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# 77. Nobuo Soma, Jun-ichi Nakazawa, Taiichiro Watanabe, Yoshio Sato, and Genshun Sunagawa : Studies on Seven-membered Ring Compounds. XXIII.*1 Reactions of Tropylium Ions Having Fused Heterocyclic System with Various Amines.

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Reactions of tropylium ions having a fused heterocyclic system with various amines were examined. Reaction of 2-phenyloxazolotropylium monomethylsulfate (I) and 2-phenylthiazotropylium chloride (XXIV) with dimethylamine produced 2-phenyl-6-dimethylamino-6*H*-cycloheptoxazole (II) and 6-dimethylamino-2-phenyl-6*H*-cycloheptathiazole (XXV), respectively. Regarding the reaction with *p*-toluidine, both I and 1-*p*-tolyl-2-phenylimidazolotropylium chloride (XXVI) gave 1-*p*-tolyl-2-phenyl-1,6-dihydrocycloheptimidazole (VI) and 1-*p*-tolyl-2-phenyl-6-*p*-tolylimino-1,6-dihydrocycloheptimidazole (VII). Reaction of I with N-methylaniline produced 2-phenyl-6-*p*-methylaminophenyl-6*H*-cycloheptoxazole (XIX) and 2-phenyl-4-*p*-methylaminophenyl-4*H*-cycloheptoxazole (XX).

From these results, it is concluded that the tropylium ions condensing a heterocycle has a priority for amination at C-6.

(Received March 29, 1966)

Some tropylium ions having a condensed oxazole, thiazole or imidazole nucleus were prepared in our preceeding paper.*1 This paper examined the reaction of these tropylium ions with various amines.

First, the reactions of 2-phenyloxazolotropylium monomethylsulfate (I) were examined. When I was allowed to react with dimethylamine in benzene, a good yield of 2-phenyl-6-dimethylamino-6*H*-cycloheptoxazole (II) was obtained. Proof of the structure of II is given by the analytical results, the similarity of the ultraviolet spectrum to that of 2-phenyl-6*H*-cycloheptoxazole, and absence of absorption bands due to carbonyl, hydroxyl or amino groups in the infrared spectrum. Furthermore, the retention of the oxazole ring in II was proved by the isolation of 2-phenyloxazole-4,5-dicarboxylic acid (III) on oxidation by potassium permanganate. The locations of the dimethylamino group and double bonds on the seven-membered ring were presumed by the examination of the NMR (nuclear magnetic resonance) spectrum which was assigned as shown in Fig. 1. To obtain the more definitive evidence on the location of the dimethylamino group, the 6-deutero-compound was prepared by the reaction of 6-deutero-2-phenyloxazolotropylium monomethylsulfate with dimethylamine and its NMR spectrum was compared with that of II. Thus, by this deuteration, the expected disappearance of a triplet of triplets centered at 7.59$\tau$ and simplification of quartets into doublets was recognized as shown in Fig. 2. Hydrogenation of II resulted in the easy uptake of three moles of hydrogen giving dimethylamine and a product, $C_{14}H_{15}ON$, which is presumed to be 2-phenyl-5,6,7,8-tetrahydro-4*H*-cycloheptoxazole (IV).

The reaction of I with methyl amine afforded a product, $C_{29}H_{23}O_2N_3$, which showed a similar ultraviolet spectrum to that of II. This analytical result indicates that two moles of I reacted with one mole of methylamine. On the basis of the results obtained in the above-mentioned reaction with dimethylamine, this product is assumed to be N,N-bis(2-phenyl-6*H*-cycloheptoxazol-6-yl)methylamine (V).

The reaction of I with arylamine proceeded differently from that described for the above alkylamines. Regarding the reaction of I with *p*-toluidine, two kinds of

