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More than Forty Years of Organosulfur Chemistry and Many Other Studies

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MORE THAN FORTY YEARS OF ORGANOSULFUR CHEMISTRY AND MANY OTHER STUDIES

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Sulfur Reports proudly presents the latest addition to its Grand Old Men of Sulfur Chemistry hall of fame, the chemical autobiography of our distinguished editorial board member Michael P. Cava. Professor Cava's most significant and impressive achievements in organic sulfur chemistry and organic chemistry at large, starting with the legendary total synthesis of strychnine and culminating with a wealth of highly topical organic metals work, are documented in a complete bibliography with 410 research papers. This high priest of chalcogenology's lasting contributions include major landwinnings in the areas of nonclassical thiophenes and a plethora of other sulfur heterocycles, exotic thiocarbonyl compounds such as thioquinones, and, for good measure, novel selenium and tellurium compounds. The autobiography proper is lucid, concise, and contagious with its pervasive love of adventure and joy of organic synthesis. While the author's contemporaries will enjoy to relive some of the great moments of the amazing development of our craft the young generation will be impressed and inspired by the rich awards a curious and independent mind can reap, both in terms of scientific achievements and as a mentor and teacher of junior scientists and collaborators.

Keywords: Benzocyclobutenes, organotellurium reagents, tetrathia- and selenafulvalenes, thia- and selenafulvenes, thieno[3,4-*c*]thiophenes, thiones

CONTENTS

1. INTRODUCTION

I was born in Brooklyn, New York, on February 13, 1926. At the tender age of seven, I received a gift of a chemistry set, which quickly became the source of my favorite amusements. I loved the colored precipitates, the hydrogen sulfide, and the small hydrogen explosions. Later, I expanded into pyrotechnics, and then discovered the endless pleasures of organic synthesis. My companion in organic chemistry during my high-school years (age 13–17) was my good friend Jerrold Meinwald (Prof. J. Meinwald of Cornell University), and we spent many happy Saturdays in an unused kitchen at his home which we made into a serious laboratory.

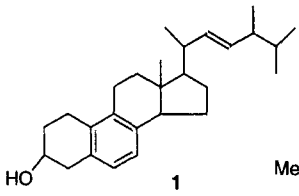
My formal chemistry training began in 1943, when I entered Harvard University as a freshman. Here, the basic chemistry courses bored me, until in my last year I took a special topics course on penicillin chemistry

taught by a fascinating young professor named Robert B. Woodward. I vowed to return to Harvard one day to work in his laboratory. Upon graduation in 1946, I returned to New York and decided to explore biochemistry as a possible alternative to organic chemistry. I studied biology and became a research assistant to Prof. Karl Meyer at Columbia University Medical School, where I worked for a year with mucopolysaccharides, the gummy constituents from such natural sources as eyeballs, cysts and umbilical cords. It was interesting, but I concluded that I preferred more conventional organic compounds. I then entered the chemistry Ph.D. program at the University of Michigan where I chose a steroid degradation project under the direction of the famous Prof. Werner E. Bachmann, who unfortunately died prematurely during my research studies. I was fortunate to be able to finish my work in 1951 under the direction of Prof. André Dreiding, then a temporary faculty member. At this point, I was lucky to receive a fellowship which enabled me to return to Prof. Woodward at Harvard, where I spent two wonderful years (1951–1953), during which time I initiated the ultimately successful first synthesis of strychnine.[1,53] After that, I was on my own as I began my first faculty position at the Ohio State University.

2. CHEMICAL RESEARCH

2.1. Steroids and Terpenoids

My graduate studies on neoergosterol **1**[21] led me to have a continuing interest in the chemistry of steroids and terpenoids. The steroid studies were centered about the conversion of natural steroids, via diazoketone precursors, into ring-contracted analogs, such as the norestrane **2**[36] and the bisnorcholestanone **3**.[87,90] Among the terpenoid excursions, the most fruitful concerned the structure determination of the classical bitter principle andrographolide **4**, a study[41,48,54,87] which resulted in a close and still ongoing connection with the chemistry department of the University of the West Indies in Jamaica.



