

The Rhodium(II) Acetate-Catalyzed Reaction of Diacyldiazomethanes with Isothiocyanates: Formation of 2-Thioxo-2*H*-1,3-oxazin-4(3*H*)-one

Hirofumi NAKANO[†] and Toshikazu IBATA*

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560

(Received July 20, 1992)

The rhodium(II) acetate-catalyzed reaction of diacyldiazomethanes such as dibenzoyldiazomethane, acetylaryldiazomethanes, diacetyldiazomethane, and diazodimedone with isothiocyanates gave 2-thioxo-2*H*-1,3-oxazin-4(3*H*)-ones through the [4+2] cycloaddition of isothiocyanates with acylketenes which were derived by the Wolff rearrangement of the diacyldiazomethanes. Migration aptitude of methyl and aryl groups was discussed in the reaction of acetylaryldiazomethanes.

Rhodium(II) acetate has been utilized as an excellent catalyst for the mild decomposition of α -diazocarbonyl compounds to generate the corresponding ketocarbonyls to avoid the Wolff rearrangement in the various reaction systems.¹⁾ In the previous paper of this series, the authors have reported the rhodium(II) acetate-catalyzed reaction of a variety of α -diazocarbonyl compounds **1** in the presence of isothiocyanates to provide 2-imino-1,3-oxathioles (**3**).²⁾ This reaction was explained by the formation of thiocarbonyl ylide through the initial attack of ketocarbonyl (**2**) on sulfur atom of isothiocyanate, followed by the intramolecular 1,5-cyclization. In this reaction system the products derived through the Wolff rearrangement were observed only in the reaction of diazodimedone. Therefore, we studied the reaction of diacyldiazomethanes with isothiocyanates in the presence of rhodium(II) acetate in order to investigate the structural effect on the reaction pathway in this reaction (Chart 1).

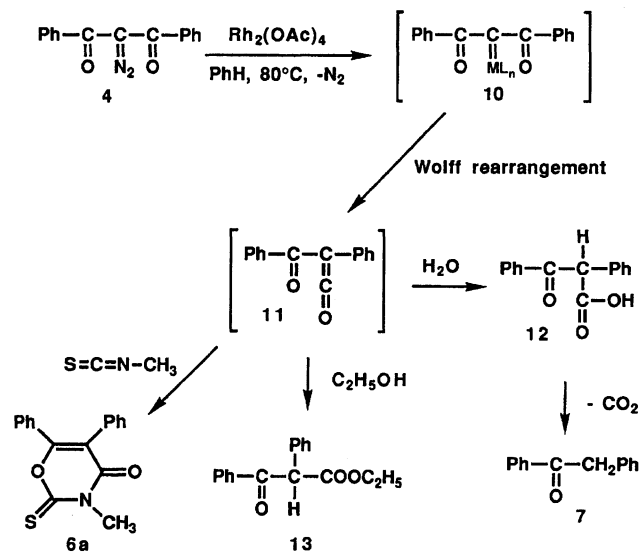
Results and Discussion

The rhodium(II) acetate-catalyzed reaction of dibenzoyldiazomethane (**4**) with methyl isothiocyanate (**5a**) gave neither 2-imino-1,3-oxathiole (**8a**) nor 1,3-oxazoline-2(3*H*)-thione (**9a**), but gave 3-methyl-5,6-diphenyl-2-thioxo-2*H*-1,3-oxazin-4(3*H*)-one (**6a**) and benzyl phenyl ketone (**7**) in 60 and 10% yields, respectively. The complete decoupling spectrum of ¹³C NMR of the thioxooxazinone **6a** is similar to that of 2-methylimino-1,3-oxathioles (**3**: R³=CH₃) described in the previous paper.²⁾ However, nondecoupling spectrum of **6a** revealed that the product does not have a structure of 2-imino-1,3-oxathiole. A quartet signal at 181.91 ppm (³J_{CH}=4.3 Hz) is not assigned to carbonyl carbon of benzoyl group on C-4 of the iminooxathiole **8a** but assigned to thiocarbonyl carbon of thioxooxazinone **6a**, because of its long-range coupling with *N*-methyl protons. Carbonyl carbon at C-4 of **6a** showed a quartet signal at 158.94 ppm (³J_{CH}=2.4 Hz, coupled

with *N*-methyl protons), C-5 showed a triplet signal at 115.09 ppm (³J_{CH}=3.9 Hz, coupled with two aromatic protons), C-6 showed a triplet signal at 161.27 ppm (³J_{CH}=3.9 Hz, coupled with aromatic protons) (Chart 2).

The formation of 2-thioxo-2*H*-1,3-oxazin-4(3*H*)-one (**6**) and benzyl phenyl ketone (**7**) is explained by the mechanism through the initial Wolff rearrangement to give an acylketene as shown below. Dibenzoylcarbenoid (**10**) generated by the rhodium(II) acetate-catalyzed decomposition of dibenzoyldiazomethane (**4**) rearranges to form the benzoylphenylketene (**11**). The conjugate oxadiene system of **11** cycloadds across the N–C double bond of isothiocyanate to yield 2-thioxo-2*H*-1,3-oxazin-4(3*H*)-one³⁾ as shown in the Scheme 1.

Small amount of water included in the reaction system attacks the acylketene **11** to produce β -keto carboxylic acid (**12**), which extrude carbon dioxide to afford benzyl phenyl ketone (**7**).⁴⁾ The intermediacy of acylketene **11** was confirmed by the formation of β -keto ester **13** in high yield in the rhodium(II) acetate-catalyzed decomposition of **4** in ethanol at 80°C.



Scheme 1.

[†]Present address: Department of Chemistry, Aichi University of Education, Kariya, Aichi 448.

