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PREPARATION OF ALDEHYDES AND KETONES BY OXIDATION OF BENZYLIC HYDROCARBONS WITH BENZENESELENINIC ANHYDRIDE

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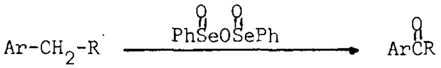
Summary: Benzeneseleninic anhydride is a mild oxidant for the conversion of benzylic hydrocarbons into aldehydes or ketones.

Although oxidation of aromatic side chains can be achieved by a variety of methods, there is still a need for new reagents which will effect this transformation. Recently benzeneseleninic anhydride has been used as a mild and versatile oxidant for a number of different organic substrates[1] and appeared to be suitable for benzylic oxidation also.



$$Ar{-}CH_2{-}R \xrightarrow{PhSe(=O)OSe(=O)Ph} ArC(=O)R$$

R = H
= Alkyl
= Aryl

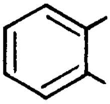
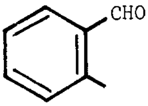
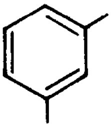
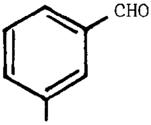
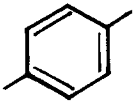
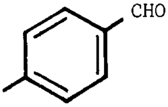
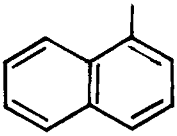
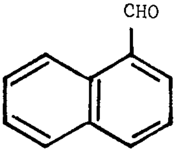
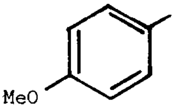
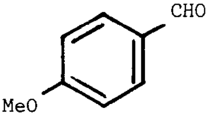
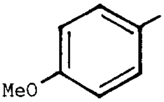
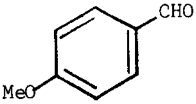
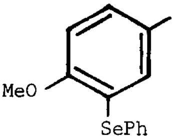
Thus we find that xylenes can be treated neat with the anhydride (0.33 mol equivalents) at 132° to give the corresponding monoaldehydes (Table). Owing to the small scale of these reactions, the aldehydes were isolated as their 2,4-DNP derivatives. In other experiments we were also able to isolate small amounts of the corresponding acid. The yields of the acid could be substantially increased when large excesses of the anhydride were used.

A number of other methyl substituted aromatics were similarly investigated (Table). Crude rate studies showed that p-nitrotoluene was inert to the anhydride while p-methoxytoluene reacted about three times faster than the xylenes. The low yield in the p-methoxytoluene reaction was accounted for by the formation of 2-phenylseleno-4-methyl anisole as a major product (40%). 1-Methylnaphthalene also on oxidation with the anhydride afforded the aldehyde together with substantial amounts of phenylselenated products.

Other compounds which were oxidised include diphenylmethane which gave benzophenone in 90% yield after 4 days. Ethyl benzene gave acetophenone in 60% yield although a significant amount of phenylglyoxal (10%) was also formed, presumably by further oxidation of acetophenone. In accord with this result, camphor gave camphorquinone in 74% after oxidation with the anhydride. Finally, it was of interest to investigate the oxidation of 9,10-dimethylanthracene in the hope of obtaining further mechanistic information. Under mild conditions, good conversion to the aldehyde was obtained. However, on extended reaction times (20 h) with more anhydride added (2 eq.) further oxidation produced anthraquinone in 64% yield.

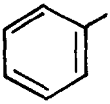
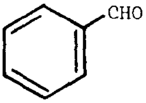
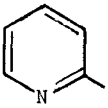
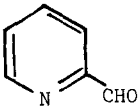
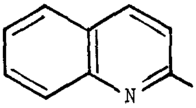
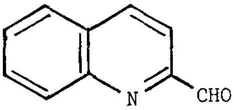
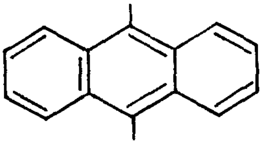
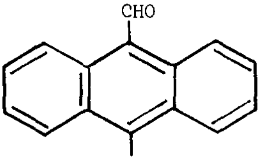
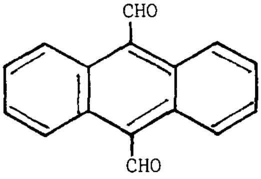
In the above reactions, at elevated temperatures, it is possible to use benzeneseleninic acid as an alternative oxidant.

