Aromatization Reactions with Selenium and Aryl Diselenides

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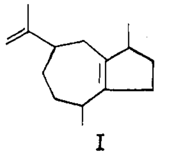
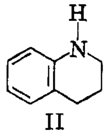
Studies of the selenium dehydrogenation reaction with guaiene, 1,2,3,4-tetrahydroquinoline, a dihydronaphthalene, and 9,10-dihydrophenanthrene show that the course of the reaction is strongly influenced by the temperature, by the number of hydrogens to be removed, and by the presence of good hydrogen acceptor molecules. At 290° and when the number of hydrogens to be removed is small, aromatization proceeds with the stoichiometric liberation of hydrogen selenide. However, disproportionation reactions occur when the number of hydrogens to be removed is large, or when the temperature is rather low, or when the reaction is carried out in the presence of a hydrogen acceptor such as oleic acid. Under certain conditions, dehydrogenation by means of aromatic diselenides resembles that achieved by elemental selenium under comparable conditions.

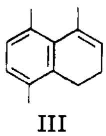
Since the initial use of selenium for dehydrogenation,[1] this element has been used extensively to achieve a variety of aromatizations. However, practically nothing has appeared in the literature on the mechanism of the reaction. In a recent study[2] it was suggested that selenium attack on a double bond is analogous to oxygen attack,[3] and that reactions involving formation of hydroperselenides and diselenides, with cleavage to give radical intermediates, are important steps in the dehydrogenation process. Thus, for example, treatment of guaiene with selenium gave much more guaiazulene than could be accounted for by the quantity of evolved hydrogen selenide.

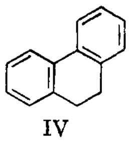
In the present study, a variety of substrates with differing degrees of aromaticity were treated with selenium alone and with selenium in the presence of a hydrogen acceptor. The compounds investigated were guaiene (I), 1,2,3,4-tetrahydroquinoline (II), 3,4-dihydro-1,5,8-trimethylnaphthalene (III), and 9,10-dihydrophenanthrene (IV):


I



II


III


IV

In addition, experiments were performed with diaryl diselenides because similar compounds were thought to be possible intermediates.

Experimental

Apparatus.—The apparatus employed for all dehydrogenation experiments has been described previously.[2] The apparatus employed for thermal decomposition experiments consisted of a 25-ml. round-bottom flask fitted with a stopcock which was connected to a vacuum pump.

Materials.—The reported preparations of guaiene (1,4-dimethyl - 7 - isopropylidene - 1,2,3,4,5,6,7,8 - octahydroazulene (I),[2] diphenyl diselenide,[4] and β,β'-dinaphthyl diselenide,[5] were repeated. Reagent grade, gray, powdered elemental selenium was obtained from Fisher Scientific Co. Eastman grade 1,2,3,4-tetrahydroquinoline was used without further treatment. The 9,10-dihydrophenanthrene obtained from Terra Chemical Co. was found to contain about 14% phenanthrene, and was used without purification. Appropriate corrections were made in the calculations. The 3,4 - dihydro - 1,5,8 - trimethylnaphthalene was prepared by B. Krabacher in this laboratory. The oleic acid used for the hydrogen acceptor experiments, was better than 99% pure.[6]

Dehydrogenation Procedure.—The materials were weighed into a reactor flask fitted with a stirring rod and attached to a lead acetate trap. The heating procedure has been described.[2] After the appropriate time at temperature, the reaction products were removed with low-boiling petroleum ether and filtered. The selenium residue was washed several times with petroleum ether, air-dried, and weighed. The lead selenide precipitate was filtered, dried overnight in a desiccator, and weighed.

In experiments involving guaiene, guaiazulene was extracted from the reaction mixture filtrate with 85% phosphoric acid, the guaiazulene was regenerated by dilution of the acid, and then it was extracted from the aqueous layer with petroleum ether. Aliquots were diluted with 95% ethanol and analyzed spectrophotometrically using absorptions at 244 and 288.5 mμ to calculate the quantity of azulene formed. In experiments involving 1,2,3,4-tetrahydroquinoline, absorptions at 300.5 and 315.5 mμ were used to calculate the quantity of quinoline and with 9,10-dihydrophenanthrene the absorption at 346 mμ of cyclohexane solutions was used to calculate the quantity of phenanthrene.

