Formation of 2-Imino-1,3-oxathioles and 2(3*H*)-Oxazolethione by the Rhodium(II) Acetate-Catalyzed Reaction of α-Diazocarbonyl Compounds with Isothiocyanates

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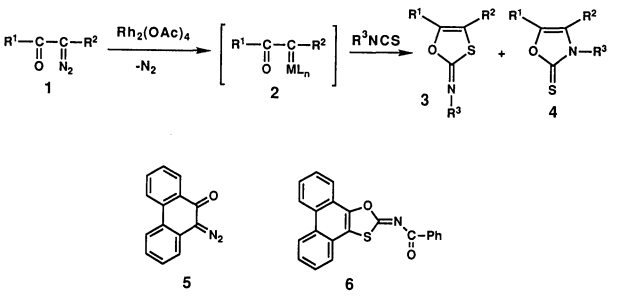
The rhodium(II) acetate-catalyzed reaction of various α-diazocarbonyl compounds with alkyl, phenyl, and benzoyl isothiocyanates gave 2-imino-1,3-oxathioles in good yields. 2(3*H*)-Oxazolethione was obtained as a by-product only in the reaction of diazodimedone with methyl isothiocyanate. The mechanism through thiocarbonyl ylide and azomethine ylide was proposed for these reactions, and preferable formation of thiocarbonyl ylide was explained by heat of formation and frontier molecular orbital calculations.

In the previous papers of this series, rhodium(II) acetate-catalyzed reaction of α-diazocarbonyl compounds with carbon disulfide was reported to give the corresponding 1,3-oxathiole-2-thiones in good yields.[1] In order to investigate the application of this reaction to the other type of heterocumulene having a sulfur atom, isothiocyanate[2] was chosen as a substrate toward α-diazocarbonyl compounds in the presence of rhodium(II) acetate. Two types of reaction are possible due to unsymmetrical structure of isothiocyanate. When the ketocarbenoid **2** attacks the sulfur atom of isothiocyanate, 2-imino-1,3-oxathiole **3** will be obtained through the intramolecular 1,5-cyclization of thiocarbonyl ylide intermediate. On the other hand, initial attack of the carbenoid **2** on nitrogen atom of isothiocyanate gives 2(3*H*)-oxazolethione **4** through azomethine ylide in a similar manner. It is of interest to investigate the preferable process of the attack of the carbenoid **2** either to form thiocarbonyl ylide or azomethine ylide, and to know the difference of the reactivity between isothiocyanate and carbon disulfide toward carbenoid **2**. Therefore, the rhodium(II) acetate-catalyzed reactions of α-diazocarbonyl compounds **1** with several isothiocyanates were carried out.

The rhodium(II) acetate-catalyzed reaction of α-diazoacetophenone (**1a**) with ten molar amounts of methyl isothiocyanate gave 2-methylimino-5-phenyl-1,3-oxathiole (**3a**) in 0.9% yield as the only isolable product. The structure of **3a** was determined by comparison of the spectroscopic data with the authentic sample prepared by the reaction of α-bromoacetophenone with sodium 1-imidazolecarboxy(methylimido)thioate according to the reported procedure.[3] The ^{1}H NMR spectrum of **3a** had a singlet signal of *N*-methyl group at δ=3.05. Its ^{13}C NMR spectrum showed quartet signals of *N*-methyl carbon and imino-carbon at δ=39.92 and 162.12, respectively. No signal of thiocarbonyl carbon was observed near δ=180. Attempts to increase the yield of **3a** by used of dichloromethane as a solvent or Cu(acac)$_2$ as a catalyst were unsuccessful.



The reactions of α-diazocarbonyl compounds **1** having various substituents R^1 and R^2 with isothiocyanates were studied to investigate the scope and limitation of the reaction. As an example of cyclic diazoketone, the reaction of 2-diazocyclohexanone (**1b**) afforded the corresponding 2-methylimino-1,3-oxathiole **3b** in 62% yield. The ^{13}C NMR spectrum of **3b** showed a signal of imino-carbon at δ=162.55 as a quartet ($^3J_{CH}$=9.8 Hz) coupled with *N*-methyl protons, signals of 4-C and 5-C of 1,3-oxathiole ring at δ=107.98 and 143.80, and a signal of *N*-methyl carbon at δ=39.94, besides four signals of methylene carbon at δ=22.19, 22.89, 23.13, and 23.15.

