ORGANOMETALLICS

Volume 1, Number 12, December 1982



# Rowland Pettit—1927–1981

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Rowland Pettit, W.T. Doherty Professor of Chemistry at the University of Texas, died of lung cancer on December 10, 1981, at the age of 54. He was a dominant figure in the rapid ascendency of organotransition-metal chemistry as a major thrust in modern chemistry. Trained as an organic chemist, he made important contributions in theoretical organic chemistry, the stabilization of transient species by metal complexation, the use of metal complexes in organic synthesis, and homogeneous catalysis.

Pettit was born in Port Lincoln, a small town in southern Australia on February 6, 1927. He completed his B.Sc. (1949), M.Sc. (1950), and *first* Ph.D. (1953) at the University of Adelaide. His graduate research was in natural products and polynuclear heterocyclic chemistry under the direction of Professors A. K. MacBeth and G. M. Badger. Always responsive to opportunity's call, he accepted an Exhibition of 1851 Overseas Fellowship (intended to bring intellectual talent from the Empire to England) to work on his *second* doctorate with Michael J. S. Dewar, a promising, new assistant professor at the University of London. During this period, his interest in theoretical organic chemistry led to synthetic and theoretical studies on non-benzenoid aromatic compounds, including the elusive tropylium ion for which he provided the first rational synthesis. Pettit's adventurous spirit was already in evidence when he set out on a hitchhiking tour of the continent only to run out of money in Spain.

Finally tiring of London's damp, dreary winter (he frequently cursed cold weather), Pettit accepted a faculty position at the University of Texas in Austin in 1957. His interest in the fledgling field of organotransition-metal chemistry having been piqued by the fascinating and provocative reports of ferrocene by Pauson, Woodward, Rosenblum, Whiting, and Wilkinson, his initial contribution to the field came in 1959 with his preparation of the first metal complexes of a nonconjugated diene, norbornadiene. His pioneering work in the stabilization of reactive molecules and ions by metal coordination followed soon thereafter with the preparation of complexes of cyclobutadiene, benzocyclobutadiene, *o*-xylylene, carbenes, and carbonium ions. The ready release of cyclobutadiene from its iron complex led to important insight into the electronic and structural nature of the free ligand and its elegant utilization in synthesis—e.g., the preparation of cubane and hypostrophene. Pettit's love of a challenge and the spirited exchange of ideas was perhaps best evidenced in his contributions on the role of orbital symmetry control in metal-catalyzed isomerizations of strained hydrocarbons.

Pettit had a great respect for and interest in industrial chemical problems. Early studies on the mechanisms of metal-catalyzed olefin isomerization and metathesis are particularly noteworthy in this respect. His unusual talent for designing novel, elegant experiments to elucidate practical questions was apparent in his more recent studies of the catalysis of carbon monoxide reduction and homologation. These studies have improved significantly our understanding of the homogeneous water gas shift reaction and heterogeneous Fisher–Tropsch process.

Pettit was an inspiring mentor to his many graduate students and postdoctoral fellows, most of whom have enjoyed considerable success and recognition in the industrial and academic sectors. His "nose" for the significant, his wonderful ability to analyze complex problems with basic chemical principles, to design novel experiments, and his sharp, critical eye were traits that have left their mark on the thinking of his chemical progeny and colleagues alike.

Pettit was author of over one hundred articles and held numerous distinguished lectureships. He was a former Alfred P. Sloan Fellow as well as a member of the National Academy of Sciences. Rolly's cleverness, warmth, fun-loving way, and underlying sensitivity will be long remembered. He lived his life intensely and, accordingly, he made a lasting imprint on all of us who knew him and his chemistry.

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# Methylenomycin B: An Efficient Synthesis from (2-Butyne)hexacarbonyldicobalt†

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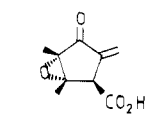
*Received June 30, 1982*

(2-Butyne)hexacarbonyldicobalt reacts at moderate temperatures with tetrahydro-2-(2-propenyloxy)pyran to give a trisubstituted cyclopentenone regiospecifically and in moderate yield. This cyclopentenone may be readily converted into the antibiotic methylenomycin B. This is the first example of regiospecificity, with respect to a simple alkene, in a cyclopentenone synthesis by this method.

The antibiotics methylenomycin A and methylenomycin B were first isolated from *Streptomyces violaceoruber* by Haneishi et al.[1] in 1974. X-ray crystallographic determination[2] of the structure (1) for the first compound was followed in 1977 by synthetic confirmation by Scarborough and Smith;[3] several further syntheses have been reported.[4] The correct structure (2) of methylenomycin B was established by Jernow et al.[5] in 1979, by means of an unambiguous synthesis. Other syntheses have appeared,[6] but all require relatively inaccessible starting materials or many steps. We report here a brief new synthesis of methylenomycin B (2) involving as the key step a regiospecific reaction between (2-butyne)hexacarbonyldicobalt (3) and tetrahydro-2-(2-propenyloxy)pyran (4).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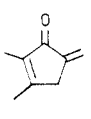
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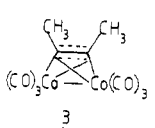
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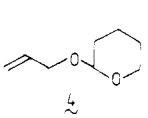
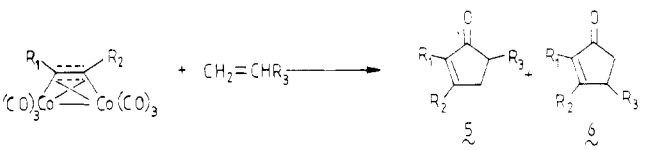

4

Scheme I


5 6

The reaction of (alkyne)cobalt complexes analogous to compound **3** with alkenes has previously been shown to be a general route to substituted cyclopentenones[7] (Scheme I). Its synthetic utility has, however, been limited by both the lack of regiospecificity observed[8] when simple unsym-

† Dedicated to the memory of R. Pettit.

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0276-7333/82/2301-1560$01.25/0 