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A NOVEL SYNTHESIS OF 2,5-DISUBSTITUTED FURANS AND SELENOPHENES VIA THE OXIDATION OF 2,4-ALKADIENOIC ESTERS WITH SeO_2

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Summary: A new synthesis of 5-alkyl-2-furancarboxylates and 5-alkyl-2-selenophenecarboxylates via the direct oxidation of 2,4-alkadienoic esters with selenium dioxide is described.

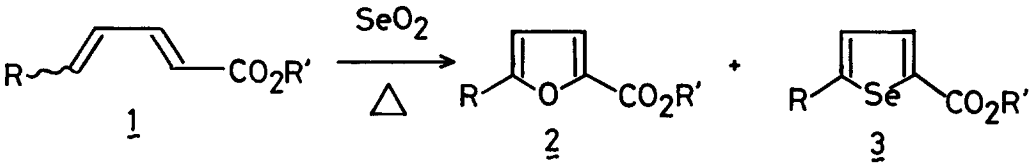
Selenium dioxide is a useful reagent for the syntheses of allylic alcohols and diketones via the oxidation of olefins and ketones.$^{1)}$ However, no reference was found on the use of selenium dioxide for furan synthesis from 2,4-alkadienoates **1**. In this communication we described a straightforward synthesis of furans and selenophenes via oxidation of 2,4-alkadienoic esters with selenium dioxide.

As a part of continuing study of conjugated alkadienoic esters **1**,$^{2)}$ we carried out the direct oxidation of **1** with SeO_2. Treatment of methyl sorbate with SeO_2 (1.1 eq.) in benzene (80 °C, 0.5 h) gave unexpectedly a mixture of methyl 5-methylfuran-2-carboxylate$^{3)}$ (46%) and methyl 5-methyl-2-selenophenecarboxylate$^{4)}$ (48%), which was easily separated by medium pressure column chromatography (SiO_2, 8:1 hexane/ethyl acetate; TLC: R_f = 0.52 and 0.61, 4:1 hexane/ethyl acetate). General applicability of this novel furan synthesis with selenium dioxide was examined for several alkadienoic esters, and these results are summarized in Table 1.

In most cases, the formation of furans was favoured. Repeated attempts revealed that prolonged reaction gives the furan predominantly. Treatments of **1** bearing small alkyl groups (R = CH_3, C_2H_5, and C_3H_7) with SeO_2 gave the oxidized products in moderate yields. With dienoic esters bearing a large alkyl group, e.g. in the attempted conversions of **1g** and **1h** to the corresponding furans, the reaction proved to be less than satisfactory despite repeated attempts to improve the yield.

Although the present method does not give a high yield of furans and selenophenes, the simplicity as well as an interest in the reaction mechanism make it considerably attractive. Noteworthy is that this procedure of 5-methyl-2-selenophenecarboxylate (**3a**) is simpler than the previously reported one.$^{4)}$ This process will also be useful for syntheses of naturally occuring 2,5-disubstituted furans.$^{5,6)}$

Table 1. Oxidation of 2,4-Alkadienoic Esters[1] with SeO_2



1[2]			SeO_2	Solvent	Temp. (^oC)	Time (h)	Yield[3] (%)	
No	R	R′					2	3
a	CH_3	CH_3	1.1	benzene	80	0.5	46	48
b	CH_3	CH_3	1.1	benzene	80	5.0	56	29
c	CH_3	C_2H_5	1.5	benzene	80	6.0	26[4]	6.2[4]
d	C_2H_5	CH_3	1.1	benzene	80	24	30	2
e	C_3H_7	C_2H_5	1.5	xylene	138	2	58	15
f	$(CH_3)_2CH$	C_2H_5	1.1	xylene	138	1.5	45	2
g	C_5H_{11}	C_2H_5	1.5	xylene	138	2	17[4,5]	3[4,5]
h	$^tBuO_2C(CH_2)_7$	CH_3	1.8	xylene	138	3	19[4]	0

1. Selenium dioxide was dried at ca. 100 °C under reduced pressure for 30 min before use. All products gave satisfactory IR and ^1H NMR spectra.
2. Geometries of 1b and 1c are [2(E),4(E)], and those of 1a and 1d-h are [2(E),4(Z)].
3. Unless otherwise indicated, determined by ^1H NMR analysis after removal of polymerized products by short-pass distillation or short column chromatography.
4. Isolated yield.
5. Ethyl 2(E),4(E)-decadienoate (4%) was isolated in addition to 2 and 3.

References

1) For example, see: N. Rabjohn, Org. React., 5, 331 (1949); R. A. Jerussi, "Selective Oxidations with Selenium Dioxide", p. 301, John Wiley, New York (1970).
2) (a) S. Tsuboi, T. Masuda, and A. Takeda, J. Org. Chem., 47, 4478 (1982).
(b) S. Tsuboi, T. Masuda, and A. Takeda, Chem. Lett., 1983, 1829.
(c) S. Tsuboi, A. Kuroda, T. Masuda, and A. Takeda, Chem. Lett., 1984, 1541.
3) B. M. Bertilsson, B. Gustafsson, I. Kuhn, K. Torssell, Acta Chem. Scand., 24, 3590 (1970).
4) Y. K. Yurêv, N. K. Sadovaya, and A. B. Ibragimova, Zhur. Obschei Khim., 29, 3647 (1959); Chem. Abstr., 54, 19644e (1960).
5) H. Okajima, K. Ishii, and H. Watanabe, Chem. Pharm. Bull., 32, 3281 (1984).
6) C. H. Fawcett, D. M. Spencer, R. L. Wain, A. G. Fallis, E. R. H. Jones, M. Le Quan, C. B. Page, V. Thaller, D. C. Shubrook, and P. W. Whitham, J. Chem. Soc. (C), 1968, 2455.

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