## Notes

Chem. Pharm. Bull. 14(12)1425~1426(1966)

UDC 547.853.07 : 547.787.31.07

**Tarozaemon Nishiwaki**: Synthesis of 2,4,6-Triphenyloxazolo-[5,4-*d*]pyrimidine-5-thione-7-one.*1

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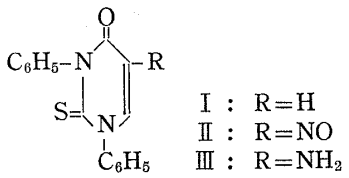
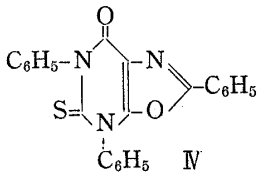
Although there are several reports[1~3] on the preparation of oxazolo[5,4-*d*]pyrimidine derivatives, none of the compounds containing sulfur has not been known. The author wishes to record here the synthesis of 5-thioxo-2,4,6-triphenyl-4,5-dihydroxazolo[5,4-*d*]-pyrimidin-7(6*H*)-one (Ⅳ) by the following scheme.



Ⅰ : R=H
Ⅱ : R=NO
Ⅲ : R=$NH_2$



Ⅳ

Nitrosation of 1,3-diphenyl-2-thiobarbituric acid (Ⅰ) afforded its 5-nitroso compound (Ⅱ), which was reduced with ammonium sulfide to 5-amino-1,3-diphenyl-2-thiobarbituric acid (Ⅲ). Ⅲ was allowed to react with benzoyl chloride and yielded Ⅳ as slightly yellow crystals. The structural assignment is based on elemental analysis and similar cyclization of 1,3-dimethyluramil with benzoyl chloride reported by Biltz, *et al.*[4]

### Experimental*3

**1,3-Diphenyl-2-thiobarbituric Acid (I)**——Diphenylthiourea (13.0 g.), malonic acid (6.0 g.), and $POCl_3$ (17.4 g.) were heated under reflux in $CHCl_3$ (90 ml.) for 5 hr. The solvent was removed and the residue was dissolved in saturated aqueous NaOAc solution and filtered. The filtrate was acidified with 6*N* HCl to give precipitates (6.7 g.), which were recrystallized several times from EtOH as light yellow needles, m.p. 242~244°. Dass, *et al.*[5] prepared this compound using acetyl chloride and recorded m.p. 245°.

**5-Nitroso-1,3-diphenyl-2-thiobarbituric Acid (II)**——To a cold solution of 1,3-diphenyl-2-thiobarbituric acid (I) (1.33 g.) in 5% aqueous NaOH (10 ml.) was added a solution of $NaNO_2$ (0.31 g) in $H_2O$ (4 ml.). Acidification of this solution with 6*N* $H_2SO_4$ gave precipitates (1.43 g.), which were recrystallized from MeOH to yield reddish-brown lustrous rods, m.p. 226~228° (decomp.). *Anal.* Calcd. for $C_{16}H_{11}O_3N_3S$ : C, 59.07; H, 3.41. Found : C, 58.72; H, 3.53.

**5-Amino-1,3-diphenyl-2-thiobarbituric Acid (III)**——To a suspension of 5-nitroso-1,3-diphenyl-2-thiobarbituric acid (1.00 g.) in $H_2O$ (10 ml.) was added commercial ammonium sulfide solution (about 20%) (10 ml.) and the mixture was left at room temperature for 1 hr. Precipitates were obtained by acidification of the resulting solution with HOAc. They were dissolved in 10% aqueous NaOH solution (30 ml.) and acidified with 6*N* $H_2SO_4$ to yield light-yellow needle (0.52 g.), m.p. 186~187° (decomp.). An additional similar treatment raised m.p. to 190~192° (decomp.). *Anal.* Calcd. for $C_{16}H_{13}O_2N_3S \cdot 2H_2O$ : C, 55.32; H, 4.93. Found : C, 54.98; H, 4.94.

**5-Thioxo-2,4,6-triphenyl-4,5-dihydrooxazolo[5,4-*d*]pyrimidine-7(6*H*)-one (IV)**——5-Amino-1,3-diphenyl-2-thiobarbituric acid (0.80 g.) was heated under reflux with benzoyl chloride (25 ml.) for 3 hr. and the resulting solution was concentrated *in vauco* to about one third volume and poured into absolute EtOH

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*1 Nomenclature is based on "The Ring Index," 174 (1960), American Chemical Society.
*2 Wakayama-Shi (西脇太郎三衛門).
*3 Melting points were taken on a Kofler block but uncorrected.

