

REACTIONS OF TRICHLOROETHYLIDENEACETOPHENONE WITH HYDRAZINES (I)

SYNTHESIS OF PYRAZOLINE AND PYRIDAZINONE DERIVATIVES

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(Received Dec. 2, 1969)

Trichloroethylideneacetophenone 과 hydrazine 들의 반응 (I) pyrazoline 및 pyridazinone 유도체의 합성

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(1969. 12. 2 접수)

요 약

trichloroethylideneacetophenone 과 hydrazine hydrate 의 반응으로 3-phenyl-5-trichloromethyl-2-pyrazoline 을 합성하였다. 또한 trichloroethylideneacetophenone 과 phenylhydrazine 또는 치환된 phenylhydrazine 의 반응으로 pyridazinone 유도체들을 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 α, β -unsaturated aldehydes and ketones⁽¹⁾. Pyridazinones are synthesized from the reaction of a γ -keto- α, β -unsaturated acid or acid derivatives with hydrazines⁽²⁾. The purpose of this work is to investigate the reaction of trichloro-

ethylideneacetophenone (I)^(3,4), an α, β -unsaturated ketone, with hydrazines.

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

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

Designation	m. p.	Infrared ^{a)} Max. (cm ⁻¹)	Analysis ^{b)}	
			Calculated	Found
3-phenyl-5-trichloromethyl-2-pyrazoline C ₁₀ H ₆ N ₂ Cl ₃	148~150°C	3320, N-H(sec.) 1600, Phenyl	C; 45.57 H; 3.14 Cl; 40.37	45.52 3.77 40.8
2,6-diphenyl-3-pyridazinone C ₁₄ H ₁₂ ON ₂	149~150°C	1660, C=O(Amide) 1590, Phenyl	C; 77.40 H; 4.87	76.93 4.92
2-(<i>p</i> -nitrophenyl)-6-phenyl-3-pyridazinone C ₁₆ H ₁₁ O ₃ N ₃	205~206°C	1680, C=O(Amide) 1600, Phenyl	C; 65.53 H; 3.78	65.55 4.16
2-(<i>p</i> -tolyl)-6-phenyl-3-pyridazinone C ₁₇ H ₁₄ ON ₂	141~143°C	1670, C=O(Amide) 1600, Phenyl	C; 77.84 H; 5.38	77.03 5.86
2-(<i>p</i> -chlorophenyl)-6-phenyl-3-pyridazinone C ₁₆ H ₁₁ ON ₂ Cl	162~165°C	1670, C=O(Amide) 1600, Phenyl	C; 67.96 H; 3.92 Cl; 1.25	67.73 4.33 1.30

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

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.

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 trichloroethylideneacetophenone in 40ml of ethanol. The colorless 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., 148~150°C, mixed m. p., 149~150°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 from 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., 205~206°C.

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 β -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 β -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., 205~206°C, mixed m. p., 205~206°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., 162~165°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.

ACKNOWLEDGEMENT

We should like to thank Dr. Keung Shik Park of the Atomic Energy Research Institute for helping the analysis of chlorine in compounds.

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