

## Oxidation of Alcohols using Benzeneseleninic Anhydride

By DEREK H. R. BARTON,\* ANDREW G. BREWSTER, RAYMOND A. H. F. HUI, DAVID J. LESTER, and STEVEN V. LEY  
(*Department of Chemistry, Imperial College, London SW7 2AY*)

and THOMAS G. BACK

(*Division of Biological Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6*)

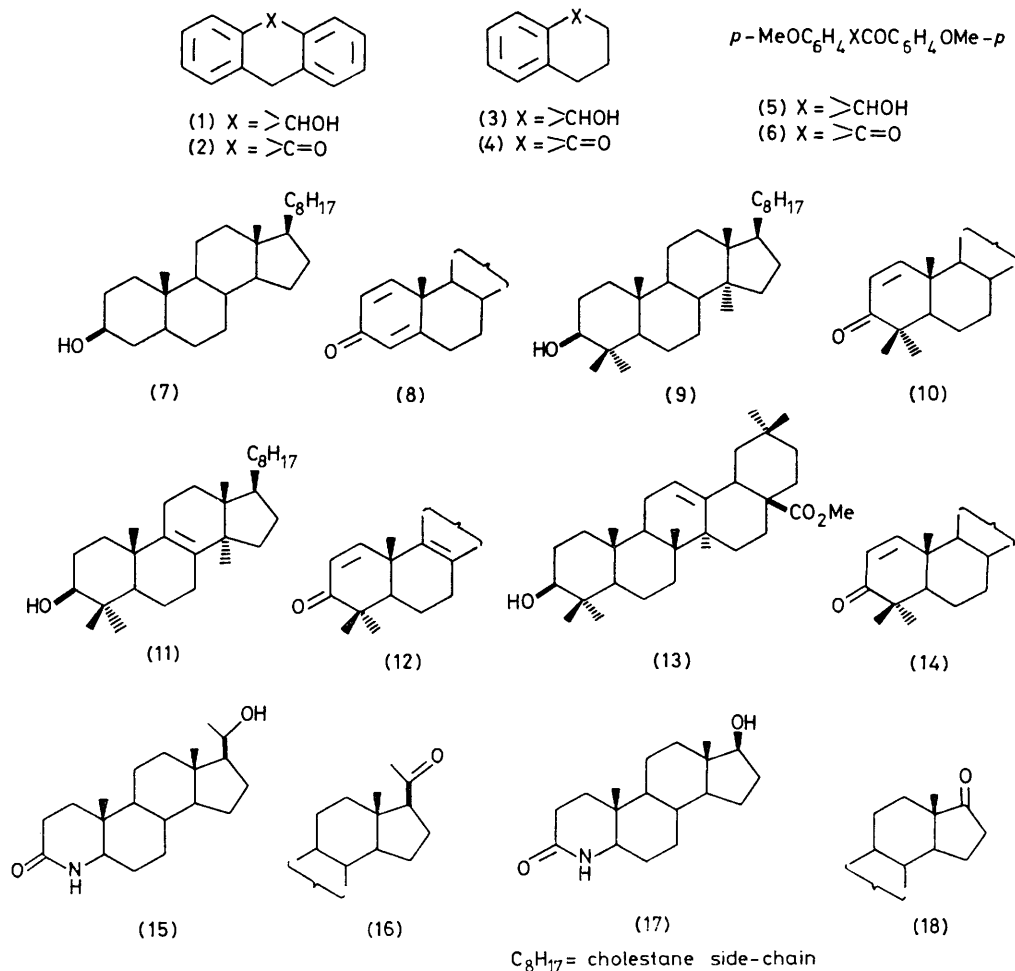
**Summary** A number of alcohols have been oxidised by benzeneseleninic anhydride to carbonyl derivatives in high yield; in appropriate cases, the corresponding dehydrogenated compounds are obtained by further oxidation.

