#### DAEHAN HWAHAK HWOEJEE

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# REACTIONS OF TRICHLOROETHYLIDENEACETOPHENONE WITH HYDRAZINES (1)

# SYNTHESIS OF PYRAZOLINE AND PYRIDAZINONE DERIVATIVES

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Youn Young Lee · Woo Young Lee · · Sae Hee Chang

Department of Chemistry, College of Liberal Arts and Sciences, Seoul National University
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# Trichloroethylideneacetophenone 과 hydrazine 돌의 반응 (I) pyrazoline 및 pyridazinone 유도체의 합성

서울대학교 문리과대학 화학과 이 윤 영·이 우 영\*·장 세 희 (1969. 12. 2 접수)

요 약

trichloroethylideneacetophenone 다 hydrazine hydrate의 반용으로 3-phenyl-5-trichloromethyl-2-pyrazoline을 합성하였다. 또한 trichloroethylideneacetophenone 과 phenylhydrazine 또는 차환된 phenylhydrazine의 반응으로 pyridazinone 유도제들을 합성하였다.

## ABSTRACT

3-Phenyl-5-trichloromethyl-2-pyrazoline was synthesized from the reaction of trichloroethylideneacetophenone with hydrazine hydrate. Pyridazinone derivatives were synthesized from the reaction of trichloroethylideneacetophenone with phenylhydrazine or substituted phenylhydrazines.

#### INTRODUCTION

The most widely used method for pyrazoline synthesis is the reaction of hydrazines with  $\alpha$ ,  $\beta$ -unsaturated aldehydes and ketones<sup>(1)</sup>. Pyridazinones are synthesized from the reaction of a  $\gamma$ -keto- $\alpha$ ,  $\beta$ -unsaturated acid or acid derivatives with hydrazines<sup>(2)</sup>. The purpose of this work is to investigate the reaction of trichloroe-

thylideneacetophenone( [ ) $^{(3,4)}$ , an  $\alpha$ ,  $\beta$ -unsaturated ketone, with hydrazines.

3-Phenyl-5-trichloromethyl-2-pyrazoline ( $\blacksquare$ ) was obtained in 85% yield from the reaction of trichloromethylideneacetophenone with hydrazine hydrate. From the reaction of trichloroethylideneacetophenone with phenylhydrazine, pyrazoline derivative was not obtained, but 2, 6-diphenyl-3-pyridazinone ( $\blacksquare$ ), which was also synthesized from the reaction of  $\beta$ -benzoylacrylic acid( $\blacksquare$ ) with phenylhydrazine by Norman et al. (5).

<sup>\*</sup> College of General Studies, Seoul National Univ.

was obtained in 72% yield. 2-(p-nitrophenyl)-(V), 2-(p-tolyl)-(V) and 2-(p-chlorophenyl)-6-phenyl-3-pyridazinone(VI) were synthesized in good yields from the reaction of trichloroethylideneacetophenone with p-nitrophenyl-, p-tolyl- and p-chlorophenylhydrazine respectively. 2-(p-Nitrophenyl)-6-phenyl-3-pyridazinone was also obtained from the reaction of  $\beta$ -benzoylacrylic acid<sup>(6)</sup> with p-nitrophenylhydrazine. Pyridazinones were produced in ethanol containing a small amount of hydrogen chloride or in acetic acid.

Since the hydrazones of  $\beta$ -benzoylacrylic acid were

not able to cyclize to form pyridazinones in alcohol containing a small amount of hydrogen chloride or in acetic acid at elevated temperature, it is quite plausible that the reaction of trichloroethyideneaceto-phenone with phenylhydrazine or other substituted phenylhydrazine would not proceed through hydrazone formation, hydrolysis to the hydrazone of  $\beta$ -benzoyl acrylic acid and ring closure, but through hydrazone formation, ring closure to carbon containing chlorine atom and hydrolysis to give pyridazinones.

The infrared spectra of 2, 6-diphenyl-3-pyridazinone synthesized through this research were identical in every detail with those obtained from the sample prepared by Norman et al. The infrared spectra of the synthesized pyridazinones were very similar each

other and the absorption bands owing to amide carbonyl group were found at 1660~1680cm<sup>-1</sup>. The absorption band owing to N-II stretching in 3 phenyl-5-triebloromethyl 2-pyrazoline was found at 3320cm<sup>-1</sup>.

TABLE 1. The Analytical and Spectral Data of Pyrazoline and Pyridazinone Derivatives

Designation	m. p.	Infrared <sup>4)</sup> Max. (cm <sup>-1</sup> )	Analys Calculated	is <sup>6)</sup> Found
3-phenyl-5-		3320, N-H(sec.)	C; 45. 57	45. 52
trichloromethyl	1 18∼150°C	1600, Phenyl	H; 3.14	3.77
-2-pyrazoline			Cl; 40.37	40.8
C10H0N2Cl3				
2, 6-diphenyl-		1660, C=O(Am	ide) C; 77.40	76. 93
3-pyridazinone	149~150°C	1590, Phenyi	H; 4-87	4. 92
$C_{14}H_{12}ON_2$				
2-(p-nitrophenyl)		1680, C=O(Am	ide) C; 65.53	65. 55
-6-phenyl-		1600, Phenyl	H; 3.78	4. 1€
3-pyridazinone	205∼206°C			
$C_{16}H_{11}O_{1}N_{3}$				
2-(p-tolyl)-		1670, C=O(Am	ide) C; 77.84	77. 03
6-phenyl-	141~143°C	1600, Phenyl	H; 5.38	5.86
3-pyridazinone				
$C_{17}H_{14}\mathrm{ON}_2$				
2-(p-chlorophenyl)		1670, C=O(Am	ide) C; 67. 96	67. 73
-6-phenyl-	162∼1 <b>65</b> °C	1600, Phenyi	H; 3.92	4. 33
3-pyridazinone			Cl; 1.25	1. 30

a) The measurement was done with Jasco iR-G using KBr pellet.

