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1-[(아릴)(페닐셀레노)메틸]벤조트리아졸과 셀렌화 6-아릴-6-(벤조트리아졸-1-일)-1-헥센일 페닐의 삼부틸틴 수소화물과의 반응메카니즘에 관한 연구

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Mechanistic Studies on the Reactions of 1-[(Aryl)(phenylseleno)methyl] benzotriazoles and 6-Aryl-6-(benzotriazol-1-yl)-1-hexenyl Phenyl Selenides with Tributyltin Hydride

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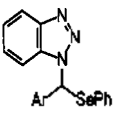
요 약. 벤조트리아졸을 보조체로 사용하는 유기합성법은 거의 대부분 이온성 반응 메카니즘으로 설명되며 라디칼 반응을 이용한 벤조트리아졸의 응용은 거의 없었다. 벤조트리아졸의 N-1의 α 위치 탄소 원자에 라디칼 중심을 만든 후 벤조트리아졸의 다섯고리를 형성하는 질소 원자중에서 질소 분자가 빠져나감으로서 생성되는 페닐 라디칼의 반응을 연구하기위해 1-[(aryl)(phenylseleno)methyl]benzotriazole, AIBN, 그리고 Bu_3SnH을 벤젠에 용해시키고 환류시켜 주었다. 이 반응 혼합물로 부터 2-aminodiphenyl selenide (16~29%), 2-aminobiphenyl (9~15%), diphenyl diselenide (30~93%), 1-(arylmethyl)benzotriazole (9~39%), 그리고 tributyltin-phenyl selenide (10~36%)을 얻었으며, AIBN없이 과량의 Bu_3SnH 존재하에 같은 조건하에서 반응시키는 경우, diphenyl diselenide (53~100%), benzotriazole (27~35%) 그리고 1-(arylmethyl)-benzotriazole (16~33%)와 함께 arylmethylidenaniline이 과량의 Bu_3S_nH에 의해 환원된 N-(arylmethyl)anilines (44~66%)이 생성되었다. 같은 조건 하에서 6-aryl-6-(benzotriazol-1-yl)-1-hexenyl phenyl selenides, AIBN, 그리고 Bu_3SnH의 반응으로부터 6-aryl-6-phenylamino-1-hexene (9~31%)과 1-aryl-1-oxo-5-pentene (15~44%)을 얻었다. 이들 생성물의 생성 메카니즘을 제시하였으며 벤조트리아졸이 합성 보조체로 이용된 경우 Bu_3SnH에 의해 벤조트리아졸의 세개의 질소 원자를 포함하는 다섯원자고리로 부터 라디칼 반응에 의해 질소 분자가 빠져나가는 것을 보여준 새로운 예이다.

ABSTRACT. Most of the reactions involving benzotriazoles as a synthetic auxiliary have been explained by ionic mechanisms, whereas benzotriazole-mediated radical reactions have received little attention. The reaction of 1-[(aryl)(phenylseleno)methyl]benzotriazole with Bu_3SnH in the presence of AIBN in benzene at reflux gave 2-aminodiphenyl selenide (16~29%), 2-aminobiphenyl (9~15%), diphenyl diselenide (30~93%), 1-(arylmethyl) benzotriazole (9~39%) and tributyltin-phenyl selenide (10~36%), whereas the compounds were treated with excess molar amount of Bu_3SnH in the absence of AIBN to afford N-(arylmethyl)anilines (44~66%) along with diphenyl diselenide (53~100%), benzotriazole (27~35%) and 1-(arylmethyl)benzotriazole (16~33%). Similarly, treatment of 6-aryl-6-(benzotriazol-1-yl)-1-hexenyl phenyl selenides with Bu_3SnH in the presence of AIBN gave 6-aryl-6-phenylamino-1-hexene (9~31%) and 1-aryl-1-oxo-5-pentene (15~44%). A mechanism for the formation of the products is proposed.

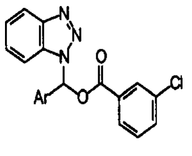
INTRODUCTION

A great deal of work has been done on exploring the potential synthetic utility of benzotriazole as a synthetic auxiliary over the last decade.[1] Up till now, most of the reactions have been explained by ionic mechanisms, whereas benzotriazole-mediated radical reactions have received little attention. Recently Kaim and his co-worker reported the generation of iminyl radicals by treatment of N-benzotriazolylimines with Bu_3SnH in benzene containing a catalytic amount of AIBN.[2] The lithiation of diaryl(benzotriazol-1-yl)methanes, followed by addition of iodine gave phenanthridines and dimers *via* the formation of diaryl (benzotriazol-1-yl)methyl radicals as intermediates.[3] The reduction of iminium cations, generated from the rapid dissociation of α-benzotriazolylalkenylamines, with samarium diiodide gave α-amino alkenyl radicals that undergo 5- or 6-exo-trig cyclizations leading to substituted cycloalkyl- or cycloheteroalkylamines.[4] Only these three papers, to the best of our knowledge, reported radical reactions of benzotriazole derivatives.

Recently we reported the reaction of 1-[(aryl)(phenylseleno)methyl]benzotriazole (1) with *m*-chloroperbenzoic acid (2 equiv.), in which 1-[(aryl)(3-chlorobenzoyloxy)methyl]benzotriazoles (2), 3-chlorobenzoyl peroxide, aromatic aldehydes, and diphenyl diselenide (3) were isolated.[5]



1



2

PhSeSePh

3

Apart from the isolation of the unusual products **2** as major compounds, which are *m*-chlorobenzoic acid incorporated compounds, the formation of diphenyl diselenide suggests that a radical mechanism may be involved in the reactions. With this in mind, the reactions of **1** with Bu_3SnH in the presence and absence of azobisisobutyronitrile (AIBN) in benzene at reflux were studied. The results are described herein.

