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Photochemically Induced Coupling Reaction of Triarylstibines with Olefins

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Abstract: Photoreaction of triarylstibines with styrenes resulted in the formation of 2-aryl-1-phenylethanols accompanied by air oxidation. Formation of the products has been explained by the valence expansion of the oxygen-antimony-styrene complex to a five-valent intermediate, followed by reductive coupling.

Keywords: *antimony and compounds ; photochemistry ; coupling reactions ; oxidation.*

Photolysis of typical metal perphenyls is known to form the corresponding metals and a phenyl radical. For example, irradiation of group 14 metal perphenyls such as tetraphenyltin and tetraphenyllead at 253.7 nm gives biphenyl.[1] Similar photochemical behavior can also be observed in group 15 metal perphenyls.[1-3] As for organoantimony compounds,[4] photolysis of pentaphenylstiborane[5] and triphenylstibine[3,6] has been reported to also form biphenyl. The initial step of these photoreactions is thought to be homolytic cleavage of the carbon-metal bond of the metal perphenyls.

We report here that the photoreaction of triarylstibines **1** with styrene **2** resulted in a coupling reaction to give the corresponding 2-aryl-1-phenylethanols **3**, probably *via* several intermediates derived from the initially formed antimony-oxygen complex **4** and *via* no radical species.

First, the photoreaction of triphenylstibine **1a** with styrene **2** was carried out under various reaction conditions and the results are summarized in Table 1. Irradiation of a mixture of **1a** and **2** with a high-pressure mercury lamp through a Pyrex filter (>300 nm) produced better results than with a low-pressure mercury lamp (253.7 nm). Irradiation with a halogen lamp (>400 nm) gave no 1,2-diphenylethanol **3a** and **1a** remained virtually unchanged. Also apparent was that the oxygen atom in the hydroxy moiety on the product originated not in water but in air, but progressive addition of oxygen by circulating dry air or oxygen into the reaction mixture suppressed the formation of **3a**, presumably because of the decomposition of **1a**. When the reaction was carried out under an aerobic oxidation condition (open) in carbon tetrachloride, the best result was obtained, giving **3a** in moderate yield (48%)[7] (run-8). Neither promotion nor inhibition of the reaction was observed when the irradiation was performed in the presence of 10% AIBN or 10% BHT (run-11, 12). The results

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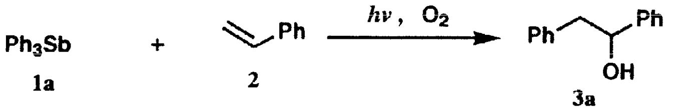
suggest that, unlike the photolysis of pentaphenylstiborane[5] and triphenylstibine[3], no radical species participates in this photoreaction.

Table I : Reaction of Triphenylstibine with Styrene

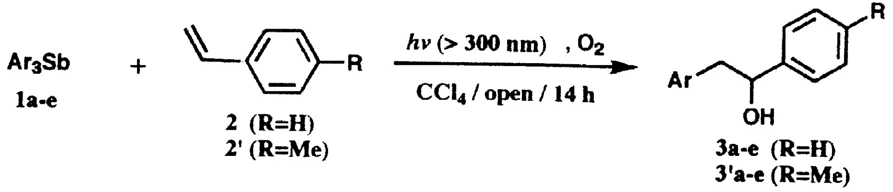


Run	Light source	Experimental conditions			Yield (%) of **3a**
1	A	acetone	open	14 h	30
2	A	acetone	dry air (20 ml/min)	14 h	8*
3	A	acetone	O_2 (20 ml/min)	2 h	rapid decomposition of **1a**
4	A	acetone / 5% H_2O	argon	10 h	3% (recovery of **1a** 90%)
5	A	CH_3CN	open	14 h	28
6	A	benzene	open	14 h	16
7	A	ether	open	14 h	13
8	A	CCl_4	open	14 h	48
9	B	CH_3CN	open	9 h	7
10	C	CCl_4	open	21 h	no reaction
11	A	acetone	open (10% AIBN)	14 h	30
12	A	acetone	open (10% BHT)	14 h	25

A; Pyrex-filtered high-presssure Hg lamp (>300 nm)
B; Quartz-filtered low-presssure Hg lamp (254 nm)
C; Halogen lamp (>400 nm)
*Bisides **3a**, 2-phenylacetophenone was formed in 12% yield.

Photoreactions of various triarylstibines **1a-e** with styrenes **2** and **2'** were also examined under the conditions shown below. In all cases, the corresponding secondary alcohols **3a-e** and **3'a-e** were obtained (Table II).