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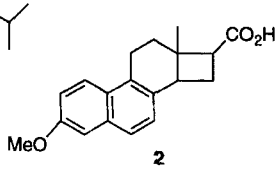

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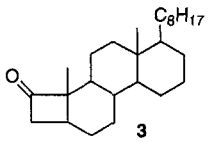

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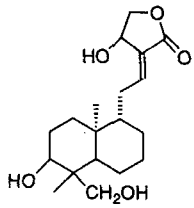

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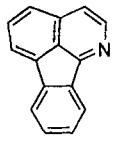
2.2. Alkaloids

My happy postdoctoral years with strychnine chemistry initiated a long-standing love of alkaloids, particularly those related to indole or to isoquinoline. Most of this work concerned isolation and structure determination. Some early work was done jointly with Prof. J.L. Beal [64,88] of the Ohio State School of Pharmacy, and a great deal involved a close collaboration with the natural products group (B. Douglas, J. Weisbach) at Smith Kline and French (now Smith Kline Beecham).[59,61,71] In addition, some alkaloids were isolated from Jamaican plants, while others derived from a research leave spent in the Brazilian Amazonian city of Manaus. Some highlights of the structural work concerned the many indole alkaloids of *Haplophyton cimicidum*, especially the remarkable indole dimer haplophytine,[171] and the new isoquinoline-derived structural types containing the azafluoranthene **5**[159] and the tropoloisoquinoline **6**[212,242] skeletons.

In more recent years, our alkaloid work has shifted to the synthesis of unusual marine alkaloids, examples of which are aaptamine **7**[313] and makaluvamine D **8**.[381]



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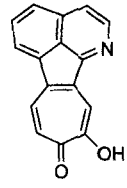

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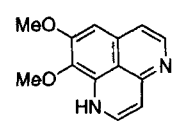

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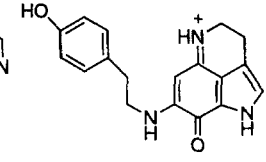

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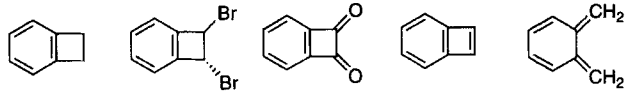
2.3. Benzocyclobutene and Related Compounds

In 1953, neither benzocyclobutene **9** nor any derivative of it was known, and there were serious doubts as to whether such compounds could be synthesized. In looking for a new area of independent research, I had the great luck to stumble upon some unpublished work in the 1909 dissertation of H. Finkelstein, a student of the great Johannes Thiele. In the course of examining the reactions of sodium iodide with various bromides, Finkelstein found that tetrabromo-*o*-xylene gave a new compound which was assigned the structure of 1,2-dibromobenzocyclobutene **10**. As a new assistant professor at Ohio State, I did not yet have a research group, but I tackled the problem myself and soon confirmed the work in the old thesis.[6,11] Several early students of mine then joined in the project, and this beginning developed into a series of about 50 publications describing the synthesis and reactions of benzocyclobutene itself and many of its simplest derivatives, including the stable "quinone" **11**[13] and the transient species benzocyclobutadiene **12**.[23] These studies also contributed a great deal to the chemistry of the hitherto unknown and highly reactive *o*-xylylene (*o*-quinodimethane, **13**) and its derivatives.[24] Since the last few decades, the literature concerning both benzocyclobutenes and *o*-xylylenes has grown enormously, and these species have even found use in complex natural product syntheses.



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

Although it was not apparent at the time, our early benzocyclobutene work led us directly into organosulfur chemistry.

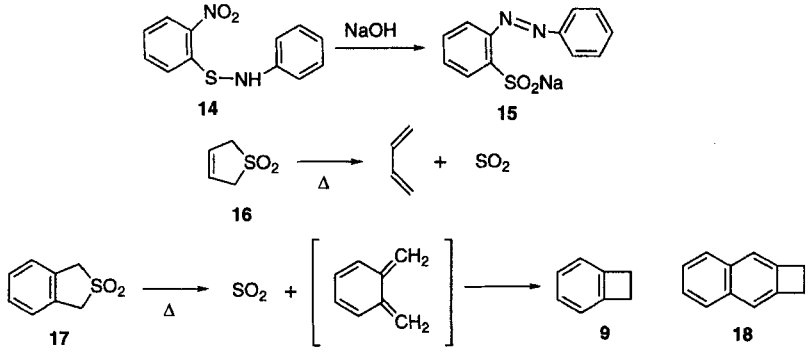
2.4. Organosulfur Compounds and Selenium Analogs

