Selenium Heterocycles. VI.[1] Mechanism of the Stereoselective Formation of 1,4-Diselenafulvenes from 1,2,3-Selenadiazoles and Base

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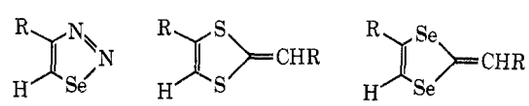
4-Substituted 1,2,3-selenadiazoles were found to react with base to form 2,ω-disubstituted 1,4-diselenafulvenes. The mechanism for the stereoselective formation of the product is discussed.

We have previously reported the synthesis of 1,2,3-selenadiazoles (I).[2] Light- and heat-induced decomposition of these new compounds produced substituted acetylenes[3] while the sulfur analog produced the dithiafulvene (II).[4] In an effort to obtain the selenium analog of II various basic reagents were examined. Good results were obtained with alcoholic solutions of potassium hydroxide or potassium ethoxide in ethanol or by the addition of potassium hydroxide pellets to ethanolic solutions of the selenadiazole. This resulted in an immediate effervesence of nitrogen gas and production of a new organoselenium compound (no reaction occurred when 5-substituted selenadiazoles were used). Elemental analysis and the mass spectra of these compounds were in agreement with a diselenafulvene structure (III). The nmr spectra of the more easily



I II III

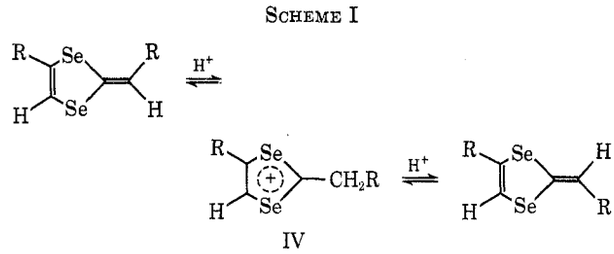
obtained fulvene from 4-aryl-1,2,3-selenadiazoles were unrevealing, since H_3 and H_ω of the ylidenes had signals in the aromatic region.

Useful spectra were obtained of the fulvenes formed from 4-alkyl derivatives such as 4-isopropylselenadiazole. Figure 1 shows the nmr spectrum of the diisopropyl-substituted derivative (III, R = isopropyl). The protons of the isopropyl groups are clearly resolved into two doublets at 1.10 ppm for the two different methyl groups and two septets for the two methine hydrogens at 2.00 and 2.66 ppm. In the low-field part of the spectrum two groups of hydrogens are observed, each integrating for one hydrogen. The signal at 6.46 ppm shows the characteristic ^{77}Se splitting pattern, with a coupling constant of 57 cps.[2] This is obviously due to the proton at position 3 in the ring, and appears to be a triplet (probably the result of the superposition of a double doublet). The signals at 5.60 ppm resolve into a doublet of doublets and a doublet. Integration shows the relative intensities of the doublet of doublets to the doublet signal to be 1:1. This spectrum can be rationalized by the presence of a mixture of two isomers. In one the two isopropyl groups are in the cis and in the other in the trans configuration. Possibly larger long-range coupling constants of the two olefinic protons in the trans configuration would result in the splitting of H_ω into a doublet and of H_3 into what appears to be a triplet.

Rapid and careful work-up of the reaction mixture resulted in a product which showed the nmr spectrum shown in Figure 2. The doublet of doublets at 5.60 ppm is reduced to a doublet and the triplet at 6.46 ppm appears now as a narrow doublet. Leaving the sample in the nmr tube for several hours resulted in the reappearance of the former spectrum (Figure 1). Clearly the product of rapid and careful work-up is a single isomer which on standing isomerizes into a mixture of the cis and the trans isomers. The rate of isomerization can be enhanced by the addition of a trace of an acid. It is noteworthy that the similar base-catalyzed dimerization of 4-phenyl-1,2,3-thiadiazole is reported to yield II (R = Ph).[5] In this series the initially obtained solid was converted to a higher melting material of the same composition on heating, a finding which was interpreted as the conversion of a cis–trans isomer mixture to the more stable isomer.[5] The possibility that the initially isolated substance was a pure isomer from a stereospecific reaction was not considered and no nmr evidence pertinent to this point was given.[6]

