ORGANIC REACTIONS

Volume 109

Organic Reactions

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Organic Reactions

VOLUME 109

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INTRODUCTION TO THE SERIES
BY ROGER ADAMS, 1942

In the course of nearly every program of research in organic chemistry, the investigator finds it necessary to use several of the better-known synthetic reactions. To discover the optimum conditions for the application of even the most familiar one to a compound not previously subjected to the reaction often requires an extensive search of the literature; even then a series of experiments may be necessary. When the results of the investigation are published, the synthesis, which may have required months of work, is usually described without comment. The background of knowledge and experience gained in the literature search and experimentation is thus lost to those who subsequently have occasion to apply the general method. The student of preparative organic chemistry faces similar difficulties. The textbooks and laboratory manuals furnish numerous examples of the application of various syntheses, but only rarely do they convey an accurate conception of the scope and usefulness of the processes.

For many years American organic chemists have discussed these problems. The plan of compiling critical discussions of the more important reactions thus was evolved. The volumes of *Organic Reactions* are collections of chapters each devoted to a single reaction, or a definite phase of a reaction, of wide applicability. The authors have had experience with the processes surveyed. The subjects are presented from the preparative viewpoint, and particular attention is given to limitations, interfering influences, effects of structure, and the selection of experimental techniques. Each chapter includes several detailed procedures illustrating the significant modifications of the method. Most of these procedures have been found satisfactory by the author or one of the editors, but unlike those in *Organic Syntheses*, they have not been subjected to careful testing in two or more laboratories. Each chapter contains tables that include all the examples of the reaction under consideration that the author has been able to find. It is inevitable, however, that in the search of the literature some examples will be missed, especially when the reaction is used as one step in an extended synthesis. Nevertheless, the investigator will be able to use the tables and their accompanying bibliographies in place of most or all of the literature search so often required. Because of the systematic arrangement of the material in the chapters and the entries in the tables, users of the books will be able to find information desired by reference to the table of contents of the appropriate chapter. In the interest of economy, the entries in the indices have been kept to a minimum, and, in particular, the compounds listed in the tables are not repeated in the indices.

The success of this publication, which will appear periodically, depends upon the cooperation of organic chemists and their willingness to devote time and effort to the preparation of the chapters. They have manifested their interest already by the almost unanimous acceptance of invitations to contribute to the work. The editors will welcome their continued interest and their suggestions for improvements in *Organic Reactions*.

INTRODUCTION TO THE SERIES
BY SCOTT E. DENMARK, 2008

In the intervening years since "The Chief" wrote this introduction to the second of his publishing creations, much in the world of chemistry has changed. In particular, the last decade has witnessed a revolution in the generation, dissemination, and availability of the chemical literature with the advent of electronic publication and abstracting services. Although the exponential growth in the chemical literature was one of the motivations for the creation of *Organic Reactions*, Adams could never have anticipated the impact of electronic access to the literature. Yet, as often happens with visionary advances, the value of this critical resource is now even greater than at its inception.

From 1942 to the 1980's the challenge that *Organic Reactions* successfully addressed was the difficulty in compiling an authoritative summary of a preparatively useful organic reaction from the primary literature. Practitioners interested in executing such a reaction (or simply learning about the features, advantages, and limitations of this process) would have a valuable resource to guide their experimentation. As abstracting services, in particular *Chemical Abstracts* and later *Beilstein*, entered the electronic age, the challenge for the practitioner was no longer to locate all of the literature on the subject. However, *Organic Reactions* chapters are much more than a surfeit of primary references; they constitute a distillation of this avalanche of information into the knowledge needed to correctly implement a reaction. It is in this capacity, namely to provide focused, scholarly, and comprehensive overviews of a given transformation, that *Organic Reactions* takes on even greater significance for the practice of chemical experimentation in the 21st century.

Adams' description of the content of the intended chapters is still remarkably relevant today. The development of new chemical reactions over the past decades has greatly accelerated and has embraced more sophisticated reagents derived from elements representing all reaches of the Periodic Table. Accordingly, the successful implementation of these transformations requires more stringent adherence to important experimental details and conditions. The suitability of a given reaction for an unknown application is best judged from the informed vantage point provided by precedent and guidelines offered by a knowledgeable author.

As Adams clearly understood, the ultimate success of the enterprise depends on the willingness of organic chemists to devote their time and efforts to the preparation of chapters. The fact that, at the dawn of the 21st century, the series continues to thrive is fitting testimony to those chemists whose contributions serve as the foundation of this edifice. Chemists who are considering the preparation of a manuscript for submission to *Organic Reactions* are urged to contact the Editor-in-Chief.

PREFACE TO VOLUME 109

> *The wings of transformation are born of patience and struggle.*
>
> Janet S. Dickens

The ability to control chemical reactivity and selectivity represents the very essence of modern synthetic organic chemistry, albeit these goals often pose complex challenges for chemists engaged in discovering new chemical reactions. For instance, highly reactive reagents often demonstrate low selectivity, limit substrate scope, and lead to competing side reactions. Consequently, many reactive intermediates are best generated from less reactive precursors under mild and often catalytic conditions to mitigate some of these detrimental issues. The ability to "mask" and "trigger" chemical reactivity provides a measurable strategic advantage that often underpins the evolution of a basic synthetic method into a sophisticated and practical process with fewer limitations. Hence, the challenges encountered in developing such a transformation are indeed "*born of patience and struggle,*" which may disguise the extensive experimentation required to enable the "metamorphosis" of a simple hypothesis into a robust chemical transformation.

