Formation of 1,3-Oxathiole-2-thione and 1,2,4-Trithiolane Derivatives by the Catalytic Reaction of α-Diazocarbonyl Compounds with Carbon Disulfide[1)]

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The rhodium(II) acetate-catalyzed decomposition of α-diazocarbonyl compounds such as substituted α-diazoacetophenones, cyclic diazoketones, cyclic diazodiketones, and α-diazo-β-ketoesters in carbon disulfide gave 1,3-oxathiole-2-thione derivatives in good yields. Diazomalonates also gave alkyl 5-alkoxy-2-thioxo-1,3-oxathiole-4-carboxylates together with 3,5-bis[bis(alkoxycarbonyl)methylene]-1,2,4-trithiolanes. The formation of 1,3-oxathiole-2-thiones can be explained by the intermediacy of zwitterionic intermediate containing rhodium(II) acetate formed by the reaction of carbon disulfide with ketocarbenoids generated in the catalytic decomposition of the diazocarbonyl compounds.

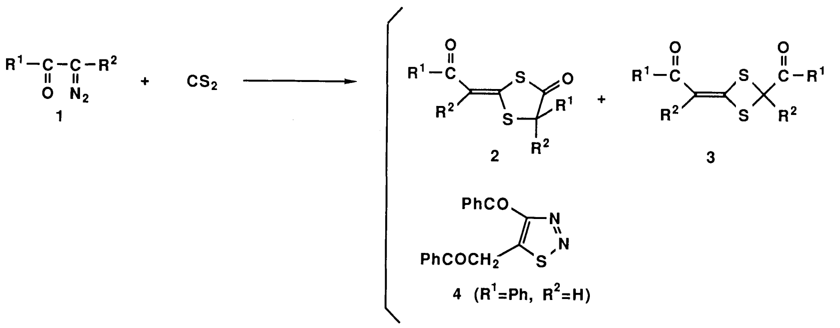
Because of its high reactivity, α-diazocarbonyl compounds have been used in many reactions in order to introduce ketocarbene moiety in organic synthesis.[2)] Reactions of α-diazocarbonyl compounds **1** with carbon disulfide in the absence of catalyst have been studied to yield 1,3-dithiolan-4-ones **2**, 2-methylene-1,3-dithietanes **3** and thiadiazoles **4** depending upon the substituents R^1 and R^2 as shown below.[3)] On the other hand, Huisgen reported that thermal and photochemical decomposition of 2,3,4,5-tetrachloro-6-diazo-2,4-cyclohexadien-1-one (**5**) in carbon disulfide yields the corresponding 1,3-benzoxathiole-2-thione (**6**).[4)]

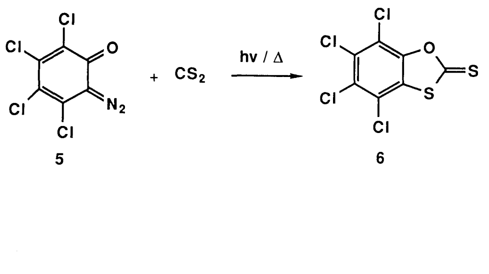
However, α-diazoacetophenone was reported to react very slowly with carbon disulfide to give a thiadiazole **4** in low yield.[3j,3k)] There is no precedent for the catalytic reaction of α-diazoacetophenone with carbon disulfide. Therefore, as a continuation of our studies on the catalytic reaction of α-diazocarbonyl compounds with hetero-unsaturated compounds,[5)] we studied the rhodium(II) acetate-catalyzed decomposition of various types of α-diazocarbonyl compounds in the presence of carbon disulfide, and found the generality of the method for the synthesis of 1,3-oxathiole-2-thione.

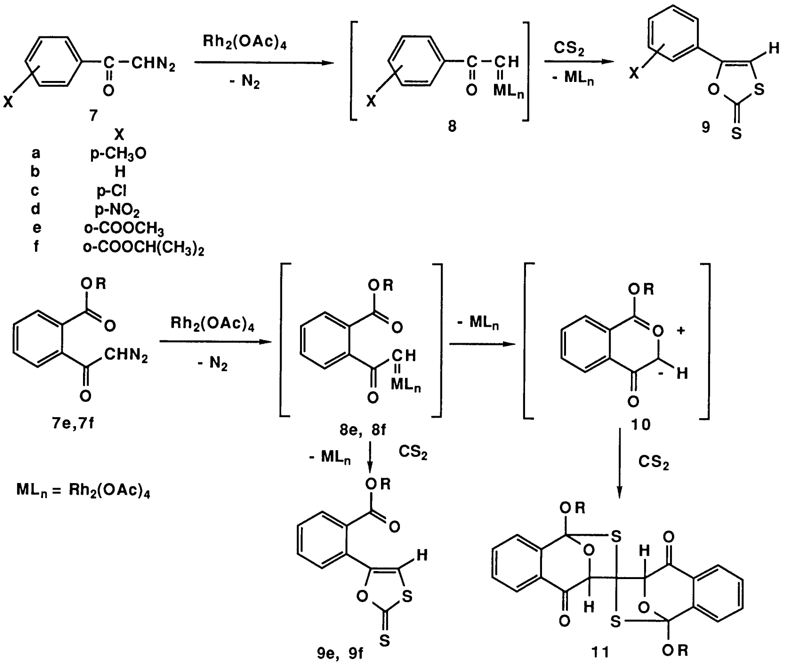
Results and Discussion

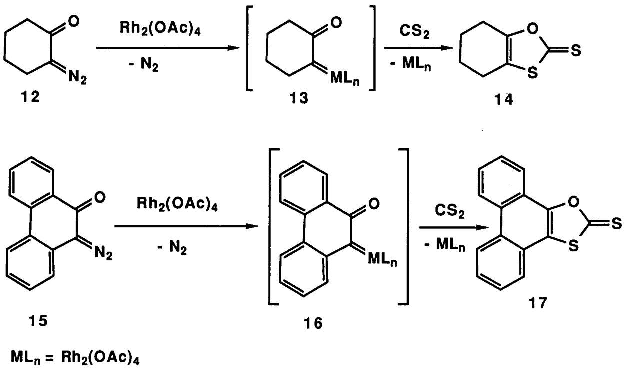
The rhodium(II) acetate-catalyzed reaction of α-diazoacetophenone (**7b**) was performed at 46 °C in carbon disulfide. The reaction mixture was separated by medium-pressure liquid chromatography on silica gel to give colorless crystals **9b**. Elemental analysis and mass spectrum measurement (M^+=194) indicate that **9b** is a 1 : 1 reaction product of the corresponding ketocarbene **8b** with carbon disulfide. IR spectrum of the product shows the presence of a thiocarbonyl group at 1197 cm^{-1} and the absence of a carbonyl group. These results and NMR data indicate that the product is 5-phenyl-1,3-oxathiole-2-thione (**9b**).[6)]

