707. *Oxidation of* 6,7-*Dihydro*-5H-*benzocycloheptene and Related Compounds by Selenium Dioxide.*

By Peter Rona.

Diselenides are obtained when the compounds named in the title are oxidized with selenium dioxide in wet pyridine. Their probable structures are established. Selenium analogues of 4,5-benzotropolone ethers have been prepared.

Selenium dioxide has been extensively used as a specific reagent for allylic oxidation of organic compounds.[1,2] Acidic and neutral solvents, such as acetic acid, benzene, and various alcohols are the usual reaction medium,[1] whereas basic solvents are rarely used in this oxidation. A few oxidations have been conducted in pyridine, but this seems to be the only basic solvent used.[3] In the dehydrogenation of botogenin acetate, pyridine was added in small quantity to the main solvent t-butyl alcohol.[4] In recent synthetic studies on compounds related to colchicine, three allylic dibenzocycloheptenols were synthesized from the corresponding olefins by oxidation with selenium dioxide in pyridine.[5]

In view of the unique stereospecificity of these oxidations further research seemed

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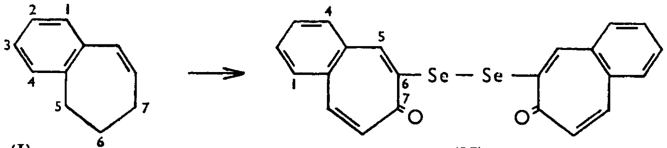
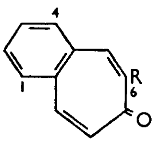
[1] Rabjohn, *Org. Reactions*, 1949, **5**, 331.
[2] Waitkins and Clark, *Chem. Rev.*, 1945, **36**, 235.
[3] Stallcup and Hawkins, *J. Amer. Chem. Soc.*, 1941, **63**, 3339; Witkop, *Annalen*, 1943, **554**, 83.
[4] Bowers, Denot, Sanchez, Neumann, and Djerassi, *J.*, 1961, 1859.
[5] Loewenthal, *J.*, 1958, 1367; 1961, 1421; Loewenthal and Rona, *Proc. Chem. Soc.*, 1958, 114; *J.*, 1961, 1429.

desirable on the possible uses of selenium dioxide–pyridine, particularly for seven-membered ring systems. Attempts were also made to investigate this oxidation with six-membered cycloalkenes. However, oxidation of 5α-cholest-1-ene, 5α-cholest-2-ene, and cholest-4-ene gave only very low yields of ill-defined products and work in this direction was discontinued.[6]

In preliminary experiments 6,7-dihydro-5*H*-benzocycloheptene (I) was oxidized with selenium dioxide in boiling pyridine with a small quantity of added water. The sole product was a light yellow seleno-organic compound, $C_{22}H_{14}O_2Se_2$. The compound has infrared carbonyl absorption at 1625 cm.$^{-1}$ and ultraviolet maxima at 281 and 345 mμ. This suggests a tropone-type structure for the product, the selenium atoms possibly forming a diselenide link connecting two equivalent parts of the molecule, as in (II).



(I) (II)



(III) R = SeO_2H
(IV) R = $SeCl_3$
(V) R = SeMe
(VI) R = $Se{\cdot}CH_2Ph$

This diselenide (II) with concentrated nitric acid at 0° gave the corresponding seleninic acid (III) which with an excess of hydrazine sulphate was reduced back to the diselenide (II).[7] When an equivalent amount of hydrazine sulphate was used, the intermediate selenic acid could not be isolated. The seleninic acid (III) resulted also from hydrolysis of the corresponding selenium trichloride derivative (IV) that was obtained by reaction of the diselenide with sulphuryl chloride.[8a] Methyl iodide reacted vigorously with the diselenide in hot methanolic potassium hydroxide; the methyl selenide (V) was isolated in low yield.[10b] The benzyl selenide (VI) was obtained by benzyl bromide in dimethylformamide. These selenides are new selenium analogues of the 4,5-benzotropolone ethers.[9]

Florey and Restivo,[10] and Baran,[11] attempted to dehydrogenate steroidal 4-en-3-ones by selenium dioxide in acetic acid, dioxan, and t-butyl alcohol–acetic acid, but obtained diselenides, the diselenide group linking two steroid molecules through position 2. Thus the selenium dioxide dehydrogenation of steriodal 4-ene-3-ones and 6,7-dihydro-5*H*-benzocycloheptene give similar products.

