Tetrahedron Vol. 49, No. 36, pp. 8241-8256, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Reductive Addition to Electron-deficient Olefins with Trivalent Iodine Compounds

Hideo Togo,* Masahiko Aoki, and Masataka Yokoyama*

Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho 1-33, Inageku, Chiba 263, Japan

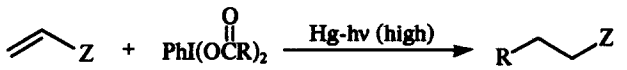
(*Received in USA* 29 *March* 1993; *accepted* 28 *April* 1993)

Abstract: (Diacyloxyiodo)arene was treated with electron-deficient olefins in the presence of hydrogen donor such as 1,4-cyclohexadiene to give the reductive addition products via alkyl radical through the radical decarboxylative pathway in good yields. Moreover, this system was able to generate either alkoxycarbonyl radicals or alkyl radicals with [bis(alkoxyoxalyloxy)iodo]benzene, which was prepared from alcohol, oxalyl chloride, and (diacetoxyiodo)benzene via two steps, depending on reaction conditions. These radicals were also utilized for C-C bond formation with electron-deficient olefins.

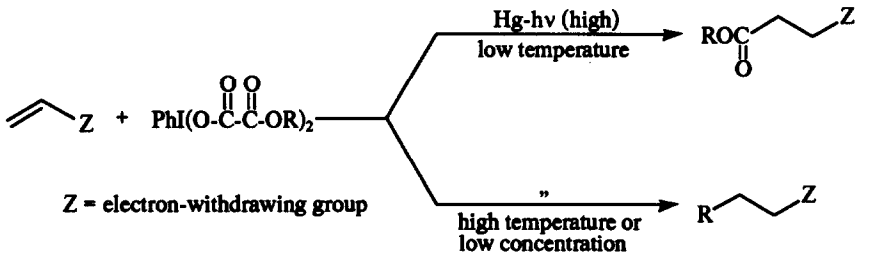
Introduction

Recently, the chemistry of hypervalent iodine compounds has been an attractive field in organic synthesis because of their powerful abilities as oxidants and carbon-carbon bond forming reagents.[1] Especially, the latter reactions are very important for synthetic organic chemistry. Among these reactions, substitution and addition reactions are the two greatest fields in organic synthesis. Previously, we have reported the alkylation onto heteroaromatic bases (substitution) with trivalent iodine compounds starting from carboxylic acids and alcohols via radical decarboxylative pathways.[2] However, the addition of alkyl radical formed via decarboxylation of (diacyloxyiodo)arene to an olefinic compound has never been studied. This radical addition reaction has a large synthetic potentiality. General method to generate alkyl radical for addition reaction is the use of alkyl halides, sulfides, selenides, and xanthates as a radical precursor with tin hydride,[3] while there are a few methods using carboxylic acids as a starting material, where one of them is a excellent method with N-hydroxy-2-thiopyridone developed by Barton.[4] In our preliminary communication,[5] we have shown that (diacyloxyiodo)benzene reacted with electron-deficient olefins in the presence of hydrogen donor such as 1,4-cyclohexadiene to obtain the reductive addition products (eq. 1). This reaction is very useful because of the non-toxicity of (diacyloxyiodo)arene as compared with organotin species, the simple experimental operation, and the good yields of reaction products.

Dedicated with gratitude to Professor Sir Derek H. R. Barton on the occasion of his 75th birthday.



(1)



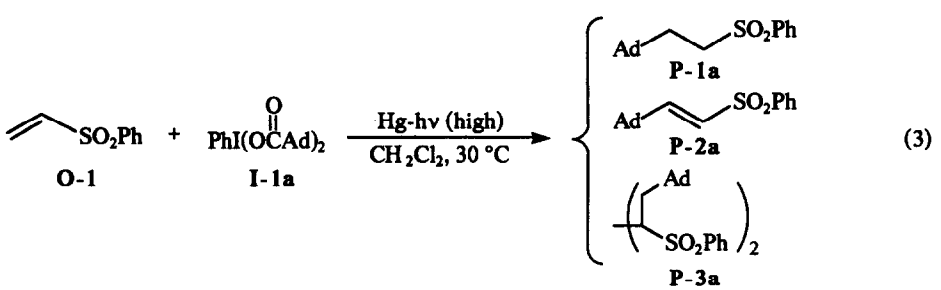
(2)

We now report full details on the reductive addition of (diacyloxyiodo)arene, which is easily prepared from carboxylic acid and (diacetoxyiodo)arene, and [bis(alkoxyoxalyloxy)iodo]arene, which is prepared from alcohol, oxalyl chloride, and (diacetoxyiodo)arene, to electron-deficient olefins (eqs. 1 and 2).

Results and Discussion

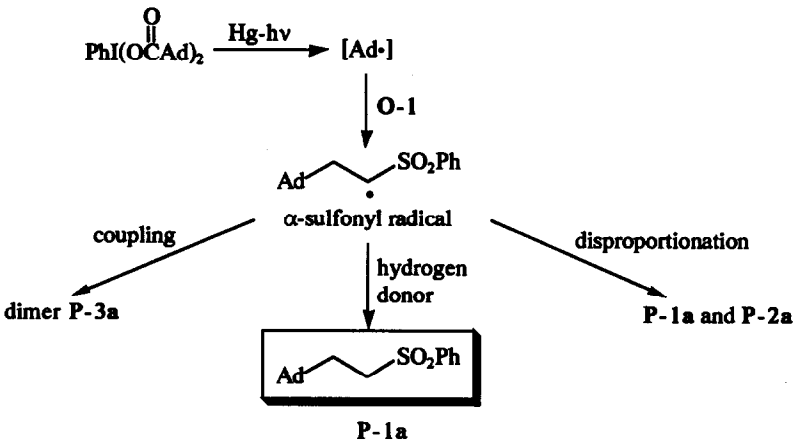
Addition Reaction to Electron-Deficient Olefins with Carboxylic Acids

A mixture of phenyl vinyl sulfone and [bis(adamantanecarboxy)iodo]benzene (**I-1a**) was irradiated with high-pressure mercury lamp in dichloromethane at 30 °C to give compounds **P-1a**, **P-2a**, and **P-3a**. This reaction did not proceed under thermal conditions at all. Here, compound **P-1a** is a reductive addition product, **P-2a** is a substitution product, and **P-3a** is a dimerized product of α-sulfonyl radical which is generated from the addition of 1-adamantyl radical to phenyl vinyl sulfone (Scheme 1). In principle, the compounds **P-1a** and **P-2a** are disproportionated products of α-sulfonyl radical intermediate. Therefore, the same amounts of **P-1a** and **P-2a** should be formed in dichloromethane. Here, the adamantyl radical via the radical decarboxylation of adamantanecarboxy radical formed by the irradiation of **I-1a** could be trapped quantitatively by 2, 2, 6, 6-tetramethyl-1-piperidinyloxy free radical (TEMPO) as shown in eq. 4 and the side products, iodobenzene and adamantanecarboxylic acid were also obtained in quantitative yields, respectively. Thus the addition of moderate hydrogen donor to α-sulfonyl radical intermediate will be expected to give the reductive addition product preferentially. The results and reaction conditions were shown in Table 1. In practice, the same amounts of



(3)

Mechanism



Scheme 1

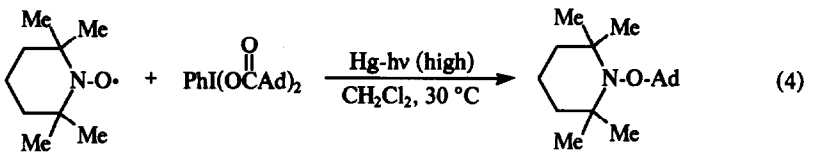
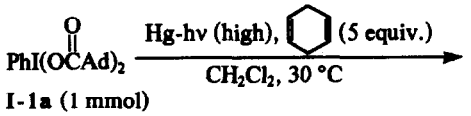


Table 1. Addition of **I-1a** to Phenyl Vinyl Sulfone (**O-1**) in the Presence of Various Hydrogen Donor[a)]

Entry	Hydrogen Donor	Conditions	Yields (%)			
			P-1a	**P-2a**	**P-3a**	Total
1	-	A	no reaction			
2	-	B	15	9	13	37
3	-	B[c)]	16	16	20	52
4	-	C	17	16	22	55
5	$CH(OMe)_3$, 1ml	B	15	12	17	44
6	Trioxane, 20 equiv.	B	17	11	15	43
7	THF, 1ml	B	37	1	3	41
8	1,3-Dioxolane, 1ml	B	52	5	5	62
9	Triethylsilane, 10 equiv.	B	54	2	0	56[d)]
10	1,4-Cyclohexadiene, 2 equiv.	B	86	-	-	86
11	1,4-Cyclohexadiene, 5 equiv.	B	99	-	-	99

a) The mole ratio of **O-1** / **I-1a** was 0.5 / 0.5 (mmol). b) Conditions A : Refluxed in benzene. B : irradiated with high-pressure mercury lamp in CH_2Cl_2. C : Irradiated with low-pressure mercury lamp in CH_2Cl_2. c) The reaction was carried out at 0-5 °C. d) Adamantane was obtained in 4 % yield.

