〃)

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*[3] The assignment of the signals due to H^4 and H^8 came from the comparison of this spectrum with that of the 8-deuterocompound which was prepared by the disproportionation reaction of the 8-deutero-2-phenyloxazolotropylium ion.

was identical with the product obtained by the above-mentioned disproportionation of IIIa, Similarly, 2-benzoylamino-7-bromotropone (XIII) gave 2-phenyl-8*H*-cycloheptoxazol-8-one (XV) when heated with dimethyl sulfate. These direct formations of the carbonyl compounds, IV and XV, can be explained by the reactivity of the oxazolotropylium ions carrying a halogen atom, considered to be intermediately formed, for methyl alcohol (Chart 3). This presumption is supported by the isolation of methyl bromide in the reaction of XIII with dimethyl sulfate. The fact that the bromotropylium ion yields

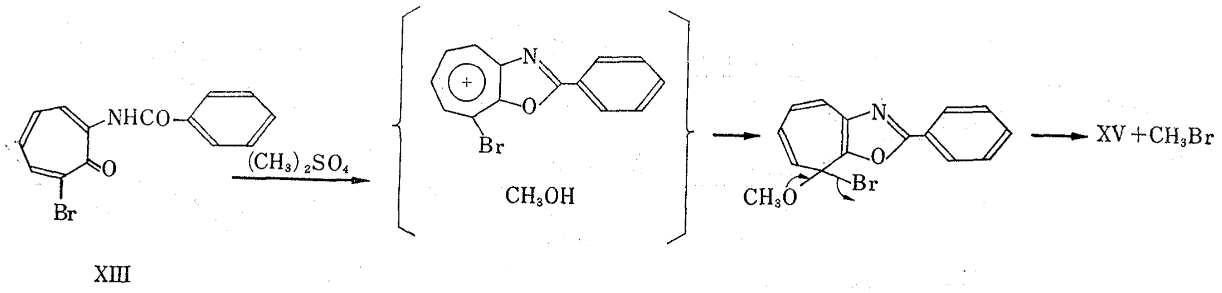

Chart 3.

tropone in the reaction with ethyl alcohol[4] also supports the above mechanism. The reaction of 2-benzoylamino-7-methoxytropone (XIV) with dimethylsulfate, similarly, gave XV.

Extending the above-described preparation of the oxazolotropylium ion, tropylium ions having fused thiazole or imidazole nucleus were prepared as follows: heating of 2-benzoylaminotroponthion (XVI) with dimethyl sulfate yielded 2-phenylthiazolotropylium monomethylsulfate (XVIIa). Furthermore, an interesting preparation of 2-phenylthiazolo-