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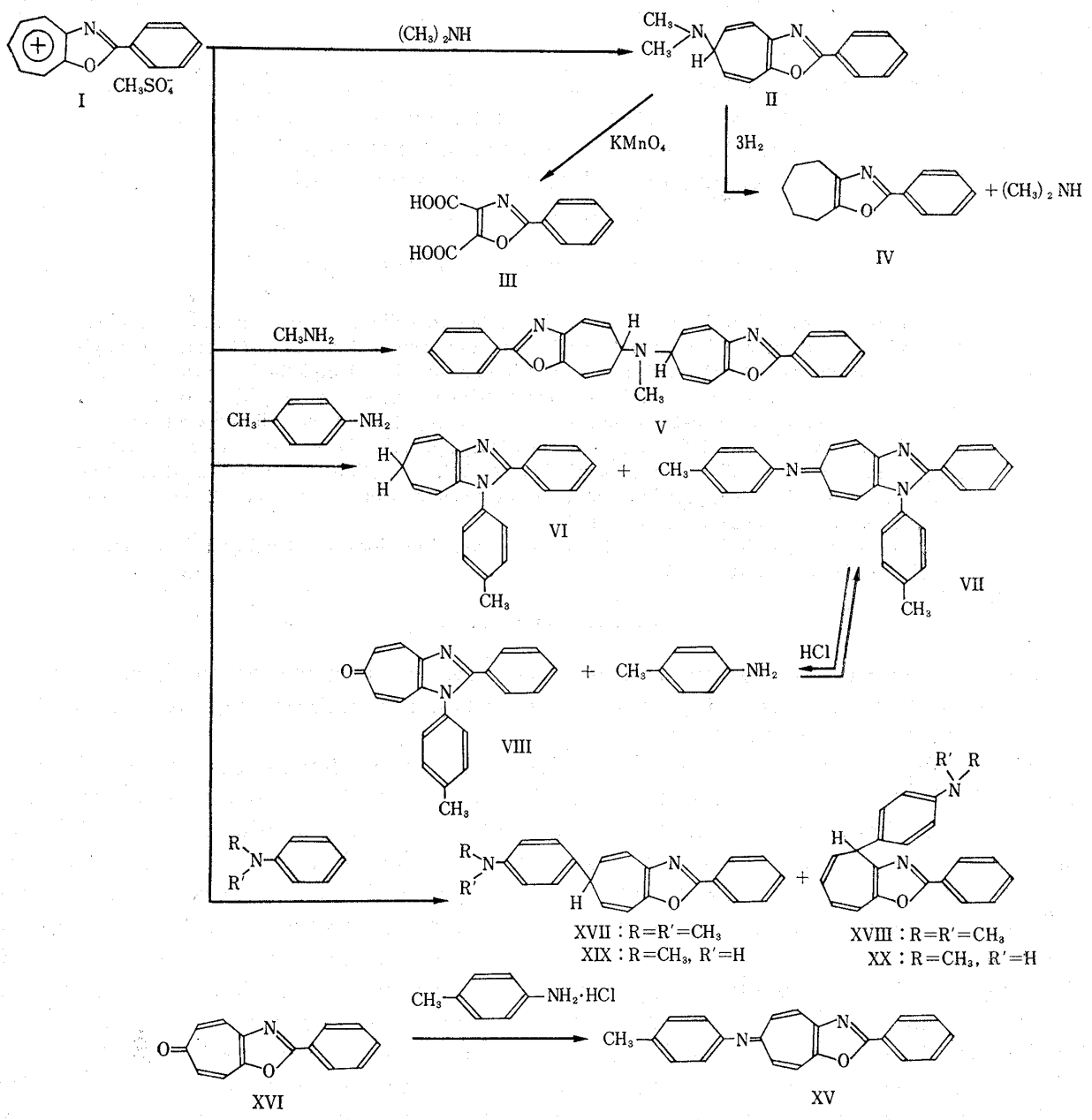


Chart 1.

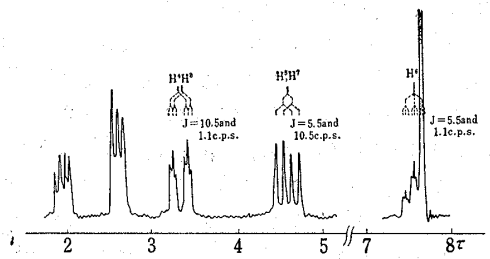


Fig. 1. NMR Spectrum of 6-Dimethylamino-2-phenyl-6*H*-cycloheptoxazole (II)

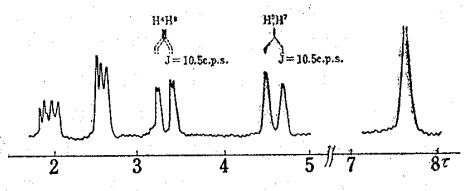


Fig. 2. NMR Spectrum of 6-Deuterio-6-dimethylamino-2-phenyl-6*H*-cycloheptoxazole

products, m.p. 122° and m.p. 181°, were obtained. The former product was proved to be 1-*p*-tolyl-2-phenyl-1,6-dihydrocycloheptimidazole (VI) by the comparison with an authentic sample.*1 The latter product, whose analytical values agreed with $C_{26}H_{23}N_3$,

was identical with the product obtained by the reaction of 1-*p*-tolyl-2-phenyl-1,6-dihydrocycloheptimidazol-6-one (Ⅷ) with *p*-toluidine. Furthermore, the acidic hydrolysis of the product gave Ⅷ and *p*-toluidine. Therefore, the latter product, m.p. 181°, is apparently 1-*p*-tolyl-2-phenyl-6-*p*-tolylimino-1,6-dihydrocycloheptimidazole (Ⅶ). The above reaction with *p*-toluidine is presumed to proceed as shown in Chart 2. Namely, the isolation of Ⅵ and Ⅶ is understood by the intermediate formation of an imidazolotropylium ion (Ⅻ) and its successive reaction with *p*-toluidine as shown in Chart 2.

