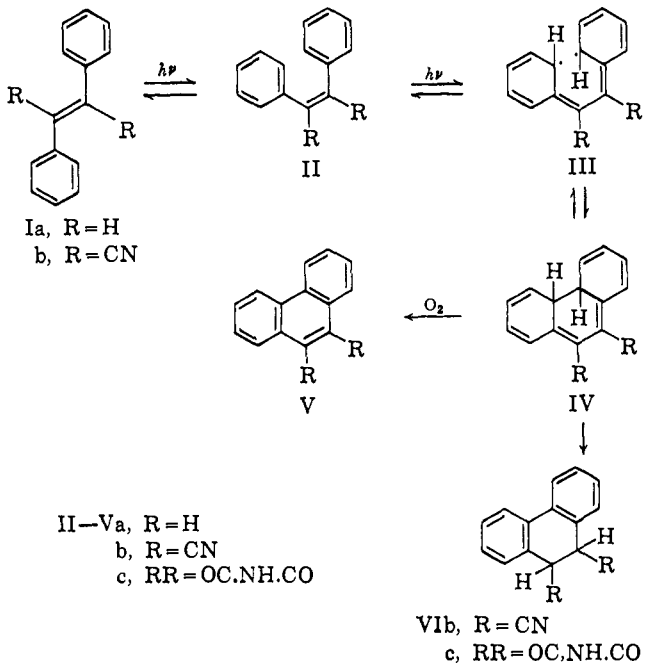

threne dicarbonitrile (Vb) and 9,10-dicyano-9,10-dihydrophenanthrene (VIb, 7%).

Compound VIb crystallized as colorless prisms from chloroform (m.p. 199–204°,[5] which varied with the rate of heating). The proton magnetic resonance spectrum exhibited a single peak equivalent to two protons at 5.58 τ in chloroform and at 4.68 τ in dimethyl sulfoxide attributed to the protons at the 9 and 10 positions. The infrared spectrum in chloroform had an aliphatic nitrile stretching mode at 2255 cm.$^{-1}$. *Anal.* Calcd. for $C_{16}H_{10}N_2$: C, 83.1; H, 4.4; N, 12.2; mol. wt., 230. Found: C, 83.1; H, 4.4; N, 12.5; mol. wt., 230. Compound VIb had previously been formulated as *cis*-$\alpha\beta$-dicyanostilbene[6] (IIb). Hydrolysis with methanolic potash gave 9-phenanthrene carboxamide (m.p. 226°[7]; lit. 226°).[8]

Photolysis of *trans*-$\alpha\beta$-dicyanostilbene in degassed[9] ethanol gave only the dihydro compound (VIb).

Diphenylmaleinimide (IIc, 7.7×10^{-3} *M*) on photolysis in ethanol for 2.5 hr. gave 9,10-phenanthrene dicarboximide (Vc) and 9,10-dicarboximido-9,10-dihydrophenanthrene (VIc, 40%). The phenanthrene (Vc) crystallized from acetone as yellow needles (m.p. 334–335°). *Anal.* Calcd. for $C_{16}H_9NO_2$: C, 77.7; H, 3.7; N, 5.7. Found: C, 77.7; H, 3.8; N, 5.7.

The dihydrophenanthrene (VIc) crystallized from chloroform as colorless prisms (m.p. 245–246° dec.) *Anal.* Calcd. for $C_{16}H_{11}NO_2$: C, 77.1; H, 4.45; N, 5.6. Found: C, 76.9; H, 4.6; N, 5.7. Recrystallization from acetone brought about dehydrogenation to the phenanthrene (Vc). Similarly, melting produced the phenanthrene, the m.p. rising to 334–335°. The proton magnetic resonance spectrum showed a single peak equivalent to two protons at 5.18 τ in dimethyl sulfoxide attributed to the protons at the 9 and 10 positions.

The electronic spectra of compounds VIb and VIc are typical of 9,10-dihydrophenanthrenes (see Table I).

(5) All melting points unless otherwise stated were determined on a Kofler block and are corrected.

(6) D. G. Coe, E. W. Garnish, M. M. Gale and C. J. Timmons, *Chem. Ind.* (London), 665 (1957).

(7) Determined in a sealed capillary tube and uncorrected.