The *Organic Reactions* series provides an enduring narrative that showcases the so-called "life-cycle" of these developments, which can be ascribed to the unique blueprint provided by Roger Adams at the outset of this venerable series in 1942. As part of this vision, the chapters are written by recognized experts in the field in a consistent and unified format to disseminate critical features of the transformation that enables the practicing synthetic organic chemist to gain the in-depth understanding and insight necessary to utilize the reaction successfully. For example, the chapters dissect crucial elements of a process within the context of the reaction mechanism and stereochemistry, scope and limitations, applications to synthesis, a comparison with other methods, and critical experimental details and procedures. For this reason, *Organic Reactions* chapters provide unparalleled insights into the various underpinnings of an important chemical reaction that would be challenging to assimilate, even with modern computerized search engines.

This single-chapter volume by Frank S. Guziec, Jr. and Lynn James Guziec provides a comprehensive treatise on extrusion reactions, which involve the loss of a small, stable inorganic molecule, such as carbon dioxide and nitrogen, or an atom, such as sulfur, from an organic precursor. Hence, the chapter deals with the notion of "unmasking" chemical reactivity to access arenes, dihydroarenes, heteroarenes, dienes, and polyenes and other challenging targets. The chapter provides an update on the extrusion of carbon dioxide and nitrogen in retro-Diels-Alder reactions (Volumes 52 and 53); however, the related Ramberg-Bäcklund reaction with the extrusion of sulfur dioxide (Volumes 25 and 62) and the Eschenmoser-type ring-contraction-extrusion reaction are not included. The introduction briefly defines extrusion and cheletropic processes, which are formally a type of pericyclic reaction that proceeds via a cyclic transition state with reorganization of σ- and π-bonds. The mechanistic aspects of these reactions remain relatively poorly understood, and most of our insight is gleaned by inference rather than actual mechanistic studies. For instance, the stereochemical outcome of thermal and photochemical extrusion of sulfur dioxide from 3-sulfolenes provides complementary stereochemistry that is ascribed to the difference in the mechanism. The thermal extrusion is a disrotatory process according to the Woodward-Hoffmann rules, whereas the corresponding photochemical process involves a conrotatory mechanism from an excited state intermediate. The mechanistic aspects of the extrusion of other groups, namely, sulfur monoxide, carbon monoxide, and molecular nitrogen illustrate the challenges in delineating a unified approach, given the subtle differences in each extrusion process. The section also describes how structural features in a series of bicyclic ketones provide insight for the observed extrusion rates, using kinetic studies and calculations.

The Scope and Limitations section is organized by the product (e.g., arenes, dihydroarenes, heterocycles, dienes, and polyenes) and then further subdivided by the type of extrusion (e.g., carbon monoxide, carbon dioxide, sulfur, sulfur dioxide, sulfur monoxide, selenium and tellurium, oxygen, and nitrogen), including reductive extrusion reactions. Notably, the extrusion process is subdivided by the nature of the dienophile often involved in the extrusion process, namely, benzynes, alkynes, alkenes, etc. A particular highlight is the extrusion of carbon monoxide from cyclopentadienone–polyacetylene adducts, which represents a powerful method for the iterative preparation of dendrimeric structures to form higher-generation dendrimers. Additional sections focus on tandem extrusion reactions and include a section on ‘click’ reactions of triazines and tetrazines that showcase both creative and useful applications of this chemistry. The chapter also contains several sections on comparative studies, which, in conjunction with the Tabular Survey, provide the reader with the additional insight needed to select the appropriate precursor for the desired extrusion reaction.

The Applications to Synthesis section describes the use of the methodology to prepare arenes, heterocycles, dienes, and polyenes that have been subsequently employed to synthesize alkaloids and pheromones. There is also an extensive section on “click and release” reactions, which have been used in the development of prodrugs in medicinal chemistry. The Comparison with Other Methods section outlines a few related strategies for the de novo synthesis of arenes and 1,3-dienes to provide the reader with a broader perspective on how the extrusion reactions compare with existing methods. The Tabular Survey incorporates reactions reported through early 2021. The organization mirrors the Scope and Limitations in that the reactions are organized by the product in the context of the type of extrusion process, which permits the identification of the optimal extrusion process for accessing a particular target. Overall, this is an excellent chapter on a venerable and important transformation relevant to modern synthetic, medicinal, and bioorganic chemistry.

I would be remiss if I did not acknowledge the entire *Organic Reactions* Editorial Board for their collective efforts in steering this volume through the editorial process' stages. I want to thank Dr. Stuart McCombie and Dr. Jin K. Cha, who served as Responsible Editors to marshal the chapter through the various phases of development. I am also deeply indebted to Dr. Danielle Soenen for her continued and heroic efforts as the Editorial Coordinator; her knowledge of *Organic Reactions* is critical to maintaining consistency in the series. Dr. Dena Lindsay (Secretary to the Editorial Board) is thanked for coordinating the authors', editors', and publishers' contributions. In addition, the *Organic Reactions* enterprise could not maintain the quality of production without the efforts of Dr. Steven M. Weinreb (Executive Editor), Dr. Engelbert Ciganek (Editorial Advisor), Dr. Landy Blasdel (Processing Editor), and Dr. Tina Grant (Processing Editor). I would also like to acknowledge Dr. Barry B. Snider (Secretary) for keeping everyone on task and Dr. Jeffery Press (Treasurer) for his fiscal diligence.

