VOLUME EDITOR: A. DE MEIJERE

201 Topics in Current Chemistry

Carbon Rich Compounds II

Macrocyclic Oligoacetylenes and Other Linearly Conjugated Systems

Springer

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Macrocyclic Oligoacetylenes and Other Linearly Conjugated Systems

Volume Editor: A. de Meijere

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As a rule, contributions are specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers are accepted for "Topics in Current Chemistry" in English.

In references Topics in Current Chemistry is abbreviated Top. Curr. Chem. and is cited as a journal.

Springer WWW home page: http://www.springer.de
Visit the TCC home page at http://www.springer.de/

ISSN 0340-1022
ISBN 3-540-65301-5
Springer-Verlag Berlin Heidelberg New York

Library of Congress Catalog Card Number 74-644622

Printed in Germany

Cover design: Friedhelm Steinen-Broo, Barcelona; MEDIO, Berlin
Typesetting: Fotosatz-Service Köhler GmbH, 97084 Würzburg

SPIN: 10649238 66/3020 – 5 4 3 2 1 0 – Printed on acid-free paper

201
Topics in Current Chemistry

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Preface

Not too long ago, graphite and diamond were the only two known modifications of carbon. That changed dramatically with the discovery of C_{60} in 1985 and all the higher fullerenes soon thereafter. Nevertheless, this breakthrough did not stand alone in paving the way to the new era of chemical and physical research into carbon rich compounds that we are now enjoying.

The last 20 years have witnessed the development of a powerful repertoire of new carbon-carbon bond forming processes, especially metal-catalyzed and metal-mediated ones. These, together with other useful organic synthetic methodologies, including important protection and deprotection procedures, have made the synthesis of new targets possible that were inconceivable previously. The whole range of modern acetylene chemistry and numerous new materials simply would not exist without these new methodologies. Along with the fast growing set of tools goes an ever increasing number of publications concerning impressive arrays – cyclic, two-dimensional and even three-dimensional – of acetylenic and diacetylenic units linked by aliphatic, aromatic or organometallic connectors. Nowadays there seems to be no limits to achieving what the fantasy of the chemist can come up with.

It appeared timely to compile recent developments in modern oligoacetylene chemistry and other new materials – such as polyparavinylenephenylenes and the like – as these carbon rich compounds and their properties bear relevance to our modern understanding of the importance of organic chemistry as well as the emerging field of organic materials science. The term "carbon rich" is used here and in the preceding volume on this topic (TCC Vol. 196) to refer to everything that has a carbon to hydrogen ratio of $1:(<1)$.

Göttingen, Januar 1999 Armin de Meijere

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Contents

Macrocyclic Structurally Homoconjugated Oligoacetylenes: Acetylene- and Diacetylene-Expanded Cycloalkanes and Rotanes

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There is ample evidence for the significance of modern acetylene chemistry and its role for the future development in several areas of organic chemistry. In this chapter, the successful syntheses and attempted approaches to macrocyclic structurally homoconjugated oligoacetylenes and oligodiacetylenes, as well as some of their physical properties, are discussed. Such compounds, which are formally derived from permethylated cycloalkanes by insertion of –C≡C– or –C≡C–C≡C– fragments between each pair of adjacent sp^3-hybridized carbon atoms, have been termed [*n*]pericyclines and expanded [*n*]pericyclines, respectively. These and analogous hydrocarbons formally derived from [*n*]rotanes (perspirocyclopropanated [*n*]pericyclines and "exploded" [*n*]rotanes) as well as heteroanalogues of [*n*]pericyclines are presented. In addition, the preparations and properties of macrocycles with mixed ethyne and butadiyne expanders as well as the attempted syntheses of perspirocyclopropanated "exploded" [*n*]rotanes are also covered. In view of the reported properties, the question of cyclic homoconjugation and homoaromaticity in these unconventional compounds is discussed. Finally, some chemical transformations of these macrocyclic oligoacetylenes and oligodiacetylenes, e.g. the conversion of diacetylene-expanded [*n*]rotanes into crowns of thiophenes, are presented.

