Formation of 1,3-Oxaselenoles *via* Pummerer Reaction in Selenium Dioxide Oxidation of Cyclic 1,2- and 1,3-Diketones, and the Preparation of 1,5,5-Trimethyl-7-selenabicyclo[2.2.1]heptane-2,3-dione

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4,5,6,7-Tetrahydro-4',4',6,6-tetramethylspiro[1,3-benzoxaselenole-2,1'-cyclohexane]-2',4,6'-trione and related 1,3-oxaselenole derivatives, and not the previously reported selenoxides of type (1), are formed in the selenium dioxide oxidation of cyclohexane-1,3-diones. The structural assignments were made on the basis of n.m.r. spectroscopy, and in the case of (5), X-ray analysis was undertaken. Oxidation of 3,3,5,5-tetramethylcyclohexane-1,2-dione with selenium dioxide yielded the bis-selenide (9) and the 1,3-ox-aselenole (10) along with the usual oxidation products, whereas the oxidation of 3,5,5-trimethylcyclo-hexane-1,2-dione gave the title, bridged selenabicyclic compound.

In the revised mechanism [1] of selenium dioxide oxidation of ketones, the proposed β-oxoseleninic acid intermediate can account for the formation of both the usual oxidation products and organic selenium compounds. Our interest in the latter reaction products was aroused during a study on the reaction of 3,3,5,5-tetramethylcyclohexane-1,2-dione with selenium dioxide, where we obtained organic selenium compounds (9) and (10) [2] along with the ring contraction products (11) and (12) (Scheme 2).[3] The selenoxide (1) and related derivatives reported [4-6] to be formed in selenium dioxide oxidation of cyclohexane-1,3-dione derivatives were considered worthy of reinvestigation, since the stoicheiometrically analogous product (10) was a selenide.

This paper describes in more detail [2,7] the selenium dioxide oxidations of 1,2- and 1,3-diketones and the organic selenium compounds formed, with their spectral properties, in the light of structural parameters obtained by X-ray analyses.[8-10]

Results and Discussion

Selenium Dioxide Oxidation of Cyclohexane-1,3-diones.—
The reaction of cyclohexane-1,3-dione derivatives (2) and (3) with selenium dioxide gave 1,3-oxaselenoles (4) and (5), and not the previously reported selenoxides of type (1).[4,6] The structural assignments were made by ^{1}H and [13]C n.m.r. spectroscopy (Table 6) and in the case of (5) by X-ray analysis.

The reaction of the trione (6) with 0.5 mol equiv. of selenium dioxide in methanol (the normal procedure of Stamm-Gossrau reaction [5]) afforded a new member of this series to which the structure (7) was assigned (Scheme 1). When the oxidation of (6) was carried out in boiling acetic acid with 2.5 mol equiv. of selenium dioxide, 3,3,5,5-tetramethylcyclo-pentane-1,2,4-trione was formed along with (7).[3] The 1,3-oxaselenole derivatives (4), (5), and (7) are golden yellow compounds and show a slight tendency to decomposition when stored in solution for an extended period of time.

Selenium Dioxide Oxidation of Cyclohexane-1,2-diones.—
When the diketone (8) was oxidized with an equimolar amount of selenium dioxide in 1,4-dioxan, small amounts of the bis-selenide (9) and the 1,3-oxaselenole (10) were isolated along with the ring-contraction products (11) and (12) (Scheme 2).[2,11] Conducted in methanol with 0.5 mol equiv. of selenium dioxide the reaction yielded (9), (10), (11), (12), and (13) in 45, 15, 3, 9, and 17% yields, respectively. The hemiacetal (13) was not isolated, but ^{1}H and [13]C n.m.r. spectra of the presumed

(1)

(2) R = H
(3) R = Me

(4) R = H
(5) R = Me

(6)

(7)
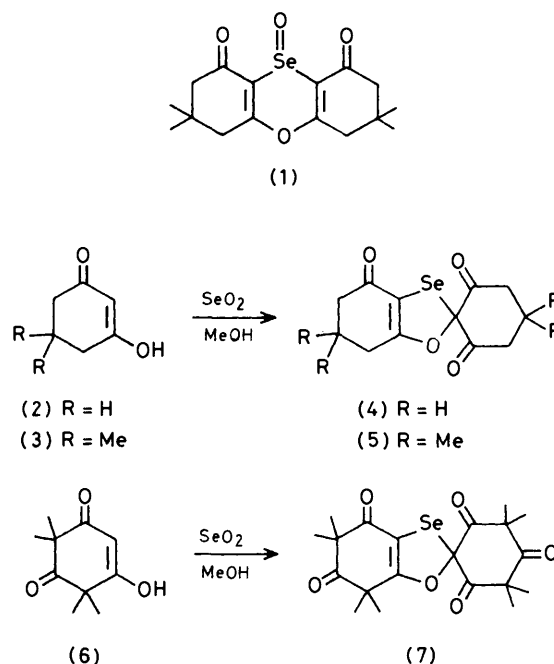
Scheme 1

mixture of (10) and (13) supported the structure (13) and the mass spectrum of the same mixture indicated the separate spectra corresponding to (10) and (13). Physical evidence for structure determination of (13) was obtained by high-resolution mass spectrometry.

The oxidation of 3,5,5-trimethylcyclohexane-1,2-dione (14) in dioxan gave the bridged selenide (15) in 6% yield along with small amounts of the elimination product (16), the main product being a polymer-like oil. To the best of our knowledge, (15) is the only reported compound of the 7-selenabi-bicyclo[2.2.1]heptane series. Its structure has been determined by X-ray analysis.[10]

