

pressure of 50 p.s.i. Hydrogenolysis was complete in 0.5 hr. The catalyst was removed by filtration and washed with hot ethanol. The combined filtrate and washings were treated with 0.5 g. of sodium carbonate. Concentration of the solution gave 1.4 g. (71%) of 1- β -cyclohexylethyl-5-amino-tetrazole, m.p. and mixture m.p. 212.5–213.5°.

Infrared spectra of the iminotetrazoline hydrochlorides and the corresponding bases were determined using a Perkin-Elmer double beam recording spectrophotometer, Model 21, and have been recorded.^{21,22} All spectra were determined

with oil mulls of the compounds at concentrations of the solid great enough to give strong absorption in the 6- μ region.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CONNECTICUT]

The Manganese Dioxide Oxidation of Allylic Alcohols

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It has been found that the rate and specificity of the manganese dioxide oxidation of allylic alcohols to allylic aldehydes is dependent on the quantity of oxidizing agent, the temperature, the solvent, and the method of preparation of the oxidizing agent. Allyl, benzyl, propyl, and isopropyl alcohols and *N,N*-dimethylaniline were oxidized with varying yields under different conditions and with a wide variety of manganese dioxides.

Manganese dioxide has been considered to be a specific reagent for the oxidation of allylic alcohols to allylic aldehydes and ketones. It has been used for the oxidation of vitamin A₁ and other polyene alcohols²; for unsaturated steroidal alcohols³; for α -santonins⁴; for alcohols in which an aromatic ring replaced the vinyl group⁵; for the determination of the stereochemistry of 10-hydroxycodine derivatives⁶; for acetylenic alcohols⁷; and for ferrocene alcohols.⁸

The nonspecificity of manganese dioxide as an oxidizing agent for allylic alcohols has recently been reported. It was found to: oxidize primary and

secondary amines to imine dimers in low yields,⁹ 2-hydroxytetrahydropyran to δ -valerolactone,⁹ aniline to azobenzene,¹⁰ *N*-methyl amines to *N*-formyl amines,¹⁰ *N*-alkyl amines to the amine and the corresponding aldehyde from the alkyl group¹⁰; dehydrogenate an *N*-alkyl amine followed by oxidative cleavage of the enamine¹⁰; cleave tetrasubstituted ethylenediamines¹⁰; oxidize aliphatic primary and secondary alcohols to the corresponding aldehydes or ketones,¹¹ aldehydes to the acids,¹¹ and 1,2-glycols in steroids to give ketones and products resulting from bond cleavage¹²; and convert an allylic methylene group into an alcoholic or ketonic grouping.¹³

Several different types of manganese dioxide have been used for the above mentioned oxidations. The first was that of Ball, Goodwin, and Morton,^{2b} followed by Attenburrow's "active" manganese dioxide;^{2a} one by Rosenkranz, Sondheimer, and Mancera;¹⁴ and two by Harfenist, Bavley, and Lazier,^{5a} who reported one of their dioxides to be specific for benzyl type alcohols but unaffactive on allyl alcohol.

The purpose of this research was to investigate the oxidation of allylic alcohols with the manganese dioxides mentioned above, others which had been reported in the literature, two commercial dioxides,

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TABLE I
 OXIDATION OF ALLYL ALCOHOL^a

