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Preparation of Cyclopentenones by Benzeneseleninic Anhydride Oxidation of Cyclopentanones

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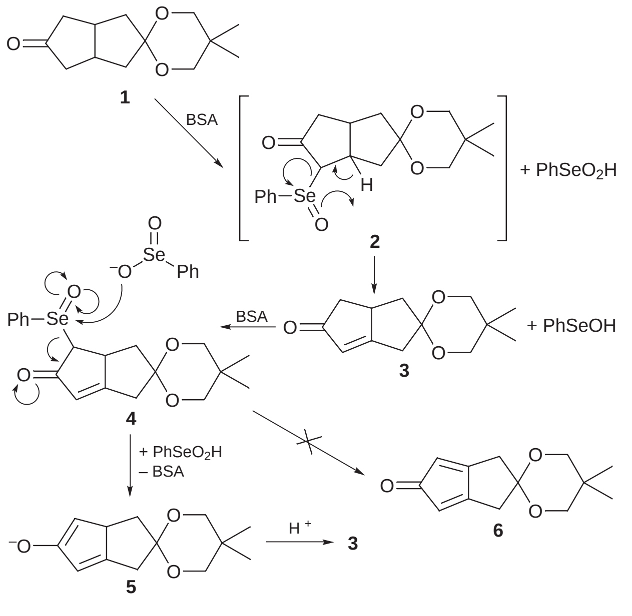
Cyclopentanones are treated with benzeneseleninic anhydride in refluxing benzene and the corresponding cyclopentenones are obtained in moderate to good yields.

Barton's group dehydrogenated a number of steroidal and triterpenoid cyclohexanones using benzeneseleninic anhydride (BSA) in chlorobenzene at 95–132 °C.[1–5] It was shown, from research on cyclohexanones, that dehydrogenation occured for as long as there were acidic hydrogen atoms (α, α' or γ) available to react with BSA, to produce dienones and trienones.[1–3] Thus, in some cases such a transformation was not of preparative value.[2] We speculated that a cyclopentanone would yield a cyclopentenone **3** (Scheme 1), and the subsequent elimination of benzeneselenenic acid would lead to an antiaromatic cyclopentadieneone **6**, which would be disfavored. For that reason any formed α-selenoxyenone **4** would react with nucleophiles present (most likely benzeneseleninic acid) to regenerate the enone **3** and, thus, further dehydrogenation would not occur.



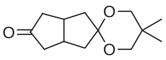
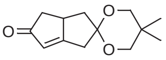
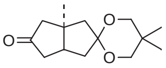
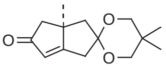
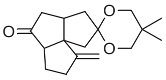
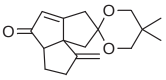
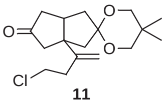
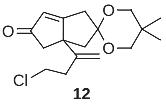
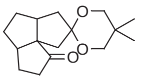
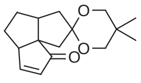
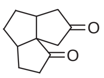
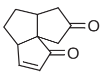
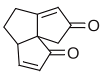
Scheme 1

The best yield of the enone **3** was obtained when a cyclopentanone was treated with 2 equiv. of BSA in refluxing benzene. It was important to add BSA in small portions over 2–2.5 h. BSA was prepared by ozonization of diphenyldiselenide.[6] The commercially available BSA reagent cannot be used in this reaction because it contains up to 30% benzeneseleninic acid.[7]

The results of the oxidations of other cyclopentanones, conducted under similar reaction conditions, are listed in Table 2. This transformation is an example of what Turner called a 'point reaction'.[8] It provided an acceptable yield only within a relatively narrow range of conditions, and an excess of reagent, increased temperature or extended reaction times significantly lowered the yield. For that reason, the given conditions may not be optimal for other substrates, and more research could improve the yield of individual reactions. Indeed, the optimal procedure for the oxidation of enedione **16** to dienedione **17** (Table 2, entry 8) is different from the optimal procedure for oxidation of the ketoketal **1** and when using that procedure the dienedione **17** was obtained in only 32% yield.