To support the position of the diselenide link and to establish the general characteristics of this reaction we studied the oxidation of some substituted benzocycloheptenes. For use as starting materials we synthesized substituted 6,7-dihydro-5*H*-benzocycloheptenes (VII—XIII) by cyclization of δ-phenylvaleric acids with polyphosphoric acid.[12] These acids were synthesized by Dreiding's method of condensing the arenealdehydes with methyl crotonate in t-butyl alcohol containing potassium t-butoxide.[13] Reduction of the resulting tetrahydrobenzocycloheptenones yielded the alcohols, which were dehydrated smoothly to the dihydrobenzocycloheptenes. The 9-methyl derivative (VII)

[6] Nussim and Rona, unpublished results.

[7] Rheinboldt and Giesbrecht, *Chem. Ber.*, 1955, **88**, 666.

[8] Rheinboldt in "Methoden der Organischen Chemie" (Houben-Weyl), Georg Thieme Verlag, Stuttgart, 1955, Vol. X, pp. (*a*) 1135, (*b*) 983, (*c*) 1109, (*d*) 1110.

[9] Tarbell and Bill, *J. Amer. Chem. Soc.*, 1952, **74**, 1234.

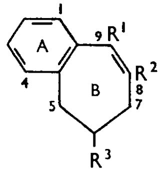
[10] Florey and Restivo, *J. Org. Chem.*, 1957, **22**, 406.

[11] Baran, *J. Amer. Chem. Soc.*, 1958, **80**, 1687.

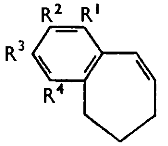
[12] Anderson, Horton, Walker, and Weiler, *J. Amer. Chem. Soc.*, 1955, **77**, 598; Horton, Hummel, and Johnson, *ibid.*, 1953, **75**, 944.

[13] General method kindly communicated by Dr. A. S. Dreiding before publication.

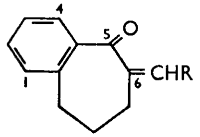
was obtained by reaction of tetrahydrobenzocycloheptenone with methylmagnesium iodide and subsequent dehydration, and the 8-methyl derivative (VIII) by reduction and dehydration of tetrahydro-6-methylbenzocyclohepten-5-one which we prepared by the procedure of Ireland and Marshall,[14] *i.e.*, conversion of the 2-hydroxymethylene-ketone



	R^1	R^2	R^3
(VII)	Me	H	H
(VIII)	H	Me	H
(IX)	H	H	Me



	R^1	R^2	R^3	R^4
(X)	H	Me	H	H
(XI)	H	H	H	Me
(XII)	H	OMe	OMe	OMe
(XIII)	OMe	OMe	OMe	H

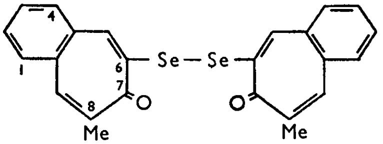


(XIV) R = OH

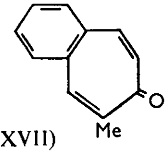
(XV) R = SBu^n

(XIV) into the n-butylthiomethylene derivative (XV). Desulphurization of this sulphide gave the methylated ketone in 70% overall yield.