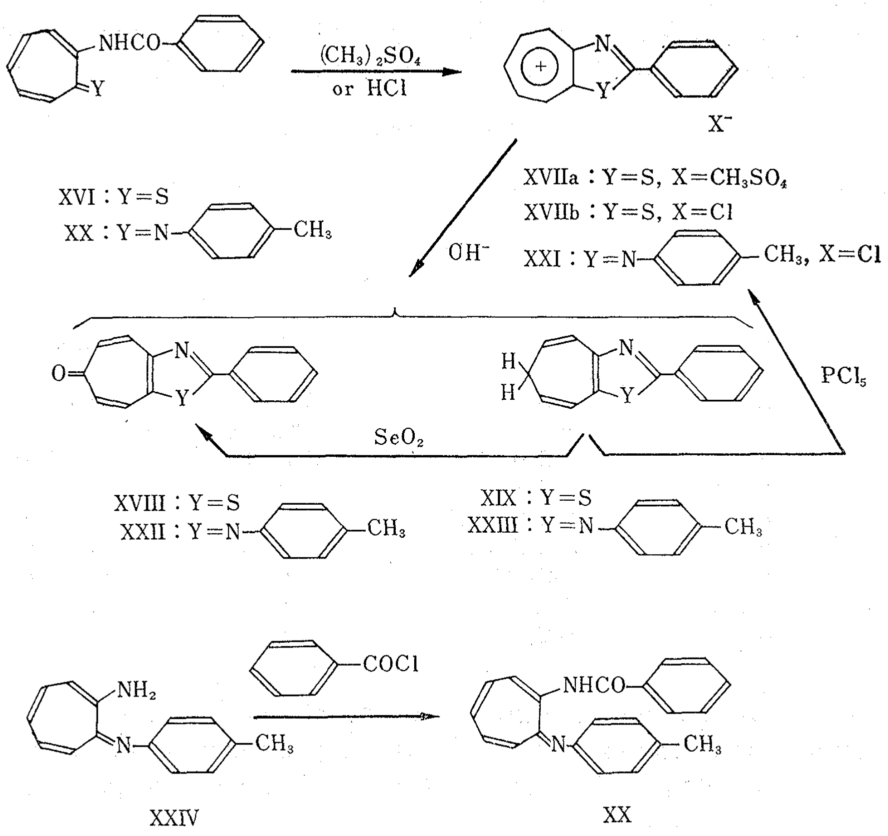

Chart 4.

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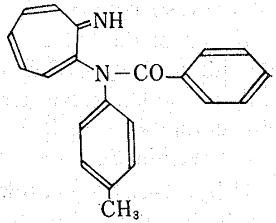
[4] H. J. Dauben, F. A. Gadecki, K. M. Hormon, D. L. Peason: J. Am. Chem. Soc., **79**, 4557 (1957).

tropylium chloride (XVIIb) from XVI was achieved by the dissolution of XVI in dilute hydrochloric acid. This was recognized by the identity of the chloroplatinate which was obtained from the hydrochloric acid solution of XVI with that derived from XVIIa. Similarly, 2-benzoylamino-N-*p*-tolyltroponeimine (XX) also gave 1-*p*-tolyl-2-phenylimidazolotropylium chloride (XXI) when dissolved in dilute hydrochloric acid. The structures of these compounds were proved by their infrared spectra in which no absorption bands due to carbonyl or amino groups were observed and by the following reactions. The treatment of both compounds, XVIIb and XXI, with aqueous alkali, resulted in the similar disproportionation reaction to that of IIIa : XVIIb gave 2-phenyl-6*H*-cycloheptathiazol-6-one (XVIII) and 2-phenyl-6*H*-cycloheptathiazole (XIX); XXI gave 1-*p*-tolyl-2-phenyl-1,6-dihydrocycloheptimidazol-6-one(XXII)and 1-*p*-tolyl-2-phenyl-1,6-dihydrocycloheptimidazole (XXIII). The treatment of XIX and XXIII with phosphorus pentachloride produced the same cations as those of XVIIa and XXI, respectively. The locations of the methylene group of XIX and XXIII were confirmed by their NMR spectra. Namely, as in the case of V, the spectrum of the seven-membered ring protons of these compounds showed three groups of signals which were assigned as follows. The spectrum consisted of a triplet in the high-field side, two sets of doublets in the low-field side, and two sets of doublet of triplets in the middle field, and these were, respectivey, assigned to the methylene protons at C-6, the protons close to the heterocycle (H^4,H^8) and the intermediate protons (H^5,H^7). (For τ-values and coupling constants, see the experimental section.) The oxidation of XIX and XXIII with selenium dioxide gave, respectively, XVIII and XXII, proving the location of the carbonyl group of these compounds.

Compound XX, the starting material of XXI, was prepared by the benzoylation of 2-amino-N-*p*-tolyltroponeimine (XXIV) in the presence of triethylamine. The assignment of structure XXV to this benzoylation product was contradicted by the fact that treatment of the product with dilute hydrochloric acid produced 2-benzoylaminotropone (I), although a poor yield, in addition to the above-mentioned XXI.