I am also indebted to past and present members of the Board of Editors and Board of Directors for ensuring the enduring quality of *Organic Reactions*. The specific format of the chapters, in conjunction with the collated tables of examples, makes this series of reviews both unique and exceptionally valuable to the practicing synthetic organic chemist.

P. Andrew Evans
Kingston
Ontario, Canada

CONTENTS

ORGANIC REACTIONS

CHAPTER 1

EXTRUSION REACTIONS AFFORDING AROMATIC SYSTEMS, DIENES AND POLYENES

Frank S. Guziec Jr. and Lynn James Guziec

Department of Chemistry and Biochemistry, Southwestern University, Georgetown, TX 78628

Edited by Stuart McCombie and Jin K. Cha

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Interlibrary Loan staffs of the University of Amsterdam and Wayne State University for their efforts on our behalf.

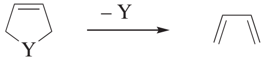
INTRODUCTION

Extrusion reactions are defined as chemical reactions in which an atom or small molecular fragment **Y** connected to two other atoms **W** and **Z** is lost from a molecule, leading to a product in which **W** becomes directly bonded to **Z** (Scheme 1).[1−7] Typically, the fragments liberated in these reactions are small, stable inorganic molecules or atoms.

$$\mathrm{W{-}Y{-}Z} \xrightarrow{-\,\mathrm{Y}} \mathrm{W{-}Z}$$

Scheme 1

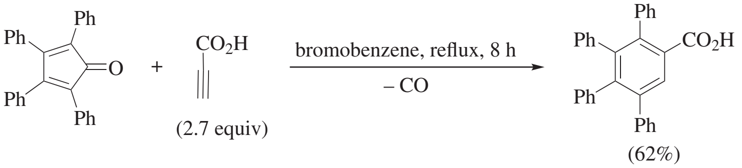
Cheletropic reactions that afford aromatic or conjugated π-systems by the loss of either a stable atomic or molecular fragment have been classified as extrusion reactions (Scheme 2).[1,2,5] For instance, many retro-Diels–Alder reactions are considered to be extrusion reactions.



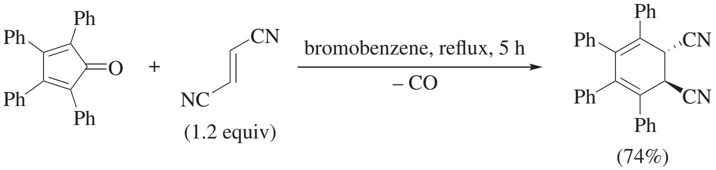
Scheme 2

This chapter deals with the generation of dienes, polyenes, and aromatic compounds by the loss of small inorganic fragments, such as CO, CO_2, SO_2, SO, S, Se, Te, O_2 and N_2. In a number of cases, the formal extrusion of O and N from molecules by reduction, followed by the loss of water or ammonia, are included for completeness. Examples in which the initial diene product is either trapped as an adduct or reacts in a further intramolecular reaction are also presented. A major review of these topics has previously been reported within the context of general extrusion processes.[6]

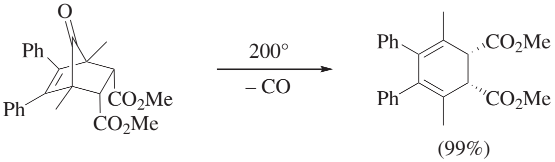
Some representative examples of CO extrusions covered in this chapter include those from in situ generated bicyclic ketones to afford arenes (Scheme 3)[8] and dihydroarenes (Scheme 4),[8] extrusions of CO from isolated bridged compounds (Scheme 5)[9] and multiple extrusions of CO (Scheme 6).[10]



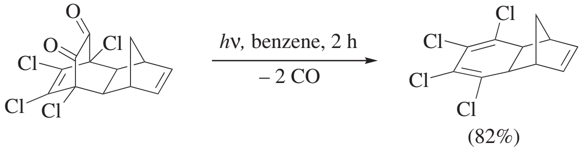
Scheme 3



Scheme 4

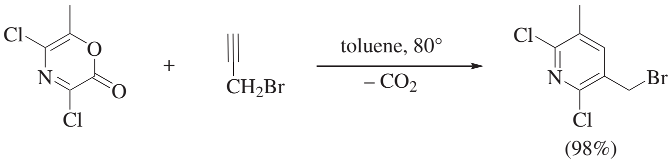


Scheme 5

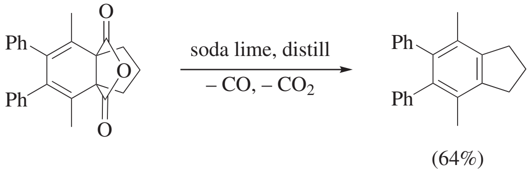


Scheme 6

Other reaction types covered include the extrusion of carbon dioxide to afford heterocycles (Scheme 7)[11] and concurrent extrusions of carbon monoxide and carbon dioxide to furnish aryl systems (Scheme 8).[12]

