

**IRON AND MANGANESE IN GROUND WATER FROM SANDSTONE
AQUIFERS IN CUMBERLAND COUNTY, TENNESSEE**

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INTRODUCTION

This paper reports results of studies of the occurrence of iron and manganese in ground water from Pennsylvanian aquifers in Cumberland County, Tennessee. The location of the area studied is in the east-central part of Tennessee on the Cumberland Plateau (Fig. 1). A study of the ground water in Cumberland County (Wilson 1965) has shown substantial difference in occurrence of iron in the water from the Sewanee and Rockcastle Conglomerates, the major aquifers in the

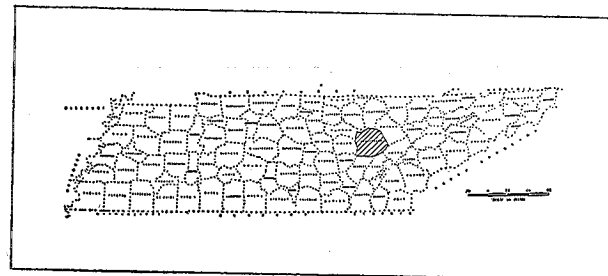


Figure 1. Map showing location of area studied.

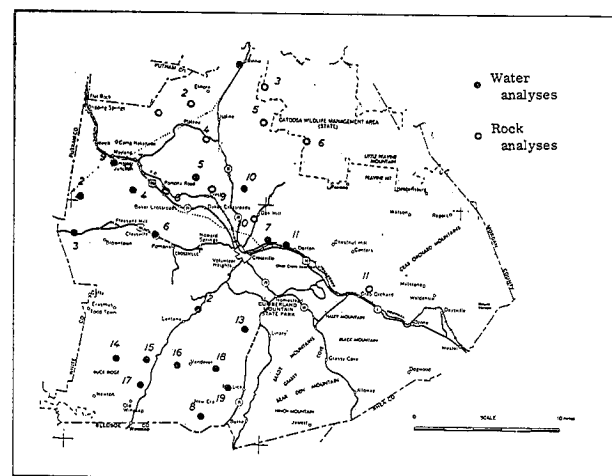


Figure 2. Map showing location of Rock and Water samples.

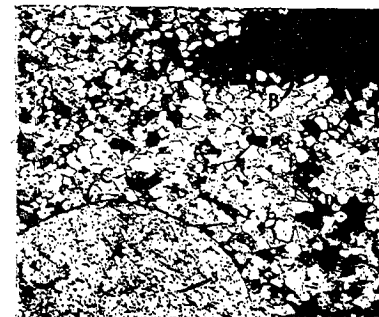
county. In the present report, 21 laboratory analyses were made of iron from two formations, and 19 laboratory analyses for total and dissolved iron were made of well water from the county. Field determinations (Fig. 2) were made of manganese, pH, temperature, and total dissolved solids in the water (Table I).

IRON AND MANGANESE CHEMISTRY

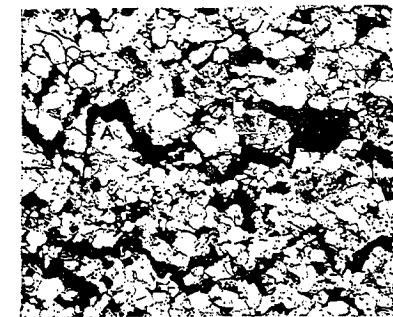
Excessive amounts of the elements iron and manganese in water can be objectionable for domestic and industrial use. More than 0.3 ppm of iron in water will result in "red water," and will stain laundry, plumbing fixtures, and other water containers. The taste of iron can be detected by most persons at the concentration of 1.8 ppm in spring water and at 3.4 ppm in distilled water (Cohen *et al* 1960). Manganese resembles iron in its chemical behavior and in its occurrence in natural water. It reacts with plumbing fixtures and laundry in the same manner as iron imparting a black or brown stain if more than 0.1 ppm is present. Excessive amounts of manganese affects the taste of beverages, particularly tea and coffee. These effects of manganese concentrations are not evaluated in this report on Cumberland County, because the iron concentrations there are usually more than two to three times those of manganese so that the effects of iron tend to overshadow those of manganese.

