Topics in Current Chemistry

119

L. A. Paquette

Recent Synthetic Developments in Polyquinane Chemistry

Springer-Verlag Berlin Heidelberg New York Tokyo

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By L. A. Paquette

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Berlin Heidelberg New York Tokyo
1984

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ISBN 3-540-11828-4 Springer-Verlag Berlin Heidelberg NewYork Tokyo
ISBN 0-387-11828-4 Springer-Verlag NewYork Heidelberg Berlin Tokyo

Library of Congress Cataloging in Publication Data.
Paquette, Leo A. Recent synthetic developments in polyquinane chemistry.
(Topics in current chemistry = Fortschritte der chemischen Forschung; 119) Bibliography: p. Includes index.
1. Quinanes. I. Title. II. Series: Topics in current chemistry; 119.
QD1.F58 vol. 119 [QD335] 530s [547'.593] 83-16722

Printed in GDR

2152/3020-543210

119 Topics in Current Chemistry

Fortschritte der Chemischen Forschung

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I Introduction

By the mid-1970's it had become clear that the area of polyquinane chemistry was on the verge of an explosive growth period. There were several underlying reasons for this surge of interest in molecules whose frameworks featured mutually fused cyclopentane rings. Perhaps the most evident was the realization that little attention had previously been paid to methodology for annulating one five-membered ring to another. The need for suitably efficient protocols of this type was arising on several fronts. On the one hand, new natural products were being isolated, the di- or triquinane skeletons of which had not heretofore been appreciated as biogenetically derivable from farnesyl pyrophosphate or related precursors. Independently and with equal intensity, a growing fascination for the possibly unusual physical and chemical properties of yet unknown spherical compounds such as dodecahedrane was gaining rapid momentum. In addition, many novel polycyclopentanoid alicyclic systems of theoretical interest were awaiting the implementation of ingenious routes to their acquisition in the laboratory.

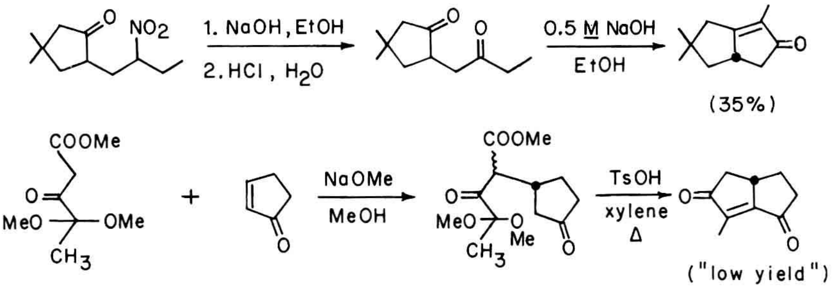
In 1979, we authored a review in Topics in Current Chemistry entitled "The Development of Polyquinane Chemistry"[1]. Numerous early experimental investigations in this field were surveyed and compiled therein. In the few, short intervening years, the level of research activity dealing with polyquinanes has literally mushroomed. Accordingly, the writing of an updated, complementary review as a means of keeping oneself abreast of the many new and imaginative developments seemed entirely appropriate and even necessary. As before, the intention has been to gather together all relevant new facets of pertinent synthetic methodology in the polyquinane field with a view to stimulating yet more exciting future scientific ventures.

