with a large volume of water, and the mixture extracted exhaustively with low boiling petroleum ether. In the distillation of the residue from these extracts, constant-boiling azeotropes of 2-methylcyclohexanol and certain of the products were obtained. The azeotrope of 2-methylcyclohexanol and N,N,2-trimethylcyclohexylamine (about 60% 2-methylcyclohexanol) had a b.p. of 162° (736 min.) (cor.), n^{25}D 1.4570, the azeotrope with N,N-diethyl-2-methylcyclohexylamine (about 40% 2-methylcyclohexanol) had a b.p. of 192° (cor.), n^{25}D 1.4500. In order to avoid these azeotropes, an excess of hydrochloric acid was added to the residue from the petroleum ether extracts, the 2-methylcyclohexanol removed by steam distillation, and the amines isolated by making the solution basic, extracting, and fractionally distilling.

The higher alcohols were removed by distillation under reduced pressure after adding an excess of acid to the reaction product. The residue was then made basic, the resulting mixture extracted with ether, and the products isolated by fractional distillation. All distillations were carried out in a 6 ft. × 13 mm. Podbielniak column except the product from 2-ethylhexanol which was distilled through a 3 ft. × 13 mm. Podbielniak column. The products isolated and yields are summarized in Table I.

Cyclohexanol from Cyclohexylamine.—A mixture of 50 g. (0.5 mole) of cyclohexylamine, 200 ml. of water and 5 g. of Harshaw Ni-0104T $^1/_8$" was placed in an Aminco bomb and, after flushing with nitrogen and venting, heated for 10 hours at 180° (no hydrogen was used). The catalyst was removed by filtration and the reaction product extracted exhaustively with low boiling petroleum ether. The extracts were dried and the solvent removed by distillation. Analysis[4] of the residue indicated that it contained 42.8% alcohol calculated as cyclohexanol, 38.6% primary amine calculated as cyclohexylamine, and 7.8% secondary amine calculated as dicyclohexylamine. This would indicate that cyclohexanol was produced in 50% yield, based on reacted cyclohexylamine.

In another experiment carried out under the same conditions, except that 100 ml. of tetrahydrofuran was added as a solvent for the reaction, analysis of the product indicated that 62% of the cyclohexylamine reacted to give cyclohexanol in 84.8% yield. Cyclohexanol was isolated by extracting an acidified aliquot of the reaction product with ether and distilling (b.p. 157–158°) (uncor.), n^{26}D 1.4631[5] and further identified by its 3,5-dinitrobenzoate, m.p. 112–113°.[6]

Acknowledgment.—The authors are indebted to Mr. L. J. Lohr for the distillations and to Dr. S. Siggia and Mr. L. J. Fraunefelder for analyses.

(4) S. Siggia, J. G. Hanna and I. R. Kervenski, *Anal. Chem.*, **22**, 1295 (1950); S. Siggia and I. R. Kervenski, *ibid.*, **23**, 117 (1951).

(5) Reported b.p. 161°, K. K. Kelley, THIS JOURNAL, **51**, 1400 (1929); reported n^{25}D 1.4642, G. S. Hiers and R. Adams, *ibid.*, **48**, 2385 (1926).

(6) Reported m.p. 112–113°, T. Reichstein, *Helv. Chim. Acta*, **9**, 799 (1926).

GENERAL ANILINE AND FILM CORP.
CENTRAL RESEARCH LABORATORY
EASTON, PENNSYLVANIA

Oxidations with Ruthenium Tetroxide

BY CARL DJERASSI AND ROBERT R. ENGLE[1]

Osmium tetroxide has been used widely in organic chemistry as a catalyst in oxidations[2] and particularly for the hydroxylation[3] of olefins. The latter reaction is usually carried out by mixing stoichiometric quantities of the olefin and osmium tetroxide in an inert solvent such as ether, with or

(1) American Platinum Works Predoctoral Fellow at Wayne University, 1952.

(2) *Inter al.*, K. A. Hofmann, *Ber.*, **45**, 3329 (1912); N. A. Milas and S. Sussman, THIS JOURNAL, **58**, 1302 (1936).

