

To summarize, the process of desulfurization-induced ring-opening polymerization provides access to a family of redox-active polymers with novel processing characteristics. The method relies on the following characteristics of the trithiaferrocenophanes: (i) one S atom in the RfcS₃ is particularly reactive toward conventional S-abstracting reagents; (ii) monomeric RfcS₂ would be strained since the S-S bond cannot easily span the inter-ring separation; and (iii) once the S-S linkage is cleaved, the C₃H₅SR rings can rotate freely.

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All-Cis Catalytic Hydrogenation of Polynuclear Aromatic Hydrocarbons by Group 5 Metal Aryloxyde Compounds

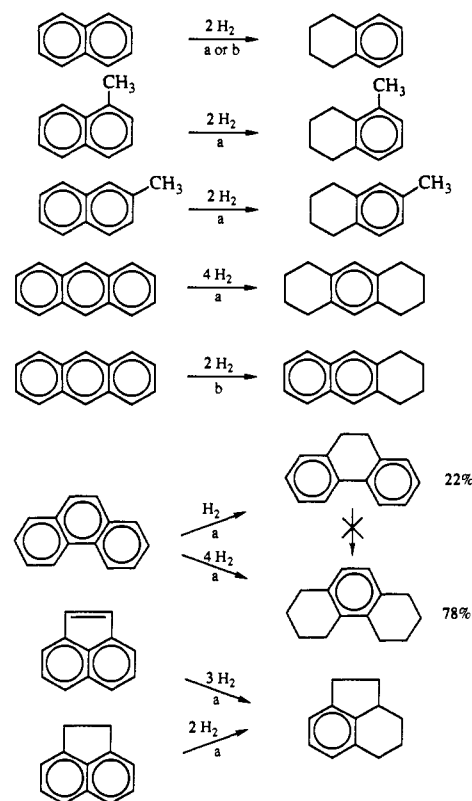
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Despite the immense success that has been achieved in the field of homogeneous catalytic hydrogenation of olefin,¹⁻³ the related field of arene hydrogenation has been underdeveloped.⁴⁻⁷ We wish to report here our discovery of a new series of arene hy-

Scheme 1^a



^a Reaction conditions: (a) [1] = 0.1 mmol, C₆H₁₂ (3 mL), H₂ (1200 psi), 80 °C, 24 h; (b) [2] = 0.1 mmol, C₆H₁₂ (3 mL), H₂ (1200 psi), 90 °C, 24 h. GC/MS analysis of the reaction mixture from hydrogenation of naphthalene by 1 showed tetralin, 95.5%, *cis*-decalin, 4.5%, and <0.3% *trans*-decalin.

drogenation catalysts. These systems exhibit not only a significant amount of regioselectivity but an extremely high degree of stereoselectivity.⁸

The niobium tris(4-methylbenzyl) compound Nb(OC₆H₃Ph₂-2,6)₂(CH₂C₆H₄-4Me)₃ (1)⁹ acts as a catalyst precursor for the hydrogenation of benzene and a variety of polynuclear aromatic hydrocarbons. A solution of 1 (0.1 mmol) in neat C₆D₆ solvent (3 mL) was found to produce C₆D₆H₆ (10% conversion) after being exposed to H₂ (1200 psi, 80 °C) for 24 h.¹⁰ Hydrolysis of the resulting solution showed that the Nb-CH₂C₆H₄-4Me groups in 1 had undergone hydrogenolysis to produce *p*-xylene, while the aryloxyde ligands had undergone hydrogenation to 2,6-dicyclohexylphenoxide groups.^{7a} Solutions of 1 in cyclohexane will carry out the efficient hydrogenation of a variety of polynuclear aromatic hydrocarbons (Scheme 1). Typical reaction conditions consist of a solution of 1 (0.1 mmol) in cyclohexane (3 mL) with 20 equiv of aromatic substrate heated at 80 °C under 1200 psi of hydrogen. After 24 h, most of the substrates are hydrogenated to the indicated products (Scheme 1) in >95% yield (NMR analysis). Anthracene was found to yield 1,2,3,4,5,6,7,8-octahydroanthracene exclusively with no detectable 9,10-dihydroanthracene. Phenanthrene is hydrogenated by 1 at a slower rate (90% conversion) than the other substrates to produce a mixture of 9,10-dihydrophenanthrene (22%) and 1,2,3,4,5,6,7,8-octahydrophenanthrene (78%). The fact that 9,10-dihydrophenanthrene is not hydrogenated by 1 indicates that this product ratio is kinetic in origin. 1-Methyl- and 2-methyl-

(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1988. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (c) Rylander, P. N. *Hydrogenation Methods*; Academic Press: London, 1985. (d) James, B. R. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 285. (e) James B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973. (f) James, B. R. *Adv. Organomet. Chem.* 1979, 17, 319.

