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BIS(*p*-METHOXYPHENYL)SELENOXIDE AS A COOXIDANT FOR SELENIUM DIOXIDE OXIDATION OF BENZYL ALCOHOLS

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The title selenoxide provides a new oxidizing system in combination with catalytic selenium dioxide for oxidation of benzyl alcohols to benzaldehydes. An effective redox cycle between selenium and the dioxide is suggested.

Selenium dioxide is widely used as a selective and valuable reagent for allylic and benzylic oxidations.1) However, these reactions suffer a serious disadvantage of the formation of colloidal selenium, being difficult to remove from the product mixtures. In addition, the quality of selenium dioxide has considerable effect on the oxidation products and yields. These problems can be overcome by use of a cooxidant which reoxidizes the reduced selenium species to the dioxide and permits the catalytic circulation of selenium dioxide reagent. Although *t*-butyl hydroperoxide and hydrogen peroxide have already been used as cooxidants, these reactions must be strictly controlled to avoid competitive oxidations with peroxide or perselenious acid.2)

We now report the novel ability of bis(*p*-methoxyphenyl)selenoxide (1) as a cooxidant. It is an extremely mild and selective oxidizing agent,3) and can oxidize selenium metal in refluxed dioxane as indicated by gradual dissolution of the metal. Thus, benzyl alcohol (3) was treated with a combination of catalytic amounts of selenium and 50% excess of 1 in refluxed dioxane for one day to give benzaldehyde (4) in 93% yield. Oxidation by use of catalytic selenium dioxide instead of selenium metal gave the quite same result.4) Previous literatures described that selenium dioxide could oxidize benzyl alcohol to benzaldehyde at ca. 200 °C without solvent.5) A comparative oxidation by purified selenium dioxide in refluxed dioxane gave just 30% yield. It should be further noted

Scheme 1.

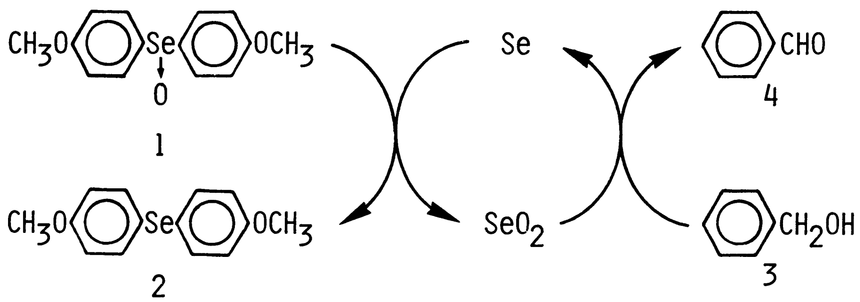
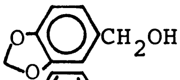
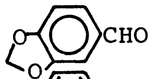
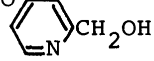
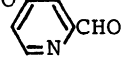
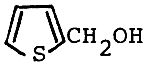
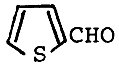


Table 1. Oxidation of benzyl alcohols to benzaldehydes by bis(*p*-methoxyphenyl) selenoxide in the presence of catalytic selenium dioxide.

Substrate	Product	Yield/%	Substrate	Product	Yield/%
$C_6H_5CH_2OH$	C_6H_5CHO	92	*p*-$NO_2C_6H_4CH_2OH$	*p*-$NO_2C_6H_4CHO$	92
p-$CH_3C_6H_4CH_2OH$	*p*-$CH_3C_6H_4CHO$	89	*m*-$NO_2C_6H_4CH_2OH$	*m*-$NO_2C_6H_4CHO$	91
o-$CH_3C_6H_4CH_2OH$	*o*-$CH_3C_6H_4CHO$	92			90
p-$CH_3OC_6H_4CH_2OH$	*p*-$CH_3OC_6H_4CHO$	92			91
p-$ClC_6H_4CH_2OH$	*p*-ClC_6H_4CHO	89			94
o-$ClC_6H_4CH_2OH$	*o*-ClC_6H_4CHO	94	$C_6H_5CH{=}CHCH_2OH$	$C_6H_5CH{=}CHCHO$	94
o-$BrC_6H_4CH_2OH$	*o*-BrC_6H_4CHO	90			

that bis(*p*-methoxyphenyl)selenoxide itself hardly reacted with benzyl alcohol under the same conditions. These results evidently support that selenoxide **1** serves as an excellent cooxidant, generating fresh and active selenium dioxide. The main by-product is bis(*p*-methoxyphenyl)selenide (**2**), which may be readily converted to **1** for reuse.[6] Some substituted benzyl alcohols and related compounds were smoothly oxidized to the corresponding aldehydes by this procedure (see Table 1).

A typical experiment is as follows; A mixture of benzyl alcohol (0.108 g, 1.0 mmol), bis(*p*-methoxyphenyl)selenoxide (0.464 g, 1.5 mmol) and selenium dioxide (2 mg) in 4 ml of dry dioxane was refluxed for one day in a nitrogen atmosphere. After evaporation of the solvent, the preparative gel-permeation liquid chromatography of the residue using chloroform as eluent gave benzaldehyde (0.098 g, 92%) following the elution of selenoxide **1** (114 mg) and selenide **2** (293 mg).

The application of the present oxidizing procedure to other selenium dioxide reactions is now under investigation.[7]

References

1) For reviews, see N. Rabjohn,"Organic Reactions," John Wiley & Sons, Inc., NY (1976), Vol. 24, Chap. 4; (1949), Vol. 5, Chap. 8.

2) M. A. Umbreit and K. B. Sharpless, J. Am. Chem. Soc., 99, 5526 (1977) and references cited therein.

3) F. Ogura, H. Yamaguchi, T. Otsubo, and T. Tanaka, Bull. Chem. Soc. Jpn., 55, 641 (1982).

4) Commercially available selenium dioxide was used without purification.

5) a) S. Astin, A. C. C. Newman, and H. L. Riley, J. Chem. Soc., 1933, 391;
b) F. Weygand, K. G. Kinkel, and D. Tietjen, Chem. Ber., 83, 394 (1950).
The yields of benzaldehyde isolated as the bisulphite adduct[a] and phenyl hydrazone[b] are 41% and 83%, respectively, based on selenium dioxide.

6) M. Cinquini, S. Colonna, and R. Giovini, Chem. Ind. (London), 1969, 1737.

7) The present procedure has proved to be effective in allylic oxidation of olefins like Sharpless' procedure using *t*-butyl hydroperoxide as a cooxidant (Ref. 2), though it required much higher temperature than the latter. In contrast, Sharpless' procedure was inapplicable to the oxidation of benzyl alcohol.

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