The Formation of 1,3-Oxaselenoles via a Pummerer Reaction. —The mechanistic postulates of Sharpless [1] and Reich [12] are assumed to apply up to the formation of the intermediate (19) (Scheme 3). The intervention of this intermediate was further
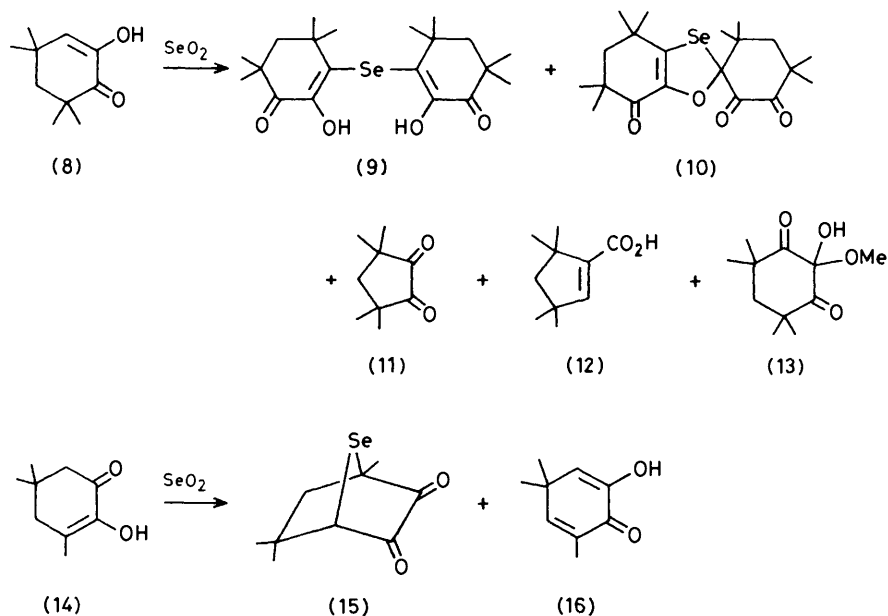
Scheme 2
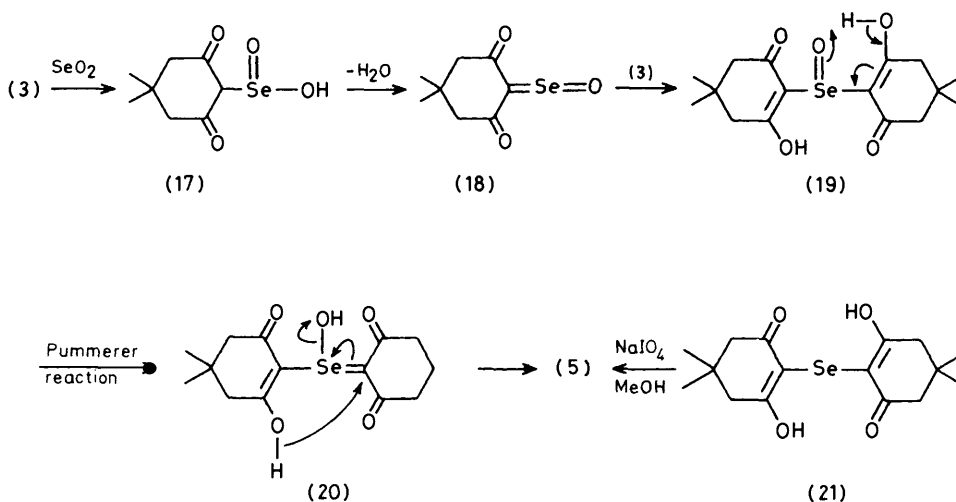
Scheme 3

supported by our observation that sodium metaperiodate oxidations of appropriate open-chain selenides produce the corresponding oxaselenoles; for example, (21) yields (5). The selenoxide (19) reacts further *via* a Pummerer reaction to produce the 1,3-oxaselenole (5), instead of through dehydration [12] yielding the selenoxide (1). The details of the Pummerer reaction are not presented in the reaction sequence, the difference from the normal route [13] being due to the internal nucleophilic participation of the enolic hydroxy-group present in the molecule. The sodium metaperiodate oxidation of (21) in methanol at room temperature yielded (5) quantitatively and the oxidation of (9) in boiling methanol afforded (10) in 35% yield.

The selenoxides where an α-hydrogen is activated by two carbonyl groups seem very prone to undergo the Pummerer reaction. Owing to the greater basicity of selenoxides compared with sulphoxides,[14] no mineral acid catalyst is needed. Actually, strongly acidic conditions prevent a Pummerer

(22)
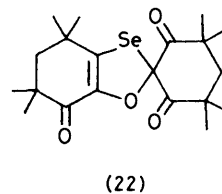
reaction in the selenium dioxide oxidation of (3) in aqueous sulphuric acid or hydrochloric acid.[15]

We would like to introduce the formation of (10) as evidence that the selenoxide–selenenate rearrangement [16] cannot explain the formation of 1,3-oxaselenoles; for if the reaction did proceed *via* a cleavage–recombination mechanism, the central carbonyl group would be the probable reaction centre [17] leading to the formation of a 1,3-oxaselenole of different structure (22) than that found.

The formation of the selenides (9) and (15) evidently proceeds via the corresponding selenoxides, though in the case of (15) the redox process cannot be rationalized on the basis of other products. The redox reaction producing (9) could be that between the selenoxide and one of the intermediates of the ring-contraction reaction,[3] namely an enediol or a reductone, both being two-electron reductants.

The reactions of cyclohexane-1,2- and -1,3-diones with selenium dioxide yielding the corresponding 1,3-oxaselenoles differ markedly with respect to reaction times and yields; the reaction of (8) in methanol during one week gave a poor yield of (10), whereas the reaction of (3) under similar conditions but with a reaction time of a few minutes produced (5) in good yield.

The reaction of (8) with 2.5 mol equiv. of selenium dioxide in refluxing acetic acid yielded the dione (11) nearly quantitatively, whereas the reaction of (6) under the same conditions afforded mainly the 1,3-oxaselenole (7).[3]

We assume that the difference in reactivity is due to the electronic nature of the 1,2- as opposed to the 1,3-diketones [see (3) and (8)]. The oxidant is electrophilic and (8) is deactivated compared with (3) towards its attack. The organic selenium compounds are dimeric products with respect to the substrate and the formation of the organic oxidation products is an intramolecular redox reaction of a selenine or β-oxoseleninic acid.[12] Because both are Pummerer reactions, the reactivity of the substrate would seem to be the main factor accounting for the divergent reaction pathways.

X-Ray Crystal Structure of (5).

—The molecular structure of (5) and the numbering scheme are shown in Figure 1. Tables 1—5 present atomic co-ordinates, interatomic distances, bond angles, selected intramolecular distances between non-bonded atoms, and deviations of atoms from least-squares planes. Lists of structure factors, thermal parameters, and atomic co-ordinates for hydrogen atoms are deposited as a Supplementary publication [SUP No. 23463 (27 pages)].*

The asymmetric unit of the structure contains two crystallographically independent molecules A and B which can be considered approximately as mirror images of each other (Figure 1). The Se(A)–Se(B) distance of 3.590(1) Å and the Se–O(3)[i] distance of 3.334(5) Å between molecules A and Se–O(3)[j] distance of 3.365(5) Å between molecules B (i = x, 1 + y, z; j = x, −1 + y, z) are shorter than the sum of the respective van der Waals radii. The bond lengths in the oxaselenole system are, within the standard deviations, the same as those in (10).[8] The bond angles of selenium atoms was found to be 82.7(3)° in A and 82.4(3)° in B, which are similar to the value in (10) and in other unsaturated five-membered rings.[18] The mean planes show the planarity of the α,β-unsaturated function including Se and O(1), and that the cyclohexanedione ring adopts a chair conformation with axial selenium. The conformation of the 1,3-oxaselenole ring is an envelope with C(1) deviating 0.43 Å (molecule A) and 0.38 Å (molecule B) from the plane of the other four atoms. The least-squares planes 1 and 2 (Table 5) are at an angle of 73.2° to each other, indicating a slight distortion from symmetrical arrangement.

