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, acetylaroyldiazomethanes, 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 acetylaroyldiazomethanes.

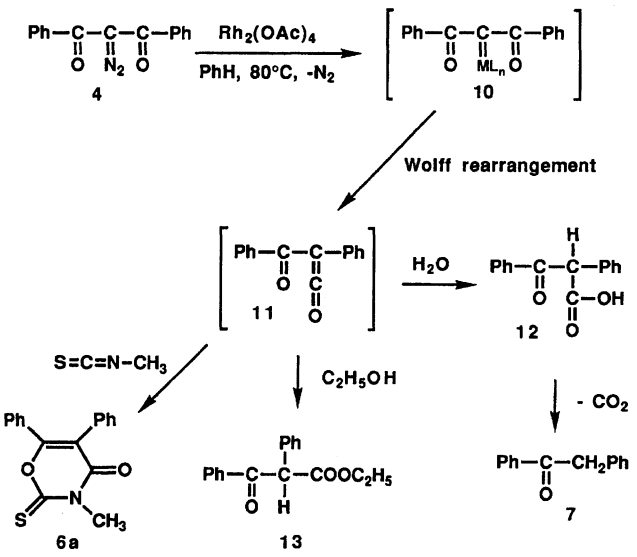
Rhodium(II) acetate has been utilized as an excellent catalyst for the mild decomposition of α-diazocarbonyl compounds to generate the corresponding ketocarbenoids to avoid the Wolff rearrangement in the various reaction systems.[1] In the previous paper of this series, the authors have reported the 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 ketocarbenoid (**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 ^{13}C NMR of the thioxooxazinone **6a** is similar to that of 2-methylimino-1,3-oxathioles (**3**: $R^3=CH_3$) 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*)-one[3] 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.

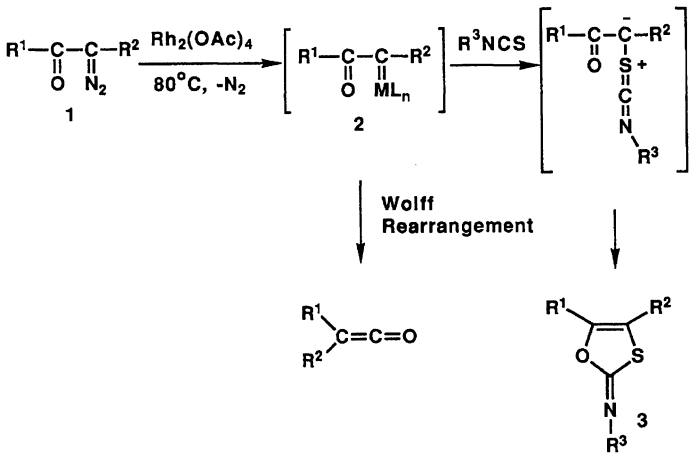


Chart 1.

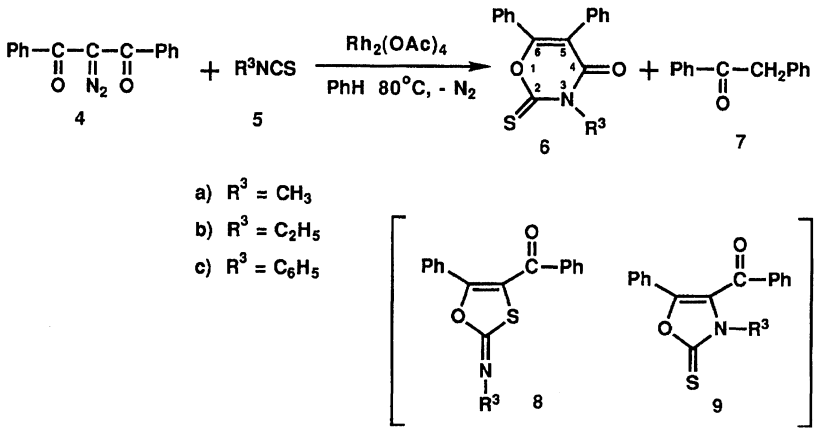


Chart 2.