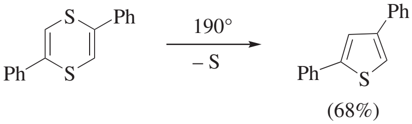


Scheme 7

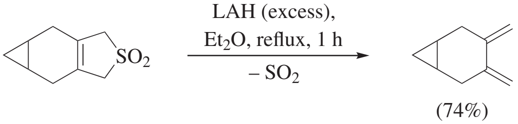


Scheme 8

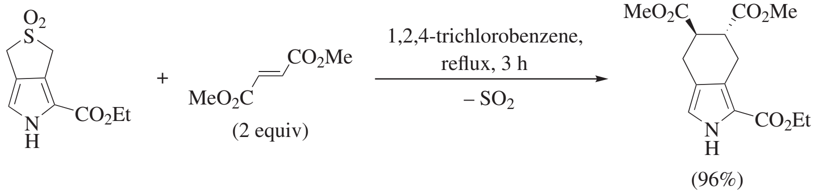
The extrusion of sulfur-derived groups is particularly well-represented in this class of reactions. For example, the direct extrusion of sulfur to generate aromatic groups is common (Scheme 9).[13] The extrusion of SO_2 from sulfolenes to afford dienes that can either be isolated (Scheme 10)[14] or trapped in situ are particularly attractive processes (Scheme 11).[15] Furthermore, the one-pot extrusion of SO_2 from Diels–Alder adducts of thiophene-1,1-dioxides (Scheme 12)[16] are also included in this chapter.



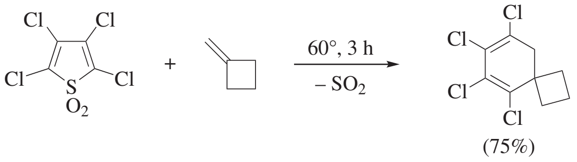
Scheme 9



Scheme 10



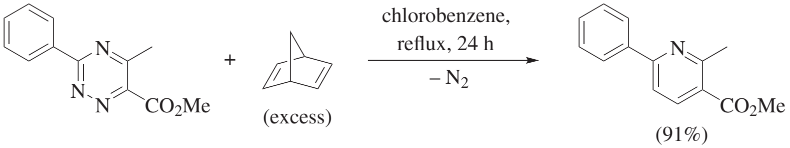
Scheme 11



Scheme 12

The liberation of molecular nitrogen in an addition-extrusion sequence is a common, synthetically useful transformation, which has been deployed in heterocyclic synthesis (Scheme 13).[17] This transformation, and a number of related extrusions of SO, O, Se and Te are also described herein.

The extrusion of SO_2 from thiirane dioxides, in particular, those derived from the Ramberg-Bäcklund reaction, have already been reviewed in *Organic Reactions*,[18,19] and will not be covered in this chapter. Eschenmoser-type ring-contraction–extrusion will also not be discussed,[20,21] and the extrusion of organic species are not



Scheme 13

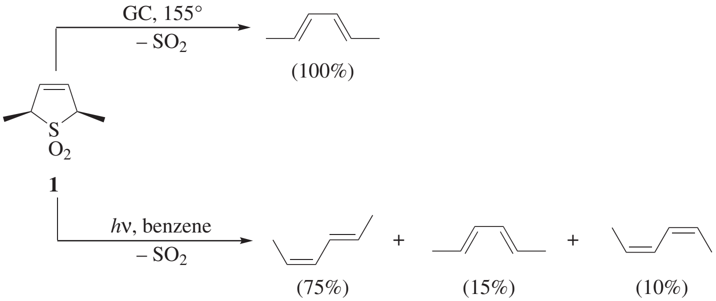
included, except when they occur in tandem with extrusions of inorganic species. Retro-Diels–Alder reactions including many CO_2 and N_2 extrusions, are updated from 1994, as they were previously reviewed in this series.[22,23]

Additional material available in the literature includes a review of the photoextrusion of small molecules,[24] extrusion of gaseous species in natural-product synthesis,[25] and a review of two-fold extrusion reactions affording alkenes and imines.[7]

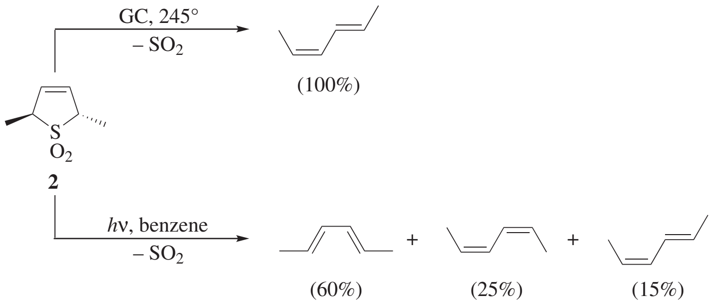
MECHANISM AND STEREOCHEMISTRY

By definition, all extrusion reactions involve the liberation of one or more small stable molecules or atoms, which are most often inorganic fragments. The ease of extrusion of several of these fragments is reported to be as follows: $N_2 > CO_2 > CO > SO > SO_2 > O_2 > S > O$, assuming similar substrates undergo extrusions by a similar reaction mechanism.[6] This order of reactivity has been confirmed in a quantitative manner based upon thermodynamic considerations.[4] At the elevated temperatures often required to facilitate extrusion reactions, such losses of small molecular or atomic fragments are also entropically favorable.