(8) C. W. Shoppee, *J. Chem. Soc.*, 37 (1933); A. Werner, *Annalen*, **321**, 248 (1902).

(9) Degassing was performed at 10^{-6} mm. with more than six freezings of the solution.

TABLE I

ELECTRONIC SPECTRA OF 9,10-DISUBSTITUTED 9,10-DIHYDROPHENANTHRENES IN EtOH

Compound	λ_{max} mμ	(ε)	λ_{max} mμ	(ε)	λ_{max}, mμ	(ε)
VIb	206	39,000	268	17,500		
	211	41,000				
	223[a]	8600				
VIc	208	35,000	265[a]	14,000	303	1200
	230[a]	10,000	275	16,000		
	240	5800	284[a]	11,500		
(±)-*trans*-9,10-Dihydroxy-9,10-dihydrophenanthrene	211	40,000	269	15,000	298[a]	2600
	225[a]	10,000				
cis-9,10-Dihydroxy-9,10-dihydrophenanthrene	208	39,500	270	16,500		
	225[a]	10,000	282[a]	11,000		
cf. VIa	209	43,500	265	17,500	290[a]	4400
	220[a]	10,000			298	4300

[a] Inflection

Proton magnetic resonance measurements on *cis*- and (±)-*trans*-9,10-dihydroxy-9,10-dihydrophenanthrene in dimethyl sulfoxide–deuterium oxide solutions showed single peaks at 5.25 and 5.22 τ, respectively, supporting the proposed structures for the photolysis products. From the resonance spectra of the aromatic protons it is tentatively suggested that the photolysis products possess the *cis* stereochemistry but this point is being investigated further.

We propose that the dihydrophenanthrenes (VIb and VIc) are rearrangement products of the photolysis intermediates IVb and IVc, the existence of which is thus further confirmed. As a result of these rearrangements the systems become stabilized by the difference in resonance energies of the biphenyl (VI) and the tricyclic hexaene (IV). Other substituted stilbenes are being investigated to see if the rearrangement is dependent on the groups R.

Acknowledgments.—We are indebted to Professor E. Boyland for a sample of *cis*-9,10-dihydroxy-9,10-dihydrophenanthrene. M. V. S. thanks Unicam Instruments Ltd., Cambridge, England, for a Research Scholarship.

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RECEIVED MAY 20, 1963

The Quinone Oxidation of Ethanol Catalyzed by Chromic Ion

Sir:

The ammonium salt of 2,5-dihydroxy-*p*-benzoquinone (denoted hereafter by Q′) reacts with a wide variety of metal ions to form complex salts which are generally insoluble[1]; chloroanilic acid, 2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone (Cl_2Q'), has been used extensively in schemes of analysis for metal ions.[2] In the hope of gaining greater insight into the interaction of transition metal ions through conjugated systems, both from the point of view of the activated complex in electron-transfer reactions[3] and of "mixed" valence states, we have undertaken an investigation of the reactions of Q′ and Cl_2Q' with chromous ion.

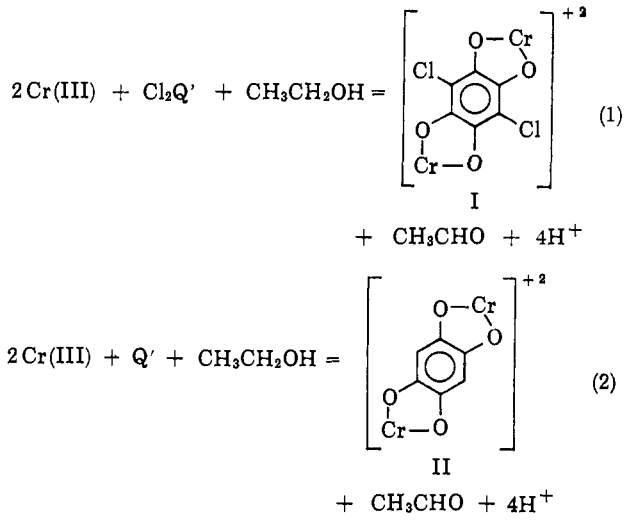
(1) R. L. Frank, G. R. Clark and J. N. Coker, *J. Am. Chem. Soc.*, **72**, 1827 (1950).