XXV

The NMR spectra of the above-described thiazolo- and imidazolotropylium ion in deuterium oxide showed further evidence for the tropylium structure of these compounds. (The determination of the spectrum of the oxazolotropylium ion, IIIa, was unsuccessful owing to the decomposition to I on standing in deuterium oxide.) In the NMR spectrum of XXI, the signals of methyl and phenyl protons appeared, respectively, at 7.41τ and near 2.4τ, whereas seven-membered ring protons did not exhibit signals at the ordinary olefine region but at $0\sim1\tau$ as shown in Fig. 2. These signals of the ring protons in a remarkably low-field corresponds to that of tropylium bromide under the same conditions (singlet at 0.44τ), indicating the tropylium ion structure of XXI. Similarly, the seven-membered ring protons of XVIIb showed absorption at $0\sim1\tau$.

The reactions of the above-described tropylium ions are now in progress.

Experimental

Oxazolotropylium Monomethylsulfates——An example is cited for 2-phenyloxazolotropylium monomethylsulfate (IIIa). Similar procedures were used in preparing the other oxazolotropylium ions shown in Table I. A mixture of 5.0 g. of 2-benzoylaminotropone (I) and 20.0 g. of dimethyl sulfate was heated at 110～120° under 30 mm. pressure, while the produced methyl alcohol and the major part of the unchanged dimethyl sulfate were gradually distilled off. (Methyl alcohol was caught in a trap cooled with dry ice-EtOH mixture and characterized as 3,5-dinitrobenzoate melting at 112°.) This required about half an hour. After cooling, benzene was added, and the crystals were filtered and washed with benzene to give 5.8 g. of pale yellow prisms. m.p. 160°(decomp.). *Anal.* Calcd. for $C_{15}H_{13}O_5NS$: C, 56.41; H, 4.10; N, 4.39; S, 10.04. Found : C, 56.26; H, 4.12; N, 4.37; S, 9.89. Chloroplatinate, m.p. >280°, was prepared by the addition of the freshly prepared aqueous solution of IIIa*[4] to an aqueous solution of chloroplatinic acid, followed by washing with acetone and benzene. *Anal.* Calcd. for $C_{14}H_{10}ONCl_3Pt_{1/2}$: C, 40.80; H, 2.45; N, 3.40; Cl, 25.80. Found : C, 40.83; H, 2.50; N, 3.46; Cl, 25.77. IR in 400~1500 cm^{-1} region (Nujol) : 1805, 1551, 1515, 1500 cm^{-1}.

Disproportionation of 2-Phenyloxazolotropylium Monomethylsulfate (IIIa) : Formation of 2-Phenyl-6*H*-cycloheptoxazol-6-one (IV) and 2-Phenyl-6*H*-cycloheptoxazole (V)——To a mixture of 80 ml. of 10% aqueous sodium hydroxide and 40 ml. of benzene was added 10.0 g. of IIIa at 10° with violent stirring. The stirring was continued for one hour. The benzene layer was separated, washed with water, and dried over Na_2SO_4. After the evaporation of benzene, the residue was treated with cyclohexane and an insoluble solid product was recrystallized from benzene giving 3.2 g. of 2-phenyl-6*H*-cycloheptoxazol-6-one (IV) melting at 158°. *Anal.* Calcd. for $C_{14}H_9O_2N$: C, 75.32; H, 4.06; N, 6.28. Found : C, 75.23; H ,4.13; N, 6.30. UV λ_{max}^{EtOH} mμ (log ε) : 261 (4.38), 270 (shoulder) (4.33), 343 (4.45). The cyclohexane soluble portion was submitted to alumina chromatography using cyclohexane as the solvent, and the crystals obtained from the eluate were recrystallized from cyclohexane to give 1.0 g. of 2-phenyl-6*H*-cycloheptoxazole (V) melting at 54°. *Anal.* Calcd. for $C_{14}H_{11}ON$: C, 80.36; H, 5.30; N, 6.69. Found : C, 80.25; H, 5.25; N, 6.70. UV λ_{max}^{EtOH} mμ (log ε) : 240 (4.14), 309 (4.20). The NMR spectrum is shown in Fig. 1.