(2) (a) Halpern, J. *Science* 1982, 217, 401. (b) Halpern, J. *Inorg. Chim. Acta* 1981, 50, 11. (c) Chang, B.-H.; Lau, C.-P.; Grubbs, R. H.; Brubaker, C. H., Jr. *J. Organomet. Chem.* 1985, 281, 213. (d) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* 1976, 15, 333. (e) Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* 1990, 112, 8621.

(3) (a) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* 1966, 1711. (b) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* 1967, 10, 67. (c) Ireland, R. E.; Bey, P. *Org. Synth.* 1973, 53, 63. (d) Jardine, F. H. *Prog. Inorg. Chem.* 1981, 28, 63. (e) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* 1976, 98, 2134, 2143, and 4450.

(4) (a) Muetterties, E. L.; Rakowski, M. C.; Hirsckorn, F. J.; Larson, W. D.; Basus, V. J.; Anet, F. A. L. *J. Am. Chem. Soc.* 1975, 97, 1266. (b) Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* 1979, 12, 324. (c) Bleeke, J. R.; Muetterties, E. L. *J. Am. Chem. Soc.* 1981, 103, 556. (d) Johnson, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* 1977, 99, 7395. (e) Bennett, M. *CHEMTECH* 1980, 444. (f) Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* 1975, 97, 1786. (g) Wilczynski, R.; Fordyce, W. A.; Halpern, J. *J. Am. Chem. Soc.* 1983, 105, 2066. (h) Linn, D. E., Jr.; Halpern, J. *J. Am. Chem. Soc.* 1987, 109, 2969.

(5) (a) Ward, M. D.; Schwartz, J. *J. Am. Chem. Soc.* 1981, 103, 5253. (b) Stobart, S. R.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* 1984, 1700. (c) Fu, P. P.; Lee, H. M.; Harvey, R. G. *J. Org. Chem.* 1980, 45, 2797. (d) Grey, R. A.; Pez, G. P.; Wallo, A. J. *J. Am. Chem. Soc.* 1980, 102, 5948. (e) Russell, M. J.; White, C.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* 1977, 427.

(6) (a) Amer, I.; Amer, H.; Ascher, R.; Blum, J.; Sasson, Y.; Vollhardt, K. C. P. *J. Mol. Catal.* 1987, 39, 185 and references therein. (b) DeWit, D. G.; Folting, K.; Streib, W. E.; Caulton, K. G. *Organometallics* 1985, 4, 1149. (c) Yalpani, M. *Chem. Ber.* 1990, 123, 983. (d) Yalpani, M.; Köster, R. *Chem. Ber.* 1990, 123, 719 and references therein.

(7) (a) Steffey, B. D.; Chesnut, R. W.; Kerschner, J. L.; Pellechia, P. J.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* 1989, 111, 378. (b) Steffey, B. D.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* 1990, 213. (c) Ankianiec, B. C.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* 1991, 113, 4710. (d) Yu, J. S.; Rothwell, I. P. Submitted for publication.

(8) The C₆H₆D₆ produced by the hydrogenation of benzene by a cobalt-allyl catalyst has been reported to contain all hydrogen atoms mutually *cis*. See ref 4a.

(9) Chesnut, R. W.; Jacob, G. G.; Yu, J. S.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* 1991, 10, 321.

(10) The reactions were performed unstirred in a Parr Minireactor 4561. The catalyst precursor, substrate, and solvent were held in a glass vessel within the reactor during the hydrogenation.

