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TETRAHEDRON

Removal of Benzotriazole Moiety from 2-[2-Aryl-2-(benzotriazol-1-yl)ethyl]tetrahydro-2*H*-pyrans and 2-[2-Aryl-2-(benzotriazol-1-yl)ethyl]-5-(methyl)tetrahydrofurans Using Lithium Naphthalene Radical Anion

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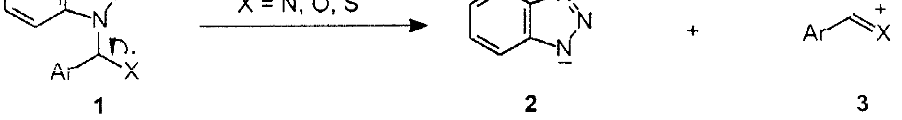
Abstract : In order to see the effects of non-bonding electrons in oxygen atoms on the cleavage of a bond between N-1 of the benzotriazole moiety and the α-carbon atom bonded to N-1 by lithium (**6a**) and sodium naphthalenides (**6b**), 2-[2-aryl-2-(benzotriazol-1-yl)ethyl]tetrahydro-2*H*-pyrans (**4**), and 2-[2-aryl-2-(benzotriazol-1-yl)ethyl]-5-(methyl)tetrahydrofurans (**5**), and 1-(benzotriazol-1-yl)-1,2-diphenylethane (**7**) were prepared. The reactions of **4** with **6a** in THF at room temperature gave 2-(2-arylethyl)tetrahydro-2*H*-pyrans (**12**) in 45 to 62 % yields along with benzotriazole and naphthalene. In addition, 2-(benzoylethyl)tetrahydro-2*H*-pyran (**15**) (12 %) was obtained only from the reaction of 2-[2-(benzotriazol-1-yl)-2-(phenyl)ethyl]tetrahydro-2*H*-pyran. Similarly, the reactions of **5** with **6a** under the same conditions afforded 2-(2-arylethyl)-5-(methyl)tetrahydrofurans (**30**) in 59 to 77 % yields along with the foregoing byproducts. Interestingly, the reaction of **7** with **6a** under the same conditions gave deoxybenzoin (**24**) in 41 % yield along with the foregoing byproducts. The results suggest that **6a** acts as a single electron-transfer agent in the reactions of **4** and **5**, and a base in the reaction of **7**. It is envisaged that for the former, Li^+ participates in the formation of a six-membered cyclic intermediate so that cleavage of α-C-N-1 bond is facilitated to give eventually **12** and **22**, whereas for the latter, **6a** abstracts a proton from α-C bonded to N-1 to generate a carbanion **19**, which extrudes a nitrogen molecule to generate a new phenyl carbanion **20**. Protonation leading to mono iminobenzoin **21**, followed by hydrolysis gives **15**. The formation of **24** can be explained based on the same mechanism as for the latter reaction.

Benzotriazole-mediated synthesis of organic compounds has been extensively studied over the last decade.[1] In particular, the benzotriazole moiety participating as a synthetic auxiliary is reported to be readily removed in the earlier stages of the reactions by a heterolytic bond cleavage between α-C and N-1 of α-substituted 1-(arylmethyl)benzotriazoles **1** to give benzotriazolate anion **2** and its counter onium ion **3** when the



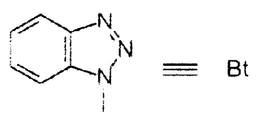
Scheme 1

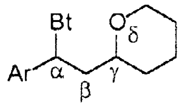
PII: S0040-4020(99)00120-9

compounds **1** have a heteroatom, i.e. N,[2] O,[3] S,[4] at α-carbon bonded to N-1 of **1** (Scheme 1). On the other hand, when there are no such heteroatoms at α-carbon, removal of the benzotriazole moiety has been mainly achieved by three methods. The first method involves the direct nucleophilic displacement of the benzotriazole group by using arylamines,[5] alkoxides,[6] alkanethiolates,[7] and Grignard reagents.[3, 8] The second method, which appears even more frequently in the literature, employs acid hydrolysis[9] or Lewis acids,[9(c), 10] i.e. acetic acid, *p*-toluenesulfonic acid, $ZnBr_2$, and $TiCl_3$/Li. A reductive cleavage[8(a), 9(a), 11] of a bond between α-C and N-1 of the benzotriazole moiety by treatment with $NaBH_4$ or $LiAlH_4$ comprises a third method. There have been other methods in which the benzotriazole moiety is spontaneously removed in the course of the reactions.[7, 12] All of the foregoing methods have to meet a special structural requirement in use, which limits their general applicability.

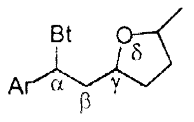
The fact that the benzotriazole moiety not only acts as a good leaving group but also takes up four electrons[13] suggests that the benzotriazole group can be removed as **2** once its anion radical is formed.

With this in mind, we have prepared 2-[2-aryl-2-(benzotriazol-1-yl)ethyl]tetrahydro-2*H*-pyrans (**4**), and 2-[2-aryl-2-(benzotriazol-1-yl)ethyl]-5-(methyl)tetrahydrofurans (**5**) and studied the reactions of the compounds **4** and **5** with lithium (**6a**) and sodium naphthalenides (**6b**) which have been utilized as single electron-transfer agents.[14] The reason for choosing compounds **4** and **5** as model compounds was that these compounds which have a δ oxygen would be expected to show different reactivities to **6** compared to the compound without δ oxygen atom such as 1-(benzotriazol-1-yl)-1,2-diphenylethane (**7**) owing to the presence of δ oxygen which might induce a strong interaction with metal ions.

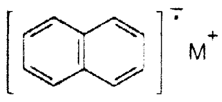




4



5



6a, M = Li
6b, M = Na

RESULTS AND DISCUSSION

(A) Synthesis

Compounds **4a** (Ar = Ph), **4b** (Ar = 4-FC_6H_4), **4c** (Ar = 4-$MeOC_6H_4$), and **4d** (Ar = 4-*tert*-BuC_6H_4), which have two chiral centers, were prepared by treatment of 1-(arylmethyl)benzotriazoles (**8**) with lithium diisopropylamide (LDA) in THF at -78 °C, followed by addition of 2-(bromomethyl)tetrahydro-2*H*-pyran (1 equiv.) (Scheme 2), and each pair of diastereomers of **4a-b**, and **4d** was separated by chromatography using a mixture of *n*-hexane and EtOAc (20 : 1) as an eluent. Diastereomers of **4c** were separated by preparative thin layer chromatography (PTLC). Quantities of the reactants and yields of **4** are summarized in Table 1 and the spectroscopic (IR, ^{1}H NMR, MS) and analytical data for **4** are presented in Table 2.

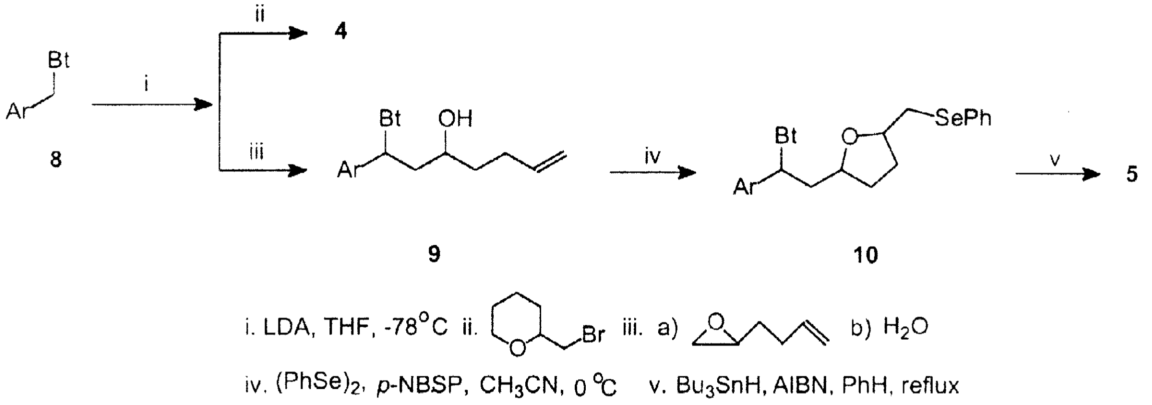
Compounds **5** were prepared by a series of reactions starting from **8**. Treatment of **8a** with LDA (1.5 equiv.) in THF at -78 °C, followed by addition of oxirane gave a mixture of diastereomers **9a** (R_f = 0.2, *n*-hexane : EtOAc = 4 : 1) and **9a'** (R_f = 0.15, *n*-hexane : EtOAc = 4 : 1), which were chromatographed using a mixture of *n*-hexane and EtOAc (5 : 1) as an eluent to give **9a** (24%) and **9a'** (23%).

Table 1. Quantities of reactants and yields of compounds 4

Compounds	Ar	mmol	LDA mmol	Yield[a] (%)		Mp[b] (°C)	
						4'	4''
8a	C_6H_5	4.06	6.09	**4a (4a'/4a'')**	59 (28/31)	107-108	128-130
8b	4-FC_6H_4	2.24	3.36	**4b (4b'/4b'')**	32 (14/18)	liquid	69-71
8c	4-$MeOC_6H_4$	3.56	5.34	**4c (4c'/4c'')**	37 (15/22)	77-78	94-95
8d	4-*tert*-BuC_6H_4	2.20	3.30	**4d (4d'/4d'')**	9 (0/9)	-	128-129

[a] Isolated yields. The ratio of diastereomers of **4c** in a mixture was determined by ^{1}H NMR spectroscopy. [b] Compounds **4a'** and **4a''** were recrystallized from MeOH and **4b''**, **4c'**, **4c''**, and **4d''** from *n*-hexane.

