



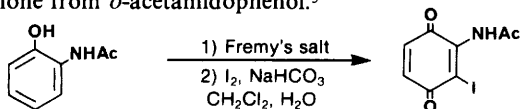
Name Reagents

Raney/Fremy/McMurry/Schwartz/Collman

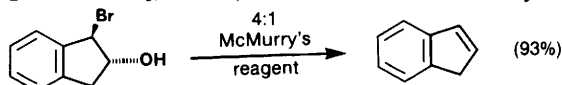
Many specialized reagents are best known by the names of the chemists who first prepared and popularized them. A good example is **Raney Nickel**[®], a hydrogenation catalyst that can be used in a variety of forms¹ for selective applications.

The chemistry of **Fremy's salt** (potassium nitrosodisulfonate), first made available by Aldrich over 20 years ago, has also been studied for many years.² Selective oxidations using **Fremy's salt** have been extended to phase-transfer systems such as the conversion of a phenol to a quinone.³

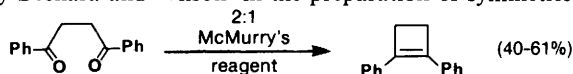
Fremy's salt has also been used in the initial step of a two-step conversion of polycyclic phenols to dihydrodiols,⁴ and in an improved synthesis of 2-acetamido-3-iodo-*p*-benzoquinone from *o*-acetamidophenol.⁵



McMurry's reagent, available as a 4:1 TiCl₃/LiAlH₄ dry mixture, has proven useful for numerous deoxygenations and reductions.⁶ Aldrich also offers **Modified McMurry's reagent**, 2:1 TiCl₃/LiAlH₄, which was recommended by Lai⁷

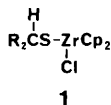


in a recent review of organic reductive coupling and utilized by Bechara and Wilson⁸ in the preparation of symmetrical



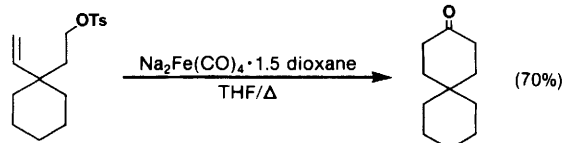
olefins from ketones. From an ESR-spectroscopy study of the reaction mechanism of Ti-induced reductive coupling of ketones to olefins, Geise and co-workers⁹ concluded that a 2:1 TiCl₃/LiAlH₄ ratio gives optimum results.

Schwartz's reagent, bis(cyclopentadienyl)zirconium chloride hydride, combines with olefins to afford organozirconium complexes which have a variety of applications in organic synthesis.^{10,11} Extension of this chemistry to thio-ketones has produced some interesting reaction sequences from the nucleophilic hydrozirconation intermediate **1**.¹² Zirconocene enolates derived from **zirconocene dichloride** promote the erythro-selective synthesis of β -hydroxycarbonyls.¹³



Collman's reagent,¹⁴ Na₂Fe(CO)₄, also effectively forms organometallic intermediates which undergo selective transformations. McMurry¹⁵ has studied the cyclocarbonylation reaction of **Collman's reagent** (dioxane adduct) with olefin tosylates and found the method effective, though limited in scope, for synthesizing five- and six-membered

rings, including some spiro compounds.



Collman's reagent has also been used to prepare stable metal-fluorocarbon complexes (R_FCO)₂Fe(CO)₄ which undergo thermal decarbonylation to *cis*-(R_F)₂Fe(CO)₄ species.¹⁶

The potassium analog of **Collman's reagent**, K₂Fe(CO)₄, has potential to be extremely useful in organic and organometallic synthesis. It can be isolated as an unsolvated, non-pyrophoric, pure solid,¹⁷ and is now available from Aldrich. It has been used to prepare mixed-metal clusters under mild conditions.¹⁸

References:

- 1) Fieser, L.F.; Fieser, M. *Reagents for Organic Synthesis* 1967, 1, J. Wiley & Sons, New York, 718, 723.
- 2) Zimmer, H.; Lankin, D.C.; Horgan, S.W. *Chem. Rev.* 1971, 71, 229.
- 3) Olson, G.L.; Cheung, H.C.; Morgan, K.; Saucy, G. *J. Org. Chem.* 1980, 45, 803.
- 4) Sukumaran, K.B.; Harvey, R.G. *ibid.* 1980, 45, 4407.
- 5) Kozikowski, A.P.; Sugiyama, K.; Springer, J.P. *Tetrahedron Lett.* 1980, 21, 3257.
- 6) McMurry, J.E.; Silvestri, M.G.; Fleming, M.P.; Hoz, T.; Grayston, M.W. *J. Org. Chem.* 1978, 43, 3249.
- 7) Lai, Y.-H. *Org. Prep. & Proc. Int.* 1980, 12, 363.
- 8) Bechara, E.J.H.; Wilson, T. *J. Org. Chem.* 1980, 45, 5261.
- 9) Dams, R.; Malinowski, M.; Westdorp, I.; Geise, H.J. *ibid.* submitted for publication.
- 10) Schwartz, J.; Labinger, J.A. *Angew. Chem., Int. Ed. Engl.* 1976, 15, 333.
- 11) Schwartz, J. *Bull. Soc. Chim. Fr.* 1980, 330.
- 12) Laycock, D.E.; Alper, H. *J. Org. Chem.* 1981, 46, 289.
- 13) Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* 1980, 21, 4607.
- 14) Collman, J.P. *Acc. Chem. Res.* 1968, 1, 136; *ibid.* 1975, 8, 342.
- 15) McMurry, J.E.; Andrus, A. *Tetrahedron Lett.* 1980, 21, 4687.
- 16) Hensley, D.W.; Wurster, W.L.; Stewart, R.P., Jr. *Inorg. Chem.* 1981, 20, 645.
- 17) Gladysz, J.A.; Tam, W. *J. Org. Chem.* 1978, 43, 2279.
- 18) Plotkin, J.S.; Alway, D.G.; Weisenberger, C.R.; Shore, S.G. *J. Am. Chem. Soc.* 1980, 102, 6156.

22,167-8	Raney Nickel [®]	100g \$16.85; 500g \$47.50
22,093-0	Fremy's salt	10g \$31.60; 50g \$126.60
22,098-1	McMurry's reagent (4:1 TiCl ₃ /LiAlH ₄)	25g \$13.85; 50g \$23.75
22,921-0	Modified McMurry's reagent (2:1 TiCl ₃ /LiAlH ₄)	10g \$9.50; 50g \$25.00
22,367-0	Schwartz's reagent	5g \$32.50; 25g \$125.00
19,621-5	Zirconocene dichloride	5g \$15.35
		25g \$49.50; 100g \$129.00
22,549-5	Collman's reagent [Na ₂ Fe(CO) ₄ ·1.5 dioxane]	10g \$13.00; 100g \$99.00
22,550-9	Dipotassium tetracarbonylferrate	5g \$9.90



chemists helping chemists in research & industry

aldrich chemical co.

P.O. Box 355, Milwaukee, Wisconsin 53201 • (414) 273-3850

RSC Publications News

NEW PUBLICATIONS

Hazards in the Chemical Laboratory



**3rd
EDITION**

EDITED BY L. BREThERICK

Hazards in the Chemical Laboratory has become established as an essential handbook on safety measures, practice and toxic effects for laboratories handling chemicals and chemical equipment. Since the 2nd Edition was published in 1977, there have been many changes on legislation, recommended safety measures, protective standards, safety equipment, measurements of toxic effects, etc., which have resulted in a real need for this new updated edition. For example, the sections dealing with hazards have been greatly revised and expanded to include the steadily increasing body of knowledge on hazardous properties—reflected by the expansion of The Toxic Substances List from 13000 compounds in 1974 to 34000 in 1978 (now retitled the Registry of Toxic Effect of Chemical Substances). Comments on the predictive value of comprehensive toxicity and carcinogenicity testing, now required for commercial chemicals, is included. A section has also been added which deals with mutagens and carcinogens in relation to health care and first aid, and also includes sources of information on toxicity and medical emergencies.

Hazards in the Chemical Laboratory is regarded by many as the most authoritative, comprehensive source of information in the field of safety in the chemical laboratory. This third edition, edited by L. Bretherick, one of the world's leading experts on hazards and safety standards, is an essential requirement for any laboratory handling hazardous chemicals.

'A minor bible' – New Scientist

Protective PVC cover 578 pp 0851864198
Price £15.00 (\$39.50) (RSC Members £9.75)



Laboratory Hazards Bulletin

Laboratory Hazards Bulletin is a new current awareness periodical which reports on safety measures, potential hazards and new legislation affecting the well-being of employees working in laboratories in the chemical and allied industries.

The vast quantity of scientific and technical literature currently being published has made the job of literature searching an extremely laborious task. Laboratory Hazards Bulletin is produced by a combination of computerised and manual techniques, developed by expert RSC staff, to save you the time, effort and expense of performing your own literature searches. A conscious effort is made to ensure that only highly topical and important items are included.

Published monthly, each issue contains approximately 30–50 references drawn from the current scientific and technical literature. The references include document titles, bibliographic citations and abstracts (concise summaries of the hazard information contained in the original articles).

