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Synthesis of 2-alkyl (and aryl)-1-aryl-2-propen-1-ones via *m*-CPBA mediated oxidation of γ-(benzotriazol-1-yl)allylic selenides

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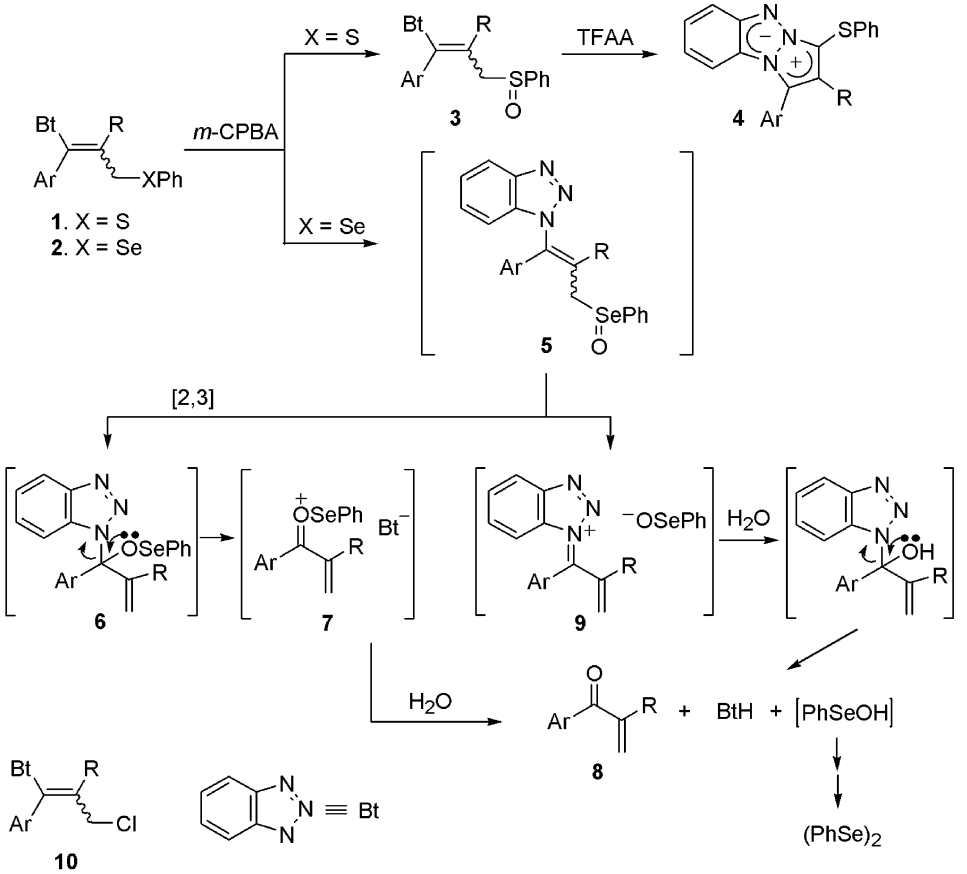
Abstract—Treatment of 2-alkyl (and aryl)-3-aryl-3-(benzotriazol-1-yl)allylic selenides with *m*-CPBA (1 equiv.) for 10 min in CH_2Cl_2 at rt gave 2-alkyl (and aryl)-1-aryl-2-propen-1-ones in excellent yields. © 2002 Published by Elsevier Science Ltd.

Very recently, we reported the synthesis of 2,3-benzo-1,3a,6a-triazapentalenes **4** through Pummerer-type reactions of γ-(benzotriazol-1-yl)allylic sulfoxides **3**, prepared by the oxidation of the corresponding sulfides **1** (X = S).[1]

In connection with the formation of such a class of mesomeric betains by treatment of **3** with trifluoroacetic anhydride (TFAA) in CH_2Cl_2 at rt, we became interested in investigating the oxidation of the corresponding allylic selenides **2** (X = Se). In contrast to stable



Keywords: benzotriazoles; enones; oxidation; selenium and compounds.