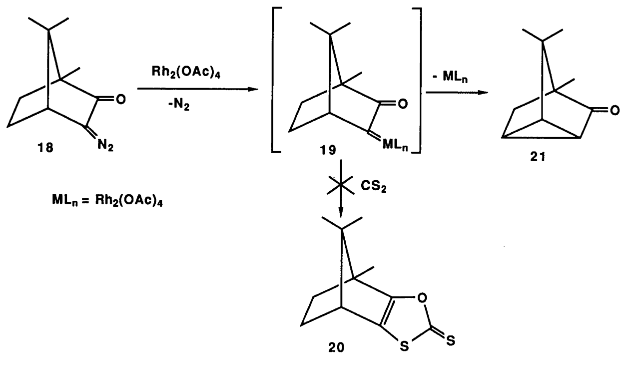
Other substituted α-diazoacetophenones **7** also gave the corresponding 1,3-oxathiole-2-thiones (**9**) in the same reaction conditions in moderate yields (Table 1). The decreased yields of 1,3-oxathiole-2-thiones (**9e** and **9f**) were observed by substitution of an alkoxycarbonyl group on ortho position to diazoacetyl group. The main pathway of these reactions was the formation of 1-alkoxy-2-benzopyrylium-4-olates (**10**) through an intramolecular carbene–carbonyl reaction,[5)] followed by 1,3-dipolar cycloaddition with carbon disulfide to











give two stereoisomers of 2:1-adducts **11**.7) Substitution on para position of diazoacetophenone by an electron-withdrawing group or an electron-releasing group did not affect dramatically the yields of **9**. The yields and spectroscopic data of **9** are listed in Table 1. There observed two types of fragmentation of **9** in its mass spectrum. One is the elimination of a carbonyl sulfide from 1,3-oxathiole-2-thione ring system to give (M^+—60) peak. The other is the elimination of HCSCS to give (M^+—89) peak.

This reaction was also applicable to cyclic diazoketones such as 2-diazocyclohexanone (**12**) and 10-diazo-9-phenanthrone (**15**) to give 1,3-oxathiole-2-thiones **14** and **17** in the yields of 71 and 66%, respectively. 1,3-Oxathiole-2-thione **14** shows a band for a thiocarbonyl group in its IR spectrum at 1191 cm^{-1} and **17** shows at 1196 cm^{-1}. ^{13}C NMR spectra of **14** and **17** show signals of C=S carbon at δ=201.05 and 203.78.

The decomposition of diazocamphor (**18**) in the presence of rhodium(II) acetate in carbon disulfide gave only intramolecular C–H insertion product, cyclocamphanone (**21**),8) without affording the expect-

Table 1. Yields and Spectroscopic Data of 5-Aryl-1,3-oxathiole-2-thione

	Yield	^{13}C NMR/δ			^{1}H NMR/δ	IR/cm^{-1}
	%	C2	C4	C5	H4	C=S
9a	71	203.09	100.42	155.86	6.56	1189
9b	67	202.78	102.76	155.67	6.74	1197
9c	72	202.36	103.41	154.46	6.75	1203, 1191
9d	51	201.23	107.27	152.98	6.99	1201
9e	6	202.57	106.34	154.73	6.67	1181
9f	7	202.66	105.99	155.28	6.61	1196

ed 1,3-oxathiole-2-thione **20**. The reaction in benzene at 46 °C gave the same tricycloketone **21**. These results indicate that the intramolecular C–H insertion of the ketocarbenoid **19** to give **21** is faster than the formation of 1,3-oxathiole-2-thione by the intermolecular reaction with carbon disulfide.

Cyclic diazodiketones such as 2-diazo-1,3-cyclohexanedione (**22a**) and diazodimedone (**22b**) gave the corresponding condensed 1,3-oxathiole-2-thiones **24a** and **24b** in 88 and 98% yields. Hadjiarapoglou reported the formation of the same compound **24b** in the $Cu(acac)_2$-catalyzed decomposition of phenyliodonium ylide of dimedone in carbon disulfide.[6c)] Similar reaction of 2,3-dihydro-3-oxo-2-(phenyliodonio)benzo[*b*]thiophen-2-ide 1,1-dioxide was also reported.[6e)] They explained this reaction by the intermediacy of ketocarbenoid generated by the catalytic decomposition of the iodonium ylide.

The reaction of an acyclic diazodiketone, 3-diazopentane-2,4-dione (**25a**), with carbon disulfide in the presence of rhodium(II) acetate yielded 4-acetyl-5-methyl-1,3-oxathiole-2-thione (**27a**) in 74% yield. The reactions of 2-diazo-3-ketoesters such as methyl (**25b**) and ethyl diazoacetoacetates (**25c**) gave only single products, 1,3-oxathiole-2-thiones **27b**, **27c**. Thione **27c** shows a band for an ester carbonyl group in its IR spectrum at $1724\,\mathrm{cm^{-1}}$ and a thiocarbonyl band at $1189\,\mathrm{cm^{-1}}$. These data indicate that the reaction-site of carbenoid **26** is not ester carbonyl group but acetyl group. Alonso and his co-workers have reported that the reaction of diazoacetoacetate with carbonyl compounds such as ketone and aldehyde in the presence of copper(II) chelate give similar type ring-closure products at acetyl group.[9)]

The reaction of diazomalonates **28** with carbon disulfide in the presence of rhodium(II) acetate gave the corresponding alkyl 5-alkoxy-2-thioxo-1,3-oxathiole-4-carboxylates (**29**) together with 3,5-bis[bis(alkoxycarbonyl)methylene]-1,2,4-trithiolanes (**30**). The structure of 1,2,4-trithiolane (**30b**) was confirmed by comparison of the spectroscopic data with those of authentic sample synthesized by the method of Wenzel.[10)] Yields of **29** and **30** decreased when substituent R becomes bulky in the order of methyl, ethyl, and isopropyl.