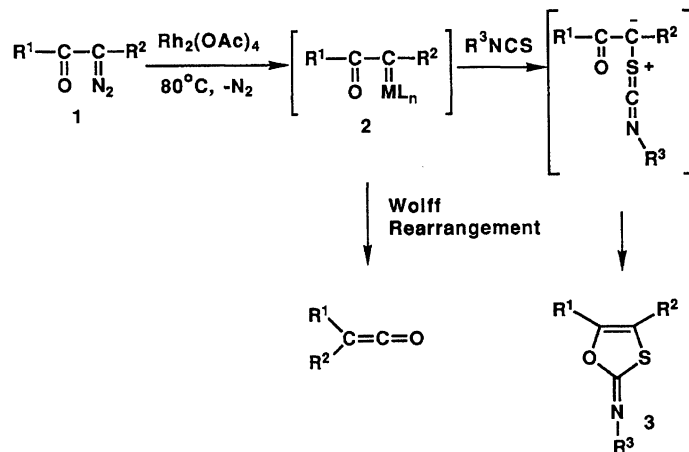


Chart 1.

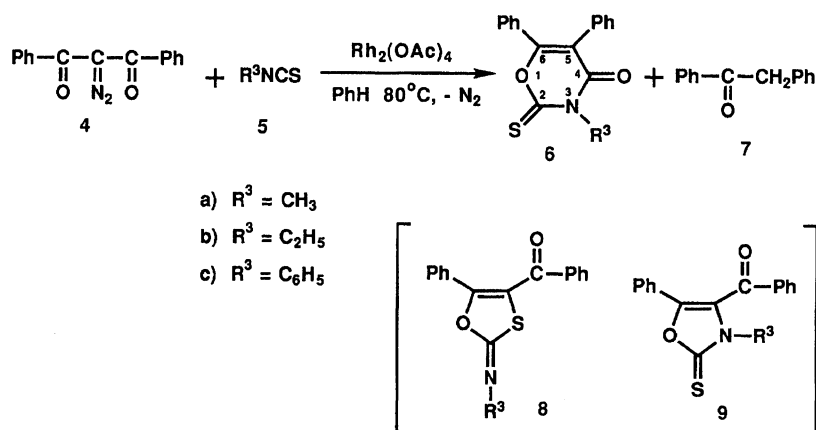


Chart 2.

The reactions of **4** with ethyl and phenyl isothiocyanates (**5b** and **5c**) also gave the corresponding 2-thioxo-2*H*-1,3-oxazin-4(3*H*)-ones **6b** and **6c** in 66 and 38% yields, respectively, together with **7**.

The catalytic reactions of unsymmetrical diacyldiazomethanes with isothiocyanates are of interest in connection with the estimation of the migratory aptitude of methyl and aryl groups in carbenoid reaction. Therefore, the rhodium(II) acetate-catalyzed reaction of acetyl(*p*-toluoyl)diazomethane (**14b**) with methyl isothiocyanates was studied in benzene at 80°C, and obtained two thioxooxazinones **18b** and **19b**. Their similar NMR spectra and the results of elemental analysis indicate that they are the isomers of 2-thioxo-2*H*-1,3-oxazin-4(3*H*)-one. The structure of the major isomer was confirmed to be 3,5-dimethyl-2-thioxo-6-(*p*-tolyl)-2*H*-1,3-oxazin-4(3*H*)-one (**18b**) on the basis of the following spectroscopic properties. The ¹H NMR spectra of **18b** and **19b** showed signals of methyl group bonding to an sp² carbon of thioxooxazinone at 2.11 and 2.20 ppm, respectively, besides signals of tolyl-methyl and *N*-methyl groups. The ¹³C NMR spectra of **18b** and **19b** showed signals of sp² carbons of C-5 and C-6 at 109.75 (q, ²*J*_{CH}=6.6 Hz) and 160.12 or 160.14 ppm for **18b** and

116.28, 163.49 ppm (q, ²*J*_{CH}=6.7 Hz) for **19b**, besides the signals of carbonyl carbon and thiocarbonyl carbons. In these compounds, the high field signals near 110 ppm are attributed to C-5 of the thioxooxazinone ring system, and the low field signals (ca. 160 ppm) are attributed to C-6 from the value of chemical shift.

Selective decoupling spectra of minor product also support the structure of 3,6-dimethyl-2-thioxo-5-(*p*-tolyl)-2*H*-1,3-oxazin-4(3*H*)-one (**19b**). When C-6-methyl proton at 2.20 ppm was irradiated, the multiplet signal at 116.28 ppm turned to triplet (coupling with two ortho-aromatic protons), and a signal at 163.49 ppm turned from quartet to singlet. When *N*-methyl protons at 3.69 ppm was irradiated, both of thiocarbonyl carbon signal at 182.23 ppm (q, ³*J*_{CH}=4.1 Hz) and a carbonyl carbon at 158.23 ppm turned to singlet (Chart 3).

In order to clarify the substituent effect on the migratory aptitude of aryl groups in the Wolff rearrangement, the reactions of acetyl(*p*-substituted benzoyl)diazomethanes **14** with methyl isothiocyanate were carried out. The reaction gave two isomeric 2-thioxo-2*H*-1,3-oxazin-4(3*H*)-ones **18** and **19** in the yields shown in Table 1. The formation of 6-aryl-3,5-dimethyl-2-thioxo-2*H*-1,3-oxazin-4(3*H*)-one (**18**) is explained by

