Oxidation of 1-[(Aryl)(phenylseleno)methyl]-, 1-[(Aryl)(arylthio)-(phenylseleno)methyl]-, and 1-[(Aryl)(diphenylseleno)-methyl]benzotriazoles with *m*-Chloroperbenzoic Acid

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During the last decade, benzotriazole (**1**) has received much attention as an excellent synthetic auxiliary [1]. Recently Katritzky, *et al.* [2] studied the oxidation of 1-(phenylthiomethyl)benzotriazole (**2a**) and 1-(2-phenyl-1-phenylthioethyl)benzotriazole (**2b**) and obtained their sulfones and sulfoxides by treatment with *m*-chloroperbenzoic acid (*m*-CPBA) and sodium periodate, respectively. No compounds derived from a heterolytic cleavage between the α-carbon and the N-1 atoms of the foregoing compounds were isolated.

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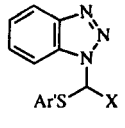
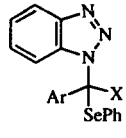
Benzotriazoles having a heteroatom with unshared electrons such as nitrogen, oxygen, and sulfur atoms bonded directly to the α-carbon on an N-1 atom have been reported to undergo a heterolytic bond cleavage, resulting in a cation and benzotriazolate anion which is stabilized by an -N=N- group in the five-membered ring of **1** [1]. The failure of heterolytic bond cleavage between N-1 and the α-carbon of compounds **2a** and **2b** suggest the investigation of the reactivities of 1-[(aryl)(phenylseleno)methyl]benzotriazole (**3**) because phenyl selenoxides formed by oxidation of phenyl selenides would be expected to rapidly undergo decomposition [3] to liberate the benzotriazolate anion by way of benzeneselenate [4]. With this in mind, **3**, 1-[(aryl)(arylthio)(phenylseleno)methyl]- **4**, and 1-[(aryl)(diphenylseleno)methyl]benzotriazoles **5** were prepared and the reactions with *m*-chloroperbenzoic acid were carried out. The results are described herein.



2a X = H Ar' = Ph
2b X = $PhCH_2$ Ar' = Ph
7 X = Ar



3 X = H
4 X = Ar'S
5 X = PhSe

Results and Discussion.

Synthesis of Compounds 3, 4 and 5.

The reaction of **1** with arylmethyl chloride gave 1-(arylmethyl)benzotriazoles **6**, which were treated with lithium diisopropylamide, followed by benzeneselenyl bromide and a slight excess amount of *n*-butyllithium in a series in tetrahydrofuran at -78° to give **3**. Physical and analytical data for compounds **6** and their spectroscopic data are summarized in Tables 1 and 2, respectively, and those of compounds **3** in Tables 3 and 4, respectively.

The 1-[(aryl)(arylthio)methyl]benzotriazoles **7** were prepared by the literature procedure [6]. Treatment of **7** with lithium diisopropylamide, followed by benzeneselenyl bromide, gave **4**. Physical and analytical data for compounds **7** and their spectroscopic data are summarized in Tables 5 and 6.

Physical and analytical data for compounds **4** and their spectroscopic data are summarized in Tables 7 and 8, respectively.

Compound **5** was prepared by treatment of **3** with lithium diisopropylamide in tetrahydrofuran, followed by the addition of benzeneselenyl bromide. Physical and analytical data for compounds **5** and their spectroscopic data are summarized in Tables 9 and 10, respectively.

Oxidation of 3 with *m*-Chloroperbenzoic Acid and its Reaction Mechanism.

From the reactions of **3** with *m*-chloroperbenzoic acid (2 equivalents) in dichloromethane at room temperature, **1**, 1-[(aryl)(3-chlorobenzoyloxy)methyl]benzotriazoles **8**, 3-chlorobenzoyl peroxide **9**, aromatic aldehydes, and diphenyl diselenide were isolated.

The structure of compound **8** was determined on the basis of the spectroscopic, mass spectral data and elemental analyses. Compound **8** is analogous to 1-[(acetoxy)-(phenyl)methyl]benzotriazole prepared by either the reaction of benzaldehyde diacetyl acetal with acid in the presence of **1** or the reaction of 1-[(hydroxy)(phenyl)methyl]-benzotriazole with acetic anhydride [7].

Compound **9** was isolated in 12% yield from the reaction of **3a** and its structure was identified by comparing its melting point with the literature value [8] in addition to its spectroscopic and analytical data. Separation of **9** from

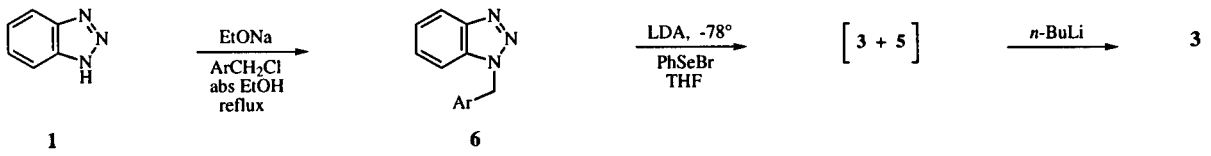


Table 1

Physical and Analytical Data for Compounds **6**

Compound	Ar	Mp [a] (°C)	Yield %	Molecular Formula	Analysis % Calcd./Found C	H	N
6c	3-$CH_3C_6H_4$	116-117	30	$C_{14}H_{13}N_3$	75.31	5.87	18.82
					75.51	5.71	18.79
6e	3-ClC_6H_4	118-120	26	$C_{13}H_{10}ClN_3$	64.07	4.14	17.24
					64.12	3.96	17.29
6f	4-FC_6H_4	68-69	45	$C_{13}H_{10}FN_3$	68.71	4.44	18.49
					68.91	4.32	18.36
6g	4-$C_5H_5C_6H_4$	184-185	11	$C_{19}H_{15}N_3$	79.98	5.30	14.73
					80.08	5.49	14.66
6h	3-CH_3(4-CH_3)C_6H_3	106-108	43	$C_{15}H_{15}N_3$	75.92	6.37	17.71
					76.03	6.51	17.59
6i	4-BrC_6H_4	118-119	23	$C_{13}H_{10}BrN_3$	54.19	3.50	14.58
					54.45	3.22	14.49
6a	C_6H_5	117-118 (115-116° [5a])	60				
6b	2-$CH_3C_6H_4$	80-81[b] (84-85° [5a])	32				
6d	4-$CH_3OC_6H_4$	78-80 (78-80° [5b])	54				

[a] From methanol; [b] From *n*-hexane.

Table 2

IR and ^{1}H NMR Spectroscopic Data for Compounds **6**

Compound	IR [a] (cm^{-1})	^{1}H NMR (deuteriochloroform) δ (ppm)
6c	1605, 1493, 1312, 951, 779, 743	2.26 (s, 3H, CH_3), 5.80 (s, 2H, CH_2), 7.02-7.44 (m, 7H, ArH)
6e	1592, 1568, 1483, 1435, 1306, 1219, 1160, 778, 754, 739	5.75 (s, 2H, CH_2), 7.00-7.40 (m, 7H, ArH), 7.95-8.10 (m, 1H, ArH)
6f	1506, 1438, 1222, 1158, 834, 738	5.80 (s, 2H, CH_2), 6.88-7.59 (m, 7H, ArH), 8.01-8.11 (m, 1H, ArH)
6g	1484, 1320, 1224, 1090, 746	5.85 (s, 2H, CH_2), 7.23-7.62 (m, 12H, ArH), 7.98-8.12 (m, 1H, ArH)
6h	2940, 1452, 1222, 1089, 781, 746	2.19 (s, 6H, $2CH_3$), 5.76 (s, 2H, CH_2), 6.98-7.37 (m, 6H, ArH) 8.00-8.11 (m, 1H, ArH)
6i	3056, 1486, 1226, 1086, 779, 744	5.79 (s, 2H, CH_2), 7.06-7.57 (m, 7H, ArH), 8.02-8.12 (m, 1H, ArH)

[a] From potassium bromide pellets.

the reactions of **3b-3i** by column chromatography failed, although thin layer chromatography (*n*-hexane:ethyl acetate = 15:1) showed the spot corresponding to **9**. In most cases, aldehydes formed during the reactions were eluted as an inseparable mixture by column chromatography. They showed a proton nuclear magnetic resonance signal at 9.92 ppm and an infrared band at 1702 cm^{-1} assignable to a proton attached to a carbonyl carbon and a carbonyl group, respectively. Physical and analytical data for compounds **8** and their spectroscopic data are summarized in Tables 11 and 12, respectively.