Thermolysis of alkyl 5-alkoxy-2-thioxo-1,3-oxathiole-4-carboxylate **29** under the conditions shown in Table 2 gave the corresponding 3,5-dimethylene-1,2,4-trithiolanes **30** in high yields. However, the rate of formation of trithiolane **30** by the thermolysis of 1,3-oxathiole-2-thione **29** is slower than that of the catalytic decomposition of diazomalonates in carbon disulfide. These results indicate that trithiolanes **30** obtained in the catalytic decomposition of diazomalonates are not the secondary product derived from 1,3-oxathiole-2-thiones **29**.

The spectroscopic data of 1,3-oxathiole-2-thiones obtained in the reaction of diazodicarbonyl compounds are summarized in Table 3. The 1,3-oxathiole-2-thiones show the strong stretching band of thiocarbonyl groups at $1172—1202\,\mathrm{cm^{-1}}$. In ^{13}C NMR spectra, a signal of thiocarbonyl carbon is observed at δ=199—201. When the thione has an alkoxyl group at C-5, the signal of thiocarbonyl carbon is observed at slightly higher field (δ=194—195).

The possible mechanism for the formation of 1,3-oxathiole-2-thiones **35** in the catalytic decomposition

Table 2. Yields of **30** Obtained in the Thermolysis of **29**

Compound	Reaction conditions	Product	Yield/%
29a	46 °C, CS_2, 40 d	**30a**	69
29b	46 °C, CS_2, 74 d	**30b**	75
29b	80 °C, C_6H_6, 12 d	**30b**	88

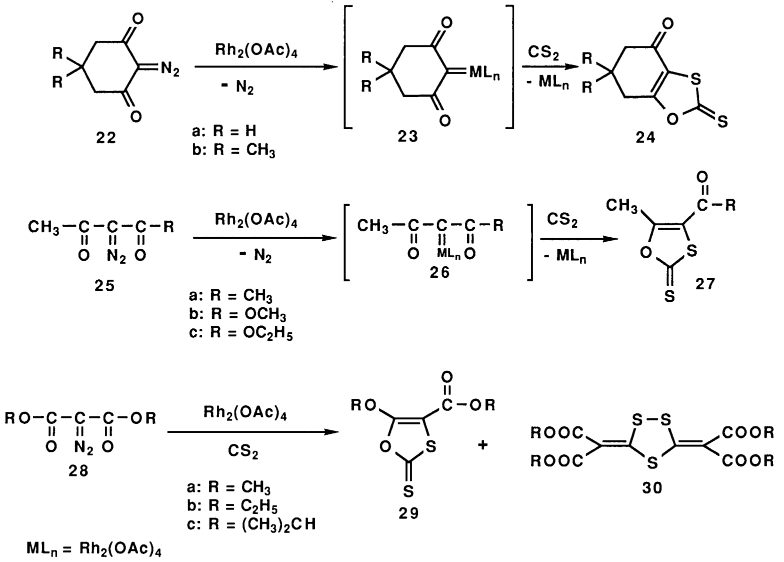
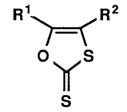
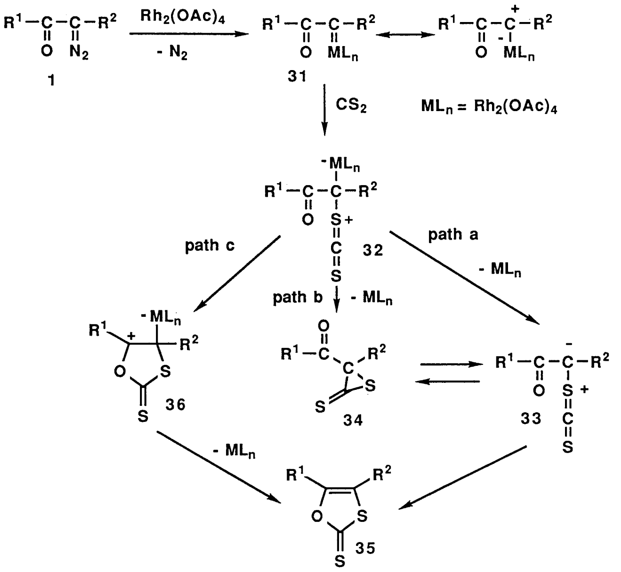


Table 3. Yields and Spectroscopic Data of 1,3-Oxathiole-2-thiones Obtained in the Reaction of Diazodicarbonyl Compounds

			IR	¹³C NMR	Yield
	R^1	R^2	C=S/cm^{-1}	C=S/δ	%
24a	$-(CH_2)_3CO-$		1176	201.09	89
24b	$-CH_2C(CH_3)_2CH_2CO-$		1202	201.41	98
27a	CH_3	$COCH_3$	1185	199.87	74
27b	CH_3	$COOCH_3$	1189	200.68	76
27c	CH_3	$COOC_2H_5$	1189	200.76	79
29a	CH_3O	$COOCH_3$	1172	194.18	49
29b	C_2H_5O	$COOC_2H_5$	1191	194.76	41
29c	$(CH_3)_2CHO$	$COOCH(CH_3)_2$	1177	195.33	31



Scheme 1.

of α-diazocarbonyl compounds in carbon disulfide is shown in Scheme 1. The reaction is initiated by the attack of ketocarbenoid **31**[2,11)] on the sulfur atom of carbon disulfide to generate zwitterion species containing rhodium(II) acetate **32**. There are three possibilities in the next step of the reaction. The first one is the elimination of rhodium(II) acetate to give thiocarbonyl ylide **33** (path a), followed by the cyclization at carbonyl oxygen and carbon atom originated from carbon disulfide to give **35**. The second possibility is that the elimination of rhodium(II) acetate to give thiirane derivative **34** in the same manner proposed for cyclopropanation of ketocarbenoid[2)] (path b), followed by the ring-opening at C–C bond to afford ylide **33**, which is in equilibrium with **34**. The third possibility is the cyclization of **32** to give a zwitterion intermediate **36** (path c), followed by elimination of rhodium(II) acetate.