Pyrolysis of Diphenyl Diselenide.—A 1.00-g. sample (3.2 moles) of diphenyl diselenide was heated for the desired length of time at the desired temperature in an evacuated flask. After cooling, boiling petroleum ether was sucked into the bulb from a syringe and the solution immediately chromatographed over alumina in a column protected from light by black paint. Red selenium deposition in the bulb, as well as on the walls of the column, indicated that decomposition of the material was occurring, but with careful exclusion of light and rapid chromatographic sepa-

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[1] O. Diels and A. Karstens, *Ber.*, **60**, 2323 (1927); O. Diels, W. Gadke, and P. Kording, *Ann.*, **459**, 1 (1927).

[2] W. T. House and M. Orchin, *J. Am. Chem. Soc.*, **82**, 639 (1960).

[3] E. H. Farmer and D. A. Sutton, *J. Chem. Soc.*, 119 (1943); F. D. Gunstone and T. P. Hilditch, *ibid.*, 1022 (1946).

[4] M. Taboury, *Bull. soc. chim.*, **29**, 761 (1903).

[5] J. Loevenich, H. Fremdling, and M. Fohr, *Ber.*, **62B**, 2856 (1929); G. Bergson, *Arkiv Kemi*, **10**, 127 (1956).

[6] J. D. Fitzpatrick and M. Orchin, *J. Am. Chem. Soc.*, **79**, 4765 (1957).

TABLE I

DEHYDROGENATIONS WITH SELENIUM

Time, hr.	Temp., °C.	Se, mmoles	Compound		Oleic, mmoles	Product			Recovered Se (mmoles)	
			Formula	mmoles		Formula	mmoles	%	As H_2Se[a]	As Se
1	290	7.5	I	2.5	15.0	G[b]	0.7	29.6	0.13	5.9
2	290	7.5	I	2.5	15.0	G	.5	21.2	.15	5.8
1	250	20.0	II	10.0	0	Q[c]	2.6	26	5.40	15.6
2	250	20.0	II	10 0	0	Q	4.7	47	9.10	13.6
1	250	10.0	II	5.0	10.0	Q	2.3	46	0.40	7
1	220	2.0	IV	2.0	0	P[d]	...	...	...	2.0
1	240	2.0	IV	2.1	0	P	0.1	4.3	.03	2.0
1	260	2.0	IV	2.0	0	P	.3	12.1	.14	1.9
1	260	2.0	IV	2.6	0	P	1.3	46.1	1.16	0.9

[a] Precipitated as PbSe. [b] Total guaiazulene. [c] Quinoline and [d] Phenanthrene, all determined by ultraviolet spectroscopy.

ration, the decomposition was held to a minimum. The first fraction eluted was diphenyl monoselenide, identified[4] as the dichloride derivative, m.p. 180–182°, followed immediately by an approximately equal amount of diphenyl diselenide, yellow crystals, m.p. and mixed m.p. 63–64°. A third fraction eluted with benzene–ligroin was isolated, consisting of about 10–15 mg. of material. This solid, m.p. 57–58°, was a yellow crystalline material, which on dissolving in all solvents gave diphenyl diselenide and selenium. Although a completely uncontaminated sample could not be obtained, it appeared that the crystalline solid was possibly an impure diphenyl triselenide. On standing for 7 days, the compound reverted to a red crystalline solid. Exposure to ultraviolet light at room temperature readily converts the solid red crystals to the yellow crystalline form. Reconversion to the red solid occurs slowly after removal of the ultraviolet irradiation. The process can be repeated indefinitely, and hence the system is completely reversible. A carbon and hydrogen analysis indicated a mixture.

Anal. Calcd. for Ph_2Se_3: C, 36.9; H, 2.58. Calcd. for Ph_2Se_2: C, 46.1; H, 3.20. Found[7]: C, 41.3; H, 2.87.

The sample could not be purified because of its instability in solvents.

Other Preparations of Impure Diphenyl Triselenide.—A 1.00-g. sample of diphenyl diselenide and selenium were heated *in vacuo* at about 290° for 24 hr. The mixture was transferred with ligroin to a chromatographic column and the mixture chromatographed in the dark. The fractions appeared to be identical with those secured from the pyrolysis of diphenyl diselenide. Heating diphenyl monoselenide and elemental selenium also gave the same yellow material. Irradiating elemental selenium at room temperature with either the monoselenide or diselenide was without effect.

