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Photochemistry of Conjugated Nitrogen–Thiocarbonyl Systems. VI.^{1a)}
Photoaddition of Olefins to 2-Thiouracil and
2-Thioquinazolin-2,4-(1*H*,3*H*)-dione^{1b)}

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Photolyses of 2-thiouracil (**1**) in the presence of olefins afforded 2-substituted products and cyclobutane products, showing dual reaction sites of the thione and the C=C bond. Photolyses of 2-thioquinazolin-2,4(1*H*,3*H*)-dione (**6**) in the presence of olefins gave 2-substituted products.

Keywords—photoaddition; olefin; thiocarbonyl system; thietane intermediate; 2-thiouracil; 2-thioquinazolin-2,4(1*H*,3*H*)-dione

In the course of studies of the photochemistry of nitrogen–carbonyl³⁾ and –thiocarbonyl⁴⁾ systems, we have reported the photochemical behavior of nitrogen–heteroaromatic thione systems. Our initial work showed that a major photoreaction of thione systems, such as 2-thiopyridone, 2-thiopyrimidine and quinoline-2-thione, is [2+2]addition predominately localized at the C=S bond.^{1,5)} Photoaddition reactions of 4-thiouracil, one of the minor bases in transfer ribonucleic acid (RNA), have been extensively studied, and the major reaction site is localized at the C=S bond.⁶⁾ Photoaddition of 4-thiouracil to the C₅=C₆ bond of cytosine is known to occur also at the thione site on irradiation of RNA containing 4-thiouridylic acid, resulting in photochemical cross-linking.⁷⁾ Generally photochemical modification is one of the useful methods in studies on the tertiary structure of biopolymers. 2-Thiouracil derivatives such as 5-methylaminomethyl-2-thiouracil are also found in transfer RNA.⁸⁾ However, the photochemical behavior of 2-thiouracil has not yet been reported. In the present paper, we describe photoaddition reactions of 2-thiouracil (**1**) and its bicyclic homologue, 2-thioquinazolin-2,4(1*H*,3*H*)-dione (**6**).

Irradiation of **1** in the presence of excess olefin **2a** or **2b** gave not only the 2-substituted pyrimidone (**3**), probably derived from the thietane intermediate,^{1a)} but also the cyclobutane product (**5**) which is the [2+2]addition product at the heterocyclic ring-incorporated C=C bond. Structures of **3** were supported by the nuclear magnetic resonance (NMR) spectral data. For example, for **3b**: a signal at 1.63 ppm due to SH disappeared and the spin–spin multiplicity of a signal (–CH(CH₃)SH) at 3.57 ppm (quintet) due to 2'-H changed to a quartet on addition of deuterium oxide, showing the presence of a 2'-mercapto-1',1'-dimethylpropyl substituent in **3b**. The positions of the three methyl substituents of **5b** were also determined from the following NMR spectral data: a signal (C₆-H) at 2.99 ppm (dd) was not affected by the addition of deuterium oxide, though the spin–spin multiplicity of the signal (C₁-H) at 3.56–3.80 ppm (multiplet) was simplified to a doublet with deuterium oxide. Therefore, these NMR data have established the expected head-to-tail orientation for **5b** as shown in Chart 1. In the pioneering work on photocycloaddition of cyclenones to an unsymmetrical olefin, Corey *et al.* observed a preference for head-to-tail over head-to-head reaction of cyclohexenone and isobutylene.⁹⁾ Thus, it is quite reasonable that **5b** is a head-to-tail addition