Spectral Properties of 1,3-Oxaselenoles.

—The ^{13}C n.m.r. chemical shifts of the studied compounds are given in Table 6. The methylene compound (23) is included to demonstrate the effect of selenium on the chemical shifts of the neighbouring carbon atoms. The assignments of carbon signals were made
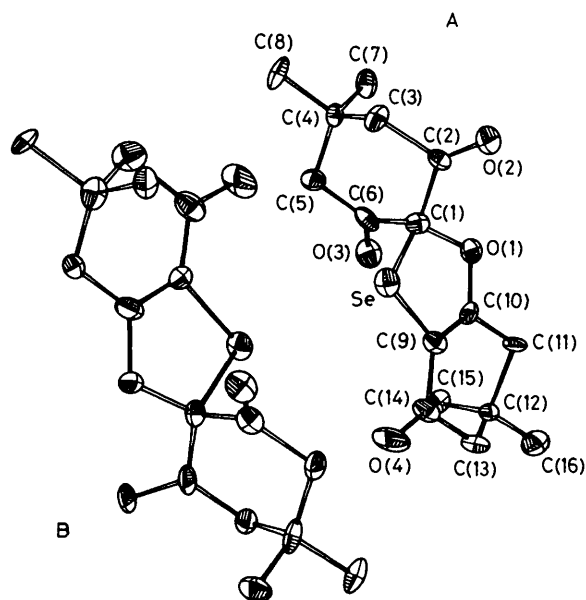

Figure 1. An ORTEP drawing of the two independent molecules of (5) with hydrogen atoms omitted. Thermal ellipsoids are drawn in 30% probability

on the basis of correlation data and of either peak intensities or of signal multiplicities in the ^1H coupled spectra.

The carbonyl carbons in (5) were assigned on the basis of peak intensities and correlation data. The olefinic carbons C(2) and C(3) were assignable by determining the peak multiplicities in the ^1H coupled spectrum and independently by considering the correlation data of α,β-unsaturated ketones and the vinyl ether effect. The magnitudes [19] of $^1J_{Se C(2)}$ and $^1J_{Se C(1')}$ of 92.5 and 58.6 Hz, respectively, lead unambiguously [20,21] to the assignments of C(2) and C(1'). In the case of the 1,3-oxaselenole (4), the spiro-carbon C(1') was independently assigned on the basis of the $^{13}C–^{13}C$ coupling constants.[22] The assignments of the methylene carbons in (5) were deduced from the peak multiplicities and intensities; and the shielding of C(6) was assumed to be very similar to the shieldings of C(3') and C(5').

The symmetry plane of the molecule of (5) renders the methyl carbons C(7) and C(8) equivalent in solution, whereas C(7') and C(8') lie in different environments regardless of whether there is a preferred conformation or an equilibrium mixture. It is reasonable to believe that the former is more likely, since one would expect the cyclohexanedione ring in solution preferably to assume a chair conformation with axial selenium owing to the longer Se–C than O–C bond and consequent smaller 1,3-diaxial interaction. That the conformation of (5) in liquid phase does not greatly deviate from that observed in the crystal was supported by the ^1H coupled ^{13}C n.m.r. spectrum where the signal arising from C(1') shows a triplet structure ($^3J_{CH}$ 5.9 Hz). This structure is presumably attributable to coupling with the equatorial protons at C(3') and C(5'), on the basis of the dependence of the magnitude of the vicinal coupling constant on the dihedral angle (Karplus equation). In the case of a rapid conformational equilibrium, the signal would be expected to appear as a quintet or as an unresolved multiplet.

In turning to the inspection of the ^1H n.m.r. spectrum of (5) it is relevant to note that the analogous sulphur compound of (5) has been prepared [23] and its spectral data (excluding ^{13}C n.m.r.) are available.[24,25] As expected, the proton chemical shifts of (5) and its sulphur analogue are practically the same,

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* For details of the Supplementary publications scheme, see Notice to Authors No. 7, J. Chem. Soc., Perkin Trans. 1, 1981, Index issue.

Table 1. Atomic co-ordinates ($\times 10^4$) for the non-hydrogen atoms of the two independent molecules of (5), with standard deviations in parentheses

	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
Se	1 451(1)	−3 379(1)	2 883(1)	1 055(1)	−1 755(1)	1 406(1)
O(1)	1 514(2)	−5 654(7)	3 917(2)	1 028(2)	413(7)	352(2)
O(2)	2 767(3)	−4 829(10)	3 927(3)	−231(3)	−192(11)	348(3)
O(3)	1 202(2)	−8 508(8)	3 131(2)	1 333(2)	3 368(8)	1 115(2)
O(4)	−60(3)	−2 101(8)	2 879(3)	2 548(3)	−3 186(9)	1 427(3)
C(1)	1 829(3)	−5 624(9)	3 357(3)	696(3)	468(10)	897(3)
C(2)	2 559(3)	−5 257(10)	3 452(3)	6(4)	223(11)	830(3)
C(3)	2 934(3)	−5 601(10)	2 889(4)	−411(3)	579(11)	1 372(4)
C(4)	2 816(4)	−7 709(11)	2 625(3)	−265(3)	2 637(10)	1 640(3)
C(5)	2 101(4)	−7 858(10)	2 467(3)	450(3)	2 797(10)	1 784(3)
C(6)	1 671(3)	−7 519(9)	3 000(3)	873(3)	2 375(10)	1 259(3)
C(7)	3 004(4)	−9 340(12)	3 069(4)	−462(4)	4 332(11)	1 214(3)
C(8)	3 212(4)	−7 943(14)	2 056(4)	−661(5)	2 841(13)	2 213(4)
C(9)	748(3)	−3 717(10)	3 424(3)	1 749(3)	−1 576(11)	864(3)
C(10)	916(3)	−4 874(10)	3 876(3)	1 618(3)	−460(10)	375(3)
C(11)	489(4)	−5 328(13)	4 414(3)	2 056(4)	−145(11)	−114(3)
C(12)	−251(4)	−5 176(11)	4 220(3)	2 745(3)	−372(10)	66(3)
C(13)	−331(3)	−3 221(12)	3 857(4)	2 845(4)	−2 273(12)	440(4)
C(14)	106(4)	−2 933(10)	3 334(4)	2 383(4)	−2 425(10)	962(4)
C(15)	−378(4)	−7 046(12)	3 847(4)	2 982(4)	1 501(12)	403(4)
C(16)	−663(4)	−5 134(15)	4 776(4)	3 191(4)	−523(13)	−488(4)