(3) *Cf.* R. Criegee, *Ann.*, **522**, 75 (1936); R. Criegee, B. Marchand and H. Wannowius, *ibid.*, **550**, 99 (1942).

without traces of pyridine, and proceeds in good yield to the corresponding *cis*-glycol *via* a cyclic osmate ester which has to be cleaved.[3] Osmium tetroxide is expensive and very poisonous, and it seemed of interest, therefore, to investigate the behavior of the corresponding ruthenium derivative, since ruthenium appears immediately above osmium in the periodic table. Ruthenium tetroxide has been prepared a number of times,[4] but its behavior toward organic compounds has not been investigated except for the observation[4] that it is reduced rapidly by alcohol, acetaldehyde and the like. Ruthenium is more readily available than osmium and there exist *a priori* two reasons why ruthenium tetroxide might be preferred to the osmium analog. Although its vapors cause irritation when inhaled, it is not poisonous to the eyes[4,5] in contrast to this very serious danger with osmium tetroxide. Furthermore, recovery problems are simplified by the fact that combustion of ruthenium dioxide in air will not yield the volatile tetroxide in contrast to the analogous osmium derivative and organic impurities can thus be removed readily. In view of the fact that the present investigation had to be interrupted,[1] we should like to report briefly our observations on the behavior of ruthenium tetroxide with some organic compounds.

The much greater oxidizing action of ruthenium tetroxide as compared to osmium tetroxide was already demonstrated in initial qualitative experiments when a search was made for suitable solvents in which the oxidations could be conducted. Thus ether, benzene and pyridine, solvents which have been found very useful in the case of osmium tetroxide,[3] reacted violently and instantaneously with ruthenium tetroxide and thus proved completely useless. Of the common organic solvents, only carbon tetrachloride and chloroform were satisfactory[6] and the former was employed throughout our experiments. In view of the very high vapor pressure of ruthenium tetroxide, the solid usually has to be stored over potassium hydroxide in an ice cooled desiccator and it was found advantageous, therefore, to keep the reagent in carbon tetrachloride solution in which it was stable for a period of over one year. The ruthenium tetroxide content was established readily in an aliquot portion by reduction with an organic compound to the insoluble solvated ruthenium dioxide and reduction of the latter with hydrogen to ruthenium metal which could be weighed.

Since phenanthrene reacts slowly (2–7 days) with osmium tetroxide[3] in benzene solution to afford in good yield the osmate ester which upon cleavage leads to the crystalline 9,10-dihydrophenanthrene-9,10-diol, this example was selected first for comparison purposes. When a carbon tetrachloride solution of ruthenium tetroxide was added to an ice-cold solution of phenanthrene, a black pre-

(4) First prepared by C. Claus, *J. prakt. Chem.*, **79**, 28 (1860); the most recent reference is that by F. S. Martin, *J. Chem. Soc.*, 2683, 3055 (1952).

(5) W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1940, p. 418.

(6) This observation was also made by Martin (ref. 4) who measured the partition coefficient of ruthenium tetroxide between water and carbon tetrachloride and found it to be 59 in favor of the latter.

cipitate separated rapidly which appeared to consist chiefly of ruthenium dioxide rather than a ruthenate ester since conventional[3] cleavage with sodium sulfite yielded only a small amount of 9,10-dihydrophenanthrene-9,10-diol. The bulk of the product was in the original carbon tetrachloride solution and consisted of 9,10-phenanthrenequinone accompanied by some unreacted phenanthrene. Whether the formation of the quinone is due to direct oxidation at the 9,10-position or involves further oxidation of an intermediate ruthenate ester cannot be decided with the information at hand and further work on the oxidation of polycyclic aromatic hydrocarbons with this reagent is contemplated.

Attention was next turned to the behavior of sulfides since they appear to be essentially inert to osmium tetroxide[7,8] under ordinary conditions. In marked contrast to osmium tetroxide,[8] diphenyl sulfide was oxidized rapidly by ruthenium tetroxide at ice-bath temperature and afforded the corresponding sulfone accompanied by some sulfoxide. That diphenyl sulfoxide was probably the intermediate in this reaction was shown by the nearly quantitative conversion of the sulfoxide to the sulfone by ruthenium tetroxide. The oxidation was not limited to a diaryl sulfide since methyl p-tolyl sulfide and methyl benzyl sulfide were also oxidized to the corresponding sulfones; no sulfoxide could be isolated in these instances. A steroidal hemithioketal, androstan-17-one ethylene hemithioketal (I)[9] was similarly oxidized rapidly to the corresponding sulfone II in somewhat better yield as compared to perphthalic acid[9] where some cleavage to the parent ketone is observed.