By similar treatment of **8b** under the same conditions, diastereomers **9b** (R_f = 0.2, *n*-hexane : EtOAc = 3 : 1) and **9b'** (R_f = 0.15, *n*-hexane : EtOAc = 3 : 1) were isolated in 21 and 27% yields, respectively. The structures of **9** were determined based on spectroscopic (IR, ^{1}H NMR, MS) data and elemental analyses, which are summarized in Table 3.



Scheme 2

Cyclization of **9** using diphenyl diselenide and *p*-nitrobenzenesulfonyl peroxide (*p*-NBSP) in CH_3CN at 0 °C[15] gave tetrahydrofuran derivatives **10**, which contained three chiral centers. So, diastereomer **9a** underwent a cyclization reaction to give a pair of diastereomers **10a** (R_f = 0.5, *n*-hexane : EtOAc = 10 : 1) and **10a'** (R_f = 0.4, *n*-hexane : EtOAc = 10 : 1) in 38 and 36% yields, respectively, whereas similar treatment of **9a'** gave a mixture of stereoisomers **10a''** and **10a'''** in 84% yield (*cis* : *trans* = 1 : 1) which was separated by PTLC. Similarly, cyclization of **9b** under the same conditions gave **10b** (R_f = 0.5, *n*-hexane : EtOAc = 10 : 1) and **10b'** (R_f = 0.4, *n*-hexane : EtOAc = 10 : 1) in 38% and 9% yields, respectively, whereas a mixture of stereoisomers **10b''** and **10b'''** (*cis* : *trans* = 1 : 1) was isolated in 74% yield from the cyclization of **9b'**. Likewise, the mixture of *cis-trans* isomers was separated by PTLC. The absolute configurations of each chiral center are unknown. Since the diastereomers **9a** and **9a'** give a pair of new diastereomers **10a** and **10a'**, and a

Table 2. IR, ^{1}H NMR, MS, and analytical data of compounds 4

Compounds	IR (neat)	^{1}H NMR (CDCl$_3$, 300 MHz)	MS (EI)	Molecular	Analysis %
	cm^{-1}	δ, ppm	m/z	Formula	Calcd/Found
4a'	3048, 2920, 2840, 1485, 1445, 1082, 1043, 741.	1.29 - 1.76 (m, 6H, 3C*H*$_2$ of ring), 2.30 (ddd, 1H, *J* = 14.2, 10.6, 3.1 Hz, 1H of BtCC*H*$_2$), 2.90 - 2.98 (m, 1H, 1H of BtCC*H*$_2$), 3.01 - 3.11 (m, 2H, OC*H*$_2$), 3.88 - 3.93 (m, 1H, C*H*O), 6.21 (dd, 1H, *J* = 11.9, 3.1 Hz, BtC*H*), 7.22 - 7.52 (m, 8H, Ar*H*), 8.06 - 8.09 (m, 1H, 1H at C-4 of Bt)	152 (17.3), 180 (71.1), 188 (100), 209 (14.4), 278 (13.3), 307 (M^+, 1.7%)	$C_{19}H_{21}N_3O$	C, 74.24 / 4.33 H, 6.89 / 6.98 N,13.67 / 13.77
4a''	3040, 2928, 2832, 1485, 1443, 1085, 1043, 745	1.36 - 1.63 (m, 6H, 3C*H*$_2$ of ring), 2.66 - 2.75 (m, 1H, 1H of OC*H*$_2$), 2.87 (ddd, 1H, *J* = 13.7, 10.7, 3.1 Hz, 1H of BtCC*H*$_2$), 3.04 - 3.11 (m, 1H, 1H of BtCC*H*$_2$), 3.34 (td, 1H, *J* = 11.5, 2.9 Hz, 1H of OC*H*$_2$), 4.01 - 4.06 (m, 1H, C*H*O), 6.07 (dd, 1H, *J* = 10.7, 4.8 Hz, BtC*H*), 7.28 - 7.43 (m, 8H, Ar*H*), 8.03 - 8.06 (m, 1H, 1H at C-4 of Bt)	152 (14.5), 180 (64.3), 188 (100), 209 (11.6), 278 (9.8), 307 (M^+, 1.1%)	$C_{19}H_{21}N_3O$	C, 74.24 / 74.39 H, 6.89 / 6.70 N, 13.67 / 13.55
4b'	3056, 2928, 2848, 1504, 1222, 1082, 835, 739	1.28 - 1.77 (m, 6H, 3C*H*$_2$ of ring), 2.25 (ddd, 1H, *J* = 14.2, 10.7, 3.1 Hz, 1H of BtCC*H*$_2$), 2.85 - 2.92 (m, 1H, 1H of BtCC*H*$_2$), 2.98 - 3.08 (m, 2H, OC*H*$_2$), 3.87 - 3.93 (m, 1H, C*H*O), 6.19 (dd, 1H, *J* = 11.9, 3.0 Hz, BtC*H*), 6.97 - 7.02 (m, 2H, Ar*H*), 7.36 - 7.50 (m, 5H, Ar*H*), 8.06 - 8.09 (m, 1H, 1H at C-4 of Bt)	170 (14.6), 198 (66.0), 206 (100), 227 (9.7), 296 (11.0), 325 (M^+, 0.9%)	$C_{19}H_{20}N_3FO$	C, 70.14 / 70.34 H, 6.20 / 6.43 N, 12.9 1/ 13.06
4b''	2928, 2832, 1504, 1222, 1085, 1043, 774, 739	1.35 - 1.79 (m, 6H, 3C*H*$_2$ of ring), 2.60 - 2.70 (m, 1H, 1H of OC*H*$_2$), 2.84 (ddd, 1H, *J* = 13.8, 10.9, 2.9 Hz, 1H of BtCC*H*$_2$), 2.99 - 3.06 (m, 1H, 1H of BtCC*H*$_2$), 3.31 (td, 1H, *J* = 11.4, 3.1 Hz, 1H of OC*H*$_2$), 4.00 - 4.05 (m, 1H, C*H*O), 6.05 (dd, 1H, *J* = 10.9, 4.7 Hz, BtC*H*), 6.98 - 7.04 (m, 2H, Ar*H*), 7.31 - 7.42 (m, 5H, Ar*H*), 8.04 (d, 1H, *J* = 8.0 Hz, 1H at C-4 of Bt)	170 (17.6), 198 (77.2), 206 (100), 227 (11.0), 296 (14.7), 325 (M^+, 0.3%)	$C_{19}H_{20}N_3FO$	C, 70.14 / 70.28 H, 6.20 / 6.35 N, 12.91 / 12.98
4c'	2928, 2832, 1504, 1450, 1075, 1040, 742	1.29 - 1.75 (m, 6H, 3C*H*$_2$ of ring), 2.27 (ddd, 1H, *J* = 14.1, 10.7, 3.3 Hz, 1H of BtCC*H*$_2$), 2.87 - 2.90 (m, 1H, 1H of BtCC*H*$_2$), 2.94 - 3.10 (m, 2H, OC*H*$_2$), 3.78 (s, 3H, C*H*$_3$O), 3.86 - 4.01 (m, 1H, C*H*O), 6.16 (dd, 1H, *J* = 11.9, 2.9 Hz, BtC*H*), 6.84 (d, 2H, *J* = 8.7 Hz, Ar*H*), 7.28 - 7.54 (m, 5H, Ar*H*), 8.08 (d, 1H, *J* = 8.4 Hz, 1H at C-4 of Bt)	167 (26.5), 210 (78.6), 224 (29.9), 238 (37.3), 294 (15.8), 308 (100), 337(M^+, 8.1%).	$C_{20}H_{23}N_3O_2$	C, 71.19 / 71.33 H, 6.87 / 6.91 N, 12.45 / 12.56
4c''	2920, 2830, 1507, 1445, 1248, 1082, 1027, 774, 740	1.36 - 1.79 (m, 6H, 3C*H*$_2$ of ring), 2.62 - 2.71 (m, 1H, 1H of OC*H*$_2$), 2.83 (ddd, 1H, *J* = 13.8, 10.7, 3.1 Hz, 1H of BtCC*H*$_2$), 3.02 - 3.11 (m, 1H, 1H of BtCC*H*$_2$), 3.33 (td, 1H, *J* = 11.3, 2.9 Hz, 1H of OC*H*$_2$), 3.77 (s, 3H, C*H*$_3$O), 4.00 - 4.05 (m, 1H, C*H*O), 6.05 (dd, 1H, *J* = 10.7, 4.8 Hz, BtC*H*), 6.83 - 6.87 (m, 2H, Ar*H*), 7.28 - 7.44 (m, 5H, Ar*H*), 8.04 (d, 1H, *J* = 8.0 Hz, 1H at C-4 of Bt)	167 (23.4), 210 (82.7), 24 (31.3), 238 (36.4), 294 (12.7), 308 (100), 337 (M^+, 7.8%).	$C_{20}H_{23}N_3O_2$	C, 71.19 / 71.22 H, 6.87 / 6.97 N, 12.45 / 12.39
4d''	2920, 2840, 1446, 1258, 1155, 1139, 1085, 832, 738	1.28 (s, 9H, 3C*H*$_3$), 1.32 - 1.62 (m, 6H, 3C*H*$_2$ of ring), 2.24 - 2.34 (m, 1H, 1H of BtCC*H*$_2$), 2.86 - 2.93 (m, 1H, 1H of BtCC*H*$_2$), 3.01 - 3.08 (m, 2H, OC*H*$_2$), 3.87 - 3.93 (m, 1H, C*H*O), 6.18 (dd, 1H, *J* = 12.0, 3.1 Hz, BtC*H*), 7.33 - 7.38 (m, 5H, Ar*H*), 7.41 - 7.47 (m, 1H, Ar*H*), 7.53 - 7.56 (m, 1H, Ar*H*), 8.06 - 8.09 (m, 1H, 1H at C-4 of Bt)	192 (38.4), 207 (13.4), 220 (38.6), 229 (48.7), 236 (100), 281 (7.6), 319 (27.6), 362 (M^+, 21.0%)	$C_{23}H_{29}N_3O$	C, 76.00 / 76.15 H, 8.04 / 8.16 N, 11.56 / 11.78

pair of diastereomers **10a''** and **10a'''**, respectively, the configurations of α-carbon to N-1 of **10a** and **10a'** are the same. By the same token, those of **10a''** and **10a'''** should be the same. The spectroscopic (IR, ^{1}H NMR) and analytical data for **10** are summarized in Table 4.

