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Reductive Addition of Alkyl Radical to Phenyl Vinyl Sulfone

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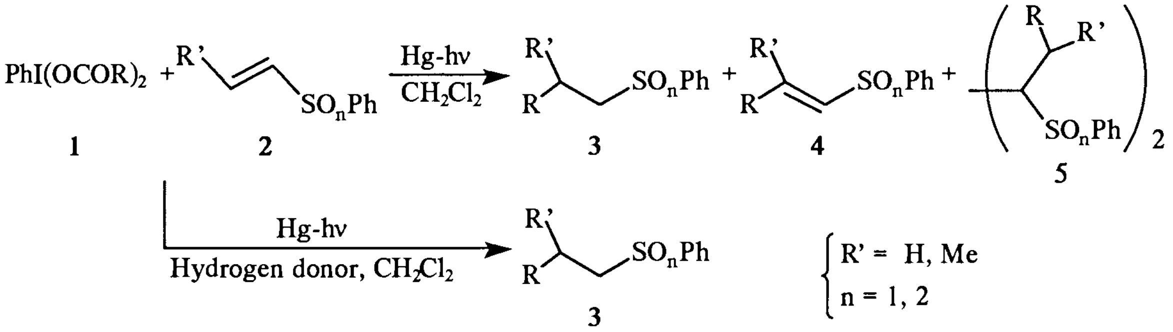
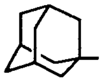
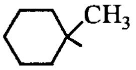
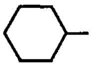
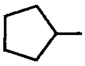
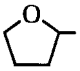
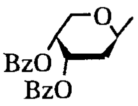
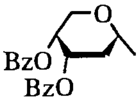
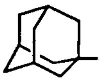
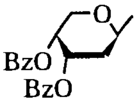
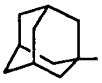
Radicals generated from (diacyloxyiodo)benzene readily added to phenyl vinyl sulfone to give 2-alkylethyl phenyl sulfone in the presence of a hydrogen donor such as 1,4-cyclohexadiene, 1,3-dioxolane, or triethylsilane. Among these donors, 1,4-cyclohexadiene was the most effective.

The addition of an alkyl radical to an electron-deficient olefin has been well studied and extensively used in organic synthesis.1) However, most of the precursors for the radicals are alkyl halides, sulfides, selenides, and xanthates. Carboxylic acids have not been studied widely as a radical precursor. One reaction is the Barton's decarboxylative reaction of N-acyloxy-2-thiopyridone,2) another is the decarboxylative reaction with N-(acyloxy)phthalimides using a complex redox system such as $Ru(bpy)_3Cl_2$ and 1-benzyl-1,4-dihydronicotinamide (BNAH).3) In the former method, 2-thiopyridyl group is always introduced to the α-position of an electron-deficient group, while hydrogen is introduced to this position in the latter method.



We report herein a simple and effective method for the addition of an alkyl radical to an electron-deficient olefin using a trivalent iodine compound. The radical reaction with trivalent iodine compounds has been extensively studied by Suárez et al.4) Recently, we and Minisci also reported a nucleophilic alkyl radical substitution of heteroaromatic bases in a decarboxylative manner by employing a trivalent iodine compound as a radical precursor.5) However, the addition of the alkyl radical formed via the decarboxylation of the trivalent iodine compound to an olefinic compound has never been studied. As shown in Table 1,6) the reaction was carried out in the presence of phenyl vinyl sulfone and various hydrogen atom donors under irradiation with a high pressure mercury lamp. When dichloromethane, trioxane, or trimethyl orthoformate was used as a hydrogen donor, a mixture of **3**, **4** (trans isomer), and **5** (a single isomer) was obtained without selectivity. Here, **3** is the reductive addition product, **4** is the substituted product, and **5** is the dimer product of α-sulfonyl radical. In principle, the compounds **3** and **4** are disproportionated products. Therefore, the same amounts of **3**

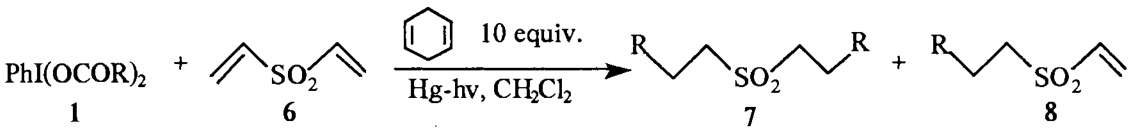
Table 1. Reaction with Phenyl Vinyl Sulfone[a]

