5 hr. with 15 cc. of acetone containing 10 mg. of *p*-toluenesulfonic acid. The solution was neutralized with Na_2CO_3 solution and concentrated under reduced pressure. The product was extracted with Et_2O, the extract was washed with H_2O, and dried over Na_2SO_4. After removal of the solvent, the crystalline residue, m.p. 140~155°, was chromatographed on alumina. Elution with petr. ether (b.p. 40~60°)-benzene (4:1) furnished 15 mg. of the acetonide, which was recrystallized from MeOH to needles, m.p. 184°. *Anal.* Calcd. for $C_{30}H_{48}O_4$: C, 76.22; H, 10.24. Found: C, 76.03; H, 10.31.

Summary

Partial synthesis of 25D,5β-spirostane-2α,3α-diol, the only unknown isomer of 25D,5β-spirostane-2,3-diols, is described.

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Hiroshi Tanida: Quinoline and Related Compounds. III.[1] The Direct N-Methylphenylamination of Quinoline 1-Oxide.

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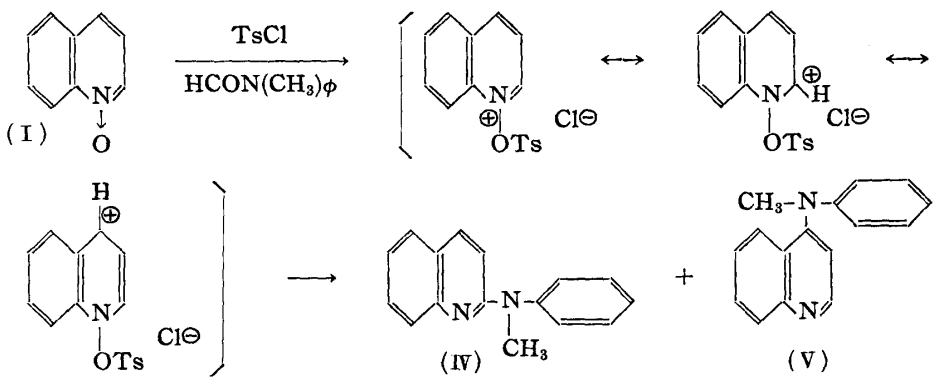
In the previous paper[2] dealing with the reaction between quinoline 1-oxide and tosyl chloride in dimethylformamide, it was shown that 2- and 4-dimethylaminoquinolines were prepared directly from quinoline 1-oxide. According to the mechanism described in that paper, it is possible to apply this reaction to various dialkylaminoformamides. The present work is one example to which this reaction was applied.

When quinoline 1-oxide (I) was heated with tosyl chloride in N-methylformanilide in the presence of boric trifluoride, a colorless oil (IV), $b.p_{0.1}$ 135~140° (Picrate: Cubic crystals, m.p. 167~168°) and a slightly yellow oil (V) (picrate of needles, m.p. 177~178°) were obtained. The composition of both picrates agreed with $C_{16}H_{14}N_2 \cdot C_6H_3O_7N_3$, and the ultraviolet absorption curves exhibited the additive curve of aminoquinoline and aniline. On the basis of these data, it seems reasonable to assume that (IV) and (V) are 2- and 4-(N-methylanilino)quinolines, respectively. The chemical proof was furnished by admixture with an authentic sample, which was prepared from chloroquinoline and methylaniline. The yield of those products was 31% of (IV) and 20% of (V).



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1) Part II: This Bulletin, 7, 887(1959).
2) H. Tanida: Yakugaku Zasshi, 78, 608(1958).

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Experimental

Reaction of Quinoline 1-Oxide (I) with Tosyl Chloride and N-Methylformanilide—Freshly distilled quinoline 1-oxide anhydride (I) (960 mg.) was dissolved in N-methylformamide (20 g.), (II) (1.37 g.) and boric trifluoride etherate (700 mg.) were added to this solution, this mixture was heated for 1 hr. at 130~135°, and for another 0.5 hr. at 140~145°, during which CO gas generated violently. Excess (III) was distilled off from the reaction mixture under a reduced pressure and the oily residue was shaken with $CHCl_3$ and 10% NH_4OH. The separated $CHCl_3$ layer was treated with 8% KOH, dried over K_2CO_3, and evaporated. The oily residue was added with 5% HCl and shaken with Et_2O. The separated HCl layer was made alkaline with K_2CO_3, and extracted consecutively with Et_2O and $CHCl_3$. The Et_2O extract (820 g.) was carefully chromatographed on alumina and the following two substances were obtained.

First fraction (from petr. ether–benzene (1:1)) : Colorless oil (IV) (480 mg.), b.$p_{0.1}$ 135~140°. Picrate, yellow cubic crystals (from AcOEt), m.p. 167~168°. *Anal.* Calcd. for $C_{16}H_{14}N_2 \cdot C_6H_3O_7N_3$: C, 57.02; H, 3.70; N, 15.11. Found : C, 56.77; H, 3.99; N, 14.98. It showed no depression on admixture with the picrate of 2-(N-methylanilino)quinoline.

Second fraction (from benzene) : Slightly yellow oil (V) (310 mg.), b.$p_{0.1}$ 150~160°. Picrate : Yellow needles (from EtOH), m.p. 177~178°. *Anal.* Calcd. for $C_{16}H_{14}N_2 \cdot C_6H_3O_7N_3$: C, 57.02; H, 3.70; N, 15.11. Found : C, 57.17; H, 3.92; N, 14.94. It showed no depression on admixture with the picrate of 4-(N-methylanilino)quinoline.

Beside these substances, (I) (170 mg.) was recovered from the $CHCl_3$ extract.

4-(N-Methylanilino)quinoline (V)—A mixture of 4-chloroquinoline (700 mg.) and methylaniline (1.37 g.) was heated for 3 hr. at 240~245°. The reaction mixture was dissolved in Et_2O and treated with Na_2CO_3 solution. Et_2O layer was dried and evaporated. The residue was purified by alumina chromatography, using benzene as a solvent. The eluate was fractionally distilled. After the starting materials distilled off, slightly yellow oil (V) (760 mg.), b.$p_{0.1}$ 150~160°, was obtained.

Summary

2- and 4-(N-Methylanilino)quinolines were obtained by the reaction between quinoline 1-oxide and tosyl chloride in N-methylformanilide. In this reaction boric trifluoride was also used as a catalytic agent.

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