RESULTS AND DISCUSSION

The reaction of 1-[(phenyl)(phenylseleno)methyl] benzotriazole (**1a**) with Bu_3SnH in the presence of AIBN in benzene at reflux gave **3**, 2-aminodiphenyl selenide (**4**), 2-aminobiphenyl (**5**), 1-(phenylmethyl)-benzotriazole (**6a**), benzotriazole (Bt) (**7**), and tributyltin-phenyl selenide (**8**) in 30, 29, 5, 13, 15, and 10% yields, respectively. The reactions of other 1-[(aryl)(phenylseleno)methyl]benzotriazoles (**1b-d**) with Bu_3SnH under similar conditions proceeded in the same fashion but yields of products **3-8** varied somewhat with the concentrations of Bu_3SnH and AIBN, and N-(arylmethyl)aniline (**9**), arylmethylidenaniline (**10**) and aldehyde (**11**) were isolated in some cases. Quantities of **1**, Bu_3SnH, and AIBN, and yields of products are summarized in *Table* 1 and the spectroscopic data and elemental analyses of **1d** and **6d** are listed in *Table* 2.

The structures of **1d** and **6d** were determined based on the spectroscopic (IR, ^1H NMR) data and elemental analyses, and those of other products were identified by comparison of their physical and spectroscopic data with those of reported values.[6]

When compound **1a** was treated with a slightly excess molar amount of Bu_3SnH in the presence of nearly equal (Entries 1 and 2) or half molar amounts of AIBN (Entry 6) in benzene at reflux, compounds **3** (30~36%), **4** (22~29%), **5** (9~13%), **6** (10~13%), **7** (15~29%), and **8** (10~36%) were isolated.

However, interestingly, compounds **9a-c** were isolated in 47~75% yields along with compounds **3**, **6a-d**, and **8** without any detectable amounts of **4** and **5** when the same reactions were carried out in the presence of catalytic amounts (Entry 3) of AIBN or in the absence of AIBN under the same conditions (Entries 4 and 5). The result indicates that compounds **4**, **5**, and **9** are formed *via* the same intermediate 12 (*vide* infra), which is trapped by both phenylselenyl radical and benzene used as a solvent in the presence of AIBN to give compounds non-formation **4** and **5**, respectively, whereas in the presence of excessive molar amounts of Bu_3SnH, the intermediate **12** would be

Table 1. Quantities of the reactants and yields of products **3-11**

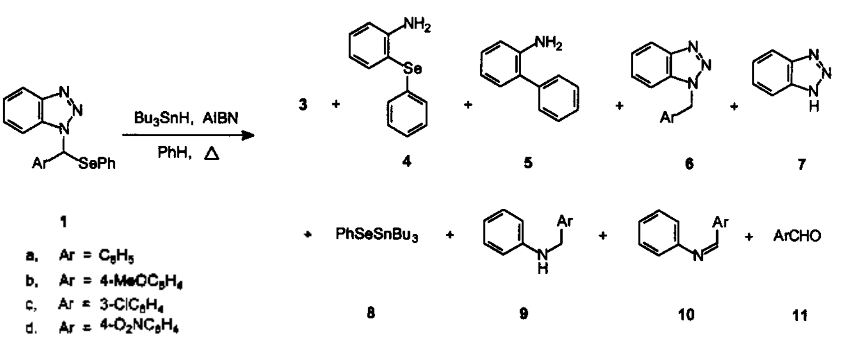
Entry	Comp	Ar	mmol	Bu_3SnH mmol	AIBN mmol	Time h	Yield (%)[b] 3	4	5[c]	6	7	8	9	10	11
1	**1a**	C_6H_5[a]	1.18	1.42	1.43	13	30	29	9	13	15	10			
2	**1a**	C_6H_5[a]	1.91	2.29	2.29	20	34	22	10	10	29	12			
3	**1a**	C_6H_5	0.743	3.72	trace	4	53	0	0	16	27	47	62		
4	**1a**	C_6H_5	0.741	2.22	0	8	82	0	0	26	34	14	47		
5	**1a**	C_6H_5	0.653	1.96	0	5	85	0	0	22	0	16	75		
6	**1a**	C_6H_5	1.18	1.42	0.706	2	36	23	13	10	18	36	0		
7	**1b**	$4\text{-}MeOC_6H_4$	0.456	5.93	0	24	100	0	0	33	0	0	66[d]		
8	**1b**	$4\text{-}MeOC_6H_4$	0.459	0.55	0	2.5	93	7	15	0	37	0	0	7[f]	39
9	**1c**	$3\text{-}ClC_6H_4$	0.937	5.62	0	19	69	0	0	19	35	34	44[e]		
10	**1c**	$3\text{-}ClC_6H_4$	0.959	1.15	0.575	2	82	16	6	9	17				
11	**1c**	$3\text{-}ClC_6H_4$	0.188	1.13	0	20	81	0	0	0	37	0	50		
12	**1d**	$4\text{-}O_2NC_6H_4$	0.691	0.829	0.414	12	72	19	0	39	35				

[a]Compounds **1a** (Entries 1 and 2), **1c** (Entry 11), and **1d** were recovered in 31, 30, 20, and 10% yields, respectively. Two reactions (Entries 5 and 11) were performed under N_2 atmosphere. [b]Isolated yields. [c]lit.,[13]. [d]lit.,[10f-g]. [e]lit.,[10b]. [f]lit.,[14].