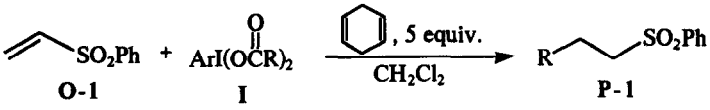
P-1a and P-2a were obtained (Entries 3 and 4). The use of triethyl orthoformate or trioxane did not bring about the expected result (Entries 5 and 6). While, in the presence of a hydrogen donor such as tetrahydrofuran (THF), 1,3-dioxolane, or triethylsilane, the reductive addition product P-1a was obtained as a major product (Entries 7-9) and especially as a sole product with 1,4-cyclohexadiene (Entries 10 and 11). The driving force for supplying a hydrogen atom to α-sulfonyl radical is the weakness of α-C-H bond neighbouring to oxygen atom in cyclic ether and Si-H bond and is aromatization in the case of 1,4-cyclohexadiene. Moreover, when THF was used as a hydrogen donor, the α-tetrahydrofuryl radical generated from THF after one hydrogen atom abstraction by α-sulfonyl radical had a powerful nucleophilicity and therefore reacted with phenyl vinyl sulfone to give phenyl 2-(α-tetrahydrofuryl)ethyl sulfone as a by-product (20-30 %). Using triethylsilane, adamantyl radical generated from I-1a abstracted a hydrogen atom from triethylsilane to give a trace amount of adamantane because Si-H bond energy is weak (Entry 9). While, 1,4-cyclohexadiene afforded a hydrogen atom very effectively and side reactions did not occur because the formed cyclohexadienyl radical preferred to release another hydrogen atom to aromatize as a benzene. The yield of the reductive addition product was improved by increasing the amount of 1,4-cyclohexadiene (Entries 10 and 11). While, the mixture of I-1a (1 mmol) and 1,4-cyclohexadiene (5 mmol) without radical acceptor such as phenyl vinyl sulfone in dry dichloromethane was irradiated to give 0.84 mmol of adamantane, along with iodobenzene and 1-adamantanecarboxylic acid. The fact indicates that one molar of I-1a generates one molar of adamantyl radical but not two molars of one. The phenyl group in (diacyloxyiodo)benzene was replaced by naphthyl group to compare the reactivity,



I-1a (1 mmol)

reaction products (mmol)	
Adamantane	0.84
PhI	0.60
Ad-COOH	0.22

(5)



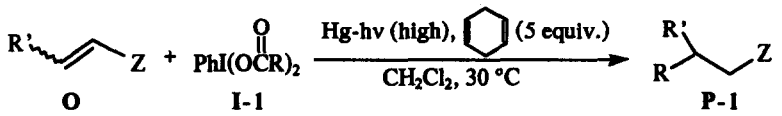
O-1 I P-1

(6)

Table 2. Relative Reactivity of (Diacyloxyiodo)arene I[a)]

Entry	Ar	R	Conditions	P-1, Yield (%)
1	phenyl (1)	1-Ad- (a)	Hg-hv (high), 30 °C	99
2	1-naphthyl (2)	"	"	92
3	pentafluorophenyl (3)	"	"	45[b)]
4	phenyl (1)	$PhCH_2CH_2$- (f)	"	44
5	1-naphthyl (2)	"	"	40

a) The mole ratio of O-1 / I was 0.5 / 0.5 (mmol). b) Phenyl vinyl sulfone was recovered in 50 % yield.

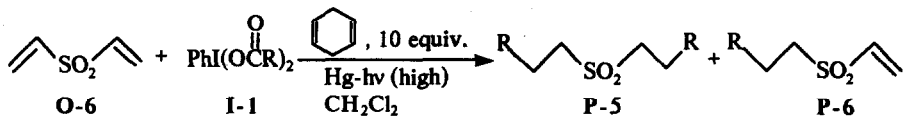


(7)

Table 3. Addition Reactions with Various Carboxylic Acids and Olefins

Entry	O	I-1, R	P-1, Yield/%
1	R' = H, Z = SO_2Ph (O-1)	Me (b)	90
2	"	(c)	88
3	"	(d)	82
4	"	(e)	85
5	"	Ph (f)	44
6	"	O (g)	67
7	R'= Me, Z = SO_2Ph (O-2)	(a)	50[a]
8	R' = H, Z = SOPh (O-3)	"	53
9	R' = H, Z = COOMe (O-4)	"	40
10	R' = H, Z = $P(O)(OEt)_2$ (O-5)	"	66
11	"	(c)	78
12	R' = H, Z = SO_2Ph (O-1)	BzO, BzO, O (h, β form)	63 (almost β form)
13	"	BzO, BzO, O (i, α form)	74 (66 : 34)[b]
14	R' = H, Z = $P(O)(OEt)_2$ (O-5)	"	58 (85 : 15)[b]

a) 2 equivalents of 1,4-cyclohexadiene were used. b) The ratio of β : α.



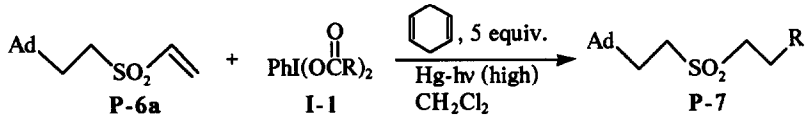
(8)

while it did not take effect so much. [Bis(adamantanecarboxy)iodo]pentafluorobenzene (**I-3a**) was less reactive than [bis(adamantanecarboxy)iodo]benzene (**I-1a**) and -naphthalene (**I-2a**) under the irradiation conditions with high-pressure mercury lamp and the addition reaction to phenyl vinyl sulfone did not proceed effectively.

Other alkyl radicals generated from (diacyloxyiodo)benzene were also added to phenyl vinyl sulfone in the presence of 1,4-cyclohexadiene to afford 2-alkylethyl phenyl sulfones in good yields. The reactivities of (diacyloxyiodo)benzene increase in order of primary < secondary < tertiary alkyl groups (Entries 1, 2, and 5 in Table 3). While, this method is applicable to other functional olefins such as phenyl vinyl sulfoxide (**O-3**), methyl acrylate (**O-4**), and diethyl vinylphosphonate (**O-5**). Especially, additions to **O-3** and **O-5** are very useful from synthetic point of view. In the former case, sulfinyl group can be easily removed from the adduct under thermal conditions to give the olefinic compound which is useful as a synthetic precursor. The latter adduct is interested in biological activities. Particularly, the adduct obtained from (diacyloxyiodo)benzene having sugar moiety is expected to be pharmaceutical activities. Practically, (diacyloxyiodo)benzene bearing sugar moiety (**I-1h** and **I-1i**) gave the addition products with **O-1** and **O-5** in good yields. The fact suggests that this reaction can be applicable to the synthesis of C-nucleoside. Furthermore, the use of less reactive phenyl 1-propenyl sulfone **O-2** having a methyl group at the reaction position gave the reductive addition product in 50 % yield (Entry 7). While, the same addition reactions of N-acyloxy-2-thiopyridone to **O-2** and **O-3** were not so effective. As anticipated from the basic theory of related radical additions to olefins, the less electrophilic methyl acrylate and phenyl vinyl sulfide than phenyl vinyl sulfone behaved poorly.[6] In the former case, polymerization occurred and the best yield from **I-1a** to the corresponding adduct was 40 %. The latter reaction was not clean and many products were formed. When divinyl sulfone (**O-6**) having two reaction positions was treated with **I-1a**, the double addition product and the single addition product were obtained as shown in Table 4. Using one equivalent of **I-1a** based on **O-6**, compounds **P-5a** and **P-6a** were obtained in 13 % and 63 % yields, respectively (Entry 1 in Table 4). However, the use of excess **I-1a** gave the double addition product **P-5a** in 87 % yield as a sole product (Entry 2). Similarly, the other double addition products were also obtained in 70 % and 78 % yields by using excess **I-1c** and **I-1d**, respectively. When single addition product **P-6a** (R = 1-adamantyl) was treated again with one equivalent of **I-1c** (R = cyclohexyl), an unsymmetrical sulfone, 2-(1-adamantyl)ethyl 2-cyclohexylethyl sulfone (**P-7**) was obtained in 70 % yield.