Oxidation of the dihydro-8-methylbenzocycloheptene (VIII) in the way described above gave smoothly a diselenide formulated as (XVI). A by-product contained four selenium atoms per molecule (see below for its structure). This successful oxidation clearly excludes the possibility of introduction of the diselenide group in the vinylic



(XVI)



(XVII)

8-position, as this is blocked in the starting material by the methyl group. It shows also the preferential oxidation of an allylic methylene group rather than an allylic methyl group. However, when the methyl and methylene groups are not in strictly equivalent positions with regard to the double bond, as in the 9-methyl derivative (VII), the site of oxidation is not the methylene but the methyl group; this compound gave a complex oily mixture and oxidation of the methyl group is suggested by the very strong absorption at 1695 cm.$^{-1}$. 6-Methylbenzocycloheptene (IX) also gave a mixture of mainly non-crystalline alcohols (at least three), but on chromatography the only ketone isolated was a small amount of 6-methylbenzocyclohepten-7-one (XVII).[15]

Oxidation of two of the ring-A-substituted compounds (XI) and (XII) gave smoothly the corresponding diselenides analogous to (XVI). The three diselenides were oxidized by cold concentrated nitric acid to the corresponding seleninic acids, *e.g.*, (XVIII). These derivatives are of importance as their molecular weights can be determined by direct titration.

The above reactions establish the main characteristics of this oxidation of 6,7-dihydro-5*H*-benzocycloheptenes, namely, introduction of an allylic carbonyl group, dehydrogenation to the benzotropone system, and introduction of the diselenide group in the homoallylic position relative to the original double bond, though this sequence listed is not necessarily that in the actual reaction.

Oxidation of the second dihydrotrimethoxybenzocycloheptene, the 1,2,3-isomer (XIII), gave a well-defined, orange compound in good yield. Its analysis corresponded

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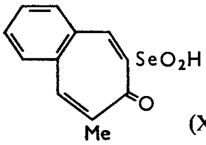
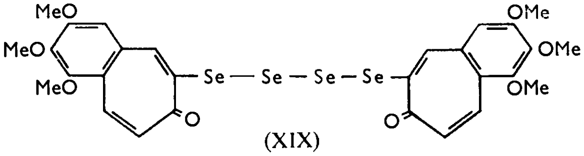
[14] Ireland and Marshall, *Chem. and Ind.*, 1960, 1534.

[15] This compound was reported without adequate characterization, by Volpin and Plate, *Doklady Akad. Nauk S.S.S.R.*, 1950, **70**, 842; *Chem. Abs.*, 1950, **44**, 6846.

with the formula $C_{28}H_{26}O_8Se_4$ and structure (XIX). In one oxidation only, a small amount of the corresponding diselenide was also isolated. Nitric acid oxidized the tetraselenide to a monoseleninic acid, which excludes the possibility of more than one C–Se bond in the molecule. Thus the polyselenide must be formulated as a straight-chain tetraselenide.



(XVIII)



(XIX)

Straight-chain triselenides are a known class of compound.[8d] However, tetraselenides seem not to have been reported hitherto; indeed alternative, less probable, formulations are possible. The tetraselenide by-product from the oxidation of compound (VIII) is analogously formulated as a straight-chain tetraselenide.

The mechanism of this oxidation is unknown, but some facts on the effect of solvents seem significant. When 6,7-dihydro-5*H*-benzocycloheptene (I) is oxidized with selenium dioxide in 3-picoline or dioxan with traces of water present, the diselenide (II) is obtained in yields comparable to those obtained with pyridine as solvent. On the other hand no diselenide could be isolated on oxidation in wet or dry benzene, t-butyl alcohol, or acetic acid.

EXPERIMENTAL

δ-Phenylvaleric Acid (*General Procedure*).—Benzaldehyde (15·9 g.) and methyl crotonate (30·6 g.) were added with cooling to a solution of potassium (12·6 g.) in t-butyl alcohol (375 ml.). The mixture became orange and solid separated. After being kept overnight at room temperature, the whole was acidified with acetic acid, and water was added. The oil which separated was extracted with ether; the extract was washed with water, dried ($MgSO_4$), and evaporated. The remaining oil was hydrogenated in ethyl acetate at 50 lb./sq. in. over 5% palladium–charcoal. The crude product obtained on filtration and removal of solvent was hydrolyzed by refluxing with 10% sodium hydroxide solution. The acid obtained by usual working-up was purified by high-vacuum distillation (18·1 g.), and after recrystallization from water had m. p. 56—57° (lit.,[16] m. p. 57°).