Relatively few detailed mechanistic studies have been conducted on extrusion processes. For the most part, these reactions appear to involve cheletropic elimination of the extrudable moiety.[26,27] A comparison of the thermal and photochemical extrusion of sulfur dioxide from 3-sulfolenes provides an indication of the impact of the mechanism on the product distribution (Schemes 14 and 15).[26,27] Notably, the thermal extrusion of sulfur dioxide from the diastereomeric sulfolenes is stereospecific, which contrasts the photochemical reaction. As expected, the thermal [4+2] retrocyclization follows Woodward–Hoffmann rules and is a disrotatory process.[28]



Scheme 14

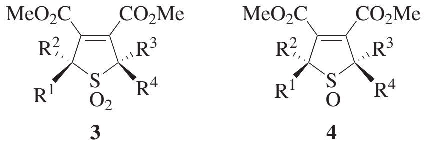


Scheme 15

The *cis*-sulfolene **1** extrudes sulfur dioxide at a considerably lower temperature than does the *trans*-isomer **2**. This result may be explained by steric repulsions in the transition state leading to sulfur dioxide extrusion from **2**. The rates of thermal decomposition of some 3-sulfolenes have been reported, along with activation parameters, and solvent and isotope effects.[29]

The photochemical extrusion reactions of the same sulfolenes (**1** and **2**) carried out using benzene as a photosensitizer (Schemes 14 and 15) are stereoselective.[26,27] These reactions form the major product primarily by a conrotatory ring opening of the sulfolene, presumably from an excited T^1 state. Interestingly the two processes can be considered as stereochemically complementary given that they each favor a different stereoisomer.

The thermal and photochemical investigation of the extrusion reactions of a series of polysubstituted 3-sulfolenes **3** and sulfoxides **4** (Figure 1) has also been described.[30] In accord with the previous study, the thermal extrusion from sulfolenes is stereospecific, whereas the photochemical extrusion and reactions of the sulfoxide analogues are only stereoselective, implying that biradical intermediates are involved in these transformations.[30]

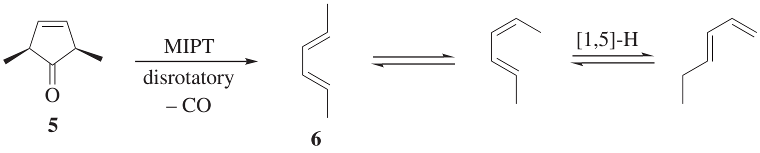


R^1, R^2, R^3, R^4 = H, Me, *t*-Bu

Figure 1. Polysubstituted sulfone and sulfoxide extrusion substrates.

Both the thermal and photochemical extrusions of carbon monoxide from 3-cyclopentenones are predicted to be conrotatory.[31] Experimental verification of this reaction course is complicated by the fact that the pyrolysis temperatures necessary for decarbonylations of simple cyclopentenones lead to thermal isomerizations of the initially formed diene products.[32,33] Importantly, employing multiphoton infrared photolysis/thermolysis prevents further thermal reactions of these products.

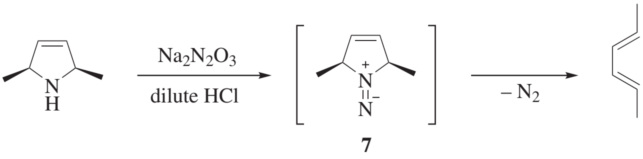
Under these thermolysis conditions, *cis*-2,5-dimethyl-3-cyclopentenone (**5**) affords the (*E*,*E*)-diene **6** exclusively, confirming that the extrusion occurs in a disrotatory manner (Scheme 16).[33] Similar stereochemical results are obtained for the extrusion of N_2 from in situ generated diazenes **7** and **8** to afford dienes (Schemes 17 and 18).[31]



5 **6**

MIPT = multiphoton infrared photolysis/thermolysis

Scheme 16



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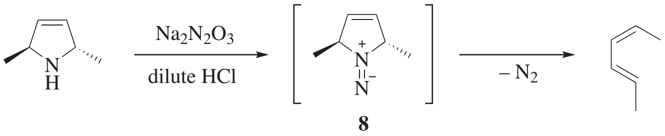
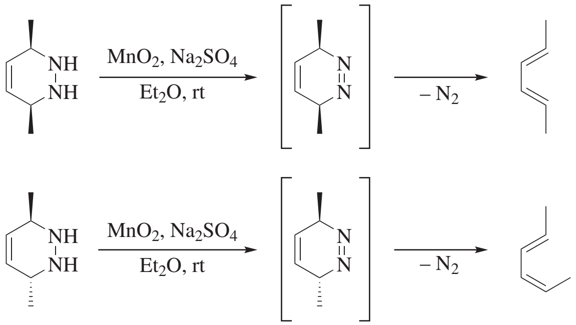
Scheme 17



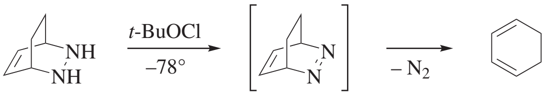
8

Scheme 18

Isomeric endocyclic diazenes also extrude N_2 in a stereospecific manner (Scheme 19).[34] In addition, the bridged diazenes illustrated in Scheme 20 extrude N_2 to form cyclic homodienes.[35] These transformations, which may be considered retro-Diels–Alder reactions, have been previously reviewed.[23]