It appears that the isomerization happens as shown in Scheme I *via* the diselenolium ion IV. Evidence for

SCHEME I



IV

the existence of IV in solution was obtained from the nmr spectrum of the pure cis or the trans isomer of III (R = Ph) in trifluoroacetic acid. In this solvent a peak appears at 4.30 ppm for the methylene protons of IV integrating for two hydrogens relative to the aromatic region's 11 hydrogens at 7.10 ppm.

An equilibrium mixture of the *cis*- and *trans*-di-*tert*-butyl derivative of III (R = *tert*-butyl) could be

(1) Part V: A. Shafiee and I. Lalezari, *J. Heterocycl. Chem.*, **8**, 835 (1971).

(2) I. Lalezari, A. Shafiee, and M. Yalpani, *Tetrahedron Lett.*, 5105 (1969); I. Lalezari, A. Shafiee, and M. Yalpani, *J. Org. Chem.*, **36**, 2836 (1971).

(3) I. Lalezari, A. Shafiee, and M. Yalpani, *Angew. Chem., Int. Ed. Engl.*, **9**, 464 (1970).

(4) W. Kirmse and L. Horner, *Justus Liebigs Ann. Chem.*, **614**, 4 (1958).

(5) R. Raap and R. G. Micetich, *Can. J. Chem.*, **46**, 1057 (1968); R. Raap, *ibid.*, **46**, 2251 (1968).

(6) We have observed a definite stereoselectivity in the conversion of the thiadiazoles to the corresponding dithiafulvenes. These findings will be reported elsewhere.

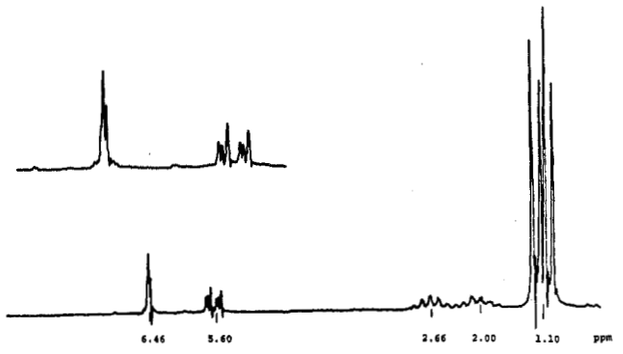


Figure 1.—Nmr spectrum of a mixture of *cis*- and *trans*-2,ω-diisopropyl-1,4-diselenafulvenes.

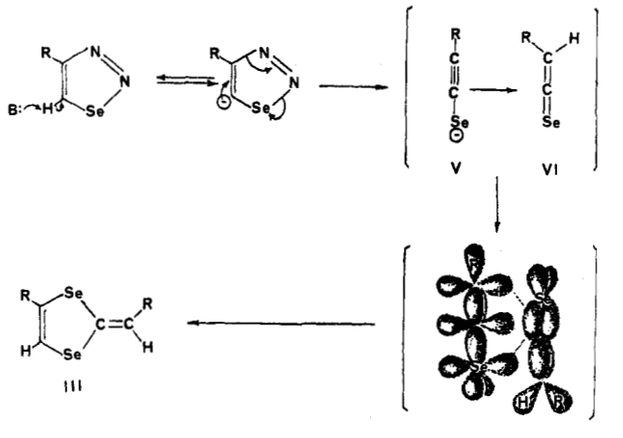
crystallized from acetone to yield one of the isomers in pure form leaving an equilibrium mixture in the mother liquor. Repeated crystallizations from the mother liquor nearly completely converted the material into the one isomer.

In analogy with the base-catalyzed decomposition of 1,2,3-thiadiazoles, the intermediate V could be obtained as an insoluble potassium salt when the reaction was carried out in dioxane using alcoholic potassium ethoxide as a base. This salt showed an acetylenic band at 2200 cm^{-1} in the ir and an ultraviolet band at 308 nm. Dissolving this salt in 95% alcohol converted it slowly but quantitatively into the same pure isomer of III that would be formed directly from the selenadiazole.