Results

Guaiene (I).—Stoichiometric quantities of selenium and I were heated for one and two hours in the presence of excess oleic acid at 290° with the results shown in Table I. Yields of guaiazulene are greatly improved over the 14% maximum reported[2] in the experiments conducted without oleic acid. Increasing the reaction time not only failed to increase the yield but, on the contrary, decreased it. Possibly the aromatic compound acts as a hydrogen acceptor or is being destroyed by side reactions.

During chromatographic separation of the selenium–guaiene–oleic acid reaction mixture, a small amount of organoselenium complex was isolated. Petroleum ether solutions of the complex, on standing, ultimately decomposed to an oil and finely dispersed elemental selenium. The complex possessed a disagreeable odor, characteristic of many organoselenium compounds, and on heating at dehydrogenation temperatures, the complex gave guaiazulene and hydrogen selenide. The ratio of selenium to complex, based on the total amount of hydrogen selenide evolved by heating at 290°, was roughly 1:5. The infrared spectrum of the selenium–guaiene complex was similar to that of guaiene except for two new peaks at 814 and 795 cm.$^{-1}$, and the disappearance of the 1640- and 888-cm.$^{-1}$ bands associated with the vinyl group.

1,2,3,4-Tetrahydroquinoline (II).—The results of experiments with II are summarized in Table I. Relatively little disproportionation occurs in either the one- or two-hour experiments since the quantity of selenium accounted for as hydrogen selenide is approximately twice that of the quinoline formed on the basis of the expected stoichiometry. However, in the presence of oleic acid the yield of quinoline at the end of one hour is almost twice as great as that observed in the absence of the hydrogen acceptor, but the amount of selenium accounted for as evolved hydrogen selenide is greatly decreased.

3,4-Dihydro-1,5,8-trimethylnaphthalene (III).—Heating equimolar quantities of selenium and III at 295° gave steady evolution of hydrogen selenide for 16 hours. About 95% of the selenium was accounted for on the basis of the ultimate yield of hydrogen selenide. The reaction mixture contained small amounts of white-gray crystals, which on attempted solvent recrystallization, decomposed to elemental selenium and an oil, most probably starting III. The crystals had a melting point of 182–183° with decomposition, and possessed a disagreeable odor. This unstable material is probably a selenium–hydroaromatic complex analogous to that obtained with guaiene. The reaction mixture remaining was vacuum distilled to give pure 1,4,5-trimethylnaphthalene in 66% yield.

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[7] Geller Laboratories, Bardonia, New York.

9,10-Dihydrophenanthrene (IV).—The results of experiments with IV are shown in Table I. Throughout the range of temperatures investigated, all the selenium other than elemental selenium, appears as hydrogen selenide. At lower temperatures, *e.g.* 240°, the yield of phenanthrene is more than three times that which would be expected on the basis of hydrogen selenide evolution. The nonstoichiometric character of the reaction at lower temperatures is similar to that obtained with guaiene. At 290° the yield of phenanthrene is much greater than at the lower temperatures and the reaction is essentially a stoichiometric one.

β,β'-Dinaphthyl Diselenide.—The successful use of an alkyl disulfide for the dehydrogenation of tetralin to naphthalene has been reported,[8] and recently diphenyl disulfide has been used as a dehydrogenation agent in the aromatization of certain sesquiterpenes such as guaiol.[9] We have found that dehydrogenation of guaiene by β,β'-dinaphthyl diselenide at 290° gave results similar to those obtained by the dehydrogenation of guaiene using elemental selenium. The results are shown in Table II. Hydrogen selenide evolution began a few minutes after initial heating and yields of guaiazulene were substantially the same (12–14% for one hour at 290°) as those found with elemental selenium. On working up the reaction mixture, a small amount of selenium–guaiene complex was isolated. The complex was identical to that obtained previously in experiments with elemental selenium. Part of the diselenide was recovered as the monoselenide. Dehydrogenation of guaiene at 200° by β,β'-dinaphthyl diselenide gave considerably lower yields of guaiazulene than those obtained at 290°. However, no hydrogen selenide evolution was observed throughout the reactions conducted at 200°, whereas appreciable quantities were evolved at 290°. There was no indication of a selenium–guiaene complex. The β,β'-dinaphthyl diselenide was recovered almost quantitatively in the 200° experiment.

