Tetrahedron Letters No. 33, pp 3079 - 3080.
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0040-4039/78/0808-3079$02.00/0

STRUCTURE OF NEW ORGANOSELENIUM COMPOUNDS FROM A SELENIUM DIOXIDE OXIDATION

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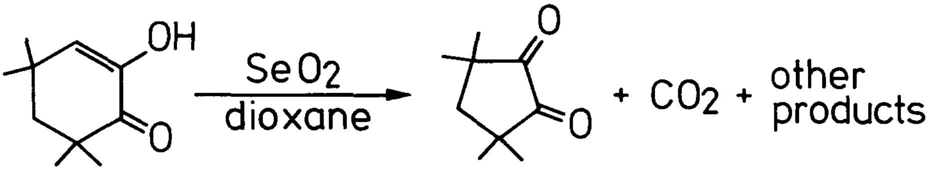
The common oxidant selenium dioxide usually oxidizes a monoketone to an α-diketone; in special cases an α,β-unsaturated ketone or an allylic oxidation product is formed instead.[1] Selenium-containing by-products are often formed during the oxidation, but are seldom characterized.[2]

We have reported earlier[3] that selenium dioxide oxidation of diosphenol I gives the diketone II in 50 % yield:



I

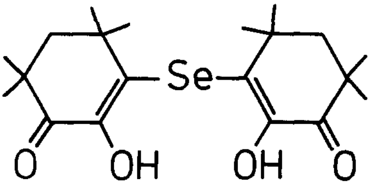
II

We now wish to report the isolation and structure determination of two new organoselenium compounds formed in the above reaction.

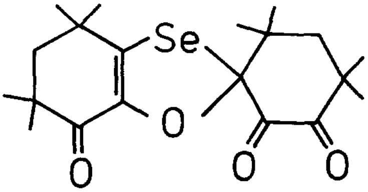
Diosphenol I treated with an equimolar amount of SeO_2 in boiling dioxane for 1.5 h, gave a white precipitate upon cooling of the reaction mixture. The crude product was purified by column chromatography and recrystallized from acetone-petroleum ether mixture in ca. 10 % yield, m. p. 190-193°C. The new selenide was assigned structure III, bis(2-hydroxy-4,4,6,6-tetramethyl-1-cyclohexen-3-one)selenide, on the basis of the following analytical and spectroscopic evidence.

The elemental analysis and mass spectrum of III are consistent with the formula $C_{20}H_{30}O_4Se$. Spectroscopic data: ir (CCl_4, cm^{-1}): 3410 (OH), 1655 (C=O), 1615 (C=C), ^{1}H-nmr ($CDCl_3$): δ 1.21 (12 H, s), 1.40 (12 H, s), 1.87 (4 H, s), 6.50 (2 H, s), ^{13}C-nmr ($CDCl_3$): δ 26.9 (off res. q), 31.0 (q), 37.4 (s), 40.2 (s), 50.1 (t), 132.5 (s), 143.5 (s), 196.2 (s). The ir, ^{1}H-nmr and ^{13}C-nmr spectra are consistent with a structure containing the intact diosphenol (I) moiety.

With longer reaction times (4-6 h), the oxidation of I with an equimolar amount of SeO$_2$ in refluxing dioxane gave the diketone II and only traces of III. After the main product (II) was sublimed, the remaining crude reaction mixture was purified by column chromatography. The yellow zone was collected and recrystallized from acetone-petroleum ether mixture to give orange-yellow crystals, m. p. 180-182°C. The new organoselenium compound was assigned structure IV, 4-oxo-5,5,7,7-tetramethyltetrahydro-2H-3,1-benzoxaselenole-2-spiro-4',4',6',6'-tetramethylcyclohexane-2',3'-dione, on the basis of X-ray diffraction analysis.[4]



III



IV

The X-ray data show the bond between Se and the cyclohexenone moiety to be somewhat shorter than that between Se and the cyclohexanedione moiety (1.89 and 2.01 Å, respectively). The calculated value of the angle between the planes of the carbonyl groups (2', 3') is 22.7°. The ir, ^{1}H-nmr, ^{13}C-nmr and uv spectra are consistent with the structure IV.

The use of different solvents in the above reaction markedly changed the product composition, e. g. the oxidation of I in t-BuOH gave mainly organoselenium compounds III and IV. Studies on the scope of the reaction as well as the mechanism of formation of IV are continuing in our laboratory.

Acknowledgement. The financial support of the E. Aaltonen Foundation is gratefully acknowledged (T.L.).

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(Received in UK 30 May 1978; accepted for publication 15 June 1978)