2.4.1. From Sulfones and Sulfoxides to Nonclassical Thiophenes

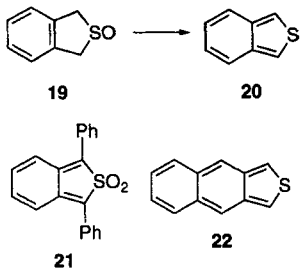
2.4.1.1. Sulfone pyrolysis

Although our first organosulfur paper concerned the base-promoted conversion of 2-nitrobenzenesulfenanilide **14** to an azobenzene-2-sulfinic acid salt **15**,[9] the door to our later sulfur studies was really opened by benzocyclobutene chemistry. Following the lead of the

well-known thermal decomposition of butadiene sulfone **16**, I wondered if the thermal decomposition of the readily prepared *o*-xylylene sulfone **17** might afford benzocyclobutene via the transient *o*-xylylene as an intermediate. This indeed worked very well in the gas phase[20] and, using the proper pyrolysis equipment, allowed us to prepare several hundred grams of benzocyclobutene for further studies. The sulfone pyrolysis reaction was then extended to other cases: for example, it afforded a useful synthesis of naphtho[*b*]cyclobutene **18**.[34]

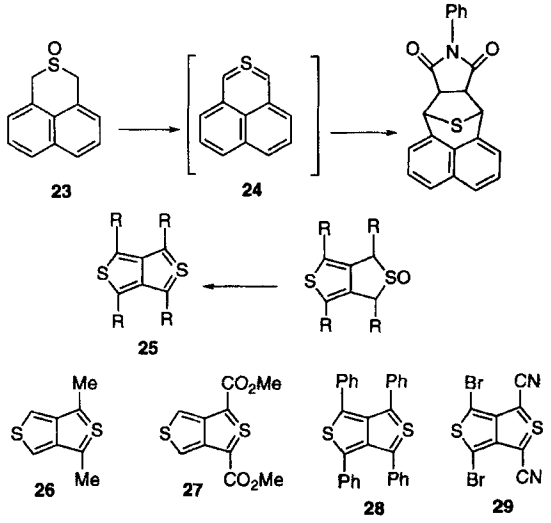


We then decided to look at the thermolysis of *o*-xylylene sulfoxide **19**, expecting that the extrusion of sulfur monoxide (SO) might take place. This was not observed, but instead a remarkably facile Pummerer dehydration occurred, affording a simple and efficient synthesis of the highly reactive benzo[*c*]thiophene **20**,[153] a compound first obtained by R. Mayer shortly before by a high temperature palladium dehydrogenation. We were attracted to this compound because of its *o*-xylylene character and we soon investigated some structural variations. For example, the novel purple sulfone **21** was generated in solution and trapped,[133] as was the naphtho[2,3-*c*]thiophene **22**.[153]



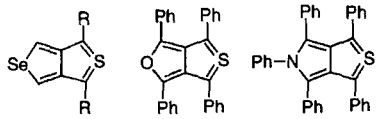
2.4.1.2. Pummerer dehydrations of sulfoxides

We then began wondering if we could generate even more unusual molecules using sulfoxide dehydrations. Indeed, dehydration of the naphthalene sulfoxide **23** generated the formally tetravalent sulfur species **24**, the existence of which was shown by its trapping *in situ* with *N*-phenylmaleimide.[116] The success of this experiment suggested the possible generation in the same way of the nonclassical thieno[3,4-*c*] thiophene system **25**, an idea which proved to be valid and which led to much interesting new chemistry. The dimethyl derivative **26** was conclusively generated and trapped with *N*-phenylmaleimide, but could not be directly observed, while the red diester **27** was marginally stable in solution.[164] On the other hand, the sterically protected tetraphenyl derivative **28** was found to be a remarkably stable deep purple crystalline compound.[165] Its symmetrical structure was confirmed by X-ray crystallography, and it proved to be a ground state singlet molecule with a theoretically interesting electronic arrangement.[201] Investigators in Japan subsequently have synthesized other sterically bulky analogs of **28**, and recently we reported the synthesis of the dibromodicyano compound **29**, which represents the first example of an isolable nonclassical thiophene stabilized only by electronic factors.[369]



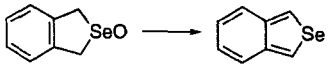
Some attention was also given to the synthesis of analogs of thieno[3,4-*c*]thiophene in which one of the sulfurs is replaced by a

different hetero atom. Thus, the unstable selenolo derivatives **30** and **31**,[213] as well as the furano derivative **32** could only be generated and trapped *in situ* as adducts, but the red perphenyl thienopyrrole **33** proved to be quite stable in the solid state.[157]