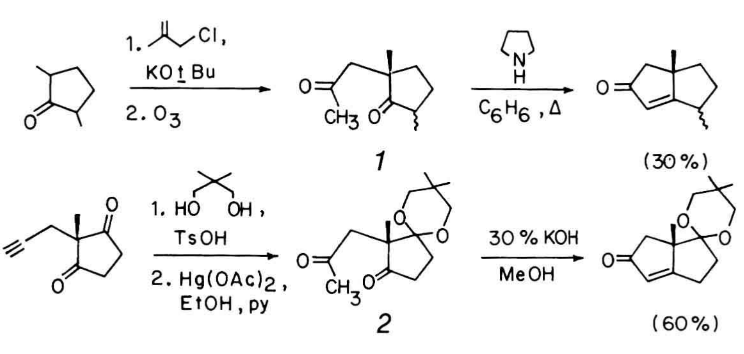
II New Synthetic Developments

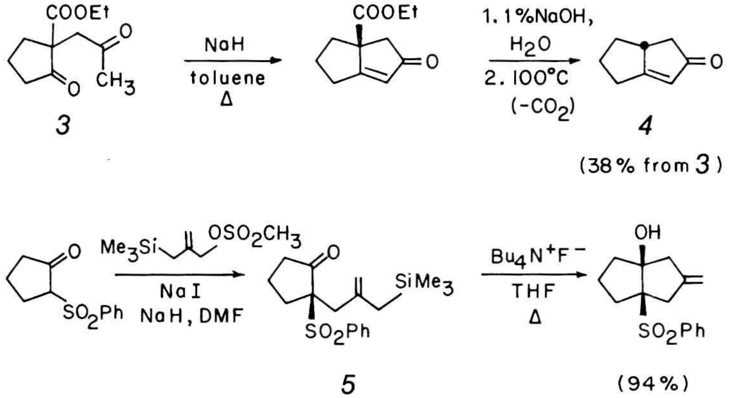
A Annulation Reactions

1 Acid- and Base-Promoted Cyclizations

Although bicyclo[3.3.0]octenones lacking angular substituents can be generated under aldol conditions [2,3], unsatisfactory yields are commonly encountered. The situation is rather dramatically altered and the process gains considerable preparative respectability when comparable cyclodehydration procedures are applied to suitably substituted analogues (Scheme I). It matters not whether the angular group is alkyl as in *1* [4] and *2* [5] or electron-withdrawing as in *3* [6] and *5* [7]. Until this phenomenon was recently appreciated, the simple bicyclic enone *4* had eluded synthesis.