Table 3. IR, ^{1}H NMR, MS, and analytical data of compounds **9**

Compounds	IR (neat) cm^{-1}	^{1}H NMR (CDCl$_3$, 300 MHz) δ, ppm	MS (EI) m/z	Molecular Formula	Analysis % Calcd/Found
9a	3375, 2925, 1489, 1448, 1272, 1158, 913, 781, 744	1.59 - 2.21 (m, 5H, C*H*$_2$C*H*$_2$C= and C*HO*), 2.29 (ddd, 1H, *J* = 14.3, 10.7, 3.3 Hz, 1H of BtCC*H*$_2$), 3.12 (ddd, 1H, *J* = 14.2, 11.9, 2.1 Hz, 1H of BtCC*H*$_2$), 3.44 (br s, 1H, O*H*), 4.92 - 5.03 (m, 2H, =C*H*$_2$), 5.72 - 5.85 (m, 1H, C*H*=), 6.27 (dd, 1H, *J* = 11.8, 3.2 Hz, BtC*H*), 7.05 - 7.45 (m, 8H, Ar*H*), 8.05 - 8.07 (m, 1H, 1H at C-4 of Bt)	152 (21.6), 180 (100), 194 (47.0), 252 (8.0), 278 (8.9), 307 (M$^+$, 4.7 %)	$C_{19}H_{21}N_3O$	C, 74.24 / 74.11 H, 6.89 / 6.67 N, 13.67 / 13.88
9a'	3365, 2925, 1449, 1159, 1077, 743, 700	1.60 - 2.19 (m, 5H, C*H*$_2$C*H*$_2$C= and C*HO*), 2.72 (ddd, 1H, *J* = 14.6, 9.3, 5.4 Hz, 1H of BtCC*H*$_2$), 2.89 (ddd, 1H, *J* = 14.0, 9.9, 3.0 Hz, 1H of BtCC*H*$_2$), 3.52 (br s, 1H, O*H*), 5.01 (m, 2H, =C*H*$_2$), 5.72 - 5.81 (m, 1H, C*H*=), 6.07(dd, 1H, *J* = 9.9, 5.3 Hz, 1H of BtC*H*), 7.25 - 7.43 (m, 8H, Ar*H*), 8.01 - 8.03 (m, 1H, 1H at C-4 of Bt)	152 (9.9), 180 (100), 194 (51.5), 252 (6.9), 278 (4.0), 307 (M$^+$, 4.8 %)	$C_{19}H_{21}N_3O$	C, 74.24 / 74.09 H, 6.89 / 6.63 N, 13.67 / 13.69
9b	3376, 2912, 1502, 1222, 1082, 780, 744, 624	1.58 - 2.17 (m, 5H, C*H*$_2$C*H*$_2$C= and C*HO*), 2.25 (ddd, 1H, *J* = 14.3, 10.7, 3.3 Hz, 1H of BtCC*H*$_2$), 3.09 (ddd, 1H, *J* = 14.2, 12.0, 2.2 Hz, 1H of BtCC*H*$_2$), 3.40 (br s, 1H, O*H*), 4.91 - 5.03 (m, 2H, =C*H*$_2$), 5.71 - 5.84 (m, 1H, C*H*=), 6.25 (dd, 1H, *J* = 11.8, 3.2 Hz, BtC*H*), 6.97 - 7.44 (m, 7H, Ar*H*), 8.05 - 8.08 (m, 1H, 1H at C-4 of Bt)	151 (20.0), 198 (100), 212 (42.5), 270 (6.0), 296 (7.7), 325 (M$^+$, 3.9 %)	$C_{19}H_{20}N_3FO$	C, 70.14 / 70.22 H, 6.20 / 6.42 N, 12.91 / 12.87
9b'	3408, 3168, 2944, 1411, 1152, 1069, 909, 730, 576	1.62 - 2.19 (m, 5H, C*H*$_2$C*H*$_2$C= and C*HO*), 2.68 (ddd, 1H, *J* = 14.3, 9.9, 5.1 Hz, 1H of BtCC*H*$_2$), 2.90 (ddd, 1H, *J* = 13.7, 10.4, 2.9 Hz, 1H of BtCC*H*$_2$), 3.54 (br s, 1H, O*H*), 4.95 - 5.06 (m, 2H, =C*H*$_2$), 5.71 - 5.83 (m, 1H, C*H*=), 6.07 (dd, 1H, *J* = 10.2, 5.1 Hz, BtC*H*), 6.96-7.46 (m, 7H, Ar*H*), 8.05 - 8.07 (m, 1H, 1H at C-4 of Bt)	170 (20.5), 198 (100), 212 (48.3), 270 (6.3), 296 (3.8), 325 (M$^+$, 6.8 %)	$C_{19}H_{20}N_3FO$	C, 70.14 / 70.18 H, 6.20 / 6.13 N, 12.91 / 12.98

Treatment of compounds **10a-a'''** and **10b-b'''** with Bu$_3$SnH in the presence of a catalytic amount of AIBN in benzene for 1.5 h at reflux gave excellent yields of tetrahydrofuran derivatives **5a-h**, respectively. Quantities of reactants and yields of **5a-h** and diphenyl diselenide are summarized in Table 5 and the spectroscopic (IR, ^{1}H NMR) and analytical data are presented in Table 6.

The relative stereochemistry between C-2 and C-5 of the tetrahydrofuran moiety of **5** was determined based on the reported ^{1}H NMR spectral data of *cis*- and *trans*-2,5-disubstituted tetrahydrofurans **11a** and **11b**.[10] That is, the *cis* diastereomer **11a** whose absolute configuration at the chiral centers is unknown exhibited a doublet at1.32 ppm assignable to methyl proton at C-5, whereas the corresponding proton signals of the *trans*