The reaction of diazodimedone (**1c**) with methyl isothiocyanate gave 6,6-dimethyl-2-methylimino-6,7-dihydro-1,3-benzoxathiol-4(5*H*)-one (**3c**) and 2(3*H*)-oxazolethione **4c** in 45 and 2.2% yields together with the products through the Wolff rearrangement.[4] The ^{1}H NMR spectrum of the major product **3c** was completely identical with that of the compound **4c** reported by Matsumura as a reaction product of 2-bromo-5,5-dimethyl-1,3-cyclohexanedione with 1,6-dimethyl-3,4-trimethylene-2,5-dithioxo[1,2,4]thiadiazolo[5,1-*e*][1,2,4]thiadiazole.[5] The ^{13}C NMR spectrum of this major product showed a signal of imino-carbon at δ=160.19 as a quartet ($^3J_{CH}$=10.1 Hz) coupled with methyl protons, which indicated the similarity of the structures between **3c** and **3a**. The chemical shifts of *N*-methyl group, ^{1}H signal at δ=3.04 and ^{13}C signal at δ=40.05, are also close to the values of the corresponding signals of **3a** described above, which supports the

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Table 1. Yields and Melting Points of the Products **3**, **4c**, **6** Obtained by the Reaction of α-Diazoketones with Isothiocyanates in the Presence of $Rh_2(OAc)_4$

Run	α-Diazoketone			Isothiocyanate	Product		
	1	R^1	R^2	R^3	**3**	Yield/%	Mp/°C
1	**1a**	Ph	H	CH_3	**3a**	0.9	101.4—103.0[a]
2	**1b**	$-(CH_2)_4-$		CH_3	**3b**	62	Oil
3	**1c**	$-CH_2CMe_2CH_2CO-$		CH_3	**3c**	45	Oil
					4c	2.2	91.2—93.4
4	**1d**	CH_3	$COOCH_3$	CH_3	**3d**	41	97.3—98.9
5	**1e**	CH_3	$COOC_2H_5$	CH_3	**3e**	59	60.2—61.3
6	**1f**	CH_3	$COOC(CH_3)_3$	CH_3	**3f**	62	52.2—53.3
7	**1d**	CH_3	$COOCH_3$	C_2H_5	**3g**	46	62.0—64.2
8	**1e**	CH_3	$COOC_2H_5$	C_2H_5	**3h**	59	Oil
9	**1f**	CH_3	$COOC(CH_3)_3$	C_2H_5	**3i**	66	Oil
10	**1e**	CH_3	$COOC_2H_5$	C_6H_5	**3j**	66	Oil
11	**1g**	C_2H_5	$COOCH_3$	CH_3	**3k**	59	44.4—45.6
12	**1a**	Ph	H	COPh	**3l**	35	164.5—166.4[b]
13	**1b**	$-(CH_2)_4-$		COPh	**3m**	51	151.9—153.3
14	**5**	c)		COPh	**6**	82	248.1—251.9
15	**1c**	$-CH_2CMe_2CH_2CO-$		COPh	**3n**	73	167.0—169.5
16	**1e**	CH_3	$COOC_2H_5$	COPh	**3o**	56	169.5—170.2[d]

a) (Lit,[5] 99—102°C). b) (Lit,[6] 159—160°C). c) 10-Diazo-9(10*H*)-phenanthrone. d) (Lit,[6] 167—169°C).

structure assignment of the major product to 2-methylimino-1,3-oxathiole **3c**.

The structure of the minor product was assigned to **4c** on the basis of ^1H NMR and ^{13}C NMR spectrum. In its ^1H NMR spectrum, *N*-methyl group showed a singlet signal at δ=3.75 which shifted down field by 0.7 ppm from that of 2-methylimino-1,3-oxathioles **3** obtained in this reaction. The ^{13}C NMR spectrum of **4c** showed four signals of sp^2-carbon at δ=123.15 (m), 159.93 (t), 179.30 (q), and 186.08 (t). Coupling pattern and the value of chemical shifts of these signals indicated that the signal at δ=179.30 is assigned to thiocarbonyl carbon, and the signal at δ=186.08 to carbonyl carbon. The quartet signal at δ=179.30 had a smaller coupling constant ($^3J_{CH}$=4.8 Hz) than that of imino-carbon of 2-methylimino-1,3-oxathioles **3**, and became singlet when a signal of *N*-methyl protons at δ=3.75 was irradiated. These results support the structure determination of our major product to **3c**, and deny the determination of the same compounds to **4c** by Matsumura.[5]

The reaction was also applicable to α-diazo-β-ketoesters **1d**—**1g**. For example, the reaction of ethyl diazoacetoacetate (**1e**) with methyl isothiocyanate gave the corresponding 2-imino-1,3-oxathiole **3e** as a sole product (59% yield). The ^{13}C NMR (δ=161.04) and IR spectra (1714 cm^{-1}) of **3e** showed the presence of ester carbonyl group. Therefore, the cyclization to give **3e** is determined to occur at the acetyl group of starting diazo compound not at ester carbonyl group.

The reaction of other α-diazo-β-ketoesters **1d**—**1g** with methyl, ethyl, and phenyl isothiocyanates also gave the corresponding 2-imino-1,3-oxathioles **3d**—**3k** in fairly good yields as shown in Table 1 (Runs 4—11). The yield of **3** changes by the substituents R^1, R^2, and R^3. When substituents R^1, R^2, and R^3 are not bulky, the yields decreased because of competing pathways such as dimer-formation and polymer-formation of ketocarbenoid. The comparison of the yields of 2-imino-1,3-oxathioles **3a**—**3k** with those of 1,3-oxathiole-2-thiones obtained by the reaction of carbon disulfide[1] suggests that carbon disulfide is more reactive than isothiocyanates toward the carbenoid intermediates.