The formation of **8** having a *m*-chlorobenzoyloxy group as one of the major products is of interest because there appears to be one report showing the formation of a product with a *m*-chlorobenzoyloxy group in the *m*-chloroperbenzoic acid mediated oxidation of sulfides. That is, treatment of 4-alkyl-2*H*-1,4-thiazin-3-ones with *m*-chloroperbenzoic acid in dichloromethane at room temperature gave 2-(*m*-chlorobenzoyloxy)-4-alkyl-2*H*-1,4-thiazin-3-ones [9] in contrast to the expectation of the formation of its sulfoxide. However, the mechanism of the reaction was not mentioned.

In order to obtain mechanistic information on the formation of **8**, 1-[(phenyl)(phenylseleno)methyl]benzotria-

Table 3

Physical and Analytical Data for Compounds **3**

Compound	Ar	Mp (°C)	Yield %	Molecular Formula	Analysis % Calcd./Found C	H	N
3a	C_6H_5	79-80 [a]	54	$C_{19}H_{15}N_3Se$	62.64	4.15	11.53
					62.55	4.02	11.33
3b	2-$CH_3C_6H_4$	59-61 [b]	41	$C_{20}H_{17}N_3Se$	63.49	4.53	11.11
					63.67	4.43	11.16
3c	3-$CH_3C_6H_4$	liquid	33	$C_{20}H_{17}N_3Se$	63.49	4.53	11.11
					63.66	4.28	11.29
3d	4-$CH_3OC_6H_4$	89-91 [b]	30	$C_{20}H_{17}N_3OSe$	60.92	4.35	10.66
					60.83	4.43	10.62
3e	3-ClC_6H_4	liquid	36	$C_{19}H_{14}ClN_3Se$	57.23	3.54	10.54
					57.45	3.88	10.84
3f	4-FC_6H_4	83-85 [b]	40	$C_{19}H_{14}FN_3Se$	59.69	3.69	10.99
					59.73	3.50	10.85
3g	4-$C_6H_5C_6H_4$	161-162 [c]	24	$C_{25}H_{19}N_3Se$	68.18	4.35	9.54
					67.97	4.25	9.77
3h	3-CH_3(4-CH_3)C_6H_3	105-107 [a]	25	$C_{21}H_{19}N_3Se$	64.29	4.88	10.71
					64.04	4.60	10.87
3i	4-BrC_6H_4	liquid	41	$C_{19}H_{14}BrN_3Se$	51.49	3.18	9.48
					51.61	3.42	9.79

[a] From methanol; [b] From *n*-hexane; [c] From ethyl ether.

zole (**3**, Ar = C_6H_5) was treated with *m*-chloroperbenzoic acid in the presence of *p*-anisic acid with the expectation of the formation of 1-[(4-methoxybenzoyloxy)(phenyl)-methyl]benzotriazole. From the reaction only **8** (Ar = C_6H_5) was isolated and **1** in 32% and 56% yields, respectively along with a mixture of benzaldehyde and diphenyl diselenide. The results indicate that compound **8** is formed *via* an intramolecular pathway. We propose a mechanism involving the formation of selenurane **11** by the reaction of selenoxide **10** (X = H) formed initially by the oxidation of **3**, with the second molecule of *m*-chloroperbenzoic acid (Scheme 1). A similar type of selenurane was proposed for the lactonization of ketoselenoxide by hydrogen peroxide and other reactions [10]. The selenurane **11** rapidly undergoes decomposition to give **8** and benzeneseleninic acid.

The formation of **1**, aromatic aldehydes, and diphenyl diselenide can be explained by an alternative pathway which involves a transformation of selenoxide **10** (X = H) to benzeneselenate **12** (X = H) as suggested in the formation of aromatic aldehydes from benzyl phenyl selenoxides [4a]. The transformation of selenoxides **10** (X = H) to benzeneselenate **12** (X = H) is further supported by the trapping of benzeneselenyl trifluoroacetate formed by oxidation of trifluoroacetoselenic ester with *m*-chloroperbenzoic acid [11]. The benzeneselenate **12** (X = H) has an oxygen atom having unshared electron pairs at the α-carbon of N-1 of **1** which would be expected to dissociate heterolytically to give benzotriazolate anion and an oxonium ion **13** in view of the relevant examples in the literature [1b]. Both the benzotriazolate anion and the oxonium ion are readily converted to **1** and aromatic aldehydes in the presence of moisture which remained in commercial *m*-chloroperbenzoic acid. Benzeneselenenic acid formed along with aromatic aldehydes undergoes a series of reactions to give diphenyl diselenide and water [12].

Oxidation of **4** with *m*-Chloroperbenzoic Acid and its Mechanism.

Treatment of **4** with *m*-chloroperbenzoic acid (2 equivalents) in dichloromethane at room temperature gave arenethiol esters **14**, **1**, and diphenyl diselenide. Physical and analytical data for compounds **14** and their spectroscopic data are summarized in Tables 13 and 14, respectively.

There have been a variety of methods for the synthesis of thiol esters which mainly consist of the reactions of alcohols [13], acid halides [14], ketones [15], or carboxylic acids [16] with thiols either in the presence of catalyst or in the absence of catalyst. Trialkylthioborane [18], alkylthiotrimethylsilane [19] and alkylthiocyanate [20] have been utilized often for the synthesis of thiol esters. However, synthesis of thiol esters utilizing *m*-chloroperbenzoic acid has not been reported. The formation of **14** can be rationalized by the hydrolysis of an oxonium ion **13** (X = SAr') formed *via* benzeneselenate **12** (X = SAr'). Benzeneselenenic acid formed along with **14** is eventually converted to diphenyl diselenide and water (Scheme 1).

Table 4

IR and ^{1}H NMR Spectroscopic Data for Compounds **3**

Compound	IR (cm^{-1})	^{1}H NMR (deuteriochloroform) δ (ppm)
3a	1615, 1595, 1495, 1455, 1440, 1360, 1300, 1270, 1250, 1220, 1165, 1140 1120, 1070, 1030, 1005, 755, 740, 695 [a]	7.03-7.55 (m, 14H, CHSe + ArH), 7.96-8.06 (m, 1H, ArH)
3b	1595, 1451, 1272, 1070, 755, 740 [a]	2.42 (s, 3H, CH_3), 7.16-7.68 (m, 13H, CHSe + ArH), 7.96-8.05 (m, 1H, ArH)
3c	1598, 1474, 1438, 1054, 779, 741, 691 [b]	2.27 (s, 3H, CH_3), 6.91-7.60 (m, 13H, CHSe + ArH), 7.96-8.08 (m, 1H, ArH)
3d	1600, 1499, 1442, 1251, 1104, 1067, 1026, 784, 773, 762, 736, 688 [a]	3.78 (s, 3H, CH_3O), 6.83 (d, 2H, J = 10 Hz, ArH), 7.01-7.45 (m, 11H, CHSe + ArH), 7.92-8.06 (m, 1H, ArH)
3e	1582, 1564, 1466, 1435, 1267, 1232, 1195, 1150, 1064, 1014, 955, 774, 736, 688 [b]	6.95-7.60 (m, 13H, CHSe + ArH), 7.95-8.10 (m, 1H, ArH)
3f	1600, 1506, 1158, 843 744, 693 [a]	6.86-7.71 (m, 13H, CHSe + ArH), 7.96-8.08 (m, 1H, ArH)
3g	1485, 1475, 1274, 1162, 1066, 851, 758, 736, 694 [a]	7.12-7.80 (m, 18H, CHSe + ArH), 7.99-8.10 (m, 1H, ArH)
3h	3060, 2945, 1449, 1272, 1056, 788, 762 [a]	2.20 (s, 6H, $2CH_3$), 7.00-7.64 (m, 12H, CHSe + ArH), 7.95-8.07 (m, 1H, ArH)
3i	3060, 1487, 1438, 1072, 1056, 788, 764 [b]	7.06-7.58 (m, 13H, CHSe + ArH), 8.00-8.09 (m, 1H, ArH)

[a] From potassium bromide pellets; [b] Neat.