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sulfoxides **3**, selenoxides **5** formed by oxidation of **2** would be expected to be unstable due to [2,3] sigmatropic rearrangement of allylic selenoxides to give unstable selenenate esters **6**,[2] which liberate benzotriazolate ion concomitant with the formation of an oxonium ion **7**.[3] Hydrolysis of **7** would give title compounds **8** together with benzotriazole and phenylselenenic acid. Alternatively, compounds **8** might be formed via hydrolysis of an intermediate **9**,[4] generated by possible elimination of benzeneselenate ion from **5**, in which the driving force for the elimination may originate from delocalization of non-bonding electrons on the N-1 of the benzotriazole moiety into the olefinic double bond. This is concomitant with the migration of the double bond to give an intermediate **9** despite the absence of β-hydrogen in view of the ready formation of olefins via a *syn*-elimination of selenoxides having a hydrogen atom at β-carbon.[5]

In order to prove the premise, we prepared the starting material **2** by treatment of 2,3-disubstituted (3-benzotriazol-1-yl)allylic chloride **10**[1] with benzeneselenol in the presence of NaOEt in THF.[6] The stereochemistry of **2** along with their (*E*)/(*Z*) ratios was determined based on NOE effects arising from the allylic protons and ortho proton(s) of Ar and R groups as described in the previous report.[1] For example, compound (*E*)-**2j** (Ar = Ph, R = *t*Bu) exhibiting a singlet at 3.95 ppm (500 MHz, $CDCl_3$), assigned to the allylic protons, has NOE effects with two *ortho* protons (7.38–7.40 ppm) of the Ph group and nine protons (1.10 ppm) of the *t*Bu group, whereas compound (*Z*)-**2j** has the NOE effects arising from the allylic protons (3.68 ppm) and the protons (1.26 ppm) of the *t*Bu group. Similar NOE effects were observed for other (*E*)- and (*Z*)-**2**. It appeared that the stereochemistry was essentially intact in the course of the conversion of **10** into **2**. The stereoisomers of **2** and **10** were separable by chromatography. Treatment of (*E*)-**2a** (Ar = R = Ph) with *m*-CPBA (1 equiv.) for 10 min in CH_2Cl_2 at rt gave enone **8a** in 85% yield[7] along with diphenyl diselenide (39%).[8] Similar treatment of (*Z*)-**2a** under the same conditions afforded **8a** and diphenyl diselenide in 87 and 36% yields, respectively. This result indicates that elimination of selenenic acid from **5** is independent of the stereochemistry of **5**. Consequently, a mixture of (*E*)- and (*Z*)-**2** was subjected to the oxidation reaction with *m*-CPBA without separation of the stereoisomers. Yields of **2** and **8** along with the (*E*)/(*Z*) ratios of **10** and **2** are summarized in Table 1.

Enones **8**, which are important as a starting material for the synthesis of various organic compounds, have been mostly prepared by the Mannich reaction followed by β-elimination.[14] Similarly, *N*,*N*,*N*′,*N*′-tetramethyldiaminomethane was found to be effective for the preparation of **8** (Ar = aryl, R = alkyl, aryl) from aryl arylmethyl ketones and alkyl aryl ketones in acetic anhydride at 40 and 90°C, respectively.[15] There exist other special methods, giving rise to **8** (Ar = alkyl, aryl, R = H) which involves the reaction of methyl ketones with trioxane in the presence of *N*-methylanilium trifluoroacetate.[9,16] Silyl enol ethers were converted to chloroenone **8** (Ar = Ph, R = Cl) in the presence of $TiCl_4$, $LiAlH_4$ in CCl_4.[17] Treatment of 3-iodo-1,2-diphenyl-1-propanone with DBU gave **8** (Ar = Ph, R = Me).[18] Siloxycyclopropane reacted with $SnCl_4$ in CH_2Cl_2 to give a stannane complex, which undergoes decomposition in DMSO to give **8** (Ar = H, R = alkyl).[19] Recently, Katritzky and co-workers reported benzotriazole-mediated synthesis of **8**.[11]

In summary, apart from the reactions of 2,3-disubstituted 3-(benzotriazol-1-yl)-2-propenyl phenyl sulfides **1** with *m*-CPBA, giving rise to the corresponding sulfoxides **3**, reactions of the analogous selenides **2** under the same conditions afforded enones **8** in excellent yields.