Table 2. Bond distances (Å) of the two independent molecules of (5)

	A	B
Se–C(1)	1.998(6)	2.016(7)
Se–C(9)	1.913(7)	1.893(7)
O(1)–C(1)	1.420(8)	1.408(8)
O(1)–C(10)	1.350(8)	1.358(8)
O(2)–C(2)	1.189(9)	1.223(10)
O(3)–C(6)	1.211(8)	1.206(8)
O(4)–C(14)	1.215(10)	1.211(10)
C(1)–C(2)	1.550(9)	1.450(11)
C(1)–C(6)	1.532(9)	1.553(9)
C(2)–C(3)	1.505(10)	1.515(11)
C(3)–C(4)	1.545(10)	1.529(10)
C(4)–C(5)	1.531(11)	1.523(10)
C(4)–C(7)	1.526(11)	1.538(10)
C(4)–C(8)	1.529(11)	1.534(11)
C(5)–C(6)	1.513(10)	1.499(9)
C(9)–C(10)	1.323(9)	1.356(10)
C(9)–C(14)	1.446(10)	1.450(10)
C(10)–C(11)	1.530(10)	1.441(10)
C(11)–C(12)	1.600(10)	1.494(10)
C(12)–C(13)	1.547(11)	1.536(11)
C(12)–C(15)	1.526(11)	1.542(11)
C(12)–C(16)	1.515(11)	1.556(11)
C(13)–C(14)	1.498(11)	1.520(12)

Table 3. Bond angles (°) of the two independent molecules of (5)

	A	B
C(1)–Se–C(9)	82.7(3)	82.4(3)
C(1)–O(1)–C(10)	110.9(5)	114.8(5)
Se–C(1)–O(1)	107.7(4)	107.2(4)
Se–C(1)–C(2)	109.8(4)	110.0(5)
Se–C(1)–C(6)	104.7(4)	102.5(4)
O(1)–C(1)–C(2)	109.3(5)	112.9(6)
O(1)–C(1)–C(6)	110.8(5)	111.3(5)
C(2)–C(1)–C(6)	114.3(5)	112.4(6)
O(2)–C(2)–C(1)	121.2(6)	121.1(7)
O(2)–C(2)–C(3)	127.2(6)	121.3(7)
C(1)–C(2)–C(3)	111.6(6)	117.6(6)
C(2)–C(3)–C(4)	112.4(6)	110.2(6)
C(3)–C(4)–C(5)	107.6(6)	109.9(6)
C(4)–C(5)–C(6)	112.3(6)	113.0(6)
O(3)–C(6)–C(1)	119.5(6)	119.7(6)
O(3)–C(6)–C(5)	125.9(6)	125.0(6)
C(1)–C(6)–C(5)	114.4(5)	115.3(5)
Se–C(9)–C(10)	110.9(5)	113.9(5)
Se–C(9)–C(14)	124.9(5)	124.7(5)
C(10)–C(9)–C(14)	124.1(7)	121.3(6)
O(1)–C(10)–C(9)	121.3(6)	116.5(6)
O(1)–C(10)–C(11)	113.7(5)	118.6(6)
C(9)–C(10)–C(11)	124.8(6)	124.9(6)
C(10)–C(11)–C(12)	109.1(6)	112.5(6)
C(11)–C(12)–C(13)	107.5(6)	111.2(6)
C(12)–C(13)–C(14)	117.2(6)	113.2(7)
O(4)–C(14)–C(9)	122.9(7)	123.4(7)
O(4)–C(14)–C(13)	123.3(7)	121.1(7)
C(9)–C(14)–C(13)	113.8(7)	115.4(7)

but our interpretation of the coupling patterns of the methylene protons in the cyclohexanedione ring is different. In the spectrum of the sulphur compound, these protons reportedly give rise to a pair of two-proton doublets (J 13.5 Hz), whereas the same protons in (5) exhibit an AA′BB′ system (J_{AB} 15 Hz; the cross-coupling constants were not examined in detail in this work). The lower field part of the AA′BB′ system is perturbed by long-range coupling. Our suggestion that the X-ray conformation of the cyclohexanedione ring is the preferred one in solution is supported by the coupling of the axial protons with the high-field methyl protons through the W-path, since the signal of the latter protons appears as a broadened singlet. The available spectral data for the sulphur compound do not allow a comparison of its conformation with that of (5).

The u.v.–visible absorption maximum at *ca.* 400 nm of the oxaselenoles (4), (5), and (7) is attributed to the spiro-conjugation effect [26] typical for structural systems where four p-orbitals are separated by an insulating atom such that approximate spiro-geometry is observed. Comparison of the u.v.–visible maxima of (5) (402 nm, ε 141) and its sulphur analogue (380 nm, ε 120) [24] suggests that the same effect is operating in both compounds. As expected, selenium causes a batho-chromic shift relative to sulphur. That the methylene compound (23) is colourless ($\lambda_{max.}$ 263 nm) supports the essential

Table 4. Selected intramolecular non-bonded distances (Å) of the two independent molecules of (5)

	A	B
Se–O(1)	2.781(5)	2.779(5)
Se–O(2)	3.732(6)	3.727(6)
Se–O(3)	3.502(5)	3.524(5)
Se–O(4)	3.250(6)	3.244(6)
Se–C(2)	2.915(7)	2.857(8)
Se–C(3)	3.418(7)	3.419(7)
Se–C(4)	4.087(7)	4.043(7)
Se–C(5)	3.407(7)	3.391(7)
O(1)–O(2)	2.661(7)	2.646(8)
O(1)–O(3)	2.667(7)	2.689(7)
O(1)–C(2)	2.424(8)	2.382(9)
C(2)–C(7)	3.001(11)	3.031(11)

were recorded on a JEOL JNM PFT100 spectrometer. I.r. spectra were obtained on a Perkin-Elmer 125 spectrometer, u.v. spectra on a Shimadzu UV-200 spectrometer, and mass spectra (70 eV) on a JEOL JMS-D 100 instrument. Solvents were evaporated on a Büchi rotavapor and the residues dried in a vacuum desiccator (over calcium chloride and paraffin waxes). The composition of mixtures of reaction products and the purity of the crude products were determined by ^{1}H n.m.r. spectroscopy. The light petroleum had a boiling range of 40—65 °C.

