ACTIVATION AND FUNCTIONALIZATION OF ALKANES

Edited by

Craig L. Hill

Emory University, Atlanta, Georgia



A Wiley-Interscience Publication JOHN WILEY & SONS New York Chichester Brisbane Toronto Singapore

Bibliothek Chemie/Materialwissenschaft Technische Universität Darmstadt

Contents

3

Ι.	Historical Evolution of Homogeneous Alkane Activation Systems A. E. Shilov	1
II.	Electrophilic Chemistry of Alkanes George A. Olah, Omar Farooq, and G. K. Surya Prakash	27
III.	Some Recent Advances in Alkane Functionalization: Metal Phosphine Catalysts and Mercury Photosensitization Robert H. Crabtree	79
IV.	Alkane Activation Processes by Cyclopentadienyl Complexes of Rhodium, Iridium, and Related Species William D. Jones	111
V.	The Homogeneous Activation of Carbon-Hydrogen Bonds by High-Valent Early d-Block, Lanthanide, and Actinide Metal Systems Ian P. Rothwell	151
<i>VI</i> .	Alkane Functionalization by Cytochromes P-450 and by Model Systems Using O_2 or H_2O_2 D. Mansuy and P. Battioni	195
VII.	Shape-Selective Oxidation of Hydrocarbons Kenneth S. Suslick	219
VIII.	Catalytic Oxygenation of Unactivated C-H Bonds: Superior Oxo-Transfer Catalysts and the "Inorganic Metalloporphyrin" Craig L. Hill	243
IX.	Selective Functionalization of Saturated Hydrocarbons by the "Gif" and "Gif-Orsay" Systems Derek H. R. Barton and Nubar Ozbalik	281
<i>X</i> .	Alkane Oxidation Studies in du Pont's Central Research Department C. A. Tolman, J. D. Druliner, M. J. Nappa and N. Herron	303
	Index	361

xi

Chapter I

HISTORICAL EVOLUTION OF HOMOGENEOUS ALKANE ACTIVATION SYSTEMS

A. E. Shilov

Institute of Chemical Physics U.S.S.R. Academy of Sciences Chernogolovka 142 432, U.S.S.R.

I.	Introduction	1
п.	Homogeneous Activation of Alkanes by Platinum(II) Complexes	3
Ш.	Alkane Reactions with Hydrides and Organometallics	11
IV.	Models of Biological Alkane Oxidation: Activation of Dioxygen	14
V.	Conclusion	24
	References	24

I. Introduction

Since the end of the 1960s a new problem has arisen in the field of homogeneous catalysis, that of homogeneous activation of saturated hydrocarbons by metal complexes. The development of coordination chemistry and catalysis had lead to increased success in the activation of various molecules by metal complexes, such as hydrogen, olefins, aromatics, carbon monoxide, and molecular nitrogen. "Activation" of a certain molecule by a metal complex, although a rather vague concept, usually means that the molecule or its part becomes a ligand in the coordination sphere of the complex and then undergoes a subsequent chemical transformation.

For some time saturated hydrocarbons remained outside of this process, which involved all the other classes of organic and inorganic substances. Meanwhile, an increasingly urgent problem involved the great resources of natural gas that necessitated the creation of new selective processes involving methane, which constitutes its primary part. At the same time, the activation of methane and its analogs is an interesting theoretical problem, since the absence of double or triple bonds, lone electron pairs, and the strength of covalent C-H and C-C σ -bonds in alkanes constitute natural difficulties in the search for desirable systems.

In 1968 J. Halpern¹, one of the leading specialists in homogeneous catalysis, described the task as "to develop a successful

1