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Oxidation Products of β-Methyl-substituted δ-Lactones Using Benzeneseleninic Anhydride and Selenium Dioxide

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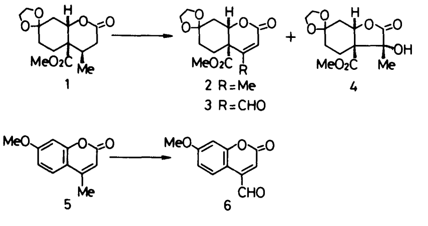
Synopsis. When 9,9-ethylenedioxy-6-methoxycarbonyl-5-methyl-2-oxabicyclo[4.4.0]decan-3-one was treated with benzeneseleninic anhydride and selenium dioxide, the former yielded preferentially the 4,5-dehydrogenated compound (**2**) together with small amounts of the 5-formyl compound (**3**) and the contraction product (**4**) of the δ-lactone ring, while the latter produced solely **2** in a poor yield.

Utility of benzeneseleninic anhydride (BSA) as an oxidizing reagent has been growing in organic synthesis concerning the preparation of aldehydes and ketones from alcohols and benzylic hydrocarbons.[1] More recently, Barton *et al.* have reported that δ-lactones such as 4-oxa-5α-cholestan-3-one reacted with BSA to form the α,β-unsaturated lactones,[2] but there has been relatively few utilization of BSA as dehydrogenating reagent for lactones and lactams. In addition to the examples, we also wish to report the pretty preparation of 9,9-ethylenedioxy-6-methoxycarbonyl-5-methyl-2-oxabicyclo[4.4.0]dec-4-en-3-one (**2**)[3] from its 4,5-dihydro compound (**1**) by the use of BSA and the investigation of the oxidation products from cyclic lactones (**1**, **2**, and **5**) with BSA and SeO$_2$.



Scheme 1.

Oxidation reaction of **1** with 1.3 molar equivalent of BSA in chlorobenzene at 80—85 °C for 42 h under N$_2$ afforded the dehydrogenated compound **2** in 70% yield along with small amounts of the aldehyde **3** and contraction product, 4,4-ethylenedioxy-9-hydroxy-1-methoxycarbonyl-9-methyl-7-oxabicyclo[4.3.0]nonan-8-one (**4**) (Run 2). This method represented better yield of **2** and one-step preparation of α,β-unsaturated δ-lactone in comparison with the previous result due to oxidation-fragmentation of the phenylseleno derivative of **1**.[3] Some results obtained from the reactions which were carried out under a range of the reaction conditions as discussed below are shown in Table 1. The longer reaction time, 95—96 h at 82—90 °C (Run 4, 5) seemed to afford improvement of the yield of **2**, but when performed with more than 1.3 molar equivalent of BSA and refluxing conditions the yield of **2** became somewhat lower (Run 10). Attempts to effect a progressive preparation of **3** from **1** or **2** by utilizing BSA under various reaction conditions were unsuccessful, suggesting little participation of BSA itself in the formation of **3**. In contrast with BSA, using SeO$_2$ to the oxidation of **1** and **2** under refluxing conditions afforded **2** in *ca.* 17% yield (Run 15) and **3** in *ca.* 26% yield (Run 13), respectively. These results noted that the methyl group on C-5 of **2** was considerably oxidizable with SeO$_2$. Furthermore, a similar allylic oxidation reaction of an α,β-unsaturated δ-lactone moiety such as 7-methoxy-4-methylcoumarin (**5**) in hot chlorobenzene containing SeO$_2$ gave an excellent yield (89%) of its 4-formyl compound **6**. All the products **2**, **3**, **4**, and **6** gave satisfactory spectroscopic data and elemental analyses. In addition, the molecular of **4** was established unambiguously by an X-ray crystal structure analysis of its acetate (Fig 1).[5]

A pathway for the formation of **2** and **4** from **1** by the use of BSA can be explained on the basis of that for BSA oxidation proposed by Barton *et al.* (Scheme 2).[2,6] On the other hand, the case of **3** is considered that it was likely produced by further oxidation of **2** with some selenoxide species such as an analog of SeO$_2$ which would be allowed in the course of the oxidation reaction in the presence of BSA.