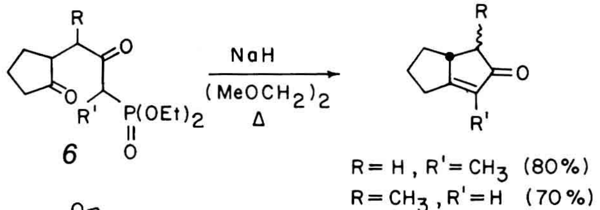


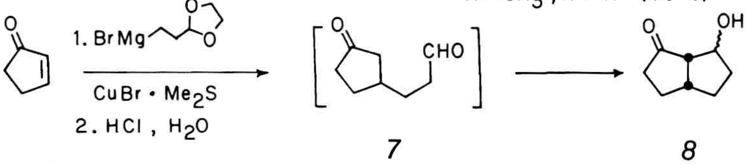


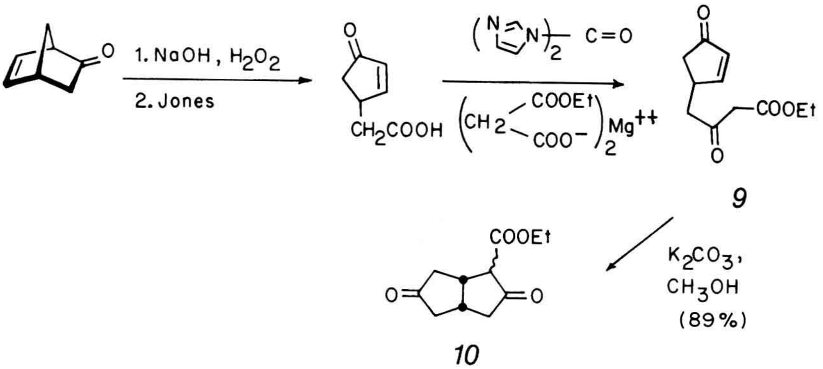


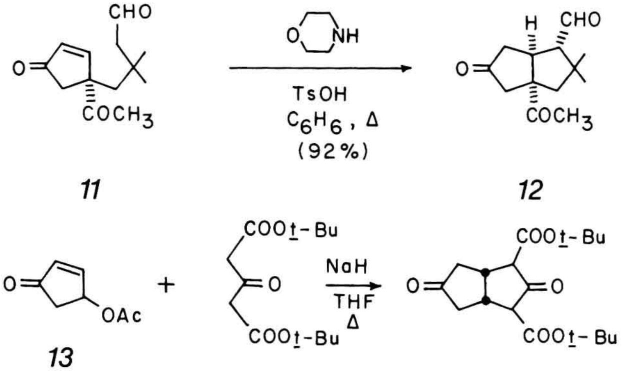
Scheme I

These difficulties can sometimes be surmounted by implementing alternative methodology. Thus, recourse to Wadsworth-Emmons reagents (e.g., *6*) has proven generally reliable, although the strongly alkaline conditions required served to dimerize *4* when arrived at in this manner [8]. Annulation also proceeds well when aldolization involves an aldehyde-containing sidechain as in *7* [9]. In most instances



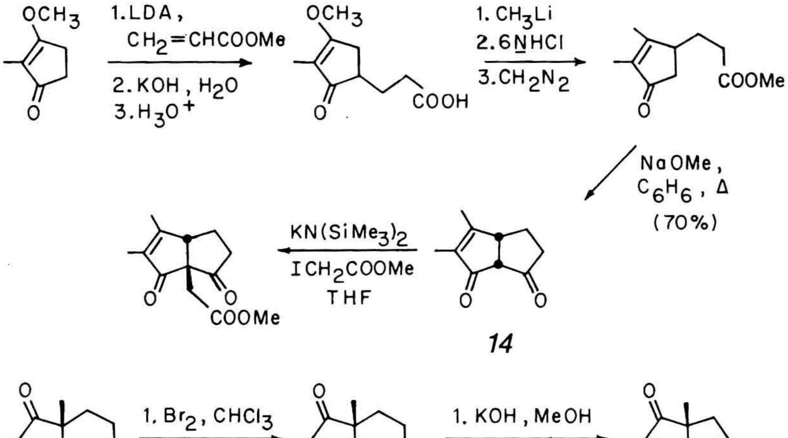


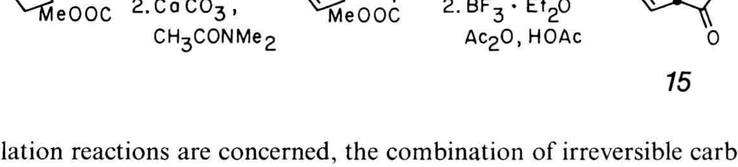




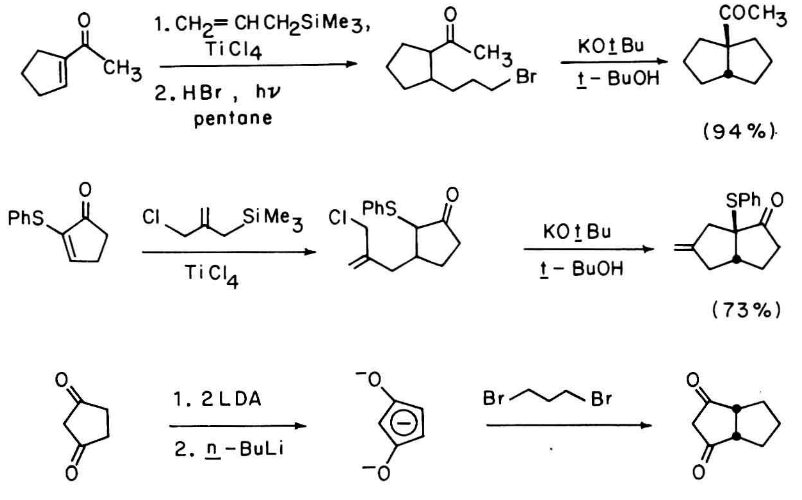
Scheme II

where β-hydroxy ketones of type *8* are formed, dehydration is not spontaneous and requires hydroxyl group activation [10]. Although less studied, intramolecular Michael additions exemplified by *9* → *10* [11] and *11* → *12* [12] give evidence of high efficiency (Scheme II). With *11* in particular, several alternative reaction pathways are possible, and reaction conditions must therefore be closely monitored. The double Michael addition options made possible by 4-acetoxy-2-cyclopentenone (*13*) are noteworthy. [13] It would appear on the basis of two reports [14, 15] that intramolecular Claisen condensations have considerable potential in delivering highly functionalized diquinanes (e.g., *14* and *15*) not readily available by other means.