I   II
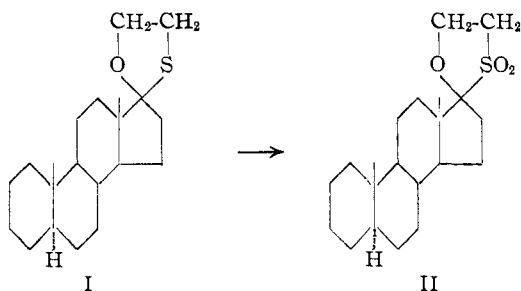
In view of this ready conversion of sulfides to sulfones or sulfoxides by means of ruthenium tetroxide under essentially neutral conditions, it seemed pertinent to investigate the behavior of triphenylmethyl phenyl sulfide toward this reagent. Knoll[10] claimed the formation of the sulfoxide by chromium trioxide oxidation of the sulfide, a reaction which could not be substantiated by Gregg and co-workers,[11] who observed that only triphenylcarbinol,[12] diphenyl disulfide and benzenesulfonic acid were formed. In spite of the fact that the entire reaction was carried out in carbon tetrachloride

(7) G. Stork, E. E. van Tamelen, L. J. Friedman and A. W. Burgstahler, THIS JOURNAL, 75, 384 (1953).

(8) Unpublished observation from this Laboratory.

(9) C. Djerassi and M. Gorman, THIS JOURNAL, 75, 3704 (1953).

(10) R. Knoll, J. prakt. Chem., 113, (N.F.), 40 (1926).

(11) D. C. Gregg, K. Hazelton and T. F. McKeon, J. Org. Chem., 18, 36 (1953), and earlier papers.

(12) It is noteworthy that the reported melting point (ref. 10) for the presumed sulfoxide (m.p. 163°) is nearly the same as that of triphenylcarbinol (m.p. 162°).

rather than acid solution, the main product (41%) of the ruthenium tetroxide oxidation was also triphenylcarbinol and no evidence for the presence of a sulfoxide or sulfone could be detected even after chromatography.

Acknowledgment.—We are indebted to the American Platinum Works, Newark, New Jersey, for support in the form of a fellowship and generous supplies of ruthenium compounds, and to Mr. Frank A. Meier of that company for helpful suggestions.

Experimental[13]

Stability of Ruthenium Tetroxide in Various Solvents.—A small amount of ruthenium tetroxide[14] (ca. 10 mg.) was tested with the following solvents: anhydrous ether—small explosion, followed by yellow flame; benzene—vigorous explosion; pyridine—no explosion, only flame; carbon tetrachloride and chloroform—reddish-orange solution, which was quite stable if preserved in stoppered flasks uncontaminated by organic matter. When a carbon tetrachloride solution (rather than the solid) of ruthenium tetroxide was added to benzene or ether, no fire or explosion was produced but an instantaneous appearance of a black precipitate of ruthenium dioxide was noted. The same observation was made when the reaction was conducted in an atmosphere of nitrogen.

Determination of Ruthenium Tetroxide in Carbon Tetrachloride Solution.—For storage or shipping purposes, ruthenium tetroxide is best handled in carbon tetrachloride solution and the following method of determination was employed. To a 4-cc. aliquot portion of the standard solution was added dropwise diphenyl sulfide or ethanol until no more black precipitate was formed. After centrifugation, the supernatant liquid was tested for the presence of unreacted tetroxide by the addition of a few drops of diphenyl sulfide and the precipitate was washed several times with carbon tetrachloride–ether. The solvated ruthenium dioxide was then transferred to a tared Rose crucible as a slurry in carbon tetrachloride (this was done to avoid losses rather than as a safety precaution since ruthenium dioxide is stable and harmless), the latter was blown off and the dioxide was reduced to ruthenium metal at red heat for 20 minutes in a slow current of hydrogen. After cooling in an atmosphere of hydrogen, the crucible was again weighed in order to determine the weight of ruthenium and the concentration of ruthenium tetroxide could thus be established accurately. A typical duplicate run gave values of 17.62 and 17.65 mg. per cc. and the accuracy of this method was tested initially with solutions of ruthenium tetroxide of known concentration.