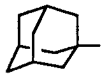
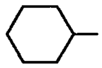
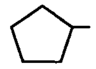
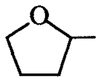
Entry	1, R-	2	Hydrogen donor	Yields / %			
				3	4	5	Total
1		R' = H, n = 2	-	15	9	13	33
2	"	"	-	16	16	20	52[b]
3	"	"	$CH(OMe)_3$, 1 ml	15	12	17	44
4	"	"	Trioxane, 20 equiv.	17	11	15	43
5	"	"	THF, 1 ml	37	1	3	41
6	"	"	1,3-Dioxolane, 1 ml	52	5	5	62
7	"	"	Et_3SiH, 10 equiv.	54	2	0	56[c]
8	"	"	 , 2 equiv.	86	-	-	86
9	"	"	" , 5 equiv.	99	-	-	99
10		"	"	90	-	-	90
11		"	"	88	-	-	88
12		"	"	82	-	-	82
13		"	"	44	-	-	44
14		"	"	67	-	-	67
15		"	"	73 (4:1)[d]	-	-	73
16		"	"	74 (1:2)[d]	-	-	74
17		R' = H, n = 1	"	53	-	-	53
18		"	"	31	-	-	31
19		R'= Me, n = 2	" , 2 equiv.	50	-	-	50

a) The mole ratio of **1** / **2** was 0.5 / 0.5 (mmol). b) The reaction was carried out at 0-5 °C.
c) Adamantane was obtained in 4% yield. d) The ratio of β / α.

and 4 are formed in dichloromethane (entry 2). However, in the presence of a hydrogen donor such as 1,3-dioxolane or triethylsilane, the reductive addition product was obtained as a major product and as a sole product with 1,4-cyclohexadiene. The addition product **3** was obtained in good to moderate yields with tertiary, secondary, and primary carboxylic acids. In addition, the compounds **1** derived from tetrahydrofurancarboxylic acid and 3,4-di-O-benzoyl-2-deoxy-D-ribopyranosecarboxylic acid also reacted with phenyl vinyl sulfone to give the corresponding adducts **3** in good yields. Thus, this result suggests that this reaction can be applied to the synthesis of C-nucleosides.

Table 2. Reaction with Divinyl Sulfone



Entry	R-	1/6 (mole ratio)	Yields / % 7	Yields / % 8
1		1	13	63
2	»	3	87	-
3		3	70	-
4		3	78	-
5		3	36	-

This method is applicable to other functionalized olefins. When **1** was treated with phenyl vinyl sulfoxide, the reductive addition product was obtained in moderate yield (entries 17 and 18), while the method with N-acyloxy-2-thiopyridone failed to react with phenyl vinyl sulfoxide effectively.[2)] Furthermore, by using phenyl 1-propenyl sulfone having a methyl group at the reaction position, the reductive addition product **3** was obtained in 50% yield (entry 19), while again the reaction with N-acyloxy-2-thiopyridone failed to give the adduct effectively. When divinyl sulfone having two reactive positions was treated with a trivalent iodine compound **1**, the double addition product **7** and single addition product **8** were obtained as shown in Table 2. Using one equivalent of **1**, compounds **7** and **8** were obtained in 13% and 63% yields, respectively (entry 1). However, the use of excess **1** gave the double addition compound **7** in 87% yield as a sole product (entry 2). When **8** (R=adamantyl) was treated again with **1** (R=cyclohexyl), an unsymmetrical sulfone, 2-adamantylethyl 2-cyclohexylethyl sulfone was obtained in 70% yield. The radical addition reaction to an electron-deficient olefins with a trivalent iodine compound is a promising new field in hypervalent iodine chemistry and is applicable to the synthesis of organic compounds. The detailed reaction mechanism and further applications are underway in this laboratory.

The typical experimental procedure is as follows: To a mixture of phenyl vinyl sulfone (0.5 mmol) and (di-1-adamantanecarboxyiodo)benzene (0.5 mmol) in dichloromethane (5 ml) was added 1,4-cyclohexadiene (2.5 mmol). The mixture was irradiated with a high pressure mercury lamp for 15 min at about 30 °C under argon atmosphere. After the reaction, the mixture was washed with sat. $NaHCO_3$ aqueous solution. The organic layer was dried over Na_2SO_4. After the removal of the solvent, the residue was chromatographed on silica gel to give 150 mg of 2-(1-adamantyl)ethyl phenyl sulfone in 99% yield. Acidification of the water layer with 2 M HCl (1 M=1 mol dm^{-3}) and extraction with ether gave 0.17 mmol of adamantanecarboxylic acid.

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6) All the compounds gave satisfactory spectroscopic and microanalytical data.

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