Where alkylation reactions are concerned, the combination of irreversible carbon-carbon bond formation and favorable kinetic considerations frequently provide

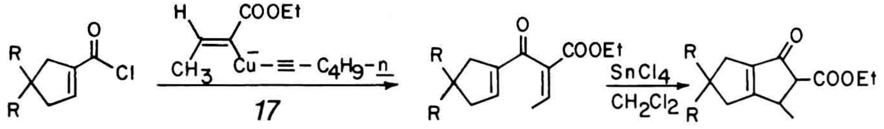


16 (13%)

Scheme III

satisfactory product yields (Scheme III).[16,17] The twofold alkylation of the cyclopentane-1,3-dione trianion with 1,3-dibromopropane to provide *16* directly is notable despite the low yield incurred.[18]

Finally, Marino and Linderman have shown that the addition of vinylcuprate *17* to cyclopentenylcarbonyl chlorides followed by Lewis acid-promoted Nazarov cyclization is a useful means of gaining access to bicyclic keto esters *18*.[19]

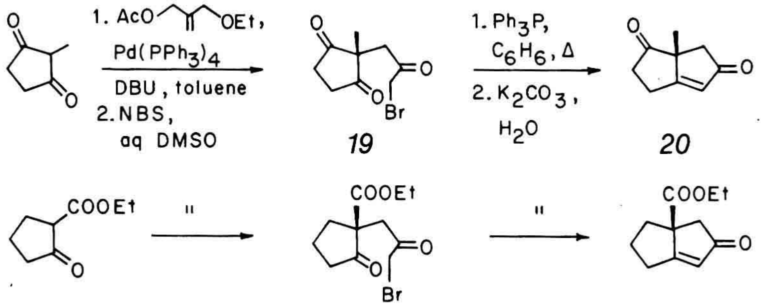


18

(R = H, 30%
R = CH_3, 30%)

2 Intramolecular Ylide Additions

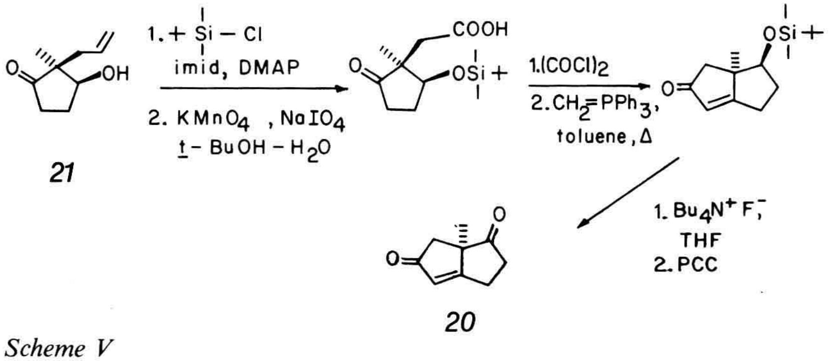
Trost and Curran have developed a cyclopentenone annulation sequence based upon an intramolecular Wittig cyclization which is both general and adaptable to asymmetric synthesis (Scheme IV).[20] Palladium(0)-catalyzed reaction of a five-ring β-dicarbonyl system with 2-ethoxy-3-acetoxy-1-propene leads in high yield to the C-alkylated product, which with N-bromosuccinimide is converted to the corresponding α-bromo ketone. Direct conversion to the phosphonium salt, followed by ylide generation at 40 °C, results in cyclization. The formation of *20* in optically active