The purity of the new compounds (7), (9), (10), and (15) was established by g.l.c. using a Carlo Erba G-1 instrument and SE-52 stationary phase in a capillary column (30 m × 0.3 mm i.d.). The retention times of (7) and (15) are 826 and 445 s, respectively. Conditions: injector/detector 230 °C, oven 100 °C (3 min)—250 °C (0 min), heating rate 20 °C/min. The

Table 5. Deviations (Å) of atoms from the best least-squares planes in (5)

(1) Plane through Se, O(1), C(9), and C(10).

	Se	O(1)	C(9)	C(10)	C(1)	C(4)	C(11)	C(14)	O(4)
Molecule A	0.00	0.00	0.00	0.00	−0.43	−1.77	0.11	−0.08	−0.26
Molecule B	0.00	0.01	0.01	−0.01	0.38	1.65	−0.05	0.12	0.33

(2) Plane through C(2), C(3), C(5), and C(6).

	C(2)	C(3)	C(5)	C(6)	C(1)	C(4)
Molecule A	0.02	−0.02	0.02	−0.02	−0.53	0.73
Molecule B	−0.01	0.01	−0.01	0.01	0.50	−0.67

(3) Plane through C(9), C(10), C(11), and C(14).

	C(9)	C(10)	C(11)	C(14)	C(12)	C(13)	O(4)
Molecule A	0.03	−0.03	0.01	−0.02	−0.56	0.10	−0.13
Molecule B	−0.02	0.02	−0.01	0.01	0.49	−0.13	0.16

role of selenium as a part of the chromophore responsible for the colour. The absorption maximum at 445 nm of (10) is evidently due to the α-diketone grouping perturbed by the proximity of selenium as reported earlier in α-selenocarbonyl compounds.[27]

Spectral Properties of (15).—The assignments of carbon-13 resonance signals of (15) were made with the help of the ^{1}H coupled spectrum, which left the peaks of C(8) and C(9) interchangeable. The assignment of C(3) was deduced from the apparent doublet structure due to the coupling with the proton attached to C(4).

The non-bonded distances Se ⋯ C(2) and Se ⋯ C(3) of 2.62 and 2.59 Å, respectively, are clearly shorter than the sum of the van der Waals radii (3.60 Å), allowing the unusual high-field resonances of the carbonyl carbons to be explained in terms of the transannular interaction.[28] The low-frequency i.r. absorption band of the carbonyl group demonstrates the weakening of the C=O linkage. The u.v.-visible absorption maximum at 304 nm (cyclohexane) is interpreted as a charge-transfer band,[29] since it shows a bathochromic shift with the increasing polarity of the solvent (311 nm, ethanol). The transannular interaction has been considered to be responsible for such bands in compounds containing suitably orientated atoms with lone pair electrons.[28,30]

The large $^1J_{CH}$ of C(4) (160 Hz) is in accord with earlier observations of the high s-character of exocyclic bonds in bicyclic compounds.[31]

Experimental

M.p.s, determined in open capillary tubes with an electro-thermal apparatus, are uncorrected. ^{1}H and ^{13}C N.m.r. spectra

retention times of (9) and (10) are 1 612 and 1 582 s, respectively. Conditions: injector/detector 230 °C, oven 50 °C (3 min) —220 °C (0 min), heating rate 10 °C/min.

Starting Materials and Reference Compounds.—Cyclohexane-1,3-dione (2) was purchased from Merck. The following compounds were prepared according to previously reported methods: (3),[32] (8),[33] (11),[3] (12),[33] (21),[34] and (23).[35] The trione (6) was prepared starting from phloroglucinol (Merck, synthetic), which was converted into phloroacetophenone,[36] methylated,[37] and hydrolysed to (6)[38] with 2M-HCl. The dione (14) was prepared starting from isophorone (Fluka, Practical), which was converted into isophorone oxide,[39] then treated with methanolic potassium hydroxide to yield the enol ether precursor of (14), which was hydrolysed in acidic solution to (14).[40] The identity of the compounds was determined by comparison of m.p. and ^{1}H n.m.r. data.

Spectral data for (23): [35] δ_H (CDCl$_3$, 100 MHz) 0.98 (3 H, s, 7'-Me), 1.11 (6 H, s, 7- and 8-Me), 1.16 (3 H, s, 8'-Me), 2.21 (2 H, s, 6-CH$_2$), 2.47 (2 H, t, J 1.9 Hz, 4-CH$_2$), 2.74 (centre of AB q, J 13.8 Hz, 3'- and 5'-CH$_2$), and 3.13 (2 H, t, J 1.9 Hz, CH$_2$); $\nu_{max.}$ (KBr) 1 740s (C=O), 1 705s (C=O), and 1 630 cm^{-1} (superimposed α,β-unsaturated ketone and C=C bands); $\lambda_{max.}$ (CHCl$_3$) 263 nm (ε 2 720).

4,5,6,7-*Tetrahydrospiro*[1,3-*benzoxaselenole*-2,1'-*cyclohexane*]-2',4,6'-*trione* (4).—The preparation conducted according to the literature method[5] gave (4) in 77% yield, m.p. 183—184 °C (lit.,[5] 180 °C, decomp.); δ_H (CDCl$_3$, 100 MHz) 1.72—2.26 (4 H, m, 5- and 4'-CH$_2$), 2.47 (2 H, apparent t, 6-CH$_2$), 2.59—3.16 (4 H, m, 3'- and 5'-CH$_2$), and 2.76 (2 H, apparent t, 4-CH$_2$); $\nu_{max.}$ (KBr) 1 727s (C=O), 1 708s (C=O), 1 652s (α,β-

Table 6. [13]C N.m.r. chemical shifts [a] of the studied compounds with the numbering scheme [b]

(4) R = H, X = Se
(5) R = Me, X = Se
(23) R = Me, X = CH$_2$

(7) (9) (10)