The liquid 2-imino-1,3-oxathioles are unstable and their color changes to dark brown during storage even at room temperature. However, **3j** is stable enough because of stabilization effect of phenyl group.

Benzoyl isothiocyanate is known to have higher reactivity than alkyl isothiocyanate in many reactions.[6] Therefore, the increase of the yields of iminooxathioles **3** is expected in the rhodium(II) acetate-catalyzed reaction of α-diazocarbonyl compounds with benzoyl isothiocyanate. The reaction of α-diazoacetophenone (**1a**) with benzoyl isothiocyanate at 80°C afforded 2-benzoylimino-1,3-oxathiole **3l** in 35% yield. Spectroscopic data and melting point of **3l** were identical with those of the product reported in the reaction of α-chloroacetophenone with methyl *N*-benzoylthiocarbamate.[7]

The reaction of benzoyl isothiocyanate with cyclic diazoketones such as 2-diazocyclohexanone (**1b**) and 10-diazo-9(10*H*)-phenanthrone (**5**) also gave the corresponding 2-imino-1,3-oxathioles **3m** and **6** in 51 and 82% yields, respectively. The reaction of diazodimedone (**1c**) with benzoyl isothiocyanate gave 2-benzoylimino-1,3-oxathiole **3n** in 73% yield. The reaction of ethyl diazoacetoacetate (**1e**) with benzoyl isothiocyanate afforded ethyl 2-benzoylimino-5-methyl-1,3-oxathiole-4-carboxylate (**3o**) in 56% yield. The structures of **3m**—**3o** and **6** were determined by the similarity of the ^{13}C NMR signals of 1,3-oxathiole ring carbons and carbonyl carbon of *N*-benzoyl group with those of **3l**. The chemical shifts of C_2 (δ=177.6—177.9), C_4 (δ=110—117), C_5 (δ=122—161), and N–CO (δ=

175.5—176.1) resemble to the corresponding values of **3l**, C_2 (δ=179.72), C_4 (δ=100.08), C_5 (δ=148.48), and N–CO (δ=176.11), respectively. In these reactions, cyclization occurs at the acetyl-oxygen in the same manner as the reactions with methyl and ethyl isothiocyanates described above. The high reactivity of benzoyl isothiocyanate increased the yields of 2-imino-1,3-oxathioles in the reactions of low reactive diazoacetophenone and diazodimedone (Table 1, Runs (1, 12) and (3, 15)).

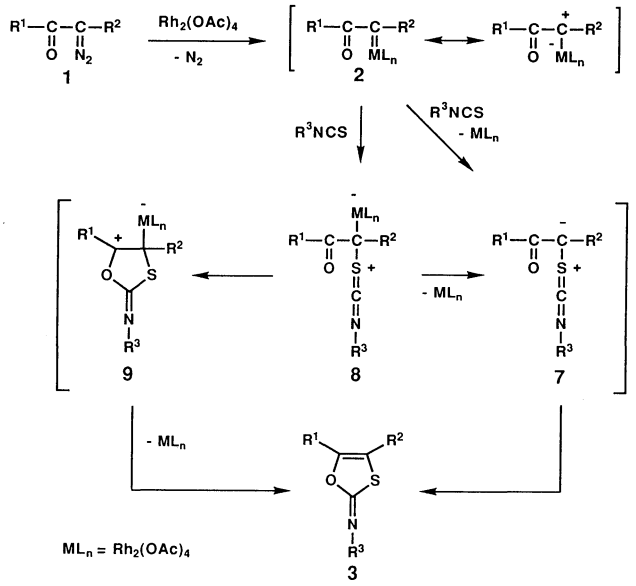
Reaction Mechanism. The reaction of diazocarbonyl compounds with isothiocyanates in the presence of rhodium(II) acetate afforded the corresponding 2-imino-1,3-oxathiole **3** dominantly. The first step of this reaction is initiated by the formation of ketocarbenoid **2** through the rhodium(II) acetate-catalyzed decomposition of α-diazocarbonyl compounds **1**.[1b] The electrophilic attack of **2** on sulfur atom of isothiocyanate generates thiocarbonyl ylide **7** or its rhodium(II) acetate coordinated species **8**. The 1,5-cyclization of these intermediates at carbonyl oxygen and isothiocyanate carbon gives the 2-imino-1,3-oxathioles **3** as shown in the tentative mechanism (Scheme 1).