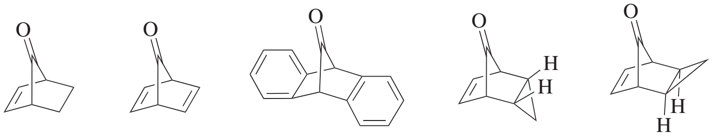


Scheme 19



Scheme 20

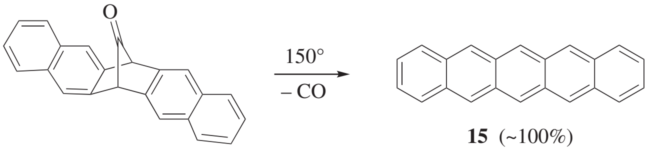
Decarbonylations of bicyclic ketones such as those represented in Figure 2 occur much more readily than decarbonylations of the corresponding monocyclic systems. The extrusion reactions of substrates **9**–**13** are all constrained to a disrotatory pathway. Extrusions of carbon monoxide from bicyclo[2.2.1]hept-2-en-7-one (**9**)[36,37] and the corresponding dienone **10**[38−40] are particularly facile relative to monocyclic system **5**. For example, norbornenone **9** is distillable at atmospheric pressure, whereas norbornadienone (**10**), which is generated photochemically, is only observable by NMR spectroscopy at 195 K and rapidly decarbonylates to afford benzene at 230 K.[39]



9 **10** **11** **12** **13**

Figure 2. Bicylic ketones as substrates for decarbonylation.

Crystallographic evidence from a variety of bicyclic 3-cyclopentenone derivatives of **9** and **10** shows both a lengthening of the α-carbon–carbonyl sigma bonds as well as a shortening of the C=O pi bond relative to a normal ketone.[33] This is consistent with the 'structure correlation principle' that indicates that structural distortions along a reaction coordinate can be present in the ground state of a molecule.[41] The decarbonylation of dibenzonorbornadienone (**11**) is less facile than that of **10**, which is the subject of kinetic studies on the parent ketone **11** and its nitro derivatives.[42] Kinetic thermal decarbonylation studies of the cyclopropane–fused 3-cyclopentenone derivatives **12** and **13** indicate that the extrusion of carbon monoxide is significantly faster in **12** than in the case of **9** and **13**. The participation of the *endo* oriented cyclopropyl moiety in **12** increases the decarbonylation rate by 10^5 relative to **9** and 10^7 relative to **13**.[36,43] It is worth noting that the norbornadienone **14** is stable at room temperature and that the decarbonylation to pentacene (**15**), which was observed by differential scanning calorimetry, occurs at elevated temperatures (Scheme 21).[44]

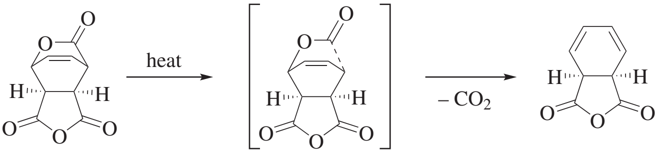


14

15 (~100%)

Scheme 21

Calculations based on kinetic data indicate that thermal decarboxylation of an α-pyrone–maleic anhydride adduct occurs by a two-stage, two-centered transition state, with cleavage at the weaker α-carbonyl carbon sigma bond (Scheme 22).[45]



Scheme 22

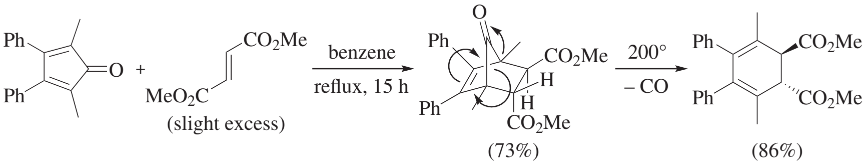
In comparison, the mechanisms of most other extrusion reactions are not particularly well-studied. Mechanistic details of some specific transformations are discussed below, within the context of the extrusion processes.

SCOPE AND LIMITATIONS

Arenes, Dihydroarenes and Other Aromatic Compounds via Extrusion Reactions

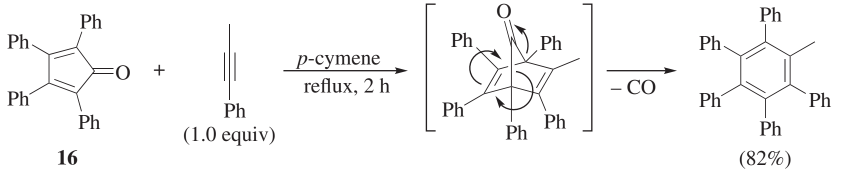
Arene and Dihydroarene Formation via Carbon Monoxide Extrusions

The extrusion of carbon monoxide from bicyclic ketones, which are either isolated or generated in situ, provides a convenient route to arenes and dihydroarenes. Several reviews dealing with extrusions of carbon monoxide from cyclopentadienone Diels–Alder adducts have been reported.[46–49] In particular, these reactions lead to highly substituted molecules that cannot be readily prepared using traditional strategies. These extrusion reactions can be most easily explained as concerted retrocyclizations, which is exemplified by the extrusion of carbon monoxide from cyclopentadienone substrates as outlined in Schemes 23[9] and 24.[50]