Type of MnO ₂	Petroleum Ether			Chloro- form 5 g.	Carbon Tetra- chloride 5 g.	Benzene 5 g.	Ethyl Ether 5 g.
	5 g.	10 g.	15 g.				
Attenburrow	99, 19 80, 2.0	92, 46		40, 1.0	66, 64	67, 1.0	75, 0.2
Ball, Goodwin, and Morton	90, 0.5	97, 0.1		1, 4.5	50, 0.2	56, 2	64, 0.2
Glemsir (No. 1) ^b		5, 22	100, 17	20, 25	45, 1.0	50, 1.0	69, 0.2
Glemsir (No. 2) ^b	89, 0.75	97, 0.5					
Harfenist, Bavley, and Lazier (No. 1)	92, 1.5	97, 0.1		81, 29.4	50, 1.0	67, 1.0	81, 19
Harfenist, Bavley, and Lazier (No. 2)	82, 1.5	89, 1.0					
Maxwell, Thirsk, and Butler (No. 1)		80, 22	100, 1.0	18, 20.7	48, 2	53, 0.2	59, 0.2
Maxwell, Thirsk, and Butler (No. 2)		40, 23	100, 17	17, 19.3	38, 2	56, 0.2	69, 0.2
Maxwell, Thirsk, and Butler (No. 3)	48, 19.5	96, 0.2					
Rosenkranz, Sondheimer, and Mancera		31, 46	100, 70	12, 19.5	34, 0.2	55, 2.5	82, 0.2
Baker Analyzed (commercial)		32, 50	41, 16	12, 20	34, 0.2	50, 0.2	78, 0.2
Baker & Adamson (commercial)	99, 19	92, 0.7		22, 26	51, 3	52, 0.2	82, 0.2
Pyrolysis of manganous nitrate	40, 57			15, 10.5	39, 0.2	55, 1.0	83, 18
Electrolysis of manganous nitrate	80, 38			22, 24.5	53, 23	61, 0.2	59, 0.2
Manganous chloride and hydrogen peroxide	39, 57			1, 10.5	32, 3	53, 0.2	88, 0.2
From manganous acetate	92, 57						
Potassium permanganate refluxed in methanol and petroleum ether	42, 24.5						
From barium permanganate	70, 24						
From manganous chromate	95, 29						
Attenburrow ^c	89, 42						
Attenburrow ^d	48, 23						
Attenburrow ^e	85, 45						
Attenburrow ^f	48, 45						
Attenburrow ^g	75, 24						
Attenburrow ^h	34, 26						
Attenburrow ⁱ	45, 20						
Attenburrow ^j	37, 20						
Attenburrow ^k	35, 22.6						

^a All oxidations were done with 50 g. of a 2% by weight solution. The first number in the columns indicates the per cent yield, and the second the time in hours. The numbers which follow the types of manganese dioxides indicate the order of preparation of the dioxides in the original article. ^b O. Glemsir, *Ber.*, 72B, 1879 (1939). ^c Washed with 15% nitric acid. ^d Washed with methanol and ether and dried at 130°. ^e Washed with water and dried at 120°. ^f Dried at 220–280°. ^g Refluxed in hydrochloric acid and reoxidized with chlorine. ^h Refluxed in methanol and ether and dried at 100°. ⁱ 3 g. of the dioxide was used. ^j 1 g. of the dioxide was used. ^k 0.5 g. of the dioxide was used.

those prepared by pyrolysis and electrolysis, and with other oxidizing agents on manganous compounds. The latter dioxides were prepared by methods which did not utilize permanganate and hence were an attempt to prepare manganese dioxide free from permanganate.

These dioxides were used to determine: (1) the time needed for complete oxidation or when the oxidation stopped, (2) the effect of solvent, (3) the quantity of oxidizing agent required for efficient oxidation, and (4) the effect of washing and drying the precipitated manganese dioxide in various ways. These results have been summarized in Table I, where the yields indicate the total amount of aldehyde produced, although the extent of oxidation was determined at various time intervals (approximately 10 minutes, 30 minutes, 1 hour,

20 hours, and 60 hours) until the oxidation was complete.

Table II depicts the rate of oxidation with three different preparations of manganese dioxide at room temperature and the absence of any change in rate when the temperature is raised by 25°. In addition, it was found that air oxidation was not important for the rate and extent of oxidation did not change in a nitrogen atmosphere.

The manganese dioxide oxidation of benzyl, propyl, and isopropyl alcohols and *N,N*-dimethylaniline in representative solvents is summarized in Table III.

