Acknowledgment. We thank Mr. H. Sato, Naka Works, Hitachi, Ltd. for the measurement of the glpc-mass spectra.

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Intramolecular and Intermolecular Oxidative Coupling Reactions by a New Iron Complex $[Fe(DMF)_3Cl_2][FeCl_4]$

Sir:

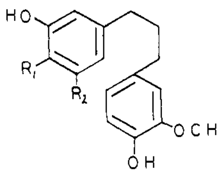
It has been known for a long time that phenols are readily oxidized by many different reagents. The products are mostly complicated mixtures of dimeric, polymeric, and quinoid compounds in nature. Oxidative phenol coupling has received considerable attention owing both to its utility as a synthetic reaction and its proposed involvement in the biosyntheses of a number of classes of natural products.[1] To date, various oxidizing agents have been investigated but with limited success;[2] we wish to report a new method for intramolecular and intermolecular oxidative coupling by a new complex prepared from ferric chloride and dimethylformamide (DMF) which gives the oxidation products in high yield under mild conditions and which avoids the formation of polymeric compounds in minimum amounts.

After trying a variety of oxidizing agents under various conditions we found ferric chloride in DMF led to fairly good results for the oxidation of compounds of type **1**. During further investigation of these reactions, a new complex[3] which has the molecular formula $[Fe(DMF)_3Cl_2][FeCl_4]$ and which is responsible for the phenol oxidation, was isolated. These observations prompted us to investigate the use of this complex for the oxidative coupling reactions in detail.

The oxidizing reagent was prepared as follows. To a solution of ferric chloride, 163 g (1 mol) in 1.6 l. of dry ether, DMF, 110 g (1.5 mol), was added with stirring. A precipitate (260 g, 95.2% yield) was obtained as a yellowish green powder[4] which was not hygroscopic and which could be recrystallized from methylene chloride and ethanol to give needles,[5] mp 220° (*Anal.* Found: C, 19.65; H, 3.94; N, 7.57; Cl, 39.38). The visible light absorption spectra of this complex either in the solid state or in the solution of nonaqueous solvents show the characteristic absorption at 530 mμ due to the $FeCl_4^-$ ion.[6] These observations reduce to the molecular formula $[Fe(DMF)_3Cl_2][FeCl_4]$ for this complex.

A typical oxidative coupling reaction using a new complex was carried out in the following manner. 1-(3,4-Dimethoxy-5-hydroxyphenyl)-3-(3-methoxy-4-hydroxyphenyl)propane (**1**) ($R_1 = R_2 = OCH_3$), bp 194–197° (0.3 mm), was prepared from the corresponding chalcone. To a solution of the complex, 5.44 g (10 mmol) in 55 ml of water, 0.318 g (1 mmol) of **1** ($R_1 = R_2 = OCH_3$) in 10 ml of ether was added and the mixture was refluxed with stirring for 1 hr. The dienone **2** ($R_1 = R_2 = OCH_3$) (mp 245–247°; ir (KBr) 3.17, 6.06, 6.13 μ; uv (C_2H_5OH) 234 (ε 17,060), 280 mμ (ε 8090)) was obtained as a crystalline precipitate in 67% yield.[7] In the same manner, by the oxidation of **1** ($R_1 = OCH_3$; $R_2 = H$), mp 103–104°, the dienone **2** ($R_1 = OCH_3$, $R_2 = H$[8]), mp 162–163°, was formed in high yield (67%), and similarly the oxidation of **1** ($R_1 = R_2 = H$), mp 58–58.5°, produced the dienone **2** ($R_1 = R_2 = H$), mp 158–160°, in 39% yield.

To illustrate additional examples, the following intermolecular oxidative coupling by the new complex was investigated. The oxidation of *p*-cresol[9] afforded only Pummerer's ketone **3** in 28% yield[7] and the oxidation of ferulic acid[10] produced a dilactone **4** in 35% yield, under similar reaction conditions. The oxidation of methyl indole-3-acetate gave an unsymmetrical coupling product **5** ($R_1 = CH_3$; $R_2 = CO_2CH_3$): mp 136–138°; nmr ($CDCl_3$) δ 3.58 and 3.70 (each s), 3.81 (s, 2 H), 5.63 (s, 1 H), 6.87 (1 H), 6.95–7.35 (m, 6 H), 7.39–7.70 (m, 2 H), 8.20 and 8.85 (each 1 H), in 50%



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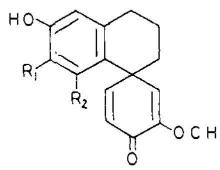

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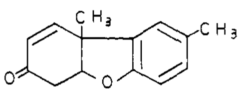

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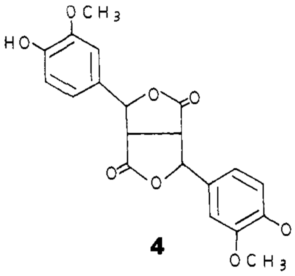

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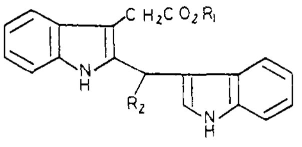

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[1] W. I. Taylor and A. R. Battersby, Ed., "Oxidative Coupling of Phenols," Marcel Dekker, New York, N. Y., 1967.