Iron. Iron generally occurs in water in either of two stages of oxidation—ferrous (bivalent) or ferric (trivalent). Under most conditions it occurs as ferrous iron. Two terms, dissolved and total, are used commonly when describing the iron content of water. Dissolved iron is iron in solution at the time of analysis, or the ferrous iron that has not been oxidized. Total iron is a combination of ferrous and ferric iron, whether suspended or in solution.

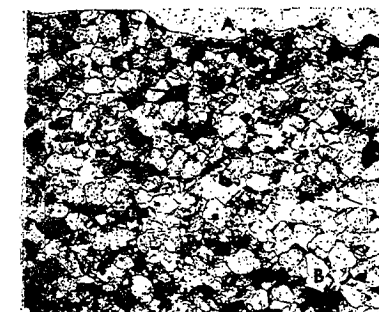
Micro-organisms are important in the development of the ferrous-ferric iron equilibrium. Some bacteria that can exist without oxygen can promote the solubility of iron, where as other types of bacteria derive their energy for life from the oxidation of ferrous to ferric



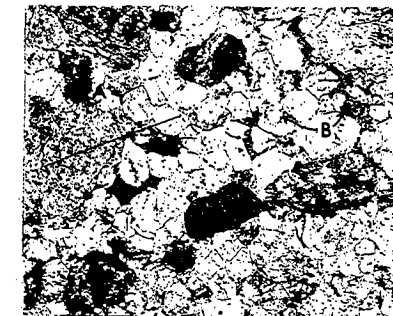
Fox Creek #1
Sewanee at 150.3'
A - Quartz pebble
B - "Shale" pebble
C - Iron oxide occurring as grain-staining



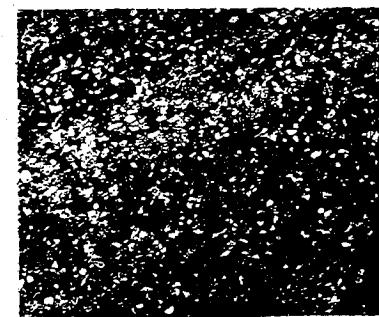
Isoline #1
Rockcastle at 39.5'
A - Iron oxide occurring as stylolitic-type structure



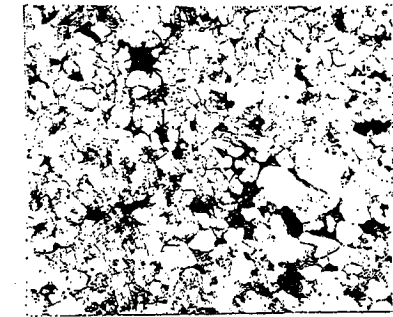
Isoline #2
Rockcastle at 34'
A - Iron oxide occurring as stylolitic-type structure
B - Iron oxide occurring interstitially



Isoline #1
Sewanee at 336'
A - Iron oxide occurring interstitially
B - Iron oxide occurring as grain-staining