The reaction of α-diazocarbonyl compounds with carbon disulfide in the presence of rhodium(II) acetate can be the general method for the preparation of 1,3-oxathiole-2-thiones different from the methods utilizing iodonium ylide[6c,6e)] and the reaction between sodium 1-imidazolecarbodithioate and substituted phenacyl bromides[6d)] because the starting materials are readily available. Further study for the determination of mechanism of the formation of 1,3-oxathiole-2-thione is now in progress.

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 (399.65 MHz and 500 MHz) and ¹³C NMR (100.40 MHz and 125.65 MHz) spectra were recorded on a JEOL GSX-400 and a GX-500 in a $CDCl_3$ solution, using TMS as an internal standard. Mass spectra were determined with a JEOL JMS-DX303 mass spectrometer. Electronic spectra were measured with a Hitachi U-3400 spectrophotometer.

Meterials. *p*-Substituted α-diazoacetophenones were prepared by the reaction of the corresponding benzoyl chlorides with an excess of diazomethane in the presence of triethylamine according to Newman's method.[12)] Methyl and isopropyl *o*-diazoacetylbenzoates were prepared by the procedure described in the previous paper.[5a)] Diazodicarbonyl compounds were prepared by the diazo group transfer reaction reported by Regitz.[13)] 10-Diazo-9-phenanthrone[14)] and 2-diazocyclohexanone[15)] were prepared according to the reported methods. Benzene was purified by distillation after reflux on CaH_2 and stored over molecular sieves 4A. Carbon disulfide was purified just before use by distillation after reflux on diphosphorus pentoxide.

General Procedure for the Rhodium(II) Acetate-Catalyzed Decomposition of α-Diazocarbonyl Compounds. A solution of diazocarbonyl compound (3.00 mmol) in dry benzene (50 ml) was added over a period of ca. 4 h to a reflux suspension of rhodium(II) acetate (4.3 mg, 9.7×10^{-3} mmol) in carbon disulfide (100 ml) under nitrogen atmosphere. The solution was heated at 46 °C until the diazo compound was no more 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 benzene–hexane or ethyl acetate–hexane).

5-(*p*-Methoxyphenyl)-1,3-oxathiole-2-thione (9a): 71% yield from **7a**; colorless crystals; mp 88.8—90.4 (lit,[6d] 85—88) °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) $\delta=3.85$ (3H, s, OCH_3), 6.56 (1H, s, CH), 6.92—6.96 (2H, m, arom-H), and 7.56—7.60 (2H, m, arom-H); ^{1}H-Selective decoupling spectrum at $\delta=3.85$ showed following assignments, ^{13}C NMR ($CDCl_3$) $\delta=55.46$ (q, OCH_3), 100.42 (d, =CH), 114.51 (d, arom-CH), 119.80 (s, arom-C), 126.75 (d, arom-CH), 155.86 (s, =C–O), 161.10 (s, CH_3O-arom-$\underline{C}$), and 203.09 (d, $^{3}J_{CH}=7.3$ Hz, C=S); IR (KBr) 3079 (C–H), 1611, 1596, 1506, 1450, 1436, 1421, 1322, 1307, 1262, 1189 (C=S), 1171, 1144, 1112, 1052, 1032, 1004, 825, 743, 713, and 666 cm^{-1}; MS (EI) *m*/*z* (rel intensity %, assignment) 226 (12, $M^{+}+2$), 225 (16, $M^{+}+1$), 224 (100, M^{+}), 164 (49, $M^{+}-COS$), 149 (81), 135 (30), 121 (18), and 77 (18). Found: C, 53.65; H, 3.65%.

5-Phenyl-1,3-oxathiole-2-thione (9b): 67% yield from **7b**; colorless crystals; mp 94.8—96.0 (lit,[6d] 91—93) °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) $\delta=6.74$ (1H, s, =CH) and 7.35—7.67 (5H, m, arom-H); ^{13}C NMR ($CDCl_3$) $\delta=102.76$ (d, =CH), 125.05 (d, arom-CH), 126.95 (s, arom-C), 129.05 (d, arom-CH), 130.16 (d, arom-CH), 155.67 (s, =C–O), and 202.78 (d, $^{3}J_{CH}=5.8$ Hz); IR (KBr) 3108 (C–H), 1567, 1489, 1445, 1197 (C=S), 1168, 1048, 1032, 1009, 735, 686, and 680 cm^{-1}; MS (EI) *m*/*z* (rel intensity %, assignment) 196 (13, $M^{+}+2$), 195 (15, $M^{+}+1$), 194 (100, M^{+}) 134 (71, $M^{+}-COS$), 105 (35), 90 (15), and 77 (27); UV (MeOH) λ_{max} (ε) 332 (1.56×10^{4}) and 223 (1.63×10^{4}) nm. Found: C, 55.82; H, 3.22%.

5-(*p*-Chlorophenyl)-1,3-oxathiole-2-thione (9c): 72% yield from **7c**; yellow crystals; mp 147.8—148.5 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) $\delta=6.75$ (1H, s, CH), 7.40—7.43 (2H, m, arom-H), and 7.56—7.60 (2H, m, arom-H); Long-range C–H cosy measurement showed following assignments, ^{13}C NMR ($CDCl_3$) $\delta=103.41$ (d, =CH–S), 125.45 (s, arom-C), 126.32 (d, *o*- of arom-CH), 129.43 (d, *m*- of arom-CH), 136.25 (s, arom-C), 154.46 (s, =C–O), and 202.36 (d, $^{3}J_{CH}=8.3$ Hz, C=S); IR (KBr) 3087 (C–H), 1603, 1487, 1406, 1283, 1211, 1203, 1191, 1184, 1164, 1093, 1052, 1020, 1009, 825, 755, and 663 cm^{-1}; MS (EI) *m*/*z* (rel intensity %, assignment) 230 (47, $M^{+}+2$), 229 (14, $M^{+}+1$), 228 (100, M^{+}), 168 (68, $M^{+}-COS$), 139 (40), 133 (22), 111 (18), 89 (15), and 75 (10). Found: C, 47.25; H, 2.41%. Calcd for $C_9H_5OS_2Cl$: C, 47.26; H, 2.20%.