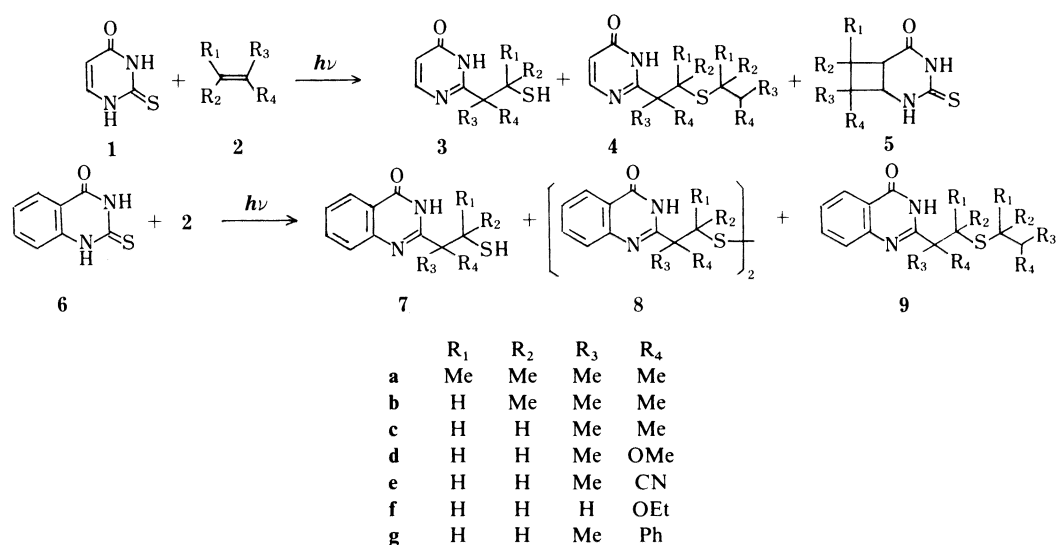


Chart 1

TABLE I. Yields of Photoproducts

Thione (mmol)	Olefin (mmol)	Time (h)	Product yield (%)				
			3	4	5	7	8
1 (1.0)	2a (10)	4	36	—	17		
1 (1.0)	2b (10)	4	10	—	12		
1 (1.0)	2c (10)	4	—	37	—		
1 (1.0)	2d (10)	4	27	—	—		
6 (1.0)	2a (10)	4				45	—
6 (1.0)	2b (10)	4				16	12
6 (1.0)	2c (10)	4				—	—
6 (1.0)	2d (10)	2				67	—
6 (1.0)	2e (10)	2				60	—
6 (1.0)	2f (10)	3				—	—
6 (1.0)	2g (10)	4				19	3

product from **1** and 2-methyl-2-butene (**2b**). Similar irradiation of **1** and isobutene (**2c**) resulted in the formation of the two-fold addition product (**4c**), though irradiation of **1** and **2d** gave only the 2-substituted pyrimidone (**3d**). The structure of the two-fold addition product (**4c**) was confirmed by the NMR spectrum and the result of Raney Ni reduction. The NMR spectrum of **4c** showed a typical signal of an isobutyl group, and the position of the dimethyl groups was confirmed to be at the 1'-position of 4(3*H*)-pyrimidone because the Raney Ni reduction of **4c** afforded 2-*tert*-butyl-4(3*H*)-pyrimidone having an identical melting point with that described in the literature.¹⁰ It was revealed that there are two reaction sites for the photoaddition of olefin to 2-thiouracil depending on the structures of the adding olefins. Namely, with tri- and tetrasubstituted olefins (**2a**, **2b**), the addition takes place not only at the C=S bond but also at the C=C bond of **1**. 2-Thiouracil (**1**) has two photochemically reactive candidate groups: an enone moiety similar to that in uracil which would undergo [2+2]cycloaddition with olefin,¹¹ and a thiocarbonyl moiety. In the study of the photochemical [2+2]cycloaddition of 2-cyclohexenones with substituted olefins,⁹ it was reported that high

reactivity is seen with those olefins which are good π -donors. On the other hand, the susceptibility of olefinic substrates to excited thiocarbonyls such as 2-thiopyridone and isoquinolin-2-thione does not significantly depend on the substituents on the olefin.^{4,5)} Therefore, it may be reasonable to assume that considerably electron-rich olefins such as **2a** and **2b** will react competitively at the C=C and C=S sites. Further, the C=S bond in **1** would be sterically more hindered than the C=C bond, and consequently, tetra- or tri-substituted olefins such as **2a**, **2b** may prefer to attack the less hindered C=C bond. Disubstituted olefins (**2c**, **2d**) afford products derived from the addition at the thione site of **1**, though **2d** is an electron-rich olefin. As reported in the preceding paper,^{1a)} the use of isobutene (**2c**) enhanced the two-fold addition giving **4c**. Photochemical addition of electron-deficient olefins, such as acrylonitrile, crotononitrile and methacrylonitrile, to 4-thiouracil derivatives occurs at the thione site,⁶⁾ whereas the reaction of electron-rich olefins has not yet been reported. Therefore, attempts were made to examine the photoaddition of the 4-thiouracil to olefins (**2a—d**). However, the photolysis afforded only complex mixtures of products. Photolysis of 2-thiouracil (**1**) and methacrylonitrile, an electron-deficient olefin, was examined, but the yields of photoaddition products were too low to allow elucidation of the stereochemical structures.