The formation of 2(3*H*)-oxazolethione **4** was observed only in the reaction of diazodimedone with methyl isothiocyanate. In order to explain the preferable formation of 2-imino-1,3-oxathiole **3** to that of 2(3*H*)-oxazolethione **4**, molecular orbital calculation of ylide intermediates was done on thiocarbonyl ylide **7** and azomethine ylide **10**. Heat of formation of thiocarbonyl

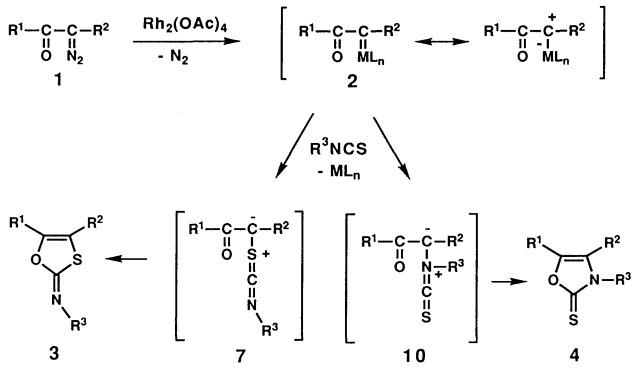
Table 2. Heat of Formation[a] of Thiocarbonyl Ylide **7** and Azomethine Ylide **10**

	Thiocarbonyl ylide **7**	Azomethine ylide **10**
R^3=CH_3	48.6	59.1
R^3=PhCO	44.2	54.0

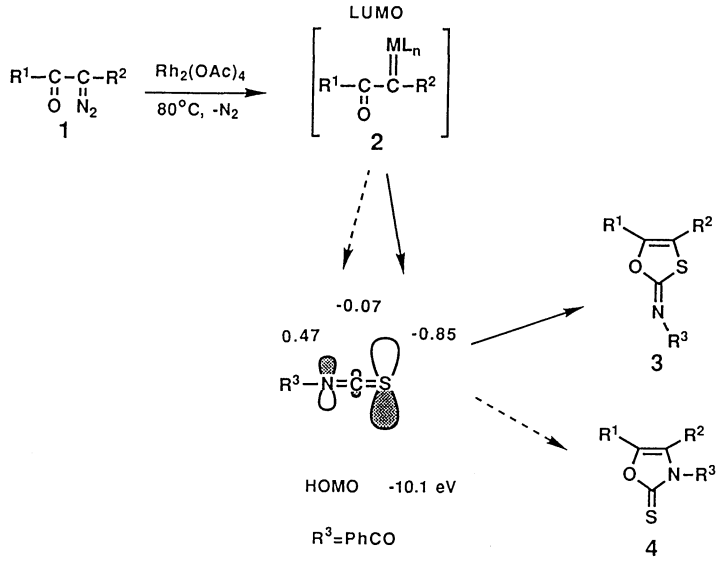
a) R^1=R^2=H, calcd by MNDOC, kcal mol^{-1}.



Scheme 1.



Scheme 2.



Scheme 3.

Table 3. Results of Elemental Analyses of the Reaction Products **3**, **4**, and **6**

Product	Found/%			Calcd/%			Molecular formula
	C	H	N	C	H	N	
3c	56.59	6.17	6.31	56.85	6.20	6.63	$C_{10}H_{13}NO_2S$
4c	56.63	6.14	6.49	56.85	6.20	6.63	$C_{10}H_{13}NO_2S$
3d	44.69	4.79	7.65	44.91	4.85	7.48	$C_7H_9NO_3S$
3e	47.65	5.42	6.96	47.75	5.51	6.96	$C_8H_{11}NO_3S$
3f	52.31	6.49	6.08	52.38	6.59	6.11	$C_{10}H_{15}NO_3S$
3g	47.71	5.46	7.02	47.75	5.51	6.96	$C_8H_{11}NO_3S$
3j	59.30	5.17	5.54	59.30	4.98	5.32	$C_{13}H_{13}NO_3S$
3k	47.34	5.26	6.73	47.75	5.51	6.96	$C_8H_{11}NO_3S$
3n	63.75	5.08	4.57	63.77	5.02	4.65	$C_{16}H_{15}NO_3S$
3o	57.67	4.51	4.87	57.72	4.50	4.81	$C_{14}H_{13}NO_4S$
6	74.31	3.87	3.93	74.35	3.69	3.94	$C_{22}H_{13}NO_2S$

ylide **7** and azomethine ylide **10** formed by the reaction of parent ketocarbene (R^1=R^2=H) with methyl isothiocyanate (R^3=CH_3) and benzoyl isothiocyanate (R^3=PhCO) were calculated by seim-empirical MNDOC method.[8] The results indicate that thiocarbonyl ylide **7** is more stable than azomethine ylide **10** independent of the substituent R^3 (Table 2). If we presume that the difference of the heats of formation between thiocarbonyl ylide **7** and azomethine ylide **10** correlates with the energy of the transition states leading to **7** and **10**, the favorable formation of the thiocarbonyl ylide **7** seems to be reasonable in the reaction of ketocarbenoid **2** with isothiocyanate.