5-(*p*-Nitrophenyl)-1,3-oxathiole-2-thione (9d): 51% yield from **7d**; yellow crystals; mp 205.1—207.5 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) $\delta=6.99$ (1H, s, CH), 7.81—7.84 (2H, m, arom-H), and 8.29—8.32 (2H, m, arom-H); ^{13}C NMR ($CDCl_3$) $\delta=107.27$ (d, =CH–S), 124.58 (d, arom-CH), 125.84 (d, arom-CH), 132.37 (s, arom-C), 148.54 (s, arom-C), 152.98 (s, =C–O), and 201.23 (d, $^{3}J_{CH}=7.2$ Hz, C=S); IR (KBr) 3115 (C–H), 1598, 1578, 1508 (N=O), 1490, 1376, 1351 (N=O), 1324, 1201 (C=S), 1184, 1157, 1111, 1054, 1018, 1010, 888, 854, 823, 763, 742, 685, and 662 cm^{-1}; MS (EI) *m*/*z* (rel intensity %, assignment) 241 (12, $M^{+}+2$), 240 (15, $M^{+}+1$), 239 (100, M^{+}), 179 (14, $M^{+}-COS$), 150 (55), 133 (16), 104 (21), 89 (32), and 76 (12). Found: C, 45.29; H, 2.32; N, 5.96%. Calcd for $C_9H_5NO_3S_2Cl$: C, 45.18; H, 2.11; N, 5.85%.

Catalytic Decomposition of Alkyl *o*-Diazoacetylbenzoate (7e and 7f) in Carbon Disulfide. A solution of alkyl *o*-diazoacetylbenzoate (3.00 mmol) in dry benzene (10 ml) was added over a period of ca. 1 h to a reflux suspension of rhodium(II) acetate (1.6 mg, 3.6×10^{-3} mmol) in carbon disulfide (20 ml) under nitrogen atmosphere. The solution was heated at 46 °C for 1.4 h. The reaction mixture was concentrated under reduced pressure. The residue was separated by medium-pressure liquid chromatography (silica gel, eluted with benzene–hexane).

Major 2:1-Adduct 11e: 65% yield from **7e**; colorless crystals; mp 236.1—237.0 °C (from benzene–hexane). Found: C, 58.93; H, 3.77%. Calcd for $C_{21}H_{16}O_6S_2$: C, 58.87; H, 3.76%.

Minor 2:1-Adduct 11e′: 10% yield from **7e**; colorless crystals; mp 200—202 °C (from benzene–hexane).

5-(*o*-Methoxycarbonylphenyl)-1,3-oxathiole-2-thione (9e): 6% yield from **7e**; pale yellow crystals; mp 120.1—121.0 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) $\delta=3.90$ (3H, s, OCH_3), 6.67 (1H, s, CH), 7.52—7.62 (3H, m, arom-H), and 7.90—7.93 (1H, m, arom-H); ^{13}C NMR ($CDCl_3$) $\delta=52.73$ (s, OCH_3), 106.34 (d, $^{1}J_{CH}=195.6$ Hz, =CH–S), 127.20 (s, arom-C), 129.94 (d, arom-CH), 130.48 (d, arom-CH), 130.50 (d, arom-CH), 130.74 (s, arom-C), 131.90 (d, arom-CH), 154.73 (s, =C–O), 166.90 (s, ester C=O), and 202.57 (d, $^{3}J_{CH}=7.0$ Hz, C=S); IR (KBr) 3092 (C–H), 1719 (ester C=O), 1598, 1450, 1432, 1299, 1288, 1250, 1181 (C=S), 1125, 1102, 1050, 1013, 956, 793, 763, 719, 687, and 666 cm^{-1}; MS (EI) *m*/*z* (rel intensity %, assignment) 254 (13, $M^{+}+2$), 253 (17, $M^{+}+1$), 252 (100, M^{+}), 221 (10), 192 (10, $M^{+}-COS$), 176 (32), 163 (50), 133 (32), 89 (10), and 77 (12). Found: C, 52.43; H, 3.20%. Calcd for $C_{11}H_8O_3S_2$: C, 52.36; H, 3.20%.

Major 2:1-Adduct 11f: 66% yield from **7f**; colorless crystals; mp 211.0—211.8 °C (from acetone). Found: C, 61.87; H, 5.23%. Calcd for $C_{25}H_{24}O_6S_2$: C, 61.96; H, 4.99%.

Minor 2:1-Adduct 11f′: 9% yield from **7f**; colorless crystals; mp 210.8—211.2 °C (from benzene–hexane). Found: C, 62.16; H, 5.04%. Calcd for $C_{25}H_{24}O_6S_2$: C, 61.96; H, 4.99%.

5-(*o*-Isopropoxycarbonylphenyl)-1,3-oxathiole-2-thione (9f): 9% yield from **7f**; yellow oil; ^{1}H NMR ($CDCl_3$) $\delta=1.34$ (6H, d, $J=6.3$ Hz, $CH_3\times2$), 5.21 (1H, sept, $J=6.3$ Hz, CH), 6.61 (1H, s, =CH), 7.50—7.60 (3H, m, arom-H), and 7.93—7.97 (1H, m, arom-H); ^{1}H-Selective decoupling spectra at $\delta=6.61$ and 5.21 showed following assignments, ^{13}C NMR ($CDCl_3$) $\delta=21.83$ (q, $CH_3\times2$), 69.68 (d, OCH), 105.99 (d, =CH–S), 127.18 (s, arom-C), 130.35 (d, arom-CH), 130.63 (d, arom-CH), 130.73 (d, arom-CH), 131.72 (s, arom-C), 131.80 (d, arom-CH), 155.28 (s, =C–O), 165.96 (s, ester C=O), and 202.66 (d, $^{3}J_{CH}=5.9$ Hz, C=S); IR(KBr) 3107 (C–H), 1715 (ester C=O), 1596, 1464, 1447, 1385, 1373, 1351, 1280, 1242, 1196, 1177, 1145, 1107, 1095, 1040, 1007, 916, 855, 753, 709, 685, and 660 cm^{-1}.