30 R = Me
31 R = CO_2Me **32** **33**

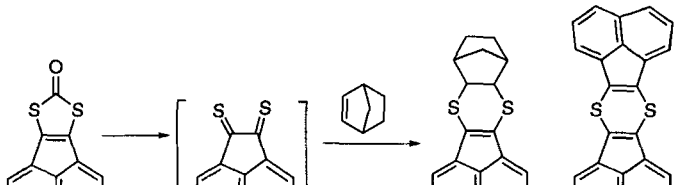
The Pummerer-type sulfoxide reactions employed above were all carried out using either acetic anhydride or mildly acidic alumina as the dehydrating agent. We later made the surprising discovery that the dehydration of sulfoxides could also be promoted by a base. Thus, both benzo[*c*]thiophene **20** and thienothiophene **28** were obtained in this way, using hot aqueous NaOH or LDA,[200] respectively. Also, the previously unknown and very labile benzo[*c*]selenophene **34** was generated from selenoxide **35** with cold aqueous NaOH.[190]



35 **34**

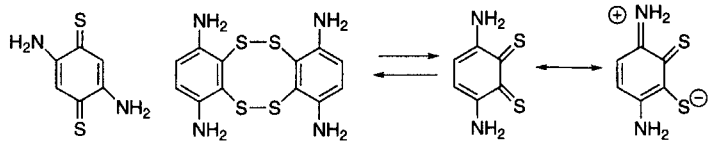
2.4.2. Thiocarbonyl Compounds: Thioquinones and Thioanhydrides

Thiocarbonyl compounds generally show quite different chemistry from their carbonyl analogs, and this led us into several studies in this area. The first of these was aimed at the synthesis of acenaphthenedithione **37**, a simple α-dithione. This could be generated photochemically from the dithiocarbonate **36**. Although it was too reactive to be isolated, it could be trapped *in situ* with norbornene to give adduct **38**; in the absence of a trapping agent the dithiine **39** was produced.[296]



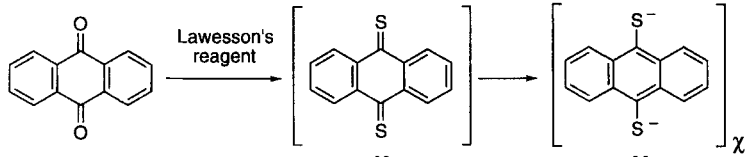
36 **37** **38** **39**

No isolable *o*-dithioquinone or *p*-dithioquinone is known, and such species have been observed only as trapping products or spectroscopically in a frozen matrix. A possible exception seemed to be a red compound reported in 1903 by Green and Perkin, and assumed to have structure **40**. We were able to prepare crystals of this compound which were suitable for X-ray crystallography, which revealed that it was actually the tetrathiocin **41**. Although **41** contains no visible chromophore, solutions of it in DMF were intensely red ($\log \varepsilon = 4.02$, λ_{max} 491 nm), leading us to conclude that the push–pull stabilized *o*-dithioquinone **42** was formed by dissociation of **41** in solution in the polar solvent.[317]



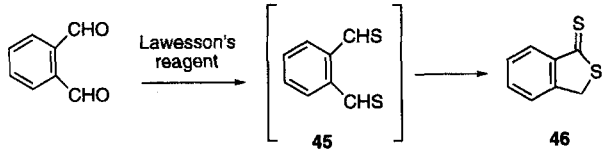
40 **41** **42**

In the search for a stable *p*-dithioquinone, we focused our efforts on 9,10-dithioanthraquinone **43**. Generation of this molecule by several different methods always afforded only a bright red product, shown to be the polymeric disulfide **44**, formed by the polymerization of thioquinone **43**.[304]

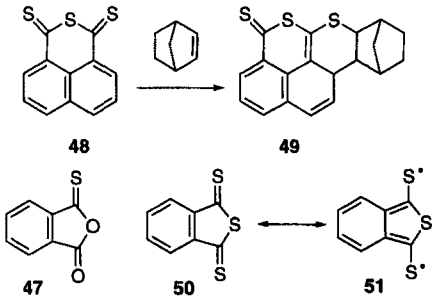


43 **44**

Thioaldehydes are generally an elusive class of compounds, and are stabilized only by strong steric hindrance or by strongly electron-donating groups. We explored the direct thionation of *o*-phthalaldehyde. In this reaction, the *o*-dithioaldehyde **45** appeared to be formed, but it rearranged *in situ* to dithiophthalide **46**. A transient absorption band at 706 nm was attributed to the intermediate **45**.[341]



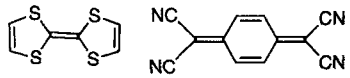
In 1984, the only known cyclic anhydride containing a thiocarbonyl group was the unstable monothionophthalic anhydride **47**. At that time, we reported the synthesis of all of the sulfur analogs of 1,8-naphthalic anhydride. The most novel of these was the stable black crystalline 1,8-trithionaphthalic anhydride **48**.[284] The most surprising reaction of **48** was its addition to norbornene at room temperature to give adduct **49**. In contrast, our attempts to prepare trithiophthalic anhydride **50** failed, affording insoluble black products.[323] This suggested that, like 9,10-dithioanthraquinone **43**, compound **50** behaves as a biradicaloid **51**.[331]