Oxidation of **5** with *m*-Chloroperbenzoic Acid and its Mechanism.

Treatment of **5** with *m*-chloroperbenzoic acid under the same conditions as in the oxidations of **3** and **4** gave 1-(aroyl)benzotriazoles **15**, **1**, and diphenyl diselenide.

Physical and analytical data for compounds **15** and their spectroscopic data are summarized in Tables 15 and 16, respectively.

Although hydrolysis of selenoketals at room temperature by mercury(II) chloride, copper(II) chloride, hydrogen peroxide, or benzeneseleninic anhydride in different solvents to give ketals have been reported [21], synthesis of 1-(acyl)benzotriazoles has been achieved by other methods which involve mostly the reactions of acid halides with 1-(trimethylsilyl)benzotriazole [22], 1-(tributylstannyl)benzotriazole [23] or 1-(hydroxymethyl)benzotriazole [24]. Compound **1** in dry pyridine treated dropwise with aroyl chlorides yielded **15** [25]. These methods are limited to the synthesis of **15a** and 1-(acetyl)benzotriazoles. Recently Katritzky, *et al.* [1e] developed two general methods for the synthesis of 1-(acyl)benzotriazoles. The first method is achieved by fusing an equimolar mixture of **1** and acid chloride at 80-100°. However, it has the drawback that a limited number of stable acid chlorides would be available. The second method involves the reaction of carboxylic acids with an equimolar amount of 1-(methanesulfonyl)benzotriazole in the presence of triethylamine at reflux.

The formation of **15** can be explained similarly by assuming a transformation of selenoxide **10** (X = SePh) to benzeneselenate **12** (X = SePh) as with the formation of **14** (Scheme 1). The benzeneselenate **12** (Scheme 2) undergoes heterolytic bond cleavage to give either selenonium ion **16** and benzeneselenate ion (path a-b) or selenonium ion **17a** and benzotriazolate anion (path a-c). In the presence of water, selenonium ion **16** is hydrolyzed to give **15** and benzeneselenol. Protonation of benzeneselenate ion becomes benzeneselenenic acid. On the other hand, selenonium ion **17a** is conceived to give benzeneseleno arene perester **18** and benzeneselenol under the same conditions as with selenonium ion **16**. However, no compound **18** was detected. Since seleno peresters are known to be unstable [26], it would be expected that compound **18**, if any, hydrolyzed to give arenecarboxylic acid **19** and benzeneselenenic acid. This possibility was confirmed by carrying out the reaction with **5c** (Ar = 4-$CH_3OC_6H_4$) from which a mixture of *m*-chlorobenzoic and *p*-anisic acids was isolated. Proton nuclear magnetic resonance spectrum (deuteriochloroform, 80 MHz) of the mixture showed a singlet at 3.88 ppm assignable to methoxy protons of *p*-anisic acid. Alternatively a heterolytic bond cleavage of **12** might give either oxonium ion **21** and benzeneselenolate (path d-e) or oxonium ion **17b**, which is a resonance form of **17a** and benzotriazolate anion (path d-c). Hydrolysis of **21** and **17b** gives compound **15** and benzeneseleno aryl esters **20**, respectively. Since no compounds **20** are detected despite their stabilities under aqueous conditions at room temperature, the

Table 5

Physical and Analytical Data for Compounds **7**

Compound	Ar	Ar'	Mp (°C)	Yield %	Molecular Formula	Analysis % Calcd./Found C	H	N	S
7a	C_6H_5	C_6H_5	80-81 [a]	21					
7b	C_6H_5	4-$CH_3C_6H_4$	122-123 [b]	23	$C_{20}H_{17}N_3S$	72.48	5.17	12.68	9.67
						72.36	5.07	12.78	9.53
7c	3-$CH_3C_6H_4$	C_6H_5	91-92 [b]	65	$C_{20}H_{17}N_3S$	72.48	5.17	12.68	9.67
						72.24	4.98	12.72	9.88
7d	4-$CH_3OC_6H_4$	C_6H_5	112-113 [b]	30	$C_{20}H_{17}N_3OS$	69.14	4.93	12.09	9.23
						69.01	4.84	12.32	9.34
7e	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	116-117 [b]	13	$C_{21}H_{19}N_3OS$	69.78	5.30	11.63	8.87
						70.02	5.58	11.49	8.96
7f	4-ClC_6H_4	4-$CH_3C_6H_4$	92-93 [b]	47	$C_{20}H_{16}ClN_3S$	65.66	4.41	11.48	8.76
						65.23	4.27	11.64	8.91
7g	4-NCC_6H_4	4-$CH_3C_6H_4$	114-115 [b]	61	$C_{21}H_{16}N_4S$	70.76	4.52	15.72	8.99
						70.51	4.43	15.94	9.14
7h	3-ClC_6H_4	4-$CH_3C_6H_4$	121-122 [b]	32	$C_{20}H_{16}ClN_3S$	65.66	4.41	11.48	8.76
						65.31	4.16	11.72	8.83

[a] From ethyl ether; [b] From methanol.

Table 6

IR and ^1H NMR Spectroscopic Data for Compounds **7**

Compound	IR [a] (cm^{-1})	^1H NMR (deuteriochloroform) δ (ppm)
7b	1444, 1268, 1068, 745	2.21 (s, 3H,CH_3), 6.70-7.72 (m, 13H, CHS + ArH), 7.95-8.10 (m, 1H, ArH)
7c	1481, 1446, 1276, 1072, 781, 741	2.31 (s, 3H, CH_3), 7.11-7.74 (m, 13H, CHS + ArH), 7.96-8.08 (m, 1H, ArH)
7d	1603, 1506, 1253, 803, 738	3.76 (s, 3H, CH_3O), 6.79-6.90 (d, 2H, J = 8 Hz), 7.14-7.72 (m, 11H, CHS + ArH), 7.96-8.05 (m, 1H, ArH)
7e	1605, 1257, 1171, 1032, 806, 774	2.19 (s, 3H, CH_3), 3.76 (s, 3H, CH_3O), 6.76-7.70 (m, 12H, CHS + ArH), 7.96-8.06 (m, 1H, ArH)
7f	1490, 1450, 1090, 1073, 1018, 768, 744	2.20 (s, 3H, CH_3), 6.84-7.69 (m, 12H, CHS + ArH), 7.99-8.10 (m, 1H, ArH)
7g	2230, 1607, 1447, 1060, 787	2.22 (s, 3H, CH_3), 6.87-7.86 (m, 12H, CHS + ArH), 8.01-8.12 (m, 1H,
7h	1595, 1490, 1451, 1074, 768, 747	ArH), 2.22 (s, 3H, CH_3), 6.96-7.67 (m, 12H, CHS + ArH), 7.96-8.11 (m, 1H, ArH)

[a] From potassium bromide pellets.

contribution of **17b** whether it is formed *via* either pathway (d-c) or **17a** may be negligible. Nevertheless we cannot rule out the involvement of the pathway (d-c) because **17a** might contribute as a major resonance form.

It is noteworthy that the sum of the yields of **15** and **1** for each reaction (Table 15) is almost quantitative and that the yields of diphenyl diselenide increase with those of **15** rather than those of **1**. These results may suggest that diphenyl diselenide is more readily formed by pathways (a-b) and (d-e) compared with pathways (a-c) and (d-c).