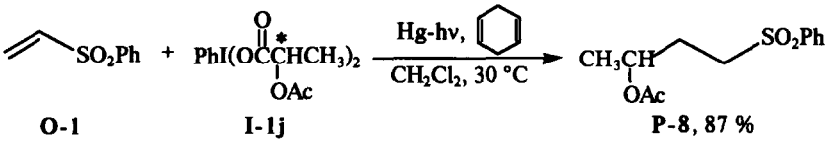
Table 4. Reaction with Divinyl Sulfone (**O-6**)

Entry	R-	**I-1** / **O-6** (mole ratio)	Yields / %	
			P-5	**P-6**
1	1-adamantyl (**a**)	1	13	63
2	"	3	87	-
3	cyclohexyl (**c**)	3	70	-
4	cyclopentyl (**d**)	3	78	-



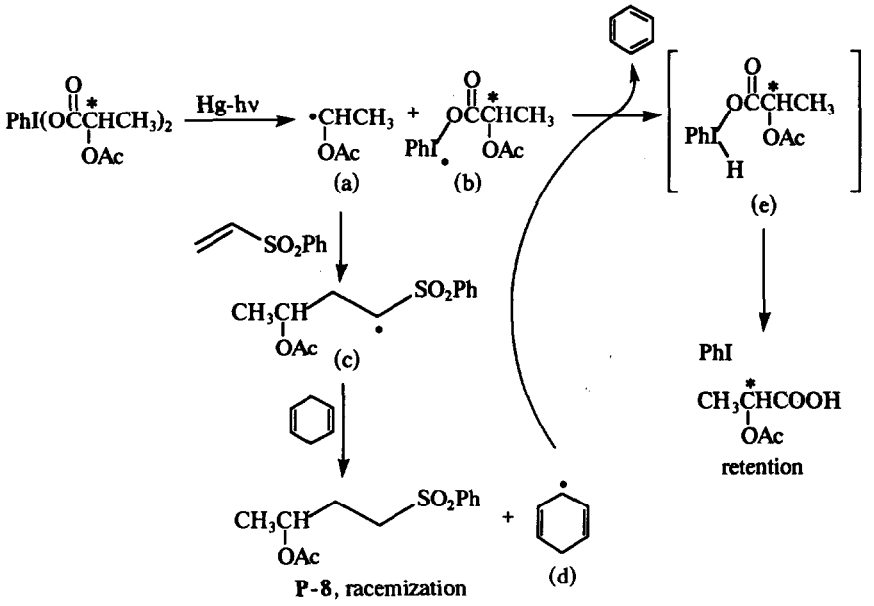
(9)

The reaction mechanism is speculated as shown in Scheme 2. The mixture of phenyl vinyl sulfone and (diacyloxyiodo)benzene **I-1j**, which was prepared from (diacetoxyiodo)benzene and chiral (L)-O-acyllactic acid, in dichloromethane was irradiated with high-pressure mercury lamp in the presence of 1,4-cyclohexadiene to give the compound **P-8** in 87 % yield. Here, the initial process of this reaction would be homolytic cleavage of I-O bond of **I-1j** to form radical (a) and (b). The alkyl radical (a), which loses chirality quickly, adds to phenyl vinyl sulfone to give radical (c), which has a radical center at the α-position of the electron-withdrawing group. Thus, the electrophilic radical (c) abstracts a hydrogen atom from 1,4-cyclohexadiene to form the reductive addition product **P-8**. Therefore, the compound **P-8** racemized completely. This fact again suggests that the reaction proceeds via radical mechanism. Cyclohexadienyl radical (d) can give another hydrogen atom to the radical (b). Thus, iodobenzene and carboxylic acid were recovered via the intermediate (e) probably. Here, the optical purity of recovered O-acyllactic acid was retained. While, cyclohexadienyl radical itself aromatizes to give benzene. In order to detect the generation of benzene, the following experiment was carried out. The mixture of



O-1 **I-1j** **P-8, 87 %** (10)

Mechanism

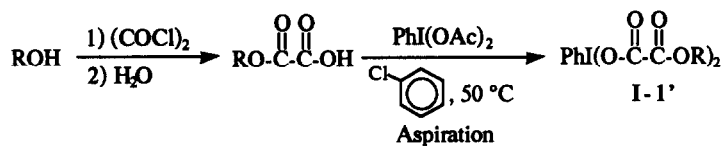


Scheme 2

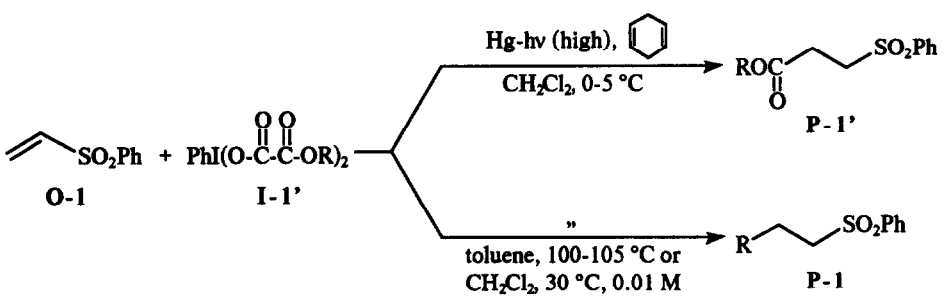
phenyl vinyl sulfone and 1-[bis(adamantanecarboxy)iodo]naphthalene (**I-2a**) in the presence of 1,4-cyclohexadiene was irradiated in dry dichloromethane. The reason why **I-2a** was used as a trivalent iodine compound is that phenyl radical might generate from **I-1a** via carbon-iodine bond cleavage. After the reaction the solvent was recovered under the reduced pressure at -78 °C and it was analyzed with gas chromatography. The recovered solvent contained benzene generated from 1,4-cyclohexadiene after hydrogen abstraction. This result indicates that the mechanism of Scheme 2 is reliable.

Addition Reaction to Electron-Deficient Olefins with Alcohols

As the addition reactions to electron-deficient olefins by carbon radicals starting from alcohols, the method of xanthates and xanthate analogues with tributyltin hydride has hitherto been studied.[7] However the study was concentrated on the effective generation of alkyl radical by this method. While, the present method with (diacetoxyiodo)benzene and oxalic acid monoalkyl ester prepared from alcohols is able to generate either alkyl radical or alkoxy carbonyl radical by changing the reaction conditions. These radicals may readily add to phenyl vinyl sulfone to give alkyl 3-(benzenesulfonyl)propionate **P-1'** and 2-alkylethyl phenyl sulfone **P-1**, respectively. The mixture of **O-1** and [bis(alkoxyoxalyloxy)iodo]benzene (**I-1'**) replaced

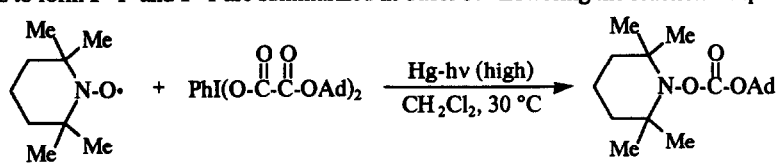


(11)



(12)

with oxalic acid monoalkyl ester was irradiated with high-pressure mercury lamp in dry dichloromethane at 30 °C to give compound **P-1** and **P-1'** without remarkable selectivity. Compound **P-1'** is a single decarboxylated product and **P-1** is a double decarboxylated product . Here, the formation of alkoxycarbonyl radical was supported by the trapping experiment with TEMPO to give carbonate derivative **P-9**. The similar reaction was carried out at low temperature (0-5 °C) in the presence of phenyl vinyl sulfone. The results and reaction conditions to form **P-1'** and **P-1** are summarized in Table 5. Lowering the reaction temperature restrains the



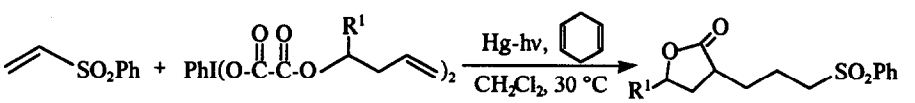
(13)

second decarboxylation and compound **P-1'** is obtained preferentially. Using primary and secondary monoalkyl esters of oxalic acid, compound **P-1'** was obtained in good yield as a sole product (Entries 4, 8, and 9). Here, alkoxy carbonyl radical coupled as a minor product to give oxalate diester in 7 % yield (Entry 4). While, to accelerate the second decarboxylation, the reaction was performed in the following two method. Method 1: The mixture of phenyl vinyl sulfone (**O-1**) and [bis(alkoxyoxalyloxy)iodo]benzene (**I-1'**) was irradiated in dry toluene under thermal conditions. Method 2: The mixture of **O-1** and **I-1'** was irradiated in dry dichloromethane under the dilution conditions (0.01 M). When secondary and tertiary monoalkyl esters of oxalic acid were used, the compound **P-1** was obtained in moderate yields (Entries 10-16).