Table 4. IR, ^{1}H NMR, MS, and analytical data of compounds **10**

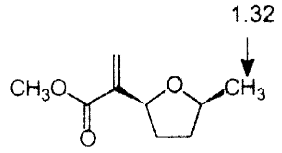
Compounds	IR (neat) cm^{-1}	^{1}H NMR (CDCl$_3$, 500 MHz) δ, ppm	Molecular Formula	Analysis % Calcd/Found
10a	1472, 1449, 1158, 1071, 1050, 1022, 742, 695	1.51 - 1.61 (m, 2H, C*H*$_2$ of ring), 1.98 - 2.13 (m, 2H, C*H*$_2$ of ring), 2.30 (ddd, 1H, *J* = 14.2, 9.9, 3.4 Hz, 1H of BtCC*H*$_2$), 2.83 (dd, 1H, *J* = 12.2, 7.0 Hz, 1H for C*H*$_2$Se), 3.01 (dd, 1H, *J* = 12.2, 5.8 Hz, 1H for C*H*$_2$Se), 3.14 (ddd, 1H, *J* = 14.3, 11.4, 2.9 Hz, 1H of BtCC*H*$_2$), 3.77 - 3.82 (m, 1H, C*H*O), 4.24 (quintet, 1H, *J* = 6.5 Hz, C*H*CH$_2$Se), 6.07 (dd, 1H, *J* = 11.5, 3.4 Hz, BtC*H*), 7.20 - 7.49 (m, 13H, Ar*H*), 8.04 - 8.05 (m, 1H, 1H at C-4 of Bt)	$C_{25}H_{25}N_3OSe$	C, 64.93 / 64.97 H, 5.03 / 5.01 N, 8.75 / 8.77
10a'	1488, 1472, 1448, 1072, 1051, 742, 698	1.58 - 1.74 (m, 2H, C*H*$_2$ of ring), 1.92 - 2.00 (m, 2H, C*H*$_2$ of ring), 2.32 (ddd, 1H, *J* = 14.1, 10.1, 3.5 Hz, 1H of BtCC*H*$_2$), 3.08 (dd, 1H, *J* = 12.4, 6.2 Hz, 1H of C*H*$_2$Se), 3.14 (dd, 1H, *J* = 12.4, 5.4 Hz, 1H of C*H*$_2$Se), 3.18 (ddd, 1H, *J* = 14.3, 11.5, 3.1 Hz, 1H of BtCC*H*$_2$), 3.67 - 3.72 (m, 1H, C*H*O), 4.04 (quintet, 1H, *J* = 6.2 Hz, C*H*CH$_2$Se), 6.07 (dd, 1H, *J* = 11.6, 3.3 Hz, BtC*H*), 7.17 - 7.33 (m, 13H, Ar*H*), 8.02 - 8.04 (m, 1H, 1H at C-4 of Bt)	$C_{25}H_{25}N_3OSe$	C, 64.93 / 65.03 H, 5.03 / 5.11 N, 8.75 / 8.88
10a''	1445, 1082, 1021, 739, 622	1.65 - 1.72 (m, 2H, C*H*$_2$ of ring), 1.96 - 2.03 (m, 2H, C*H*$_2$ of ring), 2.75 (ddd, 1H, *J* = 13.9, 9.5, 5.3 Hz, 1H of BtCC*H*$_2$), 2.89 (ddd, 1H, *J* = 13.6, 10.0, 3.5 Hz, 1H of BtCC*H*$_2$), 3.04 (dd, 1H, *J* = 12.4, 6.5 Hz, 1H of C*H*$_2$Se), 3.11 (dd, 1H, *J* = 12.4, 5.4 Hz, 1H of C*H*$_2$Se), 3.68 - 3.71 (m, 1H, C*H*O), 4.14 (quintet, 1H, *J* = 6.6 Hz, C*H*CH$_2$Se), 5.93 (dd, 1H, *J* = 10.0, 5.4 Hz, BtC*H*), 7.12 - 7.51 (m, 13H, Ar*H*), 8.02 - 8.04 (m, 1H, 1H at C-4 of Bt)	$C_{25}H_{25}N_3OSe$	C, 64.93 / 65.03 H, 5.03 / 5.08 N, 8.75 / 8.91
10a'''	1446, 1080, 1042, 738, 622	1.63 - 1.70 (m, 2H, C*H*$_2$ of ring), 2.06 - 2.19 (m, 2H, C*H*$_2$ of ring), 2.76 (ddd, 1H, *J* = 14.1, 9.2, 5.2 Hz, 1H of BtCC*H*$_2$), 2.83 - 2.93 (m, 1H, 1H of BtCC*H*$_2$), 2.98 (dd, 1H, *J* = 12.2, 6.8 Hz, 1H of C*H*$_2$Se), 3.14 (dd, 1H, *J* = 12.2, 5.7 Hz, 1H of C*H*$_2$Se), 3.79 - 3.88 (m, 1H, C*H*O), 4.28 (quintet, 1H, *J* = 6.6 Hz, C*H*CH$_2$Se), 5.98 (dd, 1H, *J* = 10.2, 5.2 Hz, BtC*H*), 7.22 - 7.57 (m, 13H, Ar*H*), 8.04 - 8.07 (m, 1H, 1H at C-4 of Bt)	$C_{25}H_{25}N_3OSe$	C, 64.93 / 65.07 H, 5.03 / 5.10 N, 8.75 / 8.88
10b	1598, 1506, 1442, 1225, 1155, 1070, 998, 741	1.55 - 1.59 (m, 2H, C*H*$_2$ of ring), 1.98 - 2.04 (m, 2H, C*H*$_2$ of ring), 2.26 (ddd, 1H, *J* = 13.9, 10.3, 3.3 Hz, 1H of BtCC*H*$_2$), 2.83 (dd, 1H, *J* = 12.3, 7.0 Hz, 1H of C*H*$_2$Se), 2.99 (dd, 1H, *J* = 12.2, 5.9 Hz, 1H of C*H*$_2$Se), 3.12 (ddd, 1H, *J* = 14.2, 11.5, 2.7 Hz, 1H of BtCC*H*$_2$), 3.72 - 3.77 (m, 1H, C*H*O), 4.24 (quintet, 1H, *J* = 6.5 Hz, C*H*CH$_2$SePh), 6.05 (dd, 1H, *J* = 11.5, 3.3 Hz, BtC*H*), 6.97 - 7.50 (m, 12H, Ar*H*), 8.04 - 8.06 (m, 1H, 1H at C-4 of Bt)	$C_{25}H_{24}N_3FOSe$	C, 62.50 / 62.77 H, 5.03 / 5.12 N, 8.75 / 8.93
10b'	1507, 1226, 1155, 1050, 835, 739	1.59 - 1.74 (m, 2H, C*H*$_2$ of ring), 1.92 - 2.00 (m, 2H, C*H*$_2$ of ring), 2.28 (ddd, 1H, *J* = 13.8, 10.5, 3.4 Hz, 1H of BtCC*H*$_2$), 3.08 - 3.14 (m, 2H, C*H*$_2$Se), 3.15 (ddd, 1H, *J* = 13.8, 11.5, 2.8 Hz, 1H of BtCC*H*$_2$), 3.63 - 3.68 (m, 1H, C*H*O), 4.04 (quintet, 1H, *J* = 6.5 Hz, C*H*CH$_2$Se), 6.05 (dd, 1H, *J* = 11.6, 3.3 Hz, BtC*H*), 6.95 - 7.55 (m, 12H, Ar*H*), 8.03 - 8.05 (m, 1H, 1H at C-4 of Bt)	$C_{25}H_{24}N_3FOSe$	C, 62.50 / 62.59 H, 5.03 / 5.11 N, 8.75 / 8.84
10b''	1501, 1083, 1021, 840, 738	1.65 - 1.78 (m, 2H, C*H*$_2$ of ring), 1.97 - 2.04 (m, 2H, C*H*$_2$ of ring), 2.70 (ddd, 1H, *J* = 13.6, 9.8, 5.2 Hz, 1H of BtCC*H*$_2$), 2.86 (ddd, 1H, *J* = 13.6, 10.3, 3.5 Hz, 1H of BtCC*H*$_2$), 3.05 (dd, 1H, *J* = 12.4, 6.2 Hz, 1H of C*H*$_2$Se), 3.11 (dd, 1H, *J* = 12.4, 5.4 Hz, 1H of C*H*$_2$Se), 3.65 - 3.67 (m, 1H, C*H*O), 4.14 (quintet, 1H, *J* = 6.4 Hz, C*H*CH$_2$Se), 5.91 (dd, 1H, *J* = 10.3, 5.1 Hz, BtC*H*), 6.97 - 7.51 (m, 12H, Ar*H*), 8.03 - 8.05 (m, 1H, 1H at C-4 of Bt)	$C_{25}H_{24}N_3FOSe$	C, 62.50 / 62.67 H, 5.03 / 4.99 N, 8.75 / 8.90
10b'''	1501, 1082, 1018, 840, 781, 738, 624	1.61 - 1.69 (m, 2H, C*H*$_2$ of ring), 2.03 - 2.17 (m, 2H, C*H*$_2$ of ring), 2.69 (ddd, 1H, *J* = 13.7, 9.9, 4.9 Hz, 1H of BtCC*H*$_2$), 2.83 (ddd, 1H, *J* = 13.7, 10.4, 3.3 Hz, 1H of BtCC*H*$_2$), 2.97 (dd, 1H, *J* = 12.2, 6.6 Hz, 1H of C*H*$_2$Se), 3.10 (dd, 1H, *J* = 12.2, 5.8 Hz, 1H of C*H*$_2$Se), 3.77 - 3.82 (m, 1H, C*H*O), 4.26 (quintet, 1H, *J* = 6.4 Hz, C*H*CH$_2$Se), 5.94 (dd, 1H, *J* = 10.5, 4.9 Hz, BtC*H*), 6.96 - 7.54 (m, 12H, Ar*H*), 8.03 - 8.05 (m, 1H, 1H at C-4 of Bt)	$C_{25}H_{24}N_3FOSe$	C, 62.50 / 62.77 H, 5.03 / 5.09 N, 8.75 / 8.66

Table 5. **Quantities of reactants** and yields of compounds **5** and diphenyl diselenide

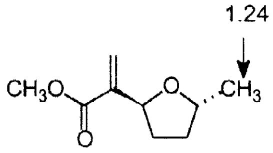
Compounds	mmol	Bu_3SnH mmol	AIBN mmol	**5**	Yield[a] (%)	$(PhSe)_2$	**5**	Mp[b] (°C)
10a	0.845	0.845	0.085	**a**	97	98	**a**	liquid
10a'	1.20	1.20	0.120	**b**	98	99	**b**	53-54
10a''	0.216	0.216	0.022	**c**	99	100	**c**	67-68
10a'''	0.199	0.199	0.020	**d**	98	99	**d**	86-87
10b	0.456	0.547	0.046	**e**	95	98	**e**	56-57
10b'	0.583	0.700	0.058	**f**	90	88	**f**	liquid
10b''	0.258	0.310	0.026	**g**	99	87	**g**	98-99
10b'''	0.243	0.292	0.024	**h**	99	90	**h**	liquid

[a]Isolated yields. [b] Recrystallized from *n*-hexane.

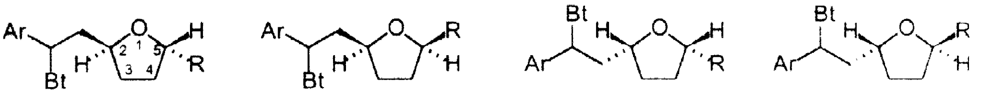
diastereomer **11b** appeared at 1.24 ppm. These ^1H NMR spectral data indicate that the signals of the *trans* methyl protons at C-5 appear upfield compared to those of the *cis* methyl protons. In the meantime, the diastereomers **5a** and **5b** exhibited a doublet at 1.14 and 1.26 ppm, respectively, assignable to the methyl protons at C-5 of the tetrahydrofuran moiety. Consequently, compounds **5a** and **5b** were assigned to be *trans* and *cis* diastereomers, respectively. This in turn suggests that compounds **10a** and **10a'**, which are precursors of **5a** and **5b**, respectively, should be *trans* and *cis* diastereomers, respectively. Likewise, compounds **5c** and **5d** were assigned to be *cis* and *trans* diastereomers based on the chemical shifts of the corresponding methyl protons appearing at 1.26 and 1.22 ppm, respectively, which in turn suggests that **10a''** and **10a'''** should be *cis* and *trans* diastereomers, respectively. Interestingly, in the case of compounds **10**, the ^1H NMR signals of the two protons at C-2 and C-5 of the tetrahydrofuran moiety of *cis* diastereomers **10a'** and **10a''** appeared upfield compared to those of the corresponding *trans* diastereomers **10a** and **10a'''**, respectively. A similar tendency in the ^1H NMR spectra of *cis*-isomers **10b'** and **10b''** and *trans*-isomers **10b** and **10b'''** was also observed.