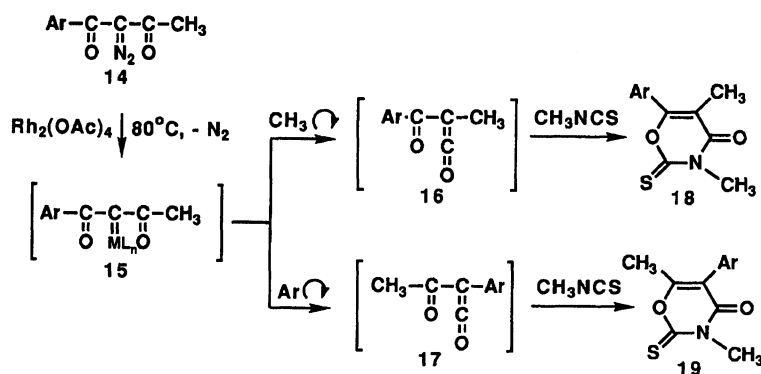


Table 1. Yields of 2-Thioxo-2*H*-1,3-oxazin-4(3*H*)-ones 18 and 19 ^{a)}

Run	14	Ar	Yield/% ^{b)}		19/(18 + 19)
			18	19	
a	14a	<i>p</i> -CH ₃ OC ₆ H ₄	23	33	0.59
b	14b	<i>p</i> -CH ₃ C ₆ H ₄	26	12	0.32
c	14c	C ₆ H ₅	26	Trace	ca. 0
d	14d	<i>p</i> -ClC ₆ H ₄	18	2	0.10

a) Reaction of 14 with methyl isothiocyanate was carried out in the conditions of General Procedure described in the Experimental. b) Yields were determined by the HPLC analysis.

the Diels-Alder reaction of methyl isothiocyanate with aroylmethylketene (16) formed by the methyl migration of diketocarbonyl (15). The formation of 5-aryl-3,6-dimethyl-2-thioxo-2*H*-1,3-oxazin-4(3*H*)-one (19) is explained by aryl group migration of the diketocarbonyl (15) to give acetylarylketene (17), followed by the same type of Diels-Alder reaction. The ratio between the yields of 18 and 19 reflects the migratory aptitude of the methyl group and aryl group, when the steps of the Diels-Alder reaction of 16 and 17 were assumed to be quantitative. The results shown in Table 1 indicate that in the reaction of acetylbenzoyldiazomethane (14) with an electron-donating group at para position of the phenyl group increased the yield of thioxoxazinone (19) due to the promotion of aryl group migration (Runs a and b).⁵⁾ In contrast, when 14 has an electron-withdrawing group, the yield of aryl migration product 19 becomes low (Run d). These results are attributed to the promotion of the aryl group migration by the introduction of an electron-donating group.

A reaction mixture of diacetyldiazomethane (20) with methyl isothiocyanate gave 3,5,6-trimethyl-2*H*-1,3-oxazine-2,4(3*H*)-dione (24) in 12% yield. The structure of the dione 24 was confirmed on the basis of NMR spectra (see Experimental). The ¹³C NMR spectrum of 24 showed signals of two carbonyl carbons at 149.09 ppm (q, ³*J*_{CH} = 2.8 Hz, C-2) and 162.74 ppm (C-4) which ruled out the structure 23 having thiocarbonyl group. The formation of 2*H*-1,3-oxazine-2,4(3*H*)-dione (24) is interpreted by the hydrolysis of 2-thioxo derivative 23

during the treatment of column chromatography. This explanation is supported by the fact that the ¹H NMR spectrum of the reaction mixture showed two methyl signals at 1.81 and 2.04 ppm (coupled to each other, *J* = 0.9 Hz), and an *N*-methyl signal at 3.00 ppm which are attributable to 23. Several attempts to isolate 23 by column chromatography were unsuccessful and gave only 24 as a pure product (Chart 4).

The rhodium(II) acetate-catalyzed reaction of diazodimedone (25) with methyl isothiocyanate at 80°C in benzene gave 2-thioxo-2*H*-1,3-oxazin-4(3*H*)-one (30) and 2*H*-1,3-oxazine-2,4(3*H*)-dione (31) in 0.9 and 5.1% yields, respectively, together with 2-methylimino-1,3-oxathiole (27) (45%) and oxazole-2(3*H*)-thione (28) (2.2%). Formation of 27 and 28 was discussed in the previous paper.²⁾ The ¹³C NMR spectrum of 30 had a signal of thiocarbonyl carbon at 183.14 ppm, which indicated that 30 has a structure of 2-thioxo-2*H*-1,3-oxazin-4(3*H*)-one. Although 31 showed a similar ¹H NMR spectrum to that of 30, its ¹³C NMR spectrum showed two signals of carbonyl carbon at 150.10 (q, C-2) and 160.17 (m, C-4) ppm. These results indicate that 31 has 2*H*-1,3-oxazine-2,4(3*H*)-dione structure (Table 2, Chart 5).

The reaction of 25 in toluene at 110°C gave 27, 28, and 30 in 36, 1.4, and 15% yields, respectively. In this reaction, 31 was not isolated, because the separation of the reaction mixture was done quickly to prevent the hydrolysis of 30 to give 31. The reaction temperature affected the ratio between the products through the Wolff rearrangement and the products through the thiocarbonyl and azomethine ylide intermediates, and the value of (30+31)/(27+28) increased from 0.13 at 80°C to 0.40 at 110°C. These results are explained by the intermediacy of rhodium carbenoid 26, which gives 27 and 28 through ylide intermediates by the attack of isothiocyanate or gives 30 via the Wolff rearrangement through acylketene 29. The pathway to give acylketene 29 by the Wolff rearrangement of ketocarbonyl 26 seems to be accelerated at high temperature. This acceleration of the Wolff rearrangement is explained by the assumption that the ketocarbonyl intermediate 26 yields free ketocarbene more easily at high temperature,

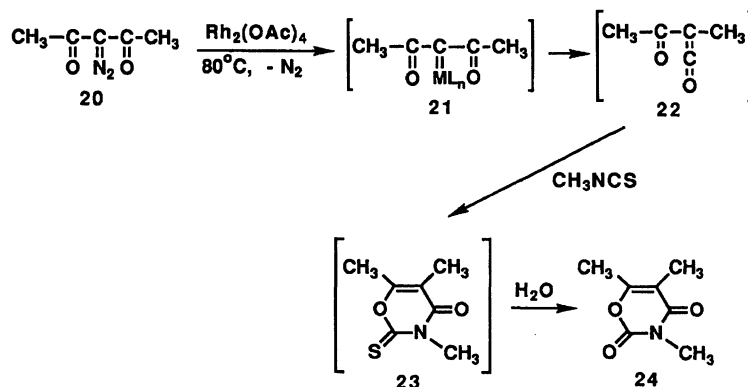


Chart 4.