The preferential formation of thiocarbonyl ylide **7** to azomethine ylide **10** is explained by the Frontier Molecular Orbital Theory. The coefficients of FMO of methyl and benzoyl isothiocyanates calculated by MNDO method are shown in Scheme 3. The electrophilic reagent usually attacks the site of the largest coefficient of HOMO in the substrate.[9] The calculation shows that HOMO coefficient of sulfur atom (0.85) is larger than that of nitrogen atom (0.47) in the isothiocyanate. Therefore, the electrophilic attack of ketocarbenoid **2** occurs on sulfur atom of isothiocyanate preferentially affording 2-imino-1,3-oxathiole **3** selectively. The formation of 2(3*H*)-oxazolethione and 2-imino-1,3-oxathiole in the reaction of diazodimedone may be attributed to the effect of two carbonyl groups bonding to carbenoid carbon.

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 and 500 MHz) and ^{13}C NMR (67.80 MHz and 125.65 MHz) spectra were recorded on JEOL EX-270 and 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 JEOL JMS-DX303 mass spectrometer.

Materials. α-Diazoacetophenone was prepared by the reaction of benzoyl chloride with an excess of diazomethane in the presence of triethylamine according to Newman's method.[10] Diazodicarbonyl compounds were prepared by the diazo group transfer reaction reported by Regitz.[11] 10-Diazo-9(10*H*)-phenanthrone[12] and 2-diazocyclohexanone[13] were prepared according to the reported methods. Methyl, ethyl, and phenyl isothiocyanates were purified by distillation of commercial reagents just before use. Benzoyl isothiocyanate was prepared by the reaction of benzoyl chloride with potassium thiocyanate.[14] Benzene was purified by distillation after reflux on CaH_2 and stored over molecular sieves 4A.

General Procedure for the $Rh_2(OAc)_4$-Catalyzed Reaction of α-Diazocarbonyl Compounds with Isothiocyanates. A solution of diazocarbonyl compound (3.0 mmol) in dry benzene (10 ml) was added dropwise over a period of ca. 4 h to a reflux suspension of $Rh_2(OAc)_4$ (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 diazo compound was detected by TLC or IR measurements. The reaction mixture was separated by medium-pressure liquid chromatography (silica gel, eluted with ethyl acetate-hexane) after removal of solvent under reduced pressure.

The reaction of α-diazoacetophenone (**1a**; 3 mmol) with methyl isothiocyanate (30 mmol) gave 2-methylimino-5-phenyl-1,3-oxathiole (**3a**): Colorless crystals; ^{1}H NMR (500 MHz) δ=3.05 (3H, s, NCH_3), 6.40 (1H, s, =CH–S), and 7.33—7.62 (5H, m, arom-H); ^{13}C NMR (125.65 MHz) δ=39.92 (q, NCH_3), 95.31 (d, =CH–S), 124.71 (d, arom-CH), 128.33 (s, arom-C), 128.80, 129.23 (each d, arom-CH), 148.36 (s, =C–O), and 162.12 (s, C=N).

The reaction of 2-diazocyclohexanone (**1b**: 3 mmol) with methyl isothiocyanate (30 mmol) gave 2-methylimino-4,5,6,7-tetrahydro-1,3-benzoxathiole (**3b**): Colorless oil; ^{1}H NMR (500 MHz) δ=1.80 (4H, m, $CH_2\times2$), 2.34 (4H, m, $CH_2\times2$), and 2.97 (3H, s, NCH_3); ^{13}C NMR (125.65 MHz) δ=22.19, 22.82, 23.13, 23.15 (each t, CH_2), 39.94 (q, NCH_3), 107.98 (s, =C–S), 143.80 (s, =C–O), and 162.55 (sq, $^3J_{CH}$=9.8 Hz, C=N); IR (neat) 2935, 2855, 1691 (s), 1662 (s), 1535, 1445, 1404, 1355, 1217, 1183, 1150, 1089, 1048, 1002, 878, and 706 cm^{-1}.

The reaction of diazodimedone (**1c**: 3 mmol) with methyl isothiocyanate (30 mmol) gave 2-methylimino-1,3-oxathiole **3c** and 2(3*H*)-oxazolethione **4c** together with two Wolff rearrangement products.

6,6-Dimethyl-2-methylimino-6,7-dihydro-1,3-benzoxathiol-4(5*H*)-one (3c): Colorless oil; ^{1}H NMR (500 MHz) δ=1.17 (6H, s, $CH_3\times2$), 2.41 (2H, s, CH_2), 2.61 (2H, s, CH_2), and 3.04

(3H, s, NCH_3); ^{13}C NMR (125.65 MHz) δ=28.39 (q, $CH_3\times2$), 34.01 (s, $\underline{C}Me_2$), 37.59 (t, CH_2), 40.15 (q, NCH_3), 50.91 (t, CH_2), 113.28 (sm, =C–S), 160.19 (sq, $^3J_{CH}$=10.1 Hz, C=N), 163.37 (st, $^2J_{CH}$=9.0 Hz, =C–O), and 189.66 (st, $^2J_{CH}$=6.4 Hz, C=O); IR (KBr) 2961, 1689 (s), 1670 (s), 1626, 1467, 1409, 1355, 1322, 1297, 1233, 1162, 1087, 1060, 1026, and 990 cm^{-1}.