[2] For recent examples, the following reagents were applied for the oxidative phenol coupling: (a) vanadium oxytrichloride and vanadium tetrachloride; W. L. Carrick, G. L. Karapinka, and G. T. Kwiatkowski, *J. Org. Chem.*, **34**, 2388 (1969); M. A. Schwartz, R. A. Holton, and S. W. Scott, *J. Amer. Chem. Soc.*, **91**, 2800 (1969); (b) manganic tris-(acetylacetonate); M. J. S. Dewar and T. Nakaya, *J. Amer. Chem. Soc.*, **90**, 7134 (1968).

[3] The formation of solvates in the reactions between DMF and various metal salts including ferric chloride is known: R. C. Poul and R. B. Sreenathan, *Indian J. Chem.*, **4**, 382 (1966); B. S. Magor and T. D. Smith, *J. Chem. Soc. A*, 1753 (1968); N. N. Dass and M. H. George, *J. Polym. Sci., Part A-1*, 269 (1969).

[4] It was a mild, exothermic reaction. The precipitate is sufficiently pure to use directly for oxidation reactions.

[5] It is a remarkable feature of this complex that it is unchanged upon recrystallization from water or acetonitrile.

[6] D. W. Meek and R. S. Drago, *J. Amer. Chem. Soc.*, **83**, 4322 (1961).

[7] The mother solution consisted mainly of starting material.

[8] The nmr spectrum of **2** ($R_1 = OCH_3$; $R_2 = H$) exhibited aromatic proton absorption consistent with a 2,4,5-trisubstituted phenol moiety, thus establishing **2** as the para–para coupling product.

[9] C. G. Hayne, A. H. Turner and W. A. Waters, *J. Chem. Soc.*, 2823 (1956); T. Kametani and K. Ogasawara, *Chem. Pharm. Bull.*, **16**, 1138 (1968).

[10] K. Freudenberg and H. Dietrich, *Chem. Ber.*, **86**, 1157 (1953); N. J. Cartwright and R. D. Haworth, *J. Chem. Soc.*, 535 (1944).

yield. Selective decarboxylation[11] was effected by the treatment of the oxidation product 5 (R_1 = CH_3; R_2 = CO_2CH_3) with 20% aqueous NaOH to give 5 (R_1 = R_2 = H, mp 203–205°) (methyl ester, mp 123–125°)[12] in 80% yield.

Studies on the application of this method to the biogenetic-type synthesis of phenolic alkaloids and indole chemistry are in progress.

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Received November 15, 1971

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(11) H-H. Stroh and H. Beitz, *Justus Liebigs Ann. Chem.*, 700, 78 (1966).

(12) All new compounds had satisfactory elemental analyses.

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*Book Reviews**

Topics in Stereochemistry. Volume 6. Edited by N. L. Allinger (University of Georgia) and E. L. Eliel (University of Notre Dame). Wiley-Interscience, New York, N. Y. 1971. xi + 296 pp. $19.95.

The latest volume in this valuable series begins with a tribute to the Nobel Laureates in Chemistry for 1969—D. H. R. Barton and O. Hassel—in the form of reprinting the most significant publication of each man in the field of conformational analysis. This is commendable not only as a gesture but as a service, for these two important papers originally appeared in journals of rather narrow circulation, and Hassel's paper, now translated, was heretofore available only in Norwegian.

The main part of this book consists of four chapters: "Pyramidal Atomic Inversion," by J. B. Lambert; "Resolving Agents and Resolutions in Organic Chemistry," by S. H. Wilen; "Stereochemistry of Nitroxides," by E. G. Janzen; and "Conformational Analysis and Configurational Effects for Chelate Complexes," by D. A. Buckingham and A. M. Sargeson. Lambert's chapter is the longest, and treats the subject from both a theoretical and experimental standpoint. Its content reflects the large amount of recent interest in inversion of tricoordinate nitrogen in cyclic compounds. Wilen's chapter, which has the longest bibliography (384 references), is principally concerned with the many new reagents available for use in classical resolution techniques. Janzen's chapter demonstrates the great rise in interest in nitroxides in recent years and the application of electron spin resonance to these stable radicals to investigate stereochemical problems. Buckingham and Sargeson's chapter is substantially concerned with calculation of the small energy differences between conformational isomers.