(15)
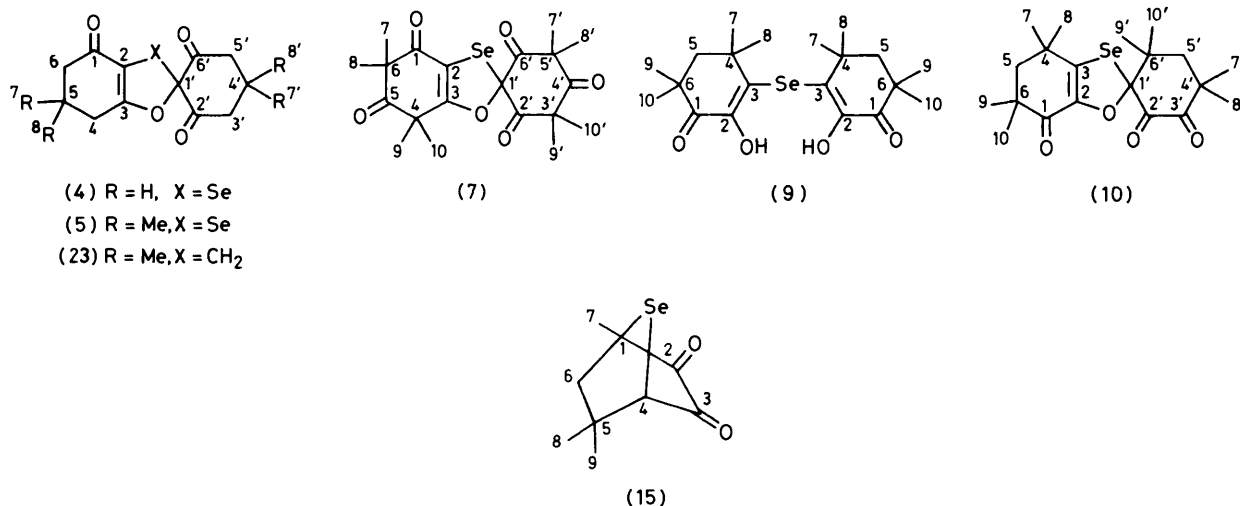
Carbon atom	(4)	(5)	(7)	(9)	(10)	(15)	(23)
1	192.8	192.2	192.6	196.2	190.7	66.8	193.9
2	107.4	106.0	105.8	143.5	145.7	188.6	109.0
3	171.2	169.9	171.3	132.5	141.6	185.9	175.8
4	25.1	38.7	48.0	37.4	38.4 [c]	67.1	37.3
5	17.2 [c]	30.4 [c]	210.6 [c]	50.1	51.5 [d]	41.6	30.6 [c]
6	36.6	50.9	56.8	40.1	42.7 [e]	50.5	50.9
1'	93.4	92.9	89.5		109.3		98.0
2'	196.7	196.6	196.4		175.2		199.6
3'	36.4	50.0	56.8		205.3		50.9
4'	21.2 [c]	34.1 [c]	208.9 [c]		45.7 [e]		34.3 [c]
5'	36.4	50.0	56.8		50.1 [d]		50.9
6'	196.7	196.6	196.4		35.2 [c]		199.6
Me [f]		25.3 (C-7')	24.4	26.9	23.3	16.7	26.8
		28.2 (C-7)	25.0	31.0	26.6	27.4	28.6
		28.2 (C-8)	25.8		27.1	29.7	29.5
		29.9 (C-8')	26.3		27.3		
					29.2		
					31.5		
Other							34.0

[a] In p.p.m. downfield from Me$_4$Si; solvent CDCl$_3$. [b] The IUPAC numbering is not followed. [c-e] The assignments may be interchangeable. [f] The signals were not assigned excepting those given in brackets.

unsaturated ketone), and 1 612s cm^{-1} (C=C); $\lambda_{max.}$ (CHCl$_3$) 398 (ε 147) and 295 nm (ε 2 010).

4,5,6,7-*Tetrahydro-4',4',6,6-tetramethylspiro*[1,3-*benzox-aselenole*-2,1'-*cyclohexane*]-2',4,6'-*trione* (5).—The preparation conducted according to literature [4] gave (5) in 90% yield, m.p. 167—169 °C (lit.,[4] 167 °C); δ_H (CDCl$_3$, 100 MHz) 0.87br (3 H, s, 7'-Me, apparently axial), 1.15 (6 H, s, 7- and 8-Me), 1.21 (3 H, s, 8'-Me, apparently equatorial), 2.33 (2 H s, 6-CH$_2$), 2.63 (2 H, s, 4-CH$_2$), and 2.77 (centre of AA'BB' system, J_{AB} 14.5 Hz, 3'- and 5'-CH$_2$; equatorial protons at 2.50 and axial protons at 3.02. The low-field part shows an unresolved multiplet structure, presumably due to long-range coupling with 7'-Me protons); $\nu_{max.}$ (KBr) 1 730s (C=O), 1 703s (C=O), 1 645s (α,β-unsaturated ketone), and 1 603s cm^{-1} (C=C); $\lambda_{max.}$ (CHCl$_3$) 402 (ε 141) and 300 nm (ε 38 70).

4,5,6,7-*Tetrahydro-3',3',5,5,5',5',7,7-octamethylspiro*[1,3-*benzoxaselenole*-2,1'-*cyclohexane*]-2',4,4',6,6'-*pentaone* (7).—A mixture of (6) (0.91 g, 5.0 mmol), selenium dioxide (0.30 g,

2.7 mmol), and methanol (5 ml) was refluxed for 30 min. The mixture was cooled and the precipitate was filtered off, washed with water, and dried *in vacuo* to give the *oxaselenole* (7) (85%), m.p. 170—171 °C (from methanol); δ_H (CDCl$_3$, 100 MHz) 1.38 (6 H, s, Me), 1.46 (6 H, s, Me), and 1.64 (12 H, s, Me); $\nu_{max.}$ (KBr) 1 752w (C=O), 1 716 (C=O), 1 697s (C=O), 1 642s (α,β-unsaturated ketone), and 1 614s cm^{-1} (C=C); $\lambda_{max.}$ (CHCl$_3$) 402 (ε 220) and 300 nm (ε 4 110) (Found: M^{+}, 440.0742. C$_{20}$H$_{24}$O$_6$Se requires M, 440.0738).