Table 2. Spectroscopic data and elemental analyses of 1-[(4-nitrophenyl)(phenylseleno)methyl]benzotriazole (**1d**) and 4-nitrophenylmethylbenzotriazole (**6d**)

Compound	mp[a] °C	IR (neat)[b] cm^{-1}	^1H NMR ($CDCl_3$, 80 MHz) δ, ppm	Molecular Formula	Anal./Found C	H	N
1d	118~119	1597, 1507, 1347, 1066, 862, 829, 771, 750, 736	6.95~7.55 (m, 11H, ArH, SeCH), 7.90~8.15 (m, 3H, ArH, H at C-4 of Bt)	$C_{19}H_{14}N_4O_2Se$	55.75 55.86	3.45 3.69	13.69 13.63
6d	128~130	1597, 1506, 1342, 1221, 1106, 1083, 856, 800, 747, 728	5.90 (s, 2H, CH_2), 7.20~7.55 (m, 7H, ArH), 8.00~8.20 (m, 1H, H at C-4 of Bt)	$C_{13}H_{10}N_4O_2$	61.41 61.65	3.96 4.11	22.04 22.10

[a]Compounds **1d** and **6d** were recrystallized from *n*-hexane and benzene, respectively. [b]IR spectra of compounds **1d**, and **6d** were taken in KBr.

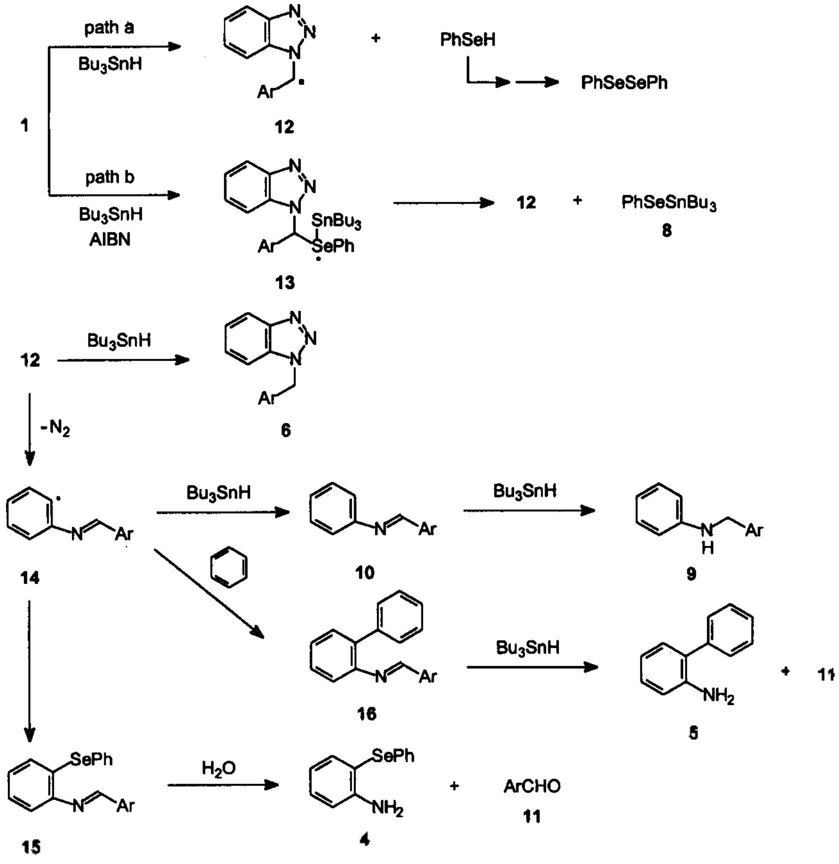


Scheme 1.

reduced to **9** *via* an imine **10**. Based on the same coherence, no formation of **4** and **5** from the reactions of **1b** (Entry 7) and **1c** (Entry 9) with a large excess of Bu_3SnH in the absence of AIBN can be explained. Instead compounds **9b** (66%) and **9c** (44%) were obtained from the former (Entry 7) and from the latter (Entry 9), respectively. However, when almost equal molar amounts of **1** and Bu_3SnH were utilized without AIBN, the propensity of the reaction changed. That is, treatment of **1b** with Bu_3SnH (1.2 equiv.) for 2.5 h (Entry 8) did not produce compounds **6**, **8**, and **9**. Instead 4-anisylmethylidenaniline (**10b**) and 4-anisaldehyde (**11b**) were isolated in 7 and 39% yields, respectively. The formation of **10b** at the expense of N-(4-anisyl) aniline (**9b**) is attributable to the low concentration of Bu_3SnH.