TABLE II

DEHYDROGENATION OF GUAIENE (1.25 MMOLES) BY β,β'-DINAPHTHYL DISELENIDE (1.25 MMOLES)

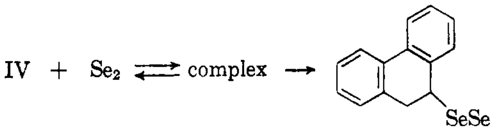
Temp., °C.	Time, min.	Total guaiazulene mmole[a]	Total guaiazulene %	Selenium as H_2Se, mmole[b]
290	30	0.19	15	0.11
290	60	.15	12	.28
290	90	.19	15	.54
290	120	.18	14	.62
200	60	.08	6	None
200	300	.11	9	None

[a] Determined by ultraviolet absorption spectroscopy. [b] Precipitated as PbSe.

Discussion

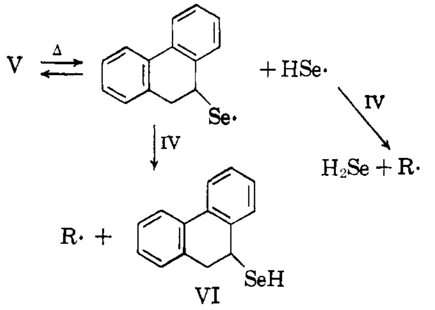
Because of the instability and reactivity of the possible organoselenium intermediates formed during the dehydrogenation reactions, it is difficult to reconstruct the sequence of reactions which occur. Nevertheless, most of the results can be rationalized on the basis of several known individual steps and by assuming reasonable intermediates.

Reversible π-complex formation between selenium and an isolated double bond or between selenium and an aromatic system is known.[2] Rearrangement of this complex is postulated to occur if allylic (or benzylic) hydrogens are available and the rearranged (sigma) complex might be a hydroperselenide.[6] Using 9,10-dihydrophenanthrene as a model, the reactions may be written as follows:



V

Thermal dissociation of V could give HSe· and RSe·, each of which is capable of hydrogen abstraction from another hydroaromatic molecule to give respectively hydrogen selenide and a selenol:

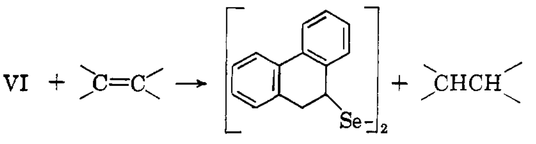


The reactive selenol could lead to aromatic product by three routes. First, there may be thermal decomposition to hydrogen selenide and an olefin:

$$\mathrm{VI} \xrightarrow{\Delta} H_2Se + \text{phenanthrene}$$

The driving force toward aromatization would facilitate hydrogen selenide elimination from these selenols already close to being completely aromatic. The stoichiometric dehydrogenation of II, III, and IV at high temperature can be explained in this manner.

A second reaction of selenols in the absence of air, may consist of oxidation to a diselenide achieved by simultaneous reduction of a double bond:



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[8] J. J. Ritter and E. D. Sharpe, *J. Am. Chem. Soc.*, **59**, 2351 (1937).

[9] J. P. Morizur and R. Pallaud, *Compt. rend.*, **251**, 2043 (1960).

Either added oleic acid or the hydroaromatic itself might function as the hydrogen acceptor. Guaiene has a particularly favorable structure for this role. It is also possible that the final aromatic compound under some conditions might be a hydrogen acceptor.

A third reaction of the selenol might consist of homolytic cleavage of the C—Se bond followed by radical disproportionation to form aromatic product:

$$2\text{VI} \longrightarrow 2\text{HSe}\cdot + \text{phenanthrene} + \text{IV}$$

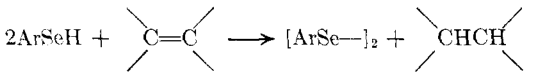
Other reaction paths that produce the hydrocarbon radical could similarly lead to disproportionations.