Next, 2-thioquinazolin-2,4(1*H*,3*H*)-dione (**6**) was subjected to similar photolysis in the presence of these olefins (**2a—g**). All the photoproducts were 2-substituted quinazoline derivatives (**7**, **8**, and **9**) apparently derived from the addition at the 2-thione site of **6**. In the case of the olefins **2c** and **2f**, two-fold addition products (**9**) were again obtained. In the addition reactions to 2-thioquinazolin-2,4(1*H*,3*H*)-dione (**6**), isobutene (**2c**) and ethyl vinyl ether (**2f**) were again the favored olefins, being relatively electron-rich and sterically less hindered, to facilitate the process of the second addition reaction. Thus, photoaddition of olefins to these bicyclic azaheterocyclic thione systems, which lack the activated ring-double bonds such as in **1**, occurs predominantly at the C=S group, leading to various aza-heterocycles with substituents introduced at the thiocarbonyl-carbon, and providing a simple synthetic method for such aza-bicyclic systems.

Experimental

Melting points were determined on a Yamato MP-21 apparatus and are uncorrected. Vacuum distillation was carried out using a Büchi Kugelrohr apparatus and boiling points are uncorrected bath temperatures. NMR spectra were taken on a JEOL JNM-FX 100 FT-NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Mass spectra (MS) were obtained with a JMS D-300 mass spectrometer. Infrared spectra (IR) were recorded with a JASCO IRA-1 infrared spectrometer. The light source was a Type EHBW1 (Eikoh-sha) 500 W high-pressure mercury lamp.

General Procedure for the Photolysis—A solution of **1** or **6** (1.0 mmol) in 100 ml of MeOH with **2** (10 mmol) was irradiated with a 500 W high-pressure mercury lamp through a Pyrex filter for 2–4 h (Table I) under an argon atmosphere. After removal of the solvent *in vacuo*, the residue was subjected to silica gel preparative layer chromatography (PLC), followed by recrystallization or distillation under reduced pressure. Spectral and elemental analysis data are given in Tables II and III.

2-(2-Mercapto-1,1,2-trimethylpropyl)pyrimidin-4-one (3a) and 7,7,8,8-Tetramethyl-3-thioxo-*cis*-2,4-diazabicyclo[4.2.0]octan-5-one (5a)—From 128 mg (1.0 mmol) of **1** and 842 mg (10 mmol) of **2a**. PLC with benzene–AcOEt (1 : 1). **3a**: colorless fine needles of mp 164–166 °C (AcOEt–*n*-hexane), 76 mg (36%). **5a**: colorless prisms of mp 223–224 °C (AcOEt–*n*-hexane), 36 mg (17%).

2-(2-Mercapto-1,1-dimethylpropyl)pyrimidin-4-one (3b) and 7,8,8-Trimethyl-3-thioxo-*cis*-2,4-diazabicyclo[4.2.0]octan-5-one (5b)—From 128 mg (1.0 mmol) of **1** and 701 mg (10 mmol) of **2b**. PLC with benzene–acetone (3 : 1). **3b**: colorless oil of bp 235 °C (bath temp.)/0.4 mmHg, 20 mg (10%). **5b**: colorless fine needles of mp 180–183 °C (benzene–*n*-hexane), 23 mg (12%).

2-(2-Isobutylthio-1,1-dimethylethyl)pyrimidine-4-one (4c)—From 128 mg (1.0 mmol) of **1** and 600 mg (10 mmol) of **2c**. PLC with *n*-hexane–acetone (10 : 3). Colorless oil of bp 210 °C (bath temp.)/0.2 mmHg, 88 mg (37%).

2-(2-Mercapto-1-methoxy-1-methylethyl)pyrimidin-4-one (3d)—From 128 mg (1.0 mmol) of **1** and 721 mg (10 mmol) of **2d**. PLC with *n*-hexane–acetone (2 : 1). Colorless fine prisms of mp 49–51 °C (AcOEt–*n*-hexane), 54 mg (27%).