Keywords: Alkynes, Coupling reactions, Macrocycles, Pericyclines, Expanded pericyclines, Cyclopropanes, Exploded [*n*]rotanes, Heteropericyclines, Homoconjugation, Homoaromaticity, Strain energy, Oligothiophenes.

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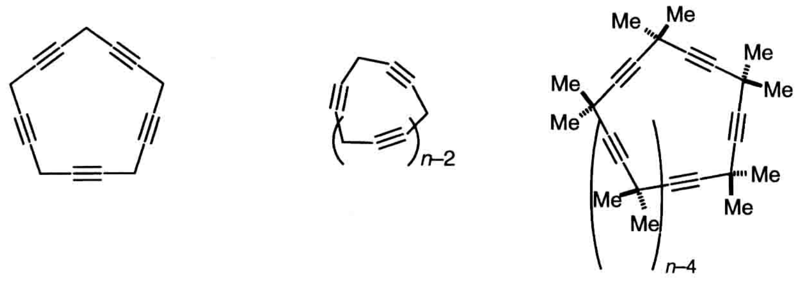
1
Introduction

The syntheses of macrocyclic oligoacetylenes with a capacity for cyclic conjugation and the investigation of their properties have once again become an active area of acetylene chemistry. After the rather quiet period following the classical work of Sondheimer et al. [1], it has gained tremendous momentum in recent years. Undoubtedly, the drastically advanced methodology of metal-catalyzed and metal-mediated cross-coupling reactions [2] has contributed to the rapid development in modern acetylene chemistry [3]. Macrocyclic, structurally homoconjugated oligoacetylenes are of special interest to evaluate the potential effects of homoconjugation and cyclic homoconjugation, particularly in neutral molecules. This account reviews the synthetic efforts that have been made towards the assembly of macrocyclic oligoacetylenes and oligodiacetylenes in which each pair of ethyne and butadiyne moieties is separated by a quaternary carbon atom, a CH_2 group or a heteroatom. Such macrocycles can also be viewed as expanded carbo- or heterocycles, in which each single bond is replaced by an ethyne or a butadiyne fragment. In addition to the synthesis of such compounds, their relevant spectroscopic and structural properties will be discussed. The few chemical transformations and insights into the chemical reactivity of these macrocycles, especially the macrocyclic oligodiacetylenes, will also be presented.

2
[*n*]Pericyclines

The preparation and chemical transformations of [*n*]pericyclines have recently been reviewed by Scott et al. [4]. This section is therefore to be considered as an update of that excellent review. The term "[*n*]pericyclines" was advanced in the pioneering work of Scott et al. [5, 6] to describe molecules containing n –C≡C– units distributed symmetrically around the perimeter of a cycle with n vertices, i.e. a cycloalkane with an ethyne moiety inserted into each single bond (Fig. 1).

The first members of this family – cyclonona-1,4,7-triyne and cyclododeca-1,4,7,10-tetrayne **2** ($n=3$, 4) – as well as their substituted analogues remain illusive to this day. In order to overcome preparative complications associated with labile hydrogens on the doubly propargylic carbon atoms, the higher [*n*]pericyclines **3**–**6** were prepared only as the fully or almost fully methylated derivatives [6].

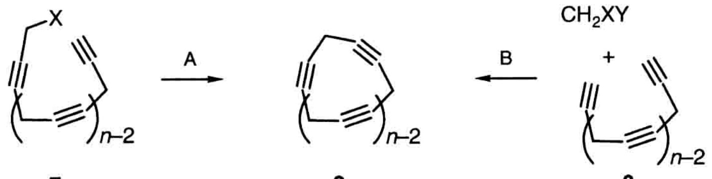


1 **2** **3** $n = 5$, **4** $n = 6$
5 $n = 7$, **6** $n = 8$

Fig. 1. [5]Pericycline **1**, pericycline **2** of order *n*, and permethylated [*n*]pericyclines **3–6** ($n = 5-8$)

2.1
Synthetic Routes to [*n*]Pericyclines

[*n*]Pericycline ring systems **2** can be prepared by a stepwise assembly of an appropriate acyclic precursor **7** with the same number of carbon atoms and its subsequent cyclization (one-component approach, pathway A) or by twofold alkynylation of a difunctional C_1-building block with an acyclic homoconjugated [*n*]oligoyne **8** (two-component approach, pathway B in Scheme 1).