2.4.3. Organic Metals: Variations on Thia- and Selenafulvenes and -fulvalenes

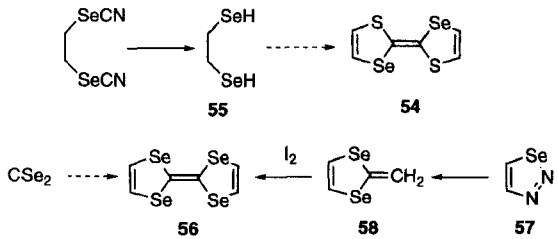
In the early 1970s, the new sulfur heterocycle tetrathiafulvalene (TTF, **52**) drew great attention from chemists and physicists alike when reports appeared that its crystalline charge-transfer salt with tetracyanoquinodimethane (TCNQ, **53**) could function as a unidimensional "organic metal" having considerable electrical conductivity. At that time, we were at the University of Pennsylvania, where physics professors A. J. Heeger and A. F. Garito were doing pioneering work with

TTF salts. They were very eager to obtain new variations on the TTF structure, especially those in which selenium replaced some or all of the sulfur atoms, and they came to our lab to try to interest me in the synthesis of such compounds. It so happened that I was off in Jamaica at the time collecting plants, since I probably would have naively rejected their proposal of collaboration on what then seemed to be dull chemistry. Fortunately, my second in command at home, Dr. M. V. Lakshmikantham, rose to the challenge of the selenafulvalenes. Thus began over 20 years of ongoing and intense activity by us on the synthesis of TTF-related heterocycles. Some highlights are reviewed below.

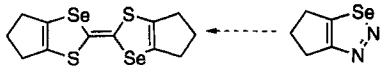


52 **53**

Dr. Lakshmikantham soon succeeded in the synthesis of her initial target molecules. Thus, the *sym*-diselenadithiafulvalene **54** was obtained from a synthesis in which the previously unknown 1,2-ethanediselenol **55** was the key intermediate.[183] An efficient synthesis of tetraselenafulvalene (TSeF, **56**) was then developed, although it required as the starting material the costly and unusually foul-smelling carbon diselenide CSe_2.[196] Many years later, we found that base treatment of 1,2,3-selenadiazole (**57**, from SeO_2 and acetaldehyde semicarbazone) gave 1,3-diselenafulvene **58**, which underwent a surprising reaction with iodine to give **56** in reasonable yields.[322]

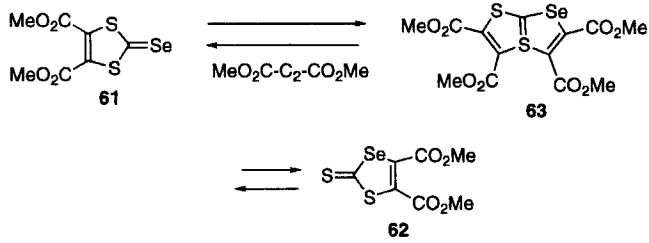


Several annelated derivatives of **54** were prepared starting from bicyclic selenadiazoles, i.e. **59** from the readily prepared **60**.[186,194]



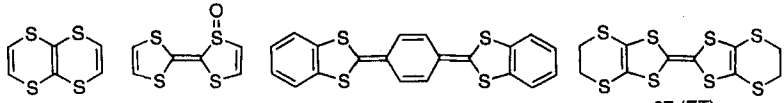
59 **60**

Some interesting and unexpected chemistry developed under the exploration of routes to thiaselenafulvalenes. A notable example was the observation that the isomeric dithiaselenocarbonates **61** and **62** were interconvertible on heating with dimethyl acetylenedicarboxylate, a reaction which must proceed via the nonclassical intermediate **63**.[195]