2-Phenyloxazole-4,5-dicarboxylic Acid (VIII)——i) From 2-phenyl-6*H*-cycloheptoxazole (V) : To a solution of 2.5 g. of V in 200 ml. of acetone, 11.0 g. of solid potassium permanganate was added at room temperature over 3 hr. After being stirred for 10 hr., the reaction product was filtered, washed with acetone, and added into 100 ml. of 10% HCl. The acidic solution was saturated with SO_2. A small amount of the insoluble product was filtered off, and the filtrate was adjusted to pH 3 with aqueous NaOH, and allowed to stand for 3 days at room temperatures. The separated crystals were filtered and treated with aqueous $NaHCO_3$. After removal of the insoluble product, the solution was adjusted to pH 2.0 with 10% HCl to give 0.2 g. of white crystals melting at 276° (decomp.) (monosodium 2-phenyloxazole-4,5-dicarboxylate hydrate). To these crystals, 5 ml. of 10% HCl and 80 ml. of EtOAc were added, and the mixture was stirred for 40 minutes at room temperature. The EtOAc layer was separated, and dried over Na_2SO_4. After removal of EtOAc, the residue was recrystallized from EtOAc to give 0.15 g. of white crystals. m.p. 215° (decomp.). *Anal.* Calcd. for $C_{11}H_7O_5N$: C, 56.66; H, 3.03; N, 6.01. Found : C, 56.61; H, 3.01; N, 6.12.

ii) From diethyl 2-phenyloxazole-4,5-dicarboxylate (IX) : A mixture of 1.5 g. of IX and 1.2 g. of KOH in 20 ml. of 75% EtOH was warmed at 40°. After removal of EtOH below 40°, 15 ml. of 10% HCl and 60 ml. of EtOAc were added to the residue, and the mixture was treated as described in (i) giving 0.5 g. of white crystals, m.p. 215° (decomp.), which were identical with the product obtained in (i) by mixed melting point determination and comparison of IR (infrared) spectra.

Ethyl 1-Ethoxy-1-phenylmethylideneaminoacetate (X)——To a suspension of 18.5 g. of benziminoethylether hydrochloride in 100 ml. of ether, a concentrated aqueous solution of 16.0 g. of K_2CO_3 was added at 5°. The mixture was stirred for 10 minutes, and the ether layer was separated. To this ethereal solution, 14 g. of ethyl glycinate hydrochloride and 8 ml. of water were added, and the mixture was stirred vigorously for 1 hr. The ether layer was seperated and dried over Na_2SO_4. After the ether was evaporated, the distillation of the residue under reduced pressure gave 6.8 g. of a colorless liquid. b.p.$_{0.06}$ 115~123°. *Anal.* Calcd. for $C_{13}H_{17}O_3N$: C, 66.36; H, 7.28; N, 5.95; OC_2H_5, 38.30. Found : C, 66.04; H, 7.16; N, 6.02; OC_2H_5 (Zeisel's method), 38.12.

Diethyl 2-Phenyloxazole-4,5-dicarboxylate (IX)——In a mixture of 5 ml. of anhydrous EtOH and 20 ml. of anhydrous ether, 1.15 g. of metallic potassium was dissolved. To this solution, 150 ml. of ether and then ethereal solution of 6.8 g. of X and 4.3 g. of ethyl oxalate were added at −10°, and the mixture was allowed to stand overnight in an ice box. The ether was evaporated, and the residue was poured into 25 ml. of hot AcOH. After cooling, 150 ml. of water was added, and the mixture was neutralized with aqueous $NaHCO_3$. The separated crystals were filtered and recrystallized from cyclohexane to give 3.0 g. of white needles. m.p. 59°. *Anal.* Calcd. for $C_{15}H_{15}O_5N$: C, 62.28; H, 5.23; N, 4.84. Found : C, 62.04; H, 5.12; N, 4.84.