In order to confirm the source of the carbonyl oxygen, the oxidation of **5c** with *m*-chloroperbenzoic acid was carried out in the presence of a small amount of H_2O^{18} (10 atom %, 0.1 ml). Mass spectral data of **15c** obtained in the absence and presence of H_2O^{18} showed 0.56% larger ratio of (m/z) $M^+ + 2$ in **15c** obtained under the latter conditions. The results indicate that the carbonyl oxygen of **15** comes from water, presumably remaining in *m*-chloroperbenzoic acid rather than either *m*-chloroperbenzoic acid or oxygen molecules in the solvent.

In summary, apart from the results obtained from the reactions of 1-[(alkyl)(phenylthio)methyl]benzotriazoles **2** with *m*-chloroperbenzoic acid, treatment of 1-[(aryl)-(phenylseleno)methyl]- **3**, 1-[(aryl)(arylthio)(phenylseleno)methyl]- **4**, and 1-[(aryl)(diphenylseleno)methyl]-benzotriazoles **5** with *m*-chloroperbenzoic acid under the same conditions gives a different type of rearranged compound as major products, which are 1-[(aryl)(3-chlorobenzoyloxy)methyl]benzotriazoles **8**, arenethiol esters **14**, and 1-(aroyl)benzotriazoles **15**, respectively. The reactions of **3** leading to compounds **8** are of interest because *m*-chlorobenzoyloxy group originated from *m*-chloroper-

Table 7

Physical and Analytical Data for Compounds **4**

Compound	Ar	Ar'	Mp (°C)	Yield %	Molecular Formula	Analysis % Calcd./Found C	H	N	S
4a	C_6H_5	C_6H_5	148-150	62	$C_{25}H_{19}N_3SeS$	63.55	4.05	8.89	6.79
						63.33	3.92	8.77	6.98
4b	C_6H_5	4-$CH_3C_6H_4$	140-142	40	$C_{26}H_{21}N_3SeS$	64.19	4.35	8.64	6.59
						64.29	4.40	8.58	6.88
4c	3-$CH_3C_6H_4$	C_6H_5	152-154	20	$C_{26}H_{21}N_3SeS$	64.19	4.35	8.64	6.59
						64.41	4.35	8.67	6.94
4d	4-$CH_3OC_6H_4$	C_6H_5	153-155	28	$C_{26}H_{21}N_3OSeS$	62.15	4.21	8.36	6.38
						62.41	4.56	8.46	6.57
4e	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	150-151	33	$C_{27}H_{23}N_3OSeS$	62.78	4.49	8.14	6.21
						62.59	4.33	8.41	6.42
4f	4-ClC_6H_4	4-$CH_3C_6H_4$	138-140	24	$C_{26}H_{20}ClN_3SeS$	59.99	3.87	8.07	6.15
						59.77	3.64	8.23	6.33
4g	4-NCC_6H_4	4-$CH_3C_6H_4$	147-149	19	$C_{27}H_{20}N_4SeS$	63.40	3.94	10.95	6.27
						63.62	4.12	11.05	6.31
4h	3-ClC_6H_4	4-$CH_3C_6H_4$	132-133	40	$C_{26}H_{20}ClN_3SeS$	59.95	3.87	8.07	6.15
						59.71	3.77	8.11	6.28

[a] From methanol.

Table 8

IR and ^1H NMR Spectroscopic Data for Compounds **4**

Compound	IR [a] (cm^{-1})	^1H NMR (deuteriochloroform) δ (ppm)
4a	1597, 1432, 1280, 1154, 1085, 741, 688	6.74-7.40 (m, 18H, ArH), 7.94-8.04 (m, 1H, ArH)
4b	1487, 1445, 1281, 1082, 807, 773, 747,723, 691	2.22 (s, 3H, CH_3), 6.77-7.40 (m, 17H, ArH). 7.97-8.10 (m, 1H, ArH)
4c	1469, 1064, 920, 824, 779, 746, 691	2.08 (s, 3H, CH_3), 6.71-7.47 (m, 17H, ArH), 7.96-8.05 (m, 1H, ArH)
4d	1605, 1507, 1467, 1258, 1176, 1026, 819, 752, 688	3.73 (s, 3H, CH_3O), 6.52-7.59 (m, 17H, ArH) 7.95-8.09 (m, 1H, ArH)
4e	1599, 1256, 1024, 785, 740	2.21 (s, 3H, CH_3), 3.73 (s, 3H, CH_3O), 6.51-7.37 (m, 16H, ArH), 7.94-8.08 (m, 1H, ArH)
4f	3072, 1592, 1483, 1280, 923, 786, 762	2.23 (s, 3H, CH_3), 6.66-7.34 (m, 16H, ArH), 7.98-8.08 (m, 1H, ArH)
4g	3064, 2232, 1597, 1486, 1445, 1285, 1128, 803, 752, 741	2.22 (s, 3H, CH_3), 6.81-7.49 (m, 16H, ArH), 7.99-8.18 (m, 1H, ArH)
4h	3072, 1590, 1486, 1197, 806, 746	2.24 (s, 3H, CH_3), 6.79-7.53 (m, 16H, ArH), 7.97-8.09 (m, 1H, ArH)

[a] From potassium bromide pellets.

1 + ArCHO + Ar'SH $\xrightarrow[\text{benzene, reflux}]{p\text{-TsOH}}$ **7** $\xrightarrow[\text{PhSeBr, THF}]{\text{LDA, -78°}}$ **4**

benzoic acid is seldom incorporated into the products. Futhermore the reactions of **3**, **4**, and **5** with *m*-chloroperbenzoic acid furnish new examples for the formation of products through the rearrangement of selenoxides to selenenates. In addition, the formation of compounds **14** in moderate to excellent yields demonstrated the usefulness of **1** as a synthetic auxiliary.

EXPERIMENTAL

The proton nuclear magnetic resonance spectra were recorded at 80 MHz in deuteriochloroform solution containing tetramethylsilane as an internal standard. Infrared spectra were recorded in potassium bromide or in thin films on potassium bromide plates. Mass spectra were obtained by electron impact at 70 eV in the Inter-University Center for Natural Sciences Research

Table 9

Physical and Analytical Data for Compounds **5**

Compound	Ar	Mp (°C)	Yield %	Molecular Formula	Analysis % Calcd./Found C	H	N
5a	C_6H_5	153-154 [a]	40	$C_{25}H_{19}N_3Se_2$	57.82	3.69	8.09
					57.96	3.91	7.63
5b	4-FC_6H_4	150-152 [b]	44	$C_{25}H_{18}FN_3Se_2$	55.88	3.38	7.82
					55.63	3.42	7.85
5c	4-$CH_3OC_6H_4$	140-142 [c]	37	$C_{26}H_{21}N_3OSe_2$	56.84	3.85	7.65
					56.58	3.89	7.62

[a] From ethanol; [b] From methanol; [c] From *n*-hexane.

Table 10

IR and ^{1}H NMR Spectroscopic Data for Compounds **5**

Compound	IR [a] (cm^{-1})	^{1}H NMR (deuteriochloroform) δ (ppm)
5a	1603, 1586, 1480, 1278, 1069, 1021, 925, 811, 781	6.62-7.39 (m, 18H, ArH), 7.93-8.05 (m, 1H, ArH)
5b	1598, 1499, 1285, 1165, 846, 794, 742, 690	6.59-7.38 (m, 17H, ArH), 7.93-8.05 (m, 1H, ArH)
5c	2944, 1597, 1523, 1174, 1022, 742	3.75 (s, 3H, CH_3O), 6.50-7.40 (m, 17H, ArH), 7.93-8.02 (m, 1H, ArH)

[a] From potassium bromide pellets.

Facilities. Elemental analyses were determined by the Korea Basic Science Center. Column chromatography was performed using silica gel (70-230 mesh, Merck).

General Procedure for the Preparation of 1-(Arylmethyl)benzotriazoles **6a-6i**.

