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.

(4) C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 482 (1957).

(5) C. R. Hauser, R. L. Pruett, and T. A. Mashburn, Jr., *ibid.*, **26**, 1800 (1961).

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

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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

(1) H. H. Sisler and S. R. Jain, *Inorg. Chem.*, **7**, 104 (1968).
(2) R. E. Highsmith and H. H. Sisler, *ibid.*, **7**, 1740 (1968).
(3) K. Utvary and H. H. Sisler, *ibid.*, **7**, 698 (1968).
(4) K. Utvary, H. H. Sisler, and P. Kitzmantel, *Monatsh. Chem.*, **100**, 401 (1969).
(5) R. E. Highsmith and H. H. Sisler, *Inorg. Chem.*, **8**, 1029 (1969).
(6) L. K. Krannich and H. H. Sisler, *ibid.*, **8**, 1032 (1969).
(7) S. R. Jain and H. H. Sisler, *ibid.*, **8**, 1243 (1969).
(8) J. C. Summers and H. H. Sisler, *ibid.*, **9**, 862 (1970).
(9) H. H. Sisler, R. M. Kren, and K. Utvary, *ibid.*, **8**, 2007 (1969).
(10) R. M. Kren and H. H. Sisler, *ibid.*, **9**, 836 (1970).
(11) H. H. Sisler, N. K. Kotia, and R. E. Highsmith, *J. Org. Chem.*, **35**, 1752 (1970).
(12) S. Keimatsu and K. Yokota, *J. Pharm. Soc. Jap.*, **50**, 531 (1930).
(13) D. G. Foster, *Recl. Trav. Chim. Pays-Bas*, **53**, 405 (1934).
(14) H. Rheinboldt and M. Perrier, *Bull. Soc. Chim. Fr.*, 759 (1950).
(15) H. Rheinboldt and E. Giesbrecht, *Ber.*, **88**, 666 (1955).
(16) M. Nakasaki, *J. Chem. Soc. Jap.*, **75**, 338 (1954).
(17) J. D. McCullough, T. W. Campbell, and E. S. Gould, *J. Amer. Chem. Soc.*, **72**, 5753 (1950).
(18) G. H. Denison, Jr., and P. C. Condit, U. S. Patent 2,528,346 (1950).
(19) O. Foss, *J. Amer. Chem. Soc.*, **69**, 2236 (1947).
(20) H. Rheinboldt and E. Giesbrecht, *Justus Liebigs Ann. Chem.*, **568**, 198 (1950).

TABLE I
RESULTS OF CHLORAMINATION REACTIONS

Reactants A	Reactants B	Reactants C[c]	Mole ratio (reactants) A:B:C or A:C	Products[a]	Mole ratio (products)	Bp (mm) or mp, °C	Yield[b] %
C_6H_5SeH		$(CH_3)_2NCl$	1.50:1.00	$C_6H_5SeSeC_6H_5$[d]		59–61[e]	87
C_6H_5SeH		$NH_3 + NH_2Cl$	1.78:1.00	$C_6H_5SeSeC_6H_5$		59–60[e]	88
n-C_4H_9SeH		$(CH_3)_2NCl$	1.48:1.00	$C_4H_9SeSeC_4H_9$		106–7(4)[f]	89
n-C_4H_9SeH		$NH_3 + NH_2Cl$	1.64:1.00	$C_4H_9SeSeC_4H_9$		114–15 (8–9)	86
C_6H_5SH	C_6H_5SeH	$(CH_3)_2NCl$	1.00:1.00:1.07	$C_6H_5SSeC_6H_5$[g,h]		57–58[e]	85
C_6H_5SH	C_6H_5SeH	$NH_3 + NH_2Cl$	1.00:1.00:1.08	$C_6H_5SSeC_6H_5$[i,h]		57–58[e]	88
n-C_4H_9SH	n-C_4H_9SeH	$(CH_3)_2NCl$	1.00:1.00:1.10	$C_4H_9SSC_4H_9$		91–92 (5.5)	
				$C_4H_9SeC_4H_9$	5.6:1.0:2.2	104–6 (5.5)	83
				$C_4H_9SeSeC_4H_9$		110–13 (5.5)	
n-C_4H_9SeH	C_6H_5SeH	$(CH_3)_2NCl$	1.00:1.00:1.14	$C_4H_9SeC_6H_5$		85–87 (2)	
				$C_4H_9SeSeC_4H_9$	1.0:1.8:2.6	93–95 (2)	81
				$C_6H_5SeSeC_6H_5$[j]		135–37 (0.5–0.6)	
n-C_4H_9SH	C_6H_5SeH	$(CH_3)_2NCl$	1.00:1.00:1.06	$C_4H_9SSC_4H_9$		69–71 (1.25)	
				$C_6H_5SeSeC_6H_5$[j]	4.0:3.5:1.0[k]	152–55 (0.8)	61
				$(C_4H_9)_2S_2SeC_6H_5$ (?)[l]		92–94 (1.0)[l]	
β-$C_{10}H_7SH$	C_6H_5SeH	$(CH_3)_2NCl$	1.00:1.00:1.06	$C_6H_5SeSeC_6H_5$	1.29:1.00	57–58	89
				β-$C_{10}H_7SS$-β-$C_{10}H_7$[m]		136–38	