Scheme 23

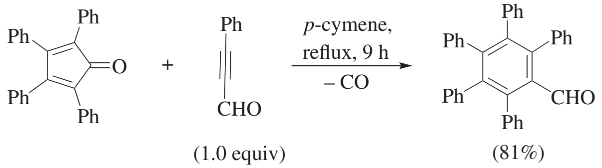
Arenes from Adducts of Cyclopentadienones. As shown in Schemes 24–26, the Diels–Alder reaction of a cyclopentadienone with an alkyne, followed by extrusion of carbon monoxide, leads to formation of an arene.[50,51] These reactions are typically carried out thermally, without isolation of the intermediate norbornadienone. The reaction is amenable to incorporating a variety of functional groups



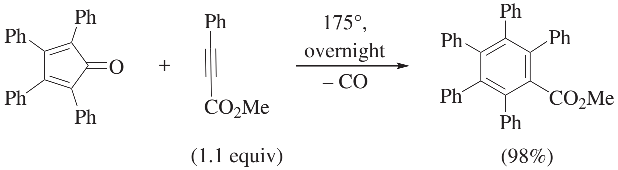
16
tetracyclone

Scheme 24

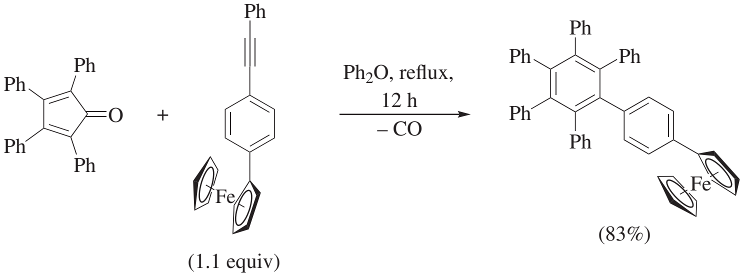
on the dienophile (Schemes 24–27),[50–52] and the cyclopentadienone derivative (Schemes 28, 29).[53,54] Aside from the utility of this method for the preparation of highly substituted aryl groups, these cycloaddition–extrusion reactions have been widely deployed for the preparation of a variety of other complex aromatic species.