11a



11b



Ar = Ph, R = CH_2SePh	**10a**	**10a'**	**10a''**	**10a'''**
→ Ar = Ph, R = CH_3	**5a**	**5b**	**5c**	**5d**
Ar = 4-FC_6H_4, R = CH_2SePh	**10b**	**10b'**	**10b''**	**10b'''**
→ Ar = 4-FC_6H_4, R = CH_3	**5e**	**5f**	**5g**	**5h**

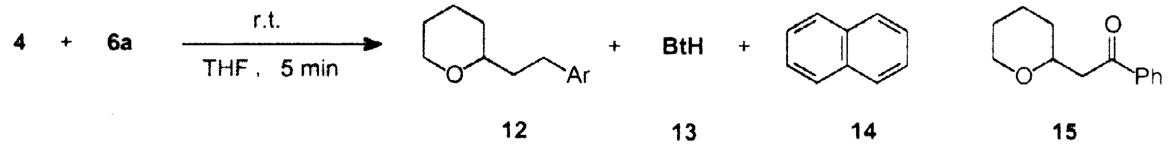
(B) The reaction of 4 with ***6a***

Upon dropwise addition of **6a** in THF (0.038 M) to the solution of **4a** in THF using a hypodermic syringe, the dark color of **6a** disppeared immediately. The addition was continued for 5 min until the dark color persisted. Quenching of the reaction mixture with water, followed by chromatography using a mixture of *n*-

Table 6. IR, ^{1}H NMR, and analytical data of compounds **5**

Compounds	IR (neat) cm^{-1}	^{1}H NMR (CDCl$_3$, 300 MHz) δ, ppm	Molecular Formula	Analysis % Calcd/Found
5a	3168, 2952, 1442, 1411, 1150, 1067, 744. 699	1.14 (d, 3H, J = 6.1 Hz, CH_3), 1.36 - 1.56 (m, 2H, CH_2 of ring), 1.99 - 2.07 (m, 2H, CH_2 of ring), 2.34 (ddd, 1H, J = 14.0, 10.1, 3.4 Hz, 1H of BtCCH_2), 3.16 (ddd, 1H, J = 14.3, 11.5, 2.9 Hz, 1H of BtCCH_2), 3.79 - 3.87 (m, 1H, CHO), 4.11 - 4.18 (m, 1H, OCHCH$_3$), 6.12 (dd, 1H, J = 11.5, 3.3 Hz, BtCH), 7.23 - 7.53 (m, 8H, ArH), 8.04 - 8.07 (m, 1H, 1H at C-4 of Bt)	$C_{19}H_{21}N_3O$	C, 74.24 / 74.52 H, 6.89 / 7.06 N, 13.67 / 13.83
5b	3056,2952, 2856, 1443, 1086, 917, 745, 698	1.26 (d, 3H, J = 6.1 Hz, CH_3), 1.40 - 1.62 (m, 2H, CH_2 of ring), 1.85 - 1.95 (m, 2H, CH_2 of ring), 2.36 (ddd, 1H, J = 13.9, 9.8, 3.5 Hz, 1H of BtCCH_2), 3.23 (ddd, 1H, J = 14.2, 11.4, 3.0 Hz, 1H of BtCCH_2), 3.62 - 3.70 (m, 1H, CHO), 3.81 - 3.91 (m, 1H, OCHCH$_3$), 6.16 (dd, 1H, J = 11.5, 3.4 Hz, BtCH), 7.28 - 7.53 (m, 8H, ArH), 8.05 - 8.08 (m, 1H, 1H at C-4 of Bt)	$C_{19}H_{21}N_3O$	C, 74.24 / 74.43 H, 6.89 / 7.03 N, 13.67 / 13.88
5c	3056, 2960, 1442, 1373, 1077,779, 742, 622	1.26 (d, 3H, J = 6.1 Hz, CH_3), 1.45 - 1.72 (m, 2H, CH_2 of ring), 1.95 - 2.03 (m, 2H, CH_2 of ring), 2.80 (ddd, 1H, J = 13.6, 9.2, 5.6 Hz, 1H of BtCCH_2), 2.92 (ddd, 1H, J = 13.6, 9.8, 3.9 Hz, 1H of BtCCH_2), 3.60 - 3.69 (m, 1H, CHO), 3.90 - 4.01 (m, 1H, OCHCH$_3$), 6.05 (dd, 1H, J = 9.8, 5.6 Hz, BtCH), 7.26 - 7.45 (m, 8H, ArH), 8.04 - 8.07 (m, 1H, 1H at C-4 of Bt)	$C_{19}H_{21}N_3O$	C, 74.24 / 74.55 H, 6.89 / 7.06 N, 13.67 / 13.89
5d	3056, 2952, 2856, 1485, 1445, 1130, 1080, 742, 698	1.22 (d, 3H, J = 6.1 Hz, CH_3), 1.41 - 1.73 (m, 2H, CH_2 of ring), 2.02 - 2.14 (m, 2H, CH_2 of ring), 2.79 - 2.85 (m, 2H, BtCCH_2), 3.80 - 3.88 (m, 1H, CHO), 4.08 - 4.19 (m, 1H, OCHCH$_3$), 6.02 (dd, 1H, J = 8.4, 7.0 Hz, BtCH), 7.26 - 7.53 (m, 8H, ArH), 8.04 - 8.07 (m, 1H, 1H at C-4 of Bt)	$C_{19}H_{21}N_3O$	C, 74.24 / 74.47 H, 6.89 / 6.99 N, 13.67 / 13.89
5e	2960, 1598, 1502, 1442, 1221, 1082, 744	1.14 (d, 3H, J = 6.1 Hz, CH_3), 1.37 - 1.60 (m, 2H, CH_2 of ring), 1.99 - 2.07 (m, 2H, CH_2 of ring), 2.29 (ddd, 1H, J = 14.0, 10.0, 3.4 Hz, 1H of BtCCH_2), 3.14 (ddd, 1H, J = 14.2, 11.5, 2.8 Hz, 1H of BtCCH_2), 3.74 - 3.82 (m, 1H, CHO), 4.09 - 4.25 (m, 1H, OCHCH$_3$), 6.10 (dd, 1H, J = 11.5, 3.3 Hz, BtCH), 6.98 - 7.51 (m, 7H, ArH), 8.05 - 8.08 (m, 1H, 1H at C-4 of Bt)	$C_{19}H_{20}N_3FO$	C, 70.14 / 70.01 H, 6.20 / 6.48 N, 12.91 / 1.09
5f	2952, 1598, 1502, 1445, 1371, 1221, 1038, 744	1.26 (d, 3H, J = 6.1 Hz, CH_3), 1.43 - 1.63 (m, 2H, CH_2 of ring), 1.89 - 2.00 (m, 2H, CH_2 of ring), 2.31 (ddd, 1H, J = 13.8, 9.9, 3.4 Hz, 1H of BtCCH$_2$), 3.21 (ddd, 1H, J = 14.2, 11.5, 2.9 Hz, 1H of BtCCH_2), 3.57 - 3.65 (m, 1H, CHO), 3.82 - 3.90 (m, 1H, OCHCH$_3$), 6.14 (dd, 1H, J = 11.5, 3.4 Hz, BtCH), 6.98 - 7.51 (m, 7H, ArH), 8.06 - 8.09 (m, 1H, 1H at C-4 of Bt)	$C_{19}H_{20}N_3FO$	C, 70.14 / 69.97 H, 6.20 / 6.35 N, 12.91 / 13.09
5g	3056, 2952, 2856. 1501, 1221, 1080, 779, 744	1.25 (d, 3H, J = 6.1 Hz, CH_3), 1.47 - 1.71 (m, 2H, CH_2 of ring), 1.91 - 2.02 (m, 2H, CH_2 of ring), 2.75 (ddd, 1H, J = 13.7, 9.5, 5.3 Hz, 1H of BtCCH_2), 2.90 (ddd, 1H, J = 13.6, 10.1, 3.7 Hz, 1H of BtCCH_2), 3.58 - 3.67 (m, 1H, CHO), 3.91 - 4.01 (m, 1H, OCHCH$_3$), 6.03 (dd, 1H, J = 10.1, 5.3 Hz, BtCH), 7.28 - 7.46 (m, 7H, ArH), 8.05 - 8.08 (m, 1H, 1H at C-4 of Bt)	$C_{19}H_{20}N_3FO$	C, 70.14 / 70.36 H, 6.20 / 6.21 N, 12.91 / 12.98
5h	3056, 2952, 2856, 1502, 1221, 1085, 746	1.21 (d, 3H, J = 6.1 Hz, CH_3), 1.42 - 1.68 (m, 2H, CH_2 of ring), 2.04 - 2.10 (m, 2H, CH_2 of ring), 2.74 (ddd, 1H, J = 14.0, 9.4, 5.4 Hz, 1H of BtCCH_2), 2.83 (ddd, 1H, J = 13.7, 9.8, 3.8 Hz, 1H of BtCCH_2), 3.77 - 3.86 (m, 1H, CHO), 4.08 - 4.18 (m, 1H, OCHCH$_3$), 6.01 (dd, 1H, J = 9.8, 5.5 Hz, BtCH), 7.28 - 7.51 (m, 7H, ArH), 8.05 - 8.07 (m, 1H, 1H at C-4 of Bt)	$C_{19}H_{20}N_3FO$	C, 70.14 / 70.11 H, 6.20 / 6.41 N, 12.91 / 13.06

hexane and EtOAc (100 : 1) gave 2-(2-phenylethyl)tetrahydro-2*H*-pyran (**12a**) (Ar = Ph) as a major product along with benzotriazole (**13**), naphthalene (**14**), 2-(benzoylmethyl)tetrahydro-2*H*-pyran (**15**) (12 %), and unknown mixtures (Scheme 3). Compound **15** was isolated only from the reaction of **4a**. Similarly compounds **12b** and **12c** were obtained from the reactions of **4b** and **4c** under the same conditions, respectively. Quantities of the reactants and yields of **12** and **13** are summarized in Table 7.