3,6,6-Trimethyl-2-thioxo-2,3,6,7-tetrahydro-1,3-benzoxazol-4(5*H*)-one (4c): Colorless prisms; ^1H NMR (500 MHz) δ=1.19 (6H, s, $CH_3\times2$), 2.43 (2H, s, CH_2), 2.73 (2H, s, CH_2), and 3.75 (3H, s, NCH_3); ^{13}C NMR (125.65 MHz) δ=28.49 (q, $CH_3\times2$), 33.59 (q, NCH_3), 35.19 (s, $\underline{C}Me_2$), 35.86 (t, CH_2) 51.97 (t, CH_2), 123.15 (sm, =C–N), 159.93 (st, $^2J_{CH}$=9.4 Hz, =C–O), 179.30 (sq, $^3J_{CH}$=4.8 Hz, C=S), and 186.08 (st, $^2J_{CH}$=6.2 Hz, C=O); IR (KBr) 2960, 1674 (s), 1449, 1380, 1352, 1305, 1295, 1276, 1036, and 971 cm^{-1}; MS (EI, rel intensity %) 212 (15, M^++1), 211 (100, M^+).

The rhodium(II) acetate-catalyzed reaction of α-diazo-β-ketoesters **1d**—**1g** with alkyl and phenyl isothiocyanates gave 2-imino-1,3-oxathioles **3d**—**3k**. The spectroscopic data of the products were shown below.

Methyl 5-Methyl-2-methylimino-1,3-oxathiole-4-carboxylate (3d): Colorless crystals; ^1H NMR (90 MHz) δ=2.46 (3H, s, CH_3), 2.99 (3H, s, NCH_3), and 3.83 (3H, s, OCH_3); IR (KBr) 2953, 1725 (s, C=O), 1690, 1672, 1634 (C=N), 1437, 1378, 1299, 1274, 1263, 1193, 1106, 1085, 793, 757, and 668 cm^{-1}; MS (EI, rel intensity %) 187 (100, M^+).

Ethyl 5-Methyl-2-methylimino-1,3-oxathiole-4-carboxylate (3e): Colorless crystals; ^1H NMR (500 MHz) δ=1.34 (3H, t, J=7.1 Hz, CH_3), 2.45 (3H, s, CH_3), 3.00 (3H, s, NCH_3), and 4.28 (2H, q, J=7.1 Hz, OCH_2); ^{13}C NMR (125.65 MHz) δ=14.02 (q, $\underline{C}H_3$–C=), 14.25 (qt, $CH_2\underline{C}H_3$), 39.75 (q, NCH_3), 61.57 (tq, $O\underline{C}H_2CH_3$), 105.45 (sq, $^3J_{CH}$=3.5 Hz, 4-C), 156.92 (sq, $^3J_{CH}$=7.4 Hz, 5-C), 159.64 (sq, $^3J_{CH}$=10.0 Hz, C=N), and 161.04 (sm, ester C=O); IR (KBr) 2979, 1714 (s, C=O), 1673 (s), 1630, 1445, 1408, 1378, 1364, 1292 (s), 1266, 1124, 1106 (s), 1086 (s), 1055, 1027, 945, 819, 758, and 669 cm^{-1}; MS (EI, rel intensity %) 202 (M^++1), 201 (100, M^+).

***t*-Butyl 5-Methyl-2-methylimino-1,3-oxathiole-4-carboxylate (3f):** Colorless crystals; ^1H NMR (90 MHz) δ=1.53 (9H, s, $C(CH_3)_3$), 2.39 (3H, s, CH_3), and 2.96 (3H, s, NCH_3); IR (KBr) 2972, 2933, 1710 (s, C=O), 1685 (s), 1670 (s), 1635, 1474, 1456, 1427, 1405, 1394, 1374, 1365, 1304 (s), 1259, 1176, 1114 (s), 1084 (s), 1057, 1036, 944, 846, 826, 755, and 666 cm^{-1}; MS (EI, rel intensity %) 229 (59, M^+), 116 (100).

Methyl 2-Ethylimino-5-methyl-1,3-oxathiole-4-carboxylate (3g): Colorless crystals; ^1H NMR (90 MHz) δ=1.26 (3H, t, J=7.2 Hz, CH_3), 2.44 (3H, s, CH_3), 3.09 (2H, q, J=7.2 Hz, NCH_2), and 3.81 (3H, s, OCH_3); IR (KBr) 2975, 2950, 2872, 1711 (s, C=O), 1690 (s), 1621 (s), 1518, 1454, 1441 (s), 1379 (s), 1355, 1292 (s), 1196 (s), 1126 (s), 1104 (s), 1062 (s), 1021, 977, 792, 753, 667, and 652 cm^{-1}.