TABLE II. Spectral Data of Photoproducts

Products	IR (Nujol) $\nu_{\max}$ (cm ⁻¹)	MS (m/z)	¹ H-NMR (CDCl ₃) δ (ppm) J (Hz)
3a	3140 (NH), 3090 (NH), 1690 (C=O), 1660 (C=N)	212 (M ⁺), 179, 138 (base), 123, 75	1.44 (6H, s), 1.49 (6H, s), 1.90 (1H, s, SH), 6.34 (1H, d, $J=6.2$), 7.93 (1H, d, $J=6.2$), 10.3 (1H, br, NH)
5a	3160 (NH), 3100 (NH), 1690 (C=O)	212 (M ⁺), 129, 84 (base), 69	1.05 (3H, s), 1.07 (3H, s), 1.11 (3H, s), 1.20 (3H, s), 3.02 (1H, d, $J=9.3$), 3.77 (1H, dd, $J=9.3$, 2.9), 7.56 (1H, br, NH), 8.37 (1H, br, NH)
3b	1660 (C=O), 1580 (C=N)	198 (M ⁺), 183, 165, 138 (base), 123, 75	1.29 (3H, d, $J=7$), 1.40 (3H, s), 1.43 (3H, s), 1.63 (1H, br, SH), 3.57 (1H, quint, $J=7$), 6.32 (1H, d, $J=6.6$), 7.96 (1H, d, $J=6.6$), 10.8—11.4 (1H, NH)
5b	3140 (NH), 1710 (C=O)	198 (M ⁺), 129 (base), 70, 55	1.04 (3H, d, $J=7$), 1.12 (3H, s), 1.17 (3H, s), 2.41 (1H, dq, $J=14, 7$), 2.99 (1H, dd, $J=15, 9$), 3.56—3.80 (1H, m), 7.62 (1H, br, NH), 8.42 (1H, br, NH)
4c	3100 (NH), 1660 (C=O), 1580 (C=N)	240 (M ⁺), 225, 183, 151 (base)	0.91 (6H, d, $J=6.6$), 1.47 (6H, s), 1.71 (1H, m), 2.34 (2H, d, $J=6.8$), 2.97 (2H, s), 6.33 (1H, d, $J=6.6$), 7.99 (1H, d, $J=6.6$), 12.1—12.4 (1H, br, NH)
3d	1680 (C=O), 1590 (C=N)	200 (M ⁺), 169, 159, 137 (base)	1.39 (1H, t, $J=8.4$, SH), 1.60 (3H, s), 3.04 (2H, d, $J=8.3$), 3.36 (3H, s), 6.34 (1H, d, $J=6.6$), 7.92 (1H, d, $J=6.6$), 10.2—10.6 (1H, br, NH)
7a	3180 (NH), 3140 (NH), 1665 (C=O), 1600 (C=N)	262 (M ⁺), 229, 188 (base)	1.48 (6H, s), 1.56 (6H, s), 1.96 (1H, s, SH), 7.38—7.54 (1H, m), 7.70—7.77 (2H, m), 8.27 (1H, dd, $J=9$), 9.8—10.2 (1H, br, NH)
7b	3160 (NH), 3120 (NH), 1670 (C=O), 1600 (C=N)	248 (M ⁺), 215, 188 (base), 173, 41	1.34 (3H, d, $J=7.0$), 1.48 (3H, s), 1.51 (3H, s), 1.61 (1H, br, SH), 3.69 (1H, quint, $J=7.0$), 7.38—7.55 (1H, m), 7.64—7.84 (2H, m), 8.27 (1H, d, $J=7.6$), 10.1—10.4 (1H, br, NH)