Bis(2-*hydroxy*-4,4,6,6-*tetramethyl*-3-*oxocyclohexenyl*) *Selenide* (9).—Refluxing of (8) (10.00 g, 0.0595 mol) and selenium dioxide (3.30 g, 0.0297 mol) in methanol (50 ml) for 1 week gave a precipitate, which was filtered off from the hot mixture, washed well with water, and dried *in vacuo* to give a grey powder (6.01 g). This was taken up in acetone, the undissolved part filtered off, and the solvent evaporated to give the *bis-selenide* (9) (5.56 g, 45%) as white powder. Recrystallization from acetone–light petroleum (1 : 4) afforded pale-yellow crystals, m.p. 191—193 °C; δ_H (CDCl$_3$, 100 MHz) 1.22

(12 H, s, Me), 1.40 (12 H, s, Me), 1.85 (4 H, s, CH₂), and 6.50 (2 H, s, OH); $v_{max.}$ (KBr) 1 660, 1 647s (doublet of α,β-unsaturated ketone), and 1 605s cm⁻¹ (C=C); $\lambda_{max.}$ (CHCl₃) 355 (ε 9920) and 289 nm (ε 12 000) (Found: $M^{+\cdot}$, 414.1319. C₂₀H₃₀O₄Se requires M, 414.1309).

4,5,6,7-*Tetrahydro*-4,4,4',4',6,6,6',6'-*octamethylspiro*[1,3-*benzoxaselenole*-2,1'-*cyclohexane*]-2',3',7-*trione* (10).—Refluxing the mixture as outlined above for the preparation of (9) for 1 week, filtering of the hot solution, evaporation of the solvent, and drying of the residue *in vacuo* gave a reddish mass, which was taken up in chloroform and filtered. After evaporation of the solvent and drying, the semisolid mass was sublimed *in vacuo* to give a mixture of three compounds: (11) (0.28 g, 3%), (12) (0.86 g, 9%), and (13) (1.19 g, 9%). Dissolution of the sublimation residue in chloroform, evaporation of the solvent, and drying of the residue gave a reddish crude product (2.78 g) contaminated with the hemiacetal (13), which appeared in the sublimate, too. The total yield (not isolated) of (13) was 17%. The ¹H and ¹³C n.m.r. spectra of the mixture of (10) and (13) and the mass spectrum of the more volatile component are consistent with structure (13). Almost pure mass spectra of the compounds (10) and (13) were obtained by direct inlet of the mixture (Found: $M^{+\cdot}$, 214.1209. C₁₁H₁₈O₄ requires M, 214.1205). Fractional recrystallization of the mixture of (10) and (13) from acetone-light petroleum (1 : 4) gave the *oxaselenole* (10) (0.67 g, 6%) as orange-yellow crystals, m.p. 181—183 °C; δ_H (CDCl₃, 100 MHz) 1.20 (6 H, s, Me), 1.21 (3 H, s, Me), 1.28 (9 H, s, Me), 1.36 (3 H, s, Me), 1.38 (3 H, s, Me), 1.69 (centre of AB q, J 15.1 Hz, CH₂), and 1.87 (centre of AB q, J 14.2 Hz, CH₂); $v_{max.}$ (KBr) 1 715 (C=O), 1 702s (C=O), 1 660s (α,β-unsaturated ketone), and 1 590s cm⁻¹ (C=C); $\lambda_{max.}$ (CHCl₃) 445 (ε 930), 351 (ε 2 380), and 300 nm (ε 7 680) (Found: $M^{+\cdot}$, 412.1141. C₂₀H₂₈O₄Se requires M, 412.1152).

Oxidation of (9) *with Sodium Metaperiodate.*—A mixture of (9) (0.2065 g, 0.50 mmol), sodium metaperiodate (0.1124 g, 0.53 mmol), and methanol (7 ml) was refluxed for 45 min. The mixture was then filtered, the solvent evaporated, and the residue dried *in vacuo* to give an orange semisolid mass. This was taken up in hot acetone-light petroleum (1 : 4); on cooling, orange crystals formed, which were identified as the oxaselenole (10) (0.072 g, 35%). Partial removal of solvent provided a further fraction of orange crystals (0.061 g) identified as a mixture of (10) and an unknown compound.

Oxidation of (21) [34] *with Sodium Metaperiodate.*—A mixture of (21) (0.1785 g, 0.50 mmol), sodium metaperiodate (0.1124 g, 0.53 mmol), and methanol (7 ml) was stirred at room temperature for 30 min. The mixture was filtered, the methanol evaporated, and the residue dried *in vacuo* to give quantitatively the oxaselenole (5) as a yellow powder. Recrystallization from acetone-light petroleum (1 : 4) afforded a pure sample, m.p 167—169 °C.

1,5,5-*Trimethyl*-7-*selenabicyclo*[2.2.1]*heptane*-2,3-*dione* (15).—A mixture of (14) (23.15 g, 0.15 mol), selenium dioxide (19.98 g, 0.18 mol), dioxan (125 ml), and water (8 ml) was refluxed for 21 h. Selenium was filtered off, the solvent evaporated, and the residue dried *in vacuo*. Purification of the oily material by column chromatography (silica gel, elution with light petroleum-diethyl ether with increasing amount of ether) gave first a small quantity of white crystals identified by ¹H n.m.r. as (16), m.p. (sublimed) 56—58 °C (lit.,⁴¹ 57 °C). After elution of (16), the yellow zone was collected to give the *bridged*

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* Correspondence concerning the *X*-ray analysis should be addressed to R. K.

selenide (15) (1.95 g, 6%), m.p. (from acetone-light petroleum) 113—115 °C; δ_H (CDCl₃, 100 MHz), 1.22 (3 H, s, Me), 1.38 (3 H, s, Me), 1.65 (3 H, s, Me), 2.07 (centre of AB q, J 14.0 Hz, CH₂), and 3.96 (1 H, s, 4-H); $v_{max.}$ (KBr) 1 732 and 1 715s cm⁻¹ (C=O); $\lambda_{max.}$ (cyclohexane) 435 (ε 415) and 304 (ε 2 470); (EtOH) 423 (ε 640) and 311 nm (ε 2 980) (Found: $M^{+\cdot}$, 231. 9988. C₉H₁₂O₂Se requires M, 232.0002).