TABLE

STARTING MATERIAL	PRODUCT(S)	REACTION CONDITIONS (d)	% YIELD
		0.33 equiv. BSA 10 h (b)	42*
		0.33 equiv. BSA 10 h (b)	62*
		0.33 equiv. BSA 10 h (b)	66*
		0.25 equiv. BSA 14 h (c)	37**
		0.33 equiv. BSA 4 h (c)	15
		2 equiv. BSA 2.5 h (c)	9
			40

/continued

Table/continued

STARTING MATERIAL	PRODUCT(S)	REACTION CONDITIONS (d)	% YIELD
		0.33 equiv. BSA 1 week (b)	38*
		0.33 equiv. BSA 2 h (a) (b)	41*
		1 equiv. BSA 15 min (a) (b)	59
$PhCH_2Ph$	PhCOPh	0.5 equiv. BSA 4 days (a) (c)	90
		1 equiv. BSA 2.5 h (a) (c)	51
			14

* *As 2,4-DNP derivative*

** *Based on starting material consumed*

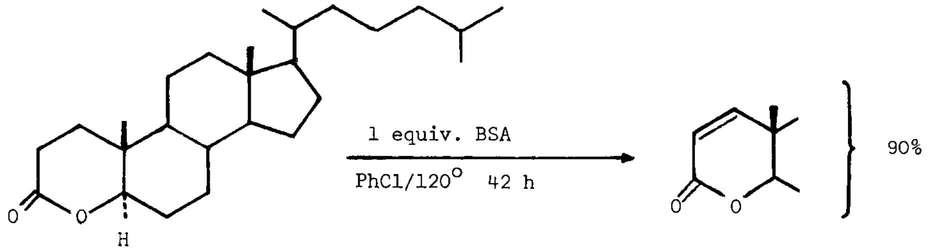
(a) *In dry chlorobenzene*

(b) *At reflux*

(c) *At 120°*

(d) *All reactions done under nitrogen or argon*

Addendum: Recently T.G. Back[1g] showed that benzeneseleninic anhydride is an excellent reagent for the dehydrogenation of cyclic lactams. We can add that it is also an excellent reagent for the dehydrogenation of cyclic lactones [(1) → (2)]. However, it is not efficient for the dehydrogenation of acyclic esters.



(1) (2)

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1. (a) D.H.R. Barton, A.G. Brewster, S.V. Ley, and M.N. Rosenfeld, J.C.S. Chem. Comm., 985 (1976); (b) M.R. Czarny, ibid., 81 (1976); D.H.R. Barton, A.G. Brewster, S.V. Ley, and M.N. Rosenfeld, ibid., 147 (1977); (c) D.H.R. Barton, D.J. Lester, and S.V. Ley, ibid., 445 (1977); (d) D.H.R. Barton, S.V. Ley, P.D. Magnus, and M.N. Rosenfeld, J.C.S. Perkin I, 567 (1977); (e) D.H.R. Barton, N.J. Cussans, and S.V. Ley, J.C.S. Chem. Comm., 751 (1977); (f) D.H.R. Barton, D.J. Lester, S.V. Ley, ibid., 131 and 276 (1978); (g) T.G. Back, ibid., 278 (1978); (h) D.H.R. Barton, N.J. Cussans, S.V. Ley, ibid., 393 (1978); (i) D.H.R. Barton, A.G. Brewster, R.A.H.F. Hui, D.J. Lester, S.V. Ley, and T.G. Back, ibid., 952 (1978).

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