8b	3160 (NH), 3120 (NH), 1660 (C=O), 1600 (C=N),	494 (M ⁺), 246, 231, 215, 188 (base), 173, 119	1.21 (3H, d, $J=7.0$), 1.33 (6H, s), 3.57 (1H, q, $J=7.0$), 7.44 (1H, d, $J=7.6$), 7.64 (1H, t, $J=7.6$), 7.79 (1H, t, $J=7.6$), 8.91 (1H, d, $J=7.6$), 8.17—8.45 (1H, br, NH)
9c	3180 (NH), 3140 (NH), 1670 (C=O), 1610 (C=N)	290 (M ⁺), 234, 233, 201 (base)	0.88 (6H, d, $J=7$), 1.54 (6H, s), 1.60—1.90 (1H, m), 2.37 (2H, d, $J=7$), 3.03 (2H, s), 7.38—7.54 (1H, m), 7.66—7.78 (2H, m), 8.22—8.32 (1H, m), 10.2—11.6 (1H, br, NH)
7d	3180 (NH), 3140 (NH), 1670 (C=O), 1620 (C=N)	250 (M ⁺), 219, 204, 203	1.43 (1H, dd, $J=9, 8$, SH), 1.67 (3H, s), 3.11 (1H, d, $J=8$), 3.14 (1H, d, $J=9$), 3.38 (3H, s), 7.41—7.77 (3H, m), 8.29 (1H, dd, $J=8, 1$), 9.5—9.9 (1H, br, NH)
7e	3170 (NH), 3140 (NH), 1665 (C=O), 1620 (C=N)	245 (M ⁺), 212, 199	1.94 (1H, dd, $J=9, 9$, SH), 1.99 (3H, s), 3.20 (1H, dd, $J=14, 9$), 3.50 (1H, dd, $J=14, 9$), 7.65—7.48 (1H, m), 7.86—7.74 (2H, m), 8.32 (1H, dd, $J=8, 1$), 11.2—11.6 (1H, br, NH)
9f	3170 (NH), 3130 (NH), 1680 (C=O), 1610 (C=N)	322 (M ⁺), 277, 249, 217, 203 (base)	1.19 (3H, t, $J=7$), 1.31 (3H, t, $J=7$), 3.00 (1H, dd, $J=14, 6$), 3.21 (1H, dd, $J=14, 4$), 3.38—3.81 (8H, m), 4.56 (1H, dd, $J=6, 4$), 7.40—7.85 (3H, m), 8.26 (1H, m), 9.5—9.8 (1H, br, NH)
7g	3160 (NH), 3120 (NH), 1670 (C=O), 1610 (C=N)	296 (M ⁺), 263, 250 (base), 234, 187, 118	1.34 (1H, t, $J=8.0$, SH), 1.88 (3H, s), 3.24 (1H, dd, $J=14, 8$), 3.52 (1H, dd, $J=14, 9$), 7.31 (5H, s), 7.40—7.57 (1H, m), 7.72—7.84 (2H, m), 8.21 (1H, d, $J=7.8$), 8.84—9.08 (1H, br, NH)
8g	3160 (NH), 3120 (NH), 1670 (C=O), 1610 (C=N)	295 (M ⁺ /2), 279, 263, 250 (base), 234, 187, 118	1.81 (6H, s), 3.22 (1H, d, $J=13.4$), 3.32 (1H, d, $J=13.2$), 3.64 (1H, d, $J=13.2$), 3.74 (1H, d, $J=13.4$), 7.23 (10H, s), 7.37—7.54 (2H, m), 7.41 (4H, d, $J=3.4$), 8.18 (2H, d, $J=7.6$), 8.86 (2H, br, NH)