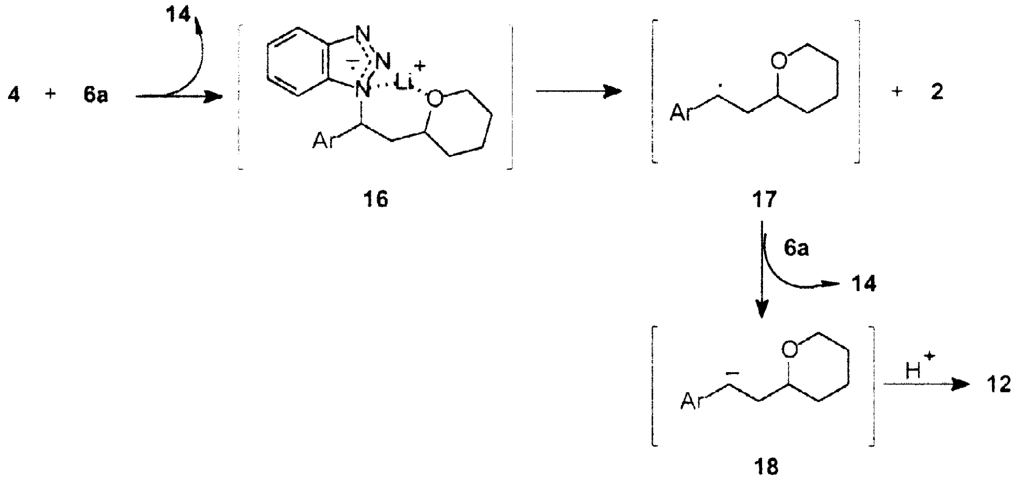
Scheme 3

Table 7. Quantities of reactants and yields of compounds 12 and 13

Compounds	Ar	mmol	6a		Yield^a (%)	
			mmol	12		13
4a	Ph	0.865	1.62	**a**	62	48
4b	4- FC_6H_4	0.418	0.758	**b**	45	78
4c	4-$MeOC_6H_4$	0.845	1.57	**c**	53	58

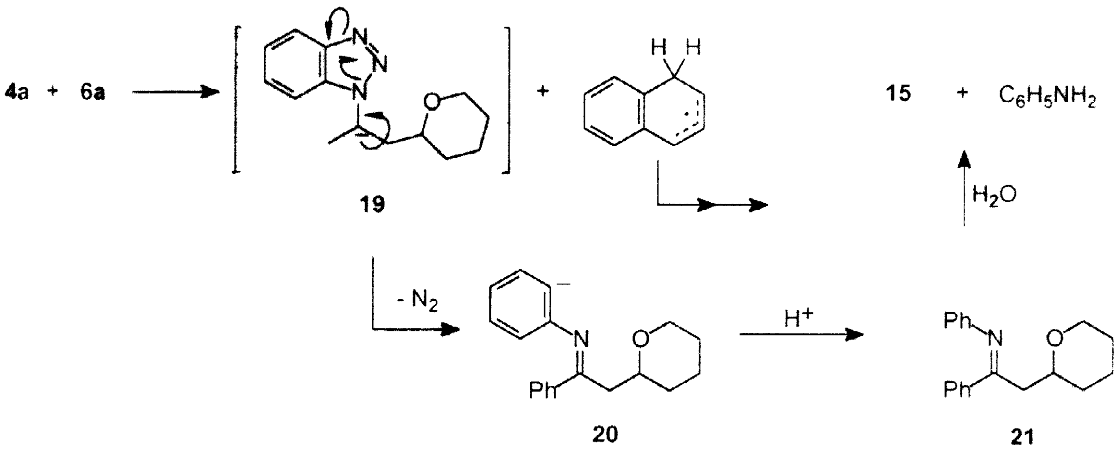
[a] Isolated yields.

The fomation of **12** may be understood by assuming a six-membered cyclic intermediate **16**, which is formed by the interaction of Li^+ with the δ oxygen and N-1 of the benzotriazole moiety. The intermediate **16** undergoes a bond reorganization to give a stable benzotriazolate ion **2** and a benzylic radical **17** (Scheme 4).



Scheme 4

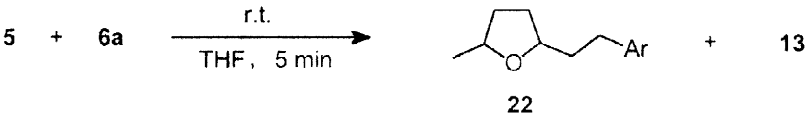
The radical **17** accepts one more electron to give a carbanion **18**, which protonates to give **12**[18]. The fomation of **15** suggests that **6a** acts as a base. That is, **6a** abstracts a proton from α-C bonded to N-1 to give a carbanion **19**, which extrudes a nitrogen molecule, followed by protonation to give an imine **21**. Hydrolysis of **21** would give **15** (Scheme 5). The formation of phenyl carbanions analogous to **20** from benzotriazole derivatives has already been proposed.[10(b),17]



Scheme 5

*(C) The reactions of 5 with **6a***

Treatment of **5a-b**, **5e-f**, a mixture of **5c** and **5d**, and a mixture of **5g** and **5h** with **6a** as for **4** gave 2-(2-arylethyl)-5-(methyl)tetrahydrofurans (**22a-h**) and **13** (Scheme 6). Yields of **22a-h** together with that of **13** are summarized in Table 8 and the spectroscopic (IR, ^{1}H NMR) and analytical data of **22a-b** and **22d-e** are presented in Table 9.



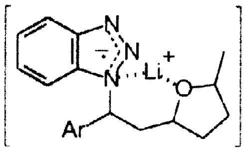
Scheme 6

Table 8. Quantities of reactants and yields of compounds **22** and **13**

Entry	Compounds	mmol	**6a**	**6b**		Yield[a] (%)	
			mmol	mmol	**22**		13
1	**5a**	0.651 (0.826)	1.19	1.48	**a**	73 (29)	78 (70)
2	**5b**	0.800 (0.898)	1.57	1.56	**b**	77 (44)	88 (68)
3	**5c** + **5d**	0.973 (0.836)	1.87	1.48	**c** + **d**	64 (43)	71 (58)
4	**5e**	0.418 (0.479)	0.710	0.823	**e**	59 (17)	64 (55)
5	**5f**	0.433 (0.615)	0.747	1.04	**f**	61 (33)	94 (63)
6	**5g** + **5h**	0.449 (0.956)	0.784	1.59	**g** + **h**	73 (39)	64 (62)

[a] Isolated yields. Numbers in the parenthesis represent data related to the reactions with sodium naphthalenide (**6b**).

Debenzotriazolated products **22**, analogous to tetrahydropyran derivatives **12**, were isolated from the reaction mixture. No products of deoxybenzoin type were obtained. Consequently, the formation of **22** can be explained by the same mechanism involving a six-membered cyclic intermediate **23**, which is analogous to the intermediate **16** (Scheme 4).

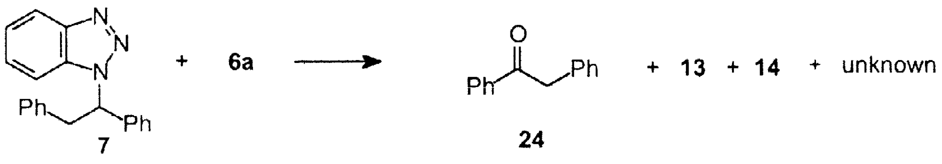


23

Table 9. IR, ^{1}H NMR, and analytical data of compounds **22**

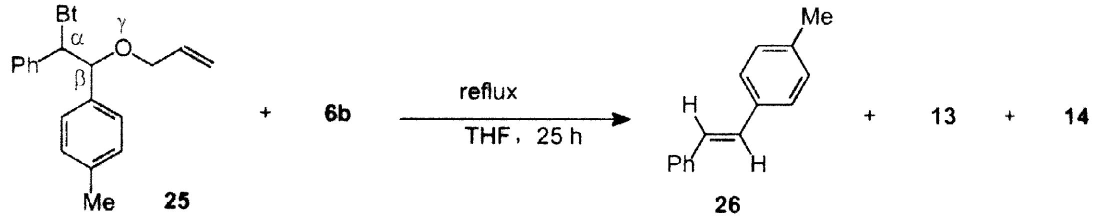
Compounds	IR (neat) cm^{-1}	^{1}H NMR (CDCl$_3$, 300 MHz) δ, ppm	Molecular Formula	Analysis % Calcd/Found
22a = **22d**	1484, 1442, 1367, 1081, 1060, 1024, 741, 695	1.29 (d, 3H, J = 6.1 Hz, CH_3), 1.45 - 1.66 (m, 2H, CH_2 of ring), 1.73 - 2.02 (m, 2H, CH_2 of ring), 2.05 - 2.14 (m, 2H, ArCH$_2$CH_2), 2.65 - 2.86 (m, 2H, ArCH_2), 4.03 - 4.23 (m, 2H, CHO and OCHCH$_3$), 7.09 - 7.35 (m, 5H, ArH)	$C_{13}H_{18}O$	C, 82.06 / 82.17 H, 9.53 / 9.78
22b = **22c**	1594, 1485, 1442, 1368, 1078, 1026 742, 694	1.34 (d, 3H, J = 6.1 Hz, CH_3), 1.45 - 2.08 (m, 6H, 2CH_2 of ring and ArCH$_2$CH_2), 2.69 - 2.89 (m, 2H, ArCH_2), 3.86 - 4.06 (m, 2H, CHO and OCHCH$_3$), 7.11 - 7.37 (m, 5H, ArH)	$C_{13}H_{18}O$	C, 82.06 / 82.22 H, 9.53 / 9.73
22d = **22h**	1502, 1442, 1371, 1216, 1149, 1082, 1067, 1011, 830, 747	1.25 (d, 3H, J = 6.1 Hz, CH_3), 1.45 - 1.56 (m, 2H, CH_2 of ring), 1.66 - 1.94 (m, 2H, CH_2 of ring), 2.02 - 2.10 (m, 2H, ArCH$_2$CH_2), 2.59 - 2.82 (m, 2H, ArCH_2), 3.97 - 4.19 (m, 2H, CHO and OCHCH$_3$), 6.93 - 7.01 (m, 2H, ArH), 7.14 - 7.19 (m, 2H, ArH)	$C_{13}H_{17}FO$	C, 74.97 / 74.89 H, 8.23 / 8.10
22e = **22f**	1595, 1506, 1443, 1366, 1216, 1077, 830, 742,	1.29 (d, 3H, J = 6.1 Hz, CH_3), 1.43 - 2.02 (m, 6H, 2CH_2 of ring and ArCH$_2$CH_2), 2.57 - 2.81 (m, 2H, ArCH_2), 3.81 - 4.06 (m, 2H, CHO and OCHCH$_3$), 6.94 - 7.02 (m, 2H, ArH), 7.14 - 7.20 (m, 2H, ArH)	$C_{13}H_{17}FO$	C, 74.97 / 74.84 H, 8.23 / 8.08