[a] Ammonium chloride or dimethylammonium chloride was formed from chloramine and dimethylchloramine, respectively, in almost quantitative yields. [b] Based on selenol and thiol taken. In cases of mixtures of two selenols and/or thiols, the overall yield is reported. [c] C added dropwise to A or to an equimolecular mixture of A and B. [d] Shining yellow crystals from hot absolute alcohol. [e] Turns deep red when heated gradually above the melting point, but returns to original yellow color on gradual cooling. [f] Light yellow liquid, offensive odor. [g] *Anal.* Calcd for $C_{12}H_{10}SSe$: C, 54.3; H, 3.7; Se, 29.7. Found: C, 53.8; H, 3.9; Se, 29.7. [h] Brilliant yellow needles recrystallized from hot methanol. [i] *Anal.* Calcd for $C_{12}H_{10}SSe$: C, 54.3; H, 3.7. Found: C, 53.4; H, 3.7. The ir spectrum for it agrees with the product referred to by footnote *g*. [j] Solidifies in condenser; hot water condenser used. [k] Appreciable quantity of black material, presumably selenium, was left in distilling flask. [l] Orange-red liquid, wt = 1.7 g (Bu_2S_2 = 3.7 g, Ph_2Se_2 = 5.65 g); ^1H nmr spectrum shows phenyl, methylene, and methyl protons (ratio of phenyl protons to methylene and methyl protons = 5:18). *Anal.* Found: C, 49.70; H, 6.88; S, 19.16; Se, 23.65. Mol wt (by vapor press osmometer) 293.7 suggests empirical formula $C_{14}H_{23}S_2Se$. The vpc shows a single broad peak only. All data available suggests two butyl and one phenyl group and two sulfur and one selenium atom in the compound. It was not further characterized ($n^{22}D$ 1.4326; d^{25}_4 1.1230). [m] Partly insoluble in ether, separated from dimethylammonium chloride using benzene in which only the disulfide is soluble. More disulfide obtained by fractional crystallization of ethereal solution. $n^{20}D$'s for Bu_2Se, PhSeBu, Bu_2Se_2, Bu_2S_2, and Ph_2Se are respectively 1.4748, 1.5684, 1.5402, 1.4908, and 1.6476. d^{25}_4's for Bu_2Se, PhSeBu, Bu_2Se_2, Bu_2S_2 are respectively, 1.1432, 1.2210, 1.3982, and 0.921.

were checked by comparison of indices of refraction[21] and densities[21] ($n^{20}D$, respectively, for PhSeH, BuSeH, BuSH, and PhSH of 1.6142, 1.4740, 1.4416, 1.5788; and d^{25}_4, respectively, for PhSeH, BuSeH, BuSH, and PhSH of 1.4856, 1.2344, 0.8428, and 1.5860), infrared spectra,[22,23] and melting or boiling points[21] with the corresponding data in the literature. All solvents used were of reagent grade and were purified by appropriate means and stored over calcium hydride, except for absolute ethanol, which was used as received.

1-Butaneselenol was prepared[24] by the reaction of selenium with butylmagnesium bromide,[25] followed by treatment with gaseous hydrogen chloride. This selenol, a light yellow liquid, distils between 113 and 115°. The commonly poor yields of this selenol are presumably a result of the rapid oxidation of this compound to the corresponding diselenide.