Subscription Details:

	18 MONTH SUBSCRIPTION July '81–Dec '82	12 MONTH SUBSCRIPTION Jan '82–Dec '82	6 MONTH SUBSCRIPTION July '81–Dec '81
1st copy	£65 00 (\$156 00)	£50 00 (\$120 00)	£26 50 (\$63 50)
*next 2–10 copies	£32 50 (\$ 78 00)	£25 00 (\$ 60 00)	£13 50 (\$32 50)
*next 11–20 copies	£26 00 (\$ 62 50)	£20 00 (\$ 48 00)	£11 00 (\$26 50)
*next 21 and over	£19 50 (\$ 47 00)	£15 00 (\$ 36 00)	£ 8 50 (\$20 50)

**ROYAL
SOCIETY OF
CHEMISTRY**

ORDERING

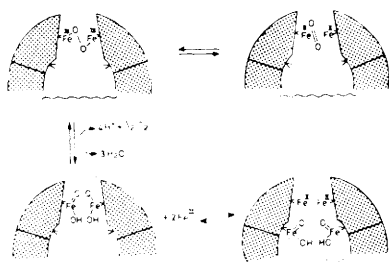
Non-RSC members orders for Hazards in the Chemical Laboratory should be sent to: The Royal Society of Chemistry, Distribution Centre, Blackhorse Road, Letchworth, Herts SG6 1HN.

RSC members orders for Hazards in the Chemical Laboratory should be sent to: The Royal Society of Chemistry, Membership Officer, 30 Russell Square, London WC1B 5DT.

All orders for Laboratory Hazards Bulletin should be sent to: The Royal Society of Chemistry, The University, Nottingham NG7 2RD.

RSC Publications

Specialist Periodical Report



Inorganic Biochemistry Vol. 1

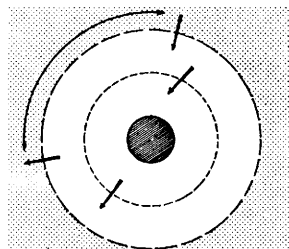
Senior Reporter: Dr H. A. O. Hill, *University of Oxford*

Inorganic Biochemistry can be defined as the biochemistry of those elements whose chemistry normally constitutes the province of inorganic chemists. Coverage is extremely wide, ranging from chemical physics to clinical medicine, and its influence is all-pervasive. There probably does not exist a single enzyme-catalysed reaction to which enzyme, substrate, product, or a combination of these is not influenced in a very direct and specific manner by the precise nature of the inorganic ions which surround and modify it.

The subject has developed dramatically this decade and it is believed that this volume, which reviews relevant work on the subject published in 1977, and those that follow in this new series will ease the burden of inorganic biochemists as they seek to relate their work to fields far beyond the confines of the traditional disciplines.

Hardcover 458 pp 8 $\frac{3}{4}$ " \times 5 $\frac{5}{8}$ " 0 85186 570 4
£36.50 (RSC Members edition £14.50)

Specialist Periodical Report



Inorganic Reaction Mechanisms Vol. 6

Senior Reporter: Professor A. McAuley,
University of Victoria, B.C., Canada

The sixth volume in this series on inorganic reaction mechanisms reviews the literature published between July 1976 and December 1977.

'This volume and its predecessors address the problem of reviewing such a large and diverse field in a constructive, realistic, and helpful way, and it is hard to see how any inorganic kineticist could be without them.'—*Anthony Poë, Journal of Organometallic Chemistry, reviewing Vol. 4.*

Brief Contents:

Part I: Electron Transfer Processes: Reactions Between Two Metal Complexes; Metal Ion-Ligand Redox Reactions; Reactions involving Oxygen and Hydrogen Peroxide

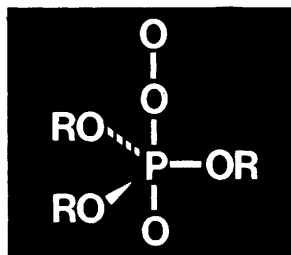
Part II: Substitution and Related Reactions: Non-metallic Elements; Inert Metal Complexes: Co-ordination Numbers Four and Five; Inert Metal Complexes: Co-ordination Number Six and Higher; Labile Metal Complexes; Solvent Effects

Part III: Reactions of Biochemical Interest

Part IV: Organometallic Compounds: Substitution; Metal-Alkyl, -Aryl, and -Allyl Bond Formation and Cleavage; Insertion Reactions; Reactions of Co-ordinated Ligands; Oxidative Addition and Reductive Elimination; Isomerization: Intramolecular Processes

Hardcover 491 pp 8 $\frac{3}{4}$ " \times 5 $\frac{5}{8}$ " 0 85186 305 1
£44.00 (RSC Members edition £17.50)

Specialist Periodical Report



Organophosphorus Chemistry Vol. 11

Senior Reporters:

Dr D. W. Hutchinson, *University of Warwick*
Professor S. Trippett, *University of Leicester*

The tenth volume in this highly successful series covers the literature published between July 1977 and June 1978.