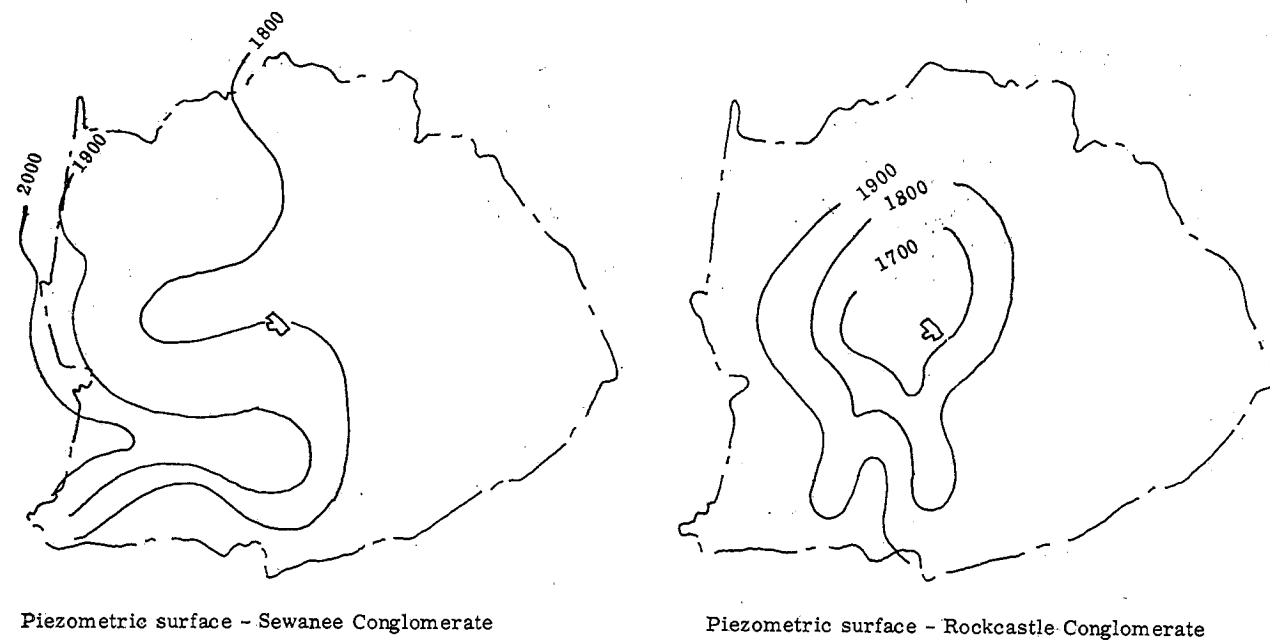


Fox Creek #1
Sewanee at 63'
Iron oxide occurring as a ferruginous-argillaceous cement



Isoline #2
Sewanee at 328'
A - Iron oxide occurring interstitially

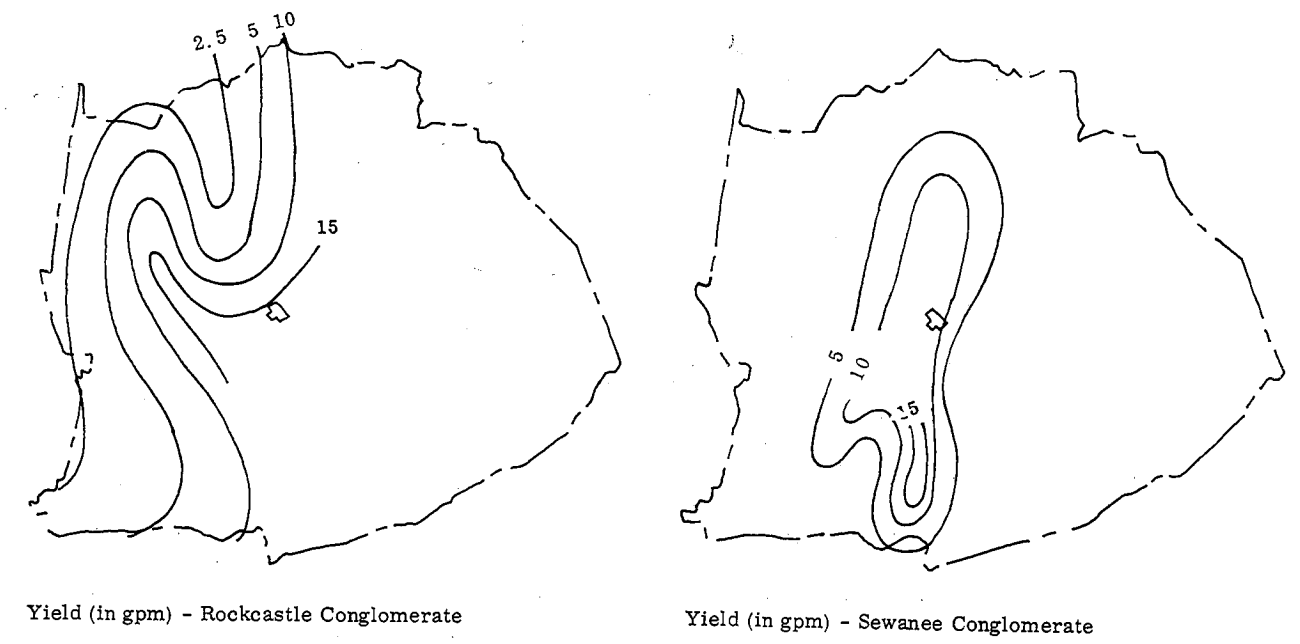
Figure 3. Photomicrographs of Pennsylvania rocks showing distribution of hydrated iron oxide (X40).