6,7,8,9-Tetrahydro-3-methyl-5H-benzocyclohepten-5-one.—δ-*p*-Tolylvaleric acid (4·6 g.) was heated in polyphosphoric acid [from 85% orthophosphoric acid (10 ml.) and phosphoric oxide (100 g.)] with stirring on the steam-bath for 1·5 hr. Ice–water was then added and the mixture extracted with benzene–ether (0·5 l.). The organic layer was washed with water, 20% potassium carbonate solution, and water, and dried ($MgSO_4$). Evaporation left the *ketone* (3·13 g.), b. p. 107°/0·01 mm. (Found: C, 82·45; H, 8·1. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%), ν(C=O) 1675 cm.$^{-1}$ (in $CHCl_3$).

6,7,8,9-Tetrahydro-6-methylbenzocyclohepten-5-one.—6-Hydroxymethylenebenzocyclohepten-5-one (XIV) was prepared from benzocyclohepten-5-one (11·1 g.) and ethyl formate (10·2 g.) in dry benzene (52 ml.), the solution being added, under helium, to dry sodium methoxide [from sodium (3·2 g.) and methanol (30 ml.); it was dried in a high vacuum at 200°]. After occasional cooling and swirling the solution was left overnight at room temperature. Ice–water was added, the water layer separated, and the benzene layer extracted twice with 20% potassium hydroxide solution. The basic extracts were added to the water layer and the whole was washed with ether, acidified with dilute hydrochloric acid, and twice extracted with ether. The ether solution was washed with saturated salt solution and dried ($MgSO_4$). Evaporation of the ether left the oily hydroxymethylene-ketone. Without purification it was treated in dry benzene (50 ml.) with naphthalene-2-sulphonic acid (100 mg.) and butane-1-thiol (8·1 ml.) and heated for 1·5 hr. under an azeotropic water-condenser. The solution was then washed with 20% potassium carbonate solution and with water and dried ($MgSO_4$). Evaporation left the oily *n-butylthio-compound* (XV) (15·8 g.), b. p. 173—175°/0·05 mm. (Found: S, 12·2. $C_{16}H_{20}OS$ requires S, 12·3%), ν(C=O) 1655 cm.$^{-1}$ (in $CHCl_3$).

The crude *sulphide* was heated in absolute ethanol and for 2·5 hr. under helium with Raney

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[16] Standinger and Muller, *Ber.*, 1923, **56**, 711.

nickel (SW-2; ∼150 g.). The nickel was then filtered off and washed with benzene. The benzene washings were added to the filtrate and the solution was evaporated. Distillation then gave the *ketone* (8·24 g.), b. p. 103°/0·03 mm. (Found: C, 82·95; H, 8·3. $C_{12}H_{14}O$ requires C, 82·72; H, 8·1%), ν(C=O) 1680 cm.$^{-1}$ (in $CHCl_3$).

6,7-*Dihydro*-5H-9-*methylbenzocycloheptene* (VII).—Tetrahydrobenzocyclohepten-5-one (5·95 g.) was added in benzene (15 ml.) to a solution of methylmagnesium iodide [from magnesium (2 g.) and methyl iodide (20 ml.)] in ether (200 ml.). The solution was heated to reflux for 3 hr. Working-up in the usual manner gave an oil which was heated in benzene (150 ml.) with naphthalene-2-sulphonic acid (0·75 g.) for 4 hr. under an azeotropic water-condenser. The solution was then washed with water, dried ($MgSO_4$), and evaporated. The oil obtained was chromatographed with hexane over alumina (60 g.). Elution with hexane gave first the *hydrocarbon* (VII), b. p. 126°/30 mm. (Found: C, 90·8; H, 8·9. $C_{12}H_{14}$ requires C, 91·1; H, 8·9%), n_D^{20} 1·5630; further elution gave back part (0·26 g.) of the starting ketone.