To a stirred solution of sodium (8.7 mmoles) in absolute ethanol (10 ml) was added a solution of benzotriazole (**1**) (8.4 mmoles) in absolute ethanol (15 ml). The mixture was stirred for an appropriate time, followed by addition of arylmethyl chloride (9 mmoles), which was heated for 3.5 hours at reflux. Quenching the mixture with water (20 ml), followed by removal of the solvent *in vacuo* gave a white residue, which was extracted with dichloromethane (3 x 50 ml). Drying of the extracts over magnesium sulfate, followed by removal of the solvent gave a residue, which was chromatographed on a silica gel column (2 x 15 cm). Elution with a mixture of *n*-hexane and ethyl acetate (4:1, 300 ml) gave white solids **6**, which were recrystallized from methanol. Consult Table 1 for physical and analytical data and Table 2 for ir and ^{1}H nmr spectroscopic data of compounds **6**.

General Procedure for the Preparation of 1-[(Aryl)(phenylseleno)methyl]benzotriazoles **3a-3i**.

To a solution of **6** (4 mmoles) in tetrahydrofuran (50 ml) at -78° under a nitrogen atmosphere was added lithium diisopropylamide (4.8 mmoles, 1.5 *M* in cyclohexane) using a hypodermic syringe. The mixture was stirred for 5 seconds to give a dark blue solution, followed by dropwise addition of benzene-

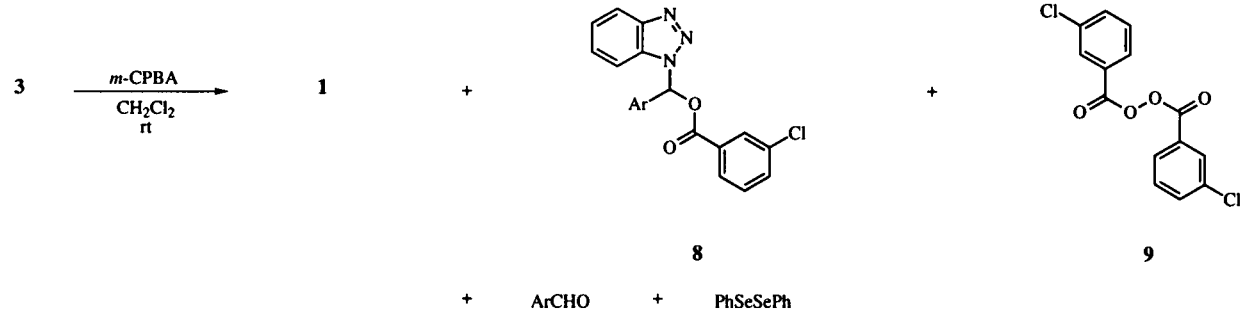


Table 11

Physical and Analytical Data for Compounds **8**

Compound	Ar	Mp (°C)	Yield %	Molecular Formula	Analysis % Calcd./Found C	H	N
8a	C_6H_5	93-94 [a]	54 (45)	$C_{20}H_{14}ClN_3O_2$	66.03	3.88	11.55
					66.25	3.60	11.21
8b	4-$CH_3OC_6H_4$	117-119 [b]	39 (41)	$C_{21}H_{16}ClN_3O_3$	64.05	4.09	10.67
					64.28	3.85	10.57
8c	4-FC_6H_4	liquid	34 (61)	$C_{20}H_{13}ClFN_3O_2$	62.92	3.43	11.01
					62.77	3.20	11.06
8d	4-$H_5C_6C_6H_4$	122-124 [c]	58 (41)	$C_{26}H_{18}ClN_3O_2$	70.99	4.12	9.55
					70.75	4.09	9.79
8e	3-$CH_3C_6H_4$	liquid	36 (63)	$C_{21}H_{16}ClN_3O_2$	66.76	4.27	11.12
					66.57	4.38	11.34
8f	3-CH_3(4-CH_3)C_6H_3	105-106 [b]	39 (61)	$C_{22}H_{18}ClN_3O_2$	67.43	4.63	10.72
					67.66	4.59	10.55
8g	4-BrC_6H_4	liquid	23 (60)	$C_{20}H_{13}BrClN_3O_2$	54.26	2.96	9.49
					54.03	3.05	9.78

[a] From ethanol; [b] From *n*-hexane; [c] From methanol; [d] Number in the parenthesis represents the yield of compound **1**.

Table 12

IR and ^{1}H NMR Spectroscopic Data for Compounds **8**

Compound	IR (cm^{-1})	^{1}H NMR (deuteriochloroform) δ (ppm)
8a	3072, 1728, 1614, 1593, 1251, 1122, 845, 778, 734, 618 [a]	7.23-8.20 (m, 13H, ArH), 8.69 (s, 1H, CHO)
8b	1728, 1604, 1245, 1177, 1060, 799, 742 [b]	3.80 (s, 3H, CH_3O), 6.96-8.15 (m, 12H, ArH), 8.65 (s, 1H, CHO)
8c	3075, 1734, 1607, 1448, 1282, 1103, 844, 768, 744, 670 [b]	7.01-8.16 (m, 12H, ArH), 8.65 (s, 1H, CHO)
8d	1733, 1282, 1244, 1104, 1120, 1058, 806, 745 [a]	7.26-8.17 (m, 17H, ArH), 8.73 (s, 1H, CHO)
8e	3065, 1734, 1607, 1589, 1448, 1242, 1059, 779, 743 [a]	2.33 (s, 3H, CH_3), 6.81-8.15 (m, 12H, ArH), 8.68 (s, 1H, CHO)
8f	3064, 2976, 1736, 1574, 1280, 1242, 1120, 1054, 798, 754, 739 [a]	2.25 (s, 6H, $2CH_3$), 7.11-8.15 (m, 11H, ArH), 8.64 (s, 1H, CHO)
8g	1738, 1282, 1245, 1105, 1062, 795, 744 [b]	7.24-8.14 (m, 12H, ArH), 8.61 (s, 1H, CHO)

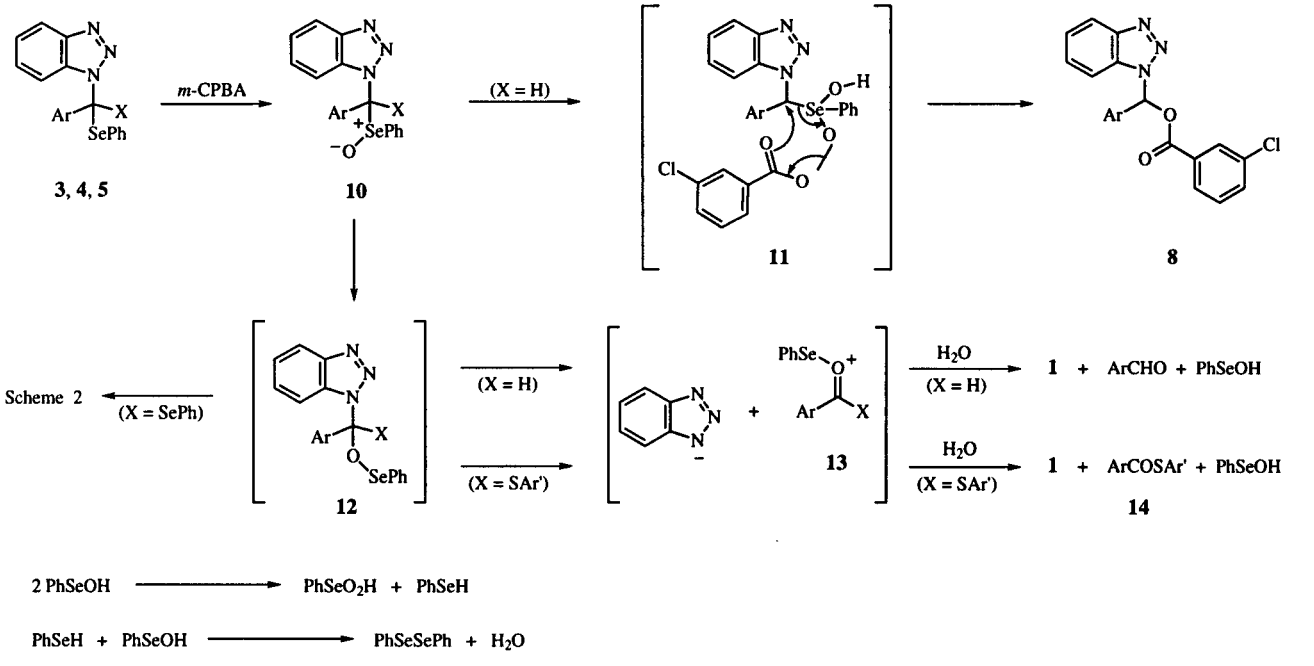
[a] From potassium bromide pellets; [b] Neat.