X-*Ray Crystal Structure Analysis of* (5).*—Weissenberg and oscillation photographs indicated orthorhombic symmetry, and from systematically absent reflections it was concluded that the space group is either centrosymmetric *Pbcm* (No. 57) or non-centrosymmetric *Pca2₁* (No. 29). Exact cell parameters were obtained and the intensity data were collected on a computer-controlled Nicolet *P3* (Fortran version) four-circle diffractometer, Mo-K_{α} = 0.71069 Å. ω-Scanning was used (5° < 2θ < 60°). The Lorentz and polarization corrections were made in the usual manner. A semi-empirical absorption correction was made and dispersion corrections for Se, $\Delta f'$, and $\Delta f''$.⁴² A total of 4 651 independent reflections were measured, and the 2 571 reflections having $F_0 > 6\sigma(F_0)$ were accepted for final refinement. The best figure of merit by MULTAN 78 program revealed the positions of the two Se atoms among the four strongest peaks. All subsequent calculations were performed using the X-RAY 76 program system (UNIVAC 1108). Full-matrix least-squares refinement of all non-hydrogen atoms with fixed hydrogen atoms (C⁻H = 1.00 Å and U_{iso} = 0.06 Å²) gave the R value 0.034 (R_w = 0.035, unit weights). Attempts to solve the structure in the centrosymmetric space group were unsuccessful.

Crystal Data for (5).—C₁₆H₂₀O₄Se, M = 355.29. Orthorhombic, a = 20.766(5), b = 6.664(1), c = 22.503(4) Å, Z = 8, U = 3114.2(10) Å³, D_c = 1.54 g cm⁻³, MoK$_{\alpha}$ radiation, λ = 0.71069 Å, μ(Mo-K_{α}) = 26.1 cm⁻¹. Space group *Pca2₁*.

References

1 K. B. Sharpless and K. M. Gordon, *J. Am. Chem. Soc.*, 1976, **98**, 300.
2 Preliminary communication, T. Laitalainen, T. Simonen, and R. Kivekäs, *Tetrahedron Lett.*, 1978, 3079.
3 T. Laitalainen, *Finn. Chem. Lett.*, 1982, 10.
4 H. Stamm and K. Gossrau, *Chem. Ber.*, 1933, **66**, 1558.
5 F. E. King and D. G. I. Felton, *J. Chem. Soc.*, 1949, 274.
6 D. S. Breslow and H. Skolnick, *Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1966, **2**, 1301.
7 Preliminary communication, T. Laitalainen, T. Simonen, M. Klinga, and R. Kivekäs, *Finn. Chem. Lett.*, 1979, 145.
8 R. Kivekäs, M. Klinga, R. Uggla, M. Sundberg, T. Laitalainen, and T. Simonen, *Cryst. Struct. Commun.*, 1978, **7**, 441.
9 M. Klinga, R. Kivekäs, T. Simonen, T. Laitalainen, R. Uggla, and M. Sundberg, *Cryst. Struct. Commun.*, 1978, **7**, 531.
10 R. Kivekäs, T. Laitalainen, and T. Simonen, *Cryst. Struct. Commun.*, 1979, **8**, 477.
11 T. Simonen and T. Laitalainen, *Finn. Chem. Lett.*, 1977, 144.
12 H. J. Reich, in 'Oxidation in Organic Chemistry,' ed. W. S. Trahanovsky, Academic Press, New York, 1978, part C, p. 118.

13 G. A. Russell and G. J. Mikol, in ' Mechanisms in Molecular Migrations,' ed. B. S. Thyagarajan, Interscience, New York, N.Y., 1968, vol. 1, p. 157—207.
14 Ref. 12, p. 25.
15 T. Laitalainen, *Finn. Chem. Lett.*, 1982, 15.
16 B. E. Norcross, J. M. Lansinger, and R. L. Martin, *J. Org. Chem.*, 1977, **42**, 369.
17 A. Schönberg and E. Singer, *Tetrahedron*, 1978, **34**, 1285.
18 A. W. Cordes, in ' Selenium,' eds. R. A. Zingaro and W. C. Cooper, Van Nostrand Reinhold Company, New York-Cincinnati-Toronto-London-Melbourne, 1974, p. 325.
19 T. Laitalainen and E. Rahkamaa, *Org. Magn. Reson.*, in the press.
20 W. McFarlane, D. S Rycroft, and C. J. Turner, *Bull. Soc. Chim. Belg.*, 1977, **86**, 457.
21 J. R. Bartels-Keith, M. T. Burgess, and J. M. Stevenson, *J. Org. Chem.*, 1977, **42**, 3725.
22 E. Rahkamaa, T. Laitalainen, and T. Simonen, ' Reports on Physical Chemistry,' Laboratory for Physical Chemistry, University of Turku, 1981, 1, 3.
23 G. D. Hope, Ph.D. Thesis, Halle, 1906.
24 G. F. Koser and Shwn-Meei Yu, *J. Org. Chem.*, 1976, **41**, 125.
25 I. W. J. Still and G. W. Kutney, *J. Org. Chem.*, 1981, **46**, 4911.
26 H. Dürr and R. Gleiter, *Angew. Chem.*, 1978, **90**, 591.
27 G. Bergson and A.-L. Delin, *Ark. Kemi*, 1961, **18**, 441.
28 J. A. Hirsch and E. Havinga, *J. Org. Chem.*, 1976, **41**, 455, and references cited therein.
29 J. A. Hirsch and A. A. Jarmas, *J. Org. Chem.*, 1978, **43**, 4106, and references cited therein.
30 I. Tabushi, Y. Tamaru, and Z. Yoshida, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1178.
31 J. B. Stothers, ' Carbon-13 NMR Spectroscopy,' Academic Press, New York and London, 1972, p. 334.
32 R. L. Shriner and H. R. Todd, *Org. Synth.*, Coll. Vol. 2, 1969, p. 200.
33 C. Sandris and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1956, 958.
34 H. Funk and W. Papenroth, *J. Prakt. Chem.*, 1960, **11**, 191.
35 I. Lielbriedis and E. Gudrinietse, *Latv. PSR Zinat. Vestis, Kim. Ser.*, 1968, 192 (*Chem. Abstr.*, 1968, **69**, 9955).
36 K. C. Gulati, S. R. Seth, and K. Venkataraman, *Org. Synth.*, Coll. Vol. 2, 1969, p. 522.
37 A. C. Jain and T. R. Seshadri, *Proc. Indian Acad. Sci., Sect. A*, 1955, **42**, 279.
38 W. Von Riedl and K. H. Risse, *Liebigs Ann. Chem.*, 1954, **585**, 209.
39 R. L. Wasson and H. O. House, *Org. Synth.*, Coll. Vol. 4, 1967, p. 522.
40 W. Treibs, *Chem. Ber.*, 1933, **66**, 1483.
41 C. Maignan, J.-C. Grandquillot, and F. Rouessac, *Bull. Soc. Chim. Fr.*, 1970, 2019.
42 ' International Tables for X-Ray Crystallography,' Vol. IV, Kynoch Press, Birmingham, 1974, p. 149.