Reaction of Phenanthrene with Ruthenium Tetroxide.—To an ice-cold solution of 2.0 g. (0.0112 mole) of phenanthrene in 100 cc. of carbon tetrachloride[15] was added dropwise with stirring over a period of 15 minutes 55 cc. of a carbon tetrachloride solution of ruthenium tetroxide containing 0.972 g. (0.0058 mole) of the tetroxide. A black precipitate formed upon addition of the first drop. After 24 hours at −5°, the precipitate was centrifuged, washed several times with carbon tetrachloride and ether, and finally was extracted with ether in a Soxhlet extractor to ensure complete removal of soluble products. The combined organic solutions were evaporated to dryness and the residue, dissolved in 100 cc. of hexane–benzene (1:1) was chromatographed on 80 g. of alumina. Unreacted **phenanthrene** (0.958 g., 48%) was eluted with the original solvent combination, while the chloroform eluates after evaporation and recrystallization from benzene afforded 0.34 g. (28% based on ruthenium tetroxide) of 9,10-**phenanthrenequinone** with m.p. 206–208°, undepressed upon ad-

(13) Melting points are uncorrected. Infrared absorption spectra were measured in chloroform solution with a Baird Associates double beam recording infrared spectrophotometer using a 0.1-mm. cell thickness.

(14) Obtained from American Platinum Works, Newark, New Jersey.

(15) The carbon tetrachloride in this and all other experiments was purified as indicated by L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., New York, N. Y., 1941, p. 365.

mixture with an authentic specimen. Identity was established further by comparison of the infrared spectra and formation of a quinoxaline derivative, m.p. 218–220°.

In another experiment,[16] the reaction was carried out as above except that equimolar proportions were used, and there was isolated 18% of phenanthrenequinone. The original black precipitate was refluxed with sodium sulfite[3] in dilute ethanol for two hours, filtered, and the filtrate was extracted thoroughly with ether. The ether residue after recrystallization from hexane–acetone furnished 11% of 9,10-dihydrophenanthrene-9,10-diol with m.p. 175–177°, undepressed upon admixture with a sample prepared with osmium tetroxide.[3]

Reaction of Diphenyl Sulfide with Ruthenium Tetroxide. —A large excess of sulfide was employed in order to isolate any intermediate oxidation product.

An ice-cold solution of 4.798 g. (0.0257 mole) of diphenyl sulfide in 150 cc. of carbon tetrachloride was treated exactly as described above with 25 cc. of a carbon tetrachloride solution of ruthenium tetroxide (containing 1.043 g., 0.0063 mole of tetroxide). Precipitation of ruthenium dioxide started immediately and after 14 hours in the refrigerator, the precipitate was centrifuged and washed thoroughly with carbon tetrachloride and ether. The residue after evaporation of the organic solvents was chromatographed on 100 g. of alumina. The unreacted sulfide was removed by the original hexane–benzene (7:3) eluates, while **diphenyl sulfone** (0.58 g., 42%) with m.p. 124.5–125.5° was obtained from the hexane–benzene (1:9) fractions. Identity was established by a mixture melting point and infrared comparison with an authentic sample; the two typical sharp sulfone bands[17] at 8.65 and 9.0 μ were present.

Anal. Calcd. for $C_{12}H_{10}O_2S$: C, 66.05; H, 4.62. Found: C, 66.32; H, 4.91.

Evaporation of the benzene and benzene–ether (1:1) eluates to dryness and recrystallization from benzene–petroleum ether furnished 0.4 g. (32%) of **diphenyl sulfoxide** with m.p. 68–69°. Identity was established in the usual manner including infrared comparison (typical[18] sulfoxide band at 9.6 μ).

Anal. Calcd. for $C_{12}H_{10}OS$: C, 71.28; H, 4.99. Found: C, 71.18; H, 5.28.

When an equimolar ratio of diphenyl sulfoxide and ruthenium tetroxide was mixed in carbon tetrachloride solution and worked up in the above manner, a 93% yield of diphenyl sulfone was realized.

Reaction of Methyl p-Tolyl Sulfide with Ruthenium Tetroxide. —Methyl p-tolyl sulfide (3.90 g., 0.0281 mole) was oxidized with 1.165 g. (0.007 mole) of ruthenium tetroxide exactly as indicated for diphenyl sulfide and purified by chromatography. **Methyl p-tolyl sulfone** was obtained in 31% yield, m.p. 85–86° (lit.[19] m.p. 86–87°) but no sulfoxide could be detected in the later eluates of the chromatogram.

Anal. Calcd. for $C_8H_{10}O_2S$: C, 56.46; H, 5.92. Found: C, 56.35; H, 5.82.

Reaction of Methyl Benzyl Sulfide with Ruthenium Tetroxide. —The oxidation was carried out in the above described manner with 0.0252 mole of methyl benzyl sulfide and 0.0067 mole of ruthenium tetroxide. **Methyl benzyl sulfone** was isolated in 58% yield, m.p. 125–126°,[20] but no sulfoxide was found in the latter chromatogram fractions.

Anal. Calcd. for $C_8H_{10}O_2S$: C, 56.46; H, 5.92. Found: C, 55.98; H, 5.69.

