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STRUCTURE OF THE DIENE-SELENIUM DIOXIDE ADDUCTS

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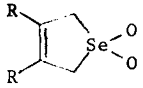
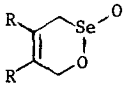
Sometime ago Backer and Strating[1] isolated a series of adducts of selenium dioxide with various substituted butadienes. These were formulated as cyclic selenones (I, R = at least one alkyl or aryl group) by analogy with the unequivocally established sulfur dioxide addition to give sulfones. The structure I has found uncritical acceptance.[2] We have reinvestigated this reaction and have obtained evidence which forces a revision of the assigned structure of the adducts.



I



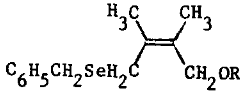
II

The unstable substance, m.p. 67-70° decomp. (lit.[1] 66°), from 2,3-dimethylbutadiene and selenous acid was isolated and found to decompose rapidly into an opaque red oil as reported.[1]

The n.m.r. spectrum was determined in deuteriochloroform and found to consist of unresolved multiplets centered at τ 8.2 (6H), 6.65 (2H) and 5.65 (2H). The chemical shift difference of the latter two resonances, assigned to methylene hydrogens, is incompatible with the symmetrical structure I. Hence, the cyclic seleninic ester structure II ($R = CH_3$), 4,5-dimethyl-1-oxa-2-selena-4-cyclohexene 2-oxide is suggested for this material.

This is supported by the infrared spectrum which shows strong absorption in potassium bromide at 836 cm^{-1} with a somewhat weaker peak at 848 cm^{-1}. This is in reasonable agreement with the $Se{=}O$ stretching frequency assignments in alkyl and aryl seleninic acids (methyl[3] 830, 810, ethyl[3] 860, phenyl[4] 828 cm^{-1}). Furthermore, diphenyl selenone is transparent in this region.

Sodium borohydride reduction of the adduct in methanol followed by benzylation ($C_6H_5CH_2Cl/Na_2CO_3$) afforded an oil formulated as IIIa. This material and its acetate, IIIb (Ac_2O/C_5H_5N), possessed the expected n.m.r. spectrum: (for IIIb in $CDCl_3$) τ 8.2 (6H), 7.93 (sharp, 3H), 6.6 (2H), 6.1 (2H), 5.3 (2H) and 2.4 (5H). Structure confirmation was supplied by



IIIa R = H

IIIb R = $COCH_3$

the mass spectrum of IIIb, which exhibited parent peaks at the calculated values 310 and 312 (corresponding to the major isotopes of selenium). Chief fragmentations of IIIb appeared to be the loss of acetic acid or benzylselenium.

On the above grounds, the selenone structure (I) is rejected in favor of II for the diene-selenium dioxide adducts.[1] Conclusions regarding the concerted mechanism of the sulfur dioxide addition to dienes[5] are not necessarily applicable to this system.

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