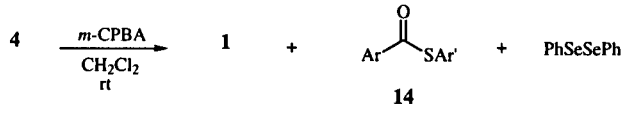
selenyl bromide (6 mmoles) to give a yellow solution. After the mixture was stirred additionally for 20 minutes, *n*-butyllithium (10 *M* in *n*-hexane, 1 equivalent) was added. The mixture was stirred for 40 minutes, followed by quenching with water (50 ml) and extracted with ethyl ether (3 x 50 ml). Drying the extracts over magnesium sulfate, followed by removal of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (2.5 x 13 cm). Elution with a mixture of *n*-hexane and ethyl acetate (6:1, 60 ml) gave a mixture of *n*-butyl phenyl selenide (0.3-0.9 mmole) and diphenyl diselenide (1.2-2.2 mmoles), an unknown mixture, and compounds **3**. Compounds **3** were recrystallized from *n*-hexane. Consult Table 3 for physical and analytical data and Table 4 for ir and ^{1}H nmr spectroscopic data of compounds **3**.

General Procedure for the Preparation of 1-[(Aryl)(arylthio)-(phenylseleno)methyl]benzotriazoles **4a-4h**.

To a solution of 1-[(aryl)(arylthio)methyl]benzotriazoles **7** (1-5 mmoles) in tetrahydrofuran (15 ml) at -78° was added lithium diisopropylamide (2-11 mmoles). The color of the solution immediately turned dark blue. Stirring of the mixture for 10 minutes, followed by dropwise addition of benzeneselenyl bromide (1-7 mmoles) gave a yellow solution, which was stirred for an additional 15 minutes. The mixture was warmed to room temperature, followed by quenching with water (10 ml), which was extracted with ethyl ether (2 x 50 ml). Drying the extracts over magnesium sulfate, followed by evaporation of the solvent gave a residue, which was chromatographed on a silica gel column (2 x 12 cm). Elution with a mixture of *n*-hexane and ethyl acetate (6:1, 60 ml) gave diphenyl diselenide (0.3-1.6 mmoles), compounds **4** (19-62%) and compounds **7** (13-61%). Compounds **4** were recrystallized from methanol. Consult Table 7 for physical and analytical data and Table 8 for ir and ^{1}H nmr spectroscopic data of compounds **4**.

Scheme 1





General Procedure for the Synthesis of 1-[(Aryl)(diphenylseleno)methyl]benzotriazoles **5a-5c**.

To a solution of **3** (1-2 mmoles) in tetrahydrofuran (15 ml) at -78° was added lithium diisopropylamide (2-5 mmoles). The color of the solution turned deep blue immediately. Stirring the mixture for 10 minutes, followed by dropwise addition of benzeneselenyl bromide (1-2 mmoles) gave a deep brown solution, which was stirred for an additional 15 minutes. The mixture was warmed to room temperature and then quenched with water (10 ml). Extraction of the mixture with ethyl ether (3 x 50 ml), followed by evaporation of the solvent gave a residue which was chromatographed on a silica gel column (3 x 9 cm). Elution with a mixture of *n*-hexane and ethyl acetate (20:1, 60 ml) gave diphenyl diselenide (0.4-0.9 mmole), compounds **5**, and unreacted compounds **3**. Consult Table 9 for physical and analytical data and Table 10 for ir and ^{1}H nmr spectroscopic data of compounds **5**.

General Procedure for the Synthesis of 1-[(Aryl)(3-chlorobenzoyloxy)methyl]benzotriazoles **8a-8g**.

To a solution of **3** (0.2-0.6 mmole) in dichloromethane (15 ml) at room temperature was added *m*-chloroperbenzoic acid (0.3-1.2 mmoles). The mixture was stirred for 50 minutes, followed by quenching with saturated sodium bicarbonate. The mixture was extracted with dichloromethane (3 x 50 ml). Drying the extract over magnesium sulfate, followed by removal of the solvent *in vacuo*, gave a residue, which was chromatographed on a silica gel column (2 x 8 cm). Elution with a mixture of *n*-hexane and ethyl acetate (7:1, 100 ml) gave a mixture of the corresponding aromatic aldehyde and 3-chlorobenzoyl peroxide. Elution with the same solvent mixture (7:1, 100 ml) gave compounds **8**. Continued elution with ethyl acetate (50 ml) gave **1**. Consult Table 11 for physical and analytical data and Table 12 for ir and ^{1}H nmr spectroscopic data of compounds **8**.

Reaction of **3a** with *m*-Chloroperbenzoic Acid in the Presence of *p*-Anisic Acid.

To a solution of **3a** (256 mg, 0.703 mmole) and *p*-anisic acid (215 mg, 1.41 mmoles) in dichloromethane (30 ml) at room temperature was added *m*-chloroperbenzoic acid (486 mg, 1.41 mmoles). The mixture was stirred for 15 minutes and worked up as in the reaction without *p*-anisic acid. Chromatography (2 x 9 cm) of the reaction mixture using a mixture of *n*-hexane and ethyl acetate (10:1, 100 ml) gave benzaldehyde contaminated with unknown compounds (24 mg), **8a** (81 mg, 32%), unknowns (19 mg), and unreacted **3a** (47 mg, 56%).

Table 13

Physical and Analytical Data for Compounds **14**

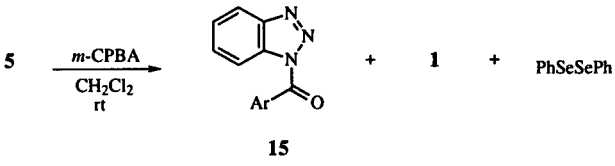
Compound	Ar	Ar'	Mp (°C)	Yield [a] %	Molecular Formula	Analysis % Calcd./Found C	H	N	S
14a	C_6H_5	C_6H_5	54-55 [b] (56° [17a])	95 (75)					
14b	3-$CH_3C_6H_4$	C_6H_5	26-27 [c]	57 (99) [d]	$C_{14}H_{12}OS$	73.65 73.41	5.30 5.29		14.04 14.51
14c	4-$CH_3OC_6H_4$	C_6H_5	90-91 [c] (94-95° [17b])	96 (82) [e]					
14d	C_6H_5	4-$CH_3C_6H_4$	70-72 [b] (75° [17a])	54 (96)					
14e	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	64-66 [c] (68° [17a])	67 (95) [f]					
14f	3-ClC_6H_4	4-$CH_3C_6H_4$	56-58 [c]	68 (84)	$C_{14}H_{11}ClOS$	64.00 63.84	4.22 4.29		12.20 12.41
14g	4-ClC_6H_4	4-$CH_3C_6H_4$	106-107 [b] (111° [17a])	63 (68)					
14h	4-NCC_6H_4	4-$CH_3C_6H_4$	115-116 [b]	84 (96) [g]	$C_{15}H_{11}NOS$	71.12 71.35	4.38 4.14	5.53 5.46	12.66 12.89

[a] Number in the parenthesis represents the yield of compound **1**; [b] From *n*-hexane; [c] From methanol; [d], [e], [f], [g] Diphenyl diselenide was isolated in 28, 15, 13 and 21% yields, respectively.