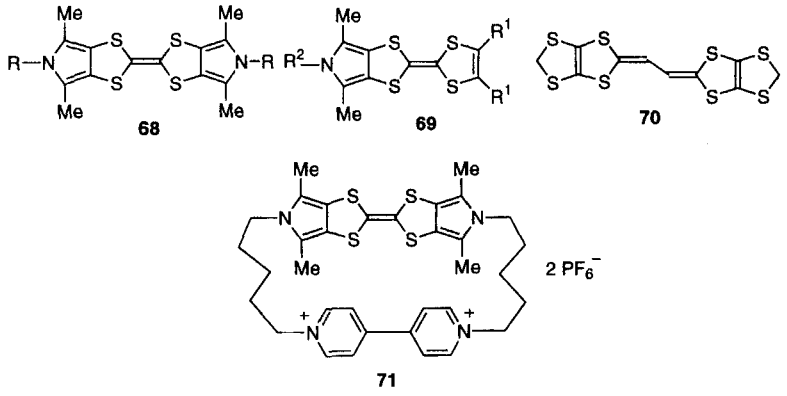
61 **63** **62**

In the period before 1980, we synthesized some variations of the TTF system which proved to be novel structures but useless donors. These included "iso-TTF" **64**,[198] TTF *S*-oxide **65**,[228] and the quinonoid analog **66**.[223] During these same years, however, we also reported a general rational approach to unsymmetrical TTF derivatives,[217] as well as the synthesis from CS_2 of the bisethylenedithio derivative **67**,[218] which we refer to as ET. In the intervening years, ET has become the most studied TTF derivative world-wide, due to the ability of some of its salts to become superconductors at low temperatures.



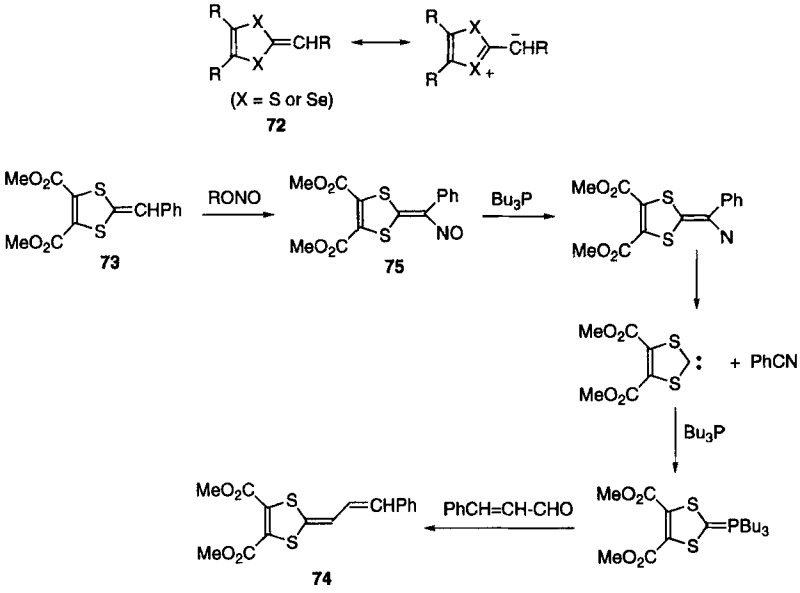
64 **65** **66** **67 (ET)**

Since 1988, our activities in TTF chemistry have taken on renewed vigor, largely due to two fortunate circumstances. First, we discovered a new class of TTF derivatives containing either one or two annelated pyrrole units (**68** and **69**), which had both excellent donor properties and the potential for extensive structural modification.[327,399] Second, we began a most fruitful collaboration with Prof. Jan Becher and his group at Odense University, which has resulted in some excellent Danish visitors working in our laboratory (especially T. Hansen, J. Lau and K. Simonsen). A few results from our joint efforts are the synthesis of the TTF vinylog **70**[343] and the synthesis of the D–A sandwich molecule **71**.[401]

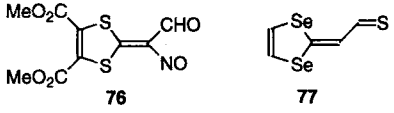


The thia- and selenafulvenes (i.e. **72**) correspond to truncated TTF-type structures, and a number of them are readily available by either Wittig reactions or from dimerization of acetylenic chalcogenides. In general, we have found that these compounds undergo facile electron-transfer substitutions at the electron-rich exocyclic carbon, i.e. nitrosation and diazonium substitution. The green nitroso compounds are particularly interesting, since they are rare examples of stable nitrosoolefins. On deoxygenation with a phosphine reagent, they generate a nitrene which fragments to a nitrile and a carbene. If excess phosphine and an aldehyde are present, the carbene reacts to produce a new fulvene via a Wittig reagent intermediate. An example of this