2-Benzoylamino-5-hydroxytropone (VI)——A mixture of 1.1 g. of 2-phenyl-6*H*-cycloheptoxazol-6-one (IV) and 1.0 g. of NaOH in 20 ml. of EtOH was heated under reflux for 1 hr. After removal of EtOH under reduced pressure, the mixture was acidified with 10% HCl. The separated crystals were filtered and recrystallized from EtOH to give 0.1 g. of white needles melting at 240°. *Anal.* Calcd. for $C_{14}H_{11}O_3N$: C, 69.70; H, 4.59; N, 5.80. Found : C, 69.40; H, 4.62; N, 6.03. UV λ_{max}^{EtOH} mμ (log ε) : 231 (4.32), 254 (4.34), 383 (4.27). IR ν_{max}^{Nujol} cm^{-1} : 3350 (NH), 2500~2800 (OH), 1690 (C=O).

2-Amino-5-hydroxytropone (VII)——A mixture of 0.8 g. of VI and 1.0 g. of NaOH in 20 ml. of 50% EtOH was heated under reflux for 2 hr. The mixture was neutralized with 10% HCl, and evaporated to dryness. The residue, after being washed with hot cyclohexane, was extracted with hot EtOH. The EtOH extract was cooled, and the separated crystals were filtered and recrystallized from EtOH to give 0.2 g. of

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*[4] Aqueous solution of IIIa seperated I when allowed to stand for a few minutes.

white needles. m.p. 205°(decomp.).[*5] *Anal.* Calcd. for $C_7H_7O_2N$: C, 61.31; H, 5.15; N, 10.21. Found : C, 61.17; H, 5.25; N, 10.42. UV λ_{max}^{EtOH} mμ (log ε) : 239 (4.37), 350 (4.16), 422 (4.05). IR ν_{max}^{Nujol} cm^{-1} : 3421, 3290, 3200~2250.

Reaction of 2-Phenyl-6*H*-cycloheptoxazole (V) with Phosphorus Pentachloride : Formation of 2-Phenyloxazolotropylium Ion——To a solution of 0.5 g. of PCl_5 in 20 ml. of CCl_4, a solution of 0.5 g. of V in the same solvent was added with stirring at room temperature. The separated solid mass was filtered, washed with CCl_4, dried in vacuo, and added to an aqueous solution of chloroplatinic acid. After being stirred for 30 minutes, the resultant crystals were filtered, and washed with EtOH and then benzene to give 0.6 g. of yellow prisms, m.p.>280°, which were identified with the chloroplatinate derived from IIIa by the comparison of IR spectra.

2-Phenyl-6*H*-cycloheptoxazol-6-one (IV) from 2-Benzoylamino-5-bromotropone (XII)——A mixture of 3.0 g. of XII and 15.0 g. of dimethyl sulfate was heated at 130° for 3 hr. Dimethyl sulfate was distilled off under reduced pressure, and water was added to the residue. The separated crystals were filtered and recrystallized from EtOH to give 1.6 g. of pale yellow prisms, m.p. 158°, which were identified with IV obtained by the disproportionation of IIIa by mixed melting point determination. In another experiment, the mixture was heated under reduced pressure as in the case of the preparation of IIIa, producing the same product IV.

2-Phenyl-8*H*-cycloheptoxazol-8-one (XV)——i) from 2-benzoylamino-7-bromotropone (XIII) : A mixture of 5.0 g. of XIII and 20.0 g. of dimethyl sulfate was heated at 140° for 1 hr. The reaction mixture was concentrated under reduced pressure, and benzene was added to the residue. The separated crystals were filtered and recrystallized from EtOH to give 2.8 g. of colorless prisms melting at 158°. *Anal.* Calcd. for $C_{14}H_9O_2N$: C, 75.32; H, 4.06; N, 6.28. Found : C, 75.33; H, 4.11; N, 6.30. Another experiment was carried out in the same manner as the above except that the heat was applied under 100 mm. pressure, and the resultant low boiling point product was collected in a trap cooled with a dry ice-EtOH mixture. The heavy oil collected was submitted to gas-chromatography (stationary phase : acetonyl acetone; column temp. : 28°) and showed the same retention time as that of authentic methyl bromide. On the other hand, the trial detection of methyl alcohol was unsuccessful in another submission to gas-chromatography(stationary phase : 30% D.O.P.; column temp. : 60°).