WE report that benzeneseleninic anhydride<sup>1</sup> is a good oxidant for a variety of alcohols giving satisfactory yields of oxidised products (Table). Benzylic alcohols are oxidised more rapidly than allylic or saturated alcohols. The major by-product of the reaction is diphenyl diselenide which can be isolated and reoxidised to the anhydride.<sup>2</sup>

TABLE

Alcohol	Product	Mol. equiv. anhydride	Solvent <sup>a</sup>	Time	% Yield
PhCH <sub>2</sub> OH	PhCHO	2	C <sub>6</sub> H <sub>6</sub>	20 min	99.5 <sup>d</sup>
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	0.5	C <sub>6</sub> H <sub>6</sub>	8 min	97
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	0.5	C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	1 day	57
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CHO	0.5	C <sub>6</sub> H <sub>6</sub>	15 min	99
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CHO	1	C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	2 days	85
PhCHOHPh	PhCOPh	1	THF <sup>c</sup>	3 h	85
(1)	(2)	0.5	C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	5.5 h	83
(3)	(4)	0.33	C <sub>6</sub> H <sub>6</sub> <sup>b</sup>	Overnight	40
PhCH=CH·CH <sub>2</sub> OH	PhCH=CHCHO	0.33	PhCl <sup>b</sup>	10 h	53 <sup>d</sup>
PhCHOHCOPh	PhCOCOPh	1	THF	3 h	92
PhCHOHCCHOHPh	PhCOCOPh	2	THF	3 h	77
(5)	(6)	1	THF	8 min	99
PhCHOHCO <sub>2</sub> Me	PhCOCO <sub>2</sub> Me	0.5	C <sub>6</sub> H <sub>6</sub>	10 min	97
(7)	(8)	4	PhCl	20 min	60
(9)	(10)	2	PhCl	12 min	65
(11)	(12)	2	PhCl	10 min	60
(13)	(14)	2	PhCl	7 min	83
(15)	(16)	1.1	THF	16 h	94
(17)	(18)	1.1	THF	20 h	86

<sup>a</sup> At reflux under nitrogen unless otherwise stated. <sup>b</sup> At room temperature. <sup>c</sup> THF = tetrahydrofuran. <sup>d</sup> Isolated as the 2,4-dinitrophenyl hydrazine derivative.



A low yield of ketone was obtained in the oxidation of  $\alpha$ -tetralol owing to contaminating side products, mainly *ortho* and *para* naphthoquinone and phenylselenated species. As an added bonus, in the oxidation of steroidal ring A alcohols dehydrogenation is also effected<sup>3</sup> to give the

commercially important 1,4-dienones. We thus effect in one step an operation that is otherwise a multistep process.

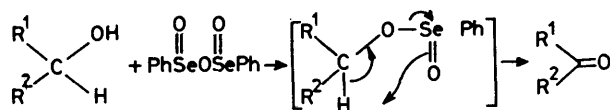
The final entries in the Table extend the oxidation to steroidal ring D and saturated side chain alcohols.

The mechanism for these reactions undoubtedly involves

fragmentation of the initially formed seleninic esters (Scheme). In reactions in which higher temperatures are involved benzeneseleninic acid can also be used as an oxidising reagent.

Clearly in the above reactions benzeneseleninic anhydride is an effective alternative reagent for the oxidation of alcohols under essentially neutral conditions.

We thank the S.R.C. and Beit Fellowships for awards to A.G.B. and D.J.L., respectively.



SCHEME

(Received, 21st July 1978; Com. 786.)

<sup>1</sup> D. H. R. Barton, N. J. Cussans, and S. V. Ley, *J.C.S. Chem. Comm.*, 1978, 393; D. H. R. Barton, D. J. Lester, and S. V. Ley, *ibid.*, p. 276; T. G. Back, *ibid.*, p. 278.

<sup>2</sup> D. H. R. Barton, S. V. Ley, P. D. Magnus, and M. N. Rosenfeld, *J.C.S. Perkin I*, 1977, 567.

<sup>3</sup> D. H. R. Barton, D. J. Lester, and S. V. Ley, *J.C.S. Chem. Comm.*, 1978, 130.