Table 5. Addition to Phenyl Vinyl Sulfone with [Bis(alkoxyoxalyloxy)iodo]benzene (**I-1'**)[a]

Entry	R-	Conditions		Yields (%) P-1'	Yields (%) P-1
1	1-Adamantyl (**a**)	CH_2Cl_2,	30 °C	41	29
2	"	",	0-5 °C	56	12
3	Cyclohexyl (**c**)	",	30 °C	50	20
4	"	",	0-5 °C	85[b]	-
5	(-)-Menthyl (**k**)	",	30 °C	53	16
6	"	",	0-5 °C	67	trace
7	2-Phenylethyl (**f**)	",	30 °C	42	13
8	"	",	0-5 °C	51	-
9	Ethyl (**l**)	",	0-5 °C	60	-
10	1-Adamantyl (**a**)	toluene,	100-105 °C	9	58
11	"	CH_2Cl_2,	30 °C, 0.01 M	12	66
12	1-Methylcyclohexyl (**b**)	CH_2Cl_2,	30 °C	-	79
13	"	",	0-5 °C	-	66
14	Cyclohexyl (**c**)	toluene,	100-105 °C	11	46
15	"	CH_2Cl_2,	30 °C, 0.01 M	28	49
16	(-)-Menthyl (**k**)	toluene,	100-105 °C	11	63
17	2-Phenylethyl (**f**)	toluene,	100-105 °C	19	21

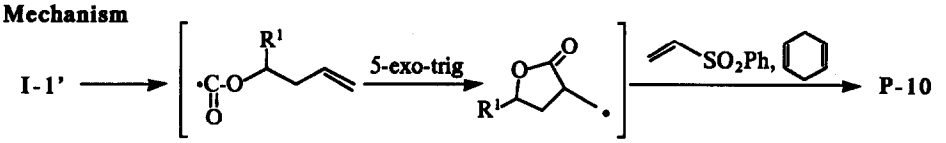
a) The ratio of **O-1** / **I-1'** was 0.5 / 0.5 mmol. b) Oxalate diester was obtained in 7 % yield.



O-1 **I-1'** **P-10** (14)

R^1	P-10 Yield (%)
Me (**m**)	47
H (**n**)	44

Mechanism



Scheme 3

When phenyl vinyl sulfone was treated with [bis(alkenoxyoxalyloxy)iodo]benzene (**I-1'**), which was replaced with oxalic acid mono-3-butenyl ester in the presence of 1,4-cyclohexadiene, the sulfone bearing lactone group was obtained in moderate yield. The alkenoxy carbonyl radical generated via one molecular decarboxylation cyclized in 5-exo-trig manner to give **P-10** (Scheme 3). This result suggests that the reaction proceeds via radical mechanism again. The lactonization is more favorable when primary oxalic acid monoalkenyl ester was used due to retard the second decarboxylation of the formed alkenoxy carbonyl radical. Now the method with [bis(alkoxyoxalyloxy)iodo]benzene will be useful in the synthesis of natural products containing lactone group.

In conclusion, the present method with (diacyloxyiodo)benzene starting from carboxylic acid is very useful for the addition of alkyl radical to electron-deficient olefins and further [bis(alkoxyoxalyloxy)iodo]benzene starting from alcohol can generate both alkoxy carbonyl and alkyl radicals freely which react with electron-deficient olefins. Therefore this system may replace the method with tributyltin hydride in the field of reductive radical addition reaction.

Experimental

Microanalyses were performed with a Perkin-Elmer 240 elemental analyser at the Chemical Analysis Center of Chiba University. IR and ^{1}H NMR spectra were measured with Hitachi 215, JEOL-MH-100, JEOL-JNM-FX270, JEOL-GSX-400 and JEOL-GSX-500 spectrometers, respectively. Mass spectra were measured with Hitachi M-60 and JEOL-HX-110. Wakogel C-200 was used for column chromatography, Kieselgel 60 F_{254} (Merck) was used for TLC, and Wakogel B-5F was used for preparative (pTLC).

Materials: The trivalent iodine compound, (diacetoxyiodo)benzene and simple organic chemicals were commercially available. Following compounds were prepared according to the procedures described in the literatures: phenyl 1-propenyl sulfone[8], 1-(diacetoxyiodo)naphthalene[9], [bis(trifluoroacetoxy)iodo]pentafluorobenzene[10], and (diacyloxyiodo)benzene[11].

General Procedure for Reductive Addition Reaction to Electron-deficient Olefins with Carboxylic Acids. The reaction was carried out with molar ratio of 0.5 / 0.5 (olefin / trivalent iodine compound). To the solution of electron-deficient olefin and (diacyloxyiodo)benzene replaced with appropriate carboxylic acid in dry dichloromethane (5 ml) was added 1,4-cyclohexadiene (5 equiv.) under argon atmosphere and the obtained mixture was irradiated with high-pressure mercury lamp (400 W) at 30 °C until the reaction was completed (about 15 minutes). After the reaction, the reaction mixture was poured into $CHCl_3$ and washed with saturated aqueous sodium hydrogen carbonate. The organic layer was dried over Na_2SO_4. After the removal of solvent under reduced pressure, the residual oil was purified by pTLC on silica gel.

To determine the amount of carboxylic acid, the remained trivalent iodine compound was removed from the reaction mixture by the short column chromatography on silica gel (eluent : ethyl acetate). The solution was washed with saturated aqueous sodium hydrogen carbonate. The water layer was acidified at about pH 1 by 2 N HCl and extracted with ether for three times. The combined extract was dried over Na_2SO_4 and the solvent was removed under reduced pressure.

Spectral and analytical data of new reductive addition compounds prepared are as follows.

2-(1-Adamantyl)ethyl phenyl sulfone (P-1a): mp 101.4-103.5 °C; IR (KBr) 2860, 1440, 1295, 1145, 1085, 760, 730, 685 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.35-1.76 (m, 14H), 1.93 (bs, 3H), 3.07 (d, 1H, J = 9.6 Hz), 3.05 (dd, 1H, J_1 = 9.6, J_2 = 3.9 Hz), 7.53-7.72 (m, 3H), 7.91 (dt, 2H, J_1 = 7.0, J_2 = 1.8 Hz); HRMS (Fab) Calcd for $C_{18}H_{25}O_2S$, m/e = 305.1574. Found: m/e = 305.1574; Anal. Calcd for $C_{18}H_{24}O_2S$: C, 71.01; H, 7.95 %. Found: C, 71.30: H, 7.73 %.

2-(1-Adamantyl)vinyl phenyl sulfone (P-2a): mp 140.5-142.0°C; IR (KBr) 2860, 1440, 1295, 1140, 840, 760, 730 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.54-1.81 (m, 12H), 2.02 (bs, 3H), 6.14 (d, 1H, J = 15.0 Hz), 6.85 (d, 1H, J = 15.0 Hz), 7.50-7.68 (m, 3H), 7.87 (dt, 2H, J_1 = 7.0, J_2 = 1.8 Hz); Anal. Calcd for $C_{18}H_{22}SO_2$: C, 71.49; H, 7.33%. Found: C, 71.36; H, 7.33..

1,4-Di(adamantyl)-2,3-di(benzenesulfonyl)butane (P-3a): mp 211-214 °C; IR (KBr) 2860, 1440, 1295, 1135, 730, 685 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.21-1.92 (m, 34 H), 4.32-4.40 (m, 2H), 7.56-7.74 (m, 6H), 7.94 (dt, 4H, J_1 = 7.0, J_2 = 1.8 Hz); HRMS (Fab) Calcd for $C_{36}H_{47}O_4S_2$, m/e = 607.2913. Found: m/e = 607.2912; Anal. Calcd for $C_{36}H_{46}O_4S_2$: C, 71.25; H, 7.64 %. Found: C, 70.90; H, 7.42 %.