The following mechanism is proposed to accommodate the foregoing (*Scheme* 2). (Aryl) (benzotriazol-1-yl)methylradical (**12**) is envisaged to be formed by a homolytic cleavage of a bond between α-carbon to N-1 of **1** and Se *via* either a Bu_3SnH-mediated reaction (path a) or a selenurane radical **13** (path b). Abstraction of a hydrogen atom by **12** would give **6**. However, extrusion of a nitrogen molecule would give 2-(arylmethylidenamino)phenyl radical **14**, which is analogous to the formation of phenyl anion from (aryl)(benzotriazol-1-yl)methyl carbanion.[7] The coupling between the radical **14** and phenylselenyl radical gives 2-(arylmethylidenamino) diphenyl selenide **15**. Either hydrolysis or reductive amination of **15** would give **4** and aldehyde **11**. In order to obtain information about the stability of **15**, 2-(phenylmethylidenamino)diphenyl selenide (**15a**) was prepared *via* an independent route: Nucleophilic displacement of a chlorine atom from *o*-chloronitrobenzene by *in situ* prepared phenylselenolate gave 2-nitrodiphenyl selenide (**17**), which was treated with tin(II) chloride dihydrate in conc. HCl at reflux to give **4**. The reaction of **4** with benzaldehyde (4 equiv.) in EtOH at reflux would be expected to give **15a** (*Scheme* 3).

After the imination reaction was completed, TLC (n-hexane : EtOAc=60 : 1) showed three spots



Scheme 2.

corresponding to **15a** ($R_f = 0.7$), benzaldehyde ($R_f = 0.6$), and 4 ($R_f = 0.5$). The ^{1}H NMR spectrum of the reaction mixture showed a 1 : 1 ratio between two peaks at δ 8.35 and 9.92 ppm, corresponding to a proton at the iminyl group of **15a** and a proton at the formyl group of benzaldehyde, respectively. After CH_2Cl_2 (5 mL) and water (5 mL) were added to the reaction mixture, stirring was continued for an additional 30 min. The ^{1}H NMR spectrum of the reaction mixture showed a 2 : 1 ratio of the same peaks mentioned above, which indicates that the formation of **15a** continues to proceed in spite of wet solution. However, it was found that **15a** underwent ready hydrolysis in the course of chromatography. As a result, only **4** and benzaldehyde were isolated by chromatography.

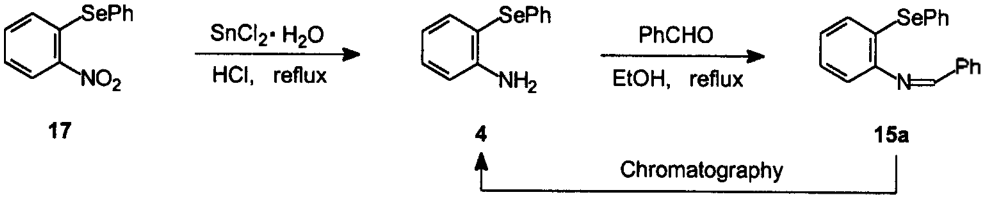
The formation of **5** can be explained by a reductive amination of 2-(arylmethylidene)biphenyl (**16**), generated by a radical substitution reaction of **14** with benzene used as a solvent.

In fact, the reduction of **16** by Bu_3SnH was confirmed by treatment of 2-(phenylmethylidenamino)-biphenyl (**16a**) with Bu_3SnH (1.2 equiv.) in the presence of AIBN (0.6 equiv.) for 2 h at reflux in a nitrogen atmosphere and in the air. Under the former conditions were isolated **5** and unreacted **16a** in 66 and 31% yields, respectively, and the yields of the corresponding compounds obtained under the latter conditions were 71 and 27%, respectively. No benzaldehyde was isolated. Consequently, hydrolysis is not likely to be involved in the formation of **5**.

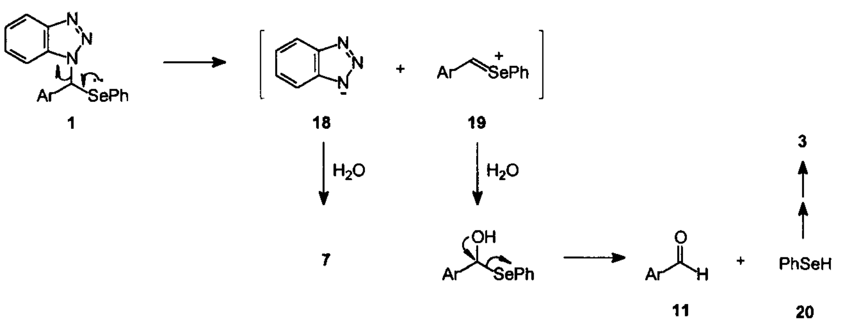
Table 1 shows that compound **7** is formed regardless of the presence (Entries 1-3, 6, 10 and 12) or absence of AIBN (Entries 4, 8, 9 and 11). A noteworthy point is that no **7** was isolated when large excess amounts of Bu_3SnH were employed (Entries 5 and 7). These results, coupled with the increased yields of **6** and **9** with the concentration of Bu_3SnH, imply that the formation of compound **7** should be achieved by a different mechanism. It is well-known that 1-(arylmethyl)benzotriazoles **6**, having a hetero atom, i.e., N, O, S, Se, at α position to N-1, undergoes a dissociation to benzotriazolate anion 18 and the corresponding onium ion.[4,5,8] Consequently, dissociation of **1** would give **18** and selenonium ion **19** (*Scheme* 4). Protonation of **18** would give **7**. Hydrolysis of **19** eventually gives aldehyde **11** and benzeneselenol **20**. The latter is readily converted to **3** in the atmosphere. Thus compounds **4-6** are formed *via* an intermediate **12**. In addition, N-(arylmethyl)anilines (**9**) are thought to be formed by reduction of arylmethylidenaniline (**10**), which is formed *via* radical **14**, in the presence of excess Bu_3SnH. When the concentration of Bu_3SnH is low, the isolation of 4-anisylmethylidenaniline (**10b**) from the reaction mixture demonstrates the involvement of Bu_3SnH (Entry 8). The formation of **9** from **10** by reduction with excess Bu_3SnH was confirmed by treatment of **10a** with Bu_3SnH (2 equiv.) from which N-(benzyl) aniline (**9a**) was isolated in 92% yield (*Scheme* 5).