The factor that controls this stereoselectivity in an apparently symmetrical intermediate is probably the steric hindrance of a relatively bulky R group on the selenaketene. This could lead to a preferred approach of the selenaketene from the hydrogen side. Consistent with this mechanism, when a smaller R group, such as methyl, was used, no matter how carefully the work-up was carried out, the product was always a mixture of the two isomers.

Scheme II shows a mechanism which would account for the products obtained. Evidence for the first step

SCHEME II



in this mechanism has been obtained in the exchange of deuterium for protium in a sample of I (5-deuterio, R = Ph) in dilute alcoholic potassium hydroxide solution. The exchange was observed to take place faster than the ring cleavage.[7] The ring scission I to V

(7) M. H. Ghandehari, D. Davallian, S. G. Shirazi, H. Partovi, and M. Yalpani, unpublished results.

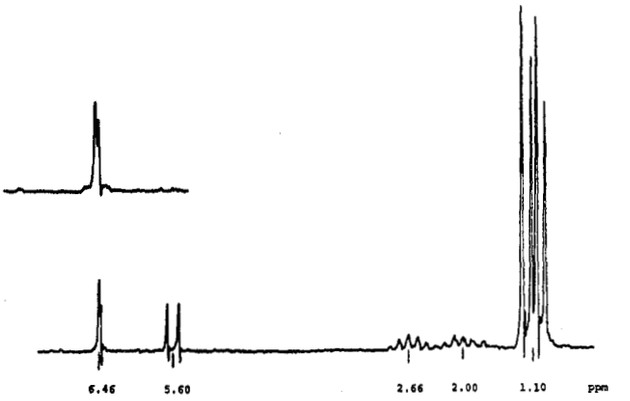


Figure 2.—Nmr spectrum of *cis*-2,ω-diisopropyl-1,4-diselenafulvene.

cannot therefore be a concerted reaction starting with the elimination of a proton by base and the C_5 carbanion species must be a discrete intermediate. The scheme also indicates that the isomer initially formed is in the cis configuration. The larger H_3–H_ω long-range coupling constants observed for the products after isomerization (see Figure 1) is in agreement with the trans configuration for the second isomer.

The initial formation of the cis isomer from the intermediate selenaketene VI is interesting because it indicates the presence of a pure C–Se double bond the π orbitals of which require a particular geometry of approach in a concerted 1,3-dipolar addition to the ethynylselenolate ion V. As indicated in Scheme II, in the transition state the approach of the selenolate ion to the selenaketene must be in the plane of the ketene substituents as well as that of the π orbitals of the C–Se double bond. This constitutes a sterically unfavorable approach relative to that of an approach 90° out of that same plane. The latter experiences the least effect of the substituents but would require orbital rearrangement subsequent to the initial Se–C bond formation, and would lead to the formation of a mixture of both geometric isomers, which was not observed. In Woodward–Hoffmann terminology the reaction is thus probably best interpreted as a symmetry-allowed one-step ($_\pi4_s + {}_\pi2_s$) cycloaddition of class C,[8] a category exemplified previously by most 1,3-dipolar cycloadditions. Examples of class C [4 + 2] cycloadditions of simple allyl anions have also been reported recently.[9]

Experimental Section

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Nmr spectra were determined using Varian A-60A and T-60 spectrometers. Infrared spectra were obtained from a Leitz Model III. Mass spectra were run on a Varian Model MAT CH5 instrument.

General Procedure for the Preparation of 1,4-Diselenafulvenes. Method A.—The selenadiazole[2] (0.1 g) was dissolved in about 3 ml of 95% ethanol and a KOH pellet was added. In most cases the evolution of N_2 gas on the surface of KOH usually commenced immediately. Heating increased the rate of the reaction. The 4-aryl derivatives, which are solids, usually crystallized in pure form out of solution at the end of the reaction and could be recrystallized from alcohol. The aliphatic derivatives are liquids and were purified by preparative tlc on silica gel using

(8) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 87.