ii) From 2-benzoylamino-7-methoxytropone (XIV) : A mixture of 2.1 g. of XIV and 10.0 g. of dimethyl sulfate was heated at 120° for 30 minutes. The reaction mixture was treated as described in (i) giving 1.0 g. of colorless prisms, m.p. 158°, which were identical with the product obtained in (i) by mixed melting point determination.

2-Phenylthiazolotropylium Ions——i) From 2-benzoylaminotroponthione (XVI). a) by the reaction with dimethylsulfate : A mixture of 7.0 g. of XVI and 30.0 g. of dimethyl sulfate was heated at 130~140° under 25 mm. pressure for 40 minutes. After evaporation of dimethyl sulfate to dryness at a pressure of about 5 mm., the residue was washed with benzene to give 4.7 g. of hydroscopic brown crystals (2-phenylthiazolotropylium monomethylsulfate (XVIIa)). The chloroplatinate was prepared by the usual method as orange crystals. m.p.>260°. *Anal.* Calcd. for $C_{14}H_{10}NSCl_3Pt_{1/2}$: C, 39.26; H, 2.35; N, 3.27. Found : C, 38.94; H, 2.37; N, 3.22. IR ν_{max}^{Nujol} cm^{-1} : no absorption at 1650~2500 cm^{-1}. b) by the reaction with HCl : A suspension of 2.4 g. of XVI in 20 ml. of 10% HCl was warmed at about 60° for 15 minutes. After being filtered from a small amount of insoluble material, the filtrate was concentrated to dryness below 60° under reduced pressure to give 1.4 g. of pale yellow crystals melting at 110°(2-phenylthiazolotropylium chloride (XVIIb)). IR ν_{max}^{Nujol} cm^{-1} : no absorption at 1650~2500 cm^{-1}. The chloroplatinate was prepared by the usual method and recrystallized from 10% HCl as yellow crystals, m.p. >280°, and identical with the chloroplatinate obtained in a) by the comparison of IR spectra.

ii) From 2-phenyl-6*H*-cycloheptathiazole (XIX) : A solution of 0.4 g. of PCl_5 in 20 ml. of CCl_4 was added to a solution of 0.3 g. of XIX in the same solvent, and the mixture was stirred for 3 hr. at room temperature. The separated crystals were filtered and dissolved in water. To this aqueous solution was added an aqueous solution of chloroplatinic acid to give the chloroplatinate, m.p. >280°, which was identical with the chloroplatinate obtained in (i) by the comparison of IR spectra.

1-*p*-Tolyl-2-phenylimidazolotropylium Ion——i) From 2-benzoylamino-N-*p*-tolyltroponeimine (XX) : In 20.0 ml. of 20% ethanolic hydrochloric acid was dissolved 3.0 g. of XX, and the mixture was concentrated below 35° under reduced pressure. The residue, after being washed with benzene, solidified on standing. The resultant solid product was dissolved in a small amount of ethanol and benzene was added to give 2.5 g. of 1-*p*-tolyl-2-phenylimidazolotropylium chloride (XXI) as hydroscopic. white crystals. m.p. 130°(decomp.). The NMR spectrum is shown in Fig. 2. IR ν_{max}^{Nujol} cm^{-1} : no absorption at 1650~2500 cm^{-1}. The fluoroborate was prepared by the usual method from an aqueous solution of XXI as white needles melting at 195°. *Anal.* Calcd. for $C_{21}H_{17}N_2BF_4$: C, 65.65; H, 4.46; N, 7.29. Found : C, 65.44; H, 4.65; N, 7.60. IR ν_{max}^{Nujol} cm^{-1} : no absorption at 1650~2500 cm^{-1}. The chloroplatinate was prepared in the same manner. m.p. 226°(decomp.).