Preparation of the 6,7-*Dihydro*-5H-*benzocycloheptenes from Tetrahydrobenzocyclohepten*-5-*ones*.—The ketone (5 g.) was dissolved in methanol (40 ml.), a few drops of water and sodium tetrahydroborate (1·5 g.) were added, and the solution was left at room temperature overnight. Next morning the solution was heated for ∼10 min. on a steam-bath, water was added, and part of the methanol evaporated. The solution was extracted with ether, and the extract was washed with water, dried ($MgSO_4$), and evaporated. The crude product left was heated in benzene (150 ml.) with naphthalene-2-sulphonic acid (0·3 g.) under an azeotropic water-condenser for 4 hr. The solution was extracted with water, dried ($MgSO_4$), and evaporated. The crude hydrocarbons listed in Table 1 were distilled under reduced pressure. Ultraviolet spectra refer to solutions in methanol.

TABLE 1.

Substituted 6,7-dihydro-5*H*-benzocycloheptenes.

Cpd.	Yield * (%)	B. p./ mm.	n_D^{20}	$\lambda_{max.}$ (mμ) (10^{-4} ε)	Found (%) C	H		Requires (%) C	H
(I)	80	124°/31	1·5883	214 (5·72) 280 (4·19)	—	—	—	—	—
(X)	83	140°/30	1·5808	216 (14·2) 257 (8·0)	90·9	8·9	$C_{12}H_{14}$	91·1	8·9
(XI)	73	138°/29	1·5810	215 (11·8) 280 (1·33)	90·3	8·8	,,	,,	,,
(IX)	62	63°/0·1	1·5665	210 (1·97) 252 (1·3)	91·0	8·8	,,	,,	,,
(VIII)	78	130°/26	1·5809	214 (11·1) 258 (8·6)	90·95	8·9	,,	,,	,,
(VII)	39	126°/30	1·5630	212 (5·8) 244 (1·4)	90·8	8·9	,,	,,	,,
(XIII)	88	125°/0·05		233 (12·0) 264 (1·8)	71·65	7·8	$C_{14}H_{18}O_3$	71·8	7·7
(XII)	96	119°/0·05		221 (15·0) 267 (2·1)	71·6	7·7	,,	,,	,,

* Calc. on the quantity of ketone reduced.

Di-(7-oxobenzocycloheptatrien-5-yl) Diselenide (II).—(*a*) *General procedure*. 6,7-Dihydro-5*H*-benzocycloheptene (0·77 g.) was dissolved in dry pyridine (6·5 ml.), water (0·1 ml.) was added, and the solution heated to the b. p. Selenium dioxide (1·15 g.; freshly sublimed) was added in small portions in 1 hr. and refluxing was continued for an additional 45 min. The mixture was cooled, benzene (75 ml.) added, and the solution decanted from the deposited selenium. The dark brown solution was washed with 20% potassium carbonate solution, dilute hydrochloric acid, and water, and dried ($MgSO_4$). Removal of the solvent left the yellow crystalline *diselenide* which was chromatographed with benzene–methylene chloride on basic alumina (40 g.) over a layer (3·5 g.) of a mixed alumina and precipitated silver (6 : 1). First a small amount of the starting material was eluted. This was followed by the product which from chloroform–benzene formed slightly yellow crystals (0·28 g.), m. p. 272° (Found: C, 55·64; H, 3·0; Se, 34·0. $C_{22}H_{14}O_2Se_2$ requires C, 56·41; H, 3·0; Se, 33·8%), ν(C=O) 1630 cm.$^{-1}$ (in KBr), $\lambda_{max.}$ 281 (ε 61,000), 345 mμ (ε 12,200) (in $CHCl_3$). An attempt to determine the molecular weight was frustrated by insolubility of the compound.