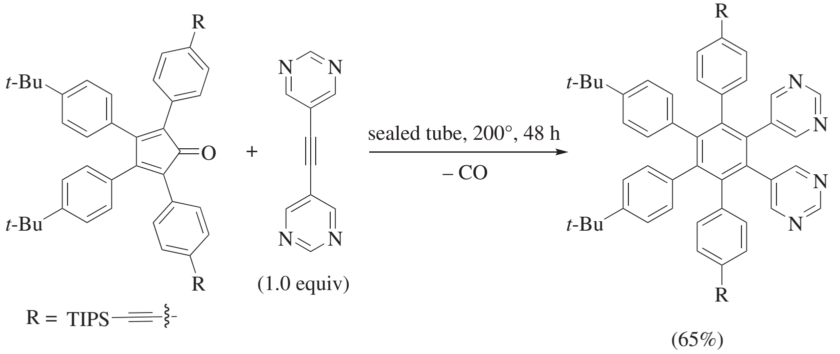
Scheme 25



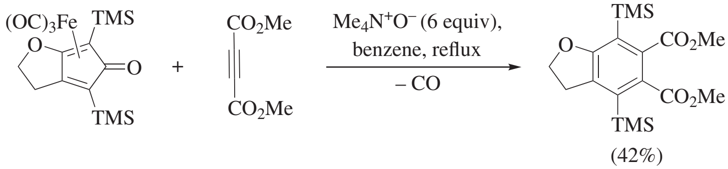
Scheme 26



Scheme 27

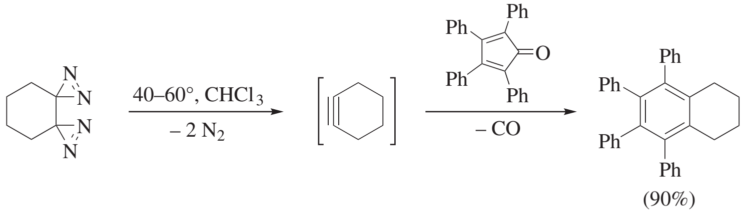


Scheme 28

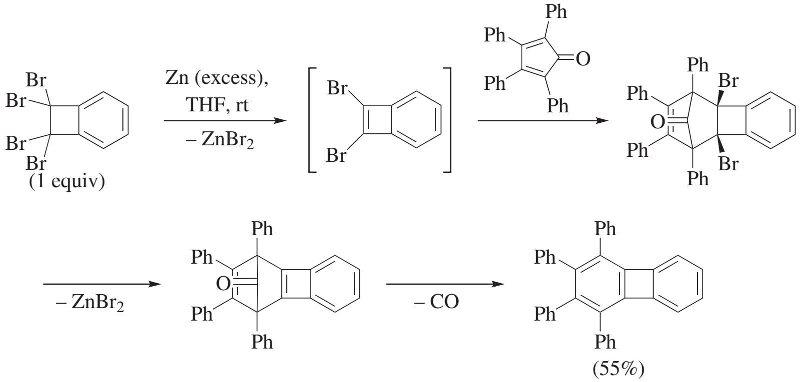


Scheme 29

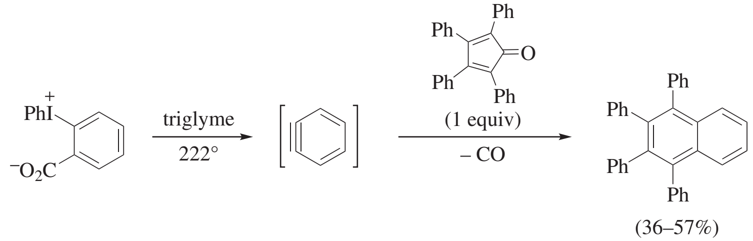
The generation of several strained cyclic alkynes is demonstrated by the formation of cyclohexyne from a bis-diazirine[55] and trapping with tetracyclone[55–61] (Scheme 30). Biphenylenes can also be prepared using cycloaddition–extrusion processes (Scheme 31).[62] Benzyne and its analogues react with cyclopentadienones to afford fused aromatic species after carbon monoxide extrusion (Scheme 32).[63] These additions are common;[63–93] in fact, trapping of the intermediate species by reaction with tetracyclone is frequently used to test for benzyne formation.[80,83–85,94–96] However, the isolation of what appears to be the product of reaction of a benzyne with tetracyclone does not necessarily prove the intermediacy of a discrete aryne.[97] In certain cases, 1,3-diphenylisobenzofuran is a more effective trapping agent for benzynes (see below).[72,98] Heteroarynes can also be trapped by the tetracyclone addition–CO extrusion reaction.[57,99,100]



Scheme 30



Scheme 31



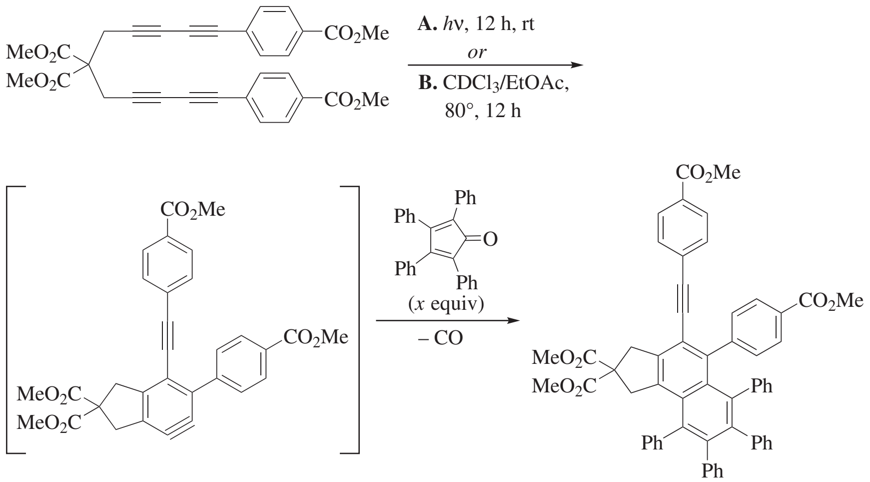
Scheme 32

Although benzynes are generally formed by elimination of adjacent substituents present on an arene molecule, an alternative strategy for benzyne formation involves a cyclotrimerization reaction of a diyne.[101–102] The benzyne generated thermally or photochemically can then be trapped in situ by tetracyclone (Scheme 33).[96,102] Bis-benzynes have also been used in these cycloaddition–extrusion reactions[77,79,103] (Scheme 34).[75]

Polyalkynes can also be deployed in these types of reactions to facilitate the preparation of a variety of extended aromatic systems (Scheme 35).[104] Bis-cyclopentadienone derivatives afford similar extended products in reactions with alkynes (Scheme 36).[105]

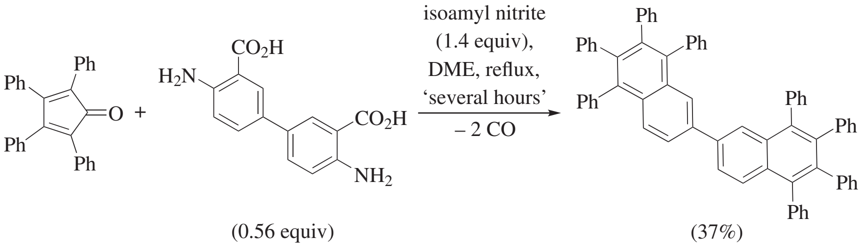
The reaction of a polyalkyne or bis-benzyne with a bis-cyclopentadienone provides a convenient route to highly aromatic polymers[75,106–113] as outlined in Scheme 37.[114] The preparation of aromatic polymers using these methods has been reviewed.[112]

The controlled polymerization of cyclopentadienone derivatives containing two acetylene groups (Figure 3) has been utilized in approaches to the preparation of nanotubes.[115]

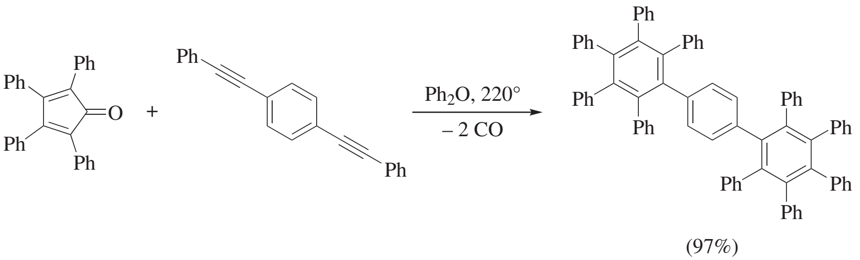


Cond	x	Yield (%)
A	2	71
B	1.5	83

Scheme 33



Scheme 34



Scheme 35