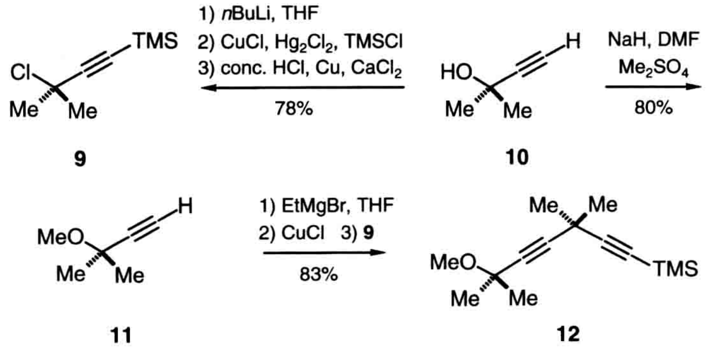


7 **2** **8**

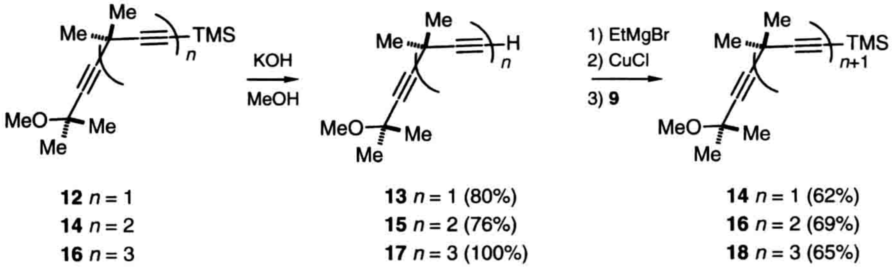
Scheme 1. Conceivable synthetic approaches to [*n*]pericyclines

Following the first of these two strategies, the whole series of permethylated [*n*]pericyclines **3–6** ($n = 5-8$) has been synthesized starting from a single building block – dimethylpropargyl alcohol **10** – which is commercially available and can easily be prepared from acetone and acetylene (Scheme 2) [4, 6].

The subsequent chain extension can be accomplished by the pedestrian step-by-step homologation sequence via the acyclic diyne **12** or by a more efficient block-to-block strategy. The step-by-step approach includes protiodesilylation of diyne **12** followed by coupling with the propargyl chloride **9** following the same protocol as for the preparation of **12** from **11** and subsequent repetitions of protiodesilylation and alkylation with chloride **9** to reach stages **16** and **18**, respectively (Scheme 3).



Scheme 2. The main building blocks for $[n]$pericyclines



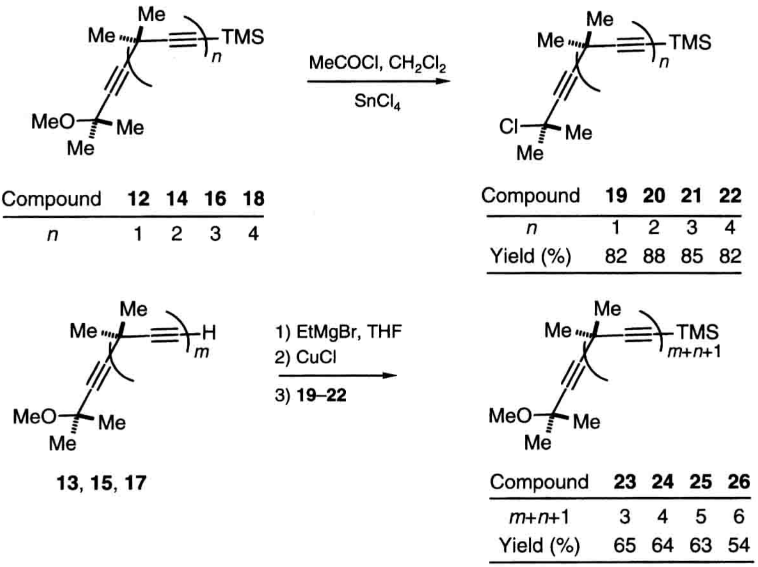
Scheme 3. Regioselective step-by-step chain lengthening of the precursor **12** to $[n]$pericyclines