The above product was obtained in the same yield on performing this experiment under helium.

(*b*) 6,7-Dihydro-5*H*-benzocycloheptene (0·77 g.) (a specially dry sample) was oxidized as described in (*a*), but without added water. The diselenide (80 mg.) was obtained.

(*c*) 6,7-Dihydro-5*H*-benzocycloheptene (0·77 g.) was oxidized with 3-picoline (6·5 ml.) as solvent, the procedure being as in (*a*). The diselenide (0·25 g.) was obtained.

(*d*) The seleninic acid (III) (0·1 g.) was suspended in a solution of hydrazine sulphate (0·1 g.) in water (4 ml.) and left overnight at room temperature. Next morning the yellow precipitate was filtered off, washed with water, dried, dissolved in chloroform, and washed with 10% potassium carbonate solution, dilute hydrochloric acid, and water, and dried ($MgSO_4$). Evaporation left the pure diselenide which after recrystallization had m. p. and mixed m. p. 269—270°. The infrared spectra of this product and that obtained by procedure (*a*) were superimposable.

Attempted Oxidations of 6,7-*Dihydro*-5H-*benzocycloheptene* (I).—(*a*) The hydrocarbon (0·96 g.) was heated in dry benzene (20 ml.), and selenium dioxide (1·63 g.) was added during 1 hr.; heating was continued for an additional hour. A semi-solid water-soluble dark mass was deposited (mainly of selenium dioxide). Working-up gave starting material (0·92 g.).

(*b*) The hydrocarbon (I) (0·50 g.) was dissolved in dry benzene (15 ml.), and water (0·2 ml.) was added. The solution was heated to the b. p. and selenium dioxide (0·8 g.) was introduced in small portions during 1 hr., reflux being continued for 47 hr. A semi-solid dark mass was deposited. Working-up gave a dark brown oily mixture (0·54 g.).

6-*Methylselenobenzocyclohepten*-7-*one* (V).—The diselenide (II) (0·24 g.) was suspended in absolute methanol and was heated to the b. p. under helium. A 25% solution of potassium hydroxide in methanol (10 ml.) was slowly added with stirring; the solution became red as the base was added. Methyl iodide (1 ml.) was then added dropwise, and heating was continued for 30 min. A second portion (5 ml.) of potassium hydroxide solution was added, followed by methyl iodide (2 ml.). The solution was boiled for an additional 1 hr., then cooled, ether and benzene were added, and the solution was washed with water until neutral, and dried ($MgSO_4$). Evaporation at reduced pressure gave a yellow oil which was chromatographed in hexane–methylene chloride on basic alumina (10 g.). The substance eluted crystallized from benzene–hexane, giving the pure *selenide* (53 mg.), m. p. 81° (Found: C, 57·6; H, 4·2%; *M*, 254. $C_{12}H_{10}OSe$ requires C, 57·8; H, 4·0%; *M*, 249), ν(C=O) 1628 cm.$^{-1}$ (in $CHCl_3$), $\lambda_{max.}$ 248 (ε 20,000), 275 (ε 22,800), 291 (ε 22,900), and 361 mμ (ε 7380) (in MeOH).

6-*Benzylselenobenzocycloheptene*-7-*one* (VI).—The diselenide (II) (0·12 g.) was quickly added to a stirred hot solution of potassium hydroxide (0·25 g.) in dimethylformamide under helium. To the resulting dark-red solution benzyl bromide (1 ml.) was added; a vigorous reaction followed and the mixture became yellow. After 30 minutes' heating a second portion (1 ml.) of benzyl bromide was added and heating continued for 30 min. The mixture was then cooled, ether was added, and the whole was washed with water until neutral, dried ($MgSO_4$), and evaporated. The yellow oil obtained was chromatographed with hexane–methylene chloride on basic alumina (8 g.). Recrystallization from ether–hexane gave the pure *selenide* (40 mg.), m. p. 105—106° (Found: C, 66·3; H, 4·4%; *M*, 362. $C_{18}H_{14}OSe$ requires C, 66·4; H, 4·3%; *M*, 325), ν(C=O) 1628 cm.$^{-1}$ (in $CHCl_3$).

