exo-**1** ($n = 2$). The flask was stoppered and stirred at 41° for 34 hr. Work-up as described above gave 150 mg of a product whose nmr spectrum was consistant with that of known *endo*-**2** ($n = 2$) and displayed no *exo*-**2** aldehydic signal at 9.1 ppm.[9] Air oxidation of the carboxaldehyde gave an acid identical with authentic bicyclo[4.1.0]heptane-7-*endo*-carboxylic acid (**4**, $n = 2$).[11]

The reaction of 30 mg of *exo*-**1** ($n = 1$) with 11 mg of lithium thiocyanate in 0.5 ml of ether at 40° for 48 hr resulted in the recovery of starting material.

Rearrangement and Epimerization Reactions of 1 in $CDCl_3$.—Samples of the epoxides **1** were dissolved in 0.4 ml of $CDCl_3$ and the nmr spectrum was recorded. Solid lithium iodide was then added to the nmr tube which was shaken briefly (the lithium iodide is only partially soluble in $CDCl_3$) and the spectrum was recorded immediately. The lithium iodide contained ether[21] (*ca.* 20% by weight) whose proton absorptions were utilized as an internal standard. Periodic scans showed changes in absorption for the epoxide and aldehydic protons (see Table I). Integration of the peaks in these regions relative to one another allowed a determination of the progress of the reaction, and integration relative to the ether proton signals substantiated the proton count. Data for the individual reactions of 55 mg of *exo*-**1** ($n = 1$) and 55 mg of *exo*-**1** ($n = 2$), both with 60 mg of lithium iodide, are listed in Table I.

A similar experiment with 53 mg of *endo*-**1** ($n = 2$) and 30 mg of lithium iodide produced a 90:10 product mixture of *exo*-**2**:-*endo*-**1** ($n = 2$) after 14 hr as determined by nmr and vpc analyses. The rates of the above reactions in $CDCl_3$ are extremely slow when the molar ratio of lithium iodide to epoxide is less than 1:5.

Silver Oxide Oxidation of *exo*-2.—Following reported procedures,[10] 60 mg of *exo*-**2** ($n = 2$) in 0.5 ml of ethanol and 0.60 g of silver nitrate in 1.0 ml of water were placed in a 10-ml round-bottom flask. To this was added dropwise with stirring a solution of 0.20 g of sodium hydroxide in 2.0 ml of water. After being stirred for 1 hr, the reaction mixture was filtered and the filtrate acidified with 3 *N* HCl. The white solid was filtered (46.4 mg) and the aqueous solution extracted with ether to yield, after evaporation, another 15.0 mg of solid. Recrystallization from hexane gave crystals which had mp 95–96° (reported[11] for bicyclo[4.1.0]heptane-7-*exo*-carboxylic acid, mp 95–96.5°).

In identical fashion, *exo*-**2** ($n = 1$) gives a white solid acid, mp 58° (reported[10] for bicyclo[3.1.0]hexane-6-*exo*-carboxylic acid, mp 58°).

Registry No.—*exo*-**1** ($n = 1$), 18684-66-7; *exo*-**1** ($n = 2$), 28541-57-3; *endo*-**1** ($n = 2$), 28541-58-4.

Acknowledgment.—The author is grateful to the Petroleum Research Fund (1207-G1) and the Research Committee, UMSL, for financial support.

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[21] The ether is not essential. Similar results are obtained with commercial anhydrous lithium iodide (Alfa Inorganics, Beverly, Mass.).

The Synthesis and Diels–Alder Reactivity of 2-Ferrocenylbutadiene[1a]

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Received September 18, 1970

We wish to report on the synthesis and characterization of 2-ferrocenybutadiene and some of its Diels–Alder adducts. The synthetic approach taken to the title compound was through dehydration of 2-hydroxy-2-ferrocenylbutene. The latter compound may be obtained in good yield from reaction of the readily available acetylferrocene and vinylmagnesium bromide. The dehydration of the alcohol is a delicate procedure because of the acid and heat sensitivity of the diene product; a variety of acid-catalyzed routes to 2-ferrocenylbutadiene were attempted without success. The method of choice is reaction with methyl chloroformate in the presence of pyridine. The intermediate carbonate decomposes under the reaction conditions to give the desired product.

The current interest in α-ferrocenylcarbonium ions[2] coupled with the possible zwitterionic character of the Diels–Alder reaction[3] prompted a study of the Diels–Alder activity of 2-ferrocenylbutadiene. Dienophiles such as maleic anhydride, *p*-benzoquinone, nitrosobenzene, and acryloylferrocene were found to add readily to form 1:1 adducts. The characterization of these compounds is given in Table I. No attempts were made to isolate minor products. Attempted reactions with dimethyl maleate and with cyclohexene were unsuccessful. The former compound appeared to catalyze decomposition of the diene to unidentified products.