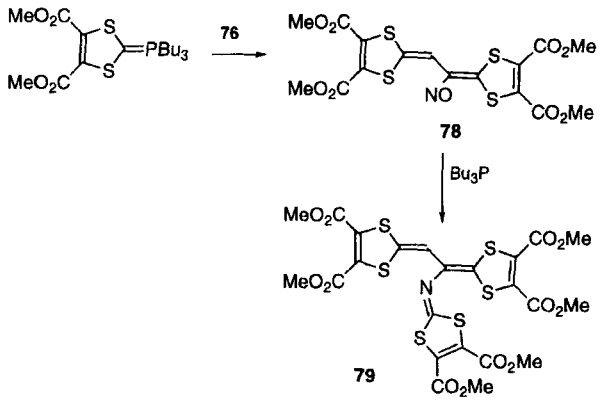
"transfulvenation" is the conversion of fulvene **73** into fulvene **74** via the nitroso compound **75**.[241,250]



Some other unusual fulvenes which we have studied are the novel nitroso aldehyde **76** and the remarkably stable brown thioaldehyde **77**.[325]



The green nitroso aldehyde **76** could be elaborated by a Wittig synthesis into the deep purple nitroso TTF vinylog **78**. Phosphine deoxygenation of **78** took an unusual course and provided the imine **79**, a product presumably derived from a nitrene–carbene addition.[403]

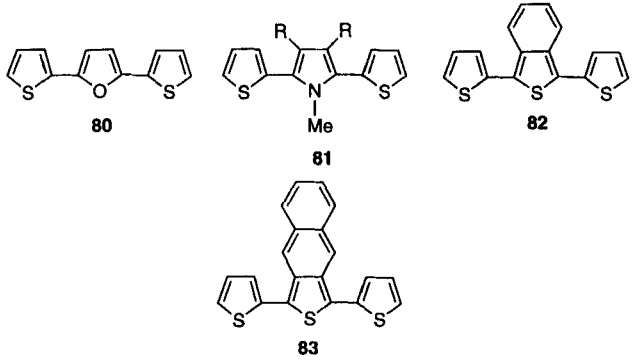


2.4.4. Organic Metals: Thiophene-Derived Oligomers and Polymers

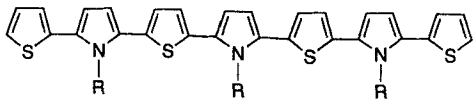
During the late 1970s, it was reported that mildly oxidized (doped) polyacetylene showed a remarkably high electrical conductivity, behaving as a true organic metal. This finding became a stimulus for extensive research programs aimed at the synthesis and electronic studies of a variety of more stable conjugated polymers, including many derived from heterocycles, especially thiophenes.

A few of our contributions to this area during the past decade are described very briefly below.

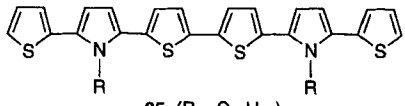
The electrochemical or chemical oxidation of symmetrical terheterocycles affords polymers of defined structure. We have made and studied the oxidation of a variety of analogs of terthiophene in which the central thiophene is replaced by a different heterocyclic unit, i.e. **80–83**.[360,361,349,364]



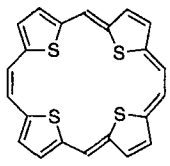
A number of longer oligomers, as well as some novel conjugated annulenes, were also synthesized. These tend to oxidize to stable cationic species, but do not afford polymers. Some examples are oligomers **84**[396] and **85**,[363] and annulenes **86**[376] and **87**.[398]



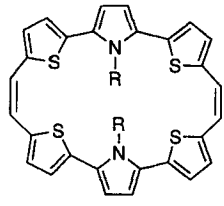
84 (R = $C_{12}H_{25}$)



85 (R = $C_{12}H_{25}$)

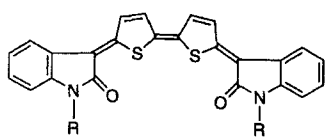


86



87

In 1882, Victor Meyer reported the discovery of thiophene from crude benzene. The isolation and purification of thiophene was followed by its reaction with isatin and sulfuric acid to give the deep blue dye indophenine. Although the marked insolubility of indophenine made it very difficult to purify, the correct gross structure **88** was eventually assigned to it, although its stereochemistry remained unknown. We found that by using *N*-heptylisatin, we could prepare and purify the nicely soluble diheptylindophenine **89**. A detailed NMR study of this material was carried out in order to assign its stereochemistry. To our surprise, our alkyl indophenine proved to be an unresolvable mixture of all six possible geometrical isomers![365]

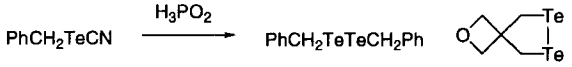


88 (R = H)
89 (R = C_7H_{15})