4,5,6,7-Tetrahydro-1,3-benzoxathiole-2-thione (14): 71% yield from **12**; colorless crystals; mp 55.6—56.8 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) $\delta=1.81$—1.91 (4H, m, $CH_2\times2$), 2.40—2.44 (2H, m, CH_2), and 2.53—2.57 (2H, m, CH_2); ^{13}C NMR ($CDCl_3$) $\delta=21.82$ (t, CH_2), 22.45 (t, $CH_2\times2$), 23.56 (t, CH_2), 117.59 (t, S–C=), 152.02 (s, O–C=), and 203.78 (s, C=S); IR (KBr) 2947, 2900, 1653, 1432, 1344, 1221, 1191 (C=S), 1172, 1154, 1131, 1081, 1066, 1051, 1000, 948, 873, 818, 690, and 658 cm^{-1}; MS (EI) *m*/*z* (rel intensity %, assignment) 174 (11, $M^{+}+2$), 173 (11, $M^{+}+1$), 172 (100, M^{+}), 144 (15, M^{+}-CO), 116 (15), 111 (28), 84 (13), 79 (10), and 71 (24). Found: C, 48.79; H, 4.64%. Calcd for $C_7H_8OS_2$: C, 48.80; H, 4.68%.

Phenanthro[9,10-*d*]-1,3-oxathiole-2-thione (17): 66% yield from **15** (after 11 d); pale yellow crystals; mp 193.9—194.8 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ=7.38—7.40 (1H, m, arom-H), 7.57—7.70 (4H, m, arom-H), 8.09—8.12 (1H, m, arom-H), and 8.52—8.55 (2H, m, arom-H); ^{13}C NMR ($CDCl_3$) δ=119.37 (s, S-C=), 120.02 (s, arom-C), 121.87 (d, arom-CH), 123.14 (d, arom-CH), 123.59 (d, arom-CH), 124.38 (s, arom-C), 124.59 (d, arom-CH), 127.12 (d, arom-CH), 127.90 (d, arom-CH), 127.96 (d, arom-CH), 128.03 (d, arom-CH), 128.50 (s, arom-C), 129.93 (s, arom-C), 149.08 (s, O-C=), and 201.05 (s, C=S); IR(KBr) 1611, 1595, 1501, 1449, 1241, 1212, 1196 (C=S), 1160, 1151, 1069, 1031, 746, and 718 cm^{-1}; MS (EI) m/z (rel intensity %, assignment) 269 (21, M^++1), 268 (100, M^+), 240 (12, M^+−CO), 208 (39, M^+−COS), 164 (23), and 163 (25). Found: C, 67.07; H, 3.28%. Calcd for $C_{15}H_8OS_2$: C, 67.14; H, 3.00%.

Cyclocamphanone (21):[8] 90% yield from **18**; ^{1}H NMR ($CDCl_3$) δ=0.80 (3H, s, CH_3), 0.90 (3H, s, CH_3), 0.96 (3H, s, CH_3), 1.43 (1H, t, J=5.3 Hz, CH), 1.71 (1H, d, J=10.8 Hz, CH), and 1.92—2.02 (3H, m, CH×3); C-H cosy spectrum showed following assignments, ^{13}C NMR ($CDCl_3$) δ=5.52 (q, 0.80-CH_3), 20.20 (q, 0.96-CH_3), 20.54 (d, ca. 2-CH), 21.00 (d, 1.43-CH), 21.09 (q, 0.90-CH_3), 33.58 (d, ca. 1.9-CH), 35.85 (t, CH_2, 1.71 CH+ca. 1.9 C-H), 43.33 (s), 48.11 (s), and 215.63 (s, C=O).

The catalytic decomposition of **18** in dry benzene gave **21** in 87% yield.

4-Oxo-4,5,6,7-tetrahydro-1,3-benzoxathiole-2-thione (24a): 89% yield from **22a**; colorless oil ^{1}H NMR ($CDCl_3$) δ=2.25 (2H, m, CH_2), 2.60 (2H, m, CH_2), and 2.91 (2H, t, J=6.3 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ=21.05 (t, CH_2), 24.13 (t, CH_2), 36.96 (t, CH_2), 120.69 (s, S-C=), 168.56 (s, O-C=), 189.08 (s, C=O), and 201.09 (s, C=S); IR (KBr) 2954, 2884, 1677 (C=O), 1618, 1451, 1422, 1352, 1326, 1302, 1209, 1176 (C=S), 1140, 1069, 1051, 1040, 958, 829, and 654 cm^{-1}; MS (EI) m/z (rel intensity %, assignment) 188 (12, M^++2), 187 (12, M^++1), 186 (100, M^+), 97 (20), 71 (10), and 55 (24).

6,6-Dimethyl-4-oxo-4,5,6,7-tetrahydro-1,3-benzoxathiole-2-thione (24b):[6c] 98% yield from **22b**; colorless crystals; mp 100.6—101.1 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ=1.21 (6H, s, CH_3×2), 2.47 (2H, s, CH_2), and 2.76 (2H, s, CH_2); ^{13}C NMR ($CDCl_3$) δ=28.32 (q, CH_3×2), 34.47 (s, $(CH_3)_2\underline{C}$), 37.80 (t, CH_2), 51.17 (t, CH_2), 119.42 (s, S-C=), 167.36 (t, $^2J_{CH}$=6.6 Hz, O-C=), 188.72 (t, $^2J_{CH}$=8.8 Hz, C=O), and 201.41 (s, C=S); IR (KBr) 2964, 2934, 2879, 1678 (C=O), 1619, 1468, 1406, 1372, 1349, 1314, 1277, 1218, 1202 (C=S), 1156, 1066, 980, and 933 cm^{-1}; MS (EI) m/z (rel intensity %, assignment) 216 (12, M^++2), 215 (14, M^++1), 214 (100, M^+), 139 (11), 111 (10), 83 (43), 70 (25), and 55 (14); UV (CH_3CN) λ_{max} (ε) 330 (2.03×10^4) nm. Found: C, 50.51; H, 4.63%.