[*5] T. Nozoe and his co-workers had previously reported that hydrogenation of the azo-coupling product of 4-hydroxytropone gave an aminoproduct, m.p. 191°. However, they made no mention of the location of its amino group. (T. Nozoe, T. Mukai, Y. Ikegami, T. Toda : Chem. Ind., **1955**, 66.)

Anal. Calcd. for $C_{21}H_{17}N_2Cl_3Pt_{1/2}$: C, 50.31; H, 3.42; N, 5.59; Pt, 19.47. Found : C, 50.28; H, 3.38; N, 5.61; Pt, 19.48. When the above reaction was worked up by dissolution of XX in 20 ml. of 10% hydrochloric acid, yellow crystals were separated. After filtration, the filtrate gave the same fluoroborate, m.p. 195°, as the above. The above-described yellow crystals were poured into water and stirred. The resulted crystals were filtered and no depression of melting point was observed on admixture with authentic sample of 2-benzoylaminotropone.

ii) From 2-phenyl-1-*p*-tolyl-1,6-dihydrocycloheptimidazole (XXIII) : To a solution of 0.5 g. of PCl_5 in 20 ml. of CCl_4, a solution of 0.5 g. of XXIII in 5 ml. of the same solvent was added and the mixture was stirred for 4 hr. and allowed to stand overnight. The separated yellow crystals were filtered and stirred in water. After removal of a small amount of an insoluble product by filtration, 20% aqueous fluoroboric acid was added to the filtrate. The separated crystals were filtered and recrystallized from EtOH to give 0.3 g. of white needles, m.p. 195°, which were identified with the fluoroborate obtained in (i) by mixed melting point determination and the comparison of IR spectra.

Disproportionation of 2-Phenylthiazolotropylium Chloride (XVIIb) : Formation of 2-Phenyl-6*H*-cycloheptathiazol-6-one (XVIII) and 2-Phenyl-6*H*-cycloheptathiazole (XIX)——To an aqueous solution of 1.4 g. of XVIIb was added a saturated aqueous solution of $NaHCO_3$, and the mixture was extracted with benzene. After evaporation of the benzene, the residue was submitted to alumina chromatography using benzene and then chloroform as the solvents. The benzene eluate, after recrystallization from benzene-cyclohexane, gave 0.4 g. of XIX as yellow crystals melting at 73°. *Anal.* Calcd. for $C_{14}H_{11}NS$: C, 74.62; H, 4.92; N, 6.21; S, 14.23. Found : C, 74.25; H, 4.87; N, 6.21; S, 14.34. UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (log ε) : 247 (4.19), 328 (4.24). NMR τ : 7.52 (2H, t, J=7.0 c.p.s.), 4.57 (1H, t-d, J=7.0 and 10.0 c.p.s.), 4.44 (1H, t-d, J=7.0 and 10.0 c.p.s.), 3.35 (1H, d, J=10.0 c.p.s.), 3.05 (1H, d, J=10.0 c.p.s.), 2.69 (3H, m), 2.09 (2H, m). The chloroform eluate, after recrystallization from EtOH, gave 0.6 g. of XVIII as yellow crystals melting at 149~150°. *Anal.* Calcd. for $C_{14}H_9ONS$: C, 70.27; H, 3.79; N, 5.85; S, 13.40. Found : C, 70.09; H, 3.90; N, 5.83; S, 13.50. UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (log ε) : 269 (4.56), 346 (4.39).

