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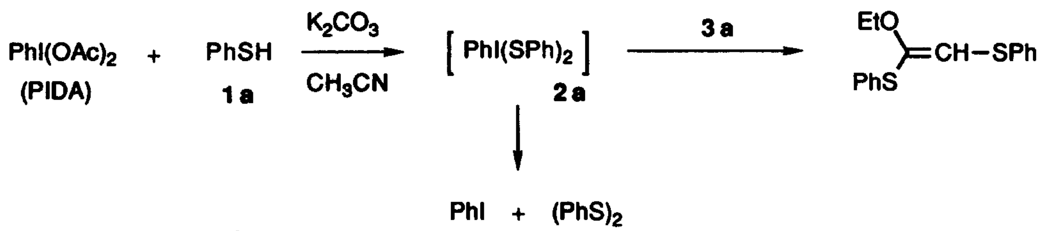
Preparation of Bis(arylthio)iodobenzene and Reaction with 1-Alkynes. A Novel Route to 1,2-Bis(arylthio)alkenes

Yasuyuki Kita,* Takayuki Okuno, Hirofumi Tohma, and Shuji Akai
Faculty of Pharmaceutical Sciences, Osaka University, 1-6, Yamada-oka, Suita, Osaka 565, JAPAN
Keita Matsumoto
Research Center, Taisho Pharmaceutical Co., Ltd., Yoshino-cho, Omiya, Saitama 330, JAPAN

Summary: The *in situ* reaction of a novel hypervalent iodine reagent **2b** having an arylthio ligand, prepared from phenyliodine diacetate and 2,3,5,6-tetrafluorothiophenol **1b** in pyridine, with 1-alkynes **3** gave 1,2-bis(arylthio)alkenes **4** in good yields.

Recently, hypervalent iodine reagents have been extensively used in organic syntheses due to their low toxicity, ready availability, and easy handling.[1] Although various types of reagents having electron negative halogen or oxygen ligands have been developed, the study of reagents having sulfur ligands has been limited[2] probably due to the easy oxidation of thiols or thiophenols to the corresponding disulfides by their reaction with hypervalent iodine reagents such as phenyliodine diacetate (PIDA).[3] We present here the preparation of a novel hypervalent iodine reagent **2b** having an arylthio ligand from PIDA and 2,3,5,6-tetrafluorothiophenol **1b** in pyridine and some reactions with 1-alkynes **3a-e** leading to 1,2-bis(arylthio)alkenes **4a-e** in good yields.

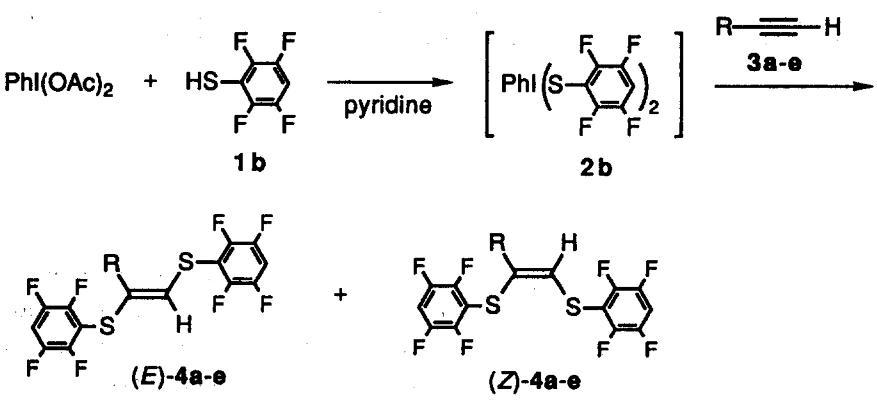
At first, we examined the preparation of bis(phenylthio)iodobenzene **2a** by the ligand exchange reaction of PIDA and 2 equiv of thiophenol **1a** in the presence of K_2CO_3 in various solvents including CH_3CN, CH_2Cl_2, THF, DMF, and CF_3CH_2OH. However, the oxidation to diphenyldisulfide was so rapid that we could not obtain any **2a**. We have, however, disclosed that similar treatment of PIDA with **1a** in CH_3CN at room temperature for 2 min followed by the addition of ethoxyacetylene **3a** provided a 30% yield of 1-ethoxy-1,2-bis(phenylthio)ethene along with a large amount of diphenyldisulfide (Scheme 1). A similar reaction of **3a**



Scheme 1

with the electron deficient chloro-, dichloro-, trichloro-, and nitrothiophenols as well as electron rich methyl- and methoxythiophenols in the presence of PIDA could not improve the yields of the 1,2-bis(arylthio)ethenes but mainly resulted in the formation of the diaryldisulfides.