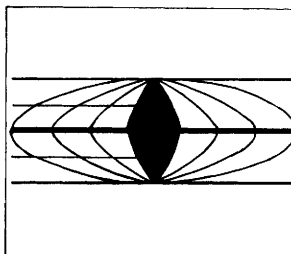
'The overall quality of the reports is high, and the scope of the literature is beyond that which would be possible for even the most indefatigable individual journal reader and note taker.'—*Bernard Miller, Journal of Medicinal Chemistry, reviewing Vol. 8*

Brief Contents:

Phosphines and Phosphonium Salts; Quinquevalent Phosphorus Compounds; Halogenophosphines and Related Compounds; Phosphine Oxides and Sulphides; Trivalent Phosphorus Acids; Quinquevalent Phosphorus Acids; Phosphates and Phosphonates of Biochemical Interest; Nucleotides and Nucleic Acids; Ylides and Related Compounds; Phosphazenes; Physical Methods

Hardcover 302 pp 8 $\frac{3}{4}$ " \times 5 $\frac{5}{8}$ " 0 85186 980 7
£54.00 (RSC Members edition £35.00)

Annual Report



Annual Reports on Analytical Atomic Spectroscopy Vol. 9

Editors: Dr J. B. Dawson *University of Leeds*,
Dr B. L. Sharp, *The Macaulay Institute, Aberdeen*

This series provides the practising analytical chemist and spectroscopist with a handbook of current practice and recent advances in instruments and methods for the determination of elements in the form of comprehensive, critical annual reports. As atomic spectrometric analysis has matured, progress in realizing the goal of precise and accurate analysis has led to the appearance of many papers in which information concerning fundamental principles, instrumentation and methodology is found within a single publication. For this reason, the structure of Volume 9 differs from its predecessors in that the two parts, 'Fundamentals and Instrumentation' and 'Methodology', have been expanded into four chapters, 'Atomization and Excitation', 'Instrumentation', 'Methodology', and 'Applications', in order to give a clearer distinction between work that is of general interest and that dedicated to a specific analysis.

Brief Contents: *Atomization and Excitation; Instrumentation; Methodology; Applications; New Books; Reviews; Meetings; References; Author Index; Subject Index*

Hardcover 357 pp 8 $\frac{1}{2}$ " \times 6" 0 85186 727 8
£34.00 (RSC Members £22.00)

CLASSIFIED ADVERTISEMENTS



DEPARTMENT OF CHEMISTRY

Postdoctoral Research Fellowship in Biosynthesis

A Fellowship is available from 1st October, 1981, renewable for a second year, for research on the biosynthesis of the polyether ionophore antibiotic monensin. The project will involve the application of C-13, H-2 and O-18 labelled precursors. Experience in organic chemistry and/or mechanistic enzymology is required.

Salary on 1A Scale within range £6,070 to £6,880 plus superannuation. Starting point dependent on age and experience.

Applications, with the names of two referees, should be sent as soon as possible to Dr. J. A. Robinson, Department of Chemistry, University of Southampton, Highfield, Southampton SO9 5NH. Please quote ref: CC.

THE UNIVERSITY OF SHEFFIELD

DEPARTMENT OF CHEMISTRY

Postdoctoral Research Assistantship in Organic Chemistry

Applications are invited from men and women for an SERC-supported position to study novel approaches in stereoselective synthesis using chiral molecular receptors of the crown ether type. Experience in synthetic and/or physical organic chemistry preferred. Tenable 1 October 1981 or soon thereafter for two years. Salary in range £6070-£6880.

Applications with curriculum vitae and names of two referees to Dr. J. F. Stoddart, Department of Chemistry, The University, Sheffield S3 7HF as soon as possible. Quote ref: R629/BG.

UNIVERSITY OF EXETER DEPARTMENT OF CHEMISTRY

Applications are invited from Organic Chemists for a Post-doctoral Research Assistantship to study a reaction of possible use in the chiral synthesis of some natural products. The post will be available from 1 October 1981 and will be for one year, at a salary in the range £6070 - £6880 per annum.

Applications (curriculum vitae; one copy with the names of two referees) should be sent to Dr. J. S. Whitehurst at the Department of Chemistry as soon as possible.

CLASSIFIED ADVERTISING

DISPLAY AND SEMI-DISPLAY
£3.50 per single col. cm. column width
43mm (10 ems)

Send your advertisements:—
**Judy Dutton, Classified Advertisements,
Burlington House, Piccadilly,
London W1V 0BN.**