Disproportionation of 1-*p*-Tolyl-2-phenylimidazolotryplium Chloride (XXI) : Formation of 1-*p*-Tolyl-2-phenyl-1,6-dihydrocycloheptimidazol-6-one (XXII) and 1-*p*-Tolyl-2-phenyl-1,6-dihydrocycloheptimidazole (XXIII)——An aqueous solution of 0.7 g. of XXI was neutralized with aqueous $NaHCO_3$. The separated solid product was filtered and submitted to alumina chromatography using benzene and then chloroform as the solvents. Benzene eluate, after recrystallization from cyclohexane, gave 0.3 g. of XXIII as white needles melting at 122°. *Anal.* Calcd. for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found : C, 84.60; H, 6.15; N, 9.39. UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (log ε) : 306 (4.13). NMR τ : 7.48 (2H, t, J=6.5 c.p.s.), 4.72 (1H, t-d, J=6.5 and 10.0 c.p.s.), 4.60 (1H, t-d, J=6.5 and 10.0 c.p.s.), 3.87 (1H, d, J=10.0 c.p.s.), 3.15 (1H, d, J=10.0 c.p.s.), 2.48~3.18 (10H). The chloroform eluate, after recrystallization from EtOH, gave 0.3 g. of XXII as white crystals melting at 181°. *Anal.* Calcd. for $C_{21}H_{16}ON_2$: C, 80.75; H, 5.16; N, 8.95. Found : C, 80.41; H, 5.26; N, 8.86. UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (log ε) : 252 (4.48), 349 (4.47).

Oxidation of 2-Phenyl-6*H*-cycloheptathiazole (XIX) : Formation of 2-Phenyl-6*H*-cycloheptathiazol-6-one (XVIII)——A mixture of 500 mg. of XIX and 296 mg. of SeO_2 in 15 ml. of 95% dioxane was heated under reflux for 3 hr. After being filtered from the separated metallic selenium, the dioxane was evaporated to dryness and the residue was extracted with benzene. The benzene was evaporated to dryness, and the residue was submitted to alumina chromatography with ether as solvent giving 190 mg. of yellow crystals. Recrystallization from EtOH gave yellow prisms, m.p. 150°, undepressed on admixture with XVIII obtained by the disproportionation reaction of XVIIb.

Oxidation of 1-*p*-Tolyl-2-phenyl-1,6-dihydrocycloheptimidazole (XXIII) : Formation of 1-*p*-Tolyl-2-phenyl-1,6-dihydrocycloheptimidazol-6-one (XXII)——To a solution of 226 mg. of SeO_2 in 3.5 ml. of 85% dioxane was added a solution of 507 mg. of XXIII in 15 ml. of dioxane and the mixture was refluxed for 3 hr. The separated metallic selenium was removed by filtration, and the dioxane was distilled off. After addition of 30 ml. of water, the mixture was extracted with chloroform. The chloroform was evaporated to dryness, and the residual dark red oil was chromatographed on alumina with ether as solvent. The resulting brown crystals (301 mg.) were recrystallized from ether to give pale brown crystals, m.p. 181°, which were not depressed on admixture with product XXII obtained by the disproportionation reaction of XXI. *Anal.* Calcd. for $C_{21}H_{16}ON_2$: C, 80.75; H, 5.16; N, 8.97. Found : C, 80.34; H, 5.19; N, 8.89.

2-Benzoylamino-N-*p*-tolyltroponeimine(XX)——To a solution of 1.3 g. of 2-amino-N-*p*-tolyltroponeimine (XXIV) and 2.0 g. of triethylamine in 20 ml. of benzene was added dropwise 1.0 g. of benzoylchloride with icewater cooling. The mixture was allowed to stand overnight, and filtered. The benzene and unchanged triethylamine were removed under reduced pressure below 30°, and the residue was recrystallized from cyclohexane to give 1.0 g. of orange needles melting at 136°. *Anal.* Calcd. for $C_{21}H_{18}ON_2$: C, 80.23; H, 5.77; N, 8.91. Found : C, 80.37; H, 5.90; N, 8.74. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1} : 3200 (NH), 1681 (C=O).

The authors are indebted to Prof. T. Nozoe and Y. Kitahara of Tohoku University and Prof. S. Uyeo of Kyoto University for guidance and encouragement throughout the course of this work. The authors are also indebted to the members of the Section of Physical Chemistry for the elemental analyses and determinations of absorption spectra