Iron content (in ppm) of water from the Sewanee Conglomerate

Iron content (in ppm) of water from the Rockcastle Conglomerate

Figure 4. Water Quality Maps.



Iron in the Sewanee Conglomerate (in % Fe)

Iron in the Rockcastle Conglomerate (in % Fe)

Figure 5. Water Quality Maps

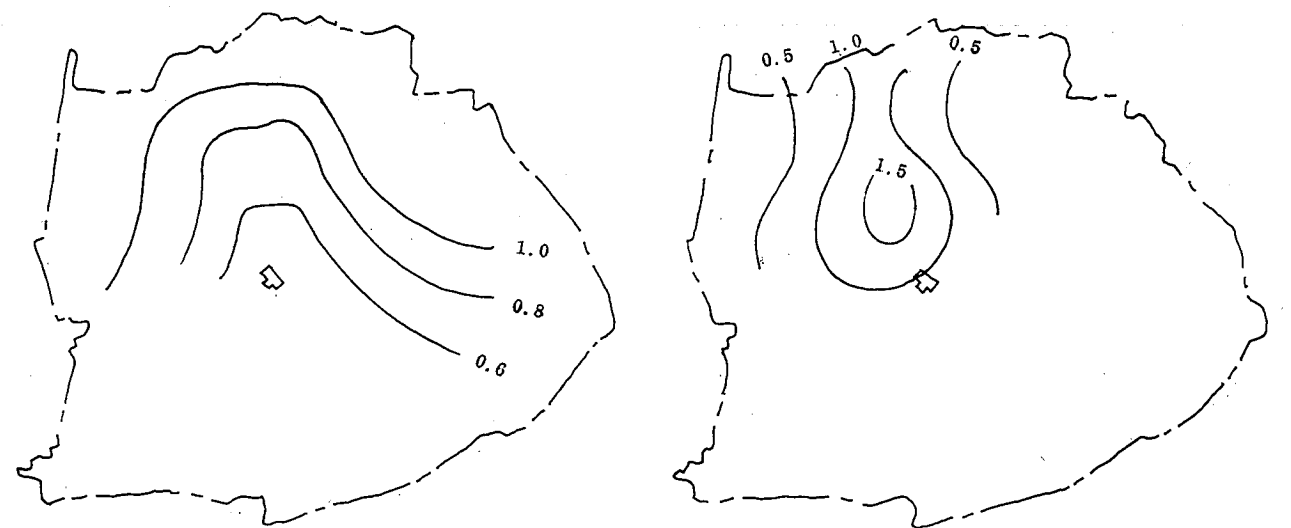




Figure 6. Water Quality Maps.

iron. The later types are partly responsible for the building of iron ore deposits.

In addition to its natural occurrence, iron may be added to the water from contact with metal, such as well casing, pumps, pipes, storage or settling tanks, and any other metal that may come in contact with the water. This is particularly true of very acid water.

Manganese. The manganese that occurs in ground water is probably the result of manganese activated by bacteria dissolving from soils and sediments. Minerals containing manganese are found commonly in sedimentary rocks and generally are associated with oxides or iron. As in the case of iron, manganese is found in two stages of oxidation, but in manganese the stages are bivalent and quadrivalent. Manganese is sometimes reported in analyses as dissolved and total, although the differences are likely to be less significant than with iron.

Manganese in excess of 1 ppm does not normally occur in ground water except when mining or industrial wastes are causative agents (California State Water Pollution Board 1952). Mine wastes may be an important factor in the few samples in Cumberland County that contain more than 1 ppm manganese (Wilson 1965).

THE OCCURRENCE OF IRON IN THE PENNSYLVANIAN AQUIFERS IN CUMBERLAND COUNTY

Rockcastle Conglomerate. The Rockcastle Conglomerate in Cumberland County is medium- to well-indurated sandstone, fine- to coarse-grained, white to yellow, brown and pink, commonly crossbedded and massive, and containing many rounded quartz pebbles. Thin zones of shale or clay occur locally. The range of

thickness of the formation is from 130 to 180 feet. In the Rockcastle Formation iron oxide is present generally as stain on the quartz grains, or in conjunction with clay as interstitial material. The occurrence of the iron (Fig. 3) is easily seen in outcrops where the color of the weathered rocks progresses from pink to red as the iron content increases. The present study confirms the findings of Hershey (1960), that weathered outcrops of the Rockcastle Formation contain more iron oxide than fresh material from drill holes.