Finally, we found a promising method using electron deficient 2,3,5,6-tetrafluorothiophenol **1b** and pyridine as the solvent and the base. Thus, under a nitrogen atmosphere, PIDA (0.31 g, 0.98 mmol) was added to a clear yellow solution of 2,3,5,6-tetrafluorothiophenol **1b** (0.155 mL, 1.30 mmol) in pyridine (3 mL) with vigorous stirring at room temperature. Within one minute, the reaction mixture turned colorless, to which was then added a solution of ethoxyacetylene **3a** (23 mg, 0.33 mmol) in pyridine (0.5 mL). The reaction mixture gradually turned yellow. After stirring for 30 min, the reaction mixture was concentrated *in vacuo* and purified by SiO_2 column chromatography (hexane-AcOEt 99:1) to give an 89% yield of the 1,2-bis(arylthio)ethene **4a** (R = EtO) as a 77:23 mixture of the (*E*)- and (*Z*)-isomers (Scheme 2). The structure of **4a** was determined by IR, ^1H NMR, and high resolution mass spectral data,[4] and its geometry was unambiguously confirmed by X-ray analysis of pure (*E*)-**4a** (Fig. 1).



Scheme 2

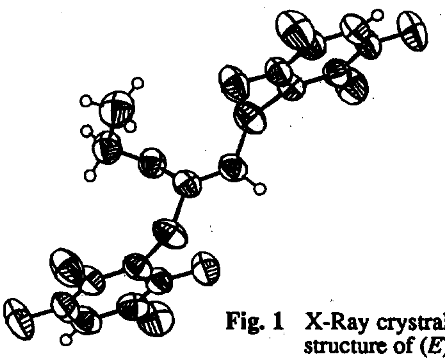


Fig. 1 X-Ray crystrallographic structure of (*E*)-**4a**

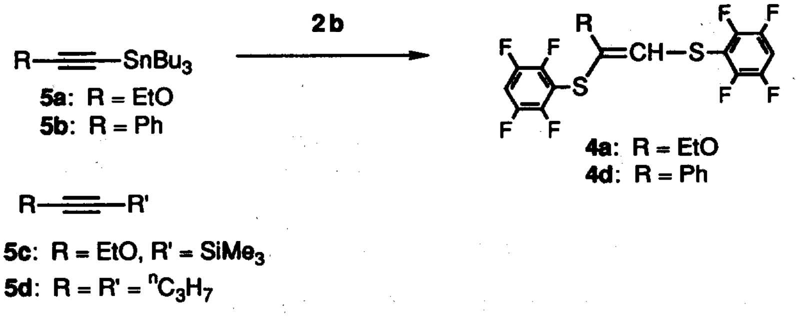
Similarly, various terminal alkynes **3b-e** reacted with **2b** to give the corresponding 1,2-bis(arylthio)-alkenes **4b-e** in good yields. The results are listed in Table 1.

Table 1. Preparation of 1,2-bis(arylthio)alkenes **4** by the reaction of PIDA, 2,3,5,6-tetrafluorothiophenol **1b**, and the alkynes **3**.