Ethyl 2-Ethylimino-5-methyl-1,3-oxathiole-4-carboxylate (3h): Colorless oil; ^1H NMR (90 MHz) δ=1.26 (3H, t, J=7.1 Hz, CH_3), 1.32 (3H, t, J=7.1 Hz, CH_3), 2.44 (3H, s, CH_3), 3.09 (2H, q, J=7.1 Hz, NCH_2), and 4.25 (2H, q, J=7.1 Hz, OCH_2); IR (KBr) 2978, 1708, 1683 (s, C=O), 1630 (s), 1467, 1373, 1284 (s), 1129, 1098 (s), 1061, 1021, 977, and 752 cm^{-1}.

***t*-Butyl 2-Ethylimino-5-methyl-1,3-oxathiole-4-carboxylate (3i):** Colorless oil; ^1H NMR (90 MHz) δ=1.25 (3H, t, J=7.2 Hz, CH_3), 1.40 (9H, s, $C(CH_3)_3$), 2.39 (3H, s, CH_3), and 3.09 (2H, q, J=7.2 Hz, NCH_2); IR (KBr) 2976, 1711 (s, C=O), 1677 (s), 1631, 1473, 1454, 1394, 1370, 1332, 1298 (s), 1260, 1170, 1110 (s), 1059, 1035, 971, 843, 826, 761, 728, and 661 cm^{-1}.

Ethyl 5-Methyl-2-phenylimino-1,3-oxathiole-4-carboxylate (3j): Colorless oil; ^1H NMR (90 MHz) δ=1.28 (3H, t, J=7.1 Hz, CH_3), 2.51 (3H, s, CH_3), 4.24 (2H, q, J=7.1 Hz, OCH_2), and 6.86—7.47 (5H, m, arom-H); IR (neat) 2981, 1717 (s), 1671 (s), 1653 (s), 1636 (s), 1594 (s), 1487, 1448, 1371, 1314 (s), 1284 (s), 1172, 1110 (s), 1076 (s), 1026, 975, 768, 697, and 670 cm^{-1}.

Methyl 5-Ethyl-2-methylimino-1,3-oxathiole-4-carboxylate (3k): Colorless crystals; ^1H NMR (90 MHz) δ=1.23 (3H, t, J=7.6 Hz, CH_3), 2.91 (2H, q, J=7.6 Hz, CH_2), 3.00 (3H, s, NCH_3), and 3.82 (3H, s, OCH_3); IR (KBr) 2983, 2957, 1722 (s), 1684 (s), 1615, 1439, 1402, 1320, 1284, 1189, 1163, 1090, 1057, 993, 798, 784, 758, and 696 cm^{-1}.

The rhodium(II) acetate-catalyzed reaction of α-diazo ketones (3.0 mmol) with benzoyl isothiocyanate (30 mmol) gave 2-benzoylimino-1,3-oxathioles in good yields.

2-Benzoylimino-5-phenyl-1,3-oxathiole (3l): Colorless crystals; ^1H NMR (270.05 MHz) δ=6.85 (1H, s, CH), 7.39—7.60 (6H, m, arom-H), 7.73—7.77, and 8.33—8.38 (each 2H, m, arom-H); ^{13}C NMR (67.80 MHz) δ=100.89 (d, =CH–S), 125.08 (dt, *o*-arom-CH), 127.22 (sm, arom-C), 128.34, 129.01, (each dd, *m*-arom-CH), 129.77 (dt, *o*-arom-CH), 129.93, 132.86 (each dt, *p*-arom-CH), 135.16 (st, arom-C), 148.48 (sm, =C–O), 176.11 (st, $^3J_{CH}$=3.7 Hz, N–C=O), and 179.72 (sd, $^3J_{CH}$=6.7 Hz, C=N); IR (KBr) 3080 (=CH), 1625, 1611, 1574 (s), 1502 (s), 1483 (s), 1448, 1323 (s), 1299 (s), 1151, 1114, 1070 (s), 1042, 1021, 909, 860, 758, 713, 688, and 665 cm^{-1}; MS (rel intensity %) 356 (19), 355 (61), and 105 (100).

2-Benzoylimino-4,5,6,7-tetrahydro-1,3-benzoxathiole (3m): Colorless crystals; ^1H NMR (500 MHz) δ=1.81—1.92 (4H, m, $CH_2\times2$), 2.47—2.59 (4H, m, $CH_2\times2$), 7.43—7.54 (3H, m, arom-H), and 8.30—8.32 (2H, m, arom-H); ^{13}C NMR (125.65 MHz) δ=22.11, 22.41, 22.51, 22.84 (each tm, CH_2), 114.33 (sm, =C–S), 128.27 (dd, arom-CH), 129.74, 132.61 (each dt, arom-CH), 135.57 (st, arom-C), 144.38 (sm, =C–O), 175.69 (st, $^3J_{CH}$=4.1 Hz, N–C=O), and 177.92 (s, C=N); IR (KBr) 2940, 1678, 1625, 1615, 1576, 1507 (s), 1484, 1452, 1437, 1346, 1334, 1319, 1296 (s), 1261, 1220, 1191, 1162, 1146, 1101, 1072, 1061, 1020, 906, 720, and 679 cm^{-1}.