6-*Methylbenzocycloheptene*-7-*one* (XVII).—To 6,7-dihydro-6-methyl-5*H*-benzocycloheptene (IX) (1·4 g.) in boiling dry pyridine (13 ml.) and water (0·1 ml.), selenium dioxide (2·3 g.) was added in small portions during 1 hr. Refluxing was continued for an additional 45 min. Working-up gave a dark oil. This was chromatographed with hexane–methylene chloride, chloroform, and methanol on basic alumina (50 g.). Twelve fractions were collected from the column; fractions 4 and 5 after several recrystallizations from isopropyl ether at −70° gave the pure *ketone* (XVII) (20 mg.), m. p. 67—68° (Found: C, 84·8; H, 6·0. $C_{12}H_{10}O$ requires C, 84·7; H, 5·9%), ν(C=O) 1630 cm.$^{-1}$ (in $CHCl_3$), $\lambda_{max.}$ 233 (ε 40,000), 271 mμ (ε 87,000) (in MeOH). Fractions 7—9 were rechromatographed together on basic alumina (30 g.) with the above solvents. The oily alcoholic product did not crystallize; it had $\nu_{max.}$ 3710vs, 1750m, 1650w cm.$^{-1}$.

Oxidation by Selenium Dioxide in Pyridine.—To 6,7-dihydro-9-methyl-5*H*-benzocycloheptene (VII) (1·4 g.) in boiling dry pyridine (10 ml.) selenium dioxide (1·75 g.) was added in small portions during 1 hr. and refluxing was continued for 45 min. The dark oil obtained was chromatographed with hexane–benzene on basic alumina (50 g.). Several fractions of a glassy aldehyde were obtained; this had ν(C=O) 1695vs, 2585w, 1625w cm.$^{-1}$ before chromatography.

Di-(8-*methylbenzocyclohepten*-6-*yl*) *Diselenide* (XVI).—To 6,7-dihydro-8-methyl-5*H*-benzocycloheptene (VIII) (1·4 g.) in boiling dry pyridine (10 ml.) and water (0·1 ml.), selenium dioxide (1·75 g.) was added in small portions during 1 hr. and refluxing was continued for 45 min. Working-up gave a yellow crystalline product that was chromatographed with hexane–methylene chloride on basic alumina (80 g.). First, part of the starting material (0·16 g.) and then the yellow product was eluted. This was rechromatographed with the same solvents over basic alumina (50 g.), three fractions being separated. The second fraction, after recrystallization from benzene–cyclohexane, gave the *diselenide* (0·15 g.), m. p. 254—255° (Found: C, 58·1; H, 3·8; Se, 31·4. $C_{24}H_{18}O_2Se_2$ requires C, 58·1; H, 3·6; Se, 31·85%), ν(C=O) 1625w cm.$^{-1}$. After numerous recrystallizations only some (0·1 g.) impure (m. p. 241—245°) product was recovered from the other fractions.

Di-(1,2,3-*trimethoxybenzocyclohepten*-6-*yl*) *Diselenide* (XIX).—6,7-Dihydro-2,3,4-trimethoxy-5*H*-benzocycloheptene (XII) (3·3 g.) was heated in dry pyridine (20 ml.), and selenium dioxide (3·35 g.) was added in small portions during 1 hr.; heating was continued for a further 2 hr. Working-up gave yellow crystals that were chromatographed on basic alumina (50 g.) on 6 : 1 alumina–precipitated silver (3·5 g.). Elution with benzene–methylene chloride and chloroform gave the pure *diselenide*. Recrystallized from chloroform–benzene (1·3 g.), it had m. p. 225—227° (Found: C, 52·4; H, 4·25; Se, 24·3. $C_{28}H_{26}O_8Se_2$ requires H, 51·7; H, 4·0; Se, 24·4%), ν(C=O) 1625 cm.$^{-1}$ (in KBr).