TABLE III. Elemental and Mass Spectral Analyses of Photoproducts

Product	Formula	Calcd (Found)			
		C	H	N	S
3a	C ₁₀ H ₁₆ N ₂ OS	56.57 (56.60)	7.60 7.65	13.19 13.12	15.10 15.05)
5a	C ₁₀ H ₁₆ N ₂ OS	56.57 (56.56)	7.60 7.63	13.19 13.03	15.10 14.93)
3b	C ₉ H ₁₄ N ₂ OS	54.52 (54.80)	7.12 7.19	14.13 13.83	16.14 15.93)
5b	C ₉ H ₁₄ N ₂ OS	54.53 (54.51)	7.12 7.23	14.13 14.04	16.14 16.20)
4c	C ₁₂ H ₂₀ N ₂ OS	59.96 (60.15)	8.38 8.43	11.65 11.36	13.32 13.18)
3d	C ₈ H ₁₂ N ₂ O ₂ S		200.06206 (200.06313)		
7a	C ₁₄ H ₁₈ N ₂ OS	64.09 (64.03)	6.92 6.93	10.68 10.54	12.22 12.27)
7b	C ₁₃ H ₁₆ N ₂ OS		248.09838 (248.09937)		
8b	C ₂₆ H ₃₀ N ₄ O ₂ S ₂	63.13 (63.03)	6.11 6.14	11.33 11.17	12.96 13.07)
9c	C ₁₆ H ₂₂ N ₂ OS	66.17 (66.31)	7.64 7.71	9.65 9.72	11.04 11.11)
7d	C ₁₂ H ₁₄ N ₂ O ₂ S	57.58 (57.75)	5.64 5.79	11.19 11.03	12.81 12.76)
7e	C ₁₂ H ₁₁ N ₃ OS	58.75 (58.90)	4.52 4.46	17.13 16.98	13.07 13.20)
9f	C ₁₆ H ₂₂ N ₂ O ₃ S	59.60 (59.46)	6.88 6.93	8.69 8.65	9.95 10.11)
7g	C ₁₇ H ₁₆ N ₂ OS		296.09848 (296.09734)		
8g	C ₃₄ H ₃₀ N ₄ O ₂ S ₂ · 1/4 C ₆ H ₁₂	69.72 (69.72)	5.51 5.36	9.15 9.02	10.47 10.49)

2-(2-Mercapto-1,1,2-trimethylpropyl)quinazolin-4(3H)-one (7a)—From 178 mg (1.0 mmol) of **6** and 842 mg (10 mmol) of **2a**. PLC with *n*-hexane–acetone (2 : 1). Colorless fine needles of mp 172–174 °C (*n*-hexane), 117 mg (45%).

2-(2-Mercapto-1,1-dimethylpropyl)quinazolin-4(3H)-one (7b) and Bis[1,2,2-trimethyl-2-(3,4-dihydro-4-oxo-2-quinazolinyl)ethyl] Disulfide (8b)—From 178 mg (1.0 mmol) of **6** and 701 mg (10 mmol) of **2b**. PLC with CHCl₃. **7b**: colorless prisms of mp 132–135 °C (*n*-hexane), 39 mg (16%). **8b**: colorless fine prisms of 224–227 °C (MeOH), 61 mg (12%).

2-(2-Isobutylthio-1,1-dimethylethyl)quinazolin-4(3H)-one (9c)—From 178 mg (1.0 mmol) of **6** and 600 mg (10 mmol) of **2c**. PLC with *n*-hexane–acetone (3 : 1). Colorless solid of bp 230 °C (bath temp.)/0.45 mmHg, 76 mg (26%).

2-(2-Mercapto-1-methoxy-1-methylethyl)quinazolin-4(3H)-one (7d)—From 178 mg (1.0 mmol) of **6** and 721 mg (10 mmol) of **2d**. PLC with *n*-hexane–acetone (2 : 1). Colorless fine needles of mp 111–113 °C (AcOEt–*n*-hexane), 167 mg (67%).

2-(1-Cyano-2-mercapto-1-methylethyl)quinazolin-4(3H)-one (7e)—From 178 mg (1.0 mmol) of **6** and 671 mg (10 mmol) of **2e**. PLC with *n*-hexane–acetone (2 : 1). **7e**: colorless fine needles of mp 157–159 °C (AcOEt–*n*-hexane), 147 mg (60%).

2-[1-Ethoxy-2-(2-ethoxyethylthio)ethyl]quinazolin-4(3H)-one (9f)—From 178 mg (1.0 mmol) of **6** and 721 mg (10 mmol) of **2f**. PLC with *n*-hexane–acetone (2 : 1). Colorless needles of mp 79–81 °C (*n*-hexane), 167 mg (52%).

2-(2-Mercapto-1-methyl-1-phenylethyl)quinazolin-4(3H)-one (7g) and Bis[2-methyl-2-phenyl-2-(3,4-dihydro-4-oxo-2-quinazolinyl)ethyl] Disulfide (8g)—From 178 mg (1.0 mmol) of **6** and 1.18 g (10 mmol) of **2g**. PLC with *n*-hexane–AcOEt (3 : 1). **7g**: colorless fine prisms of mp 168–172 °C (AcOEt–*n*-hexane), 57 mg (19%). **8g**: colorless fine prisms of mp 223–229 °C (AcOEt–*n*-hexane), 19 mg (3%).

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