2-(1-Methylcyclohexyl)ethyl phenyl sulfone (P-1b): oil; IR (neat) 2850, 1430, 1290, 1140, 1080, 735, 685 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.80 (s, 3H), 1.07-1.46 (m, 10H), 1.62 (dd, 1H, J_1 = 9.2, J_2 = 4.3 Hz), 1.64 (d, 1H, J = 9.2 Hz), 3.04 (dd, 1H, J_1 = 9.2, J_2 = 4.3 Hz), 3.06 (d, 1H, J = 9.2 Hz), 7.53-7.72 (m, 3H), 7.93 (dt, 2H, J_1 = 7.1, J_2 = 1.5 Hz); Anal. Calcd for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32 %. Found: C, 67.62; H, 8.50 %.

2-(Cyclohexyl)ethyl phenyl sulfone (P-1c): oil; IR (neat) 2860, 2820, 1435, 1290, 1140, 1080, 735, 685 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.76-0.98 (m, 2H), 1.00-1.36 (m, 4H), 1.50-1.76 (m, 7H), 3.09 (dd, 1H, J_1 = 7.8, J_2 = 4.5 Hz), 3.12 (d, 1H, J = 7.8 Hz), 7.52-7.72 (m, 3H), 7.91 (dt, 2H, J_1 = 7.0, J_2 = 1.6 Hz); Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99 %. Found: C, 66.38; H, 7.87 %.

2-(Cyclopentyl)ethyl phenyl sulfone (P-1d): mp 68.4-68.8 °C; IR (KBr) 2900, 1440, 1280, 1140, 1080, 800, 740, 685 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.95-1.16 (m, 2H), 1.40-1.96 (m, 9H), 3.03-3.16 (m, 2H), 7.53-7.72 (m, 3H), 7.91 (dt, 2H, J_1 = 7.0, J_2 = 1.3 Hz); Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61 %. Found: C, 65.50; H, 7.56 %.

2-(Cyclobutyl)ethyl phenyl sulfone (P-1e): mp 68.1-68.8 °C; IR (KBr) 2895, 1440, 1280, 1135, 1080, 805, 740, 690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.53-1.69 (m, 2H), 1.78-1.92 (m, 4H), 1.98-2.14 (m, 2H), 2.27 (Septet, 1H, J = 7.7 Hz), 2.96 (dd, 1H, J_1 = 7.3, J_2 = 3.9 Hz), 2.99 (d, 1H, J = 7.3 Hz), 7.54-7.70 (m, 3H), 7.90 (dt, 2H, J_1 = 7.9, J_2 = 1.3 Hz); Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19 %. Found: C, 64.03; H, 6.95 %.

2-(2-Tetrahydrofuryl)ethyl phenyl sulfone (P-1g): oil; IR (neat) 2825, 2890, 1430, 1280, 1135, 1050, 740, 685 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.34-1.53 (m, 1H), 1.70-2.10 (m, 5H), 3.14 (ddd, 1H, J_1 = 14.3, J_2 = 11.2, J_3 = 5.4 Hz), 3.30 (ddd, 1H, J_1 = 14.3, J_2 = 11.2, J_3 = 5.4 Hz), 3.60-3.90 (m, 3H), 7.90

(dt, 2H, J_1 = 7.0 Hz, J_2 = 1.4 Hz),7.49-7.70 (m, 3H); Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71 %. Found: C, 59.64; H, 6.56 %.

3-(Acetoxy)butyl phenyl sulfone (P-8): oil; IR (neat) 2900, 1720, 1440, 1365, 1300, 1235, 1145, 750, 690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.22 (d, 3H, J = 6.3 Hz), 1.90-2.10 (m, 2H), 1.99 (s, 3H), 3.01-3.24 (m, 2H), 4.93 (sixtet, 1H, J = 6.3 Hz), 7.55-7.73 (m, 3H), 7.92 (dt, 2H, J_1 = 7.0, J_2 = 1.3 Hz); Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29 %. Found: C, 56.16; H, 6.29 %.

Phenyl 4-(phenyl)butyl sulfone (P-1f): mp 57.5-59.5 °C; IR (neat) 2900, 1435, 1285, 1140, 740, 685 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.57-1.85 (m, 4H), 2.58 (t, 2H, J = 7.1 Hz), 3.10 (t, 2H, J = 7.1 Hz), 7.04-7.30 (m, 5H), 7.49-7.71 (m, 3H), 7.86 (dt, 2H, J_1 = 7.1, J_2 = 1.4 Hz); Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61 %. Found: C, 69.76; H, 6.48 %.

2-(1-Adamantyl)propyl phenyl sulfone (P-1o): oil; IR (neat) 2885, 2850, 1450, 1310, 1155, 1100, 760, 740, 700 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.03 (d, 3H, J = 7.0 Hz, 3H), 1.16-2.00 (m, 16H), 2.71 (dd, 1H, J_1 = 14.2, J_2 = 9.7 Hz), 3.29 (d, 1H, J = 14.2 Hz), 7.50-7.68 (m, 3H), 7.88-7.96 (m, 2H); Anal. Calcd for $C_{19}H_{26}O_2S$: C, 71.65; H, 8.23 %. Found: C, 71.43; H, 7.93 %.

2-(1-Adamantyl)ethyl phenyl sulfoxide (P-1p): mp 81.4-82.1 °C; IR (KBr) 2850, 1435, 1040, 750, 690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.20-1.74 (m, 14H), 1.92 (bs, 3H), 2.60-2.88 (m, 2H), 7.44-7.57 (m, 3H), 7.58-7.68 (m, 2H); Anal. Calcd for $C_{18}H_{24}OS$: C, 74.95; H, 8.39 %. Found: C, 74.58; H, 8.10 %.

Methyl 3-(1-adamantyl)propionate (P-1q): oil; IR (neat) 2830, 1725 1430, 1150 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.40-1.48 (m, 8H), 1.56-1.76 (m, 6H), 1.96 (bs, 3H), 2.24-2.31 (m, 2H), 3.68 (s, 3H); HRMS (Fab) Calcd for $C_{14}H_{23}O_2$, m/e = 223.1697. Found: m/e = 223.1698.

Diethyl 2-(1-adamantyl)ethylphosphonate (P-1r): oil; IR (neat) 2820, 1235, 1020, 950, 785 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.32 (t, 6H, J = 6.9 Hz),1.28-1.78 (m, 16H), 1.96 (bs, 3H), 4.02-4.18 (m, 4H); HRMS (Fab) Calcd for $C_{16}H_{30}O_3P$, m/e = 301.1933. Found: m/e = 301.1939.

Diethyl 2-(cyclohexyl)ethylphosphonate (P-1s): oil; IR(neat) 2850, 1435, 1235, 1020, 950 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.34 (t, 6H, J = 7.4 Hz), 1.28-1.76 (m, 12H), 1.96 (bs, 3H), 4.00-4.16 (m, 4H); HRMS (Fab) Calcd for $C_{12}H_{26}O_3P$, m/e = 249.1618. Found: m/e = 249.1614.

2-(3,4-Di-O-benzoyl-2-deoxy-D-ribopyranosyl)ethyl phenyl sulfone: (α form) (P-1t): oil; IR (neat) 1700, 1250 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.01-2.09 (m, 4H, $H^{2'}$ and sugar-$\underline{CH_2}CH_2$), 3.21-3.28 (m, 1H, sugar-$CH_2\underline{CH_2}$), 3.35-3.42 (m, 1H, sugar-$CH_2\underline{CH_2}$), 3.61 (quintet, 1H, J = 6.4 Hz, $H^{1'}$), 3.68 (dd, 1H, J_1 = 13.2, J_2 = 0.9 Hz, $H^{5'}$), 4.20 (dd, 1H, J_1 = 13.2, J_2 = 2.2 Hz, $H^{5'}$), 5.27-5.33 (m, 1H, $H^{3'}$), 5.46 (bs, 1H, $H^{4'}$), 7.34 (t, 2H, J = 7.9 Hz), 7.46-7.52 (m, 3H,), 7.57-7.63 (m, 3H), 7.65-7.69 (m, 1H), 7.88 (d, 2H, J = 8.0 Hz), 7.93 (d, 2H, J = 8.0 Hz), 8.07 (d, 2H, J = 8.0 Hz), NOE ($H^{1'}$ ↔ $H^{4'}$) was observed.