(2) W. G. Hart, *Org. Chem. Bull.*, **33**, 3 (1961).

(3) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 25 (1959).

The products of these reactions are characterized by a series of intense absorption bands in the visible region of the spectrum. As might be anticipated on the basis of oxidation–reduction potentials and of the "capture" property which Cr^{+2} has on being oxidized to Cr(III), each of the products contains two moles of chromium per mole of quinone. We wish to report here that the product obtained when chromic ion is added to either of the two quinones in ethanol is identical with that obtained from the reaction of chromous ion with that of quinone. Further work is in progress to elucidate the nature of the reactions, including a kinetic study of the processes, but we feel that the systems are of sufficient interest to warrant a preliminary report of the observations.

With the proviso that chelation is assumed rather than established, we believe the net reaction may be represented by eq. 1 or 2



(1)

I

(2)

II

The presence of two chromium atoms per quinone was established by titrating alcoholic $Cr(H_2O)_6(ClO_4)_3$ into a constant amount of the quinone, diluting to a standard volume and measuring the optical density due to the product complex after no further change was observed to take place. Values obtained were Cr/Q′ = 1.94; Cr/Cl_2Q' = 2.13. That ethanol was oxidized to acetaldehyde was confirmed by distilling the solvent from a reaction mixture and analyzing for carbonyl groups by the method of Eitel.[4] The carbonyl yield found, based on one mole per mole of the quinone added, was 72%. Since the amount of carbonyl compound found corresponded to oxidation of only 0.08% of the ethanol present, another sample was analyzed by mass spectrometric methods; all major peaks observed could be assigned to either ethanol, acetaldehyde or CO_2 (the latter present in the sample in small amount because of the method of handling).

There are several interesting features of these reactions that merit discussion. Alcohols can be converted to aldehydes by the Oppenauer reaction, although its use for primary alcohols is generally limited[5]; in such a process, using quinones as hydrogen acceptors, the oxidation "may" be rapid,[6] although we know of no report of a quantitative measure of such a reaction rate. In the presence of a large excess of chromic ion, we have established that the half-life of Cl_2Q' in ethanol is about 15 min. at 25°. This rate has a large temperature coefficient; thus we find that the half-life at 35° is reduced to 4 min. As measured by the appearance of the spectrum of I, the reaction takes place readily with *n*-propyl alcohol, *n*-butyl alcohol, and isopropyl alcohol ($t_{1/2} \cong 7$ min. at 25° for the latter), but not with *t*-butyl alcohol or methanol; Q′ reacts similarly, but more slowly. It should be noted that in the absence of the metal ion, no reaction occurred between Cl_2Q' and ethanol after heating at 50° for 6 days.

By studying the rate of formation of I as a function of the chromic ion concentration, we have observed that with sufficient excess of chromic ion, the rate becomes independent of the concentration of chromic ion. The implication of this is that the rate of substitution into the first coördination sphere of chromic ion is not rate-determining, and that this substitution is *rapid* in ethanol. This result is highly surprising when compared to the rates of substitution of various ligands on chromic ion in aqueous solution.[7] Research is currently in progress to determine if the rapid substitution in ethanol is general or is due to specific reactivity of the organic molecule; preliminary experiments with Cl^- as a ligand show the formation of $CrCl^{+2}$ to be rapid also.

A related observation is that various ligands cause a diminution in the rate of formation of I; water or methanol exerts this effect as does Cl^-, Br^- or CCl_3COO^-. Table I shows the effect of Cl^-. It appears that these ligands either interfere with the substitution process or with the ability of the system to transfer electrons from the ethanol to the quinone. In any event it is remarkable that a single Cl^- for each Cr^{+3} can have such a profound effect on the rate.

TABLE I

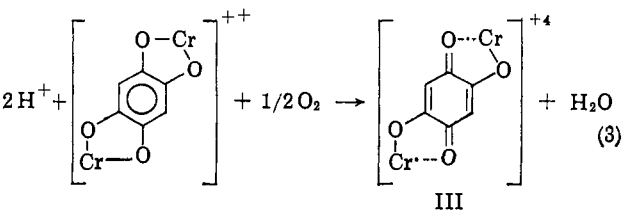
EFFECT OF Cl^- ON RATE OF FORMATION OF I

$Cr^{+3} = 1.78 \times 10^{-2}$ *M*; $Cl_2Q' = 5.1 \times 10^{-5}$ *M*; $H_2O \cong 0.1$ *M*

Cl^-	$t_{1/2}$ (min.) at 25°
0	30[a]
0.78×10^{-2} *M*	54
1.57×10^{-2} *M*	200
2.20×10^{-2} *M*	1200

[a] Variation in water concentration explains the difference of this $t_{1/2}$ from that mentioned in the text.