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 ^{1}H NMR spectra of **18b** and **19b** showed signals of methyl group bonding to an sp^2 carbon of thioxooxazinone at 2.11 and 2.20 ppm, respectively, besides signals of tolyl-methyl and *N*-methyl groups. The ^{13}C NMR spectra of **18b** and **19b** showed signals of sp^2 carbons of C-5 and C-6 at 109.75 (q, $^2J_{CH}$=6.6 Hz) and 160.12 or 160.14 ppm for **18b** and 116.28, 163.49 ppm (q, $^2J_{CH}$=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, $^3J_{CH}$=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

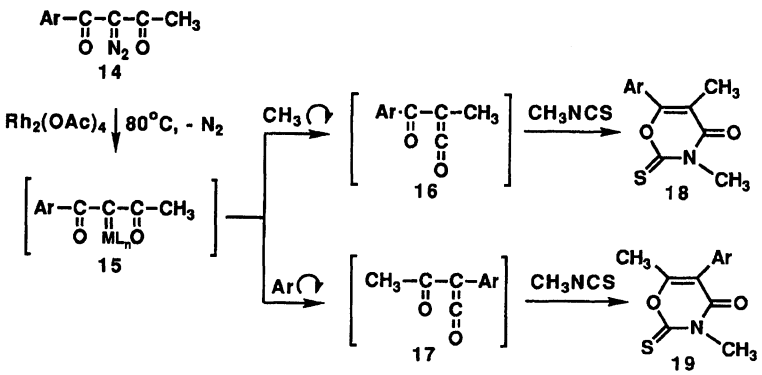


Chart 3.

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**	*p*-$CH_3OC_6H_4$	23	33	0.59
b	**14b**	*p*-$CH_3C_6H_4$	26	12	0.32
c	**14c**	C_6H_5	26	Trace	ca. 0
d	**14d**	*p*-ClC_6H_4	18	2	0.10

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

the Diels-Alder reaction of methyl isothiocyanate with aroylmethylketene (**16**) formed by the methyl migration of diketocarbenoid (**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 diketocarbenoid (**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 thioxooxazinone (**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 ^{13}C NMR spectrum of **24** showed signals of two carbonyl carbons at 149.09 ppm (q, $^3J_{CH}=2.8$ 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 ^{13}C 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 ^{13}C 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 ketocarbenoid **26** seems to be accelerated at high temperature. This acceleration of the Wolff rearrangement is explained by the assumption that the ketocarbenoid intermediate **26** yields free ketocarbene more easily at high temperature,

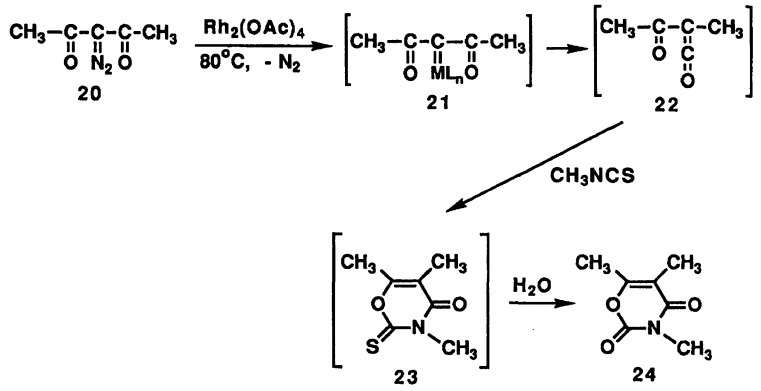


Chart 4.