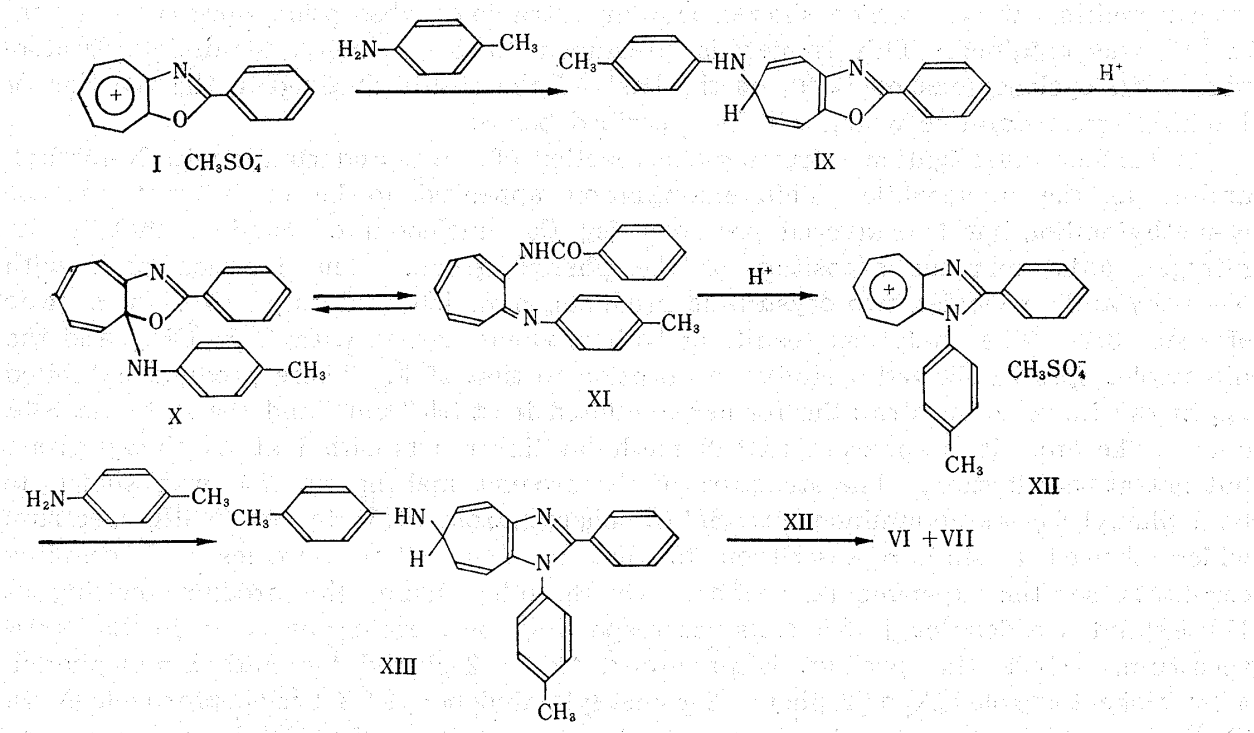


Chart 2. A Possible Route for the Formation of Ⅵ and Ⅶ from I

This presumption is supported by the reaction of 1-*p*-tolyl-2-phenylimidazolotropylium chloride (XXⅥ) with *p*-toluidine to give Ⅵ and Ⅶ which will be described later. The formation of 1-*p*-tolyl-2-phenylimidazolotropylium chloride from Ⅺ by proton*[1] also supports above presumption. Regarding the formation of Ⅺ, the adoption of an intermediate Ⅸ is considered to be more preferable than direct formation from I, on the basis of the priority for amination at C-6 of I observed in the above-described reaction with dimethylamine, and the experiment that 2-phenyl-6-amino-6*H*-cycloheptoxazole derivatives yield Ⅻ by the reaction with *p*-toluidine which will be fully reported in a later paper. In addition to the above route shown in Chart 2, some other routes can be postulated for the formation of Ⅵ and Ⅶ. One of these is the route in which the reaction of I with *p*-toluidine to give 2-phenyl-6*H*-cycloheptoxazole (XⅣ) and 2-phenyl-6-*p*-tolylimino-6*H*-cycloheptoxazole (XV), and the consecutive reconstruction of the oxazole ring of these compounds into the imidazole ring by *p*-toluidine to give the final products, Ⅵ and Ⅶ, are included. However, this route was rejected because experiment showed that the attempted reactions of either XIV or XV with *p*-toluidine under the same conditions resulted in the recovery of the materials. This experiment also excluded the other possible routes in which the reactions between I and XIII or between Ⅸ and Ⅻ were included. Compound XV which was used in the above reactions was prepared by the reaction of 2-phenyl-6*H*-cycloheptoxazol-6-one (XⅥ) with *p*-toluidine hydrochloride.