Run	Alkyne 3		1,2-Bis(arylthio)alkene 4			
					yield (%)[a]	(*E*) : (*Z*)
1	EtO—≡—H	**3a**	R = EtO	**4a**	89	77 : 23[b]
2	ᵗBuO—≡—H	**3b**	R = ᵗBuO	**4b**	48	98 : 2[c]
3	PhS—≡—H	**3c**	R = PhS	**4c**	87	66 : 34[c]
4	Ph—≡—H	**3d**	R = Ph	**4d**	88	43 : 57[c]
5	$^{n}C_6H_{13}$—≡—H	**3e**	R = $^{n}C_6H_{13}$	**4e**	48	80 : 20[d]

[a] Isolated yield by SiO_2 column chromatography is shown. [b] The geometry was determined by X-ray analysis of pure (*E*)-**4a**. [c] The geometry was estimated by similarity of their ^1H NMR data to those of **4a**. [d] The geometry was determined by the NOE experiment.

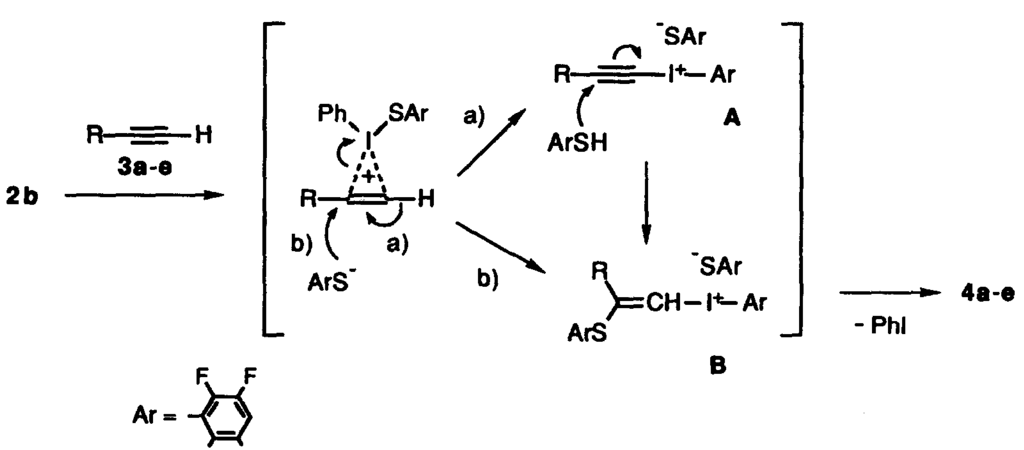
The reaction of 1-stannylalkynes **5a, b** with **2b** gave the protodestannylated 1,2-bis(arylthio)alkenes **4a, d**, but the yields were lower (64% and 34% yields, respectively) than those of the terminal alkynes **3a, d**.[5] The 1-silylalkyne **5c** and the internal alkyne **5d** did not react with **2b** at all (Scheme 3).



Scheme 3

Although the isolation of the iodine reagent **2b** having an arylthio ligand failed due to its fast decomposition to the disulfide, we consider the formation of **2b** to be attained by the following observations: (i) a yellow color of the anion of **1b** in pyridine turned colorless when PIDA was added and (ii) the use of a slight excess of PIDA for generation of **2b** is essential for good yields of **4**. In this case, the excess PIDA is recovered. The subsequent reaction of **2b** with **3** may be announced to proceed through the alkynyliodonium salt **A** and/or the alkenyliodonium salt **B** to give **4** similar to the reactions of alkynes with PIDA[6] and (hydroxy)-

tosyloxyiodobenzene[1g] and related reactions through vinyliodonium salts[7] (Scheme 4). Studies of the generality of this reaction and the reaction mechanism preferentially giving (*E*)-**4** are in currently progress.



Scheme 4

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4. (*E*)-**4a**: mp 46-46.5 °C (hexane-CH_2Cl_2); IR ($CHCl_3$) 1632, 1495 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.27 (3 H, t, $J = 7$ Hz), 4.10 (2 H, q, $J = 7$ Hz), 6.03 (1 H, s), 7.01-7.17 (2 H, m); HRMS calcd for $C_{16}H_8OF_8S_2$: 431.9888, found: 431.9908. (Z)-**4a**: ^{1}H NMR ($CDCl_3$) δ 1.12 (3 H, t, $J = 7$ Hz), 3.91 (2 H, q, $J = 7$ Hz), 5.50 (1 H, s), 6.95-7.17 (2 H, m).
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