Table 2. Results of Elemental Analysis of the Reaction Products

Products	Found/%			Calcd/%			Molecular formula
	C	H	N	C	H	N	
6a	69.36	4.60	4.96	69.13	4.44	4.74	C ₁₇ H ₁₃ NO ₂ S
6b	69.93	5.02	4.56	69.88	4.89	4.53	C ₁₈ H ₁₅ NO ₂ S
6c	74.08	4.38	3.90	73.93	4.23	3.92	C ₂₂ H ₁₅ NO ₂ S
18a	59.27	5.01	5.25	59.30	4.96	5.32	C ₁₃ H ₁₃ NO ₃ S
18b	63.08	5.32	5.69	63.13	5.30	5.66	C ₁₃ H ₁₃ NO ₂ S
19b	62.80	5.28	5.56	63.13	5.30	5.66	C ₁₃ H ₁₃ NO ₂ S
18c	62.02	4.81	6.10	61.78	4.75	6.10	C ₁₂ H ₁₁ NO ₂ S
24	54.18	5.84	9.29	54.19	5.85	9.03	C ₇ H ₉ NO ₃
30	56.94	6.13	6.65	56.85	6.20	6.63	C ₁₀ H ₁₃ NO ₂ S
31	60.84 ^{a)}	6.67	7.39	61.53	6.71	7.17	C ₁₀ H ₁₃ NO ₃

a) The discrepancy of the value with the calculated one was attributed to the difficulty of purification due to the low yield and oily nature of **31**.

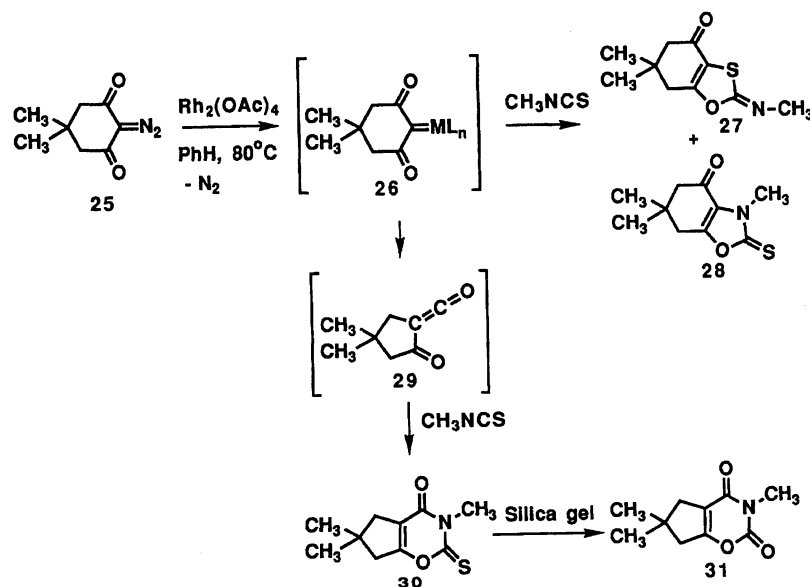


Chart 5.

which affords the Wolff rearrangement products.⁶⁾

The ability of the Wolff rearrangement seems to be in the following order: acyclic diacyldiazomethanes (100% rearrangement) > cyclic 2-diazo-1,3-diketones (11–29% rearrangement) ≫ α-diazoketones (no rearrangement), on the basis of relative yields of thioxoxazinone to 2-

imino-1,3-oxathiole. Since rhodium(II) acetate is well known as a catalyst for the decomposition of α-diazo-carbonyl compounds without affording the product of Wolff rearrangement, the present reaction provides a special case. The similar reactions of diacetyldiazomethane (**20**), diazodimedone (**25**), and 2-cy-

clohexanedione catalyzed by rhodium(II) acetate in the presence of carbon disulfide gave 1,3-oxathiole-2-thione derivatives as a sole product in high yields through the thiocarbonyl ylide intermediates, and no product through the Wolff rearrangement was obtained.⁷⁾ The reason why the Wolff rearrangement was favorable for the present reaction system may be attributed to the generation of free ketocarbene promoted by effective coordination of the reactants such as isothiocyanate, water, and ethanol onto the rhodium metal, in contrast to the case of carbon disulfide. Although the photochemical or thermal Wolff rearrangement of α -diazocarbonyl compounds is well known, the photolysis or thermolysis of diacyldiazomethanes in the presence of isothiocyanates gave only a mixture of unseparable tarry products.

Experimental

Melting points were measured with a Yanagimoto Melting-point Apparatus and were not corrected. IR spectra were recorded on a Perkin-Elmer model 983. ¹H NMR (270.05 MHz and 500 MHz) and ¹³C NMR (67.80 MHz and 125.65 MHz) spectra were recorded on a JEOL EX-270 and a GX-500 in a CDCl₃ solution using TMS as an internal standard. A Varian EM-390 (90 MHz) was also used for measurements of ¹H NMR spectra. Mass spectra were determined with a JEOL JMS-DX303 spectrometer.