In the block-to-block strategy, the direct conversion of the methoxy group in compounds of type **12**, **14**, etc., to a chloride leaving group leads to propargylic chlorides **19**–**22** with the appropriate chain length which can be coupled with acetylenic cuprates derived from compounds **13**, **15** or **17** under the conditions mentioned above to give oligoynes **23**–**26** (Scheme 4). These, in turn, are converted to the corresponding chlorides **27** in 82–93% yields. Accordingly, a set of only two to three standard repetitive operations was used in both types of preparations of the acyclic oligoacetylenic compounds for eventual cyclization [4–6].

The acyclic oligoynes **23**–**26** can be cyclized under Friedel-Crafts conditions, i. e. by treatment with $AlCl_3$ in CS_2, which presumably proceeds via the intermediate tertiary propargylic **27** and β-silyl-substituted vinylic carbocations of type **28** (Scheme 5).

The yield of the macrocycle drops steadily as the ring size increases from 35% for **3** ($n=5$) to 22% for **4** ($n=6$), 6.2% for **5** ($n=7$) and 1.5% for **6** ($n=8$). By an analogous sequence, octamethyl[5]pericycline **30** has also been prepared, albeit in lower yield than the permethylated analogue **3** (Scheme 6) [6].

The two-component approach has been elaborated for the preparation of $[n]$pericycline derivatives with $n=4$ and $n=8$, and 10. These compounds are not easily or not at all accessible along the one-component route. In principle, the appropriate acyclic precursors can be prepared in the same manner as the ones for



