THESIS

Entitled

REACTIONS WITH PYRIDAZINONES

Submitted by

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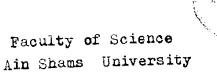
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REACTIONS WITH PYRIDAZINONES

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VITAE

Omar Aly Sherif was born in December 8,1947 in Farhonia, Ashmoon, Menofia, Egypt. He attended Ashmoon Secondary School from 1963 till 1966 and got the Secondary School Certificate in 1966. He was then enrolled in the Faculty of Science; Ain Shams University, Cairo, Egypt, where he majored in chemistry and received the degree of Bachelor of Science with second class honours in 1970.

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SUMMARY OF THE ORIGINAL WORK Reactions with 3(2H)-pyridazinones

6-p-Tolyl 3(2H)-pyridazinene (Ia) and its dihydroderivative (IIa) react with ethyl bromoacetate yielding acetic acid ethyl ester derivative Ib and IIb, respectively.

$$\begin{array}{c}
C_6^{H_4CH_3-p} \\
N_{-CH_2COOC_2H_5} \\
0
\end{array}$$
(Ib)
$$\begin{array}{c}
C_6^{H_4CH_3-p} \\
N_{-CH_2COOC_2H_5} \\
0
\end{array}$$
(IIb)

Hydrolysis of Ib gives the corresponding acetic acid derivative Ic, which undergoes decarboxylative acylation with acetic anhydride in pyridine to give 2-propanone derivative Id.

Reaction of Ib and IIb with hydrazine affords the corresponding hydrazides III & IV.

The hydrazide III condenses with aromatic aldehydes to give the arylidene derivatives V.

(V)

Cyanoethylation of Ia and IIa gives the cyanoethy-lated products VI and VII.

$$\begin{array}{c} C_6^{H_4CH_3-p} \\ \hline N \\ O \end{array}$$

$$\begin{array}{c} C_6^{H_4CH_3-p} \\ \hline O \\ O \end{array}$$

$$\begin{array}{c} C_6^{H_4CH_3-p} \\ \hline O \\ O \end{array}$$

$$\begin{array}{c} C_6^{H_4CH_3-p} \\ \hline O \\ O \end{array}$$

Hydrolysis of VI and VII give the corresponding acid VIII and IX respectively.

Condensation of IIa with aldehydes yields the 4-arylidene derivatives (X).

(X)

Both Ia and IIA undergo Mannich reaction at the ring nitrogen with the formation of the Mannich bases XIII & XIV.

$$\begin{array}{cccc}
C_6^{H_4CH_3-P} & & & & & \\
N_{-CH_2}R & & & & & \\
N_{-CH_2}R & & & & & \\
(XIII) & & & & \\
\end{array}$$

2 Phenyl-6-p-tolyl-4,5-dihydro-3(2H)-pyridazinone (XI) undergoes a Mannich condensation at the Politica to give XV.

Ia and IIa react with Grignard reagents (ArMgX) yielding XIX and XVIII respectively.

$$\begin{array}{c}
C_6^{H_4CH_3-p} \\
N \\
Ar
\end{array}$$
(XVIII)
$$\begin{array}{c}
C_6^{H_4CH_3-p} \\
N \\
N \\
N \\
N \end{array}$$

On the other hand, Ia reacts with phenylmagnesium bromide in 1:1 THF-ether mixture to give 5-phenyl-6-p-tolyl-4,5-dihydro-3(2H)-pyridazinone(XX).

(XX)

Reaction of 6-p-tolyl-3-chloropyridazine(XXIII), with aromatic amines gives the 3-arylamino-6-p-tolyl-, pyridazines (XXIV), which react with acetyl chloride to give XXV.

XXIII reacts with anthranilic acid to give XXVI.

6-p-Telyl-3-chloropyridazine (XXIII) condenses with hydrazine hydrate to give 6-p-tolyl-3-hydrazinopyri-dazine (XXVII).

(IIVXX)

3-Hydrazinopyridazine(XXVII) reacts with nitrous acid to give 3-azidopyridazine XXVIII, which also obtain by a reaction of 3-chloropyridazine (XXIII) with sodium azide.

$$\begin{array}{c}
C_6^{H_4CH_3-p} \\
N \\
N \\
N
\end{array}$$
(XXIX)

Heating 3-hydrazinopyridazine (XXVII) with glacial acetic acid and sodium acetato glvus triazolopyridazine lerivative (XXX).

(XXX)

Reaction of hydrazinopyridazine (XXVII) with acetylacetone gives 3-(3,5-dimethylpyrazol-l-yl) 6-p-tolylpyridazine (XXXI).

(IXXX)

3-Hydrazinopyridazine XXVII, condenses with -c-acetobenzoic acid to give 2(lH)-phthalazinone derivative (XXXII).

(XXXII)

Treatment of 3-chloropyridazine (XXIII) with phenols and p-thiocresol in the presence of potassium carbonate yields the ether XXXIII, and thioether XXXIV derivatives respectively.

$$\begin{array}{c}
C_6^{H_4CH}_3^{-p} \\
\hline
0 \\
R
\end{array}$$

$$\begin{array}{c}
C_6^{H_4CH}_3^{-p} \\
\hline
0 \\
C_6^{H_4CH}_3^{-p}
\end{array}$$

$$\begin{array}{c}
C_6^{H_4CH}_3^{-p} \\
C_7^{H_4CH}_3^{-p}
\end{array}$$

$$\begin{array}{c}
C_7^{H_4CH}_3^{-p} \\
C_7^{H_4CH}_3^{-p}
\end{array}$$

$$\begin{array}{c}
C_7^{H_4CH}_3^{-p} \\
C_7^{H_4CH}_3^{-p}
\end{array}$$

Reaction of XXIII with methanol and ethanol in the presence of potassium hydroxide gives XXXV.