Analyses.—The Galbraith Microanalytical Laboratory, Knoxville, Tenn., conducted the elemental analyses. Molecular weights were determined by vapor pressure osmometer (Model 320, Mechrobal Inc.). Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded with a Beckman Model IR-10 grating infrared spectrophotometer. ^1H nmr spectra were recorded with a Varian A-60 spectrometer.

All the sulfides, selenides, or selenosulfides prepared show bands in the region 300–700 cm^{-1} of the infrared spectrum. However, the infrared spectra are of limited use in these compounds, since only small differences in frequencies are found for the C–S, C–Se, S–S, S–Se, and Se–Se stretchings in the 300–700-cm^{-1} region. Moreover, the bands are frequently weak or poorly defined.

Synthesis of Chloramines.—Anhydrous chloramine was prepared by the method of Sisler and Mattair[26] which involves the gas-phase chlorination of ammonia. Ethereal solutions of chloramine were prepared by the procedure of Sisler and Gilson[27] and stored over calcium hydride at 0–5°. Dimethylchloramine was prepared by a procedure analogous to the Raschig synthesis of chloramine.[28] It was dissolved in diethyl ether and stored over calcium chloride.

General Procedure for Chloramination Reactions.—All manipulations were performed in an efficient hood or in an all-glass vacuum line. Chloramine and dimethylchloramine concentrations in reacting solutions were estimated iodometrically. An ethereal solution of chloramine or dimethylchloramine was added dropwise to a solution of the selenol (or a mixture of selenols or a mixture of a selenol and a thiol) in dry diethyl ether with constant stirring. The reactions were carried out at 25°, unless stated otherwise. Air and moisture were excluded. The reaction mixture soon became warm, dense white fumes were evolved, and a white precipitate formed immediately. In the initial stages, color changes of the reaction mixture from light yellow to orange-red were observed. The reaction mixture was stirred overnight, and was then refluxed for periods of from 1 to 2 hr. Ammonium chloride or dimethylammonium chloride, as the case may be, was removed by filtration. All the diselenides or selenosulfides reported herein are soluble in ether, except di-β-naphthyl disulfide. Ether and excess of chloramine were removed by reducing the pressure and trapping them in Dry Ice–acetone cooled traps. The products obtained were characterized by melting or boiling points,[29] infrared and proton magnetic resonance spectra, analytical data, and molecular weights. All analyses, unless otherwise noted, had percentages of C and H and molecular weights within 0.5% of the calculated values. The indices of refraction and densities (Table I) agree with reported literature values.[30,31] In cases of mixtures of compounds, fractional crys-

(21) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 1, Chemical Publishing Co., Inc., New York, N. Y., 1958, pp 62–69.
(22) N. Sheppard, *Trans. Faraday Soc.*, **46**, 429 (1950).
(23) N. Sharghi and I. Lalezari, *Spectrochim. Acta*, **20**, 237 (1964).
(24) E. P. Painter, *J. Amer. Chem. Soc.*, **69**, 229 (1947).
(25) H. Gilman and C. Meyers, *Org. Syn.*, **4**, 59 (1924).
(26) R. Mattair and H. H. Sisler, *J. Amer. Chem. Soc.*, **73**, 1619 (1951).
(27) I. T. Gilson and H. H. Sisler, *Inorg. Chem.*, **4**, 273 (1965).
(28) A. Berg, *Ann. Chim. Phys.*, **3**, 319 (1894).
(29) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 3, Chemical Publishing Co., Inc., New York, N. Y., 1958, pp 395–417.
(30) G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, 2089 (1962).
(31) M. Nardelli and L. Chierici, *Ann. Chim. (Rome)*, **42**, 111 (1952).

tallization or distillation was employed to separate the components, as shown in the Table I. The solids were recrystallized from appropriate solvents.