All of the oxidations were followed by infrared analysis of a 2% solution of the alcohols and amine in neutral solvents. When an alcohol was studied, the rate was measured by the gradual decrease of the

TABLE II
 EFFECTS OF TEMPERATURE AND ATMOSPHERE^a

Type of MnO ₂	Normal	Nitrogen Atmosphere	40° ± 0.2°	45° ± 0.2°	50° ± 0.2°	66° ± 1°
			Attenburrow	51, 0.12 65, 0.5 80, 1.0 99, 19	48, 0.12 53, 0.7 89, 13	
Ball, Goodwin, and Morton	85, 0.12	70, 0.12				
	90, 0.5 92, 0.75	70, 0.7				
Rosenkranz, Sondheimer, and Mancera	22, 6 ^b	30, 0.18	30, 0.18	35, 0.18	34, 0.12	31, 0.12
	31, 46	32, 1.7 36, 29	43, 11.25 45, 23	42, 10.75 44, 25.7	41, 10.25 43, 24.5	89, 10.5 100, 26
Pyrolysis of manganous nitrate	0, 0.18		28, 0.18	22, 0.18	32, 0.18	17, 0.21
	14, 1.5 21, 6 40, 57		32, 11.75 43, 25.25	30, 12 38, 24	37, 10 45, 27	43, 15.7 49, 23.25 92, 36.75

^a 5 g. of MnO₂ was used. The first number indicated per cent yield and the second the time in hours. The temperature was controlled with a Thermocap Relay. ^b 10 g. of MnO₂ was used.

 TABLE III
 OTHER OXIDATIONS WITH 5 g. OF MnO₂^a

Compound	Benzyl Alcohol		1-Propanol		2-Propanol	N,N-Dimethyl aniline
	Petroleum Ether	Carbon Tetrachloride	Petroleum Ether	Carbon Tetrachloride	Carbon Tetrachloride	Carbon Tetrachloride
Type of MnO ₂						
Attenburrow	63, 2.7	69, 4.3	13, 30	78, 47	62, 26	45, 33.5
Ball, Goodwin, and Morton	60, 2.7	49, 4	17, 29	22, 47	38, 26	18, 31.5
Electrolysis of manganous nitrate	62, 2.7	71, 20	25, 29	58, 47	31, 26	13, 32.5
Glemsir (No. 1)	67, 0.1	56, 20	30, 25	28, 47		
Rosenkranz, Sondheimer, and Mancera	60, 2.7	52, 3.7	5, 30	27, 47		
Pyrolysis of manganous nitrate	60, 2.7	50, 0.2	5, 29	26, 47		
Attenburrow ^b			25, 36.5	40, 26	92, 26	

^a The first number indicates the per cent yield and the second indicates time in hours. ^b 10 g. of the dioxide was used.

oxygen-hydrogen peak at 3.0 microns, and the rate of amine oxidation was determined by the decrease of the carbon-hydrogen peak at 3.5 microns. This was possible, since it was determined that both the oxygen-hydrogen and carbon-hydrogen peaks were inversely proportional to the carbonyl peak.

Discussion of Results. The results of this study are not in complete agreement with those reported previously. In many cases these discrepancies can be attributed to differences in experimental techniques. The excellent yields obtained in the short times are possibly due to an improvement in technique. All reaction mixtures were stirred continuously with a Teflon-covered stirring bar and magnetic stirrer. This permits a constant change in the surface of the manganese dioxide and enabled the unoxidized portion of the alcohol in solution to make contact with the surface of the dioxide. Previous techniques placed the alcohol and solvent in a stoppered flask which contained the manganese

dioxide, and the reaction mixture was agitated at different time intervals. A good yield of product required six to twelve days.

The data in Table I indicates that some manganese dioxides give efficient oxidation of allyl alcohol in petroleum ether when 10 g. of the dioxide (to 1 g. of alcohol) is used in one half to twenty-four hours. The initial rate is decreased when 5 g. of oxidant is used, but comparable yields can still be obtained in approximately the same time. Further decrease in the quantity of dioxide resulted in diminished oxidation. Other dioxides failed to give efficient oxidation when 10 g. was used. When the amount of oxidizing agent was increased to 15 g., a comparable yield of acrolein was obtained. These results clearly prove the previous suggestion of Henbest¹⁰ that the yield of aldehyde depends on the quantity of oxidizing agent. In addition the rates of oxidation have been determined (Table II).¹

The dioxides which give rapid oxidation and high yields utilize permanganate or chromate in their preparation. This suggests the presence of permanganate or other higher oxidation states of manganese or chromium which are absorbed and occluded when the manganese dioxide is precipitated. Other evidence for possible permanganate oxidation is indicated by the fact that the dioxides which utilized no permanganate in their preparation failed to give a large yield of acrolein in the early stages of oxidation. Attempts to detect the presence of permanganate by x-ray and ultraviolet analysis were unsuccessful.