TABLE I

PROPERTIES OF THE DIELS–ALDER ADDUCTS OF 2-FERROCENYLBUTADIENE[a]

Dienophile[d]	Adduct mp, °C	Adduct nmr, δ
Maleic anhydride (12504-80-2)	147	5.95 (s, 1, vinyl), 4.26 (m, 4, ferrocenyl), 4.11 (s, 5, ferrocenyl), 3.40 (m, 2, methine), 2.55 (m, 4, methylene)
p-Benzoquinone (12504-81-3)	137–138	6.69 (s, 2, vinyl), 5.83 (m, 1, vinyl), 4.20 (m, 9, ferrocenyl), 3.30 (m, 2, methine), 2.60 (m, 4, methylene)
Nitrosobenzene[b] (12504-82-4)	86–87	7.22 (m, 5, phenyl), 5.92 (m, 1, vinyl), 4.48 (m, 2, methylene), 4.36 (m, 2, ferrocenyl), 4.21 (m, 2, ferrocenyl), 4.11 (s overlapping m, 7, ferrocenyl and methylene)
Acryloylferrocene[c] (12504-89-1)	161–162	5.96 (m, 1, vinyl), 4.82 (m, 2, ferrocenyl), 4.51 (m, 2, ferrocenyl), 4.33 (m, 2, ferrocenyl), 4.21 (s, ferrocenyl), 4.10 (s, ferrocenyl); total area 4.21 + 4.10 = 12

[a] Satisfactory analysis for C, H, and Fe were obtained for the adducts in this table. The data were made available to the referees and to the editor. [b] The expected product is 2-phenyl-5-ferrocenyl-3,6-dihydro-1,2-oxazine. See ref 2. [c] The expected product is 1-ferrocenyl-4-ferrocenoylcyclohexene-1. See ref 3d. [d] Registry numbers appear in parentheses.

It is concluded that 2-ferrocenylbutadiene is an active diene with a variety of dienophiles. More detailed studies are necessary to adequately weigh the electronic and steric effects of the 2-ferrocenyl group.

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[1] (a) This work was sponsored by the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract DAAH01-70-C-0146. (b) Rohm and Haas Co., Spring House, Pa. 19477.

[2] See J. Feinburg and M. Rosenblum, *J. Amer. Chem. Soc.*, **91**, 4324 (1969), and references cited therein.

[3] For recent discussions on the mechanism of the Diels–Alder reaction, see (a) S. Seltzer, *Advan. Alicycl. Chem.*, **2**, 1 (1968); (b) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970; (c) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967); (d) J. A. Titov, *Russ. Chem. Rev.*, 267 (1962).

Experimental Section

The melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Unless noted all nmr spectra were obtained on a Varian A-60 spectrometer, with deuteriochloroform as solvent and tetramethylsilane as the internal standard.

Preparation of 2-Hydroxy-2-ferrocenylbutene.—A 2.13 *M* vinylmagnesium bromide solution in tetrahydrofuran (12 ml) was added over a 20-min period to a solution of 5.0 g of acetylferrocene[4] in 40 ml of dry tetrahydrofuran. The solution was refluxed for 2 hr and then allowed to cool to room temperature. A solution of aqueous ammonia saturated with ammonium chloride was added until a solid precipitated from solution. The mixture was filtered, and the residue was washed with ether and combined with the filtrate. The combined ether solution was washed with water until neutral and dried ($MgSO_4$), and the solvent removed under reduced pressure to leave a deep red oil. This material was stored at 0° and used without purification. The yield was 5.2 g (93%); ir (CCl_4) 3400, 3100, 1635, 1100, 998, and 815 cm^{-1}; nmr (CCl_4) 6.15 (m, 2, vinyl), 4.10 (m, 9, ferrocenyl), 2.62 (s, 1, hydroxyl), 1.48 (s, 3, methyl).

