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APPLICATION OF BIS(*p*-METHOXYPHENYL)SELENOXIDE AS AN OXIDIZING AGENT OF KORNBLUM OXIDATION

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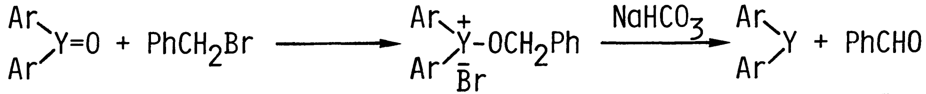
The title selenoxide was found to serve as a suitable agent for Kornblum oxidations of various benzyl bromides to the corresponding carbonyl compounds. On the other hand, the analogous sulfoxide and telluroxide hardly promoted such oxidations.

Most of dimethyl sulfoxide oxidations involve an alkoxysulfonium salt as intermediate which subsequently reacts with a base to give a carbonyl product.$^{1)}$ Formation of the alkoxysulfonium salt by direct nucleophilic displacement of a halide with dimethyl sulfoxide (Kornblum oxidation) often requires severe conditions.$^{2)}$ Recent attention has been paid to the oxidizing capacity of other chalcogenoxides such as selenoxide$^{3)}$ and telluroxide.$^{4)}$ Since the basicity of the oxygen atoms of triadic chalcogenoxides increases in order of S=O, Se=O, and Te=O,$^{5)}$ the initial stage of Kornblum reaction may be expected to be facilitated by use of selenoxide or telluroxide as an alternative nucleophile. Although common selenoxides and telluroxides are unfavorable owing to their smell and/or lability, bis(*p*-methoxyphenyl)selenoxide (1a)$^{3)}$ and telluroxide (1b)$^{4)}$ have turned out to be practical materials, especially useful for selective oxidations. Here we report the Kornblum oxidation of benzyl bromide to benzaldehyde by them as another application.



$$\mathrm{Ar_2Y{=}O} + \mathrm{PhCH_2Br} \longrightarrow \mathrm{Ar_2\overset{+}{Y}{-}OCH_2Ph\ \overset{-}{Br}} \xrightarrow{\mathrm{NaHCO_3}} \mathrm{Ar_2Y} + \mathrm{PhCHO}$$

1a, Y=Se
1b, Y=Te
1c, Y=S
Ar=p-$CH_3OC_6H_4$

2

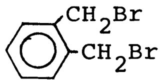
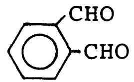
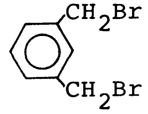
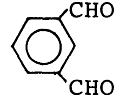
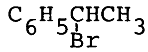
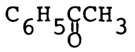
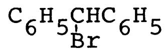
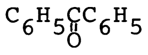
3a, Y=Se
3b, Y=Te

4

5

Original Kornblum reactions were carried out at high temperatures of 100 to 150 °C in a neat state of dimethyl sulfoxide itself.$^{2)}$ Dimethyl sulfoxide and bis(*p*-methoxyphenyl)sulfoxide (1c) were unreactive to benzyl bromide (2) in a usual solvent such as acetonitrile, tetrahydrofuran, or dioxane. In contrast, selenoxide (1a), combined with sodium bicarbonate, smoothly reacted with 2 in acetonitrile at 75 °C or in tetrahydrofuran under reflux to give benzaldehyde (5) in an excellent yield, together with bis(*p*-methoxyphenyl)selenide (4). The reaction proceeded with a considerable yield (51%) of 5 even in the absence of

Table 1. Kornblum oxidation of benzyl bromides to carbonyl compounds by bis(*p*-methoxyphenyl)selenoxide 1a[a]

Material	Product	Yield/%	Material	Product	Yield/%
$C_6H_5CH_2Br$	C_6H_5CHO	89(93)[b]			84
o-$CH_3C_6H_4CH_2Br$	*o*-$CH_3C_6H_4CHO$	88			
m-$CH_3C_6H_4CH_2Br$	*m*-$CH_3C_6H_4CHO$	93			90
m-$BrC_6H_4CH_2Br$	*m*-BrC_6H_4CHO	86	 $C_6H_5\underset{Br}{C}HCH_3$	 $C_6H_5\underset{O}{\overset{\|}{C}}CH_3$	85
p-$BrC_6H_4CH_2Br$	*p*-BrC_6H_4CHO	86			
m-$NO_2C_6H_4CH_2Br$	*m*-$NO_2C_6H_4CHO$	85	 $C_6H_5\underset{Br}{C}HC_6H_5$	 $C_6H_5\underset{O}{\overset{\|}{C}}C_6H_5$	87
p-$NO_2C_6H_4CH_2Br$	*p*-$NO_2C_6H_4CHO$	90	$C_6H_5CH{=}CHCH_2Br$	$C_6H_5CH{=}CHCHO$	83

a) Reaction time, 5 h; Solvent, CH_3CN at 75 °C.

b) Reaction time, 10 h; Solvent, THF under reflux.

the base. It is thus accepted that the enhanced basicity of selenoxide (1a) relative to sulfoxides facilitated the formation of the intermediate (3a). On the other hand, a similar reaction with telluroxide (1b) did not afford benzaldehyde (5). Prolonged treatment in refluxed toluene (1 d) led ultimately to only 6% yield of 5, and the main product was benzyl alcohol (90%). Although selenonium salt (3a) could not be detected in the preceding reaction, the ready formation and high stability of telluronium salt (3b) were recognized on NMR measurement; 3b demonstrated NMR signals at δ 3.66(s, CH_3O), 4.52(s, CH_2), 6.73 and 7.70(A_2B_2m, ArH), and 7.22(s, PhH) in deuteriochloroform. It is, therefore, understandable that a reaction of 1b and 2 readily gave telluronium salt (3b), which was, however, too stable to undergo further fission into two products (4) and (5), and finally hydrolyzed to benzyl alcohol during work-up.

As shown in Table 1, the present method using bis(*p*-methoxyphenyl)selenoxide (1a) was conveniently applicable to oxidations of various benzyl bromides to the corresponding carbonyl compounds. It may be thus noted that selenoxide (1a) is a suitable agent for Kornblum oxidations owing to its rather moderate basicity. Further investigation on the scope is now in progress.

References

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