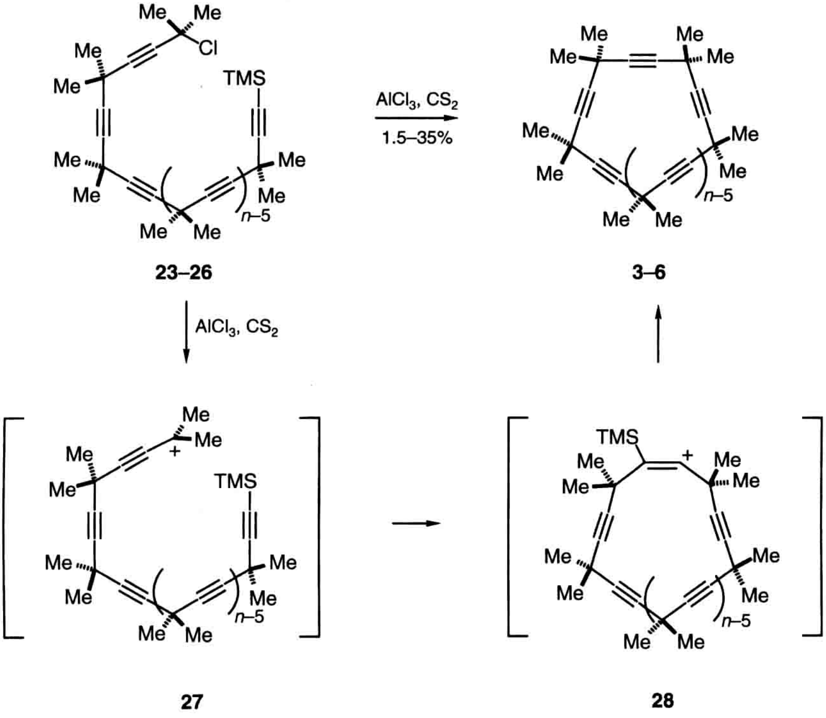
Compound	12	14	16	18
n	1	2	3	4

Compound	19	20	21	22
n	1	2	3	4
Yield (%)	82	88	85	82

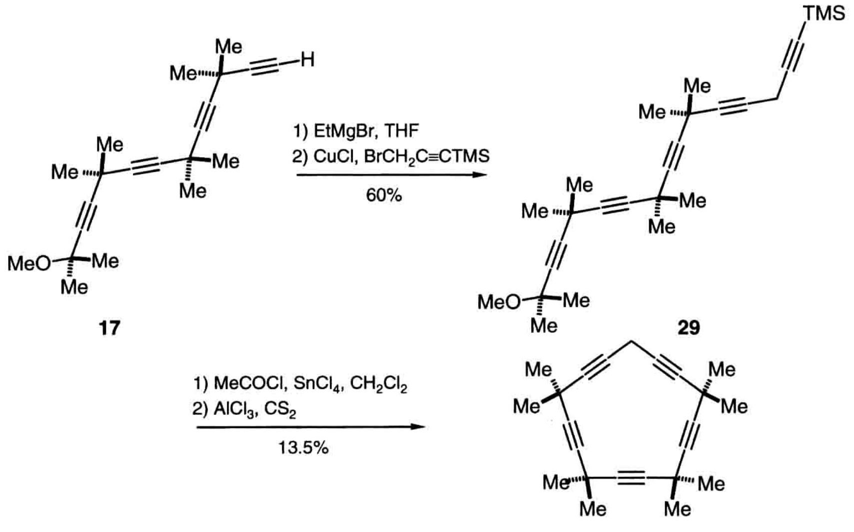
13, 15, 17

Compound	23	24	25	26
m+n+1	3	4	5	6
Yield (%)	65	64	63	54

Scheme 4. Starting materials for [*n*]pericyclines



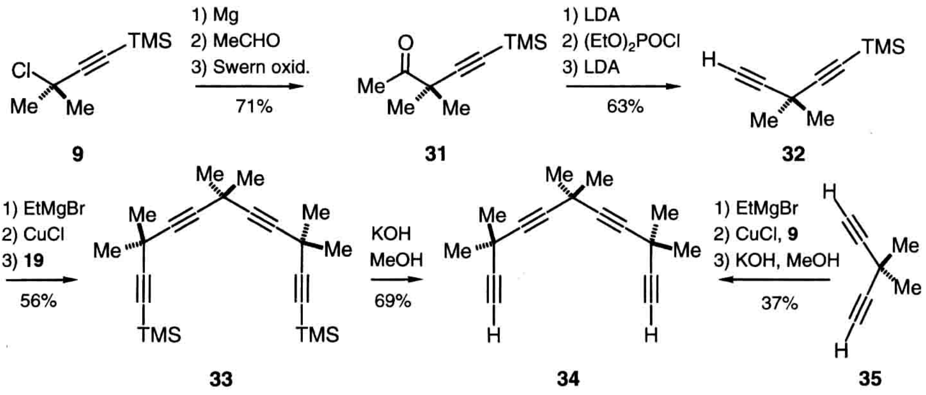
Scheme 5. Synthesis of [*n*]pericyclines and possible mechanistic rationalization