A solution of **10a**, Bu_3SnH (1.2 equiv.), and AIBN (0.6 equiv.) in a mixture of benzene (10 mL) and water (0.15 mL) was heated in order to see how **10a** is sensitive to water under the reaction conditions. From the reaction mixture, **9a** and benzaldehyde were isolated in 49 and 9% yields, respectively. On the other hand, heating **10a** without Bu_3SnH and AIBN in the same solvent mixture gave benzaldehyde (28%) along with unreacted **10a** (61%) (*Scheme* 6).

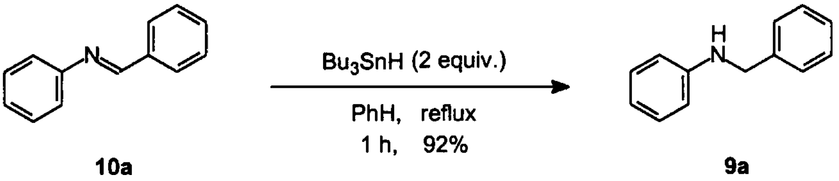
The results indicate that **10a** is readily reduced to **9a** by Bu_3SnH but manifests considerable



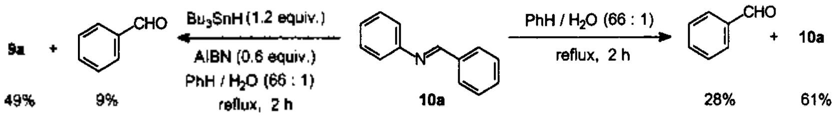
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

resistance to hydrolysis.

In view of the generation of radical **12**, it would be expected that 6-aryl-6-(benzotriazol-1-yl)-1-hexenyl radical (**22**) is formed by treatment of 6-aryl-6-(benzotriazol-1-yl)-1-hexenyl phenyl selenides (**21**) with Bu_3SnH in the presence or absence of AIBN (*Scheme* 7).

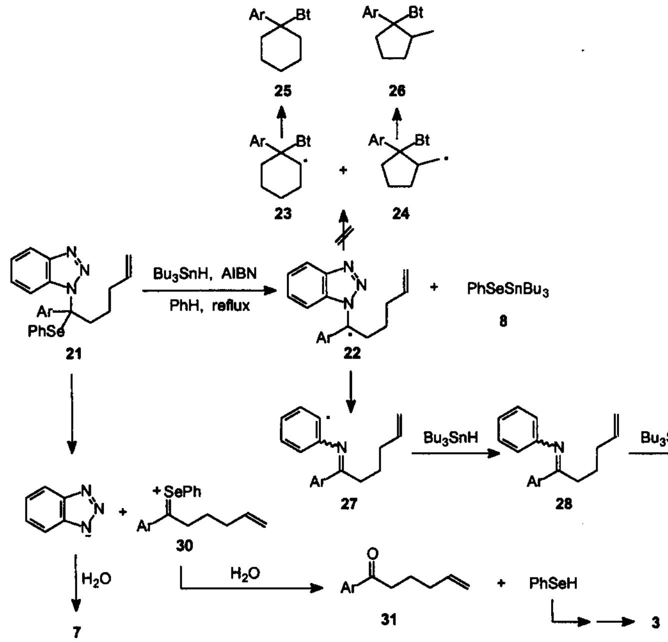
One might conceive that the radical **22** undergoes either intramolecular cyclization to give compounds **25** and/or **26** *via* radicals **23** and **24**, respectively, or elimination of a nitrogen molecule to give a new radical species **27** which is analogous to radical **14** in *Scheme* 2. Hydrogen abstraction by **27** followed by reduction in the presence of excess Bu_3SnH would give an amine **29**. This possibility was examined by subjecting the three compounds **21a-c** to the same conditions. Quantities of the reactants, reaction conditions and yields of products are summarized in *Table* 3, and the spectroscopic data and elemental analyses of compounds **29** and **31** are listed in *Table* 4.

Since neither cyclization products **25** and **26** or products derived from radicals **23** and **24** were detected, radical **22** undergoes reactions to give **29** in the same fashion as radical **12**. The formation of **31** can be explained by a dissociation mechanism as shown in *Scheme* 4. However, the non-isolation of **8** (*Table* 3, Entries 1, 3-4), along with the isolation of a lesser amount of **8** (*Table* 3, Entry 2), suggests that the formation of selenurane radical analogous to **13** (*Scheme* 2) from **21** may be less important than the formation of **13** from **1**.

This may be attributable to the stability of the more stable radical **22** which is tertiary, compared to radical **12** which is secondary.

EXPERIMENTAL

The ^1H NMR spectra were recorded at 80 MHz in $CDCl_3$ containing tetramethylsilane as an internal standard. IR spectra were recorded in KBr or in thin films on KBr plates. Elemental analyses were



Scheme 7.