A procedure was utilized to remove any adsorbed or occluded permanganate and other manganese oxides from two dioxides and the results indicate that the oxidation rate in the early stages of reaction is decreased appreciably. When 25- and 100-mg. samples of potassium permanganate were added to 5 g. of dioxide the initial oxidation rate showed a slight increase. The present study has revealed that washing and drying of the precipitate exerts an influence on the oxidizing power of the dioxide. When the precipitate is washed with organic solvents the yield is lowered, possibly because any adsorbed permanganate or other species which cause rapid oxidation are removed to a greater extent by the organic solvent than by water. This could reduce the oxidizing power of the dioxide. Thus, the manganese dioxide which was prepared from potassium permanganate refluxed in petroleum ether and methanol, showed poor initial oxidation and a comparatively low yield of acrolein after twenty-four hours of reaction. Washing with nitric acid does not appear to have any appreciable effect, but drying at high temperature causes a decrease in oxidizing power. This result substantiates Henbest's¹⁰ and Evans's¹⁵ statements that the manganese dioxide must be partially hydrated for efficient oxidation.

Attenburrow stated that the oxidizing power of his dioxide was due to precipitation in an alkaline media.^{2a} This is inconsistent with the results of this study, since effective dioxides which utilized permanganate in their preparations were precipitated either from neutral or acid media.

The dioxides prepared from manganous chloride and hydrogen peroxide, the electrolysis and pyrolysis of manganous nitrate, and manganous acetate and ammonium persulfate are essentially free from permanganate contamination. The present results indicate that the initial rate of oxidation is considerably less in comparison to the dioxides which appear to be contaminated by permanganate. The yields of acrolein after fifty-seven hours of oxidation are also lower.

The possibility of air oxidation in the reaction was investigated by conducting the oxidations in an

atmosphere of nitrogen. The results imply that air oxidation is negligible.

The results of the temperature study on the oxidation of allyl alcohol appear in Table II. The results between 40°, 45°, and 50° would indicate that there is no Arrhenius temperature effect. When the oxidation was carried out at reflux temperature (63°), the oxidizing power of these two dioxides was increased by approximately 60% over the normal rate indicating a definite increase in oxidation when there is a sufficient increase in the temperature.

The effect of solvent on the oxidation rate was extensively investigated with a variety of dioxides. The results indicate that the extent of oxidation is reduced from 50 to 70% when chloroform or carbon tetrachloride is used in place of petroleum ether and that the dioxides which show possible permanganate contamination are affected more than the dioxides which are essentially permanganate free. In benzene the effect is not so pronounced, for the oxidation rate is decreased by 20 to 30%. In ether, all the dioxides gave increased yields, but these results are not accurate since the high volatility of ether hindered quantitative measurements.

The present investigation was also extended to another allylic alcohol, benzyl alcohol. The results in Table III indicate that the yields of benzaldehyde in petroleum ether, though less than acrolein, are about 65% after three hours of oxidation when the benzyl alcohol is present in about one half the concentration of allyl alcohol. The simultaneous increase of the hydroxyl and carbonyl peaks in the infrared suggests some oxidation to benzoic acid. The results in carbon tetrachloride are comparable to those of allyl alcohol in the same solvent, which indicates that there are several inconsistencies with those communicated in the literature. Turner^{5b} attempted the oxidation of benzyl alcohol with the dioxide of Rosenkranz, Sondheimer, and Mancera¹⁴ and reported that the alcohol could not be oxidized. The present study shows a 60% yield of benzaldehyde is obtained after three hours with the same dioxide.

Padilla and Herran¹² tested the oxidizing power of several dioxides and their findings indicated the dioxide of Rosenkranz, Sondheimer, and Mancera¹⁴ to be the most efficient. The present results indicate the dioxides of Attenburrow^{2a} and of Ball, Goodwin, and Morton^{2b} to be superior to that of Rosenkranz, Sondheimer, and Mancera in the oxidation of benzyl and allyl alcohol.