Table 1. Yields of **2** and **8**, and the (*E*)/(*Z*) ratios of **10** and **2**

Entry	Ar	R	Yield[a] (%)		
			10 (*E*/*Z*)[b]	**2** (*E*/*Z*)[b]	**8**[c]
a	Ph	Ph	(4.86:1)	85 (4.83:1)	86 (96)[9]
b	2-MeC_6H_4	Ph	(2.11:1)	83 (2.10:1)	85 (100)[10]
c	2-MeC_6H_4	4-MeC_6H_4	(2.99:1)	83 (2.97:1)	84 (82)[11]
d	2-$MeOC_6H_4$	4-MeC_6H_4	(1.91:1)	81 (1.87:1)	85[13]
e	4-$MeOC_6H_4$	4-MeC_6H_4	(1.04:1)	82 (1.11:1)	92 (98)[11]
f	4-$MeOC_6H_4$	β-Naphthyl	(2.68:1)	82 (2.46:1)	93[13]
g	4-FC_6H_4	Ph	(3.61:1)	87 (3.65:1)	90[13]
h	4-FC_6H_4	2,5-$Me_2C_6H_3$	(2.85:1)	83 (2.91:1)	88[13]
i	Ph	Me	(8.01:1)	81 (7.41:1)	85 (85)[9]
j	Ph	*t*Bu	(2.41:1)	82 (2.45:1)	89 (78)[12]

[a] Isolated yields.

[b] The ratios of stereoisomers were determined based on the ^1H NMR absorptions of the allylic protons ((*E*)-**2**: 3.95–4.44 ppm; (*Z*)-**2**: 3.64–4.05 ppm; (*E*)-**10**: 4.28–4.87 ppm; (*Z*)-**10**: 4.02–4.45 ppm).

[c] The number in parentheses represents yield in the literature.