2.5. Adventures with Tellurium

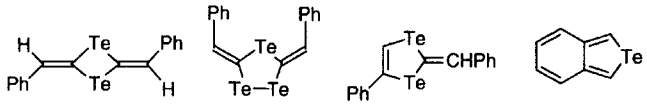
2.5.1. Tellurium Heterocycles

By 1975, we began thinking about tellurium, the relatively neglected member of the chalcogen family. For example, alkali metal thiocyanates and selenocyanates were already known in the last century, but the corresponding tellurocyanates refused to form under the usual conditions. Dr. Lakshmikantham solved the mystery when she found that tellurium dissolved in a dimethyl sulfoxide solution of potassium cyanide. The resulting KTeCN was stable only in DMSO solution and could not be isolated, but it reacted with benzyl chloride to give benzyl tellurocyanate **90**, the first alkyl tellurocyanate available for further study.[205] The most interesting reaction of **90** was its reduction by H_3PO_2 to dibenzyl ditelluride **91**, a compound so light-sensitive that it could be worked with only under red darkroom lights.[211] Years later, KTeCN was also the key reagent in the synthesis of the first stable 1,2-ditellurolane **92**. In this compound, the two p-orbitals of the two telluriums are coplanar and forced to overlap, resulting in a bathochromic visible shift of almost 300 nm compared to an acyclic ditelluride (690 nm vs 395 nm)![352]



90 **91** **92**

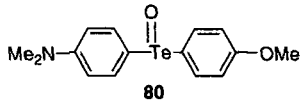
We have also studied the synthesis and properties of a number of novel unsaturated tellurium-containing heterocycles. All four compounds **93–96** [251,253] can be isolated after acidification of PhC≡CTeLi solutions, the major products depending upon the conditions used. Quite recently, we succeeded in achieving the first synthesis of the reactive and elusive benzo[*c*]tellurophene **97**.[400]



93 **94** **95** (*cis*) **96** (*trans*) **97**

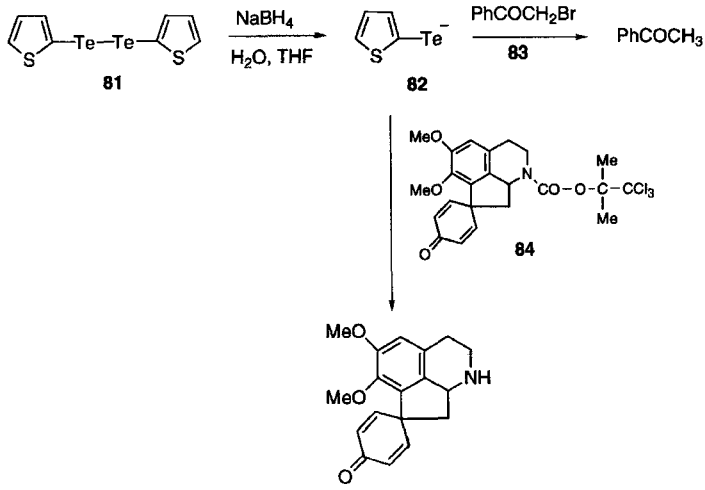
2.5.2. *Tellurium Reagents*

Among our other tellurium studies, several have resulted in reagents useful in general synthesis. For example, the readily prepared aromatic telluroxide **80** can function as a mild and selective aldol catalyst. The electron-donating substituents of **80** are essential for the activity, since diphenyl telluroxide has no activity.[290]



80

2,2′-Dithienyl ditelluride (**81**) is a nicely crystalline organic compound which is easily synthesized from thiophene.[260] It is rapidly reduced by sodium borohydride to 2-thiophenetellurolate anion **82**, which behaves as a supernucleophile. The tellurolate attacks the halogen of an α-bromo ketone[262] or a chlorine of a trichloro-BOC protected amine,[309] and the initially formed tellurenyl halide immediately reacts with anion **82** to regenerate ditelluride **81**. The reagent **81** can therefore be used in catalytic amounts, with only sodium borohydride being consumed stoichiometrically. The entire cycle is sufficiently fast so that ketonic products are formed faster than they are reduced by the borohydride. Examples using ketones **83** and **84** are shown below.



Acknowledgments

All of the studies described here, and many others as well, were carried out by a talented and enthusiastic group of graduate students, post-doctorals, and senior scientists, whose names appear in the publication list. Particular recognition is given to my long-time senior associate, Dr. M. V. Lakshmikantham, who must be credited with initiating and carrying out some of our most challenging projects. Finally, most of our chalcogen studies would not have been possible without the decades-long continuous support from the U.S. National Science Foundation.

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