Dissimilarities also occur with the results of Harfenist, Bawley, and Lazier.^{5a} These investigators found that their dioxide (No. 1) would oxidize benzyl alcohol to benzaldehyde, but would not oxidize allyl alcohol to acrolein. This study indicates that the dioxide (No. 1) is more efficient for the oxidation of allyl alcohol than (No. 2).

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The specificity of manganese dioxide for allylic alcohols was investigated with 1-propanol, 2-propanol, and *N,N*-dimethylaniline. The results in Table III indicate that nonallylic compounds can be oxidized with manganese dioxide, but usually not so well as allylic compounds. This is in excellent agreement with the findings of Abel-Wahab, El-Sadr, and Barakat¹¹ and the results of Highet and Wildman.⁹

The present results do not permit us to make any definite statements about the mechanism of this oxidation. Several pertinent facts are evident: Allyl and benzyl alcohols are oxidized more readily than saturated alcohols, which would indicate that the π -electrons of the double bond have some effect; allyl alcohol is oxidized more readily than benzyl alcohol, which might indicate a steric effect; and Rapoport⁶ has found that *cis*-10-hydroxy-dihydrodesoxycodeine is oxidized more readily than the *trans* alcohol. One aspect which hinders the clarification of this oxidation is that the fate of the manganese dioxide is not known. It is anticipated that future work will permit us to clarify some of the mechanistic aspects of the reaction.

EXPERIMENTAL

Reagent. The following reagents were used in the preparation of the manganese dioxides: manganous chromate (British Drug House), manganous sulfate (Baker and Adamson), manganous acetate (Fisher Analytical Reagent), manganous nitrate (Mallinckrodt), manganous chloride (Mallinckrodt), barium permanganate (British Drug House), potassium permanganate (Baker and Adamson), ammonium persulfate (Baker and Adamson), manganous carbonate (Baker Analyzed Reagent), manganous oxalate (British Drug House), and hydrogen peroxide (30%, Baker and Adamson).

The following materials were distilled through a 16-in. silvered column packed with glass helices: petroleum ether (Fisher White Label, b.p. 63–64°), which was dried for 12 hr. over sodium sulfate, carbon tetrachloride (Baker and Adamson, b.p. 76–77°) which was washed with concentrated sulfuric acid and water and dried over a mixture of sodium sulfate and Drierite, chloroform (Baker and Adamson, b.p. 58–60°) which was washed with concentrated sulfuric acid and water and dried over a mixture of sodium sulfate and Drierite, allyl alcohol (Eastman White Label, b.p. 96–97°, n_D^{20} 1.4135), benzyl alcohol (Eastman Yellow Label, b.p. 76.7° at 4.5 mm., n_D^{20} 1.5395), 1-propanol (Eastman White Label, b.p. 97–98°, n_D^{20} 1.3854), 2-propanol (Mallinckrodt, b.p. 82–83°, n_D^{20} 1.3776), and *N,N*-dimethylaniline (Fairmount Chemicals, b.p. 72° at 3.8 mm., n_D^{20} 1.5582). Acrolein (Eastman Yellow Label, b.p. 52.5°) was distilled through a small Claisen apparatus and immediately added to petroleum ether to retard polymerization.

Variations in preparation of manganese dioxides reported in the literature. The following variations were performed on manganese dioxide prepared by the method of Attenburrow: (1) It was washed with 15% nitric acid and dried at 220° to 280° according to the method of Harfenist, Bavley, and Lazier;^{8a} (2) It was washed with methanol and ether and dried at 130° by the method of Rosenkranz, Sondheimer, and Mancera;¹⁴ (3) It was dried at 120° after washing with water; (4) It was dried at 220° to 280°; (5) Manganese dioxide (50 g.) was refluxed in 100 ml. of concentrated hydrochloric acid until it was reduced to manganous chloride (green coloration of solution). This also reduced

any permanganate which was present. The solution was then neutralized with concentrated sodium hydroxide, while the manganous chloride solution was stirred in an ice bath. Chlorine gas (purified with sulfuric acid) was admitted into the solution and oxidized the manganese back to the plus four state. The manganese dioxide was washed with 3 l. of water and dried at 100° for 2 days; (6) Manganese dioxide (50 g.) was added to a solution of 50 ml. of methanol and 50 ml. of petroleum ether, and refluxed for 24 hr. The manganese dioxide was dried between 80° and 100° for 2 days.