Materials. Diacyldiazomethanes were prepared by the diazo group transfer reaction reported by Regitz.⁸⁾ Benzene was purified by distillation after reflux on CaH₂ and stored over molecular sieves 4A. Commercial isothiocyanates were purified by distillation just before use.

General Procedure for the Rhodium(II) Acetate-Catalyzed Decomposition of Diazodicarbonyl Compound in the Presence of Isothiocyanate. A solution of diacyldiazomethane (3.0 mmol) in dry benzene (10 ml) was added over a period of ca. 4 h to a reflux solution of rhodium(II) acetate (13.3 mg, 3.0 × 10⁻² mmol) and isothiocyanate (30 mmol) in benzene (20 ml) under nitrogen atmosphere. The solution was heated at 80°C until no more diazo compound was detected by TLC or IR spectrum. The resulting reaction mixture was concentrated under reduced pressure. The residue was separated by medium pressure liquid chromatography (silica gel, eluted with ethyl acetate-hexane).

The Rh₂(OAc)₄-catalyzed reaction of dibenzoyldiazomethane (**4**) with methyl isothiocyanate gave benzyl phenyl ketone (**7**: 11% yield) and **3-methyl-5,6-diphenyl-2-thioxo-2H-1,3-oxazin-4(3H)-one (6a)**: 60% yield; colorless crystals; mp 112.0–113.5°C (from benzene-hexane); ¹H NMR (500 MHz) δ =3.75 (3H, s, NCH₃) and 7.19–7.37 (10H, m, arom-H); ¹³C NMR (125.65 MHz) δ =34.91 (q, NCH₃), 115.09 (st, ³J_{CH}=3.9 Hz, 5-C), 128.35 (dd, *m*-arom-CH), 128.70 (dd, *m*-arom-CH), 128.73 (dt, *p*-arom-CH), 129.44 (dt, *o*-arom-CH), 129.82 (st, arom-C), 130.42 (sdd, arom-C), 130.66 (dt, *o*-arom-CH), 131.33 (dt, *p*-arom-CH), 158.94 (sq, ³J_{CH}=2.4 Hz, 4-C=O), 161.27 (std, 6-C), and 181.91 (sq, ³J_{CH}=4.3 Hz, 2-C=S); IR (KBr) 2926 (C-H), 1690 (s, C=O), 1630, 1573, 1488, 1437, 1370 (s), 1349 (s), 1314 (s), 1149, 1107, 1075, 770, 697, and 660 cm⁻¹;

MS (EI, assignment, rel intensity %) 295 (M⁺, 22), 222 (M⁺ - MeNCS, 77), 105 (100), and 77 (28).

The Rh₂(OAc)₄-catalyzed reaction of **4** with ethanol (30 mmol) gave **ethyl 3-oxo-2,3-diphenylpropanoate (13)**: 95% yield; colorless crystals; mp 91.2–91.7°C (from benzene-hexane); ¹H NMR (90 MHz) δ =1.21 (3H, t, *J*=7.1 Hz, CH₃), 4.17 (2H, q, *J*=7.1 Hz, OCH₂), 5.58 (0.96H, s, COCHCO), 7.1–8.0 (10H, m, arom-H), and 13.59 (0.04H, s, =C-OH); IR (KBr) 1741 (s, C=O), 1674 (s, C=O), 1369, 1328, 1317, 1265, 1188, 1161, 726, 702, and 688 cm⁻¹.

The Rh₂(OAc)₄-catalyzed reaction of **4** with ethyl isothiocyanate (**5b**) gave **7** (4.4% yield) and **3-ethyl-5,6-diphenyl-2-thioxo-2H-1,3-oxazin-4(3H)-one (6b)**: 65% yield; colorless crystals; mp 131.5–132.9°C (from ethyl acetate-hexane); ¹H NMR (270.05 MHz) δ =1.39 (3H, t, *J*=7.0 Hz, CH₃), 4.66 (2H, q, *J*=7.0 Hz, NCH₂), and 7.17–7.36 (10H, m, arom-H); ¹³C NMR (67.80 MHz) δ =11.15 (q, CH₃), 43.62 (t, NCH₂), 115.35 (st, ³J_{CH}=3.0 Hz, 5-C), 128.34 (dd, arom-CH), 128.68 (dd, arom-CH), 128.71 (dt, *p*-arom-CH), 129.45 (dt, arom-CH), 129.85 (sm, arom-C), 130.39 (sm, arom-C), 130.69 (dt, *o*-arom-CH), 131.33 (dt, *p*-arom-CH), 158.47 (st, ³J_{CH}=3.0 Hz, 4-C=O), 161.24 (std, 6-C), and 181.91 (st, ³J_{CH}=5.5 Hz, 2-C=S); IR (KBr) 1690 (s, C=O), 1631 (C=C), 1600, 1490, 1440, 1401, 1379 (s), 1370 (s), 1353, 1310, 1275 (s), 1221, 1144, 1086, 964, and 769 cm⁻¹.

The Rh₂(OAc)₄-catalyzed reaction of **4** with phenyl isothiocyanate (**5c**) gave **7** (1.3% yield) and **3,5,6-triphenyl-2-thioxo-2H-1,3-oxazin-4(3H)-one (6c)**: 38% yield; colorless crystals; mp 231.5–232.6°C (from ethyl acetate-hexane); ¹H NMR (270.05 MHz) δ =7.23–7.56 (m, arom-H); ¹³C NMR (67.80 MHz) δ =115.00 (st, ³J_{CH}=3.5 Hz, 5-C), 127.75 (dt, arom-CH), 128.33 (dd, arom-CH), 128.54 (dt, arom-CH), 128.69 (d, arom-CH), 129.72 (s, arom-C), 129.93 (s, arom-C), 130.69 (dt, arom-C), 131.43 (dt, arom-CH), 137.98 (stt, arom-C), 159.07 (s, 4-C=O), 161.73 (st, ³J_{CH}=3.8 Hz, 6-C), and 182.17 (s, 2-C=S); IR (KBr) 3035, 1703 (s, C=O), 1629 (s), 1597, 1574, 1488, 1445, 1384 (s), 1345 (s), 1305 (s), 1202 (s), 1185, 1169, 1158, 1142, 1073, 1063, 1026, 1002, 969, 923, 801, 783, 761, 750, 696, and 664 cm⁻¹.

