

Reactions of Trichloroethylideneacetophenone with Hydrazines (II)

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(Received April 25, 1971)

Trichloroethylideneacetophenone 과 Hydrazine 들의 반응(II)

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(1971. 4. 25접수)

Abstract 2,6-Disubstituted-3-pyridazinones were synthesized from the reaction of trichloroethylideneacetophenone with substituted phenylhydrazines. Trichloroethylideneacetophenone 2,4-dinitrophenylhydrazone was isolated from the reaction of trichloroethylideneacetophenone with 2,4-dinitrophenylhydrazine and it gave 2-(2,4-dinitrophenyl)-6-phenyl-3-pyridazinone through ring closure. This indicates that pyridazinones are produced through hydrazone formation and ring closure as suggested previously. The effect of substituents of phenylhydrazine on the reaction was also discussed.

As a part of the studies on the reaction of trichloroethylideneacetophenone^{1,2} with hydrazines³, 2,6-disubstituted-3-pyridazinones were synthesized from the reaction of trichloroethylideneacetophenone with substituted phenylhydrazines. 2-(*o*-Tolyl)-, 2-(*m*-tolyl)-, 2-(*o*-nitrophenyl)-, 2-(*m*-nitrophenyl)-, 2-(2,4-dinitrophenyl)-, 2-(*m*-chlorophenyl)-, and 2-(*p*-bromophenyl)-6-phenyl-3-pyridazinone were obtained in good yields from the reactions of trichloroethylideneacetophenone with *o*-tolyl-, *m*-tolyl-, *o*-nitrophenyl-, *m*-nitrophenyl-, 2,4-dinitrophenyl-, *m*-chlorophenyl- and *p*-bromophenylhydrazine respectively in ethanol containing a small amount of hydrochloric acid or

in acetic acid.

In the previous paper³, we have suggested that the reaction would proceed through hydrazone formation and ring closure to give pyridazinones. Although hydrazones have not been isolated yet from the reaction of trichloroethylideneacetophenone with phenylhydrazine or monosubstituted phenylhydrazines, 2,4-dinitrophenylhydrazone was isolated from the reaction of trichloroethylideneacetophenone with 2,4-dinitrophenylhydrazine and it gave 2-(2,4-dinitrophenyl)-6-phenyl-3-pyridazinone on refluxing in ethanol-acetone mixture containing a small amount of hydrochloric acid or in acetic acid. It might be expected that the

reactions of trichloroethylideneacetophenone with phenylhydrazine or other substituted phenylhydrazines would proceed through hydrazone formation and ring closure to give pyridazinones.

In a series of reaction with substituted phenylhydrazines, phenylhydrazines containing electron-withdrawing group such as nitro and halogen on the phenyl group reacted more readily than those containing electron-releasing group such as methyl on the phenyl group. It might be expected that the presence of electron-withdrawing groups on the phenylhydrazine would reduce the basic strength of the hydrazine and increase the concentration of free hydrazine, and, accordingly, enhance the nucleophilic attack on the carbonyl group at the slow step for

hydrazone formation. The slower rate of 2-(*o*-nitrophenyl)-6-phenyl-3-pyridazinone formation relative to the meta and para compounds is likely due to ortho effect of the nitro group on the *o*-nitrophenylhydrazine.

The infrared spectra of synthesized 2-(*p*-bromophenyl)-6-phenyl-3-pyridazinone in this research were identical in every detail with those obtained from the sample prepared by Norman et al⁴. The infrared spectra of the synthesized pyridazinones were quite similar with strong amidecarbonyl band at 1660-1680 cm^{-1} . The absorption band owing to N-H stretching in trichloroethylideneacetophenone 2, 4-dinitrophenylhydrazone was found at 3250 cm^{-1} . The summary of the infrared spectra of compounds synthesized is as follows.

Summary of infrared spectra of compounds

2-(<i>o</i> -nitrophenyl)-6-phenyl-3-pyridazinone	C=O(amide)	1677 cm^{-1}
	C=C(conjugated)	1598
2-(<i>m</i> -nitrophenyl)-6-phenyl-3-pyridazinone	C=O(amide)	1675
	C=C(conjugated)	1602
2-(2, 4-dinitrophenyl)-6-phenyl-3-pyridazinone	C=O(amide)	1675
	C=C(conjugated)	1603
2-(<i>o</i> -tolyl)-6-phenyl-3-pyridazinone	C=O(amide)	1675
	C=C(Conjugated)	1600
2-(<i>m</i> -tolyl)-6-phenyl-3-pyridazinone	C=O(amide)	1668
	C=C(conjugated)	1603
2-(<i>m</i> -chlorophenyl)-6-phenyl-3-pyridazinone	C=O(amide)	1670
	C=C(conjugated)	1601
2-(<i>p</i> -bromophenyl)-6-phenyl-3-pyridazinone	C=O(amide)	1668
	C=C(conjugated)	1600
trichloroethylideneacetophenone 2, 4-dinitrophenylhydrazone	N-H(sec.)	3250
	C=N	1616
	C=C(conjugated)	1595

Experimental

2-(*o*-tolyl)-6-phenyl-3-pyridazinone A mixture of 2.5g of trichloroethylideneacetophenone and 1.5g of *o*-tolylhydrazine hydrochloride in

80ml of ethanol was heated under reflux for 2 hrs. Water was added until the solution became turbid. Colorless needles were crystallized out after standing the solution at room temperature. The product was recrystallized

from 70% ethanol. The yield was 1.8g(73%). m. p., 113—115°C; Anal. Calcd. for $C_{17}H_{14}ON_2$: C, 77.84; H, 5.38; N, 10.68; Found: C, 77.26; H, 5.93; N, 10.49;