Reaction of 2-Sulfenamidopyridine with 2-Mercaptopyridine.—2-Sulfenamidopyridine (mp 79–80°) was prepared by the method of Hurley and Robinson[32] involving the reaction of an aqueous solution of chloramine with an aqueous solution of the sodium salt of 2-mercaptopyridine. 2-Sulfenamidopyridine was dissolved in diethyl ether and an equivalent amount of 2-mercaptopyridine (mp 127–28°) in diethyl ether was added to it dropwise at 0–5°. When the reaction mixture was allowed to stand for 2 hr and the ether evaporated, 2,2′-dipyridyl disulfide (mp 51–52°) was obtained in almost quantitative yields.

Results and Discussion

The synthesis of Se–Se and S–Se bonded compounds by the chloramination of corresponding selenols or mixtures of selenols and thiols is recommended because of its simplicity and the fact that the diselenide or selenosulfide is easily obtained in high purity and good yield.

The monoselenides reported in Table I might have been formed from the diselenides with the elimination of selenium ($R_1R_2Se_2 \rightarrow R_1R_2Se + Se$).

The exclusive formation of diphenyl selenosulfide from the chloramination of a mixture of thiophenol and selenophenol may reasonably be attributed to reactions of selenenyl halide (formed as an intermediate) and thiophenol or sulfenyl halide and selenophenol.

$$C_6H_5SCl + C_6H_5SeH \longrightarrow C_6H_5SSeC_6H_5 + HCl$$
$$C_6H_5SeCl + C_6H_5SH \longrightarrow C_6H_5SSeC_6H_5 + HCl$$

A possible alternative explanation[33] is that one of the reactants (*e.g.*, R′SH) may react with one of the symmetrical diselenides to produce the unsymmetrical compound RSSeR′. Since exchange is possible,[34,35] the distribution of diselenide and disulfide may have resulted in part from such disproportionation reactions as follow.

$$RSSR + R'SeSeR' \rightleftharpoons 2RSSeR'$$
$$RSSR + R'SeH \rightleftharpoons RSSeR' + RSH$$
$$RSeSeR + R'SH \rightleftharpoons RSSeR' + RSeH$$

However, the mild conditions of the reactions make such exchanges improbable.

It was observed that at room temperature the liquid diselenides are, in general, bright orange in color, but this coloration becomes less intense as the temperature is lowered. This suggests partial dissociation into RSe radicals, which increases with rising temperature. However, in our present investigations free radical mechanisms are improbable since the reactions have been studied in ether and at low temperature (25° or lower). Furthermore, it has been shown that the reactions proceed almost instantaneously even in the dark and there seems to be no induction period. This rules out the free radical mechanism for the formation of disulfides, diselenides, and selenosulfides.

Diselenides resemble the disulfides in their chemical properties. Thus, there is no cleavage of the Se–Se bond when diphenyl diselenide or di-*n*-butyl diselenide is treated with chloramine or dimethylchloramine in ether under various sets of experimental conditions (temperatures varying between 0 and 25°, reaction times up to 72 hr, and a variety of ratios of concentrations of reactants). The diselenide was almost quantitatively recovered in all such experiments. It was reported earlier[11] that sulfur–sulfur bonds are not cleaved by the action of chloramines on disulfides. This suggests that the formation of disulfide or diselenide is not the first step in the chloramination of thiols and selenols. Otherwise it is difficult to explain the formation of both sulfenamide and disulfide[11] by the action of chloramine on thiols in other media.

A possible mechanism may be the formation of the sulfenamide or selenenamide as the first step in the reaction equation

$$RXH + NR_2'Cl \xrightarrow[R' = H, CH_3]{X = S, Se} RXNR_2' + HCl$$

followed by the reaction with an additional molecule of RXH to form diselenide, disulfide, or selenosulfide.

$$RXH + RXNR_2' \xrightarrow[= \text{same or different}]{R \text{ and } X} RXXR + R_2'NH$$

The reaction of 2-sulfenamidopyridine with 2-pyridinethiol resulting in the formation of 2,2′-dipyridyl disulfide and also the reported formation of sulfenamides by reactions of aqueous solutions of chloramine over aqueous alkali mercaptides[32,36–38] support the above mechanism. Also reactions of sulfenamides resulting in the formation of disulfides have been reported in the literature.[36,38,39]

It is assumed in this mechanism that the reaction of the sulfenamide or selenenamide with thiol or selenol to form disulfide, diselenide, or selenosulfide is relatively fast in comparison with the reaction of chloramine with thiol or selenol to form sulfenamide or selenenamide.