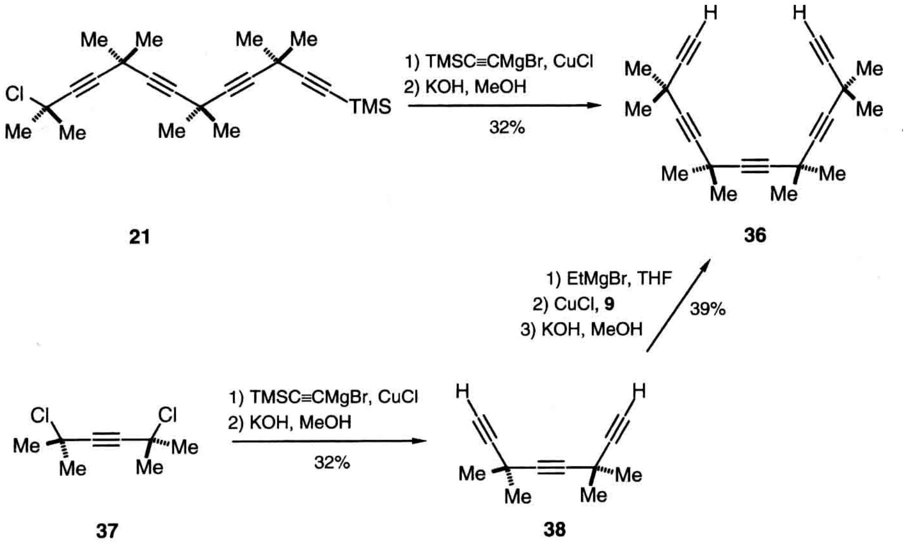
Scheme 6. Preparation of octamethyl[5]pericycline **30** **30**

the one-component approach from the building block **9**, yet acyclic oligoynes with even and odd numbers of triple bonds were synthesized along two different routes. For example, hexamethylundecatetrayne **34** was assembled starting from **9** in five steps with 17% overall yield [3, 7], or, more efficiently, in two steps from dimethylpentadiyne **35** which unfortunately is less easily available (Scheme 7) [7, 8].

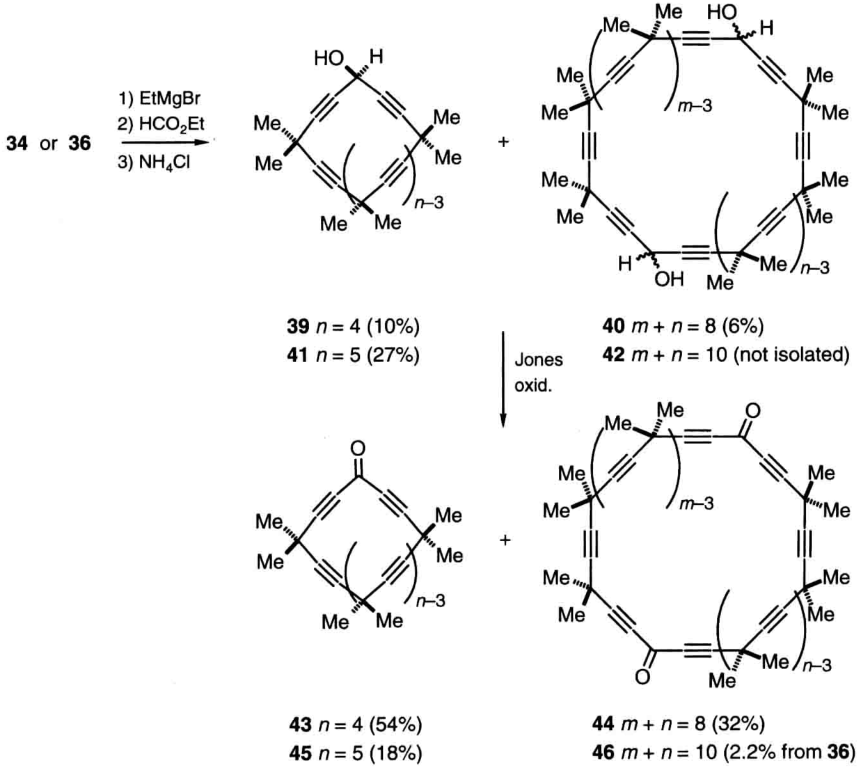
The acyclic octamethyltetradecapentayne **36** was constructed either from chlorotetrayne **21** by adding one dimethylethynyl unit or starting from 2,5-dichloro-2,5-dimethyl-3-hexyne (**37**) by coupling with one ethynyl unit on either side (Scheme 8) [4].



Scheme 7. Starting materials for [*n*]pericyclines via a two-component approach



Scheme 8. Starting materials for [*n*]pericyclines via a two-component approach



Scheme 9. Pericyclinols and pericyclinones via a two-component approach