Preparation of 2-Ferrocenylbutadiene.—To a solution of 15.0 g (59 mmol) of 2-hydroxy-2-ferrocenylbutene and 11.5 g (145 mmol) of pyridine in 300 ml of dry benzene, a solution of 12.3 g (130 mmol) of methyl chloroformate in 50 ml of benzene was added over a 1-hr period. The temperature was controlled at 5° during the addition. After the addition was complete, the solution was allowed to warm to ambient temperature and the stirring continued until gas evolution ceased (about 16 hr). The reaction solution was washed three times with 250-ml portions of water and dried ($MgSO_4$), and the solvent removed under reduced pressure without heating. The resulting oil was extracted with 500 ml of pentane. Methylene chloride (16 ml) was added to the pentane solution, and the resulting solution passed through a silica gel (100–200 mesh) column cooled to 5°. The 2-ferrocenylbutadiene is the only component of the reaction solution which passed through the column under these conditions. After solvent removal at low temperature, 5.6 g (40%) of a deep red, heavy oil is obtained: ir (CCl_4) 3110, 1650, 1585, 1105, 1000, 918, and 818 cm^{-1}; nmr ($CDCl_3$) 7.0–5.0 (m, 5, vinyl), 4.35 (m, 2, ferrocenyl), 4.22 (m, 2, ferrocenyl), 4.10 (s, 5, ferrocenyl).

Anal. Calcd for $C_{14}H_{14}Fe$: C, 70.62; H, 5.93; Fe, 23.46. Found: C, 70.96; H, 6.03; Fe, 23.80.

This compound was stored at 0° as a 25% solution in benzene.

Preparation of Acryloylferrocene.—β-Dimethylaminopropionylferrocene hydrochloride was prepared by the method of Hauser, Pruett, and Mashburn[5] from acetylferrocene, formaldehyde, and dimethylamine hydrochloride. The hydrochloride salt was dissolved in water and neutralized with sodium hydroxide, and the free amine extracted into ether. Methyl iodide (1 equiv) was added to the ether solution and the mixture allowed to stand for 12 hr. The resulting quaternary ammonium salt was then filtered from the ether and suspended in a two-phase solution of methylene chloride and sodium hydroxide-water. The sodium hydroxide was in fivefold excess. The three-phase system was stirred until the solid disappeared and a deep red color developed. The organic layer was then separated and dried ($MgSO_4$), and the solvent removed under reduced pressure leaving a red oil which can be crystallized from ethanol–water. (It was sometimes necessary to chromatograph the oil through silica gel before recrystallization.) Yields varied from 30 to 70%. The product melted at 72.5–73° (lit.[5] 73.5–74°).

General Procedure for the Preparation of the Diels–Alder Adducts.—The dienophile (1 equiv) was added to a 25% solution of 2-ferrocenylbutadiene in benzene. The reaction solution was stirred at ambient temperature until the diene ir peaks at 918 and 880 cm^{-1} vanished (15 min–20 hr). In the case of maleic anhydride, the product precipitated from the reaction mixture after 15 min. With acryloylferrocene and *p*-benzoquinone, the products precipitated when the reaction solution was poured into a 20-fold excess of pentane. With nitrosobenzene, the solvent was stripped from the reaction mixture and the resulting oil passed through a silica gel (100–200 mesh) column. The product was eluted with a pentane–methylene chloride ratio of 5:1. All the adducts were recrystallized from hot ethanol.

Registry No.—2-Ferrocenylbutadiene, 12-504-78-8; 2-hydroxy-2-ferrocenylbutene, 12504-79-9.

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The Formation of Sulfur–Selenium and Selenium–Selenium Bonds by Chloramination

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Received September 25, 1970

The various reactions of chloramines R_2NCl ($R =$ alkyl or H) with amines, phosphines, arsines, and stibines have been extensively investigated in this laboratory.[1-10] Sisler, *et al.*,[11] have recently shown that chloramines bring about the oxidative coupling of thiols to yield disulfides, RSSR. We were interested in determining whether similar chloramination reactions with selenols or mixtures of thiols and selenols would yield RSeSeR′ or RS–SeR′ compounds (R or R′ is an aryl or alkyl group and R and R′ may be identical or different).

There are numerous references[12-18] to the preparation of diselenides by methods other than chloramination. Likewise, the formation of compounds containing sulfur–selenium bonds by methods[16,19,20] other than chloramination have been reported.

We have, therefore, studied the reactions of chloramine and of dimethylchloramine with several selenols and with mixtures of thiols and selenols and have found that these reactions provide methods for the synthesis of diselenides and selenosulfides which are more convenient than previously described methods and which, in a number of instances, give a purer product in higher yields.

Experimental Section

Materials.—Selenophenol, thiophenol, and 1-butanethiol were obtained from Eastman Organic Chemicals. Magnesium turnings, selenium powder, and *n*-butyl bromide were obtained from Fischer Scientific Co., and 2-naphthalenethiol was obtained from J. T. Baker Chemical Co. The purities of the thiols and selenols

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