Next, the reaction of I with N,N-dimethylaniline was examined, since the ability of N,N-dimethylaniline as a nucleophile at its *p*-position is well known. This reaction

yielded a crystalline product, $C_{22}H_{20}ON_2$, which showed no $\nu_{C=O}$ or $\nu_{NH}$ in the infrared spectrum and had a similar ultraviolet absorption spectrum to that of II. The NMR spectrum of the seven-membered ring protons of this product showed a similar situation to that of II, although the overlap of the signals in the lower field with those of phenyl protons was observed. (For $\tau$-values and coupling constants, see the experimental section.) Accordingly, it is apparent that the product is 2-phenyl-6-*p*-dimethylaminophenyl-6*H*-cycloheptoxazole (XVII). In addition to this product, a small amount of an isomer melting at 142°, which showed similar ultraviolet absorption spectrum to that of XVII, was obtained. This isomer is presumed to be 2-phenyl-4-*p*-dimethylaminophenyl-4*H*-cycloheptoxazole (XVIII), on the basis of the result obtained in the reaction of I with N-methylaniline which will be described below.

A further investigation regarding the reaction of I was undertaken with N-methylaniline as the nucleophile. This examination appeared to be of interest because N-methylaniline has two favored positions for the nucleophilic reaction, that is, its nitrogen atom and the *p*-position of the phenyl group. The reaction of I with N-methylaniline yielded two crystalline products, m.p. 150° and m.p. 118°, in a ratio of about 3:2. The analytical results of both products agreed with $C_{21}H_{18}ON_2$, and the ultraviolet spectra showed a similar absorption to that of II. These products exhibited $\nu_{NH}$ in the infrared spectra : the former exhibited it at 3463 $cm^{-1}$ and the latter at 3438 $cm^{-1}$. Therefore it is apparent that N-methylaniline reacts with I at its phenyl group but not at its nitrogen. The structure of the product melting at 150° was shown to be 2-phenyl-6-*p*-methylaminophenyl-6*H*-cycloheptoxazole (XIX) by its NMR spectrum which showed a similar absorption to that of XVII. (For $\tau$-values and coupling constants, see the experimental section.) On the other hand, the product melting at 118° exhibited a doublet (J=6.5 c.p.s.) corresponding one proton at 5.10$\tau$ in its NMR spectrum. Hence, this product is presumed to be 2-phenyl-4-*p*-methylaminophenyl-4*H*-cycloheptoxazole (XX) or 2-phenyl-8-*p*-methylaminophenyl-8*H*-cycloheptoxazole (XXI). To decide which structure is assignable to the product, the NMR spectrum was compared with that of the 4-deutero-product which was derived from 4-deutero-2-phenyloxazolotropylium monomethylsulfate by the same reaction, and a substantial disappearance of this doublet in the spectrum of 4-deutero-product was recognized. Therefore, it is apparent that the above product melting at 118° is not XXI but XX. More specifically, the assignment of the structure, 2-phenyl-3a-*p*-methylaminophenyl-3a*H*-cycloheptimidazole (XXII) or 2-phenyl-8a-*p*-methylaminophenyl-8a*H*-cycloheptimidazole (XXIII) was rejected because the position of above-mentioned doublet is too high and

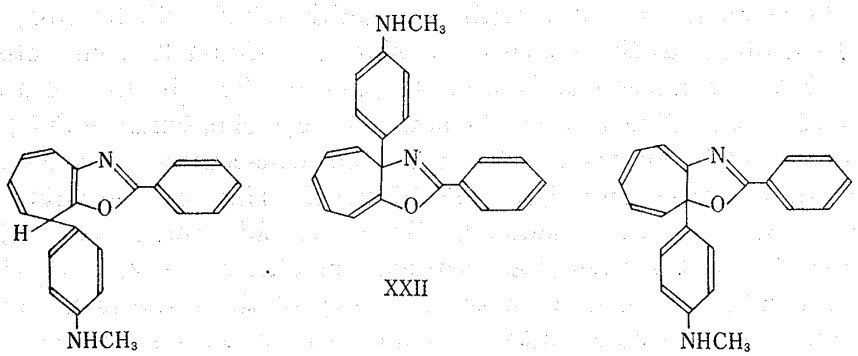


Chart 3.

the coupling constant is too small for either of these structures. The mutual conversion of the products, XIX and XX, was not recognized, when heated in ethyl alcohol with

or without hydrochloric acid. Consequently, it is apparent that I is attacked by N-methylaniline at its two positions, namely, C-6 and C-4.