The additional possibility of formation of compounds of the type RSCl or RSeCl as intermediates may also be considered.[36,40] This would be in accord with the the colors observed (from light yellow to orange-red) during the course of the reaction.[17,19] It is possible that the sulfenamide or selenenamide formed from the chloramination of selenol and thiol may be cleaved by hydrogen chloride[41,42] to give the corresponding sulfenyl or selenenyl chlorides. In this case, the sulfenyl or selenenyl chlorides so formed could react spontaneously with the thiols or selenols to give the disulfides, diselenides, or selenosulfides.[43–45]

Registry No.—$C_6H_5SeSeC_6H_5$, 1666-13-3; $C_4H_9SeSeC_4H_9$, 20333-40-8; $C_6H_5SSeC_6H_5$, 28622-58-4; C_4H_9-

(32) T. J. Hurley and M. A. Robinson, *J. Med. Chem.*, **8**, 888 (1965).
(33) H. Lecher, *Ber.*, **53B**, 591 (1920).
(34) G. Gorin, G. Doughterty, and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **71**, 3551 (1949).
(35) D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *ibid.*, **73**, 3627 (1951).
(36) E. L. Carr, G. E. P. Smith, and G. Alliger, *J. Org. Chem.*, **14**, 921 (1949).
(37) S. B. Greenbaum, *J. Amer. Chem. Soc.*, **76**, 6052 (1954).
(38) J. A. Baltrop and K. J. Morgan, *J. Chem. Soc.*, 3072 (1957).
(39) H. Lecher, *Ber.*, **58B**, 409 (1925).
(40) W. S. Cook and R. A. Donia, *J. Amer. Chem. Soc.*, **73**, 2275 (1951).
(41) J. H. Billman and E. O'Mahony, *ibid.*, **61**, 2340 (1939).
(42) M. L. Moore and T. B. Johnson, *ibid.*, **58**, 1091, 1960 (1936).
(43) H. Brintzinger and H. Schmahl, *Ber.*, **87**, 314 (1954).
(44) S. Magnusson, J. E. Christian, and G. L. Jenkins, *J. Amer. Pharm. Ass., Sci. Ed.*, **36**, 257 (1947).
(45) I. B. Douglass and C. E. Osburne, *J. Amer. Chem. Soc.*, **75**, 4582 (1953).

SSC_4H_9, 629-45-8; $C_4H_9SeC_4H_9$, 14835-66-6; $C_4H_9SeC_6H_5$, 28622-61-9; β-$C_{10}H_7SS$-β-$C_{10}H_7$, 5586-15-2.

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A Mechanistic Study of 1,2-Glycol Cleavage with Nickel Peroxide

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It has previously been found by Nakagawa, Igano, and Sugita[2] that nickel peroxide[3] is a useful oxidant for the oxidative cleavage of 1,2-diols and related compounds, as are periodic acid, lead tetraacetate, phenyliodoso acetate, and sodium bismuthate. In connection with mechanistic studies[4] on nickel peroxide oxidations reported recently, which explained the oxidative action of nickel peroxide in terms of its having characteristic abilities for both hydrogen abstraction and OH radical donation, we have investigated the mechanism of the unusual oxidative cleavage of 1,2-diols with nickel peroxide.

The fact that the oxidation of *meso*-hydrobenzoin with nickel peroxide (50°, 1 hr) gives benzaldehyde in 85% yield, while that of pinacol (70°, 3 hr) gives acetone in 61% yield[2] indicates that elimination of the hydrogen on the α position of the 1,2-glycol is not necessary in the oxidative cleavage of 1,2-diols with nickel peroxide. In order to establish this, the isotope effects in the oxidative cleavage of *meso*-1,2-diphenyl-1,2-dideuterioethane-1,2-diol and *meso*-2,3-dideuteriobutane-2,3-diol were examined, since the oxidation of a monohydric alcohol with nickel peroxide begins with hydrogen abstraction at the α position of the alcohol (k_H/k_D = 7.4 on the oxidation of benzhydrol).[4] The values of the pseudo-first-order reaction rate constants determined by a thermoanalytical technique[5] are shown in Table I. The data suggest that no isotope effect occurs in either reaction within the experimental error.