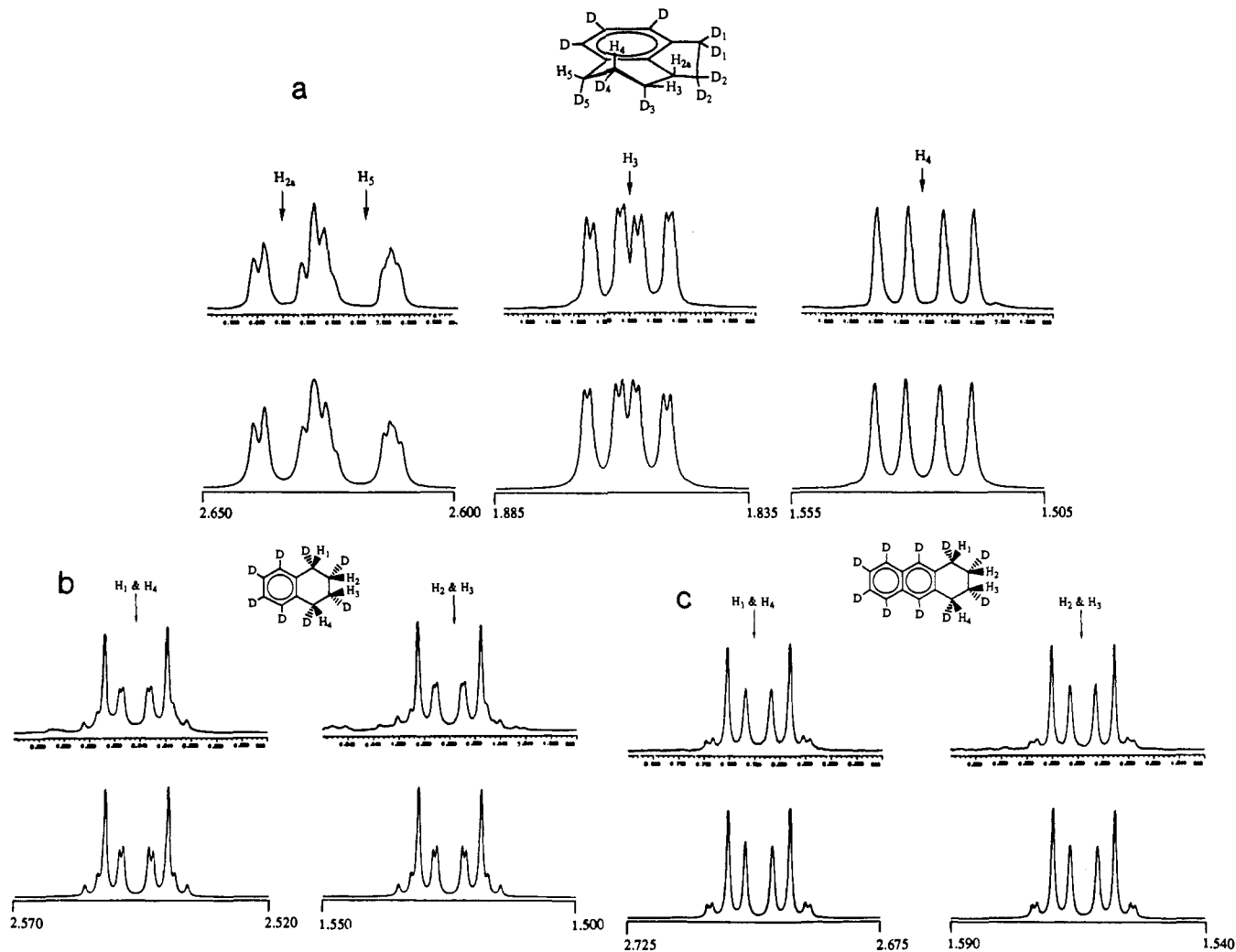


Figure 1. Observed and simulated ^2H -decoupled 500-MHz ^1H NMR spectra for (a) $\text{C}_{12}\text{D}_{10}\text{H}_4$ obtained by hydrogenation of acenaphthene- d_{10} by **1**, (b) $\text{C}_{10}\text{D}_8\text{H}_4$ obtained by hydrogenation of naphthalene- d_8 by **1**, (c) $\text{D}_{14}\text{D}_{10}\text{H}_4$ obtained by hydrogenation of anthracene- d_{10} by **2**. Each segment is 25 Hz wide.

naphthalene are hydrogenated at the unsubstituted ring, while acenaphthylene and acenaphthene are both converted to 1,2,2a,3,4,5-hexahydroacenaphthylene.