The reaction of 2-phenylthiazolotropylium chloride (XXIV) with dimethylamine under similar conditions to those of I with the same amine gave a crystalline product, $C_{16}H_{16}N_2S$, which showed a similar ultraviolet absorption to that of 2-phenyl-6*H*-cycloheptathiazole and no absorption band due to carbonyl, hydroxyl or amino groups in

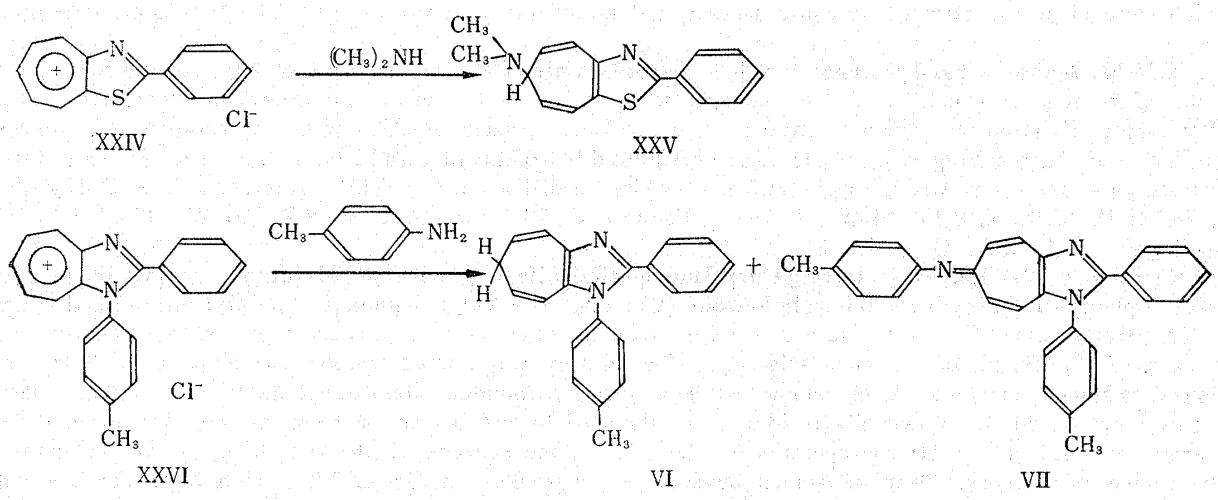


Chart 4.

the infrared spectrum. The NMR spectrum of seven-membered ring protons showed a similar situation to that of II. (For $\tau$-values and coupling constants, see the experimental section.) Therefore, the product is, apparently, 6-dimethylamino-6*H*-cycloheptathiazole (XXV).

Last, the reaction between 1-*p*-tolyl-2-phenylimidazolotropylium chloride (XXVI) and *p*-toluidine was examined. This reaction produced two products, $C_{21}H_{18}N_2$, and $C_{28}H_{23}N_3$. These products were identical with VI and VII, respectively, which were obtained in the above-described reaction of I with *p*-toluidine. This indicates the accuracy of the route shown in Chart 2.

The above results demonstrate the priority of tropylium ions having a condensed heterocyclic system for amination at C-6. Further reactions of these tropylium ions are now being studied

## Experimental

**2-Phenyl-6-dimethylaminocycloheptoxazole (II)**——To a suspension of 4.0 g. of 2-phenyloxazolotropylium monomethylsulfate (I) in 20 ml. of benzene was added a solution of 1.6 g. of dimethylamine in 20 ml. of benzene at 10~15°, and the mixture was stirred for 1 hr., during which time it became two layers. The benzene layer was separated and concentrated under reduced pressure below 50°. The resulting crystals were recrystallized from cyclohexane to give 2.8 g. of white leaflets melting at 112°. *Anal.* Calcd. for $C_{16}H_{16}ON_2$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.01; H, 6.31; N, 11.01. UV $\lambda_{max}^{EtOH}$ mμ (log ε): 240 (4.04), 312 (4.12). The NMR spectrum is shown in Fig. 1.