1) H. Biltz : Ann., **404**, 181 (1914).
2) E. Falco, G. B. Elion, E. Burgi, G. Hitchings : J. Am. Chem. Soc., **74**, 4897 (1952).
3) G. Haeger, C. Kaiser : J. Am. Pharm. Assoc., **44**, 193 (1955).
4) H. Biltz, K. Strufe : Ann., **404**, 170 (1914).
5) I. Daas, S. Dutt : Proc. Indian Acad. Sci., **8A**, 145 (1938) (C. A., **33**, 620 (1939).

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(50 ml.). After standing overnight the solution deposited crystals (0.52 g.), which were filtered off and recrystallized several times from toluene as slightly yellow rods, m.p. 264~265° (decomp.), UV $\lambda_{max}^{CHCl_3}$ 32 mμ (log ε 4.41) (an inflection : 341 mμ (log ε 4.22)). *Anal.* Calcd. for $C_{23}H_{15}O_2N_3S$ : C, 69.50; H, 3.80; N, 10.57; S, 8.07. Found : C, 69.46; H, 3.78; N, 10.29; S, 8.28. Major IR absorptions (Nujol) were at 1727, 1645, 1597, 1566, 1493, 1326, 1309, 1250, 1072, 890, 829, and 683 $cm^{-1}$.

(Received March 25, 1966)

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[Chem. Pharm. Bull. 14(12)1426~1430(1966)]

*UDC 547.924.07.02*

## Tokuo Kubota, Keiji Yoshida, and Fumihiko Watanabe : The Configuration of the Products obtained from Hydroxylation of Steroidal $\Delta^{1,4}$-3-Ketones with Osmium Tetroxide.

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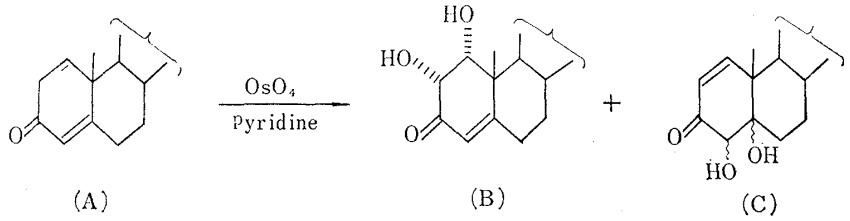
Previously, in connection with thes ynthesis of A-norsteroid derivatives,[1] several steroidal $\Delta^{1,4}$-3-ketones (A) have been hydroxylated with osmium tetroxide in pyridine. Each of the compounds afforded the corresponding two isomeric products, 1,2-dihydroxy-$\Delta^4$-3-one (B) and 4,5-dihydroxy-$\Delta^1$-3-one (C), for which the $\alpha$-configuration of the introduced hydroxyl groups had been assigned.

Out of these assignment, the 1$\alpha$,2$\alpha$-dihydroxyl configuration in the former isomers (B) was firmly settled by the optical rotatory dispersions (ORD), which have been studied thoroughly by Kuriyama, *et al.*,[2] and by the chemical correlation of the derivative from 25D-spirosta-1,4-dien-3-one with the previously known epimer, 1$\beta$,2$\beta$-dihydroxy-25D-spirost-4-en-3-one.[3]




(A) (B) (C)

Chart 1.

In analogy, the hydroxy groups of the 4,5-dihydroxy-$\Delta^1$-3-ones (C) had been assigned as $\alpha$-configuration, based on the assumption that bulky osmium tetroxide should approach the double bond from the less hindered $\alpha$-side. Although this was supported by the ORD curves showing negative Cotton effect which resembles to that of cholest-1-en-3-one, no example sufficient for discussion was existed and some doubt had been remained on the assign of $\alpha$-configuration in (C).

For the purpose of preparing 4$\alpha$,5$\alpha$,17$\beta$-trihydroxyandrostan-3-one in the subject of other investigation, the 4,5-dihydroxy derivative (Id) prepared previously from osmylation of 17$\beta$-hydroxyandrosta-1,4-dien-3-one, was subjected to catalytic hydrogenation on palladium charcoal. There was obtained a dihydro product, m.p. 164~166°,

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1) T. Kubota, K. Yoshida, F. Hayashi, K. Takeda : This Bulletin, **13**, 50 (1965).
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3) T. Kubota, K. Takeda : Tetrahedron, **10**, 1 (1960).

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