Aryl Diselenides.—The dehydrogenation of guaiene by β,β'-dinaphthyl diselenide at lower temperatures may proceed by dissociation of the diselenide to organoselenium radicals:

$$\text{ArSeSeAr} \overset{\Delta}{\rightleftharpoons} 2\text{ArSe}\cdot$$

The radicals in the presence of a hydrogen donor (guaiene) abstract hydrogen to give the selenol. Regeneration of the diselenide may occur by reaction of the selenol with the external double bond of guaiene and guaiazulene is finally produced by radical disproportionation:

$$\text{ArSe}\cdot + \text{guaiene} \longrightarrow \text{ArSeH} + \text{R}\cdot$$



$$2\text{ArSeH} + {>}\text{C}{=}\text{C}{<} \longrightarrow [\text{ArSe}\text{—}]_2 + {>}\text{CHCH}{<}$$

$$2\text{R}\cdot \longrightarrow \text{saturate} + \text{aromatic}$$

At higher temperatures (290°), the dehydrogenation of guaiene with the diselenide was essentially similar to that observed with elemental selenium. Presumably, the aryl diselenide decomposes to elemental selenium and monoselenide.

Thermal decomposition of diphenyl diselenide alone at the same temperature gives diphenyl monoselenide and what appears to be an impure new compound which may be a diphenyl triselenide, since it readily decomposes to elemental selenium and diphenyl diselenide:

$$\begin{tikzcd}\text{ArSeSeAr} \arrow[r, shift left, "\Delta"] & \text{ArSe}_3\text{Ar} + \text{ArSeAr} \arrow[l, shift left] \arrow[d, shift right] \\ & \text{ArSeSeAr} + \text{Se} \arrow[u, shift right]\end{tikzcd}$$

Heating stoichiometric amounts of diphenyl monoselenide and elemental selenium, as well as diphenyl diselenide and elemental selenium to 280–300° gave the same mixture believed to contain the triselenide. Diphenyl diselenide has been prepared by heating diphenyl monoselenide with selenium, and diphenyl diselenide gives diphenyl monoselenide on heating,[10] so apparently all the reactions are reversible. Since at about 290° elemental selenium, mono-, di-, and triselenide coexist, the similarity in the dehydrogenations of guaiene with elemental selenium and with the aryl diselenide is not unexpected. Although other diaryl triselenides are known,[11] diphenyl triselenide has not been prepared. Our compound, presumed to be impure diphenyl triselenide, apparently exists in two forms. The unstable form (yellow) is prepared by irradiating the stable form (red) with ultraviolet light. Although we have no basis on which to propose structures at this time, it is possible that the red and yellow forms of the triselenide represent a cyclic and open chain structure, respectively.

Acknowledgment.—The authors wish to thank the National Science Foundation for a grant (NSF-G-14459) which made this work possible.

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[10] H. Bauer, *Ber.*, **46**, 92 (1913).

[11] H. Rheinboldt and E. Giesbrecht, *ibid.*, **88**, 1 (1955).

Preparation and Reactions of Some Phosphobetaines[1]

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Triphenylphosphine has been allowed to react with chloroacetic acid, β-chloropropionic acid, and γ-chlorobutyric acid. In each case the carboxyalkyltriphenylphosphonium salt was obtained. The salt from chloroacetic acid decarboxylated on heating or on treatment with base. The two other salts on treatment with base gave stable phosphobetaines. The chemistry of these materials is discussed. Triphenylphosphine and bromoacetic acid reacted, under several sets of conditions, to give triphenylphosphine oxide and acetyl bromide.

There have been several reports concerning the preparation of phosphobetaines, I, $n = 1$.[3] The data concerning these substances was quite sparse and there was reason for doubting the structural assignments.

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[1] A preliminary account appeared in *Chem. Ind.* (London), 290 (1961).

[2] National Science Foundation Coöperative Graduate Fellow, 1959–1960.

[3] (a) A. Michaelis and H. v Gimborn, *Ber.*, **27**, 272 (1894); (b) D. E. Worrall, *J. Am. Chem. Soc.*, **52**, 2933 (1930); (c) A. Michaelis, *Ann.*, **293**, 288 (1896); (d) A. H. Meyer, *Ber.*, **4**, 734 (1871).