**Oxidation of 2-Phenyl-6-dimethylamino-6*H*-cycloheptoxazole (II): Isolation of 2-Phenyloxazole-4,5-dicarboxylic Acid (III)**——To a solution of 25 g. of II in 500 ml. of acetone was added 100 g. of solid potassium permanganate at room temperature over a period of 3 hr. After stirring for 10 hr., the mixture was treated in a manner similar to that described for the permanganate oxidation of 2-phenyl-6*H*-cycloheptoxazole in our preceding paper.*[1] The resulting white needles (1.0 g.), m.p. 215°(decomp.), were identified with the authentic sample of III by mixed melting point determination and the comparison of spectra.

**Hydrogenation of 2-Phenyl-6-dimethylamino-6*H*-cycloheptoxazole (II)**——Two grams of II were hydrogenated by the usual method in 50 ml. of EtOH with 0.1 g. of platinic oxide. After the rapid uptake of 3 moles of hydrogen, the absorption stopped. The catalyst was filtered off, and the filtrate was concentrated under atmospheric pressure and the distillate was collected in EtOH containing HCl. The residual

oily product was submitted to distillation under reduced pressure (b.$p_{0.06}$ 111°) and was then recrystallized from petroleum-ether to give white needles melting at 34~36°. *Anal.* Calcd. for $C_{14}H_{15}ON$ (2-phenyl-5,6,7,8-tetrahydro-4*H*-cycloheptoxazole (IV)): C, 78.84; H, 7.09; N, 6.57. Found: C, 78.47; H, 7.25; N, 6.68. UV $\lambda_{max}^{EtOH}$ mμ (log ε): 281 (4.25). Picrate: m.p. 163°; *Anal.* Calcd. for $C_{20}H_{18}O_8N_4$: C, 54.30; H, 4.10; N, 12.67. Found: C, 54.18; H, 4.22; N, 12.68. The distillate collected as above was concentrated to dryness, and the residue was dissolved in a small amount of water and filtered from the insoluble product. The aqueous solution was neutralized with aqueous NaOH, and an aqueous solution of picric acid was added. Separated crystals were filtered and recrystallized from EtOH to give 0.8 g. of yellow prisms melting at 162°, which were identified with an authentic sample of dimethylamine picrate by mixed melting point determination.

**N,N-bis(2-phenyl-6*H*-cycloheptoxazol-6-yl)methylamine (V)**——A solution of 2.0 g. of methylamine in 30 ml. of benzene was added at 15° to a suspension of 6.7 g. of 2-phenyloxazolotropylium monomethylsulfate (I) in 30 ml. of the same solvent. After stirring for 1 hr., benzene solution was concentrated under reduced pressure and the resulting oily product was crystallized by treatment with MeOH. The crude product (3.0 g.) was recrystallized from MeOH to give 1.5 g. of white needles melting at 145°. *Anal.* Calcd. for $C_{29}H_{23}O_2N_3$: C, 78.18; H, 5.20; N, 9.43; M.W., 445.50. Found: C, 78.01; H, 5.21; N, 9.32; M.W., 425. UV $\lambda_{max}^{EtOH}$ mμ (log ε): 244 (4.37), 316 (4.55).

**Reaction of 2-Phenyloxazolotropylium Monomethylsulfate (I) with *p*-Toluidine: Formation of 1-*p*-Tolyl-2-phenyl-1,6-dihydrocycloheptimidazole (VI) and 1-*p*-Tolyl-2-phenyl-6-*p*-tolylimino-1,6-dihydrocycloheptimidazole (VII)**——A solution of 8.7 g. of *p*-toluidine in 20 ml. of benzene was added to a suspension of 6.0 g. of I in 50 ml. of the same solvent. The mixture was stirred at room temperature for 3 hr., and allowed to stand overnight. After removal of the resulting *p*-toluidine monomethylsulfate by filtration, benzene was evaporated and the brown oily residue was submitted to alumina chromatography with benzene and then chloroform as solvent. After evaporation of the solvent, the benzene eluate left 3.5 g. of yellow crystals which gave, after recrystallization from *n*-hexane, yellow needles melting at 122° which were identified with an authentic sample of VI by mixed melting point determination and comparison of the IR spectra. The solvent was evaporated from the chloroform eluate, and the residue was dissolved in 10% HCl and extracted with chloroform. The chloroform solution was shaken with aqueous $NaHCO_3$, washed with water, and dried over $Na_2SO_4$. Chloroform was evaporated, and the residue was recrystallized from EtOH to give VII in the form of orange needles melting at 181°. *Anal.* Calcd. for $C_{28}H_{23}N_3$: C, 83.76; H, 5.77; N, 10.47. Found: C, 83.36; H, 5.84; N, 10.24. UV $\lambda_{max}^{EtOH}$ mμ (log ε): 353 (4.48), 248 (4.49).