(β form) (P-1t): oil; $[\alpha]_D^{24}$ 66.18 (*c* 1.30, $CHCl_3$) IR (neat) 1700, 1250, 1080, 710 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.81 (ddd, 1H, J_1 = 14.5, J_2 = 11.7, J_3 = 2.5 Hz, $H^{2'}$), 1.83-1.91 (m, 1H, sugar-$\underline{CH_2}CH_2$), 1.96-2.02 (m, 1H, sugar-$\underline{CH_2}CH_2$), 2.10 (ddd, 1H, J_1 = 14.5, J_2 = 3.7, J_3 = 2.5 Hz, $H^{2'}$), 3.23 (ddd, 1H, J_1 = 14.1, J_2 = 10.5, J_3 = 5.2 Hz, sugar-$CH_2\underline{CH_2}$), 3.37 (ddd, 1H, J_1 = 14.1, J_2 = 10.5, J_3 = 4.9 Hz, sugar-$CH_2\underline{CH_2}$), 3.81-3.86 (m, 2H, $H^{1'}$ and $H^{5'}$), 4.01 (dd, 1H, J_1 = 10.7, J_2 = 5.2 Hz, $H^{5'}$), 5.20 (ddd, 1H, J_1 = 10.7, J_2 = 5.2, J_3 = 2.5 Hz, $H^{4'}$), 5.75 (q, 1H, J = 2.5 Hz, $H^{3'}$), 7.32 (t, 2H, J = 7.8 Hz), 7.47-7.51 (m, 3H), 7.56-7.67 (m, 4H), 7.85 (d, 2H, J = 7.8 Hz), 7.92 (d, 2H, J = 7.8 Hz), 8.06 (d, 2H, J = 7.8 Hz);

HRMS (Fab) Calcd for $C_{27}H_{27}O_7S$, m/e = 495.1478. Found: m/e = 495.1478.

Diethyl 2-(3,4-di-O-benzoyl-2-deoxy-D-ribopyranosyl)ethylphosphonate: (α form) (P-1u): oil; IR (neat) 1705, 1250, 1180, 1020, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, 6H, J = 7.0 Hz, $P(OCH_2\underline{CH_3})_2$), 1.81-2.00 (m, 3H, sugar-CH_2CH_2 and $H^{2'}$), 2.05-2.07 (m, 3H, sugar-CH_2CH_2 and $H^{2'}$), 3.58-3.62 (m, 1H, $H^{1'}$), 3.73-3.77 (m, 1H, $H^{5'}$), 4.07-4.17 (m, 5H, $P(O\underline{CH_2}CH_3)_2$ and $H^{5'}$), 4.26 (dd, 1H, J_1 = 13.2, J_2 = 2.1 Hz, $H^{5'}$), 5.32-5.37 (m, 1H, $H^{3'}$), 5.49 (bs, 1H, $H^{4'}$), 7.34 (t, 2H, J = 7.8 Hz), 7.46-7.53 (m, 3H), 7.59-7.63 (m, 1H), 7.88-7.91 (m, 2H), 8.09-8.12 (m, 2H).

(β form) (P-1u): oil; $[\alpha]_D^{24}$ 56.71 (*c* 0.89, $CHCl_3$) IR (neat) 1700, 1250, 1190, 1020, 950, 720, 710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (td, 6H, J_1 = 7.0, J_2 = 1.1 Hz, $P(OCH_2\underline{CH_3})_2$), 1.74-1.89 (m, 4H, sugar-CH_2CH_2 and $H^{2'}$), 1.96-2.06 (m, 1H, sugar-$CH_2\underline{CH_2}$), 2.13 (ddd, 1H, J_1 = 14.5, J_2 = 3.9, J_3 = 2.9 Hz, $H^{2'}$), 3.81-3.86 (m, 1H, $H^{1'}$), 3.93 (t, 1H, J = 10.8 Hz, $H^{5'}$), 4.04-4.15 (m, 5H, $P(O\underline{CH_2}CH_3)_2$ and $H^{5'}$), 5.26 (ddd, 1H, J_1 = 10.8, J_2 = 5.4, J_3 = 2.9 Hz, $H^{4'}$), 5.78 (q, 1H, J = 2.9 Hz, $H^{3'}$), 7.33 (t, 2H, J = 7.8 Hz), 7.46-7.52 (m, 3H), 7.61 (tt, 1H, J_1 = 6.8, J_2 = 1.3 Hz), 7.86-7.89 (m, 2H), 8.07-8.10 (m, 2H); HRMS (Fab) Calcd for $C_{25}H_{32}O_8P$, m/e = 491.1833. Found: m/e = 491.1832.

Addition Reaction to Divinyl Sulfone. To the solution of divinyl sulfone and (diacyloxyiodo)benzene in dry dichloromethane (5 ml) was added 1,4-cyclohexadiene under argon atmosphere. The mixture was irradiated at 30 °C for 30 minutes (400 W high-pressure mercury lamp). After the reaction, the solvent was removed and the residue was chromatographed on silica gel. The molar ratio of divinyl sulfone / (diacyloxyiodo)benzene / 1,4-cyclohexadiene was 0.5 / 1.5 / 5 when the double addition reaction was carried out, while in the case of the single addition reaction it was 0.5 / 0.5 / 2.5.

Bis[2-(1-adamantyl)ethyl] sulfone (P-5a): mp 237-241 °C (decomp); IR (KBr) 2875, 1445, 1295, 1285, 1250, 1120 cm^{-1} ^1H NMR (270 MHz, $CDCl_3$) δ 1.42-1.78 (m, 28H), 1.98 (m, 6H), 2.91 (dd, 1H, J_1 = 8.8, J_2 = 4.4 Hz), 2.93 (d, 1H, J = 8.8 Hz); Anal. Calcd for $C_{24}H_{38}O_2S$: C, 73.79; H, 9.81 %. Found: C, 73.72; H, 9.51 %.

2-(1-Adamantyl)ethyl vinyl sulfone (P-6a): mp 86.3-87.3 °C; IR (KBr) 2860, 1440, 1290, 1120, 975, 800 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.40-1.79 (m, 14H), 2.00 (bs, 3H), 2.95 (dd, 1H, J_1 = 9.2, J_2 = 4.0 Hz), 2.97 (d, 1H, J = 9.2 Hz), 6.19 (d, 1H, J = 9.5 Hz), 6.45 (d, 1H, J = 16.1 Hz), 6.65 (dd, 1H, J_1 = 16.1, J_2 = 9.5 Hz, 1H); Anal. Calcd for $C_{14}H_{22}O_2S$: C, 66.10; H, 8.72 %. Found: C, 66.23; H, 8.75 %.

Bis(2-cyclohexyl)ethyl sulfone (P-5c): mp 114.5-116 °C; IR (KBr) 2870, 2820, 1435, 1260, 1125, 765 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.74-0.96 (m, 4H), 1.02-1.38 (m, 8H), 1.44-1.80 (m, 14H), 2.87 (dd, 1H, J_1 = 8.2, J_2 = 4.1 Hz), 2.90 (d, 1H, J = 8.2 Hz); Anal. Calcd for $C_{16}H_{30}O_2S$: C, 67.08; H, 10.56 %. Found: C, 67.46, H, 10.75 %.

Bis(2-cyclopentyl)ethyl sulfone (P-5d): mp 69.0-71.5 °C; IR (KBr) 2900, 2840, 1270, 1110 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.00-1.24 (m, 4H), 1.40-1.72 (m, 8H), 1.73-1.98 (m, 10H), 2.88-3.04 (m, 4H); Anal. Calcd for $C_{14}H_{26}O_2S$: C, 65.07; H, 10.14 %. Found: C, 64.62; H, 9.84 %.

2-(1-Adamantyl)ethyl 2-(cyclohexyl)ethyl sulfone (P-7): mp 149.0-152.0 °C; IR (KBr) 2850, 2810, 1440, 1290, 1270, 1120 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.82-1.03 (m, 2H), 1.08-1.84 (m, 25H), 1.97 (bs, 3H), 2.82-3.02 (m, 4H); Anal. Calcd for $C_{20}H_{34}O_2S$: C, 70.95; H, 10.12 %. Found: C, 70.82; H, 9.81 %.

General Procedure for Addition Reaction to Phenyl Vinyl Sulfone with Oxalic Acid

Monoalkyl Esters. Esterification of phenyl vinyl sulfone: To the mixture of phenyl vinyl sulfone (0.5 mmol) and [bis(alkoxyoxalyloxy)iodo]benzene replaced with oxalic acid monoalkyl ester (0.5 mmol) in dry dichloromethane (5 ml) was added 1,4-cyclohexadiene (5 equiv.). The mixture was cooled at 0 °C and irradiated with high-pressure mercury lamp at about 0 °C under argon atmosphere. After the reaction, the mixture was washed with saturated aqueous sodium hydrogen carbonate and the organic layer was dried over Na_2SO_4. After the removal of solvent under reduced pressure, the residue was chromatographed on silica gel.