Acknowledgements

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4. Upon addition of *m*-CPBA, the spot (R_f=0.38–0.56, EtOAc:*n*-hexane=1:4) corresponding to **2** had completely disappeared and a new spot appeared at origin, which was indicative of the formation of a polar intermediate such as **7** and/or **9**. Work-up with water gave **8**.
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6. Typical procedure: Sodium (32 mg, 1.38 mmol) was placed in absolute EtOH (15 mL), followed by addition of benzeneselenol (217 mg, 1.38 mmol). The mixture was stirred for 5 min, followed by addition of a solution of 1-(3-chloro-1,2-diphenylpropenyl)-1*H*-benzotriazole **10a** (159 mg, 0.46 mmol) in THF (30 mL) at rt. The mixture was additionally stirred for 2 h, followed by addition of water (50 mL), which was extracted with CH_2Cl_2 (30 mL×3). The extracts were dried over $MgSO_4$. Removal of the solvent in vacuo gave a residue, which was chromatographed on a silica gel column (3×10 cm, EtOAc:*n*-hexane=1:5) to give compound **2a** (182 mg, 85%): Viscous liquid; (*E*)/(*Z*)=4.83:1; IR (neat) 3040, 2912, 1600, 1569, 1475, 1436, 1374, 1267, 1224, 1153, 1067, 905, 737, 692, 520 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.93 (s, 2H, CH_2Se, *Z*), 4.28 (s, 2H, CH_2Se, *E*), 6.88–7.43 (m, 18H, ArH, *E* and *Z*), 7.93 (d, J=7.7 Hz, 1H, ArH, *E*), 8.12 (dd, J=10.0, 2.0 Hz, 1H, ArH, *Z*). Anal. calcd for $C_{27}H_{21}N_3Se$: C, 69.52; H, 4.54; N, 9.01. Found: C, 69.60; H, 4.52; N, 8.97.
7. Typical procedure: To a solution of (*E*)-**2a** (121 mg, 0.35 mmol) in CH_2Cl_2 (25 mL) was added *m*-CPBA (45 mg, 0.35 mmol) at rt. The mixture was stirred for 10 min, followed by addition of aqueous $NaHCO_3$ (10%), which was extracted with CH_2Cl_2 (30 mL×3). The combined extracts were dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was chromatographed on a silica gel column (2×10 cm, EtOAc:*n*-hexane=1:7) to give diphenyl diselenide (21 mg, 39%): mp 61–63°C (CH_2Cl_2/*n*-hexane) (lit. mp 60–62°C) and compound **8a** (63 mg, 85%): liquid; IR (neat) 3048, 2920, 1656, 1588, 1486, 1438, 1323, 1208, 1174, 912, 770, 696, 588, 520 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.76 (s, 1H of =CH_2), 6.09 (s, 1H of =CH_2), 7.32–7.39 (m, 3H, ArH), 7.41–7.50 (m, 4H, ArH), 7.54–7.59 (m, 1H, ArH), 7.92–7.98 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 121.2, 127.5, 128.8, 129.0, 130.4, 133.5, 137.4, 137.5, 148.7, 197.9 (signal of one aromatic C atom not visible); MS (70 eV) (*m*/*z*) 208 (M^+, 78.8%), 179 (6.7), 165 (5.0), 105 (100.0), 77 (52.2), 51 (12.7). Anal. calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.43; H, 5.75. Refer to reference for mp of PhSeSePh: Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434–5447.
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13. **8d**: Liquid; IR (neat) 3008, 2920, 1659, 1590, 1504, 1476, 1452, 1428, 1320, 1273, 1246, 1200, 1112, 1019, 973, 820, 753, 521 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.38 (s, 3H, CH_3), 3.74 (s, 3H, OCH_3), 5.74 (s, 1H of =CH_2), 5.99 (s, 1H of =CH_2), 6.92 (d, J=8.5 Hz, 1H, ArH), 7.01 (dd, J=7.5, 0.7 Hz, 1H, ArH), 7.18 (d, J=7.9 Hz, 2H, ArH), 7.33 (d, J=8.0 Hz, 2H, ArH), 7.41–7.47 (m, 1H, ArH), 7.52 (dd, J=7.5, 1.7 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 56.0, 111.9, 120.8, 124.4, 128.2, 129.3, 130.4, 132.8, 134.7, 138.2, 150.6, 158.2, 198.1 (signal of one aromatic C atom not visible); MS (70 eV) (*m*/*z*) 252 (M^+, 30.0%), 135 (100.0), 115 (8.8), 92 (8.3), 77 (13.3), 51 (2.3). Anal. calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.99; H, 6.43. **8f**: Mp 107–109°C (CH_2Cl_2/*n*-hexane); IR (KBr) 3040, 2928, 1644, 1587, 1497, 1449, 1304, 1251, 1161, 1022, 976, 841, 776, 515 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.86 (s, 3H, OCH_3), 5.67 (s, 1H of =CH_2), 6.14 (s, 1H of =CH_2), 6.93 (d, J=7.0 Hz, 2H, ArH), 7.46–7.50 (m, 2H, ArH), 7.63 (dd, J=8.6, 1.8 Hz, 1H, ArH), 7.77–7.89 (m, 4H, ArH), 8.00 (d, J=8.8 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.9, 114.2, 119.3, 124.7, 126.7, 126.8, 128.0, 128.9, 130.3, 132.9, 133.5, 133.7, 134.8, 148.9, 164.2, 196.7 (signals of two aromatic C atoms not visible); MS (70 eV) (*m*/*z*) 288 (M^+, 32.3%), 152 (15.2), 135 (100.0), 92 (10.5), 77 (17.1). Anal. calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.24; H, 5.63. **8g**: Liquid; IR (neat) 3048, 2912, 1657, 1587, 1491, 1401, 1320, 1224, 1148, 977, 849, 780, 692, 580, 505 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.65 (s, 1H of =CH_2), 6.07 (s, 1H of =CH_2), 7.12 (t, J=7.5 Hz, 2H, ArH), 7.33–7.47 (m, 5H, ArH), 7.93–8.00 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 116.0 (^2J=21.8 Hz), 120.8, 127.4, 129.0, 129.1, 133.0 (^3J=9.3 Hz), 133.8 (^4J=2.9 Hz), 137.2, 148.6, 166.2 (^1J=253.8 Hz), 196.3; MS (70 eV) (*m*/*z*) 226 (M^+, 100.0%), 197 (9.0), 183 (6.7), 123 (100.0), 95 (72.9), 77 (34.0), 51 (12.4). Anal. calcd for $C_{15}H_{11}FO$: C, 79.63; H, 4.90. Found: C, 79.70; H, 4.94. **8h**: Liquid; IR (neat) 3016, 2912, 1651, 1587, 1489, 1440, 1198, 1313, 1225, 1148, 977, 846, 809, 784, 590, 516 cm^{-1}; ^1H NMR

($CDCl_3$, 300 MHz) δ 2.17 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 5.99 (dd, $J=11.8$, 1.1 Hz, 2H, $=CH_2$), 7.05–7.17 (m, 5H, ArH), 7.90–7.99 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.4, 21.3, 115.9 ($^2J=21.7$ Hz), 127.8, 129.6, 130.6, 130.7, 132.7, 132.8 ($^3J=9.2$ Hz), 133.9 ($^4J=3.0$ Hz), 136.0, 138.4, 149.6, 165.8 ($^1J=252.9$ Hz), 195.4; MS (70 eV) (m/z) 254 (M^+, 100%), 131 (35.7), 123 (55.5), 115 (17.0), 95 (19.1), 91 (14.2). Anal. calcd for $C_{17}H_{15}FO$: C, 80.29; H, 5.95. Found: C, 80.21; H, 5.99.

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