Table 14

IR and ^1H NMR Spectroscopic Data for Compounds **14**

Compound	IR (cm^{-1})	^1H NMR (deuteriochloroform) δ (ppm)
14b	3065, 1676, 1477, 1246, 1023, 939, 786, 745, 691 [a]	2.41 (s, 3H, CH_3) 7.30-7.50 (m, 7H, ArH), 7.75-7.98 (m, 2H, ArH)
14f	1667, 1562, 1402, 1194, 922, 806, 765, 691 [b]	2.39 (s, 3H, CH_3), 7.17-7.60 (m, 6H, ArH), 7.91-8.02 (m, 2H, ArH)
14h	3065, 2232, 1678, 1488, 1203, 906, 851, 765, 656 [a]	2.40 (s, 3H, CH_3), 7.19-7.80 (m, 6H, ArH) 8.05-8.15 (m, 2H, ArH)



[a] Neat; [b] From potassium bromide pellets.

Table 15

Physical and Analytical Data for Compounds **15**

Compound	Ar	Mp [a] (°C)	Yield %	Molecular Formula	Analysis % Calcd./Found C	H	N
15a	C_6H_5	110-112 (112-113° [1d])	62 (37)				
15b	4-FC_6H_4	110-112	37 (57)	$C_{13}H_8FN_3O$	64.73 64.90	3.34 3.55	17.42 17.49
15c	4-$CH_3OC_6H_4$	110-111	95 (trace)	$C_{14}H_{11}N_3O_2$	66.40 66.31	4.38 4.21	16.59 16.88

[a] From methanol; [b] Number in the parenthesis represents the yield of benzotriazole isolated.

Table 16

IR and ^{1}H NMR Spectroscopic Data for Compounds **15**

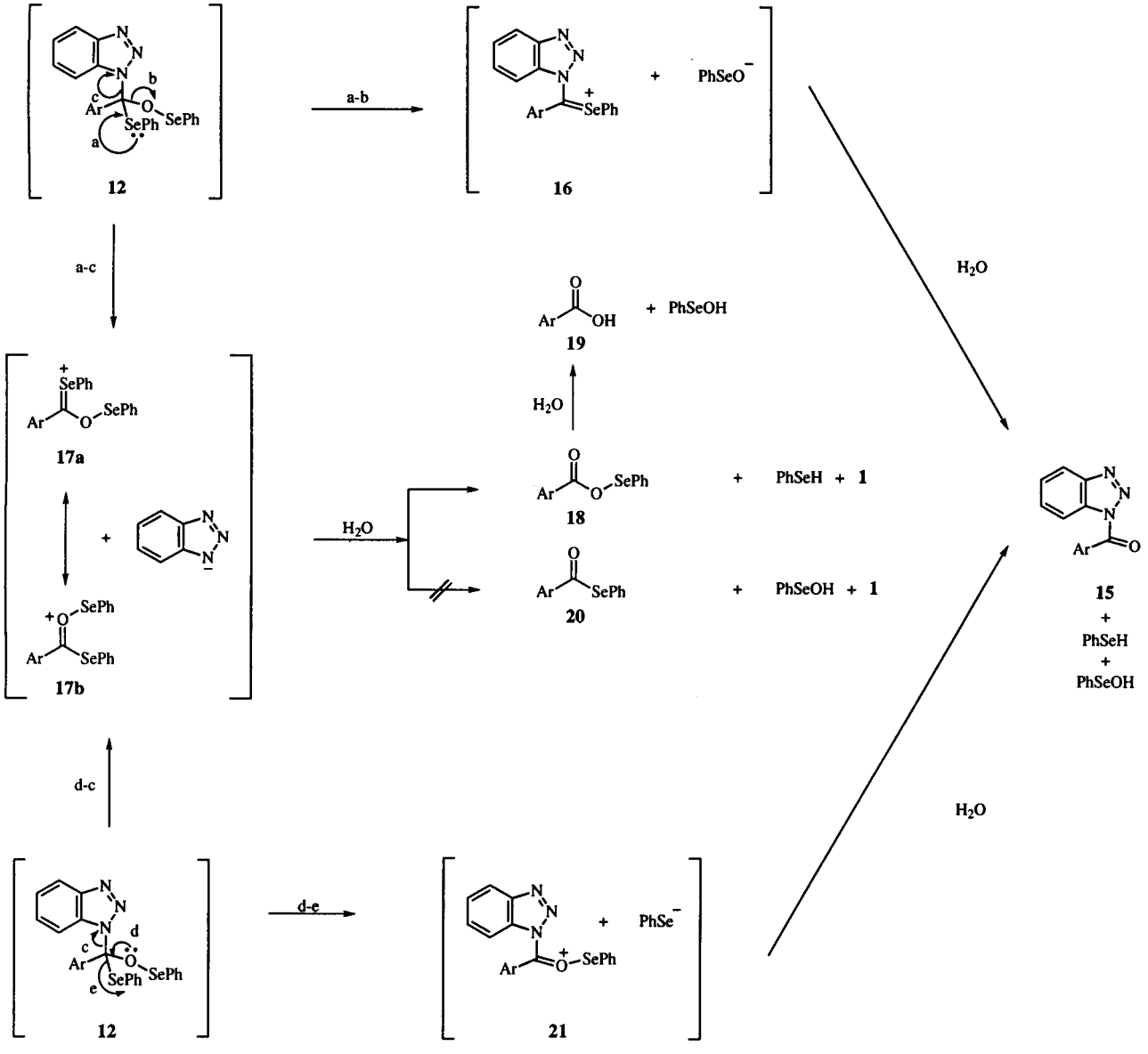
Compound	IR [a] (cm^{-1})	^{1}H NMR (deuteriochloroform) δ (ppm)
15b	3088, 1710, 1604, 1504, 1446, 1288, 1042, 752	7.14-8.43 (m, 8H, ArH)
15c	3088, 2848, 1692, 1606, 1375, 1253, 1049, 940, 753	3.89 (s, 3H, CH_3O), 7.02 (d, 2H, J = 8 Hz, ArH), 7.37-7.73 (m, 2H, ArH), 8.08-8.43 (m, 4H, ArH)

[a] From potassium bromide pellets.

General Procedure for the Synthesis of Arenethiol Arenecarboxylates **14a-14h**.

To a solution of **4** (0.2 mmole) in dichloromethane (15 ml) at room temperature was added *m*-chloroperbenzoic acid (0.4 mmole). The mixture was stirred for 10 minutes, followed by quenching with saturated sodium bicarbonate and extracted with dichloromethane (2 x 50 ml). The extracts were washed with water (50 ml) and then dried over magnesium sulfate. Removal of the solvent *in vacuo*, followed by chromatography on a silica gel column (2 x 13 cm) using a mixture of *n*-hexane and ethyl acetate (50:1, 100 ml) gave compounds **14**. Continued elution with ethyl acetate (50 ml) gave **1**. Consult Table 13 for physical and analytical data and Table 14 for ir and ^{1}H nmr spectroscopic data of compounds **14**.

Scheme 2



General Procedure for the Synthesis of 1-(Aroyl)benzotriazoles **15a-15c**.

To a solution of **5** (0.2-0.3 mmole) in dichloromethane (10 ml) at room temperature was added *m*-chloroperbenzoic acid (0.4-0.6 mmole). The mixture was stirred for 5 minutes. The color of the solution turned immediately yellow and diphenyl diselenide was formed. The reaction was quenched with saturated sodium bicarbonate. The reaction mixture was extracted with dichloromethane (3 x 50 ml) and the extracts were washed with water. Drying the extract over magnesium sulfate, followed by removal of the solvent gave a residue, which was chromatographed on a silica gel column (2 x 10 cm). Elution with a mixture of *n*-hexane and ethyl acetate (30:1, 100 ml) gave diphenyl diselenide (0.1-0.3 mmole). Elution with the same solvent mixture (5:1, 60 ml) gave **15**. Elution with ethyl acetate (50 ml) gave **1**. Consult Table 15 for physical and analytical data and Table 16 for ir and ^{1}H nmr spectroscopic data of compounds **15**.

Preparation of ^{18}O Labeled 1-(4-Methoxybenzoyl)benzotriazole **15c**.