Table 3. Reactions of 6-aryl-6-(benzotriazol-1-yl)-1-hexenyl phenyl selenides (**21**) with Bu_3SnH in the presence of AIBN

Entry		Compound R	mmol	Bu_3SnH mmol	AIBN mmol	Time h	Yield (%)				
							29	**31**	**7**	**3**	**8**
1	**21a**	C_6H_5	0.245	0.735	0.025	3	31	25	40	94	
2	**21b**	4-$MeOC_6H_4$	0.670	0.804	0.067	3	22	50		70	11
3	**21b**	4-$MeOC_6H_4$	0.132	0.396	0.013	5	23	15	54	83	
4	**21c**	3,4-$(Me)_2C_6H_3$	0.122	0.366	0.012	2	9	44	49	68	

[a]Isolated yields.

determined by the Korea Basic Science Center. Column chromatography was performed using silica gel (70~230 mesh, ASTM). 1-(Arylmethyl) benzotriazoles **6a-c** and 1-[(aryl)(phenylseleno) methyl]benzotri-azoles **1a-c** were prepared according to procedures in the literature.[5] Similarly, 1-[(4-nitrophenyl)-methyl]benzotriazole (**6d**) and 1-[(4-nitrophenyl)(phenylseleno)methyl]benzotriazole (**1d**) were prepared. Consult *Table* 2 for physical and analytical, IR, and ^1H NMR spectroscopic data for **6d** and **1d**.

General Procedure for the Reactions of 1-[(Arylseleno)(phenyl)methyl]benzotriazole (**1**) with Tribuytyltin Hydride (Bu_3SnH) in the Presence of Azobisisobutyronitrile (AIBN).

AIBN (0~2.3 mmol), followed by Bu_3SnH (0.55~5.9 mmol), was added to a solution of **1** (0.19~1.9 mmol) in dried benzene (20 mL). The mixture was heated for an appropriate time at reflux. The solvent was removed *in vacuo* and the residue was chromatographed on a silica gel (2×10 cm). Elution with *n*-hexane gave a mixture of diphenyl diselenide (**3**) and tributyltin-phenylselenide (**8**), which was analyzed by ^1H NMR spectroscopy. Elution with a mixture of *n*-hexane and EtOAc (300 : 1) gave 2-aminodiphenyl selenide (**4**), and 2-aminobiphenyl (**5**). When 4-anisylidenaniline (**10b**) was formed, the compound was eluted with the same solvent mixture after the elution of **5**. 4-Anisaldehyde (**11**) (Ar=4-$MeOC_6H_5$) was eluted with a mixture of *n*-

Table 4. Spectroscopic data of 6-aryl-6-(N-phenyl)-1-hexenes (**29**) and 1-aryl-1-oxo-5-pentenes (**31**)

Compound	IR (neat), cm^{-1}	^1H NMR ($CDCl_3$, 80 MHz), δ, ppm
29a	a	1.25~2.18 (m, 6H, $CH_2CH_2CH_2$), 3.98 (s, br, 1H, NH), 4.20 (t, J=6.4 Hz, 1H, NCH), 4.86~5.09 (m, 2H, CH_2=), 5.60~6.02 (m, 1H, =CH), 6.43~7.48 (m, 10H, ArH)
29b	3410, 1603, 1460, 1506, 1283	1.26~2.17 (m, 6H, $CH_2CH_2CH_2$), 3.74 (s, 3H, OMe), 3.97 (s, br, 1H, NH), 4.24 (t, J=6.4 Hz, 1H, NCH), 4.86~5.07 (m, 2H, =CH_2), 5.54~6.11 (m, 1H, =CH), 6.42~7.37 (m, 8H, ArH)
31a	a	1.54~2.18 (m, 4H, CH_2CH_2), 2.92 (t, J=7.2 Hz, 2H, CH_2), 4.86~5.10 (m, 2H, CH_2=), 5.60~6.02 (m, 1H, =CH), 6.92~7.43 (m, 3H, ArH), 7.86~8.04 (m, 2H, ArH)
31b	1676, 1576, 1418, 1312, 1255, 1170, 1030	1.54~2.29 (m, 4H, CH_2CH_2), 2.93 (t, J=7.2 Hz, 2H, CH_2), 3.83 (s, 3H, OMe), 4.89~5.14 (m, 2H, CH_2=), 5.60~6.09 (m, 1H, =CH), 6.91 (d, J=8.0 Hz, 2H, ArH), 7.94 (d, J=8.0 Hz, 2H, ArH)
31c	1679, 1609, 1448, 1408, 1162	1.72~2.20 (m, 4H, CH_2CH_2), 2.29 (s, 6H, 2Me), 2.94 (t, J=8.0 Hz, 2H, CH_2), 4.91~5.15 (m, 2H, CH_2=), 5.52~6.10 (m, 1H, =CH), 7.13~7.24 (m, 1H, ArH), 7.65~7.72 (m, 2H, ArH)

[a] IR spectra of pure **29a** and **31a** could not be recorded.

hexane and EtOAc (30 : 1). Elution with the same solvent mixture (n-hexane : EtOAc=5 : 1) gave 1-(arylmethyl)benzotriazole (**6**) and benzotriazole (**7**). Consult *Table* 1 for quantities of the reactants, reaction conditions and yields of each compound **3-11**.

Phenylmethylidenaniline (10a). Aniline (1.09 g, 11.7 mmol) was added to a solution of benzaldehyde (1.04 g, 9.80 mmol) in dried benzene (20 mL). Upon addition of aniline, white solids were formed and the color of the solution turned yellow. The mixture was stirred for 40 min at room temperature and the water formed was dried over $MgSO_4$. Evaporation of the solvent gave a residue, which was chromatographed on a silica gel (3×5 cm). Elution with a mixture of n-hexane and CH_2Cl_2 gave **10a** (1.69 g, 95%) (lit.,[9] 52 °C)

N-(Benzyl)aniline (9a). Bu_3SnH (646 mg, 2.22 mmol) was added to a solution of **10a** (201 mg, 1.11 mmol) in dried benzene (10 mL) at 50 °C. The mixture was heated for 1 h at reflux until the spot corresponding to **10a** had disappeared. After the solvent was evaporated off, the residue was chromatographed on a silica gel (2×10 cm). Elution with n-hexane gave excess Bu_3SnH. Subsequent elution with a mixture of n-hexane and CH_2Cl_2 (3 : 2) gave **9a** (187 mg, 92%)(lit.,[10a-c,e] 34~35 °C).

