SYNTHESIS OF 4,5-DIHYDRO-11H-PYRROLO[3,2-a]-PHENOTHIAZINE DERIVATIVES

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We have found that the hydrogen atom in the α position relative to the carbonyl group is replaced by an o-nitroarylmercapto group (III, IV) on fusion or heating (in dioxane solution) of 4-oxotetrahydroindole derivatives (I, II) with o-nitrobenzenesulfenyl chloride or with their benzene-substituted derivatives. It is expedient to use N-substituted 4-oxotetrahydroindoles, since a mixture of derivatives V and VI is formed with unsubstituted I.

Compounds III and IV are converted to the previously unknown 4,5-dihydro-11H-pyrrolo[3,2-a]phenothiazines (VII and VIII), which are isolated as the hydrochlorides, by reduction with zinc dust in acetic acid in the presence of sodium acetate.

I R=H; II R=CH₃; III R=CH₃, R'=R"=H; IV R=CH₃, R'=H, R"=Br; V R=R"=H, R'=CH₃; VI R=o-NO₂C_eH₄S, R'=CH₁, R"=H; VII R"=H; VIII R"=Br

EXPERIMENTAL

 $\frac{1,3-\text{Dimethyl-}2-\text{carbethoxy-}4-\text{oxo-}5-(2-\text{nitrophenylthio})-4,5,6,7-\text{tetrahydroindole (III)}. \text{ This compound was obtained in }51\% \text{ yield and had mp }169-170^{\circ} \text{ (from alcohol)}. \text{ Found: }C 58.7; \text{ H }4.9; \text{ N }7.2; \text{ S }8.5\%. \\ C_{19}\text{H}_{20}\text{N}_{2}\text{O}_{5}\text{S.} \text{ Calculated: }C 58.7; \text{ H }5.2; \text{ N }7.2; \text{ S }8.3\%. }$

 $\frac{1,3-\text{Dimethyl-}2-\text{carbethoxy-}4-\text{oxo-}5-(2-\text{nitro-}4-\text{bromophenylthio})-4,5,6,7-\text{tetrahydroindole (IV)}.}{\text{This compound was obtained in }80\% \text{ yield and had mp }196-197^{\circ} \text{ (from alcohol)}.}$ Found: C 49.0; H 4.1; Br 16.9; N 6.0; S 6.8%. C₁₉H₁₉BrN₂O₅S. Calculated: C 48.8; H 4.1; Br 17.1, N 6.0; S 6.9%.

 $\frac{2,6,6-\text{Trimethyl-}2-\text{carbethoxy-}4-\text{oxo-}5-(2-\text{nitrophenylthio})-4,5,6,7-\text{tetrahydroindole (V)}.}{\text{pound was obtained in 34\% yield and had mp 169-170° (from alcohol)}.}$ Found: C 59.9; H 5.4; N 7.0; S 8.3%. C $_{20}\text{H}_{22}\text{N}_{2}\text{O}_{5}\text{S}$. Calculated: C 59.7; H 5.5; N 7.0; S 8.0%.

 $\frac{1,5-Bis(2-nitrophenylthio)-3,6,6-trimethyl-2-carbethoxy-4-oxo-4,5,6,7-tetrahydroindole (VI). This compound was obtained in 43% yield and had mp 157-158° (from alcohol). Found: C 56.2; H 4.7; N 7.5; S 11.3%. <math>C_{26}H_{25}N_3O_7S_2$. Calculated: C 56.2; H 4.5; N 7.6; S 11.5%.

1,3-Dimethyl-2-carbethoxy-4,5-dihydro-11H-pyrrolo[3,2-a]phenothiazine Hydrochloride (VII). This compound was obtained in 43% yield and had mp 104-105° (from acetone). Found: C 60.5; H 6.0; N 7.4; S 8.6%. $C_{19}H_{20}N_2O_2S \cdot HCl$. Calculated: C 60.5; H 5.6; N 7.4; S 8.5%.

1,3-Dimethyl-2-carbethoxy-9-bromo-4,5-dihydro-11H-pyrrolo[3,2-a]phenothiazine Hydrochloride (VIII). This compound was obtained in 70% yield and had mp 97-98° (from acetone). Found: C 50.0; H 4.6; Br 17.4; N 6.1; S 6.9%. $C_{19}H_{19}BrN_2O_2S \cdot HCl$. Calculated: C 50.1; H 4.4; Br 17.5; N 6.1; S 7.0%.

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