2-(*m*-tolyl)-6-phenyl-3-pyridazinone A mixture of 2.5g of trichloroethylideneacetophenone and 1.5g of *m*-tolylhydrazine hydrochloride in 80ml of ethanol was heated under reflux for 2 hrs. Water was added until the solution became turbid. Crystals were obtained after standing the solution at room temperature. The product was recrystallized from 70% ethanol. The yield was 2.0g (81%). m. p., 109—111°C; Anal. Calcd. for $C_{17}H_{14}ON_2$: C, 77.84 H, 5.38; N, 10.68; Found. C, 77.32. H, 5.82; N, 10.27;

2-(*o*-nitrophenyl)-6-phenyl-3-pyridazinone A mixture of 1.6g of trichloroethylideneacetophenone and 1.2g of *o*-nitrophenylhydrazine hydrochloride in 50ml of ethanol was heated under reflux for 1 hr. The reaction mixture was transferred to evaporating dish and evaporated to one-third of original volume at room temperature. The crystals separated from the solution were recrystallized from 80% ethanol. The yield was 0.9g (49%). m. p., 121—123°C; Anal. Calcd. for $C_{16}H_{11}O_3N_3$: C, 65.53; H, 3.78; N, 14.33; Found: C, 65.32; H, 4.03; N, 14.02;

2-(*m*-nitrophenyl)-6-phenyl-3-pyridazinone A mixture of 2.4g of trichloroethylideneacetophenone and 1.8g of *m*-nitrophenylhydrazine hydrochloride in 80ml of ethanol was heated under reflux for 20 min. Crystals were obtained after cooling the solution at room temperature. The product was recrystallized from 95% ethanol. The yield was 1.7g (61%). m. p., 176—178°C; Anal. Calcd. for $C_{16}H_{11}O_3N_3$: C, 65.53; H, 3.78; N, 14.33; Found: C, 65.07; H, 4.59; N, 14.06;

2-(*m*-chlorophenyl)-6-phenyl-3-pyridazinone

A mixture of 2.0g of trichloroethylideneacetophenone and 2.0g of *m*-chlorophenylhydrazine sulfate in 30ml of ethanol was heated under reflux for 1 hr. Crystals were obtained after cooling the solution at room temperature. The product was recrystallized from 80% ethanol. The yield was 1.6g (71%). m. p., 141—144°C; Anal. Calcd. for $C_{16}H_{11}ON_2Cl$: C, 67.96; H, 3.92; N, 9.91; Cl, 12.50; H, 4.14; N, 10.03; Cl, 13.0;

2-(*p*-bromophenyl)-6-phenyl-3-pyridazinone A mixture of 2.0g of trichloroethylideneacetophenone and 2.0g of *p*-bromophenylhydrazine hydrochloride in 80ml of ethanol was heated under reflux for 1 hr. Colorless crystals were obtained after cooling the solution at room temperature. The product was recrystallized from 95% ethanol. The yield was 1.2g(46%). m. p., 174—175°C (lit., 174—176°C);

Trichloroethylideneacetophenone 2,4-dinitrophenylhydrazone To a hot solution of 2.0g of trichloroethylideneacetophenone in 50ml of methanol was added a hot solution of 1.6g of 2,4-dinitrophenylhydrazine and 3.0ml of conc. hydrochloric acid in 50ml of methanol. The orange crystals were obtained after cooling the solution at room temperature. The product was recrystallized from acetone-ethanol mixture (2 : 1). The yield was 2.0g (58%). m. p., 153—155°C d; Anal. Calcd. for $C_{16}H_{11}O_4N_4Cl_3$: C, 44.68; H, 2.58; N, 13.03; Cl, 24.74; Found: C, 44.19; H, 3.35; N, 12.68; Cl, 24.9;

2-(2,4-dinitrophenyl)-6-phenyl-3-pyridazinone 1. A mixture of 1.0g of trichloroethylideneacetophenone and 1.0g of 2,4-dinitrophenylhydrazine in 4.0 ml of glacial acetic acid was heated under reflux for 5 min. Water was added until the solution became turbid. Crystals were obtained after standing the solution at room temperature. The product was

recrystallized from 80% acetic acid. The yield was 0.9g(67%). m. p., 208—210°C;

2. 1.2g of trichloroethylideneacetophenone 2,4-dinitrophenylhydrazone in 40 ml of glacial acetic acid was heated under reflux for 2 min. Water was added until the solution became turbid. Yellow crystals were obtained after standing the solution at room temperature. The product was recrystallized from 80% acetic acid. The yield was 0.6g (64%). m. p., 208—210°C;

3. A mixture of 0.6g of trichloroethylideneacetophenone 2,4-dinitrophenylhydrazone and 3 ml of conc. hydrochloric acid in 80ml of acetone-ethanol mixture was heated under reflux for 20 min. The reaction mixture was transferred to evaporating dish and evaporated the solvent. The product was recrystallized from 80% acetic acid. The yield was 0.3g (64%). m. p., 208—210°C; mixed m. p., 208—210°C; Anal. Calcd. for $C_{16}H_{10}O_5N_4$: C, 56.81; H, 2.98; N, 16.57; Found: C, H, 3.83; N, 16.12; 56.30;

Carbon, hydrogen and nitrogen were determined by microanalysis using Coleman Model 33 C&H, and N Analyzer. Chlorine was determined by neutron activation analysis using TRIGA Mark II Reactor at AERI.

Acknowledgement

I should like to thank Professor Sae Hee Chang of the Department of Chemistry, Seoul National University for advising this research throughout. I also thank Mr. Chul Lee of the Atomic Energy Research Institute for helping the analysis of chlorine in the compounds.

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