It is of interest to note that a possibility for a cyclic series of reactions exists with this system since the compound II can be oxidized by oxygen to a red compound, presumably the binuclear quinone complex



(3)

III

or combining eq. 2 and 3

$$CH_3CH_2OH + 1/2O_2 \xrightarrow{Cr^{+3};\ Q'} CH_3CHO + H_2O \quad (4)$$

In an experiment starting with 0.53 mmole of Q′, 1.7 mmoles of $Cr(H_2O)_6(ClO_4)_3$ and 75 ml. of ethanol, adding

(4) A. Eitel, *J. Prakt. Chem.*, **159**, 292 (1942); see also J. Mitchell, Jr., in "Organic Analysis," Vol. 1, J. Mitchell, I. M. Kolthoff, E. S. Proskauer and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y. 1953.

(5) C. Djerassi in "Organic Reactions," R. Adams, Ed., Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951.

(6) H. Adkins and R. C. Franklin, *J. Am. Chem. Soc.*, **63**, 2381 (1941).

(7) D. R. Stranks in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York N. Y., 1960.

oxygen in three separate steps, enough being added in each step to oxidize II to III, we found a total of 2.06 mmoles of carbonyl.

Acknowledgment.—This work was supported by the National Science Foundation under Grant No. 20954. Funds for the purchase of the spectrophotometer were also made available by the National Science Foundation under Grant No. 22611. R. G. L. wishes to express thanks for fellowship support by the Eastman Kodak Company and the National Science Foundation.

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RECEIVED MAY 31, 1963

BOOK REVIEWS

Les Cyclitols. Chimie, Biochimie, Biologie. Actualités Scientifiques et Industrielles 1294. By THÉODORE POSTERNAK, Professeur a l'Université de Genève. Editions Hermann, 115, Boulevard Saint-Germain, Paris VI, France. 1962. 491 pp. 17.5 × 24 cm. Price, 48 NF.

Although the prototype cyclitol, *myo*-inositol, was discovered in muscle tissue more than a century ago, no rapid progress in cyclitol chemistry was possible until the configuration of this key compound was determined. This difficult task was finally accomplished by Théodore Posternak of the University of Geneva during the period 1928–1942, stimulated by earlier work of his father, S. Posternak. Professor T. Posternak later elucidated the configuration and chemistry of numerous other cyclitols, and it is most fitting that the first major treatise on this subject now appears under his authorship.

The word cyclitol was at first applied only to ordinary inositol and a few closely related substances. Now in a much broader sense *cyclitol* might be taken to include any monoalicyclic compound whose ring bears at least one hydroxyl group and may also bear other groups. The results of cyclitol research now conveniently available in Posternak's book are of value in many areas of science, and this excellent monograph should be useful to a wide circle of chemists, biochemists and biologists.

The cyclitols are old friends to teachers and students of organic chemistry, because the nine isomers of inositol have long served as favorite illustrations of the stereoisomerism (and more recently, conformational analysis) of polysubstituted cyclic molecules. These isomers were already the basis of extensive classroom discussions at a time when most of the actual compounds were still unknown and the paths leading to their ultimate synthesis could not even be foreseen.

The study of cyclitols is a fascinating and challenging subject for the synthetic or structural chemist because of their complex stereoisomerism, numerous functional groups of similar reactivity, and special susceptibility to conformational analysis. The treatment of these compounds in "Les Cyclitols" benefits by the rather complete configurational knowledge now available. To a greater extent than in most previous reviews, Posternak has placed the structurally selective and stereospecific reactions of cyclitols on a rational basis made possible by modern conformational theory. Only brief mention is made of the application of n.m.r. and optical rotation predictions to these compounds, and it does seem that greater emphasis should be placed on these exciting new physical methods.