The following variations were performed on manganese dioxide prepared by the method of Ball, Goodwin, and Morton^{2b}: (1) It was reduced to manganous chloride and reoxidized to the plus four oxidation state with chlorine; (2) It was washed with methanol and ether and dried at 130° by the method of Rosenkranz, Sondheimer, and Mancera.¹⁴

The dioxide of Rosenkranz, Sondheimer, and Mancera¹⁴ was refluxed in methanol and petroleum ether for 24 hr. and dried between 80° and 100° for 2 days.

Other methods used in the preparation of manganese dioxide.

A. Preparation of manganese dioxide from manganous acetate. Manganous acetate (114.2 g.) was dissolved in 2 l. of water to which 200 ml. of sulfuric acid (2*N*) were added. The solution was heated to boiling and ammonium persulfate (226 g.) was added over a 30-min. period. The manganese dioxide precipitated after 15 min. It was filtered, washed with water till the washings were neutral, and dried at 60° for 2 days.

B. Preparation of manganese dioxide from pyrolysis of manganous nitrate. Manganous nitrate was heated gradually to 400° and maintained at 400° for 1 hr. The manganese dioxide was then washed with water (1 l.) and dried at 60° for 2 days.

C. Preparation of manganese dioxide from electrolysis of manganous nitrate. Equal volumes of concentrated nitric acid and manganous nitrate were placed in a 1-l. vessel. Two platinum electrodes connected to a 6-volt transformer were placed in the solution and the current turned on low until the decomposition voltage was reached. Complete deposition of manganese dioxide took 3–4 days. The manganese dioxide was filtered, washed with water until the washings were neutral, and dried at 60° for 2 days.

D. Preparation of manganese dioxide from potassium permanganate. Potassium permanganate (25 g.) was added to a solution of 300 ml. of methanol and 100 ml. of petroleum ether and the resulting mixture was refluxed with stirring for 2 days. The permanganate was reduced to manganese dioxide which was filtered, washed with water until the washings ran clear, and dried at 60° for 2 days.

E. Preparation of manganese dioxide from manganous chloride. Manganous chloride (300 g.) was dissolved in 2 l. of water. The solution was made slightly alkaline by addition of sodium hydroxide (6*N*). Hydrogen peroxide (453 g. of a 30% solution) was then added with a dropping funnel for 1.5 hr. and the solution was stirred at 10-min. intervals. The brown manganese dioxide was collected by filtration, washed with water until the washings were neutral, and dried at 60° for 2 days.

F. Preparation of manganese dioxide from barium permanganate. Barium permanganate (453 g.) was dissolved in water (1 l.) and 300 ml. of sulfuric acid (concentrated) was added slowly with stirring. The permanganate was reduced to manganous chloride which was collected by filtration, washed with water until the washings were clear, and dried at 60° for 2 days.

G. Preparation of manganese dioxide from manganous chromate. Manganous chromate (50 g.) was dissolved in 1 l. of water. 100 ml. of 2*N* sulfuric acid was added, and the solution was heated to boiling. Ammonium persulfate (113 g.) was added over a period of 0.5 hr. to the hot solution. The black manganese dioxide was collected by filtration, washed with hot water till the washings were clear (6 to 7 l.), and dried at 60° for 2 days.

Construction of the infrared standardization curves. Accurately weighed amounts of the four alcohols, acrolein, and the tertiary amine were added to 49 g. of the appropriate solvent to give the required percentage solution. The infrared spectra (Perkin-Elmer Model 21) of the solutions were obtained in a 0.5-mm. sodium chloride absorption cell with a reference of solvent in a 0.5-mm. cell. This method gave excellent resolution of the peaks due to oxygen-hydrogen stretching at 3.00 microns in the alcohols, carbon-oxygen double bond stretching at 5.85 microns in the aldehydes, and the carbon-hydrogen stretching at 3.50 microns in the amine. The percentage transmissions of the oxygen-hydrogen, carbon-oxygen double bond, and the carbon-hydrogen peaks were determined for the various concentrations, and these were plotted against concentration to give the standardized curves. The curves showed both positive and negative deviations from Beer's Law, but subsequent determinations indicated that the curves were accurate to $\pm 2\%$.