Samples of Rockcastle material analyzed for iron content include composite of seven coal test core holes drilled by the Tennessee Division of Geology and a composite sample of cuttings from an oil test well (Table II).

Sewanee Conglomerate. The Sewanee Conglomerate in Cumberland County is medium to coarse-grained, white to brown, yellow and pink, crossbedded massive sandstone with rounded quartz pebbles. In some areas it is a fine-grained, thinbedded sandstone. The thickness ranges from 60 to 230 feet. Iron in the Sewanee Formation occurs as grain-staining, interstitial material, and as ferruginous-argillaceous cement (Fig. 3). This cement is partly responsible for the hardness of the Sewanee Formation. The color in weathered Sewanee outcrops depends directly on the iron content. Hershey (1960) observed that at several localities the weathered material contains less iron oxide than fresh drill-hole samples.

Analyses of Sewanee included in this report are composite samples from nine core holes and two test wells (Table I).

The Sewanee Conglomerate is mined for glass sand by the Sewanee Silica Sand Company near Sewanee.

TABLE I
DETERMINATION OF WATER QUALITY

Report Number	Owner	Total Depth	Aquifer	Date Collected	pH	Temp.	Field Determinations		Laboratory Determinations	
							Manganese (ppm)	Total Dissolved Solids (ppm)	Total Iron (ppm)	Dissolved Iron (ppm)
1	O. Smith	150	Ps	6-23-65	6.65	67	.25	49.4	.20	.13
2	E. Burkes	130	Ps	6-22-65	7.90	62	.35	195.0	.5	.06
3	C. Dodson	100	Ps	6-22-65	6.46	62	.45	84.5	.3	.05
4	K. Tanner	120	Ps	6-22-65	6.52	58	.65	55.3	.75	.12
5	W. Mullins	190	Ps	6-23-65	5.83	58	.30	13.0	.40	.06
6	H. Smith	100	Pr	6-22-65	6.52	62	.50	58.5	8.6	.03
7	B. Jones	169	Ps	6-23-65	6.60	63	.20	95.6	.05	.04
8	S. Blaylock	72	Ps	6-23-65	6.70	66	.80	100.8	.35	.07
9	D. Phillips	60	Pr	6-22-65	5.95	56	.45	65.7	.25	.20
10	N. Tabor	103	Pr	6-22-65	5.85	65	.33	20.8	1.9	.10
11	C. Crye	100	Pr	6-22-65	5.85	61	.40	61.8	1.7	.08
12	A. Clement	125	Pr	6-23-65	6.92	68	.30	120.3	.4	.03
13	C. Brown	95	Pr	6-23-65	6.00	63	.90	33.8	1.7	.12
14	F. Kinser	72	Pr	6-23-65	5.60	63	.50	22.1	.05	.04
15	J. Burgess	70	Pr	6-23-65	5.85	66	0	39.7	4.5	.40
16	C. Burgess	135	Pr	6-23-65	5.90	67	.60	14.0	.5	.06
17	H. Wood	102	Pr	6-23-65	5.87	68	.45	39.0	.7	.05
18	C. Lowe	85	Pr	6-23-65	5.82	63	.60	27.3	5.0	.20
19	W. Bradley	96	Pr	6-23-65	5.85	67	.25	33.8	.13	.06