Reaction of 10a with Bu_3SnH in the Presence of AIBN. Bu_3SnH (407 mg, 1.40 mmol) was added to a solution of **10a** (211 mg, 1.16 mmol) in a mixture of benzene (10 mL) and water (0.15 mL). The mixture was heated for 2 h at reflux and dried over $MgSO_4$. Evaporation of the solvent, followed by chromatography (2×11 cm) with a mixture of n-hexane and CH_2Cl_2 (2 : 1) as an eluent gave benzaldehyde (11 mg, 9%) and **9a** (104 mg, 49%).

Hydrolysis of 10a. A solution of **10a** (211 mg, 1.16 mmol) in a mixture of benzene (10 mL) and water (0.15 mL) was heated for 2 h at reflux. The reaction mixture was worked up as usual. Chromatography (2×8 cm) of the reaction mixture using CH_2Cl_2 gave benzaldehyde (35 mg, 28%) and unreacted **10a** (128 mg, 61%).

2-Nitrodiphenyl Selenide (17). To a solution of benzeneselenol (296 mg, 1.88 mmol) in EtOH (8 mL) was added $NaBH_4$ (89 mg, 2.35 mmol), which was stirred for 3 min at room temperature. 2-Chloronitrobenzene (247 mg, 1.57 mmol) was added to the *in situ* generated sodium benzeneselenolate and then the mixture was refluxed for 2.5 h. The cooled reaction mixture was extracted with CH_2Cl_2

(50 mL × 3) and the extracts were washed with water (50 mL × 3) and dried over $MgSO_4$. Removal of the solvent gave a residue which was chromatographed on a silica gel (3 × 11 cm). Elution with a mixture of *n*-hexane and EtOAc (100 : 1) gave diphenyl diselenide (163 mg) and **17** (347 mg, 79%): mp 87~88 °C (MeOH) (lit.,[11] 91 °C).

2-Aminodiphenyl Selenide (4). A mixture of **17** (264 mg, 0.949 mmol) and tin(II) chloride dihydrate (1.07 g, 4.74 mmol) in a mixture of conc. HCl (1 mL) and water (15 mL) was heated for 1.5 h at reflux. The mixture was neutralized with NaOH solution, which was extracted with CH_2Cl_2 (50 mL × 3). The extracts were washed with water (100 mL × 3) and dried over $MgSO_4$. After the solvent was removed *in vacuo*, the residue was chromatographed on a silica gel (3 × 8 cm). Elution with a mixture of *n*-hexane and EtOAc (300 : 1) gave an unknown (12 mg), **17** (53 mg, 20%), and **4** (60 mg, 26%): liquid; IR (neat) 3464, 3360, 1606, 1576, 1475, 1438, 1306, 1158, 1066, 1019, 914, 738 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) 4.05 (s, br, 2H, NH_2), 6.60~6.83 (m, 2H, ArH), 7.10~7.32 (m, 6H, ArH), 7.51~7.63 (m, 1H, ArH). Anal. Calcd for $C_{12}H_{11}NSe$: C, 58.07; H, 4.47; N, 5.64. Found: C, 58.13; H, 4.55; N, 5.46.

Attempted Preparation of 2-(Phenylmethylidenamino)diphenyl Selenide (15a). A mixture of **4** (50 mg, 0.201 mmol) and benzaldehyde (85 mg, 0.804 mmol) in EtOH (5 mL) was heated for 1 he at reflux. TLC (*n*-hexane : EtOAc=60 : 1) showed three spots corresponding to **15a** (R_f=0.7), benzaldehyde (R_f=0.6), and **4** (R_f=0.5). CH_2Cl_2 (20 mL × 3), followed by water (20 mL), was added to the mixture, which was additionally stirred for 30 min at room temperature. The mixture was dried over $MgSO_4$. Gas chromatographic analyses of the reaction mixture (column; HP-5, 0.53 mm × 10 m; injector temp. 100 °C, column temp. 250 °C) showed three peaks corresponding to **4**, benzaldehyde and **15a**. Integration ratios, which had previously been 1 : 3 : 5, changed to 18 : 21 : 5 after column chromatography (CH_2Cl_2). The attempt to separate **15a** was unsuccessful.

2-(Phenylmethylidenamino)biphenyl (16a). A mixture of 2-aminobiphenyl (**5**) (581 mg, 3.43 mmol) and benzaldehyde (1.09 g, 10.3 mmol) in absolute EtOH (18 mL) was heated for 4 h at reflux. The mixture was worked up as for **10a**. Chromatography of the reaction mixture gave **16a** (662 mg, 75%):

Reaction of 16a with Bu_3SnH in the Presence of AIBN

(i) in nitrogen atmosphere; A mixture of **16a** (403 mg, 1.57 mmol), Bu_3SnH (547 mg, 1.88 mmol), and AIBN (155 mg, 0.942 mmol) in benzene (10 mL) was heated for 2 h under nitrogen atmosphere at reflux. The mixture was worked up as described for the formation of **9a**. Compound **16a** (124 mg, 31%) and **5** (177 mg, 66%) were isolated by column chromatography.