Methods used in this study. One-gram samples of the four alcohols and *N,N*-dimethylaniline were weighed in a weighing bottle. The solvent (49 g.) and the manganese dioxide were weighed on a triple beam balance and placed in a flask equipped with a condenser and a sidearm that permitted samples to be taken. The compound was transferred from the weighing bottle to the flask with a hypodermic syringe. The reaction mixture was stirred with a Teflon-covered stirring bar and a magnetic stirrer. At the desired time stirring was stopped, the rubber bulb capping the sidearm was removed, and a sample was taken with a hypodermic syringe and transferred to the infrared cell. The per cent transmission of the sample was then determined.

When the reaction was carried out in a nitrogen atmosphere, a hypodermic needle which extended below the surface of the reaction mixture was pushed through the rubber bulb on the sidearm. Nitrogen was then passed through the solution for 0.5 hr. to remove the air present. The condenser was equipped with a mercury bubbler which was then closed to prevent air from entering the system. Samples were taken with a hypodermic syringe through the rubber bulb covering the sidearm.

In those reactions carried out at elevated temperatures a flask with a sidearm and a thermometer well was used. The reaction mixture was prepared in the usual manner. The temperature was controlled to $\pm 0.2^\circ$ by a Thermocap Relay (Niagara Electron Laboratories) which was attached to a thermometer placed in the thermometer well of the flask, which was heated with a heating mantle. To ensure better

thermal conductivity some mercury was placed in the thermometer well. The samples were obtained in the same manner as above.

X-ray study. An attempt was made to detect traces of the suspected permanganate in the dioxide of Attenburrow; Ball, Goodwin, and Morton; Maxwell, Thirsk, and Butler (No. 3); Baker Analyzed (Commercial); Glemsir (No. 2); and the dioxide prepared from the pyrolysis of manganous nitrate, by x-ray diffraction. An x-ray diffraction pattern (Phillips Standard Unit with Cu radiation) was first taken of potassium permanganate and this was used as a standard. The lines on the x-ray pictures of the above dioxides did not show any similarity to the lines produced by the potassium permanganate. In many instances the lines were blurred and this is in agreement with the analysis reported by Maxwell, Thirsk, and Butler¹⁶ who obtained dark brown pictures. The x-ray information is limited since it is difficult to detect materials present in concentrations of less than 5%.¹⁷

Ultraviolet study in the visible range. An attempt was made to detect the suspected permanganate in the above manganese dioxides with an ultraviolet spectrophotometer (Beckman Model DU). A preliminary study was made on permanganate in a mineral oil suspension, and it was found that absorption occurred between 540 and 545 m μ . The samples were prepared by suspending 100 mg. of the dioxides in 2.97–3.00 g. of mineral oil. The dioxides failed to give any absorption in the permanganate region, but this could be due to the inability of the apparatus to detect traces of permanganate present in concentrations less than 2%.¹⁸

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Structure and Antimicrobial Activity of the 3-Aminorhodanines

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Some *N*-substituted derivatives of 3-aminorhodanine have been synthesized by the cyclization of the corresponding carboxymethyl dithiocarbazates and their structures confirmed by infrared and ultraviolet spectra. Within this series, the most active compounds in producing inhibition of the growth of *A. niger* are the *p*-haloanilinerhodanines.

The antimicrobial activity¹ of the 3-phenyl- (IA) and 3-benzylrhodanines (IB) suggested the investigation of other 3-substituted rhodanines. By the principle of isosterism,² the 3-anilinerhodanines (IC) would be expected to resemble the

3-benzylrhodanines in activity. It was also anticipated that the presence of the amino group would perhaps lead to the possibility of salt formation and hence greater water solubility, since 3-amino-2,4-thiazolidine (ID) has been isolated as a hydrochloride salt.³

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