#### PERIMENTAL

## 3-phenyl-5-trichloromethyl-2-pyrazoline(III)

To a solution of 2ml of hydrazine hydrate in 10ml of ethanol was added a solution of 2.0g of trichloro-ethylideneacetophnone in 40ml of ethanol. The color-less needles were crystallized after standing the solution for 2 hrs. at room temperature. The product was recrystallized from 60% ethanol.

The yield was 1.8g (85%), m.p., 148~150°C. 2,6-diphenyl-3-pyridazinone(IV)

1. A mixture of 4.0g of trichloroethylideneacetophenone and 2.0g of phenylhydrazine hydrochloride in 40ml of ethanol was heated under reflux for 1.5 hrs. Water was added until the solution became turbid and the colorless crystal was obtained after cooling the solution at room temperature. The product was recrystallized from 80% ethanol.

The yield was 2.6g (72%), m. p., 149~150°C(lit.,

150~151°C)

2. Three grams of trichloroethylideneacetophenone and 1.5g of phenylhydrazine were dissolved in 40ml of glacial acetic acid and the mixture was heated under reflux for 30 min. The mixture was transferred to an evaporating dish and evaporated at room temperature. The separated crystal was recrystallized from 80% ethanol.

The yield was 1.8g (72%), m.p.,  $148\sim150^{\circ}$ C, mixed m.p.,  $149\sim150^{\circ}$ C

## 2-(p-nitrophenyl)-6-phenyl-3-pyridazinone(V)

1. Two grams of trichloroethylideneacetophenone and 1.2g of p-nitrophenylhydrazine were dissolved in 30ml of glacial acetic acid and the yellow crystal was separated form the solution after standing overnight at room temperature. The product was recrystallized from 80% acetic acid.

The yield was 1.2g (51%), pale yellow needle, m. p.,  $205\sim206^{\circ}$ C.

b) Carbon and hydrogen were determined by microanalysis at the Korean Institute of Science and Technology. Chlorine was determined by neutron activation analysis at the Atomic Energy Research Institute.

2. A mixture of 1.6g of trichloroethylideneacetophenone and 1.2g of p-nitrophenylhydrazine hydrochloride in 30ml of ethanol was heated under reflux for 20 min. The separated crystal was recrystallized from 80% acetic acid.

The yield was 0.9g (48%), m.p., 206~207°C.

3. Two grams of  $\beta$ -benzoylacrylic acid and 2.0g of p-nitrophenylhydrazine were dissolved in 60ml of glacial acetic acid and the mixture was heated under reflux for 30 min. p-Nitrophenylhydrazone of  $\beta$ -benzoylacrylic acid (K) was obtained in 45%(1.4g) yield after standing the solution for 24 hrs. at room temperature. The product was recrystallized from 80% ethanol; yellow crystal, m. p., 210~212°C.

A solution of 1.0g of p-nitrophenylhydrazone of β-benzoylacrylic acid in 40ml of acetic anhydride and 0.5g of sodium acetate was heated under reflux for 1 hr. The reaction mixture was cooled and poured into 200ml of cold water. The precipitate was separated and recrystallized from 80% acetic acid.

The yield was 0.85g (80%), m.p.,  $205\sim206^{\circ}$ C, mixed m.p.,  $205\sim206^{\circ}$ C.

#### 2-(p-tolyl)-6-phenyl-3-pyridazinone(VI)

A mixture of 3.0g of trichloroethylideneacetophenone and 1.8g of p-tolylhydrazine hydrochloride in 60ml of ethanol was heated under reflux for 2 hrs. Water was added until the solution became turbid. The colorless needles were crystallized out after standing the solution at room temperature. The product was recrystallized from 70% ethanol.

The yield was 2.4g (76%), m. p., 141~143°C.

2-(p-chlorophenyl)-6-phenyl-3-pyridazinone(VII)

A mixture of 2.0g of trichloroethylideneacetophenone

and 2.0g of p-chlorophenylhydrazine hydrochloride in 60ml of ethanol was heated under reflux for 1 hr. Colorless needles were obtained after cooling the solution at room temperature. The product was recrystallized from 70% ethanol.

The yield was 1.2g(53%), m.p.,  $162\sim165^{\circ}$ C.

#### CONCLUSION

3-Phenyl-5-trichloromethyl-2-pyrazoline was synthesized in good yields from the reaction of trichloroethylideneacetophenone with hydrazine hydrate. The reaction of trichloroethylideneacetophenone with phenylhydrazine or substituted phenylhydrazine gave in good yields the pyridazinone derivatives. The method described for pyridazinone synthesis was very convenient.

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