1-Adamantyl 3-(benzenesulfony)propionate (P-1'a): oil; IR (neat) 2850, 1700, 1290, 1225, 1120, 1040, 730, 680 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.56-1.70 (m, 6H), 1.96-2.20 (m, 9H), 2.66 (t, 2H, J = 7.9 Hz), 3.40 (t, 2H, J = 7.9 Hz), 7.52-7.74 (m, 3H), 7.92 (dt, 2H, J_1 = 7.2, J_2 = 1.5 Hz); Anal. Calcd for $C_{19}H_{24}O_4S$: C, 65.49; H, 6.94 %. Found: C, 65.33; N, 6.88 %.

Cyclohexyl 3-(benzenesulfonyl)propionate (P-1'c): oil; IR (neat) 2895, 1705, 1300, 1240, 1140, 730, 685 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.10-1.86 (m, 10H), 2.74 (t, 2H, J = 7.9 Hz), 3.45 (t, 2H, J = 7.9 Hz), 4.64-4.80 (m, 1H), 7.56-7.76 (m, 3H), 7.92 (dt, 2H, J_1 = 7.2, J_2 = 1.5 Hz); Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80 %. Found: C, 61.06; H, 6.95 %.

(-)-Menthyl 3-(benzenesulfonyl)propionate (P-1'k): oil; IR (neat) 2900, 1720, 1305, 1240, 1150, 740, 690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.72 (d, 3H, J = 7.0 Hz), 0.87 (d, 3H, J = 7.0 Hz), 0.89 (d, 3H, J = 7.0 Hz), 0.70-1.96 (m, 9H), 2.69-2.79 (m, 2H), 3.44 (t, 2H, J = 7.5 Hz), 4.66 (td, 1H, J_1 = 6.4, J_2 = 4.3 Hz), 7.56-7.73 (m, 3H), 7.89-7.97 (m, 2H); Anal. Calcd for $C_{19}H_{28}O_4S$: C, 64.74; H, 8.01 %. Found: C, 64.87; H, 7.92 %.

2-Phenylethyl 3-(benzenesulfonyl)propionate (P-1'f): mp 53.1-55.5 °C; IR (KBr) 2900, 1710, 1290, 1240, 1140, 735, 690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.72 (t, 2H, J = 7.6 Hz), 2.89 (t, 2H, J = 7.0 Hz), 3.38 (t, 2H, J = 7.6 Hz), 4.24 (t, 2H, J = 7.0 Hz), 7.10-7.37 (m, 5H), 7.49-7.72 (m, 3H), 7.84-7.94 (m, 2H); Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70 %. Found: C, 64.15; H, 5.63 %.

Ethyl 3-(benzenesulfonyl)propionate (P-1'l): oil; IR (neat) 2900, 1720, 1305, 1245, 1140, 740 690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.23 (t, 3H, J = 7.2 Hz), 2.76 (t, 2H, J = 7.9 Hz), 3.45 (t, 2H, J = 7.9 Hz), 4.10 (q, 2H, J = 7.2 Hz), 7.54-7.73 (m, 3H), 7.89-7.96 (m, 2H); Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82 %. Found: C, 54.62; H, 6.13 %.

Alkylation of Phenyl Vinyl Sulfone. The reaction was carried out as follows. Method 1: To the solution of phenyl vinyl sulfone (0.5 mmol) and [bis(alkoxyoxalyloxy)iodo]benzene (0.5 mmol) in dry toluene (5 ml) was added 1,4-cyclohexadiene (5 equiv.). The mixture was heated to about 100 °C and irradiated with high-pressure mercury lamp under thermal conditions. Method 2: To the solution of phenyl vinyl sulfone (0.5 mmol) and [bis(alkoxyoxalyloxy)iodo]benzene (0.5 mmol) in dry dichloromethane (50 ml, *c*0.01 M) was added 1,4-cyclohexadiene (5 equiv.) under argon atmosphere and the mixture was irradiated with high-pressure mercury lamp at 30 °C. After the reaction in each method, the residue was worked up by usual way using pTLC on silica gel.

2-[(-)-Menthyl]ethyl phenyl sulfone (P-1k): oil (diastereomeric mixture, 79 : 21); IR (neat) 2860, 1440, 1290, 1140, 1080, 735, 685 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.58 and 0.65 (d, 3H, J = 12.7 and J = 7.1 Hz), 0.73-0.98 (m, 8H), 1.22-1.94 (m, 10H), 2.94-3.20 (m, 2H), 7.52-7.68 (m, 3H), 7.84-7.95 (m, 2H); HRMS (Fab) Calcd for $C_{18}H_{29}O_2S$, m/e = 309.1887. Found: m/e = 309.1891; Anal. Calcd for $C_{18}H_{28}O_2S$: C, 70.08; H, 9.15 %. Found: C, 70.24; H, 9.46 %.

Lactonization of Phenyl Vinyl Sulfone. The reaction was carried out with molar ratio of 0.5 / 0.5 / 2.5 (mmol) (phenyl vinyl sulfone / [bis(alkenoxyoxalyloxy)iodo]benzene / 1,4-cyclohexadiene). To the solution of phenyl vinyl sulfone and [bis(alkenoxyoxalyloxy)iodo]benzene in dry dichloromethane (5 ml) was added 1,4-cyclohexadiene and the resulting mixture was irradiated with high-pressure mercury lamp. The residue was worked up by the same procedure described above.

5-Methyl-3-(3-benzenesulfonylpropyl)tetrahydro-2-furanone.(P-10m): oil (diastereomeric mixture, 76 : 24); IR (neat) 2900, 1740, 1440, 1280, 1175, 1130, 950, 730, 690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.36 and 1.41 (d, 3H, J = 6.5 and J = 6.0 Hz), 1.50-1.63 (m, 1H), 1.80-2.08 (m, 4H), 2.44-2.67 (m, 2H), 3.10-3.17 (m, 2H), 4.42-4.55 and 4.63-4.75 (m, 1H), 7.57-7.72 (m, 3H), 7.85-7.95 (m, 2H); Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43 %. Found: C, 59.49; H, 6.45 %.

3-(3-Benzenesulfonylpropyl)tetrahydro-2-furanone.(P-10n); oil; IR (neat) 2900, 1750, 1440, 1290, 1150, 1020, 740, 700 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.58-1.67 (m, 1H), 1.82-2.01 (m, 4H), 2.35-2.60 (m, 2H), 3.10-3.19 (m, 2H), 4.18 (td, 1H, J_1 = 8.6, J_2 = 7.1 Hz), 4.35 (td, 1H, J_1 = 8.6, J_2 = 2.7 Hz), 7.57-7.72 (m, 3H), 7.90 (dt, 2H, J_1 = 7.1, J_2 = 1.5 Hz); Anal. Calcd for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01 %. Found: C, 58.45; H, 6.11 %.

Reaction to Trap Alkyl Radical with TEMPO. The mixture of TEMPO and (diacyloxyiodo)benzene {or [bis(alkoxyoxalyloxy)iodo]benzene} in dry dichloromethane (5 ml) was irradiated at 30°C. After the reaction, the mixture was worked up by usual way.

(P-4): mp 87-90°C; IR (KBr) 2850, 1440, 1345, 1130, 1050, 920, 710 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.00-1.65 (m, 12H), 1.08 (s, 6H), 1.18 (s, 6H), 1.85-1.95 (m, 6H), 2.13 (bs, 3H); HRMS (Fab) Calcd for $C_{19}H_{34}NO$, m/e = 292.2639. Found: m/e = 292.2640.

(P-9): oil; IR (neat) 2860, 1720, 1440, 1340, 1210, 1180, 1025 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.10 (s, 6H), 1.15 (s, 6H), 1.30-1.80 (m, 11H), 2.10-2.18 (m, 10H); HRMS (Fab) Calcd for $C_{20}H_{34}NO_3$, m/e = 336.2537. Found: m/e = 336.2539.

References

1) Reviews: Varvoglis, A. *Synthesis*, **1984**, 709-726; Ochiai, M.; Nagao, Y. *J. Synth. Org. Chem., (Japan)*, **1986**, *44*, 660-673; Umemoto, T. *ibid*, **1983**, *41*, 251-265; Moriarty, R. M.; Vaid, R. K. *Synthesis*, **1990**, 431-447.

Papers: Decomposition of (Diacyloxyiodo)arenes: Leffler, J. E.; Story, L. J. *J. Am. Chem. Soc.*, **1967**, *89*, 2333-2338; Leffler, J. E.; Ward, D. C.; Burduroglu, A. *ibid.*, **1972**, *94*, 5339-5341.