* Ps—Sewanee; Pr—Rockcastle

TABLE II
RESULTS OF ANALYSES OF ROCK SAMPLES

Report Number	Core or Well Identification	Formation	Iron (Fe) (percent of rock)	Iron (Fe ₂ O ₃) (percent of rock)
1a	Campbell Junction #3-A	Rockcastle	.89	1.27
1b	Campbell Junction #3-A	Sewanee	1.00	1.43
2	Isoline #5	Sewanee	1.02	1.46
3a	Isoline #1	Rockcastle	1.23	1.27
3b	Isoline #1	Sewanee	1.23	1.76
4a	Isoline #3	Rockcastle	.82	1.17
5a	Isoline #2	Rockcastle	.40	.57
5b	Isoline #2	Sewanee	.88	1.26
6	Fox Creek #1	Sewanee	1.16	1.66
7a	Campbell Junction #6	Rockcastle	.39	.56
8a	Campbell Junction #8	Rockcastle	1.23	1.76
8b	Campbell Junction #8	Sewanee	.98	1.42
9a	Isoline #7	Rockcastle	1.64	2.32
9b	Isoline #7	Sewanee	.75	1.07
10a	Sutton oil test	Rockcastle	.78	1.11
10b	Sutton oil test	Sewanee	.61	.87
11	Peterson oil test	Sewanee	.67	.96

TESTS FOR IRON

A total of 18 composite samples of rock from the two aquifers were collected from oil test well cabletool chips and from cores of holes drilled for coal tests by the Tennessee Division of Geology. Composite sampling was selected for the purpose of giving an overall look at the iron concentrations in the two sandstones. Chip samples were collected from the cores at two to four foot intervals for the length of the section of each formation penetrated by the well. These samples were ground and analyzed for iron as Fe. Conversion to Fe₂O₃ was made, and both determinations are reported (Table II).

The average iron concentrations for the two formations in fresh samples are very similar: the Sewanee ranged from 0.61 to 1.16% Fe, with an average of 0.88. These results bear out the statement made by Hershey (1960), that the Sewanee seemed to have more iron in subsurface samples than the outcrop. However, it is difficult to compare these composite analyses with single-out-crop analyses as reported by Hershey. The contours drawn on equal iron values in the Sewanee (Fig. 5) indicate that the iron is somewhat scattered with relation to the ground-water maps. The contours drawn on equal iron values in the Rockcastle (Fig. 6) coincide with the contours on water values in the north half of Cumberland County.

QUALITY MAPS

Maps have been drawn for both formations connecting areas of water with equal mineral quality; also, piezometric maps of the water level, and maps of the yield in gallons per minute (gpm) (Figs. 4, 5, 6). The maps show clearly what happens to ground water as it travels from recharge areas in the formations. The piezometric map of the Rockcastle (Fig. 4) shows that the most likely recharge areas are either outside the county or on the fringes of it, and the water discharge area is in a roughly circular basin. The total iron and total dissolved solids increase in concentration as the water flows toward the center of the ground water basin

(Figs. 4, 5, 6). There is a decrease of acidity in the water, and an increase in well yields toward the center of the basin (Fig. 6).

The four quality-of-water maps of the Sewanee Formation present a picture almost as uniform. In the Sewanee Formation the recharge area is a ridgelike structure, which trends roughly north-south through Cumberland County, and the water apparently moves from this ridge inward (Fig. 4). The concentrations of iron and total dissolved solids reflect this movement of water by increasing as the water moves from recharge to discharge areas (Figs. 4, 5, 6).

There is an increase in alkalinity from this ridge inward (Fig. 6), and the well yields increase toward the discharge areas (Fig. 5).

CONCLUSIONS

From the evidence reported, the writer concludes that the striking difference in amounts of iron in water from the Sewanee and Rockcastle conglomerates is due to the direction of ground-water movement in fractures in these formations. The amount of iron present is determined by the length of time the water is in the ground between recharge and discharge so that the iron concentration is directly proportioned to the distance of travel.

The writer wishes to thank Robert E. Hershey and Robert J. Floyd of the Tennessee Division of Geology, who read the manuscript critically and gave suggestions. D. F. Farrar made the chemical determinations on the rock samples and the laboratory tests on the water samples.

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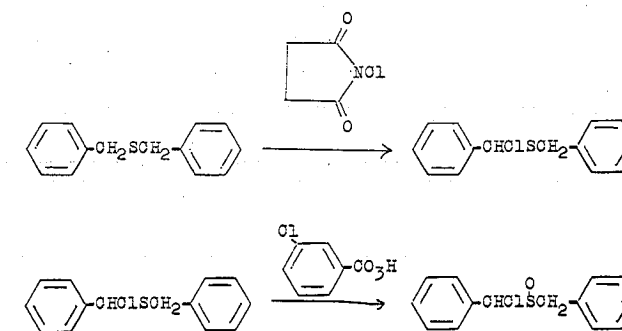
BENZYL ALPHA-CHLOROBENZYL SULFOXIDE

