# Dehydrogenation of Steroidal Ketones using Benzeneseleninic Anhydride

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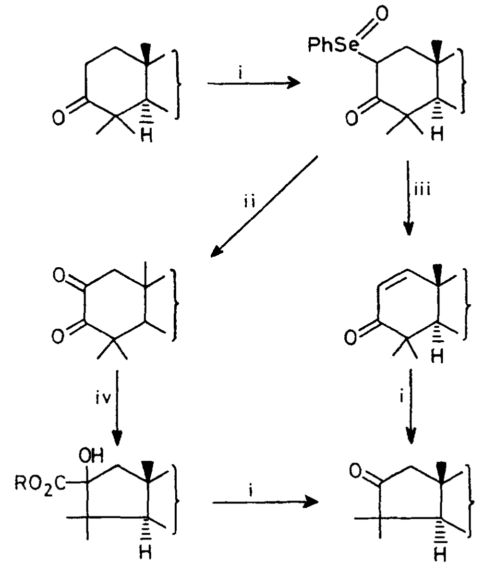
*Summary* A number of steroidal ketones have been dehydrogenated in excellent yield and under mild conditions using benzeneseleninic anhydride; in some cases A-nor ketones were also formed.

Although dehydrogenation of steroidal ketones can be achieved by a variety of methods,[1] there is still a need for improvement. Here we describe the use of benzeneseleninic anhydride[2] as a suitable reagent to effect this transformation.

TABLE. Reaction of steroidal ketones with benzeneseleninic anhydride (BSA).

| | Reaction conditions | | | Products | | |
|---|---|---|---|---|---|---|
| Ketone | Temp./ °C | BSA/ equiv. | Time | Enone (%) | A-Nor-3-one/ % | 2-Phenylseleno ketone/% |
| Lanostanone | 95 | 1 | 45 min | 1-Enone (67) | 13 | 4 |
| Cholest-4-en-3-one | 132 | 1 | 40 min | 1,4-Dienone (92) | — | — |
| 4,4-Dimethylcholest-5-en-3-one | 95—100 | 1 | 35 min | 1,5-Dienone (67) | Trace | — |
| „ „ | 95—100 | 2 | 17 h | „ (31) | 28 | — |
| α-Amyrone | 95—100 | 1 | 25 min | 1-Enone (74) | — | — |
| „ | 95—100 | 2 | 17 h | „ (39) | 39 | — |
| β-Amyrone | 95—100 | 1 | 15 min | 1-Enone (54) | 9 | 6 |
| „ | 95—100 | 2 | 17 h | „ (21) | 36 | — |
| Hecogenin acetate | 132 | 2 | 50 min | 9(11)-Enone (91) | — | — |
| Lupeone | 95—100 | 1 | 15 min | 1-Enone (58) | — | — |
| Cholestan-3-one | 132 | 2 | 3 h | 1,4-Dienone (82) | — | — |
| Cholest-1-en-3-one | 95 | 1 | 45 min | 1,4-Dienone (76) | — | — |

In a typical experiment, the ketone was treated with the anhydride in chlorobenzene at 95—100 °C and the products were separated by preparative layer chromatography. Of particular interest are the yields of dehydrogenated products from hecogenin acetate, cholestan-3-one, and cholest-4-en-3-one which are noticeable improvements over existing literature reactions.[3] The results are presented in the Table.



SCHEME. i, PhSe(O)OSe(O)Ph; ii, Pummerer-type reaction; iii, *syn*-elimination; iv, benzilic acid rearrangement.

In a number of experiments, especially where more than 1 equiv. of the anhydride and longer reaction times are used, other products such as A-nor ketones or phenylselenated species can be isolated. Lanost-1-en-3-one, in a separate experiment, was converted into the A-nor-3-one by treatment with benzeneseleninic anhydride in 48% yield. Undoubtedly the A-nor compounds arise *via* benzilic acid rearrangement of the corresponding 1,2-dicarbonyl species[4] themselves being derived as outlined in the Scheme for which ample precedence exists.[5]

In accord with these proposals, benzilic acid can be converted into benzophenone (yield 95%) after reaction with the anhydride in chlorobenzene at 95—100 °C overnight. The phenylseleno ketones are probably formed by reaction of the starting ketone with a partially reduced form of the anhydride, *e.g.* PhSeOSe(O)Ph. Authentic 2-phenylselenolanostan-3-one was also prepared by reaction of the enolate with phenylselenenyl chloride.

In conclusion, we feel that benzeneseleninic anhydride is an attractive alternative, particularly to selenium dioxide, for the dehydrogenation of steroidal ketones. The major byproduct of the reaction, diphenyl diselenide, can be easily separated and reoxidised to the anhydride. Additionally the anhydride, in contrast to selenium dioxide, is relatively unreactive towards the ethylenic linkage.

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