For comparison of this reaction with a typical radical reaction of 1,2-glycols, azoisobutyronitrile was allowed to react with *meso*-hydrobenzoin to give benzil exclusively. Furthermore, investigation of the product distribution in the oxidation of *meso*-hydrobenzoin and *meso*-1,2-diphenyl-1,2-dideuterioethane-1,2-diol with nickel peroxide in order to reveal the difference between the radical oxidation and the oxidative cleavage with nickel peroxide was carried out to obtain the results as listed in Table II. Benzil did not react at all with nickel peroxide at 30°. This means that benzaldehyde is not afforded from benzil with nickel peroxide. The fact[3] that benzoin reacts with nickel peroxide to give a 98% yield of benzil suggests that the production of benzil from *meso*-hydrobenzoin with nickel peroxide would be attributable to the abstraction of α hydrogen of the glycol, which is the ordinary radical oxidation type, to yield benzoin followed by the oxidation of it. The substitution of deuterium for α hydrogen would make slowly the abstraction reaction at the α position to yield benzil.

For clarification of the characteristic of the reaction of 1,2-glycols with nickel peroxide, the relative oxidation rates of *meso*-hydrobenzoin, benzhydrol, and benzylphenylcarbinol are shown in Table I. The results suggest that substitution of the α-hydroxybenzyl group for the benzyl group increases the reactivity to nickel peroxide by about 800 times.

Subsequently, it could be assumed that the oxidative cleavage of 1,2-glycols with nickel peroxide takes place by way of a cyclic complex in a similar manner to that with lead tetraacetate and periodic acid.[6] However, if this were the case, a sharp distinction between the cis and trans glycols would be expected. Table III, where the reaction rates of the oxidation of *cis*- and *trans*-cyclopentane-1,2-diol with nickel peroxide are compared, shows that the behavior of 1,2-glycols with nickel peroxide, which is a one-electron oxidant type, is remarkably different from that with lead tetraacetate, the valence of which is immediately reduced

TABLE I

RATE CONSTANTS FOR THE OXIDATION OF 1,2-GLYCOLS AND RELATED COMPOUNDS WITH NICKEL PEROXIDE

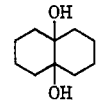
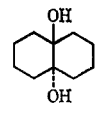
Substrate	Registry no.	Temp, °C	k, sec^{-1}
$(C_6H_5C(OH)H-)_2$	579-43-1	31	4×10^{-2}
$(C_6H_5C(OH)D-)_2$	28795-90-6	31	5×10^{-2}
$(CH_3C(OH)H-)_2$	5341-95-7	1	6.8×10^{-4}
$(CH_3C(OH)D-)_2$	28795-91-7	1	9.1×10^{-4}
$C_6H_5CH_2CH(OH)C_6H_5$	614-29-9	30	5.2×10^{-5}
$C_6H_5CH(OH)C_6H_5$	91-01-0	30	5.3×10^{-4}
$C_6H_5CH(OH)CH(CH_3)C_6H_5$	28795-94-0	30	1.5×10^{-5}
	28795-95-1	1	4.7×10^{-5}
		20	No reaction

TABLE II

PRODUCT DISTRIBUTION ON THE OXIDATION OF *meso*-HYDROBENZOIN AND *meso*-1,2-DIPHENYL-1,2-DIDEUTERIOETHANE-1,2-DIOL WITH NICKEL PEROXIDE[a]

Compd	Temp, °C	Products, % yield— Benzaldehyde	Benzil
$(C_6H_5C(OH)H-)_2$	30	84.4	8.1
	1	71.2	31.8
	−11[b]	21.9	53.1
$(C_6H_5C(OH)D-)_2$	30	100	0
	−11[b]	45.3	Trace

[a] In benzene. [b] Unchanged 1,2-glycols were recovered.

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(2) K. Nakagawa, K. Igano, and J. Sugita, *Chem. Pharm. Bull.*, **12**, 403 (1964).

(3) K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).

(4) R. Konaka, S. Terabe, and K. Kuruma, *ibid.*, **34**, 1334 (1969).

(5) I. Takashima, K. Yoneyama, and K. Watanabe, *Kogyo Kagaku Zasshi*, **69**, 1672 (1966).

(6) C. A. Bunton in "Oxidation in Organic Chemistry," part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter 6.