The results of oxidation of the same polyquinane ketones by the procedure of Saegusa and coworkers[9,10] are also listed in Table 2. A comparison between the results obtained by the BSA oxidation and those obtained by Saegusa's method shows that the latter often provided higher yield (entries 1, 3, 4). However, in several examples the BSA method was superior by providing either a higher yield (entries 2, 6)

Table 2 Preparation of enones from ketones

Entry	Ketone	BSA (equiv.)	Product	Solvent T / °C	Yield (%)[a]	Yield (%)[b]
1	 **1**	2	 **3**	C_6H_6, 80	55 (15)[c]	72
2	 **7**	2	 **8**	C_6H_6, 80	51 (35)[c]	42(9)
3	 **9**	2	 **10**	C_6H_6, 80	0[d]	73
4	 **11**	2	 **12**	C_6H_6, 80	0[d]	—
5	 **13**	2	 **14**	C_6H_6, 80	62	74
6	 **15**	2	 **16**	$CHCl_3$, 60	40	10[e]
7	**15**	4	 **17**	$CHCl_3$, 60	17	20[e]
8	**16**	6	**17**	C_6H_6, 80	32	42

[a] BSA method. [b] Saegusa's method. [c] Yield of recovered starting ketone is given in parentheses. [d] A mixture of unidentified products was obtained. [e] A single conversion of **15** provided **17** and **16** in yields of 20 and 10%, respectively.

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or a better material balance (entry 8). Thus, the dienedione **17** was obtained in 59% overall yield after the recovered enedione **16** was recycled twice. The advantage of BSA method is that, unlike Saegusa's method, the formation of the intermediates is reversible. Therefore, any α-selenoxy ketone that could not eliminate to a cyclopentenone will be converted to the starting cyclopentenone, which can undergo the reaction with BSA again until the satisfactory conversion to cyclopentenone is achieved.

Therefore, BSA oxidation of cyclopentenones represents a complementary method to Saegusa's procedure. A limitation of this procedure is that enones with additional isolated double bonds provided a complex mixture of products, most likely due to the allylic oxidation of the olefin by the benzeneseleninic acid,[11,12] which was one of the byproducts of the reaction.

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Techniques used: IR, ^{1}H and ^{13}C NMR, LRMS, HRMS

References: 15

Tables: 2 (Oxidation of the ketoketal **1**, Preparation of enones from ketones)

Schemes: 3

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References cited in this synopsis

1 D. H. R. Barton, D. J. Lester and S. V. Ley, *J. Chem. Soc., Chem Commun.*, 1978, 130.
2 D. H. R. Barton, D. J. Lester and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2209.
3 D. H. R. Barton, J. W. Morzycki, W. B. Motherwell and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 1981, 1044.
4 D. H. R. Barton, R. A. H. F. Hui, S. V. Ley and D. J. Williams, *J. Chem Soc., Perkin Trans. 1*, 1982, 1919.
5 D. H. R. Barton, C. R. A. Godfrey, J. W. Morzycki and W. B. Motherwell, *J. Chem Soc., Perkin Trans. 1*, 1982, 1947.
6 G. Ayrey, D. Barnard and D. T. Woodbridge, *J. Chem. Soc.*, 1962, 2089.
7 Aldrich Chemical Co., **21,301-2** Benzeneseleninic anhydride, 70%. Contains ≈ 30% benzeneseleninic acid.
8 S. Turner, *Design of Organic Syntheses,* Elsevier, Amsterdam, 1976, pp. 21 and 22.
9 Y. Ito, T. Hirao and T. Saegusa, *J. Org. Chem.*, 1978, **43**, 1011.
10 Y. Ito, H. Aoyama, T. Hirao, A. Mochizuki and T. Saegusa, *J. Am. Chem. Soc.*, 1979, **101**, 494.
11 D. H. R. Barton and D. Crich, *Tetrahedron*, 1985, **41**, 4359.
12 T. Hori and K. B. Sharpless, *J. Org. Chem.*, 1978, **43**, 1689.