To a solution of **5c** (175 mg, 0.319 mmole) in dichloromethane (10 ml) was added two drops (0.1 ml) of H_2O^{18} (10% atom), followed by addition of *m*-chloroperbenzoic acid (220 mg, 0.638 mmole). The color of the solution turned immediately yellow. The mixture was stirred for 5 minutes at room temperature, followed by addition of water (50 ml) and was extracted with dichloromethane (3 x 50 ml). Drying the extract over magnesium sulfate, followed by removal of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (3 x 6 cm). Elution with a mixture of *n*-hexane and ethyl acetate (8:1, 60 ml) gave diphenyl diselenide (66 mg, 0.211 mmole), **15c** labeled and nonlabeled with ^{18}O at the carbonyl oxygen (17 mg, 88%), a mixture of *m*-chloroperbenzoic acid and *p*-anisic acid and compound **1** (6 mg, 16%).

Mass spectroscopy of **15c** and ^{18}O-labeled **15c**; ms: m/z (relative intensity) of **15c**, 253 (M^+, 100), 255 ($M^+ + 2$, 1.63); ms: m/z (relative intensity) of ^{18}O-labeled **16c**, 253 (M^+, 100), 255 ($M^+ + 2$, 2.19).

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REFERENCES AND NOTES

[1a] A. R. Katritzky, S. Perumal and W.-Q. Fan, *J. Chem. Soc., Perkin Trans. 2*, 2059 (1990); [b] A. R. Katritzky, S. Rachwal and G. J. Hitchings, *Tetrahedron*, **47**, 2683 (1991); [c] A. R. Katritzky, Z. Yang and J. N. Lam, *Tetrahedron*, **48**, 4971 (1992); [d] A. R. Katritzky, N. Shobana, J. Pernak, A. S. Afridi and W.-Q. Fan, *Tetrahedron*, **48**, 7817 (1992); [e] A. R. Katritzky, S. Rachwal, B. Rachwal and P. J. Steel, *J. Org. Chem.*, **57**, 4925 (1992); [f] A. R. Katritzky, M. F. Gordeev, J. V. Greenhill and P. J. Steel, *J. Chem. Soc., Perkin Trans. 1*, 1111 (1992); [g] A. R. Katritzky, J. Li and M. F. Gordeev, *J. Org. Chem.*, **58**, 3038 (1993); [h] A. R. Katritzky, G. Yao, X. Lan and X. Zhao, *J. Org Chem.*, **58**, 2086 (1993); [i] A. R. Katritzky, X. Lan and Z. Zhang, *J. Heterocyclic Chem.*, **30**, 381 (1993); [j] A. R. Katritzky, Z. Yang and J. N. Lam, *J. Org. Chem.*, **58**, 1970 (1993); [k] A. R. Katritzky, S. C. Jurczyk, M. Szajda, I. V. Shcherbakova and J. N. Lam, *Synthesis*, 499 (1994); [l] A. R. Katritzky and X. Lan, *Chem. Soc. Rev.*, 363 (1994); [m] A. R. Katritzky, Q. Hong and Z. Yang, *Organometallics*, **14**, 734 (1995); [n] A. R. Katritzky, L. Xie, D. Toader and L. Serdyuk, *J. Am. Chem. Soc.*, **117**, 12015 (1995); [o] A. R. Katritzky and L. Xie, *J. Org. Chem.*, **60**, 3707 (1995); [p] A. R. Katritzky, H. Lang, Z. Wang and Z. Lie, *J. Org. Chem.*, **61**, 7551 (1996); [q] A. R. Katritzky, L. Xie and L. Serdyuk, *J. Org. Chem.*, **61**, 7564 (1996).

[2] A. R. Katritzky, S. Rachwal, K. C. Caster, F. Mahni, K. W. Law and O. Rubio, *J. Chem. Soc., Perkin Trans. 1*, 781 (1987).

[3] T. Hori and K. B. Sharpless, *J. Org. Chem.*, **43**, 1689 (1978).

[4a] I. D. Entwistle, R. A. W. Johnstone and J. H. Varley, *J. Chem. Soc., Chem. Commun.*, 61 (1976); [b] M. Shimizu and I. Kuwajima, *Tetrahedron Letters*, 2801 (1979); [c] I. Kuwajima, M. Shimizu and H. Urabe, *J. Org. Chem.*, **47**, 837 (1982).

[5a] M. S. Gibson, *J. Chem. Soc.*, 1076 (1956); [b] A. R. Katritzky, X. Lan and J. N. Lam, *Chem. Ber.*, **124**, 1819 (1991).

[6a] A. R. Katritzky, A. S. Afridi and W. Kuzmierkiewicz, *Helv. Chim. Acta.*, **74**, 1931 (1991); [b] A. R. Katritzky, L. Xie, A. S. Afridi, W.-Q. Fan and W. Kuzmierkiewicz, *Synthesis*, **47** (1993).

[7] A. R. Katritzky, S. Rachwal and B. Rachwal, *J. Chem. Soc., Perkin Trans. 1*, 791 (1987).

[8a] G. Tsuchihashi, S. Miyajima, T. Otsu and O. Simamura, *Tetrahedron Letters*, **21**, 1039 (1965); [b] A. G. Hortmann, A. J. Aron and A. K. Bhattacharya, *J. Org. Chem.*, **43**, 3374 (1978).

[9] M. Hojo, R. Masuda, K. Yoshinaga and S. Munehira, *Synthesis*, 312 (1982).

[10a] B. M. Trost, P. Buhlmayer and M. Mao, *Tetrahedron Letters*, 1443 (1982); [b] C. Paulmier, Selenium Reagents and Intermediates in Organic Synthesis, Pergamon Press, Oxford, 1986 Chapter V, p 128-131.

[11a] D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 100 (1974); [b] H. J. Reich, *J. Org. Chem.*, **39**, 428 (1974); [c] K. Uneyama, K. Maeda, Y. Tokunaga, N. Itano and M. Aki, The 4th International Conference on Heteroatom Chemistry, July 30-Aug. 4, 1995, Seoul, Korea, OA-13.

[12] H. Rheinboldt and E. Giesbrecht, *Chem. Ber.*, **85**, 357 (1952).

[13] J. Y. Gauthier, F. Bourdon and R. N. Young, *Tetrahedron Letters*, **27**, 15 (1986).

[14] D. P. N. Satchell, *Quart. Rev., Chem. Soc.*, **17**, 160 (1963).

[15] J. March, Advanced Organic Chemistry, 4th Ed., John Wiley and Sons, New York 1992, p 767.

[16] M. Ueda and H. Mori, *Bull. Chem. Soc. Japan*, **65**, 1636 (1992).

[17a] C. A. Kingsbury and G. Ebert, *Phosphorus Sulfur*, **9**, 315 (1981); [b] P. A. Grieco, Y. Yokoyama and E. Williams, *J. Org. Chem.*, **43**, 1285 (1978).

[18] A. Pelter, T. E. Levitt, K. Smith and A. Jones, *J. Chem. Soc., Perkin Trans. 1*, 1672 (1977).

[19] T. Mukaiyama, T. Takeda and K. Atsumi, *Chem. Letters*, 187 (1974).

[20] J. March, Advanced Organic Chemistry, 4th Ed, John Wiley and Sons, New York, NY, 1992 p 552.

[21] A. Burton, L. Hevesi, W. Dumont, A. Cravador and A. Krief, *Synthesis*, 877 (1979).

[22] J. P. Gasparini, R. Gassend, J. C. Maire and J. Elguero, *J. Organomet. Chem.*, **188**, 141 (1980).

[23] R. Gassend, J. C. Maire and C. Pommier, *J. Organomet. Chem.*, **137**, 185 (1977).

[24] N. G. Gaylord, *J. Am. Chem. Soc.*, **76**, 285 (1954).

[25] A. Krentzberger and E. Dietz, *Arzneim-Forsch.*, **20**, 1723 (1970); *Chem. Abstr.*, **74**, 53663c (1971).

[26] W. Jenny, *Helv. Chim. Acta.*, **41**, 317 (1958).