4-Acetyl-5-methyl-1,3-oxathiole-2-thione (27b): 74% yield from **25a**; yellow oil; ^{1}H NMR ($CDCl_3$) δ=2.40 (3H, s, CH_3) and 2.61 (3H, s, CH_3CO); ^{1}H-Selective decoupling spectra at δ=2.40 and 2.61 showed following assignments, ^{13}C NMR ($CDCl_3$) δ=15.11 (q, CH_3), 30.08 (q, CH_3CO), 122.09 (s, S-C=), 159.99 (s, O-C=), 187.59 (s, C=O), and 199.87 (s, C=S); IR (KBr) 2925, 1658 (C=O), 1607, 1422, 1382, 1362, 1305, 1185 (C=S), 1105, 1041, 1003, 956, and 676 cm^{-1}; MS (EI) m/z (rel intensity %, assignment) 174 (100, M^+), 114 (18, M^+−COS), 88 (12), 72 (10), 45 (16), and 43 (58, CH_3CO^+). Found: C, 41.06; H, 3.43%. Calcd for $C_6H_6OS_2$; C, 41.36; H, 3.47%.

Methyl 5-Methyl-2-thioxo-1,3-oxathiole-4-carboxylate (27b): 76% yield from **25b**; yellow oil; ^{1}H NMR ($CDCl_3$) δ=2.60 (3H, s, CH_3), and 3.85 (3H, s, CH_3O); ^{1}H-Selective decoupling spectrum at δ=2.60 showed following assignments, ^{13}C NMR ($CDCl_3$) δ=14.36 (q, CH_3), 52.86 (q, CH_3O), 112.18 (q, $^3J_{CH}$=3.3 Hz, S-C=), 159.54 (q, ester C=O), 162.08 (q, $^2J_{CH}$=7.3 Hz, O-C=), and 200.68 (s, C=S); IR (KBr) 2951, 1723 (ester C=O), 1638, 1432, 1376, 1302, 1238, 1189 (C=S), 1105, 1056, 993, 957, 793, 757, and 669 cm^{-1}. Found: C, 37.62; H, 3.12%. Calcd for $C_6H_6OS_2$: C, 37.88; H, 3.18%.

Ethyl 5-Methyl-2-thioxo-1,3-oxathiole-4-carboxylate (27c): 79% yield from **25c**; yellow oil; ^{1}H NMR ($CDCl_3$) δ=1.34 (3H, t, J=7.1 Hz, CH_3), 2.60 (3H, s, CH_3), and 4.31 (2H, q, J=7.1 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ=14.09 (q, $\underline{C}H_3CH_2$), 14.28 (q, CH_3), 62.19 (t, CH_2O), 112.55 (s, S-C=), 159.05 (s, ester C=O), 161.75 (s, O-C=), and 200.76 (s, C=S); IR (KBr) 2981, 1724 (ester C=O), 1628, 1462, 1427, 1371, 1319, 1287, 1240, 1189 (C=S), 1099, 1056, 1012, 990, 944, 854, 821, 757, and 670 cm^{-1}; MS (EI) m/z (rel intensity %, assignment) 206 (12, M^++2), 205 (12, M^++1), 204 (100, M^+), 163 (13), 159 (13, M^+−OC_2H_5), 116 (21), 88 (25), and 43 (47, CH_3CO^+). Found: C, 40.92; H, 3.93%. Calcd for $C_7H_8O_3S_2$; C, 41.16; H, 3.95%.

Methyl 5-Methoxy-2-thioxo-1,3-oxathiole-4-carboxylate (29a): 49% yield from **28a**; yellow crystals; mp 69.0—71.5 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ=3.80 (3H, s, CH_3) and 4.21 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ=52.41 (q, OCH_3), 60.25 (q, OCH_3), 87.31 (s, S-C=O), 158.94 (s), 159.21 (s), and 194.18 (s, C=S); IR (KBr) 2957, 2945, 1719 (C=O), 1637, 1455, 1436, 1358, 1253, 1172, (C=S), 1104, 1090, 1004, 952, 895, 793, 755, and 713 cm^{-1}; MS (EI) m/z (rel intensity %, assignment) 206 (68, M^+), 180 (76), 175 (25), 149 (26), 147 (19, M^+−$COOCH_3$), 142 (26), 133 (97), 117 (12), 116 (19), 115 (47), 101 (50), 88 (17), 85 (19), 75 (65), 74 (40), 69 (43), 59 (100), 58 (37), and 43 (63). Found: C, 34.91; H, 2.98%. Calcd for $C_6H_6O_4S_2$: C, 34.94; H, 2.93%.

3,5-Bis[bis(methoxycarbonyl)methylene]-1,2,4-trithiolane (30a): 50% yield from **28a**; colorless crystals; mp 214.5—215.2 °C (from chloroform); ^{1}H NMR ($CDCl_3$) δ=3.73 (6H, s, OCH_3×2) and 3.88 (6H, s, CH_3×2); ^{13}C NMR ($CDCl_3$) δ=52.85 (q, OCH_3), 53.05 (q, OCH_3), 110.88 (s), 164.68 (s, ester C=O), 166.33 (s, ester C=O), and 174.19 (s); IR (KBr) 2690, 1681, 1650, 1440, 1422, 1412, 1296, 1271, 1126, 1005, 792, and 755 cm^{-1}; MS (EI) m/z (rel intensity %, assignment) 382 (19, M^++2), 381 (19, M^++1), 380 (100, M^+), 349 (18, M^+−CH_3O), 321 (14, M^+−$COOCH_3$), 305 (17), 293 (11), 206 (14), 189 (21), 143 (53), 99 (13), 75 (14), and 59 (44). Found: C, 37.56; H, 3.09%. Calcd for $C_{12}H_{12}O_8S_3$; C, 37.89; H, 3.18%.

