

Trichloroethylideneacetone 과 Hydrazine 들의 반응 (I)

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Reactions of Trichloroethylideneacetone with Hydrazines (I)

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Abstract 2, 6-Disubstituted-3-pyridazinones were synthesized from the reaction of trichloroethylideneacetone with substituted phenylhydrazines. From the reaction of trichloroethylideneacetone with *o*-nitrophenylhydrazine, pyridazinone derivative was not obtained, but γ, γ -dichloro- γ -(*o*-nitrophenylhydrazino)-ethylideneacetone was obtained in 24% yield.

In the previous study^{1,2}, 2, 6-disubstituted-3-pyridazinones were synthesized from the reaction of trichloroethylideneacetophenone with phenylhydrazine or substituted phenylhydrazines. The same reaction was applied to synthesize 2, 6-disubstituted-3-pyridazinones from trichloroethylideneacetone^{3,4,5} and substituted phenylhydrazines. 2-(*m*-Nitrophenyl)-, 2-(*p*-nitrophenyl)-, 2-(*p*-chlorophenyl)- and 2-(*p*-bromophenyl)-6-methyl-3-pyridazinone were obtained from the reactions of trichloroethylideneacetone with *m*-nitrophenyl-, *p*-nitrophenyl-, *p*-chlorophenyl- and *p*-bromophenylhydrazine respectively in ethanol containing a small amount of hydrochloric acid. The yields of pyridazinones obtained from trichloroethylideneacetone were a little lower compared to those obtained from trichloroethylideneacetophenone, because the former polymerized to give tarred material at elevated

temperature, especially in the presence of acid. However, in the case of 2-(*p*-nitrophenyl)-6-methyl-3-pyridazinone synthesis, the method described was more convenient than that by Overend *et al.*⁶, and, the yield of product was also higher than that obtained by them.

From the reaction of trichloroethylideneacetone with *o*-nitrophenylhydrazine, 2-(*o*-nitrophenyl)-6-methyl-3-pyridazinone was not obtained, but γ, γ -dichloro- γ -(*o*-nitrophenylhydrazino)-ethylideneacetone was obtained in 24% yield. It might be expected that the nucleophilic attack of *o*-nitrophenylhydrazine would be occurred on the trichloromethyl group instead of the carbonyl group on account of less positive character of the carbonyl group due to the effect of electron-releasing methyl group, and ortho effect of nitro group on the *o*-nitrophenylhydrazine.

The infrared spectra of the pyridazinones synthesized were quite similar with strong amide-carbonyl band at 1660–1680cm⁻¹. The

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absorption bands owing to N—H and C=O stretching in γ, γ -dichloro- γ -(*o*-nitrophenylhydrazino)-ethylideneacetone were found at 3230cm^{-1}

and 1657cm^{-1} respectively. The summary of the infrared spectra of compounds synthesized is as follows.

Summary of Infrared Spectra of Compounds

2-(<i>m</i> -nitrophenyl)-6-methyl-3-pyridazinone	C=O(amide)	1667cm^{-1}
	C=C(conjugated)	1605
2-(<i>p</i> -nitrophenyl)-6-methyl-3-pyridazinone	C=O(amide)	1680
	C=C(conjugated)	1610
2-(<i>p</i> -chlorophenyl)-6-methyl-3-pyridazinone	C=O(amide)	1680
	C=C(conjugated)	1608
2-(<i>p</i> -bromophenyl)-6-methyl-3-pyridazinone	C=O(amide)	1675
	C=C(conjugated)	1604
γ, γ -dichloro- γ -(<i>o</i> -nitrophenylhydrazino)-ethylideneacetone	N—H(sec.)	3230
	C=O(ketone)	1657
	C=C(conjugated)	1608

Experimental

2-(*m*-nitrophenyl)-6-methyl-3-pyridazinone

A mixture of 2.0g of trichloroethylideneacetone and 1.6g of *m*-nitrophenylhydrazine hydrochloride in 50ml of ethanol was heated under reflux on the water bath for 20 min. Pale yellow crystals were obtained after cooling the solution at room temperature. The product was recrystallized from 95% ethanol. The yield was 1.2g (62%). m. p., $181\text{--}183^\circ\text{C}$; Anal. Calcd. for $\text{C}_{11}\text{H}_9\text{O}_3\text{N}_3$: C, 57.14; H, 3.92; N, 18.18; Found: C, 56.71; H, 4.65; N, 17.81;

2-(*p*-nitrophenyl)-6-methyl-3-pyridazinone

A mixture of 2.5g of trichloroethylideneacetone and 2.0g of *p*-nitrophenylhydrazine hydrochloride in 60ml of ethanol was heated under reflux on the water bath for 30 min. Crystals were obtained after standing the solution at room temperature for 24 hrs. The product was recrystallized from 50% acetic acid. The yield was 1.2g (49%). m. p., $184\text{--}185^\circ\text{C}$ (lit. $184\text{--}185^\circ\text{C}$); Anal. Calcd. for $\text{C}_{11}\text{H}_9\text{O}_3\text{N}_3$: C, 57.14; H,

3.92; N, 18.18; Found: C, 56.91; H, 4.26; N, 17.93;

2-(*p*-chlorophenyl)-6-methyl-3-pyridazinone

A mixture of 2.5g of trichloroethylideneacetone and 2.0g of *p*-chlorophenylhydrazine hydrochloride in 60ml of ethanol was heated under reflux on the water bath for 30 min. Water was added until the solution became turbid. Crystals were obtained after standing the solution at room temperature to permit the evaporation of nearly all the ethanol in the evaporating dish. The product was recrystallized from 30% ethanol. The yield was 1.0g (41%). m. p., $99\text{--}101^\circ\text{C}$; Anal. Calcd. for $\text{C}_{11}\text{H}_9\text{ON}_2\text{Cl}$: C, 59.88; H, 4.11; N, 12.72; Found: C, 59.52; H, 4.36; N, 12.96;

2-(*p*-bromophenyl)-6-methyl-3-pyridazinone

A mixture of 1.3g of trichloroethylideneacetone and 1.5g of *p*-bromophenylhydrazine hydrochloride in 30ml of ethanol was heated under reflux on the water bath for 40 min. Water was added until the solution became turbid. Crystals were obtained after standing the solution at room temperature to permit the evapor-

ation of nearly all the ethanol in the evaporating dish. The product was recrystallized from 30% ethanol. The yield was 0.6g(34%). m. p., 93—94°C; Anal. Calcd. for $C_{11}H_9ON_2Br$: C, 49.83; H, 3.42; N, 10.57; Found: C, 49.62; H, 3.93; N, 10.03;

γ, γ -dichloro- γ -(*o*-nitrophenylhydrazino)-ethylideneacetone A mixture of 2.0g of trichloroethylideneacetone and 1.6g of *o*-nitrophenylhydrazine hydrochloride in 60ml of ethanol was heated under reflux on the water bath for 40 min. Yellow needles were obtained after cooling the solution at room temperature. The product was recrystallized from ethanol. The yield was 0.6g(24%). m. p., 154—155°C d; Anal. Calcd. for $C_{11}H_{11}O_3N_3Cl_2$: C, 43.44; H, 3.65; N, 13.82; Cl, 23.32; Found: C, 42.61; H, 3.66; N, 13.34; Cl, 23.5;

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.

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