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	$C_{17}H_{13}NO_2S$
6b	69.93	5.02	4.56	69.88	4.89	4.53	$C_{18}H_{15}NO_2S$
6c	74.08	4.38	3.90	73.93	4.23	3.92	$C_{22}H_{15}NO_2S$
18a	59.27	5.01	5.25	59.30	4.96	5.32	$C_{13}H_{13}NO_3S$
18b	63.08	5.32	5.69	63.13	5.30	5.66	$C_{13}H_{13}NO_2S$
19b	62.80	5.28	5.56	63.13	5.30	5.66	$C_{13}H_{13}NO_2S$
18c	62.02	4.81	6.10	61.78	4.75	6.10	$C_{12}H_{11}NO_2S$
24	54.18	5.84	9.29	54.19	5.85	9.03	$C_7H_9NO_3$
30	56.94	6.13	6.65	56.85	6.20	6.63	$C_{10}H_{13}NO_2S$
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**.

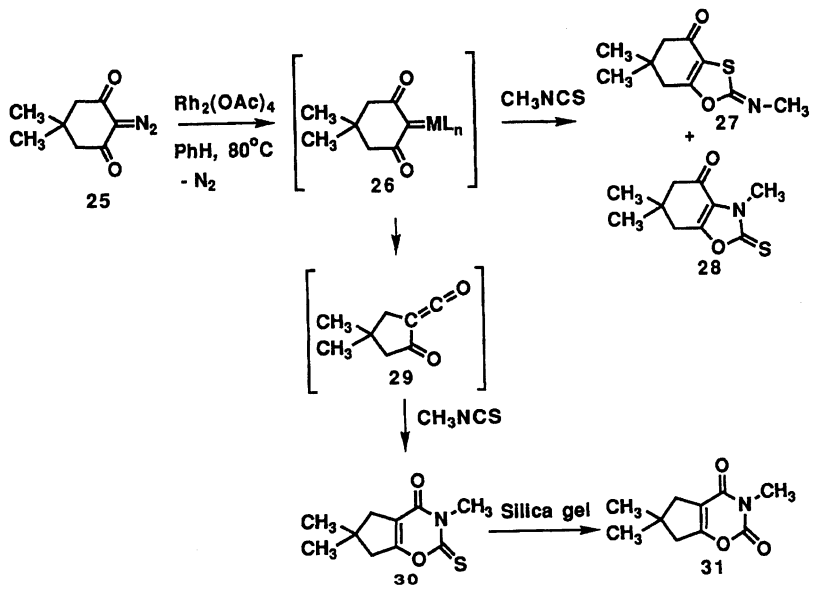


Chart 5.