The material assembled in this volume should be of especially great value to the carbohydrate chemist, for whom the cyclitols are useful model substances with which to study typical secondary-alcohol group behavior of sugars, in the absence of ring-opening complications. The alicyclic or steroid chemist will also find much of interest here, since the cyclitols conveniently display many properties of the six-membered ring.

The Première Partie (272 pages) of this book consists of 14 chapters on "Chimie des Cyclitols." After a long introductory chapter on basic characteristics of the entire family of compounds (stereochemistry, conformation, reactivity, physical properties) there are individual chapters dealing with: *myo*-inositol; the other inositols; the pentols, tetrols and triols; the methyl ethers; cycloses; anhydro and unsaturated derivatives; halogen and nitrogen derivatives; carboxylic acids; and phosphate esters. Although part of a "Natural Products" series, Posternak's book gives thorough coverage to synthetic cyclitols, and in fact these comprise the great majority of compounds mentioned.

In the Deuxième Partie (110 pages) there are ten chapters on "Biochimie and Biologie." These provide a useful review of a great variety of fascinating topics, including: occurrence in plants and animals; metabolism; biosynthesis; inositol lipids; antagonists of *myo*-inositol; lipotropic action; inosituria; effect on tumors.

The potentially great importance of inositols to the biochemist or biologist arises in part from the fact that *myo*-inositol occurs in every living cell, so far as is known. Perhaps even more important is the fact that *myo*-inositol belongs to that very select group of 22 organic compounds (including 13 amino-acids) which are *necessary and sufficient* for the survival and growth of isolated human cells. Although the essential cellular role of *myo*-inositol is not well understood, there can be little doubt that it is deeply involved in important biochemical processes.

The primary coverage of "Les Cyclitols" extends through 1959, but 50 additional papers from 1960 and 1961 are reviewed in 11 pages of *Addenda*. Altogether, not less than 1200 original articles were examined. Citations to these are given both in fine-print footnotes and in a 40-page alphabetized bibliography. This bibliography and the subject index and table of contents together consume not less than 85 large-type, single-column pages at the end of the book. This format, space-consuming though it may be, is a refreshing change from the supercondensed multicolumn style which afflicts so much of today's scientific literature.

The author of any work on cyclitols faces some vexing problems of nomenclature, since the ways of naming these substances are almost as numerous as the groups working on them. Although uniformity is much needed, it appears that nearly every proposed nomenclature has some good features, which might well be preserved in the ultimate uniform system.

The difficulties arise primarily in designating the very numerous stereoisomers (*e.g.*, 32 for an aminodeoxyinositol). Three principal notations have been advocated, and since Posternak makes some use of all three, the reader has an opportunity to judge their relative effectiveness. The first notation uses 8 rather arbitrary prefixes (allo, muco, neo, etc.) for the cyclohexanehexols, 10 other prefixes for the cyclohexanepentols, and so on. The second notation tries to name nearly all cyclitols in terms of the 8 inositol configurations. The third notation employs fractional symbols, as in the name "*14/23*-cyclohexanetetrol." In the reviewer's opinion, this fractional notation, being nearly self-explanatory to any organic chemist, is by far the best system.

It does seem unfortunate that Dr. Posternak has chosen to perpetuate the name "*meso*-inositol" for the most common isomer, since seven *meso*-inositols are possible and all are now known. Although "*myo*-inos," meaning literally "muscle-muscle" (the Greeks had two words for it), is redundant, the name *myo*-inositol proposed by Fletcher, Anderson and Lardy is already widely accepted, and now seems the most practical way to escape the ambiguity.

This volume is unusually free of typographical or other errors. However, 1,2,4,5-cyclohexanetetrol (p. 121) should be credited with five (not four) theoretically possible diastereomers—the last of these were prepared this year. Also, more than one 1,2,4-triol (p. 126) has been reported in earlier literature. Also formula 115 (p. 100) needs revision.

"Les Cyclitols" is an attractively printed and bound paperback, which well deserves its selection by a French Graphic Arts Committee as one of "les 50 plus beaux livres de l'année" (non-scientific books included). The present volume is one of a promising series on the Chemistry of Natural Substances, to be edited by Professor Edgar Lederer, Director of the new Institut de