Reaction of Triphenylmethyl Phenyl Sulfide and Ruthenium Tetroxide. —The oxidation of the triphenylmethyl phenyl sulfide[11] was carried out in the standard manner except that equimolar amounts were employed. As in the above-described cases, ruthenium dioxide separated immediately upon addition of the tetroxide. After centrifugation, the carbon tetrachloride solution was evaporated to dryness yielding a residue with m.p. 77–87° which was par-

titioned between water[21] and ether. The ether solution was washed until neutral, dried, evaporated and dissolved in warm cyclohexane from which 33% of triphenylcarbinol (m.p. 160–162°) separated. The filtrate was evaporated and the residue was chromatographed on alumina yielding 13% of recovered sulfide and an additional 8% of triphenyl carbinol. No disulfide[11] was found in any chromatogram fractions. Acidic products formed were not investigated.

Reaction of Androstan-17-one Ethylene Hemithioketal (I) and Ruthenium Tetroxide. —A mixture of 0.48 g. (0.0011 mole) of the hemithioketal (I)[9] and 0.34 g. (0.0021 mole) of ruthenium tetroxide in carbon tetrachloride was left in the refrigerator overnight. After centrifugation the supernatant liquid was evaporated to dryness and triturated with acetone yielding 0.35 g. of the **sulfone II** with m.p. 187–190°. Two recrystallizations from acetone raised the m.p. to 199–200°, undepressed upon admixture with an authentic sample[9] prepared by perphthalic acid oxidation of I. The infrared spectra of the two specimens were identical.

(21) The ruthenium tetroxide probably contains a small amount of water since it is obtained by co-distillation with water. It is therefore not necessary to postulate that the hydrogen necessary for the formation of triphenylcarbinol is furnished during the ether–water partition. Indeed, direct chromatography of the carbon tetrachloride residue gave essentially the same results.

DEPARTMENT OF CHEMISTRY
WAYNE UNIVERSITY
DETROIT 1, MICHIGAN

Δ⁵-Pregnen-20-one[1]

BY MARGARET A. DAUS AND H. HIRSCHMANN

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In a study of the hydrogenolyses of toluenesulfonates with lithium aluminum hydride Schmid and Karrer[2] observed that the tosylate of cholesterol yielded both Δ⁵-cholestene and 3,5-cyclocholestane. In contrast reduction of the tosylate of Δ⁵-pregnen-3β-ol-20-one followed by reoxidation of the 20-hydroxy group furnished only a single pure product[3] of the composition $C_{21}H_{32}O$. This was held probably to be the hitherto undescribed[4] Δ⁵-pregnen-20-one, as it showed a well-defined infrared absorption maximum in the region of the bending vibrations of hydrogen attached to a trisubstituted double bond. However, the spectrum which possessed absorption maxima near 12.67 and 12.37 μ failed to conform to the generalizations which had emerged from a study of the spectra of Δ⁵-unsaturated steroids.[5] These compounds showed in general two maxima in this region that could be associated with the presence of the double bond. If no functional group other than one at C-3 was present in the vicinity of the double bond one of these peaks was close to 12.50 μ (800 cm.⁻¹) while the position of the other depended on the nature and the configuration of the substituent at C-3. Since Δ⁵-cholestene showed maxima at 12.52, 12.37 (w) and 12.01 μ (799, 809, 833 cm.⁻¹) an absorption peak near 12.50 μ was to be expected also for the spectrum of Δ⁵-pregnen-20-one. As it

(1) Supported by grants from the Hanna Research Fund and from the National Cancer Institute of the National Institutes of Health, Public Health Service.

(2) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32**, 1371 (1949).

(3) P. Karrer, H. Asmis, K. N. Sareen and R. Schwyzer, *ibid.*, **34**, 1022 (1951).

(4) The preparation of this substance has been recorded in the patent literature (R. E. Marker and E. L. Wittle, U. S. Patents 2,397,424, 2,397,425 and 2,397,426). However, the product was not characterized in any way.

(5) H. Hirschmann, THIS JOURNAL, **74**, 5357 (1952).

(16) This experiment was performed at the University of Mexico with Dr. Alberto Sandoval.

(17) K. C. Schreiber, *Anal. Chem.*, **21**, 1168 (1949).

(18) D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

(19) R. Otto, *Ber.*, **18**, 154 (1885).

(20) Reported, m.p. 124.5° (A. Freiman and S. Sugden, *J. Chem. Soc.*, 263 (1928)).