The tantalum trihydride compound $\text{Ta}(\text{OC}_6\text{H}_3\text{cy}_2-2,6)_2(\text{H})_3(\text{PMe}_2\text{Ph})_2$ (**2**)^{7c} will also carry out the hydrogenation of naphthalene and anthracene in cyclohexane solution to produce 1,2,3,4-tetrahydronaphthalene and 1,2,3,4-tetrahydroanthracene, with a small amount of 1,2,3,4,5,6,7,8-octahydroanthracene in the latter case.

The hydrogenation (H_2 gas) of naphthalene- d_8 and acenaphthene- d_{10} by **1** and of naphthalene- d_8 and anthracene- d_{10} by **2** produces the corresponding hydrogenated products. Analysis of the products by mass spectrometry showed that no H/D scrambling had occurred, and the ^{13}C NMR spectra of the products showed the aliphatic groups to be exclusively CHD. In the case of the hydrogenation of acenaphthene- d_{10} by **1**, the ^1H NMR and ^2H NMR spectra indicate that the four hydrogen atoms have been introduced mutually cis, i.e., all on one face of the arene ring (supplementary material).¹¹ The $\{^2\text{H}\}^1\text{H}$ NMR spectrum of the aliphatic region can be simulated to yield all of the ^1H - ^1H coupling constants within the ground-state half-chair conformation of this molecule (Figure 1).¹¹ The $\{^2\text{H}\}^1\text{H}$ NMR spectra of the 1,2,3,4-tetrahydronaphthalene- d_8 and 1,2,3,4-tetrahydroanthracene- d_{10} produced by **1** and **2** show single (>95%) AA'XX' patterns at 500 MHz (Figure 1). Of the six possible isotopomers for these molecules, four can generate this symmetric pattern. Simulation of the spectra yields coupling constants between the four hydrogen atoms whose magnitudes are very close to the cis

coupling constants reported for cyclohexene.¹¹⁻¹³ Hence, this work shows that these arene hydrogenation catalysts show not only a significant degree of regioselectivity, but more importantly are

(11) The aliphatic region of the ^1H NMR spectrum (500 MHz, C_6D_6) of 1,2,2a,3,4,5-hexahydroacenaphthylene consists of 11 multiplets. The four nonequivalent benzylic protons at the 1 and 5 positions and the methine proton at 2a all overlap, while the other six protons are well resolved and can be separated into those occupying axial (upfield) positions and equatorial (downfield) positions. In the product obtained by hydrogenation of acenaphthene- d_{10} , only four protons are observed (Figure 1). The chemical shifts identify them as H_{2a} at δ 2.634 ppm (which is locked into a pseudo-axial position), the equatorial proton on C_3 (1.859 ppm), the axial proton on C_4 (1.529 ppm), and the equatorial proton on C_5 (2.619 ppm). The following six coupling constants were used in the simulation (Figure 1): $^3J_{2a,3} = 4.82$ Hz; $^4J_{2a,4} = 0.20$ Hz; $^5J_{2a,5} = 1.0$ Hz; $^3J_{3,4} = 3.10$ Hz; $^4J_{3,5} = 0.65$ Hz; $^3J_{4,5} = 6.53$ Hz. The tetralin obtained by hydrogenation of naphthalene- d_8 contains two multiplets at δ 1.525 (H_2 and H_3) and 2.546 ppm (H_1 and H_4) in the ^2H -decoupled ^1H NMR spectrum (Figure 1). Simulation of the AA'XX' pattern yielded the following coupling constants: $^3J_{1,2} = ^3J_{3,4} = 5.62$ Hz; $^4J_{1,3} = ^4J_{2,4} = 0.59$ Hz; $^3J_{2,3} = 2.99$ Hz; $^5J_{1,4} = 0.82$ Hz. Analysis of the AA'XX' spectrum obtained for the product of hydrogenation of anthracene- d_{10} (Figure 1) yielded the following data: $\delta(\text{H}_1, \text{H}_4) = 2.699$ ppm; $\delta(\text{H}_2, \text{H}_3) = 1.564$ ppm; $^3J_{1,2} = ^3J_{3,4} = 5.62$ Hz; $^4J_{1,3} = ^4J_{2,4} = 0.52$ Hz; $^3J_{2,3} = 3.50$ Hz; $^5J_{1,4} = 0.31$ Hz. In both 1,2,3,4-tetrahydronaphthalene and 1,2,3,4-tetrahydroanthracene, the $^3J_{2,3}$ and $^3J_{1,2}$ ($^3J_{3,4}$) couplings are close to the cis couplings of 2.95 and 5.67 Hz found for the corresponding protons in cyclohexene (ref 12, p 16) (der Hyde, W. A.; Löttke, W. *Chem. Ber.* 1978, 111, 2384). Simulation of an AA'XX' spectrum containing a trans (8 Hz) coupling between H_2 and H_3 results in a very different pattern. Analysis of this data shows the spectra obtained in this study are >95% due to the all-cis isotopomer. For a discussion of the stereochemistry of hydrogenation of quinoline, see: Fish, R. H.; Baralt, E.; Smith, S. J. *Organometallics* 1991, 10, 54 and references therein.