(ii) in the air; A mixture of **16a** (152 mg, 0.592 mmol), Bu_3SnH (207 mg, 0.710 mmol), and AIBN (58 mg, 0.355 mmol) in benzene (10 ml) was heated for 2 h at reflux in the air. **16a** (41 mg, 27%) and **5** (71 mg, 71%) were obtained from the reaction.

General Procedure for the Synthesis of 6-Aryl-6-(benzotriazol-1-yl)-1-hexenyl Phenyl Selenide (21). LDA (1.02~3.88 mmol) was added to a solution of **1** (0.408~1.55 mmol) in THF (10 mL) at − 78 °C, the solution turned bright blue. 5-Bromo-1-pentene (2.0~3.2 mmol) was immediately added. The mixture was stirred for 20 min and then extracted with ether (50 mL × 3). The extracts were washed with water (50 mL). Evaporation of the solvent gave a residue, which was chromatographed on a silica gel (3.5 × 6 cm). Elution with a mixture of *n*-hexane and EtOAc (10 : 1) gave a mixture of **3** and 5-bromo-1-pentene, **21** and unreacted **1**. Elution with the same solvent mixture (2 : 1) gave 1-[(benzoyl)(phenyl)methyl]-benzotriazole (37%) (**32**)[15] in the case of **1** (Ar=Ph).

6-Phenyl-6-(benzotriazol-1-yl)-1-hexenyl Phenyl Selenide (21a); 24% yield; liquid; IR (neat) 3060, 2935, 1474, 1444, 1155, 1113, 741, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 1.17~1.64 (m, 2H, CH_2), 1.84~2.14 (m, 2H, CH_2), 2.66~2.85 (m, 2H, CH_2), 4.81~5.01 (m, 2H, $=CH_2$), 5.54~5.86 (m, 1H, =CH), 6.72~7.58 (m, 13H, ArH), 7.98~8.09 (m, 1H, H at

C-4 of BtH). Anal. Calcd for $C_{24}H_{23}N_3Se$: C, 66.66: H, 5.36: N, 9.72. Found: C,66.73: H, 5.42: N, 9.75.

6-(4-Methoxyphenyl)-6-(benzotriazol-1-yl)-1-hexenyl Phenyl Selenide (21b); 82% yield; liquid; IR (neat) 3080, 2936, 2848, 1610, 1510, 1256, 1034, 918, 742, 694 cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz) δ 1.33~1.63 (m, 2H, CH_2), 1.84~2.12 (m, 2H, CH_2), 2.62~2.83 (m, 2H, CH_2), 3.76 (s, 3H, MeO), 4.79~5.02 (m, 2H, $=CH_2$), 5.47~5.94 (m, 1H, =CH), 6.72~7.30 (m, 12H, ArH), 7.96~8.08 (m, 1H, H at C-4 of BtH). Anal.Calcd for $C_{25}H_{25}N_3OSe$: C, 64.93: H, 5.45: N, 9.09. Found: C, 64.02: H, 5.48: N, 9.02.

6-(3,4-Dimethylphenyl)-6-(benzotriazol-1-yl)-1-hexenyl Phenyl Selenide (21c); 30% yield; liquid; IR (neat) 3072, 2944, 1115, 742, 693, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 1.30~1.64 (m, 2H, CH_2), 1.87~2.05 (m, 2H, CH_2), 2.16 (s, 3H, Me), 2.23 (s, 3H, Me), 2.64~2.83 (m, 2H, CH_2), 4.82~5.02 (m, 2H, $=CH_2$), 5.47~5.96 (m, 1H, =CH), 6.67~7.32 (m, 11H, ArH), 7.95~8.10 (m, 1H, H at C-4 of BtH). Anal.Calcd for $C_{26}H_{27}N_3Se$: C, 67.82: H, 5.91: N, 9.13. Found: C, 67.90: H, 5.93: N, 9.17.

1-[(Benzoyl)(phenyl)methyl]benzotriazole (32); 37% yield; mp 162~163 °C (MeOH); IR (KBr) 3040, 2925, 1690, 1594, 1448, 1225, 756, 737 cm^{-1}; ^1H NMR ($CDCl_3$, 80 MHz) δ 7.22~7.64 (m, 11H, ArH), 7.82~8.03 (m, 4H, ArH). Anal. Calcd for $C_{20}H_{15}N_3O$: C, 76.66; H, 4.82; N, 13.41. Found: C, 76.76; H, 5.05; N, 13.41.

General Procedure for the Reactions of 21 with Bu_3SnH. AIBN (0.012~0.067 mmol) was added to a solution of **21** (0.12~0.67 mmol) in benzene (20 mL). The solution was maintained at 50 to 60 °C and then Bu_3SnH (0.37~0.80 mmol) was added. The mixture was stirred until no spot corresponding to **21** was observed on TLC (*n*-hexane : EtOAc=7 : 1). Evaporation of the solvent, followed by chromatography (3 × 10 cm) using a mixture of *n*-hexane and EtOAc (50 : 1) gave 6-aryl-6-phenylamino-1-hexene **(29)** and 1-aryl-1-oxo-5-pentene **(31)**. Elution with EtOAc gave **7**. Consult *Table* 3 for quantities of the reactants, reaction conditions and yields of each products and *Table* 4 for spectroscopic data for compounds **29** and **31**.

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