**1-*p*-Tolyl-2-phenyl-1,6-dihydrocycloheptimidazol-6-one (VIII)**——1-*p*-Tolyl-2-phenyl-6-*p*-tolylimino-1,6-dihydrocycloheptimidazole (VII) (0.5 g.) was heated under reflux for 8 hr. in 25 ml. of EtOH containing 3 ml. of conc. HCl. After the evaporation of EtOH, the residue was stirred vigorously in a mixture of benzene and aqueous $NaHCO_3$. The benzene solution was separated and concentrated. Recrystallization of the residue gave orange needles melting at 180~181° which were identified with an authentic sample of VIII by mixed melting point determination and comparison of the spectra.

**Reaction of 1-*p*-Tolyl-2-phenyl-1,6-dihydrocycloheptimidazol-6-one (VIII) with *p*-toluidine: Formation of 1-*p*-Tolyl-2-phenyl-6-(*p*-tolylimino)-1,6-dihydrocycloheptimidazole (VII)**——A mixture of 0.3 g. of VIII and 0.14 g. of *p*-toluidine hydrochloride in 10 ml. of EtOH was refluxed for 8 hr. After evaporation of EtOH, the residue was dissolved in chloroform and the solution was shaken with aqueous $NaHCO_3$. Chloroform was evaporated and the recrystallization of the residue gave orange needles, m.p. 180°, which was not depressed on admixture with the product VII obtained by the reaction of I with *p*-toluidine.

**Reaction of 2-Phenyloxazolotropylium Monomethylsulfate (I) with N,N-Dimethylaniline**——To a suspension of 5.0 g. of I in 100 ml. of benzene was added 4.2 g. of N,N-dimethylaniline, and the mixture was stirred for 48 hr. at room temperatures. The mixture was filtered from the insoluble material and formed two layers. The upper benzene layer was treated with charcoal and the benzene was distilled off. The residue was submitted to alumina chromatography with cyclohexane and then benzene-cyclohexane mixture (6:4) as the solvents. The cyclohexane eluate gave unchanged N,N-dimethylaniline. The cyclohexane-benzene eluate, after evaporation of the solvent, left 1.1 g. of yellow crystals, which were recrystallized from cyclohexane to give yellow needles melting at 128°. *Anal.* Calcd. for $C_{22}H_{20}ON_2$ (2-phenyl-6-(*p*-dimethylaminophenyl)-6*H*-cycloheptoxazole, (XVII)): C, 80.46; H, 6.14; N, 8.53. Found: C, 80.27; H, 6.20; N, 8.38. UV $\lambda_{max}^{EtOH}$ mμ (log ε): 250 (4.44), 308 (4.37). NMR τ: 7.08 (6H, s), 6.92 (1H, t-t, J=6.0 and 1.5 c.p.s.), 4.52 (1H, d-d, J=6.0 and 10.0 c.p.s.), 4.50 (1H, d-d, J=6.0 and 10.0 c.p.s.), 3.52~2.80 (6H, m), 2.60 (3H, m), 1.94 (2H, m). The lower blue oil was chromatographed on alumina with cyclohexane-benzene mixture (6:4) as a solvent. The resulting yellow oil (52 mg.) was dissolved in a small amount of cyclohexane and the solution was allowed to stand in an ice-box. Separated crystals were filtered and recrystallized from cyclohexane to give yellow needles melting at 142°. *Anal.* Calcd. for $C_{22}H_{20}ON_2$ (2-phenyl-4-*p*-dimethylaminophenyl-4*H*-cycloheptoxazole (XVIII)): C, 80.46; H, 6.14; N, 8.53. Found: C, 80.18; H, 6.00; N, 8.49. UV $\lambda_{max}^{EtOH}$ mμ: 250, 310.

**Reaction of 2-Phenyloxazolotropylium Monomethylsulfate (I) with N-Methylaniline**——A mixture of 5.7 g. of N-methylaniline and 7.0 g. of I in 100 ml. of benzene was stirred for 48 hr. at room temperatures. After removal of insoluble material by filtration, 10% HCl was added and the mixture was vigorously stirred