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) $\gg\alpha$-diazoketones (no rearrangement), on the basis of relative yields of thioxooxazinone to 2-imino-1,3-oxathiole. Since rhodium(II) acetate is well known as a catalyst for the decomposition of α-diazocarbonyl 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-diazo-1,3-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. ^{1}H NMR (270.05 MHz and 500 MHz) and ^{13}C NMR (67.80 MHz and 125.65 MHz) spectra were recorded on a JEOL EX-270 and a GX-500 in a $CDCl_3$ solution using TMS as an internal standard. A Varian EM-390 (90 MHz) was also used for measurements of ^{1}H 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 CaH_2 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 $Rh_2(OAc)_4$-catalyzed reaction of dibenzoyldiazomethane (**4**) with methyl isothiocyanate gave benzyl phenyl ketone (**7**: 11% yield) and **3-methyl-5,6-diphenyl-2-thioxo-2*H*-1,3-oxazin-4(3*H*)-one (6a)**: 60% yield; colorless crystals; mp 112.0—113.5°C (from benzene–hexane); ^{1}H NMR (500 MHz) δ=3.75 (3H, s, NCH_3) and 7.19—7.37 (10H, m, arom-H); ^{13}C NMR (125.65 MHz) δ=34.91 (q, NCH_3), 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 $Rh_2(OAc)_4$-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); ^{1}H NMR (90 MHz) δ=1.21 (3H, t, J=7.1 Hz, CH_3), 4.17 (2H, q, J=7.1 Hz, OCH_2), 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 $Rh_2(OAc)_4$-catalyzed reaction of **4** with ethyl isothiocyanate (**5b**) gave **7** (4.4% yield) and **3-ethyl-5,6-diphenyl-2-thioxo-2*H*-1,3-oxazin-4(3*H*)-one (6b)**: 65% yield; colorless crystals; mp 131.5—132.9°C (from ethyl acetate–hexane); ^{1}H NMR (270.05 MHz) δ=1.39 (3H, t, J=7.0 Hz, CH_3), 4.66 (2H, q, J=7.0 Hz, NCH_2), and 7.17—7.36 (10H, m, arom-H); ^{13}C NMR (67.80 MHz) δ=11.15 (q, CH_3), 43.62 (t, NCH_2), 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 $Rh_2(OAc)_4$-catalyzed reaction of **4** with phenyl isothiocyanate (**5c**) gave **7** (1.3% yield) and **3,5,6-triphenyl-2-thioxo-2*H*-1,3-oxazin-4(3*H*)-one (6c)**: 38% yield; colorless crystals; mp 231.5—232.6°C (from ethyl acetate–hexane); ^{1}H NMR (270.05 MHz) δ=7.23—7.56 (m, arom-H); ^{13}C 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 $Rh_2(OAc)_4$-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-2*H*-1,3-oxazin-4(3*H*)-one (18a): 23% yield; colorless needles; mp 152.8—153.6°C (from ethyl acetate–hexane); ^{1}H NMR (90 MHz) δ=2.13 (3H, s, CH_3), 3.71 (3H, s, NCH_3), 3.87 (3H, s, OCH_3), 6.9—7.1 (2H, m, arom-H), and 7.5—7.7 (2H, m, arom-H); ^{13}C NMR (125.65 MHz) δ=11.92 (q, CH_3), 34.73 (q, NCH_3), 55.51 (q, OCH_3), 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-2*H*-1,3-oxazin-4(3*H*)-one (19a): 33% yield; ^{1}H NMR (500 MHz) δ=2.12 (3H, s, CH_3), 3.69 (3H, s, NCH_3), 3.84 (3H, s, OCH_3), 6.95—6.97 (2H, m, arom-H), and 7.16—7.18 (2H, m,

arom-H); ^{13}C NMR (125.65 MHz) δ=18.17 (q, CH_3), 34.82 (q, NCH_3), 55.36 (q, OCH_3), 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 $Rh_2(OAc)_4$-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)-2*H*-1,3-oxazin-4(3*H*)-one (18b): 26% yield; colorless needles; mp 109.7—110.3°C (from ethyl acetate–hexane); ^1H NMR ($CDCl_3$, 500 MHz) δ=2.11 (3H, s, CH_3), 2.42 (3H, s, arom-CH_3), 3.71 (3H, s, NCH_3), 7.29 (2H, d, J=8.3 Hz, arom-H), and 7.52 (2H, d, J=8.3 Hz, arom-H): ^{13}C NMR (125.65 MHz) δ=11.84 (q, CH_3), 21.54 (qt, $^3J_{CH}$=4.4 Hz, arom-CH_3), 34.72 (q, NCH_3), 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)-2*H*-1,3-oxazin-4(3*H*)-one (19b): 12% yield; colorless needles; mp 108.0—108.8°C (from ethyl acetate–hexane); ^1H NMR ($CDCl_3$, 500 MHz) δ=2.20 (3H, s, CH_3), 2.38 (3H, s, arom-CH_3), 3.69 (3H, s, NCH_3), 7.12—7.14 (2H, m, arom-H), and 7.23—7.24 (2H, m, arom-H); ^{13}C NMR ($CDCl_3$, 125.65 MHz) δ=18.13 (q, CH_3), 21.29 (qt, $^3J_{CH}$=4.4 Hz, arom-CH_3), 34.79 (q, NCH_3), 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 $Rh_2(OAc)_4$-catalyzed reaction of acetylbenzoyldiazomethane (**14c**) with methyl isothiocyanate gave a mixture of **18c** and **19c**.