highly stereoselective, introducing four hydrogen atoms onto the same face of acenaphthene, naphthalene, and anthracene.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8915573) for support of this research. J.S.Y.

(12) For a discussion of the coupling constants in molecules in this type, see: Anet, F. A. L. In *The Conformational Analysis of Cyclohexenes, Cyclohexadienes, and Related Hydroaromatic Compounds*; Rabideau, P. W., Ed.; V. C. H. Publishers: New York, 1989.

(13) The spectra of a number of isomers of naphthalene tetrachloride have been analyzed: (a) de la Mare, P. B. D.; Johnson, M. D.; Lomas, J. S.; Sanchez del Olmo, V. *J. Chem. Soc., Chem. Commun.* **1965**, 483. (b) de la Mare, P. B. D.; Johnson, M. D.; Lomas, J. S.; Sanchez del Olmo, V. *J. Chem. Soc. B* **1966**, 827. (c) de la Mare, P. B. D.; Koenigsberger, R.; Lomas, J. S. *J. Chem. Soc. B* **1966**, 834.

gratefully acknowledges the award of a David Ross Fellowship from the Purdue Research Foundation, while B.C.A. would like to thank the SERC for the award of a NATO Postdoctoral Fellowship. We also thank C. Zambrano and D. Carlson for technical assistance in obtaining the ^2H NMR spectra and Prof. John Grutzner for helpful discussions.

Supplementary Material Available: ^1H , ^2H , ^{13}C , and $\{^1\text{H}\}^{13}\text{C}$ NMR spectra of the products of hydrogenation (H_2) of acenaphthene- d_{10} , simulations of the spectra expected for cis and trans isotopomers of $\text{C}_{10}\text{D}_8\text{H}_4$ and $\text{C}_{14}\text{D}_{10}\text{H}_4$ for comparison with the observed spectra, and comparison of the 3J coupling constants for cyclohexene and the products shown in Figure 1 (20 pages). Ordering information is given on any current masthead page.

Additions and Corrections

Effect of Allylic Substituents on the Face Selectivity of Diels-Alder Reactions of Semicyclic Dienes [*J. Am. Chem. Soc.* **1990**, *112*, 8472]. S. C. DATTA, R. W. FRANCK,* R. TRIPATHY, G. J. QUIGLEY, L. HUANG, S. CHEN, and A. SIHAED

Page 8473, Table I, entry 11: The stereochemistry of adduct **16** was reported as 100% syn when, in fact, it is 100% anti. In the discussion, in the left-hand column at the bottom of page 8474, it is correctly reported as anti.

Stereospecificity of the β -Hydroxyl Elimination from the (Hydroxyalkyl)chromium Complex $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}-\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{OH}^{2+}$ [*J. Am. Chem. Soc.* **1991**, *113*, 5292]. HAIM COHEN,* ALEXANDER FELDMAN, RUTH ISH-SHALOM, and DAN MEYERSTEIN*

Page 5295, Figure 2a: The X coordinate should have the dimensions $[\text{H}_3\text{O}^+] \times 10$ and not $[\text{H}_2\text{O}] \times 10^3$.

Page 5297, Figure 5: \square should be % 1-butene and \blacksquare % *trans*-2-butene.