Table II : Reactions of Triarylstibines with Styrenes

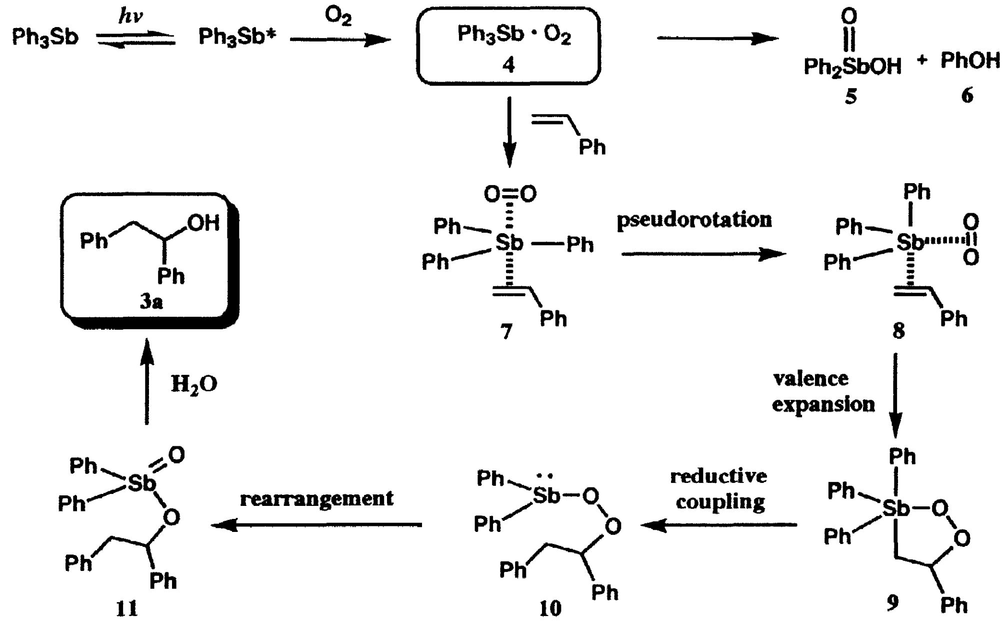


	Ar	R	Yield (%)
a	Ph	H	48
		Me	35
b	*o*-Tol	H	40
		Me	29
c	*p*-Tol	H	27
		Me	27
d	*p*-anisyl	H	32
		Me	25
e	*p*-fluorophenyl	H	40
		Me	14

Air oxidation of trivalent organophosphorous compounds is known to be stimulated more at the excited state than at the ground state by UV irradiation.[9] Razuvaev *et al.* have recently reported that triphenylstibine **1a**, excited at 253.7 nm, forms a labile reversible antimony-oxygen complex **4**, which converts into diphenylstibinic acid **5** and phenol **6** *via* rearrangement and hydrolysis.[6] We also found that the irradiation of triphenyl-, tri-*p*-tolyl-, and tri-*p*-fluorophenyl-stibine with a Pyrex-filtered high-pressure mercury lamp in carbon tetrachloride in air in the absence of styrene gave the corresponding phenols in 10~15 % yields. These results suggest that the antimony-oxygen complex **4** should be involved as a key intermediate in the present coupling reaction.

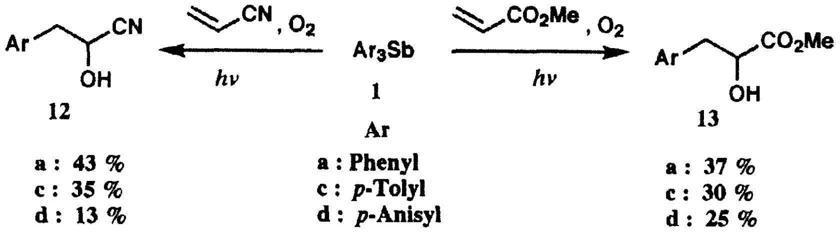
A plausible mechanism of this coupling reaction is shown in Scheme 1. The styrene molecule may approach the antimony-oxygen complex **4** from an apical direction due to non-bonding interaction. The intermediate **7** thus formed could be isomerized to **8** by pseudorotation[10] of the five substituents on the antimony atom, and the resulting **8** converts into the more stable five-valent cyclic peroxide intermediate **9**. Formation of the intermediate **9** might be attributed to the superior ability of valence expansion of the group 15 heavier elements.[4c,11] The reductive coupling of an apical phenyl substituent with the apical styrene moiety on the intermediate **9** affords the three-valent antimony intermediate **10**, which undergoes rearrangement into **11**, followed by hydrolysis to give rise to 1,2-diphenylethanol **3a**.[12] It is noteworthy that the formation of phenol is not observed in the present photo-coupling reaction, indicating the antimony-oxygen complex **4** is highly reactive with olefins and the formation of the antimony-styrene complex **7** predominates over the rearrangement into **5** and **6**.

Scheme I



We have also demonstrated that this reaction ca be applied to the formation of cyanohydrines and α-hydroxy esters. Irradiation of triarylstibines **1** in the presence of acrylonitrile or methyl acrylate instead of styrene under similar conditions gave the corresponding cyanohydrines **12** or α-hydroxy esters **13**, respectively[13, 15] (Scheme II).

Scheme II



In summary, we have found that irradiation of triarylstibines in the presence of styrenes in air resulted in a coupling reaction to give 2-aryl-1-phenylethanols and the mechanism of this new photo-coupling reaction was discussed. Further details of the mechanism of this coupling reaction are now under investigation.

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References and Notes

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[7] In a typical procedure, a solution of triphenylstibine **1a** (8.00 mmol) and styrene **2** (80.0 mmol) in 400 ml of carbon tetrachloride was irradiated for 14 h with a Pyrex-filtered mercury lamp (400W, Ushio Inc.). After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel (hexane : ethyl acetate = 9 : 1) to give 1,2-diphenylethanol **3a** (760 mg, 48%), mp 64~65℃ (lit.[8] mp 63.5~65℃).

[8] Hoeg DF, Lusk DI. J. Organometal. Chem. 1966;5:1-12.

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[12] As noted above, photolysis of triphenylstibine in the absence of olefins resulted mainly in decomposition to form only phenol in low yield. The relatively low yields of **3** in the present reaction may be caused by this unspecified decomposition.

[13] For example, the reaction of triphenylstibine **1a** (8.00 mmol) and acrylonitrile (80.0 mmol) gave 2-hydroxy-3-phenylpropanenitrile **12a** (506 mg, 43%), mp 56~57℃ (lit.[14] mp 56~58℃).

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[15] However, the reaction of **1** with electron-rich ethyl vinyl ether gave a complex mixture and no characterizable products.