Ethyl 5-Ethoxy-2-thioxo-1,3-oxathiole-4-carboxylate (29b): 41% yield from **28b**; yellow crystals; mp 56.5—57.0 °C (from benzene–hexane); ^{1}H NMR ($CDCl_3$) δ=1.31 (3H, t, J=7.1 Hz, CH_3), 1.50 (3H, t, J=7.1 Hz, CH_3), 4.26 (2H, q, J=7.1 Hz, CH_2), and 4.56 (2H, q, J=7.1 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ=14.23 (q, CH_3), 14.90 (q, CH_3), 61.58 (t, CH_2), 70.70 (t, CH_2), 88.39 (s), 158.62 (s), 158.97 (s), and 194.76 (s, C=S); IR(KBr) 2979, 2936, 2904, 1726 (C=O), 1686, 1626, 1448, 1417, 1383, 1346, 1252, 1191 (C=S), 1127, 1098, 1082, 1010, 997, 859, 840, 816, and 761 cm^{-1}; MS (EI) m/z (rel intensity %, assignment) 236 (19, M^++2), 235 (21, M^++1), 234 (94, M^+), 202 (76), 189 (21), 157 (73), 156 (58), 146 (83), 130 (28), 118 (98), 112 (33), 102 (99), 100 (84), 90 (100), 86 (56), 85 (94), 84 (68), 69 (48), 64 (80), 58 (39), and 45 (89); UV (CH_3CN) λ_{max} (ε) 336 (1.62×10^4), 281 (4.87×10^3), and 266 (4.38×10^3) nm. Found: C, 41.08; H, 4.22%. Calcd for $C_8H_{10}O_4S_2$: C, 41.01; H, 4.30%.

3,5-Bis[bis(ethoxycarbonyl)methylene]-1,2,4-trithiolane (30b):

38% yield from **28b**; colorless crystals; mp 144.0—145.9 (lit,[10] 139) °C (from benzene-hexane); ^{1}H NMR ($CDCl_3$) δ=1.34 (6H, t, J=7.1 Hz, $CH_3\times2$), 1.36 (6H, t, J=7.1 Hz, $CH_3\times2$), 4.31 (4H, q, J=7.1 Hz, $CH_2\times2$), and 4.34 (4H, q, J=7.1 Hz, $CH_2\times2$); ^{13}C NMR ($CDCl_3$) δ=14.11 (q, CH_3), 14.16 (q, CH_3), 61.93 (t, CH_2), 62.14 (t, CH_2), 111.70 (s), 164.20 (s, ester C=O), 165.85 (s, ester C=O), and 174.38 (s); IR (KBr) 2978, 2936, 1722, 1672, 1636, 1409, 1384, 1368, 1283, 1141, 1107, 1029, 929, 865, and 793 cm^{-1}; MS (EI) m/z (rel intensity %, assignment) 438 (17, M^++2), 437 (21, M^++1), 436 (100, M^+), 391 (23), 364 (19), 335 (11), 320 (14), 318 (19), 292 (16), 274 (14), 248 (16), 246 (32), 234 (19), 190 (13), 157 (40), 146 (11), 129 (11), 102 (12), and 85 (70). Found: C, 44.06; H, 4.62%.

Isopropyl 5-Isopropoxy-2-thioxo-1,3-oxathiole-4-carboxylate (29c): 31% yield from **28c**; pale yellow crystals; mp 56.9—62.2 °C (from ethyl acetate-hexane); ^{1}H NMR ($CDCl_3$) δ=1.29 (6H, d, J=6.2 Hz, $CH_3\times2$), 1.47 (6H, d, J=6.2 Hz, $CH_3\times2$), 5.06 (1H, sept, J=6.2 Hz, CH), and 5.10 (1H, sept, J=6.2 Hz, CH); ^{13}C NMR ($CDCl_3$) δ=21.83 (q, $CH_3\times2$), 22.35 (q, $CH_3\times2$), 69.49 (d, OCH), 80.32 (d, OCH), 90.55 (s, S–C=), 158.24 (s), 158.59 (s), and 195.33 (s, C=S); IR(KBr) 2981, 2935, 2875, 1723 (C=O), 1696, 1630, 1466, 1452, 1384, 1322, 1240, 1177 (C=S), 1145, 1090, 989, 896, 839, 796, 759, 721, and 665 cm^{-1}; MS (EI) m/z (rel intensity %, assignment) 262 (11, M^+), 220 (79, $M^+-(CH_3)_2CH$), 178 (75, $M^+-(CH_3)_2CH\times2$), 161 (21), 118 (100), 100 (28), 90 (22), 43 (76), and 41 (22). Found: C, 45.79; H, 5.28%. Calcd for $C_{10}H_{14}O_4S_2$: C, 45.78; H, 5.38%.

3,5-Bis[bis(isopropoxycarbonyl)methylene]-1,2,4-trithiolane (30c): 18% yield from **28c**; colorless crystals; mp> 300 °C (from ethyl acetate-hexane); ^{1}H NMR ($CDCl_3$) δ=1.32 (12H, d, J=6.2 Hz, $CH_3\times4$), 1.33 (12H, d, J=6.2 Hz, $CH_3\times4$), 5.14 (2H, sept, J=6.2 Hz, $CH\times2$), and 5.19 (2H, sept, J=6.2 Hz, $CH\times2$); ^{13}C NMR ($CDCl_3$) δ=21.82 (q, $CH_3\times4$), 21.86 (q, $CH_3\times4$), 69.66 (d, $OCH\times2$), 69.96 (d, $OCH\times2$), 112.65 (s), 163.79 (s, C=O), 165.31 (s, C=O), and 170.66 (s); IR (KBr) 2981, 2934, 2875, 1714 (C=O), 1693, 1658, 1460, 1387, 1374, 1354, 1336, 1270, 1250, 1181, 1138, 1098, 972, 953, 905, 841, 830, 786, 756, and 673 cm^{-1}; MS (EI) m/z (rel intensity %, assignment) 494 (17, M^++2), 493 (25, M^++1), 492 (85, M^+), 433 (30,), 406 (20), 364 (33), 346 (12), 322 (21), 320 (13), 304 (19), 288 (11), 280 (26), 278 (23), 262 (22), 260 (12), 246 (12), 236 (20), 218 (17), 178 (22), 161 (19), 147 (19), 129 (31), 102 (16), 85 (11), and 43 (100). Found: C, 48.82; H, 5.62%. Calcd for $C_{20}H_{28}O_8S_3$: C, 48.76; H, 5.73%.

Thermolysis of 29a and 29b. Compounds **29a** and **29b** were subjected to the reaction conditions shown in Table 2 and worked-up similarly, giving **30a** and **30b**, respectively, in the yields shown in the Table.

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