Molecular Recognition by Circular Oligonucleotides: Increasing the Selectivity of DNA Binding [*J. Am. Chem. Soc.* **1991**, *113*, 6265–6266]. ERIC T. KOOL

Page 6265, ref 7: The correct concentration for oligomer and template is 50 μM each.

Models of the Cytochromes *b*. 8. Two-Dimensional Nuclear Overhauser and Exchange Spectroscopy Studies of Paramagnetic "Cavity" Type (Tetraphenylporphinato)iron(III) Complexes of Planar Ligands [*J. Am. Chem. Soc.* **1991**, *113*, 8652–8657]. F. ANN WALKER* and URSULA SIMONIS

Page 8653: The definition of acquisition time A_t in the last paragraph should read $A_t = N/F$, where N is the number of real data points and F is the spectral bandwidth. Thus, for the example quoted, in the t_2 dimension, where $N = 256$, A_t is 14 ms and the digital resolution in f_2 ($1/A_t$) is 70 Hz, whereas in the t_1 dimension, A_t is 7 ms and the digital resolution in f_1 is 141 Hz. The digital resolution in f_1 was improved by zero-filling once before Fourier transformation.

Book Reviews*

Neutron, X-Ray and Light Scattering: Introduction to an Investigative Tool for Colloidal and Polymeric Systems. Edited by P. Lindner (Institut Laue-Langevin, Grenoble) and Th. Zemb (C. E. A. Saclay, France). North Holland: Amsterdam. 1991. viii + 376 pp. \$100.00. ISBN 0-444-88946-9.

This book contains the Proceedings of the European Workshop on Neutron, X-Ray and Light Scattering as an Investigative Tool for Colloidal and Polymeric Systems held in Bombannes, France, May 27–June 2, 1990. It consists of 17 papers organized under the following headings: I. Using General Principles; II. Solving Inverse Problems; III. Studying Surfaces and Interfaces; IV. Focussing on Large Scales; V. Investigating Non-Equilibrium Systems; VI. Using Light. At the end there is a dictionary of terms, an author index, and a subject index.

Cell Signalling: Experimental Strategies. Edited by Eric Reid (Guilford Academic Associates) and G. M. W. Cook and J. P. Luzzio (University of Cambridge, U.K.). The Royal Society of Chemistry: Cambridge, U.K. xiv + 446 pp. £84.50. ISBN 0-85186-436-8.

This book contains the Proceedings of the Twelfth International Subcellular Methodology Forum entitled Cell Signalling Experimental Strategies, held in Guildford, U.K., September 4–7, 1990. There are 33 papers with discussions in typescript form organized under the following sections: A. The Signalling Scene, and Response Initiation; B. Cyto-

plasmic Transmission Systems, and Some Agonist Effects; C. Hormone Origination and Actions, Especially Insulin and Glucagon; D. Individual-Cell Studies, Especially on Ca^{2+} ; E. Fibrinolytic, Oncogenic, Junctional and Neural Phenomena; F. Location and Transit of Proteins (Besides 'PKC'). There is a subject index; affiliations of the authors are given at the headings of the papers.

Organic Materials for Non-linear Optics II. Edited by R. A. Hann (ICI Imagedata, Manningtree) and D. Bloor (University of Durham). The Royal Society of Chemistry: Cambridge, UK. 1991. £52.50. xii + 396 pp. ISBN 0-85136-397-3.

This book contains the proceedings of the conference on Organic Materials for Non-linear Optics held in Oxford, September 4–6, 1990. It consists of an Introduction by Bloor and 45 papers in typescript form organized under the following headings: Theory; Small Organic Molecules; Metal-organic Compounds; Polymers; Devices. Affiliations of authors are given at the headings of each paper. There is a subject index.

Enzymes in Industry—Productions and Applications. Edited by Wolfgang Gerhartz (Ullmann's Encyclopedia of Industrial Chemistry). VCH Publishers: New York. 1990. xvii + 321 pp. \$95.00 (hardback). ISBN 0-89573-937-2.

In the course of just under 300 pages of text, various experts contribute short reviews of important topics concerning enzyme production and use. This is accomplished in an encyclopedic approach that will no doubt be found to be inadequate by researchers working in any of the many spe-

*Unsigned book reviews are by the Book Review Editor.