(9) T. Kauffmann and E. Koeppelmann, *Angew. Chem., Int. Ed. Engl.*, **11**, 291 (1972).

chloroform or less polar solvents. Chromatographic purification always lead to the formation of the two geometrical isomers.

Method B.—The selenadiazole was dissolved in 10% KOH or potassium ethoxide in ethanol. The reaction product was purified as described in method A.

2,ω-Di-*tert*-butyl-1,4-diselenafulvene.—4-*tert*-Butyl-1,2,3-selenadiazole (0.5 g, 2.6 mmol) was dissolved in 10 ml of 95% ethanol and a pellet of KOH was added. After the gas evolution had ceased water was added and extracted with chloroform. The chloroform layer after drying was evaporated to yield 0.3 g (72%) of an oil: nmr (CCl_4) 6.45 (s, 1 H), 5.90 (s, 1 H), 1.20 (s, 9 H), 1.10 (s, 9 H); upon standing for some times 6.45 (s, 0.5 H), 6.44 (d, J = 1.5 Hz, 0.5 H), 5.97 (d, J = 1.5 Hz, 0.5 H) 5.90 (s, 0.5 H), 1.29 (two lines, 9 H), 1.10 (two lines, 9 H). Repeated recrystallization from acetone gave a product: mp 78–80° (*Anal.* Calcd for $C_{12}H_{20}Se_2$: C, 44.72; H, 6.21. Found: C, 44.81; H, 6.02.); nmr (CCl_4) 6.44 (d, J = 1.5 Hz, 1 H) 5.97 (d, J = 1.5 Hz, 1 H), 1.21 (s, 9 H) 1.10 (s, 9 H); mol wt (mass spectrum) m/e 324.

2,ω-Diphenyl-1,4-diselenafulvene.—4-Phenyl-1,2,3-selenadiazole (2.2 g, 0.01 mol) was dissolved in about 15 ml of ethanol, and a few pellets of KOH were added. Upon heating the solution slightly, gas evolution commenced. Yellowish crystals began to separate when gas evolution ceased. These crystals, ir (KBr) 912 (w), 900 (w), 890 (m), 821 (w), 846 (w), 840 (m), 835 (s), 692 (m), 512 cm^{-1} (m) (yield 1.5 g, 90%; another 0.1 g of material could be obtained from the mother liquor by trituration with water), had mp 139–140° and upon cooling and reheating melted at 219–220°: ir (KBr) 890 (m), 832 (m), 820 (m), 735 (s), 682 (s), 510 cm^{-1} (s); uv (EtOH) 340 nm (ϵ 1.8 × 10^4) (*Anal.* Calcd for $C_{16}H_{12}Se_2$: C, 53.04; H, 3.32. Found: C, 52.85; H, 3.06.); mol wt (mass spectrum) m/e 364.

2,ω-Diisopropyl-1,4-diselenafulvene.—4-Isopropyl-1,2,3-selenadiazole (1.0 g, 5.7 mmol) was dissolved in 10 ml of 95% ethanol, and a few pellets of KOH were added. After gas evolution had ceased, water was added and the solution was extracted with chloroform. From the chloroform extracts 0.6 g (79%) of an oil was isolated. The oil was purified on silica gel plates using petroleum ether as solvent, nmr shown in Figure 1, mol wt (mass spectrum) m/e 296. The nmr of the oil without purification on silica gel and obtained immediately after the reaction is shown in Figure 2.

Potassium 2-Phenylethyneselenolate.—4-Phenyl-1,2,3-selenadiazole (0.5 g, 2.4 mmol) was added to a solution of 50 mmol of potassium ethoxide in 50 ml of dioxane containing 2 ml of ethanol. After the gas evolution had ceased the precipitate was filtered under a dry atmosphere and washed with dry ether to give the white potassium salt, ir (KBr) 2200 cm^{-1}, uv (EtOH) 308 mm (ϵ 2.1 × 10^4). This salt, which was always formed contaminated with, apparently, some potassium ethoxide (the weight of material isolated was always more than the theoretically calculated amount and the percentage of potassium in the sample was variable, but always in excess of that calculated) rapidly turned yellow on standing in moist air. Dissolution of this salt in 10 ml of ethanol gave 0.42 g (99% based on 4-phenyl-1,2,3-selenadiazole) of III, mp 139–140°.