Di - (2,3,4 - *trimethoxy* - 7 - *oxobenzocyclohepten* - 6*yl*) *Tetraselenide*.—6,7 - Dihydro -1,2,3 - trimethoxy-5*H*-benzocycloheptene (XIII) (1·95 g.) was treated in boiling dry pyridine (19 ml.) and water (0·2 ml.) with selenium dioxide (4·16 g.) during 1 hr. and heating was continued for an additional 2 hr. Working-up gave a crystalline product that was chromatographed with benzene–methylene chloride on basic alumina (100 g.) over 6 : 1 alumina–precipitated silver (3·5 g.). The orange *tetraselenide*, recrystallized from benzene–cyclohexane (0·54 g.), had m. p. 205° (Found: C, 41·6; H, 3·5; Se, 39·0. $C_{28}H_{24}O_8Se_4$ requires C, 41·75; H, 3·5; Se, 39·3%), ν(C=O) 1605 cm.$^{-1}$ (in KBr).

In one experiment fractions after the second were mixed and crystallization gave white rosettes among the orange crystals of the main product. The former were removed manually and recrystallized from benzene–cyclohexane. This gave the *diselenide* (15 mg.), m. p. 170—174° (sintering at 112°) (Found: Se, 24·1. $C_{28}H_{26}O_8Se_2$ requires Se, 24·4%), ν(C=O) 1610 cm.$^{-1}$ (in KBr).

7-*Oxobenzocycloheptene*-6-*seleninic Acid* (III).—The diselenide (II) (70 mg.) was dissolved in chloroform (0·5 ml.), sulphuryl chloride (0·4 ml.) was added, and the selenium trichloride which was immediately precipitated was filtered off, washed with cold chloroform, and dried in desiccator. The crude dry trichloride was suspended in cold water (1 ml.). Reaction occurred immediately and the product was precipitated; it was filtered off and dried in a desiccator. On recrystallization, the seleninic acid, m. p. and mixed m. p. 255—256° (sintering 162°) (see below), was obtained.

TABLE 2.

Substituted 7-oxobenzocycloheptene-6-seleninic acids.

		Yield	Found (%)					Requires (%)			
Subst.	M. p.	(%)	C	H	Se	Equiv.		C	H	Se	Equiv.
None	255—256°	51	49·6	3·0	29·6	281	$C_{11}H_8O_3Se$	49·4	3·0	29·6	267
6-Me	232 (sint. 166)	29	50·9	3·9	—	269	$C_{12}H_{10}O_3Se$	51·2	3·5	28·4	282
1-Me	210	47	50·8	3·7	—	295	$C_{12}H_{10}O_3Se$	51·2	3·5	28·4	282
1,2,3-OMe	195	48	47·2	4·0	22·0	352	$C_{14}H_{14}O_6Se$	47·0	3·9	22·2	357
2,3,4-OMe	177—178	26	46·4	3·9	—	351	$C_{14}H_{14}O_6Se$	47·0	3·9	22·2	357

General Preparation of 7-*Oxo*-7H-*benzocycloheptene*-6-*seleninic Acids by Oxidation of the Diselenides*.—The diselenide (0·25 g.) was added in portions to cold (0°) concentrated nitric acid (4 ml.). The mixture was stirred for about 0·5 min.; when the diselenide dissolved, the solution was poured into ice–water. The pale yellow seleninic acid was precipitated; it was filtered off, washed with water, dried in a desiccator, and recrystallized from chloroform–isopropyl ether with a few drops of ethanol added. The *products* are listed in Table 2.

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CHEMISTRY DEPARTMENT, ISRAEL INSTITUTE OF TECHNOLOGY, HAIFA, ISRAEL.
[Present address: ISRAEL ATOMIC ENERGY COMMISSION LABORATORIES,
REHOVOTH, ISRAEL.]

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