The Rh₂(OAc)₄-catalyzed reaction of acetyl-*p*-anisoyldiazomethane (**14a**) with methyl isothiocyanate gave a mixture of **18a** and **19a**.

2-Thioxo-6-(*p*-methoxyphenyl)-3,5-dimethyl-2H-1,3-oxazin-4(3H)-one (18a): 23% yield; colorless needles; mp 152.8–153.6°C (from ethyl acetate-hexane); ¹H NMR (90 MHz) δ =2.13 (3H, s, CH₃), 3.71 (3H, s, NCH₃), 3.87 (3H, s, OCH₃), 6.9–7.1 (2H, m, arom-H), and 7.5–7.7 (2H, m, arom-H); ¹³C NMR (125.65 MHz) δ =11.92 (q, CH₃), 34.73 (q, NCH₃), 55.51 (q, OCH₃), 109.02 (sq, ²J_{CH}=6.6 Hz, 5-C), 114.14 (dd, arom-CH), 122.38 (st, arom-C), 130.65 (dd, arom-CH), 160.20 (sm, 4-C or 6-C), 160.91 (sm, 4-C or 6-C), 161.97 (sm, arom-C), and 182.39 (sq, ³J_{CH}=4.3 Hz, 2-C=S); IR (KBr) 2931, 1688 (s, C=O), 1644 (C=C), 1605, 1568, 1509, 1437, 1417, 1370 (s), 1348 (s), 1311 (s), 1298, 1261 (s), 1216, 1177, 1152, 1111, 1050, 1017, 837, 755, and 627 cm⁻¹; MS (EI, assignment, rel intensity %) 263 (M⁺, 47), 190 (29), and 135 (100).

5-(*p*-Methoxyphenyl)-3,6-dimethyl-2-thioxo-2H-1,3-oxazin-4(3H)-one (19a): 33% yield; ¹H NMR (500 MHz) δ =2.12 (3H, s, CH₃), 3.69 (3H, s, NCH₃), 3.84 (3H, s, OCH₃), 6.95–6.97 (2H, m, arom-H), and 7.16–7.18 (2H, m,

arom-H); ¹³C NMR (125.65 MHz) δ =18.17 (q, CH₃), 34.82 (q, NCH₃), 55.36 (q, OCH₃), 114.20, 116.01, 122.12, 131.32, 158.39, 159.98, 163.49 (sq, ²J_{CH}=6.9 Hz, C-6), and 182.24 (sq, ³J_{CH}=4.3 Hz, 2-C=S).

The Rh₂(OAc)₄-catalyzed reaction of acetyl(*p*-toluoyl)diazomethane (**14b**) with methyl isothiocyanate gave a mixture of **18b** and **19b**.

3,5-Dimethyl-2-thioxo-6-(*p*-tolyl)-2H-1,3-oxazin-4-(3H)-one (18b): 26% yield; colorless needles; mp 109.7–110.3°C (from ethyl acetate–hexane); ¹H NMR (CDCl₃, 500 MHz) δ =2.11 (3H, s, CH₃), 2.42 (3H, s, arom-CH₃), 3.71 (3H, s, NCH₃), 7.29 (2H, d, *J*=8.3 Hz, arom-H), and 7.52 (2H, d, *J*=8.3 Hz, arom-H); ¹³C NMR (125.65 MHz) δ =11.84 (q, CH₃), 21.54 (qt, ³J_{CH}=4.4 Hz, arom-CH₃), 34.72 (q, NCH₃), 109.75 (sq, ²J_{CH}=6.6 Hz, 5-C), 127.35 (st, 1'-arom-C), 128.82 (dd, 2'-arom-CH), 129.35 (ddq, 3'-arom-CH), 141.91 (sdq, 4'-arom-C), 160.12 (sm, 4-C or 6-C), 160.16 (sm, 4-C or 6-C), and 182.36 (sq, ³J_{CH}=4.3 Hz, 2-C=S); IR (KBr) 1691 (s, C=O), 1647 (C=C), 1612, 1443, 1384, 1370, 1350, 1316, 1307, 1157, 817, 758, and 652 cm⁻¹; MS (EI, assignment, rel intensity %) 247 (M⁺, 50), 174 (M⁺–MeNCS, 27), 146 (14), and 119 (100).

3,6-Dimethyl-2-thioxo-5-(*p*-tolyl)-2H-1,3-oxazin-4-(3H)-one (19b): 12% yield; colorless needles; mp 108.0–108.8°C (from ethyl acetate–hexane); ¹H NMR (CDCl₃, 500 MHz) δ =2.20 (3H, s, CH₃), 2.38 (3H, s, arom-CH₃), 3.69 (3H, s, NCH₃), 7.12–7.14 (2H, m, arom-H), and 7.23–7.24 (2H, m, arom-H); ¹³C NMR (CDCl₃, 125.65 MHz) δ =18.13 (q, CH₃), 21.29 (qt, ³J_{CH}=4.4 Hz, arom-CH₃), 34.79 (q, NCH₃), 116.28 (sm, 5-C), 127.07 (st, 1'-arom-C), 129.35 (dd, 2'-arom-CH), 129.90 (ddq, 3'-arom-CH), 138.77 (sm, 4'-arom-C), 158.23 (sq, C=O), 163.49 (sq, ²J_{CH}=6.7 Hz, 6-C), and 182.23 (sq, ³J_{CH}=4.1 Hz, 2-C=S); IR (KBr) 2922, 1697 (s, C=O), 1658 (C=C), 1615, 1513, 1440, 1388, 1346, 1309, 1209, 1156, 1126, 1110, 1095, 1042, 951, 932, 839, 812, 784, 774, and 717 cm⁻¹; MS (EI, assignment, rel intensity %) 247 (M⁺, 39), 174 (M⁺–MeNCS, 100), and 132 (81).