2-Benzoyliminophenanthro[9,10-*d*]-1,3-oxathiole (6): Yellow prisms; ^1H NMR (270.05 MHz) δ=7.51—7.66 (3H, m, arom-H), 7.70—7.8 (4H, m, arom-H), 7.85—7.91 (1H, m, arom-H), 8.37—8.46 (3H, m, arom-H), and 8.70—8.76 (2H, m, arom-H); ^{13}C NMR (67.80 MHz) δ=116.90 (s, =C–S), 120.47 (s, arom-C), 121.86, 123.40, 123.74, (each d, arom-CH), 125.70 (s, arom-C), 127.02, 127.89 127.94, 128.15, 128.48 (each d, arom-CH), 128.72 (s, arom-C), 130.01 (d, arom-CH), 130.33 (s, arom-C), 133.21 (d, arom-CH), 135.02 (s, arom-C), 142.46 (s, =C–O), 176.12 (s, N–C=O), and 177.92 (s, C=N); IR (KBr) 1637 (s), 1612, 1599, 1576, 1523 (s), 1486, 1450, 1385, 1316, 1295 (s), 1242, 1145, 1124, 1073, 1064, 1040, 1025, 891, 863, 752, 719, 710, 687, and 669 cm^{-1}.

2-Benzoylimino-6,6-dimethyl-6,7-dihydro-1,3-benzoxathiol-4(5*H*)-one (3n): Colorless crystals; ^1H NMR (270.05 MHz) δ=1.20 (6H, s, $CH_3\times2$), 2.47 (2H, s, CH_2), 2.79 (2H, s, CH_2), 7.44—7.61 (3H, m, arom-H), and 8.27—8.32 (2H, m, arom-H); ^{13}C NMR (67.80 MHz) δ=28.25 (qm, $CH_3\times2$), 34.38 (sm, $Me_2\underline{C}$), 37.10 (tm, CH_2), 51.13 (tm, CH_2), 116.76 (sm, =C–S), 129.36 (dd, *m*-arom-CH), 129.84 (dt, *o*-arom-CH), 133.23 (dt, *p*-arom-CH), 134.53 (s, arom-C), 161.45 (st, $^3J_{CH}$=9.2 Hz, =C–

O), 175.53 (st, $^3J_{CH}$=4.4 Hz, N–C=O), 178.22 (s, C=N), and 190.22 (st, $^3J_{CH}$=6.4 Hz, C=O); IR (KBr) 2960, 1671 (s, C=O), 1640 (s, N–C=O), 1616, 1598, 1576 (s), 1529 (s), 1486, 1466, 1450, 1428, 1389, 1354, 1313 (s), 1291 (s), 1257, 1226, 1174, 1153, 1142, 1069, 1030 (s), 1015 (s), 939, 909, 863, 714 (s), and 681 (s) cm^{-1}; MS (EI, rel intensity %) 301 (21, M^+), 105 (100).

Ethyl 2-Benzoylimino-5-methyl-1,3-oxathiole-4-carboxylate (3o): Colorless crystals; ^1H NMR (500 MHz) δ=1.37 (3H, t, J=7.2 Hz, CH_3), 2.66 (3H, s, CH_3), 4.37 (2H, q, J=7.2 Hz, OCH_2), 7.45—7.57 (3H, m, arom-H), and 8.29—8.31 (2H, m, arom-H); ^{13}C NMR (125.65 MHz) δ=13.81 (q, $\underline{C}H_3$–C=), 14.17 (qt, $CH_2\underline{C}H_3$), 61.99 (tq, $O\underline{C}H_2CH_3$), 110.41 (sm, =C–S), 128.42 (dd, arom-CH), 129.92 (dt, arom-CH), 133.13 (dt, arom-CH), 134.90 (st, arom-C), 155.61 (sm, =C–O), 166.66 (sm, ester C=O), 176.13 (st, $^3J_{CH}$=4.4 Hz, N–C=O), 177.60 (s, C=N); IR (KBr) 2981, 1698 (C=O), 1642, 1619, 1598, 1574, 1512 (s), 1485, 1476, 1451, 1430, 1400, 1382, 1371, 1315, 1298 (s), 1272, 1233, 1179, 1162, 1125, 1116, 1084 (s), 1070, 1038, 970, 865, 762, 721, and 688 cm^{-1}; MS (EI, rel intensity %) 291 (28, M^+), 105 (100, $PhCO^+$).

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