In order to see the effects of metal ions which are conceived to be involved in making a six-membered cyclic intermediate, compounds **5** were treated with sodium naphthalenide (**6b**) in the same manner as for the reactions with **6a**. The results are summarized in Table 8. Yields of **22** decreased remarkably but there were no significant differences in yields of **13**. The differences in yields of **22** are envisaged to reflect the more efficient interaction of Li$^+$ with unshared electrons on the oxygen atom of the tetrahydrofuran moiety and on the N-1 atom of the benzotriazole moiety in the intermediate than with Na$^+$,[19] presumably due to the predominant existence of solvent-separated ion pairs of **6a**, whereas the contact ion pairs of **6b** are the dominant species in THF. In the meantime, the reaction of **7** with **6a** in THF under the same conditions as for **4** gave deoxybenzoin (**24**) (41%) along with **13** (28%) and an unknown mixture (Scheme 7).



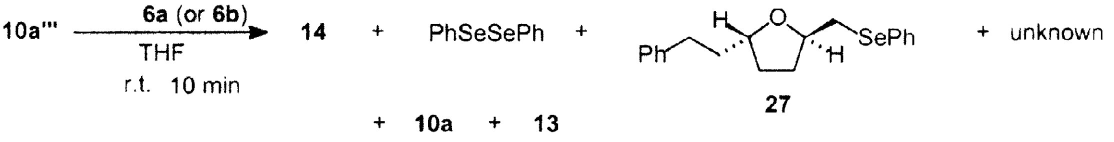
Scheme 7

The formation of **24** may be explained by the same mechanism as that for the formation of **15**. On the other hand, treatment of **25** having a γ-oxygen atom with **6b** for 25 h at reflux gave a mixture of **14** and *trans* olefin from which *trans* isomer **26** was isolated in 71% yield by rinsing the mixture with MeOH (Scheme 8).



Scheme 8

The stereochemistry of **26** was identified by comparing its melting point with the literature value[20] in addition to its spectroscopic data. In order to obtain **22** directly from **10**, compound **10a'''** was treated with **6a** (1.2 equiv.) for 10 min at room temperature. However, the reaction yielded **10a'''** (10%) and **27** (14%) in addition to **14** (89%), diphenyl diselenide (23%), and **13** (36%) (Scheme 9). Similar treatment with **6b** gave **10a'''** (15%), **27** (9%), **14** (85%), diphenyl diselenide (20%), and **13** (34%). The stereochemistry of 27 was assigned based on that of **10a'''**.



Scheme 9

The results suggest that 1.2 molar equivalents of **6a** and **6b** are insufficient quantities for removing both the benzotriazole moiety and the benzeneselenyl group. Attempted nucleophilic displacement of the benzotriazole moiety from **9c** using *N*,*N*-dimethylaniline (5 equiv.) under the same conditions as those employed for the reaction of 1-[(4-*N*,*N*-dialkylaminophenyl)methyl]benzotriazole with *N*,*N*-dialkylanilines[illegible] was not at all successful.

EXPERIMENTAL

^{1}H NMR spectra were recorded at 80 MHz, 300 MHz, and 500 MHz in $CDCl_3$ solution containing tetramethylsilane as an internal standard. Infrared (IR) spectra were obtained in KBr or as thin films on KBr plates. Mass spectral data were obtained by electron impact at 70 eV. Column chromatography was performed using silica gel (70-230 mesh, Merck). Thin layer chromatography was carried out on Merck chromatogram sheets (Kiesel gel 60 F_{254}). Chromatograms were visualized by using a mineral UV lamp. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected.

1-(Benzotriazol-1-yl)-1,2-diphenylethane (**7**)[5(a),10(b)] and 1-(arylmethyl)benzotriazoles (**8**)[12(c)] were prepared according to the literature procedures:

1-(Benzotriazol-1-yl)-1,2-diphenylethane (7): 147-148 °C (MeOH); IR (KBr) 3016, 2912, 1483, 1442, 1208, 1152, 1066, 853, 741 cm^{-1}. ^{1}H NMR (80 MHz, $CDCl_3$) 3.49 - 4.28 (m, 2H, C*H*$_2$), 5.87 - 6.05 (m, 1H, ArC*H*), 7.05 - 7.58 (m, 13H, Ar*H*), 7.96 - 8.08 (m, 1H, Ar*H*). Anal. Calcd for $C_{20}H_{17}N_3$: C, 80.24; H, 5.72; N, 14.04. Found: C, 80.45; H, 5.80; N, 14.01.

1-(4-*tert*-Butylphenylmethyl)benzotriazole (8d): 119-120 °C (MeOH); IR (KBr) 2944, 1504, 1442, 1218, 1080, 835, 738, 717 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) 1.28 (s, 9H, 3C*H*$_3$), 5.81 (s, 2H, C*H*$_2$), 7.21 - 7.26 (m, 2H, Ar*H*), 7.30 - 7.44 (m, 5H, Ar*H*), 8.05 - 8.08 (m, 1H, Ar*H*). Anal. Calcd for $C_{17}H_{19}N_3O$: C, 76.95; H, 7.22; N, 15.84. Found: C, 76.86; H, 7.44; N, 15.81.

General Procedure for the Synthesis of 2-[2-Aryl-2-(benzotriazol-1-yl)ethyl]tetrahydro-2*H*-pyrans (4).

LDA was added to a solution of **8** in THF (15 mL) at -78 °C, followed by addition of 2-(bromomethyl)tetrahydro-2*H*-pyran. The mixture was stirred for 10 min and then the temperature was raised to room temperature. The reaction mixture was quenched with water (50 mL), followed by extraction with CH_2Cl_2 (3 × 60 mL). The extracts were dried over $MgSO_4$. Removal of the solvent *in vacuo*, followed by chromatography on a silica gel (3 × 13 cm) using a mixture of *n*-hexane and EtOAc (20 : 1) gave diastereomers **4'** and **4''**, excluding **4c**. Diastereomers **4c'** and **4c''** were separated by preparative thin layer chromatography. Consult Table 1 for quantities of reactants and yields of diastereomers **4'** and **4''**, including the melting point of **4**, and Table 2 for the spectroscopic (IR, ^{1}H NMR, MS) and analytical data for diastereomers 4' and 4''.

General Procedure for the Synthesis of 1-Aryl-1-(benzotriazol-1-yl)-6-hepten-3-ol (9).

LDA (6.65 mmol, 3.3 mL) was added to a solution of 1-(phenylmethyl)benzotriazoles (**8a**) (928 mg, 4.43 mmol) in THF (25 mL) at -78 °C. The solution immediately turned deep blue. 1,2-Epoxy-5-hexene (522 mg, 5.32 mmol)was immediately added to the colored solution. The mixture was stirred for 20 min. The purple reaction mixture was quenched by adding water (50 mL), followed by extraction with CH_2Cl_2 (3 × 80 mL). The reaction mixture was worked up as usual. Chromatography (3 × 7 cm) using a mixture of *n*-hexane and EtOAc (10 : 1) gave unknown mixtures. Elution with the same solvent mixture (5 : 1) gave 1-(benzotriazol-1-yl)-1-phenyl-6-hepten-3-ol (**9a**) (331 mg, 24%) and **9a'** (319 mg, 23%). The melting point of **9a** was 206-207 °C (*n*-hexane + EtOAc) and that of **9a'** was 100-101 °C (*n*-hexane + EtOAc). Similarly, from the reaction mixture obtained from 1-(4-fluorophenylmethyl)benzotriazole (**8b**) (2.52 g, 11.1 mmol), LDA (16.7 mmol), and 1,2-epoxy-5-hexene (1.31 g, 13.3 mmol), were isolated diastereomers, 1-(benzotriazol-1-yl)-1-(4-fluorophenyl)-6-hexen-3-ol (**9b**) (746 mg, 21%) and **9b'** (971 mg, 27%), and unreacted **8b** (654 mg, 26%). The melting point of **9b** was 96-98 °C (*n*-hexane) and that of **9b'** was a liquid. Consult Table 3 for the spectroscopic (IR, ^{1}H NMR, MS) data for **9a**, **9a'**, **9b**, and **9b'**.

General Procedure for the Synthesis of 2-[2-Aryl-2-(benzotriazol-1-yl)ethyl]-5-(phenylselenomethyl)tetrahydrofurans (10).