Registry No.—*cis*-III (R = Bu), 36912-13-7; *trans*-III (R = Bu), 36912-17-1; *cis*-III (R = Ph), 36912-14-8; *trans*-III (R = Ph), 36912-18-2; *cis*-III (R = *i*-Pr), 36912-15-9; *trans*-III (R = *i*-Pr), 36912-16-0; potassium 2-phenylethyneselenolate, 36928-61-7; 1,2,3-selenadiazole, 26223-16-5.

Sensitized Photolyses of DDT and Decyl Bromide

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The photolysis of alkyl halides can be sensitized by aromatic amines in oxygenated or degassed solutions. The photoproducts from irradiation of diethylaniline in the presence of decyl bromide in cyclohexane are decane (22.7%), *N*-ethylaniline (3.6%), *o*-decyl-*N*,*N*-diethylaniline (48.5%), *p*-decyl-*N*,*N*-diethylaniline (30.8%), and diethylaniline hydrobromide (88%). Similar yields are formed in solvents methanol, dimethylformamide, and benzene and the quantum yields for decyl bromide disappearance are similar to the value of 0.19 found for methanol solution. This photolysis is not quenched by oxygen or piperylene and decyl bromide photolysis is not sensitized by benzophenone. This implicates the excited singlet state of diethylaniline as the first reactive intermediate. A mechanism involving decyl radicals is proposed. Diethylaniline also sensitizes DDT degradation. In aerated methanol the following photoproducts are formed: DDD, DDE, DDCO, diethylaniline hydrochloride, methyl 1,1-bis(*p*-chlorophenyl)acetate, *cis*- and *trans*-1,1,4,4-tetrakis(*p*-chlorophenyl)-2,3-dichloro-2-butene, 1,1-bis(*p*-chlorophenyl)-2-(*p*-diethylaminophenyl)-2-methoxyethylene, and 1,1-bis(*p*-chlorophenyl)-2,2-bis(*p*-diethylaminophenyl)ethylene. Mechanistic hypotheses involving the 2,2-bis(*p*-chlorophenyl)-1,1-dichloromethyl radical are given. It is shown that in degassed solutions of DDT in ethanol or cyclohexane a radical chain reaction is initiated by 310-nm light which efficiently converts DDT to DDD. This reaction can be inhibited by dibutyl sulfide or hexyl mercaptan, and is quenched by oxygen. Oxygen quenching may explain the inefficiency of DDT degradation by sunlight.

It has been observed that aromatic amines can induce the photodecomposition of alkyl halides.[1-4] It seemed that this process might be applicable to halogenated pesticide degradation. We have, therefore, initiated a study of pesticide photolyses with particular attention to sensitization. It was hoped that new designs for degradable pesticides[5] and information about natural degradation pathways would result.

This paper reports results which enucleate this problem. Thus we have explored the feasibility of degrading the persistent pesticide DDT with several photosensitizers both under air and under nitrogen and we have studied the photolysis of a simple alkyl halide in order to gain more mechanistic insight into the processes available to halogenated pesticides.

The photosensitization of pesticide degradation has not escaped attention by other chemists. Casida and Ivie[6] placed mixtures of known photosensitizers and pesticides on silica gel and found that several pesticides, including halogenated compounds, were degraded in sunlight. They also investigated the solar decomposition of chlorinated pesticides on bean leaves as accelerated by rotenone, triphenylamine, and other insecticides.

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(5) H. J. Liu, P. J. Silk, and J. Unger, *Can. J. Chem.*, **50**, 55 (1972).
(6) G. W. Ivie and J. E. Casida, *Science*, **167**, 1620 (1970); G. W. Ivie and J. E. Casida, *J. Agr. Food Chem.*, **19**, 405 410 (1971).