A commendably detailed subject index and a cumulative index of titles of chapters in previous volumes conclude the book.

Biological Techniques in Electron Microscopy. By Clinton J. Dawes (University of South Florida). Barnes & Noble, Inc., New York, N. Y. 1971. xiv + 193 pp. $4.95.

This is a laboratory manual with much practical information about preparation of biological samples, a short reading list, and a useful appendix listing commercial sources of materials.

Cours de Chimie. Volume II. By J. Amiel (Faculté des Sciences de Paris). Dunod, Paris. 1971. viii + 600 pp. 74 F.

This is a textbook of general chemistry, devoted largely to the descriptive side, about half inorganic half organic.

Laboratory Course in Organic Chemistry. By D. H. Rosenblatt and G. T. Davis (Johns Hopkins University). Allyn & Bacon, Inc., Boston, Mass. 1971. xiv + 320 pp. $10.25.

This introductory manual has two unusual features. The experiments are divided into two groups, "Main Sequence" and "Optional," in which the latter are not simply advanced experiments but are alternates or supplements. The experiments are keyed to specific chapters of Morrison and Boyd's "Organic Chemistry," in an attempt to surmount one of the commonest complaints about organic laboratory courses—that they are out of phase with the lecture course. There are literature footnotes to each experiment and there is an appendix of particular value to the instructor, listing required supplies and equipment and their sources.

General Organic Chemistry. By R. B. Seymour (University of Houston). Barnes & Noble, Inc., New York, N. Y. 1971. xvi + 557 pp. $5.95.

This is a textbook designed for a one-semester terminal course. It covers the subject in 14 chapters, of which the last is devoted to characterization of organic compounds. There are many examples taken from industrial chemistry throughout, chosen for the purpose of creating interest, and three of the later chapters attempt to balance this with subjects of biological interest, such as cardiac glycosides and nucleic acids. There are problems, an appendix that gives the answers, and a good index. The volume is softbound.

Science and Archaeology. Edited by R. H. Brill (The Corning Museum of Glass). MIT Press, Cambridge, Mass. 1971. xvi + 288 pp. $30.00.

There have been several symposia on archaeological chemistry sponsored by the Division of History of Chemistry of the American Chemical Society, devoted in general to the application of chemical and physical methods to the solution of archaeological problems. The 22 papers given at the 1968 symposium are printed in this book, which is beautifully illustrated with full-page plates, many in color. Analysis plays the largest role in such work, and neutron activation is prominent among the methods, but there are interesting contributions on ceramics, metal working, dating techniques, and chemical changes during storage. This is the sort of book that can bring the results of sophisticated science to the appreciation of the layman, not unaided by the attractive presentation.

Principles of Mass Spectrometry and Negative Ions. By C. E. Melton (University of Georgia). Marcel Dekker, Inc. New York, N. Y. 1970. 313 pp.

This text presents the fundamental details of both instrumentation and the ionization and fragmentation process. Problems are included at the end of chapters. The book is not directed to the needs of the experimentalist (especially organic) but might be used as a supplementary text in a course on mass spectrometry.

M. M. Green, *University of Michigan*

Topics in Organic Mass Spectrometry. Edited by A. L. Burlingame (University of California). Wiley-Interscience Publishers, New York, N. Y. 1969. 471 pp. $22.50.

This volume, edited by A. L. Burlingame, consists of a series of excellent critical reviews of high interest to any chemist concerned with the mass spectra of organic molecules.

M. M. Green, *University of Michigan*

Les Hauts Polymères Thermostables. Publications de L' Institut Francais du Pètrole. Collection Colloques et Sèminaires. No. 20. Edited by J. Gole. Éditions Technip, Paris. 1971. xv + 152 pp. 48.00 F.

This is a collection of five lectures presented in May of 1970 at a conference held at the National Institute of Applied Sciences in Lyon. It is a concise and cohesive overview of thermally stable polymers. Topics included are: physical, chemical, and mechanical properties of polymer structures (G. de Gaudemaris); synthesis and properties of known thermally stable materials (B. Sillion); aeronautic and space applications (P. Giuliani); heat resistant fibers (J. Corbiere); and, applications of polyimides (M. Mallet).

Daniel T. Longone, *University of Michigan*

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* Unsigned book reviews are by the Book Reviews Editor.