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The oxidation of alpha-chloro sulfides with ozone, (1, 2) peroxybenzoic acid (3) and monoperoxyphthalic acid (4) has been employed to prepare chloromethyl aryl sulfoxides, (1, 4) chloromethyl ethyl sulfoxide, (2, 4) bis(chloromethyl) sulfoxide (3) and bis(1-chloroethyl) sulfoxide. (3) We have synthesized benzyl alpha-chlorobenzyl sulfoxide by the oxidation of benzyl alpha-chlorobenzyl sulfide (5) with *m*-chloroperoxybenzoic acid.

A solution of benzyl sulfide in carbon tetrachloride was treated at room temperature with *N*-chlorosuccinimide to produce benzyl alpha-chlorobenzyl sulfide. Succinimide was removed by filtration and the solvent was removed at reduced pressure. The chloro sulfide was dissolved in ether and oxidized with an equivalent amount of *m*-chloroperoxybenzoic acid, to afford the chloro sulfoxide in 72% yield based on starting sulfide.



The nmr (60 Mc.) spectrum of the chloro sulfoxide (in deuteriochloroform) displays, in addition to the aromatic region, a singlet at 5.22 ppm, assigned to the methinyl hydrogen, and a doublet of doublets centered about 4.08 ppm ($J=14$ cps) assigned to the methylene hydrogens. The methylene protons are rendered non-equivalent by the sites of asymmetry present in the molecule. The major infrared absorption (assigned to the SO moiety) occurs at 1040 cm^{-1} .

As the chloro sulfoxide contains two potentially asymmetric centers (at carbon and sulfur), the possibility of diastereoisomerism exists. Initially, we felt that purification might have separated the isomers. However, the line width of the sharp methinyl singlet in the nmr spectra is the same for the crude chloro sulfoxide and for the purified material. The chloro sulfoxide was treated with acidic dioxane at room temperature, (6) to attempt to convert the chloro sulfoxide to a mixture of the diastereomers. This treatment resulted in the decomposition of the sulfoxide and the formation of benzaldehyde.

We can not, therefore, currently state whether an *erythro-threo* mixture is formed or if the oxidation is a stereospecific process. It seems rather unlikely that the oxidation is totally stereospecific. The possibility that the chemical shifts of the methinyl hydrogens in the two diastereomers are identical also seems improbable. It may well be that the reaction is stereoselective, and that the concentration of the less abundant diastereomer is such that it was not discerned in the nmr spectra.

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research, and to the National Science Foundation for a grant (GP 1683) used to purchase the A-60 nmr spectrometer.

EXPERIMENTAL

To a solution of benzyl sulfide (10.0 g., 0.0467 mole) in 50 ml. of spectrograde carbon tetrachloride was added *N*-chlorosuccinimide (6.23 g., 0.0467 mole). The mixture was stirred magnetically at room temperature; after one hour succinimide was removed by filtration and the solvent was removed by the use of a vacuum pump (use of a water aspirator caused extensive hydrolysis of the chloro sulfide). The residue was dissolved in 50 ml. of anhydrous ether. The ethereal solution was stirred and maintained at 2-4 C while a solution of *m*-chloroperoxybenzoic acid (8.06 g.) in 50 ml. of anhydrous ether was added over a one hour period. The mixture was stirred overnight, washed several times with aqueous sodium bicarbonate solution, washed with water and dried over magnesium sulfate. Removal of the solvent and recrystallization from hexane gave the chloro sulfoxide, m.p. 109-111 C (8.93 g., 72%). Further recrystallization from hexane afforded material of m.p. 112-113 C. (Found: C, 63.33; H, 4.86. C₁₄H₁₃ClOS requires C, 63.51; H, 4.95 per cent.)

A solution of the chloro sulfoxide (0.5 g.) in acidic 1,4-dioxane prepared by mixing 16 ml. of dioxane with 8 ml. of concentrated hydrochloric acid was allowed to stand at room temperature for 24 hours. Neutralization was effected with aqueous sodium hydroxide solution; extraction was ether and evaporation of the ethereal layer afforded benzaldehyde as the only immediately recognizable product.

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