Thus, the use of BSA seems to be an effective way in view of the simple handling procedure in order to obtain α,β-unsaturated δ-lactones from its saturated lactones. It was also found that BSA is not convenient

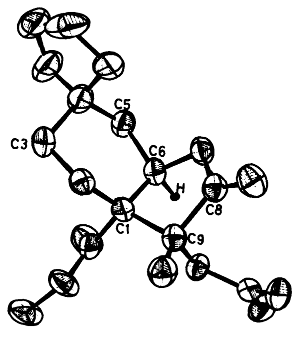
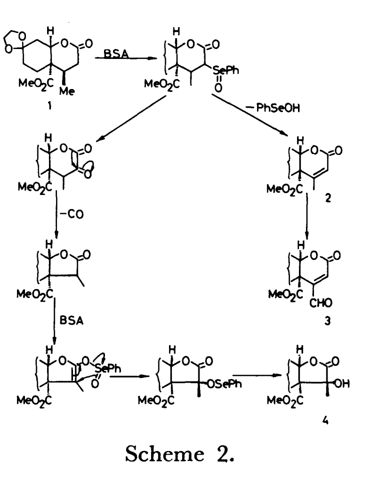


Fig. 1. ORTEP drawing of the molecular structure of acetate of **4**.[4]



Scheme 2.

TABLE 1. YIELDS OF **2** AND **3**[a)]

Run	Compd	BSA or SeO_2[b)]	Reaction temp/°C and time/h		Yield[c)]/%	
					2	**3**
1[d)]	**1**	1.30 BSA	65—67	40	17	None
2	**1**	1.30 BSA	80—85	42	70	Trace
3	**1**	1.29 BSA	90—95	42	69	Trace
4	**1**	1.30 BSA	82—88	95	75	Trace
5	**1**	1.30 BSA	78—90	96	78	Trace
6[d)]	**1**	0.51 BSA	83—88	44	26	None
7[d)]	**1**	0.86 BSA	82—87	42	41	None
8[d)]	**1**	1.13 BSA	84—88	42	50	Trace
9	**1**	1.31 BSA	Reflux	20	41	6
10	**1**	2.50 BSA	Reflux	20	33	7
11[d)]	**2**	1.28 BSA	Reflux	20		7
12[d)]	**2**	2.50 BSA	Reflux	20		5
13[d)]	**2**	1.25 SeO_2	Reflux	20		26
14[d)]	**1**	2.50 SeO_2	Reflux	20	9	None
15[d)]	**1**	1.20 SeO_2	Reflux	20	17	None

a) The reactions were carried out in chlorobenzene except those of Run 13 and 15 in *o*-xylene. b) Molar ratio of BSA or SeO_2 to the starting material. c) Determined by column chromatographic separation. d) These reactions, Run 1, 6—8, and 11—15 gave recovery of the starting material in 59, 51, 35, 44, 26, 68, 53, and 51%, respectively.

for the oxidation of allylic methyl group in comparison with SeO_2.

Experimental

IR and NMR spectra were measured in $CHCl_3$ and $CDCl_3$, respectively. Chemical shifts are given in δ values (ppm) downfield from the internal TMS reference. The X-ray diffraction data were obtained on an Enraf-Nonius CAD-4 automated four-circle diffractometer with a SDP program package.