The Rh₂(OAc)₄-catalyzed reaction of acetylbenzoyldiazomethane (**14c**) with methyl isothiocyanate gave a mixture of **18c** and **19c**.

3,5-Dimethyl-6-phenyl-2-thioxo-2H-1,3-oxazin-4-(3H)-one (18c): 26% yield; colorless needles; mp 148.1–148.8°C (from ethyl acetate–hexane); ¹H NMR (500 MHz) δ =2.11 (3H, s, CH₃), 3.75 (3H, s, NCH₃), 7.47–7.52 (3H, m, arom-H), and 7.61–7.62 (2H, m, arom-H); ¹³C NMR (125.65 MHz) δ =11.78 (q, CH₃), 34.74 (q, NCH₃), 110.27 (sq, ²J_{CH}=6.6 Hz, 5-C), 128.68 (dd, *m*-arom-CH), 128.84 (dt, *o*-arom-CH), 130.19 (st, arom-C), 131.33 (dt, *p*-arom-CH), 160.03 (sm, 4-C or 6-C), 161.00 (sm, 4-C or 6-C), and 182.26 (sq, ³J_{CH}=4.3 Hz, 2-C=S); IR (KBr) 2960 (C–H), 1689 (s, C=O), 1645 (C=C), 1597, 1572, 1492, 1444, 1389, 1370 (s), 1346 (s), 1315 (s), 1301 (s), 1284, 1208, 1150 (s), 1121, 1051, 1028, 1001, 975, 772, 755, 696, and 670 cm⁻¹; MS (EI, assignment, rel intensity %) 234 (M⁺+1, 11), 160 (M⁺–MeNCS, 33), 105 (PhCO⁺, 100).

3,6-Dimethyl-5-phenyl-2-thioxo-2H-1,3-oxazin-4-(3H)-one (19c): ¹H NMR (270.05 MHz) δ =2.20 (3H, s, CH₃), 3.69 (3H, s, NCH₃), and 7.22–7.47 (5H, m, arom-H); ¹³C NMR (CDCl₃, 67.80 MHz) δ =14.04 (q, CH₃), 34.74 (q, NCH₃), 116.26 (sm, 5-C), 128.78 (d, arom-CH), 128.85 (d, arom-CH), 129.99 (d, arom-CH), 135.84 (dt, *p*-arom-CH), 158.07 (sq, ³J_{CH}=2.1 Hz, C=O), 163.64 (sq, ²J_{CH}=6.8 Hz,

6-C), and 182.08 (sq, ³J_{CH}=4.2 Hz, 2-C=S).

The Rh₂(OAc)₄-catalyzed reaction of acetyl(*p*-chlorobenzoyl)diazomethane (**14d**) with methyl isothiocyanate gave a mixture of **18d** and **19d**.

6-(*p*-Chlorophenyl)-3,5-dimethyl-2-thioxo-2H-1,3-oxazin-4(3H)-one (18d): 18% yield; ¹H NMR (270.05 MHz) δ =2.10 (3H, s, CH₃), 3.71 (3H, s, NCH₃), and 7.46–7.60 (4H, m, arom-H); ¹³C NMR (67.80 MHz) δ =11.73 (q, CH₃), 34.67 (q, NCH₃), 110.41 (sq, ²J_{CH}=6.7 Hz, 5-C), 128.37 (s, arom-C), 128.95 (d, arom-CH), 130.07 (d, arom-CH), 137.51 (s, arom-C), 159.66 (sm, 4-C or 6-C), 159.70 (sm, 4-C or 6-C), and 181.84 (sq, ³J_{CH}=4.3 Hz, 2-C=S).

5-(*p*-Chlorophenyl)-3,6-dimethyl-2-thioxo-2H-1,3-oxazin-4(3H)-one (19d): 2% yield; ¹H NMR (270.05 MHz) δ =2.22 (3H, s, CH₃), 3.68 (3H, s, NCH₃), 7.19–7.23 (2H, m, arom-H), and 7.30–7.43 (2H, m, arom-H); ¹³C NMR (67.80 MHz) δ =18.09 (q, CH₃), 34.67 (q, NCH₃), 115.19 (sm, 5-C), 128.47 (s, arom-C), 128.81 (d, arom-CH), 131.37 (d, arom-CH), 134.84 (s, arom-C), 157.80 (sq, ³J_{CH}=2.4 Hz, C=O), 163.69 (sq, ²J_{CH}=6.7 Hz, 6-C), and 181.72 (sq, ³J_{CH}=4.3 Hz, 2-C=S).

The Rh₂(OAc)₄-catalyzed reaction of diacetyldiazomethane (**20**) with methyl isothiocyanate gave a mixture of **23** and **24**.

3,5,6-Trimethyl-2-thioxo-2H-1,3-oxazin-4(3H)-one (23): ¹H NMR (90 MHz) δ =1.81 (3H, q, *J*=0.9 Hz, CH₃), 2.01 (3H, q, *J*=0.9 Hz, CH₃), and 3.00 (3H, s, NCH₃).