3,5-Dimethyl-6-phenyl-2-thioxo-2*H*-1,3-oxazin-4(3*H*)-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, CH_3), 3.75 (3H, s, NCH_3), 7.47—7.52 (3H, m, arom-H), and 7.61—7.62 (2H, m, arom-H); ^{13}C NMR (125.65 MHz) δ=11.78 (q, CH_3), 34.74 (q, NCH_3), 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-2*H*-1,3-oxazin-4(3*H*)-one (19c): ^1H NMR (270.05 MHz) δ=2.20 (3H, s, CH_3), 3.69 (3H, s, NCH_3), and 7.22—7.47 (5H, m, arom-H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ=14.04 (q, CH_3), 34.74 (q, NCH_3), 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 $Rh_2(OAc)_4$-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-2*H*-1,3-oxazin-4(3*H*)-one (18d): 18% yield; ^1H NMR (270.05 MHz) δ=2.10 (3H, s, CH_3), 3.71 (3H, s, NCH_3), and 7.46—7.60 (4H, m, arom-H); ^{13}C NMR (67.80 MHz) δ=11.73 (q, CH_3), 34.67 (q, NCH_3), 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-2*H*-1,3-oxazin-4(3*H*)-one (19d): 2% yield; ^1H NMR (270.05 MHz) δ=2.22 (3H, s, CH_3), 3.68 (3H, s, NCH_3), 7.19—7.23 (2H, m, arom-H), and 7.30—7.43 (2H, m, arom-H); ^{13}C NMR (67.80 MHz) δ=18.09 (q, CH_3), 34.67 (q, NCH_3), 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 $Rh_2(OAc)_4$-catalyzed reaction of diacetyldiazomethane (**20**) with methyl isothiocyanate gave a mixture of **23** and **24**.

3,5,6-Trimethyl-2-thioxo-2*H*-1,3-oxazin-4(3*H*)-one (23): ^1H NMR (90 MHz) δ=1.81 (3H, q, J=0.9 Hz, CH_3), 2.01 (3H, q, J=0.9 Hz, CH_3), and 3.00 (3H, s, NCH_3).

3,5,6-Trimethyl-2*H*-1,3-oxazine-2,4(3*H*)-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, CH_3), 2.20 (3H, q, J=0.9 Hz, CH_3), and 3.32 (3H, s, NCH_3); ^{13}C NMR (125.65 MHz) 10.21 (q, CH_3), 16.84 (q, CH_3), 28.54 (q, NCH_3), 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 (CH_3CO^+, 79).

The $Rh_2(OAc)_4$-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(3*H*)-one (30): 0.9% yield; colorless prisms; mp 57.2—59.6°C; ^1H NMR (270.05 MHz) δ=1.23 (6H, s, CH_3×2), 2.52 (2H, t, J=1.7 Hz, CH_2), 2.66 (2H, t, J=1.7 Hz, CH_2), and 3.64 (3H, s, NCH_3); ^{13}C NMR (67.80 MHz) δ=29.57 (qm, CH_3×2), 34.48 (q, NCH_3), 36.52 (s, $\underline{C}(CH_3)_2$), 40.62 (tm, CH_2), 45.65 (tm, CH_2), 113.00 (stt, $^2J_{CH}$=6.4 Hz, $^3J_{CH}$=4.3 Hz, =$\underline{C}$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(3*H*)-dione (31): 5.1% yield; colorless oil; ^1H NMR (270.05 MHz) δ=1.22 (6H, s, CH_3×2), 2.49 (2H, t, J=1.8 Hz, CH_2), 2.59 (2H, t, J=1.8 Hz, CH_2), and 3.33 (3H, s, NCH_3); ^{13}C NMR (67.80 MHz) δ=28.54 (q, NCH_3), 29.73 (qm, CH_3×2), 36.54 (s, $\underline{C}(CH_3)_2$), 40.54 (tm, CH_2),

45.47 (tm, CH_2), 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).