4-Nitrobenzenesulfonyl peroxide (4-NBSP) (0.73 - 0.93 mmol) was added to a solution of diphenyl diselenide (0.73 - 0.93 mmol) in dried CH_3CN (30 mL) at 0 °C. The mixture was stirred for 10 min. A solution of compound 9 (1.4 - 1.8 mmol) in CH_3CN (10 mL) was dropwise added to the above mixture. The color of the solution turned slowly from red to brown. The mixture was stirred for 2 h at 0 °C. After water (50 mL) was added, the mixture was extracted with CH_2Cl_2 (3 × 80 mL). The extracts were worked up as usual. Chromatography (3 × 12 cm) using a mixture of *n*-hexane and EtOAc (20 : 1) gave diphenyl diselenide. Elution with the same solvent mixture (10 : 1) gave unknown mixtures and diastereomer **10a**. Diastereomer

10a' was eluted with the same solvent mixture (5 : 1). In the case of diastereomers **10a"** and **10a'''**, chromatography (3 × 8 cm) using a mixture of *n*-hexane and EtOAc (10 : 1) gave diphenyl diselenide. Elution with the same solvent mixture (10 : 1) gave **10a"** and **10a'''** in a mixture which were separated by PTLC. Similarly, diastereomers **10b** and **10b'**, **10b"** and **10b'''** were obtained. The melting point of **10a"** was 84-85 °C (*n*-hexane) and that of **10b'''** was 79-80 °C (*n*-hexane). The other diastereomers prepared were liquids. Consult Table 4 for the spectroscopic (IR, ^{1}H NMR) and analytical data for each diastereomer.

General Procedure for the Synthesis of 2-[2-Aryl-2-(benzotriazol-1-yl)ethyl]-5-(methyl)tetrahydrofurans (5).

A catalytic amount of azobisisobutyronitrile (AIBN) (0.046 - 0.178 mmol) was added to a solution of **10** (0.456 - 1.78 mmol) in benzene (10 mL). The mixture was heated to 50 °C, followed by addition of Bu_3SnH (0.547 - 2.14 mmol), which was heated for 1.5 h at reflux. Removal of the solvent *in vacuo*, followed by chromatography (2 × 13 cm) of the residue using *n*-hexane gave unreacted Bu_3SnH. Elution with a mixture of *n*-hexane and EtOAc (20 : 1) gave diphenyl diselenide. Elution with the same solvent mixture (5 : 1) gave **5**. Consult Table 5 for quantities of reactants and yields of **5** and diphenyl diselenide, including the melting point of **5**, and Table 6 for the spectroscopic (IR, ^{1}H NMR) and analytical data for **5**.

Preparation of Lithium Naphthalenide (6a).

Compound **6a** was prepared by treatment of naphthalene (**14**) (6.76 mmol) in THF (30 mL) with granular lithium metal (10.9 mmol) in THF (30 mL) at room temperature. The color of the solution turned pale yellow in 5 min and then deep green in 15 min. After additional stirring for 40 min, the reaction mixture was quenched with water to determine the concentration of **6a** formed. Chromatography of the reaction mixture gave **14** (82%) and 1,4-dihydronaphthalene (17%), which in turn suggested the concentration of **6a** to be 0.038 M.

General Procedure for the Reactions of 4 with 6a.

Compound **6a** (0.038 M, 15-34 mL) in THF was dropwise added to a solution of **4** (0.4-0.9 mmol) in THF (8 mL) by using a hypodermic syringe. The mixture was stirred for 5 min and then quenched by addition of water (50 mL). The reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL). The extracts were dried over $MgSO_4$ and worked up as usual. Chromatography (2 × 13 cm) of the reaction mixture using *n*-hexane gave **14**. Elution with mixture of *n*-hexane and EtOAc (100 : 1) gave 2-(2-arylethyl)tetrahydro-2*H*-pyrans (**12**). 2-(Benzoylmethyl)tetrahydro-2*H*-pyran (**15**) formed in the reaction of 2-[2-phenylethyl-2-(benzotriazol-1-yl)ethyl]tetrahydro-2*H*-pyran (**4a**) was eluted by using a mixture of *n*-hexane and EtOAc (30 : 1) after 2-(2-phenylethyl)tetrahydro-2*H*-pyran (**12a**) was eluted. The structures of **12a**[23] and **15**[24] were identified by comparing their spectroscopic data with the literature values. Consult Table 7 for quantities of reactants and yields of **12** and benzotriazole (**13**).

2-[2-(4-Fluorophenethyl)]tetrahydro-2*H*-pyran (**12b**) : liquid; IR (neat) 2928, 2832, 1501, 1440, 1216, 1082, 1040, 880, 826, 739 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) 1.25 - 1.87 (m, 8H, 3CH_2 of ring and ArCH$_2$CH_2), 2.59 - 2.81 (m, 2H, ArCH_2), 3.19 - 3.28 (m, 1H, 1H of OCH_2), 3.43 (td, 1H, J = 11.3, 2.8 Hz, 1H of OCH_2), 3.98 - 4.04 (m, 1H, OCHCH$_2$), 6.94 - 7.01 (m, 2H, ArH), 7.13 - 7.28 (m, 2H, ArH); MS (m/z) 109 (100), 148 (14.8), 161 (8.4), 190 (3.1), 208 (M^+,39.0%). Anal. Calcd for $C_{13}H_{17}FO$: C, 74.97; H, 8.23. Found: C, 74.71; H, 8.11.

2-[2-(4-Anisylethyl)]tetrahydro-2*H*-pyran (**12c**) : liquid; IR (neat) 2920, 2830, 1507, 1448, 1371, 1239, 1172, 1085, 877, 812 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) 1.27 - 1.88 (m, 8H, 3CH_2 of ring and ArCH$_2$CH_2), 2.58 -

2.79 (m, 2H, ArCH_2), 3.22 - 3.30 (m, 1H, 1H of OCH_2), 3.40 - 3.48 (m, 1H, 1H of OCH_2), 3.81 (s, 3H, CH_3O), 4.01 - 4.06 (m, 1H, OC*H*CH$_2$), 6.85 (d, 2H, *J* = 8.5 Hz, Ar*H*), 7.14 (d, 2H, *J* = 8.5 Hz, Ar*H*); MS (m/z) 121 (97.8), 147 (79.5), 161 (5.0), 174 (4.3), 201 (1.1), 220 (M^+, 100%). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.54; H, 9.29.

General Procedure for the Reactions of 5 with 6a.

The procedure is the same as that described for the reactions of 4 with **6a**. Consult Table 8 for quantities of reactants and yields of 2-(2-arylethyl)-5-(methyl)tetrahydrofurans (**22**) and **13**, and Table 9 for the spectroscopic (IR, ^{1}H NMR) and analytical data for **22**.

Reaction of 1-(Benzotriazol-1-yl)-1,2-diphenylethane (7) with 6a.

The same procedure as described for the reaction of **4** with **6a** was applied. Elution with a mixture of *n*-hexane and EtOAc (100 : 1) gave deoxybenzoin (**24**) (60 mg, 41%)[22] and unknown mixtures. Treatment of the aqueous layer with concentrated HCl, followed by extraction with CH_2Cl_2 gave **13** (25 mg, 28%).

Reaction of [2-(Benzotriazol-1-yl)-2-phenyl-1-(4-tolyl)]ethyl Allyl Ether (25) with Sodium Naphthalenide (6b).

To a solution of **25** (213 mg, 0.577 mmol) in THF (8 mL) was dropwise added **6b** (0.960 mmol, 35 mL), prepared *in situ* by treatment of Na (251 mg, 10.9 mmol) with naphthalene (866 mg, 6.76 mmol) in THF (35 mL), by using a hypodermic syringe. The mixture was heated for 2 h at reflux and quenched by addition of water (50 mL). The mixture was extracted with CH_2Cl_2 (3 × 80 mL) and the extracts were worked up as usual. Chromatography (3 × 10 cm) of the reaction mixture using *n*-hexane gave **14** (342 mg). Subsequent elution with a mixture of *n*-hexane and EtOAc (5 : 1) gave a mixture of **14** and *trans*-1-phenyl-2-(4-tolyl)ethene (**26**), which was washed with MeOH to give **26** (80 mg, 71%). The melting point of **26** was 115-116 °C (MeOH) (lit.,[20] 119 °C). According to the method described above for the reaction of **7** with **6a**, compound **13** (69 mg, 100%) was isolated from the aqueous layer.

Reaction of 10a''' with 6a.

Compound **6a** (0.187 mmol) was dropwise added to a solution of **10a'''** (75 mg, 0.162 mmol) in THF (8 mL) by using a hypodermic syringe. The mixture was stirred for 10 min at room temperature and then quenched by addition of water (50 mL). The mixture was worked up as usual. Chromatography (2 × 14 cm) of the reaction mixture using *n*-hexane and EtOAc (100 : 1) gave diphenyl diselenide (6 mg, 23%), 2-phenethyl-5-(phenylselenomethyl)tetrahydrofuran (**27**) (8 mg, 14%), an unknown mixture (24 mg) and reactant **10a'''** (8 mg, 10%). According to the method described above for the reaction of **7** with **6a**, compound **13** (7 mg, 36%) was isolated from the aqueous layer.

Compound **27** : liquid; IR (neat) 3024, 2912, 1472, 1248, 1046, 739, 688 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 1.61 - 2.07 (m, 4H, 2CH_2 of ring), 2.64 - 2.84 (m, 2H, ArCH$_2$CH_2), 3.00 (dd, 1H, *J* = 12.0, 7.5 Hz, 1H of CH_2Se), 3.20 (dd, 1H, *J* = 12.1, 5.3 Hz, 1H of CH_2Se), 3.78 - 4.29 (m, 4H, ArCH_2 + C*H*O + C*H*CH$_2$Se), 7.12 - 7.33 (m, 8H, Ar*H*), 7.55 - 7.58 (m, 2H, Ar*H*); MS (m/z) 91 (100), 105 (9.3), 131 (15.0), 157 (32.9), 175 (17.2), 189 (3.2), 345 (M^+, 2.3%), 346 (M^+ + 1, 20.2), 347 (M^+ + 2, 4.3), 348 (M^+ + 3, 4.0). Anal. Calcd for $C_{19}H_{22}OSe$: C, 66.08; H, 6.42. Found: C, 65.98; H, 6.23.

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