General Procedure for the Oxidation of δ-Lactones Using BSA. A mixture of starting material and BSA in dry chlorobenzene was stirred under N_2. After removal of the solvent *in vacuo*, the residue was separated and purified by chromatographic work-up on silica gel with a mixture of benzene and ethyl acetate. **2**: Colorless plates, mp 105—107 °C (ethyl acetate–hexane); IR: 1735, 1720, and 1645 (weak) cm^{-1}; ^1H-NMR: 1.4—1.8 and 2.0—2.2 (6H, m, 3×$-CH_2-$), 2.07 (3H, s, C_5-CH_3), 3.76 (3H, s, $-CO_2CH_3$), 3.96 (4H, s, ethylenedioxy group), 5.04 (1H, dd, *J*=6 and 10 Hz, C_1-H), and 5.96 (1H, s, C_4-H); ^{13}C-NMR: 19.9 (q, C_5-CH_3), 26.9, 31.5, and 37.2 (each t, C_7, C_8, and C_{10}), 49.8 (s, C_6), 53.2 (q, $-CO_2\underline{C}H_3$), 64.6 (t, ethylenedioxy group), 77.6 (d, C_1), 107.1 (s, C_9), 120.0 (d, C_4), 155.2 (s, C_5), 162.7 (s, C_3), and 171.9 (s, $-\underline{C}O_2CH_3$); MS: *m/z* 282 (M^+); Found: C, 59.79; H, 6.51%. Calcd for $C_{14}H_{18}O_6$: C, 59.56; H, 6.43%. **3**: Colorless needles, mp 144—145.5 °C (ethyl acetate–hexane); IR: 2850, 2750 (weak), 1740, 1720, and 1620 (weak) cm^{-1}; ^1H-NMR: 1.3—1.6, 1.9—2.3, and 2.4—2.7 (6H, m, 3×$-CH_2-$), 3.75 (3H, s, $-CO_2CH_3$), 3.98 (4H, s, ethylenedioxy group), 5.04 (1H, dd, *J*=6 and 8 Hz, C_1-H), 6.76 (1H, s, C_4-H), and 9.73 (1H, s, $-CHO$); ^{13}C-NMR: 26.0, 31.1, and 37.2 (each t, C_7, C_8, and C_{10}), 47.3 (s, C_6), 53.4 (q, $-CO_2\underline{C}H_3$), 64.9 (t, ethylenedioxy group), 79.4 (d, C_1), 106.8 C_9), 134.0 (d, C_4), 150.0 (s, C_5), 161.9 (s, C_3), 171.0 (s, $-\underline{C}O_2CH_3$), and 191.3 (d, $-CHO$); MS: *m/z* 296 (M^+); Found: C, 56.93; H, 5.55%. Calcd for $C_{14}H_{16}O_7$: C, 56.75; H, 5.44%. **4**: Colorless plates, mp 183.5—185.5 °C (ethyl acetate–hexane); IR: 3600, 1780, and 1740 cm^{-1}; ^1H-NMR: 1.5—2.3 (6H, m, 3×$-CH_2-$), 1.50 (3H, s, C_9-CH_3), 3.21 (1H, s, OH), 3.78 (3H, s, $-CO_2CH_3$), 3.92 (4H, s, ethylenedioxy group), and 5.20 (1H, t, *J*=4 Hz, C_6-H); ^{13}C-NMR: 17.7 (q, C_9-CH_3), 25.2, 30.8, and 33.9 (each t, C_2, C_3, and C_5), 52.5 (q, $-CO_2\underline{C}H_3$), 55.2 (s, C_1), 64.2 and 64.7 (each t, ethylenedioxy group), 77.5 (d, C_6), 78.6 (s, C_9), 106.3 (s, C_4), 170.5 (s, $-\underline{C}O_2CH_3$), and 174.8 (s, C_8); MS: *m/z* 286 (M^+); Found: C, 54.61; H, 6.35%. Calcd for $C_{13}H_{18}O_7$: C, 54.55; H, 6.29%. This compound was obtained in less than 10% yield. Acetate of **4**: Colorless plates, mp 129—130.5 °C (ethyl acetate–hexane); IR: 1790, 1750, and 1740 cm^{-1}, ^1H-NMR: 1.5—2.3 (6H, m, 3×$-CH_2-$), 1.66 (3H, s, C_9-CH_3), 2.00 (3H, s,$-OCOCH_3$), 3.79 (3H, s, $-CO_2CH_3$), 3.92 (4H, s, ethylenedioxy group), and 5.15 (1H, t, *J*=4 Hz, C_6-H); MS: *m/z* 328 (M^+); Found: C, 54.96; H, 5.85%. Calcd for $C_{15}H_{20}O_8$: C, 54.87; H, 6.14%.

4-Formyl-7-methoxycoumarin (6). A mixture of **5** (480 mg, 2.53 mmol), SeO_2 (400 mg, 3.60 mmol; purified by sublimation method) in dry chlorobenzene (70 ml) was refluxed for 20 h under N_2. After the usual work-up, the crude solid was chromatographed on silica gel using dichloromethane as the eluent to afford 460 mg of **6**; yellow needles, mp 204—206 °C recrystd from dichloromethane (lit,[7)] mp 195 °C). IR: 2850, 2750 (weak), 1750 sh, 1720, and 1615 cm^{-1}; ^1H-NMR: 3.89 (3H, s, $-OCH_3$), 6.76 (1H, s, C_3-H), 6.91 (1H, d, *J*=3 Hz, C_8-H), 7.02 (1H, dd, *J*=3 and 8 Hz, C_6-H), 8.54 (1H, d, *J*=8 Hz, C_5-H), and 10.14 (1H, s, $-CHO$), MS: *m/z* 204 (M^+); Found: C, 64.92; H, 3.90%. Calcd for $C_{11}H_8O_4$: C, 64.70; H, 3.95%.

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3) Compound **2** has been synthesized in 49% yield by α-phenylselenenylation of **1** with lithium diisopropylamide and benzeneselenenyl chloride, followed by oxidation of the phenylseleno derivative with H_2O_2; J. D. White, T. Matsui, and J. A. Thomas, *J. Org. Chem.*, **46**, 3376 (1981).

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