

## New Method for Carbon–Carbon Bond Formation: Biogenetic-type Synthesis of Safranal

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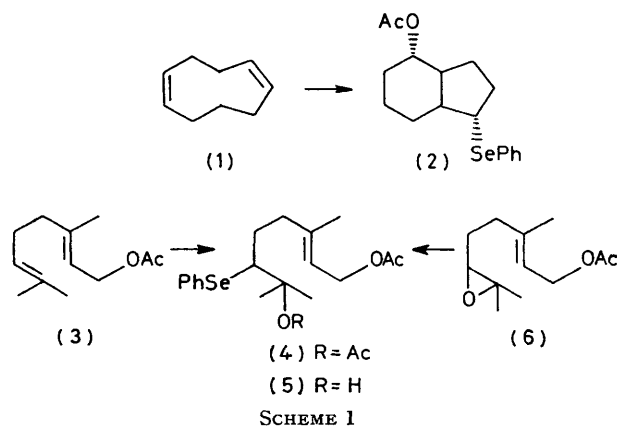
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**Summary** Acid catalysed cyclisation of the olefinic  $\beta$ -hydroxy selenide (5) afforded the cyclic compound (7) which was converted into safranal (16) *via* the olefinic alcohol (12), diolefinic alcohol (14), and aldehyde (15).

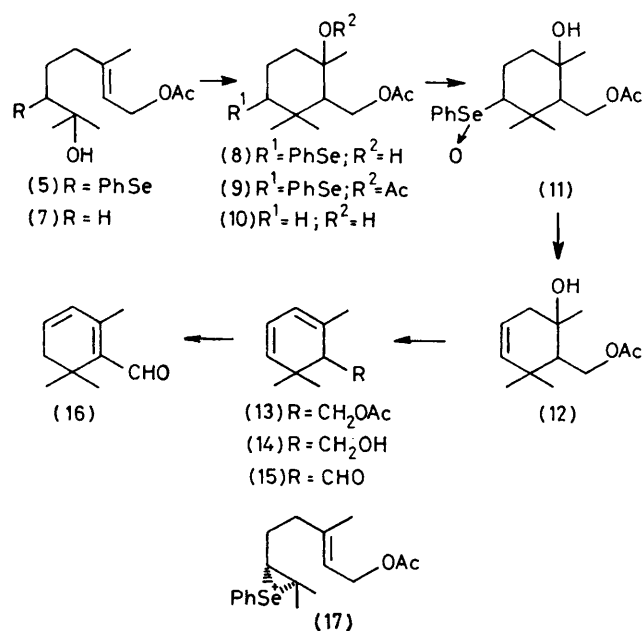
(5) and not the expected cyclic compounds (8) or (9). Compound (5) was alternatively synthesised by epoxidation of (3) using *m*-chloroperbenzoic acid followed by treatment of the resulting epoxide (6) with phenylselenium anion.<sup>8</sup>

FUNCTIONAL group manipulation using organoselenium reagents has been thoroughly investigated and the chemistry of such reagents is of current interest.<sup>1</sup> In contrast to the well studied<sup>2–4</sup> synthesis of heterocycles by cyclisation reactions involving the use of organoselenium reagents, studies<sup>5</sup> concerned with carbon–carbon bond formation using selenium reagents are limited. Of prime importance to our study was that a cyclisation reaction be found which would provide a product suitably functionalised to further elaboration. Although a considerable amount of investigation in the area of polyolefin cyclisation has been reported,<sup>6,7</sup> we became interested in developing cyclisation reactions induced by organoselenium reagents because of the versatility of the selenyl functional groups.<sup>1</sup> We now report a new selenium-assisted cyclisation reaction resulting in carbon–carbon bond formation.

To determine whether the cyclisation (1)  $\rightarrow$  (2) reported by Clive<sup>3</sup> is generally applicable for carbon–carbon bond formation, a preliminary experiment was carried out in which geranyl acetate (3) was treated with PhSeCl in AcOH in the presence of NaOAc under the same conditions.<sup>3</sup> However, the products isolated were shown to be (4) and



Since cyclisation of (3) could not be achieved under the conditions described, our interest turned to possible cyclisation of (5). The carbonium ion generated by acid treatment of (5) may be established by participation of the phenylselenyl group with *in situ* formation of the seleniranium ion (17).<sup>9</sup> Thus, treatment of (5) with



SCHEME 2

CF<sub>3</sub>CO<sub>2</sub>H in CH<sub>2</sub>Cl<sub>2</sub> gave, in 65% yield, the cyclic compound (8)† [δ (CDCl<sub>3</sub>) 0.97, 1.18, 1.30 (9H, each s, 3 × Me), 2.03 (3H, s, MeCO), 3.01 (1H, dd, *J* 2.5 and 5 Hz, PhSeCH), 4.1–4.7 (2H, m, CH<sub>2</sub>OAc), and 7.2–7.7 (5H, m, PhSe)]. When the alcohol (7) was subjected to the same treatment, the product obtained, although uncharacterised, was shown not to be the corresponding cyclic compound (10). This remarkable difference in the reactivity of compounds (5) and (7) may be attributed to participation of the phenylselenenyl group as already described. In order to demonstrate the easy manipulation of the functional groups thus introduced, the cyclic compound (8) was converted into safranals (16) as follows. Oxidation of (8) with 30% H<sub>2</sub>O<sub>2</sub> gave the oxide (11), m.p. 139–140.5 °C, which on heating in CCl<sub>4</sub> afforded the olefin (12). The diene alcohol (14) was obtained by dehydration of (12) using SOCl<sub>2</sub> in pyridine, followed by hydrolysis of the resulting acetate (13) with 1 N KOH in MeOH. Oxidation of (14) with CrO<sub>3</sub> in pyridine yielded the aldehyde (15) which, on reflux in pyridine, furnished safranals (16) with identical n.m.r. spectra<sup>10</sup> to those of an authentic sample. All steps‡ in the reaction sequence from (8) to safranals (16) proceeded in moderate to high yield.

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† Although the stereochemistry of this compound (7) remains unknown, it was shown to be homogeneous, namely, it showed a single spot (*R<sub>f</sub>* 0.46) on t.l.c. analysis using silica gel 60 F<sub>254</sub> with benzene–ethyl acetate (4:1) as developer.

‡ The spectral data for the new compounds appearing in this paper are in agreement with the proposed structures.

<sup>1</sup> For a review see D. L. J. Clive, *Tetrahedron*, 1978, **34**, 1049; H. J. Reich, *Accounts Chem. Research*, 1979, **12**, 22. References cited herein.

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