Scheme IV

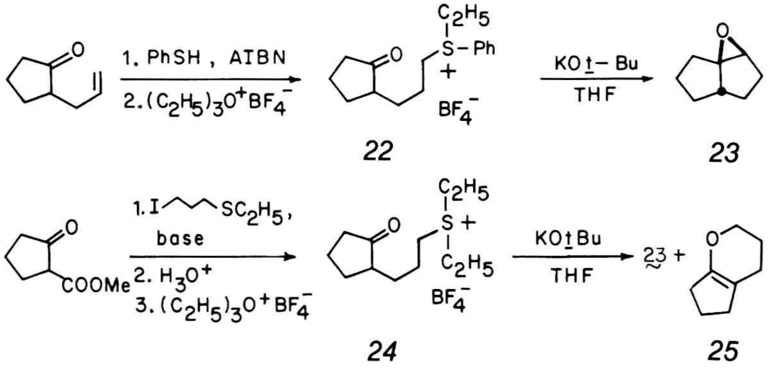
form by condensation of *19* with various optically active phosphines and subsequent exposure to aqueous K_2CO_3 eventuates in poor-to-good chirality transfer (0–77% ee) [21]. A transition state model has been advanced in an effort to rationalize the interdependency of optical induction and phosphine structure. [20, 21]

In an alternative solution to the problem of obtaining optically active *20*, Brooks and coworkers first subjected *21* (and the corresponding propyl and propargyl derivatives as well) to microbial reduction with baker's yeast [22]. The resulting ketol (*21*), obtained in greater than 98% enantiomeric purity (the absolute configuration was also established), was subsequently converted in seven steps to enantiomerically pure bis-nor-Wieland-Miescher ketone (*20*, Scheme V).



Scheme V

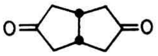
The utility of intramolecular sulfur ylide-carbonyl condensations for achieving cyclopentane epoxyannulation was simultaneously reported by two research groups. [23, 24] Crandall's approach relies upon regioselective thiophenol addition to 2-allylcyclopentanone under free radical conditions and sulfonium salt formation with triethyloxonium fluoroborate (Scheme VI). Under strongly basic conditions, epoxide formation proceeds readily and in good yield. The sulfur substitution plan in *22* appears more suited than that found in *24* since a 1:1 ratio of *23* and *25* is encountered in the last instance. [24]



Scheme VI

3 Weiss-Cook Condensations

Although Weiss' original study of the condensation of dimethyl 3-ketoglutarate with 1,2-dicarbonyl compounds was made public in 1968, [25] it remained for Bertz, Rihs, and Woodward to develop a workable, large-scale laboratory preparation of the parent bicyclo[3.3.0]octan-3,7-dione (*26*) from glyoxal only last year. [26] During the



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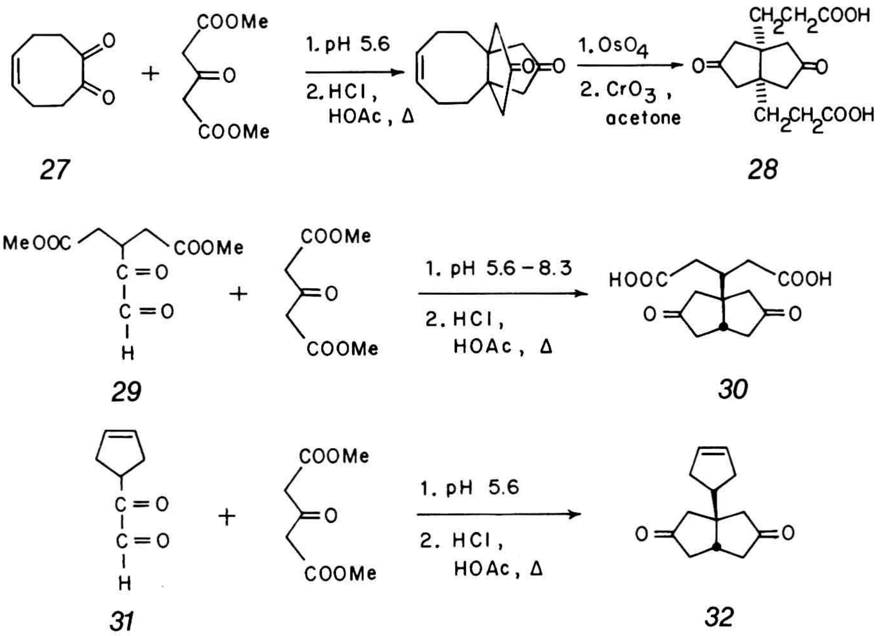

Scheme VII