for 30 minutes, and then filtered. The crystals obtained were shaken in a mixture of benzene and aqueous $NaHCO_3$, until they disappeared. The benzene solution was separated, concentrated and chromatographed on alumina with benzene as the solvent. The resulting raw product (1.76 g.) was recrystallized from benzene to give yellow needles melting at 150°. *Anal.* Calcd. for $C_{21}H_{18}ON_2$ (2-phenyl-6-*p*-methylaminophenyl-6*H*-cycloheptoxazole (XIX)): C, 80.23; H, 5.77; N, 8.91. Found: C, 80.17; H, 5.72; N, 9.04. UV $\lambda_{max}^{EtOH}$ mμ (log ε): 246.5 (4.14), 308 (4.06). NMR τ: 7.21 (3H, s), 6.97 (1H, t-t, J=5.8 and 1.5 c.p.s.), 6.42 (1H, broad), 4.59 (1H, d-d, J=9.5 and 5.8 c.p.s.), 4.57 (1H, d-d, J=9.5 and 5.8 c.p.s.), 3.45~2.75 (6H, m), 2.60~1.77 (5H, m). IR $\nu_{max}^{CCl_4}$ $cm^{-1}$: 3463 (NH). After standing, from the above-mentioned filtrate an insoluble oily product separated. This oil was stirred in a mixture of benzene and aqueous $NaHCO_3$, and the benzene solution was dried over $Na_2SO_4$. The benzene was evaporated and the residue (2.0 g.) was submitted to alumina-chromatography with benzene as the solvent and then recrystallization from a benzene-cyclohexane mixture (1:1) to give yellow needles melting at 118°. *Anal.* Calcd. for $C_{21}H_{18}ON_2$ (2-phenyl-4-(*p*-methylaminophenyl)-4*H*-cycloheptoxazole (XX)): C, 80.23; H, 5.77; N, 8.91. Found: C, 79.97; H, 5.90; N, 9.16. UV $\lambda_{max}^{EtOH}$ mμ (log ε): 243 (4.28), 340 (4.28). NMR τ: 7.27 (3H, s), 6.59 (1H, broad), 5.10 (1H, d, J=6.5 c.p.s.), 4.17~2.74 (8H), 2.57 (3H, m), 1.95 (2H, m). IR: $\nu_{max}^{CCl_4}$ $cm^{-1}$: 3428 (NH).

**2-Phenyl-6-dimethylamino-6*H*-cycloheptathiazole (XXV)**——A solution of 2.3 g. of dimethylamine in 30 ml. of benzene was added to a suspension of 4.6 g. of 2-phenylthiazolotropylium chloride (XXIV) in 70 ml. of the same solvent and the mixture was stirred for 5 hr. at room temperature. After being filtered from the resulting dimethylamine hydrochloride, the benzene was evaporated, and the residual oily product was dissolved in petroleum-ether and allowed to stand overnight. Separated crystals were filtered and recrystallized from petroleum-ether to give 2.2 g. of white needles melting at 86~88°. *Anal.* Calcd. for $C_{16}H_{16}N_2S$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.62; H, 6.00; N, 10.35. UV $\lambda_{max}^{EtOH}$ mμ (log ε): 250 (4.17), 322 (4.17). NMR τ: 7.62 (6H, s), 7.47 (1H, t-t, J=5.5 and 1.5 c.p.s.), 4.31 (1H, d-d, J=5.5 and 10.5 c.p.s.), 4.22 (1H, d-d, J=5.5 and 10.5 c.p.s.), 3.26 (1H, d-d, J=1.5 and 10.5 c.p.s.), 2.98 (1H, d-d, J=1.5 and 10.5 c.p.s.), 2.47 (3H, m), 1.87 (2H, m).

**Reaction of 1-*p*-Tolyl-2-phenylimidazolotropylium Chloride (XXVI) with *p*-toluidine: Formation of 1-*p*-Tolyl-2-phenyl-1,6-dihydrocycloheptimidazole (VI) and 1-*p*-Tolyl-2-phenyl-6-(*p*-tolylimino)-1,6-dihydrocycloheptimidazole (VII)**——A solution of 5.0 g. of *p*-toluidine in 50 ml. of benzene was added to a suspension of 1.2 g. of XXVI in 10 ml. of benzene, and the mixture was stirred at room temperature for 7 hr. Dilute hydrochloric acid was added, and the mixture was shaken vigorously, and during this time reddish orange crystals separated. The crystals were filtered, and the benzene solution was separated from the filtrate. The benzene solution, after concentration, was submitted to alumina chromatography with benzene as the solvent. Removal of benzene from the eluate gave 0.1 g. of VI, which was characterized as its picrate, m.p. 202°(decomp.), not depressed by admixture with an authentic sample. The above-described reddish orange crystals were dissolved in chloroform and the solution was shaken with 5% $NaHCO_3$. After evaporation of the chloroform, the residue was recrystallized from EtOH to give 0.15 g. of yellow-orange crystals melting at 181° which were identified with the product VII obtained by the reaction of I with *p*-toluidine by mixed melting point determination and comparison of the spectra.

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