Carbon-Carbon Bond Formations: Karelsky, M.; Pausacker, K. H. *Aust. J. Chem.*, **1958**, *11*, 39-41; Sandin, R. B.; Brown, R. K. *J. Am. Chem. Soc.*, **1947**, *69*, 2253-2254; Hernández, R.; Marrero, J. J.; Suárez, E. *Tetrahedron Lett.*, **1989**, *30*, 5501-5504; Dektar, J. L.; Hacker, N. P. *J. Org. Chem.*, **1990**, *55*, 639-647; Callinan, A; Chen, Y.; Morrow, G. W.; Swenton, J. S. *Tetrahedron Lett.*, **1990**, *31*, 4551-4552.

Functionalization and Fragmentation: Furuta, K.; Nagata, T.; Yamamoto, H. *Tetrahedron Lett.*, **1988**, *29*, 2215-2218; Concepción, J. I.; Francisco, C. G.; Freire, R.; Hernández, R.; Salazar, J. A.; Suárez, E. *J. Org. Chem.*, **1986**, *51*, 402-404; Singh, R.; Just, G. *Synth. Commun.*, **1988**, *18*, 1327-1330; Concepción, J. I.; Francisco, C. G.; Hernández, R.; Salazar, J. A.; Suárez, E. *Tetrahedron Lett.*, **1984**, *25*, 1953-1956; Freire, R.; Marrero, J. J.; Rodriguez, M. S.; Suárez, E. *ibid*, **1986**, *27*, 383-386; Freire, R.; Hernández, R.; Rodriguez, M. S.; Suárez, E. *ibid*, **1987**, *28*, 981-984; Stang, P. J.; Boehshar, M.; Wingert, H.;

Kitamura, T. *J. Am. Chem. Soc.*, **1988**, *110*, 3272-3278; Brimble, M. A.; Williams, G. M.; Baker, R.; James, M. *Tetrahedron Lett.*, **1990**, *21*, 3043-3046; Armas, P.; Carrau, R.; Concepción, J. I.; Francisco, C. G.; Hernández, R.; Suárez, E. *ibid*, **1985**, *26*, 2493-2496; Francisco, C. G.; Freire, R.; Rodriguez, M. S.; Suárez, E. *ibid*, **1987**, *28*, 3397-3400; Hernández, R.; Marrero, J. J.; Suárez, E. *ibid*, **1988**, *29*, 5979-5982; Barret, R.; Daudon, M. *ibid*, **1990**, *31*, 4871-4872; Ellwood, C. W.; Pattenden, G. *ibid*, **1991**, *32*, 1591-1594; Boto, A.; Betancor, C.; Prange, T.; Suárez, E. *ibid*, **1992**, *33*, 6687-6690; Kita, Y.; Tohma, H.; Inagaki, M.; Hatanaka, K.; Yakura, T. *ibid*, **1991**, *32*, 4321-4324; Galatsis, P.; Millan, S. D. *ibid*, **1991**, *32*, 7493-7496; Tingoli, M.; Tiecco, M.; Chianelli, D.; Balducci, R.; Temperini, A. *J. Org. Chem.*, **1991**, *56*, 6809-9813; Boutin, R. H.; Loudon, G. M. *J. Org. Chem.*, **1984**, *49*, 4277-4284; Motherwell, W. B.; Wilkinson, J. A. *Synlett*, **1991**, 191-192.

2) Carboxylic acid: Togo, H.; Aoki, M.; Yokoyama, M. *Tetrahedron Lett.*, **1991**, *32*, 6559-6562; Minisci, F.; Vismara, E.; Fontana, F.; Barbosa, M. C. N. *ibid*, **1989**, *30*, 4569-4572.

Alcohol: Togo, H.; Aoki, M.; Yokoyama, M. *Chem. Lett.*, **1991**, 1691-1694.

3) Giese, B. "Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds," ed by Baldwin, J. E. Pergamon Press, Oxford (1986); Curran, D. P. *Synthesis*, **1988**, 417-439 and 489-513; Giese, B., "Tetrahedron Symposia-In-Print," *Tetrahedron*, **1985**, *41*, 3887-4302; Ueno, Y. *J. Synth. Org. Chem*, **1984**, *42*, 1121-1131; Ramaiah, M. *Tetrahedron*, **1987**, *43*, 3541-3676.

4) Reviews: Reaction with Acyl Derivatives of N-Hydroxy-2-thiopyridone: Barton, D. H. R.; Zard, S. Z. *Pure Appl. Chem.*, **1986**, *58*, 675; Barton, D. H. R. *Aldrichimica Acta*, **1990**, *23*, 3-10; Crich, D.; Quintero, L. *Chem. Rev.*, **1988**, *89*, 1413-1432; Crich, D. *Aldrichimica Acta*, **1987**, *20*, 35-43; Togo, H.; Fujii, M.; Yokoyama, M. *J. Synth. Org. Chem., (Japan)*, **1990**, *48*, 644-657.

Papers: Addition to Vinyl Sulfone Derivatives: Barton, D. H. R.; Togo, H.; Zard, S. Z. *Tetrahedron Lett.*, **1985**, *26*, 6349-6352; Barton, D. H. R.; Sarma, J. C. *ibid*, **1990**, *31*, 1965-1968; Padwa, A.; Murphree, S. S.; Yeske, P. E. *ibid*, **1990**, *31*, 2983-2986; Boivin, J.; Crépon, E.; Zard, S. Z. *ibid.*, **1991**, *32*, 199-202; Barton, D. H. R.; Chern, C-Y.; Jaszberenyi, J. Cs. *ibid*, **1991**, *32*, 3309-3312; Okada, K.; Okamoto, K.; Morita, N.; Okubo, K.; Oda, M. *J. Am. Chem. Soc.*, **1991**, *113*, 9401-9402; Barton, D. H. R.; Boivin, J.; Sarma, J.; Silva, E.; Zard, S. Z. *Tetrahedron Lett.*, **1989**, *30*, 4237-4240.

5) Togo, H.; Aoki, M.; Yokoyama, M. *Chem. Lett.*, **1992**, 2169-2172.

6) Inamoto, N.; Masuda, S. *Chem. Lett.*, **1982**, 1007-1010.

7) Thiocarbonate Type: Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1574-1585; Barton, D. H. R.; Motherwell, W. B.; Stange, A. *Synthesis*, **1981**, 743-746; Barton, D. H. R.; Hartwig, W.; Hay-Motherwell, R. S.; Motherwell, W. B.; Stange, A. *Tetrahedron Lett.*, **1982**, *23*, 2019-2022.

Methyl Oxalate Type: Lemieux, R. P.; Beak, P. *J. Org. Chem.*, **1990**, *55*, 5454-5460; Dolan, S. C.; MacMillan, J. *J. Chem. Soc., Chem. Commun.*, **1985**, 1588-1589.

N-Hydroxy-2-thiopyridone: Barton, D. H. R.; Crich, D. *Tetrahedron Lett.*, **1985**, *26*, 757-760; Barton, D. H. R.; Crich, D. *J. Chem. Soc., Chem. Commun.*, **1984**, 774-775; Crich, D.; Fortt, S. M. *Synthesis*, **1987**, 35-37; Togo, H.; Fujii, M.; Yokoyama, M. *Bull. Chem. Soc. Jpn.*, **1991**, *64*, 57-67; Togo, H.; Yokoyama, M. *Heterocycles*, **1990**, *31*, 437-441.

8) Parham, W. E.; Blake, F. D.; Theissen, D. R. *J. Org. Chem.*, **1962**, *27*, 2415-2419; Tarbell, D. S.; McCall, M. A. *J. Am. Chem. Soc.*, **1952**, *74*, 48-56.

9) Pausacker, K. H. *J. Chem. Soc.*, **1953**, 107-109; Gustafsson, J.; Rondahl, L.; Bergman, *J. Biochemistry*, **1979**, *18*, 865-870.

10) Schmeisser, M.; Dahmen, K.; Sartori, P. *Chem. Ber.*, **1967**, *100*, 1633-1637.

11) Stang, P. J.; Boehshar, M.; Wingert, H.; Kitamura, T. *J. Am. Chem. Soc.*, **1988**, *110*, 3272-3278; Merkushev, E. B.; Novikov, A. N.; Makarchenko, S. S.; Moskalchuk, A. S.; Glushkova, V. V.; Kogai, T. I.; Polyakova, L. G. *Zh. Org. Khim.*, **1975**, *11*, 1259-1262.