3,5,6-Trimethyl-2H-1,3-oxazine-2,4(3H)-dione (24): 12% yield; colorless needles; mp 79.3–80.8°C (from ethyl acetate–hexane); ¹H NMR (500 MHz) δ =1.92 (3H, q, *J*=0.9 Hz, CH₃), 2.20 (3H, q, *J*=0.9 Hz, CH₃), and 3.32 (3H, s, NCH₃); ¹³C NMR (125.65 MHz) 10.21 (q, CH₃), 16.84 (q, CH₃), 28.54 (q, NCH₃), 107.58 (sm, 5-C=), 149.09 (sq, ³J_{CH}=2.8 Hz, 2-C=O), 159.24 (sm, 6-C=), and 162.74 (sm, 4-C=O); IR (KBr) 2933, 1750 (C=O), 1685 (C=O), 1667 (C=C), 1399, 1377, 1329, 1174, 1152, 1092, 1062, 763, 695, and 665 cm⁻¹; MS (EI, assignment, rel intensity %) 156 (M⁺+1, 12), 155 (M⁺, 100), 98 (M⁺–MeNCS, 66), 83 (45), 70 (58), 56 (39), and 43 (CH₃CO⁺, 79).

The Rh₂(OAc)₄-catalyzed reaction of diazodimedone (**25**) with methyl isothiocyanate gave **30**, and **31** together with **27** (45% yield), **28** (2.2% yield).¹⁾

3,6,6-Trimethyl-2-thioxo-2,5,6,7-tetrahydrocyclopenta[e]-1,3-oxazin-4(3H)-one (30): 0.9% yield; colorless prisms; mp 57.2–59.6°C; ¹H NMR (270.05 MHz) δ =1.23 (6H, s, CH₃×2), 2.52 (2H, t, *J*=1.7 Hz, CH₂), 2.66 (2H, t, *J*=1.7 Hz, CH₂), and 3.64 (3H, s, NCH₃); ¹³C NMR (67.80 MHz) δ =29.57 (qm, CH₃×2), 34.48 (q, NCH₃), 36.52 (s, C(CH₃)₂), 40.62 (tm, CH₂), 45.65 (tm, CH₂), 113.00 (stt, ²J_{CH}=6.4 Hz, ³J_{CH}=4.3 Hz, =C=O), 157.03 (sm, C=O), 167.42 (stt, ²J_{CH}=8.6 Hz, ³J_{CH}=5.0 Hz, O=C=), and 183.14 (sq, ³J_{CH}=4.4 Hz, C=S); IR (KBr) 2955, 2867, 1717 (s, C=O), 1670 (s), 1447 (s), 1398 (s), 1368, 1338, 1293 (s), 1228, 1168, 1144 (s), 1079, 966, 895, 853, 776, and 750 cm⁻¹; MS (EI, assignment, rel intensity %) 212 (M⁺+1, 18), 211 (M⁺, 100), 138 (M⁺–MeNCS, 77), and 123 (98).

3,6,6-Trimethyl-6,7-dihydrocyclopenta[e]-1,3-oxazine-2,4(3H)-dione (31): 5.1% yield; colorless oil; ¹H NMR (270.05 MHz) δ =1.22 (6H, s, CH₃×2), 2.49 (2H, t, *J*=1.8 Hz, CH₂), 2.59 (2H, t, *J*=1.8 Hz, CH₂), and 3.33 (3H, s, NCH₃); ¹³C NMR (67.80 MHz) δ =28.54 (q, NCH₃), 29.73 (qm, CH₃×2), 36.54 (s, C(CH₃)₂), 40.54 (tm, CH₂),

45.47 (tm, CH₂), 110.65 (stt, ²J_{CH}=6.4 Hz, ³J_{CH}=4.3 Hz, =C-C=O), 150.10 (sq, ³J_{CH}=3.1 Hz, N-C=O), 160.17 (sm, =C-C=O), and 164.80 (stt, ²J_{CH}=8.6 Hz, ³J_{CH}=5.5 Hz, O-C=); IR (KBr) 2957, 2867, 1762 (s, C=O), 1700 (s, C=O), 1448 (s), 1400, 1368, 1339, 1313, 1271, 1234, 1171, 1100, 1058, 1007, 904, 757, and 677 cm⁻¹; MS (EI, assignment, rel intensity %) 195 (M⁺, 53), 138 (M⁺-MeCNO, 99) and 123 (100).

The authors are grateful to Mr. Hiroshi Moriguchi, Faculty of Engineering, Osaka University for the measurement of mass spectra.

References

- 1) A. Padwa and S. F. Hornbuckel, *Chem. Rev.*, **91**, 263 (1991), and references cited therein.
 - 2) T. Ibata and H. Nakano, *Bull. Chem. Soc. Jpn.*, **65**, 3088 (1992).
 - 3) a) G. Desimoni and G. Tacconi, *Chem. Rev.*, **75**, 651 (1975); b) D. L. Boger and S. M. Weinreb, "Hetero Diels-Alder Methodology in Organic Synthesis," Academic Press, New York (1987).
 - 4) a) H. Meier and K.-P. Zeller, *Angew. Chem., Int. Ed. Engl.*, **14**, 32 (1975); b) "The Chemistry of Diazonium and Diazo Groups," ed by S. Patai, John Wiley & Sons, New York (1978).
 - 5) K.-P. Zeller, H. Meier, and E. Muller, *Tetrahedron*, **28**, 5831 (1972); G. Hayes and G. Holt, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 1206.
 - 6) M. Takebayashi, T. Ibata, H. Kohara, and B. H. Kim, *Bull. Chem. Soc. Jpn.*, **40**, 2392 (1967).
 - 7) T. Ibata and H. Nakano, *Chem. Express*, **4**, 93 (1989); T. Ibata and H. Nakano, *Bull. Chem. Soc. Jpn.*, **63**, 3096 (1990).
 - 8) M. Regitz, *Chem. Ber.*, **99**, 3128 (1966).
-