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PROFESSOR S SWAMINATHAN 60TH BIRTHDAY COMMEMORATION LECTURE—1994

SELECTIVE INTRAMOLECULAR CARBON-CARBON BOND FORMATION IN POLYCARBOCYCLIC SYNTHESIS: FROM CATIONIC TO RADICAL INDUCED PROCESSES

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Some developments of the regio- and stereo-selective carbon-carbon bond formations involving intramolecular aromatic cyclialkylation, metal-catalyzed keto-carbenoid insertion and addition, and acid-induced intramolecular cyclization-rearrangements of α-diazomethyl ketones within the context of total synthesis of structurally diverse polycarbocyclic diterpenoids incorporating quaternary centres and the related bridged-ring compounds, based upon the results reported from the author's laboratories, have been briefly reviewed. The critical role of the nature of aromatic ring substituents in the open chain substrates in acid-catalyzed cyclialkylation reaction through a 2-2(arylethyl)-1,3,3-trimethylcyclohexyl cation generating the respective *trans*- and the *cis*-podocarpatrienes has been evaluated leading to a simple and highly stereoselective synthesis of a large number of naturally occurring tricyclic diterpenoids. Highly regioselective intramolecular keto-carbenoid insertion and addition reactions have been utilized towards the synthesis of key intermediates for some pentacyclic diterpene alkaloids and glibberellins. A new acid-catalyzed cyclization-rearrangement reaction of some β,γ-unsaturated polycyclic hydroaromatic α-diazomethyl ketones has been shown to afford unsaturated cyclobutanones, pentalenoannulated tetralins and bridged hydroxycyclopentanones, in excellent yields, depending upon the reagents and reaction conditions. An account of an on-going investigation on a conceptually new general and convergent stereocontrolled synthesis of six-, seven-, eight- and nine-membered linearly annulated condensed hydroaromatic systems, using highly regioselective 6-*endo*-, 7-*endo*, 8-*endo*- and 9-*endo*-*trig* aryl radical cyclizations, is presented along with an intramolecular Heck-type ring closure giving different selectivities.

Key Words: Aromatic Cyclialkylations; Podocarpatriene Diterpenoids; Keto-carbenoids, Diterpene Alkaloids; Gibberellins; α-Diazomethyl Ketone; Alkylation-Rearrangements; Six to Nine-*endo* Cyclizations; Aryl Radical, Intramolecular Heck-Reaction

Introduction

I feel greatly honoured for being invited by the Indian National Science Academy to deliver the 'Professor S Swaminathan 60th Birthyday Commemoration Lecture—1994'. Professor Swaminathan, a highly respected teacher and an outstand-

*At the INSA premises, New Delhi.

ing Organic Chemist has many adorable and distinctive qualities. Over the last twenty years I have been fortunate for having personal contact with him which has endowed me further to develop a profound admiration and respect for his enviable professional rigour and academic excellence. To express my deep appreciation to his outstanding contribution in establishing a simple methodology to complex polycarbocyclic systems[1], as an originator of the so called 'anionic oxy-Cope rearrangement,' I have chosen to highlight some aspects of selective works from our laboratories, on intramolecular carbon-carbon bond formations within the context of their utilities in the synthesis of such structurally diverse compounds.

Background

The synthetic and stereochemical problems associated with the complex polycyclic systems with quaternary carbon centres provide with a rich harvest of developing new and simpler methodologies. In fact, the development of simple and selective carbon-carbon bond formation under mild conditions, which can be extended to the constructions of complex polycyclic and bridged-ring systems of structurally diverse families of natural products, is one of the central objectives of synthetic organic chemistry. These concepts have been extensively explored in our laboratories as a major successful strategy, particularly in the development of the regio- and stereo-specific carbon-carbon bond formation leading to the construction of quaternary carbon centres through acid-induced intramolecular cationic cyclization, metal-catalyzed keto-carbenoid insertion or addition, acid-catalyzed intramolecular cyclization and rearrangements of diazomethyl ketones, in addition to a number of methodologies. Though cationic, anionic (not included in the present review) and carbenoid reactions clearly dominated the scene, the use of carbon centered radicals and organometallic intermediates in efficient chemoselective carbon-carbon bond formations have dramatically increased within the last decade. Amongst many reagents, tri-*n*-butyltin hydride (TBTH) and Pd(O)-based complex are most commonly used to conduct free radicals and organopalladium induced bond formations. In this presentation, I will first highlight key aspects of some selective examples, from our work, within the context of total synthesis of structurally diverse polycarbocyclic diterpenoids and some bridged-ring compounds involving the aforementioned types of the cationic and carbenoid reactions. The remaining part of my lecture will focus on the immense possibilities of a conceptually novel and a potentially general convergent synthetic route to linearly condensed hydroaromatic carbocyclics incorporating six to nine-membered rings through a radical initiated annulation reaction, currently under investigation in our laboratories. A few related examples on intramolecular Pd(O) induced Heck reaction will also be illustrated.

Intramolecular Cationic Cyclization

The acid-catalyzed intramolecular cyclialkylation reaction constitutes one of the simplest and most widely used methods for the synthesis of ring-C-aromatic resin acids[2,3] and various naturally occurring diterpenoids having podocarpa-8,11,13-triene skeleton[4]. Despite the simplicity and converging nature of this method con-

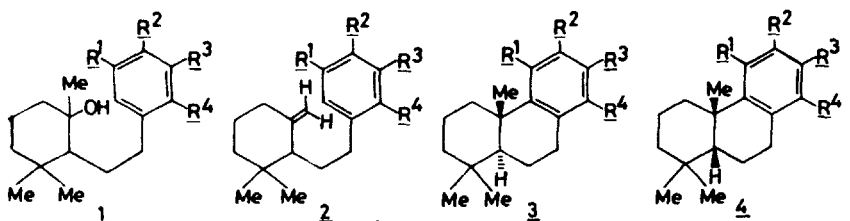
siderable confusion existed[5,6] until recently, regarding the unpredictable stereochemical outcome of the cyclization products. We have now established the critical role of the aromatic ring substituents[7-9] in the open chain substrates in acid-catalyzed cyclization under mild conditions, on a large number of easily accessible alcohols **1** and *exo*-olefins **2** in determining the distribution of the respective *trans*- and the *cis*-cyclized products **3** and **4**.

Our extensive results (Table I) on the stereochemistry of cyclialkylation of the cyclohexanols **1a-d, h-j** and the olefins **2a-d, h-j**, particularly under mild condition using $MeSO_3H$-P_2O_5 as the reagent[10], provide with some important generalizations. Thus, cyclizations of the olefins **2a-c, i, j** with the unactivated aromatic

Table I

Cyclization of the cyclohexanols ***1a-d, h-j*** *and methylene-cyclohexanes* ***2a-d, h-j*** *with* $MeSo_3P_2O_5$
Ratio of trans- and cis-podocarpatrienes ***3a-d, h-j*** *and* ***4a-d, hj***

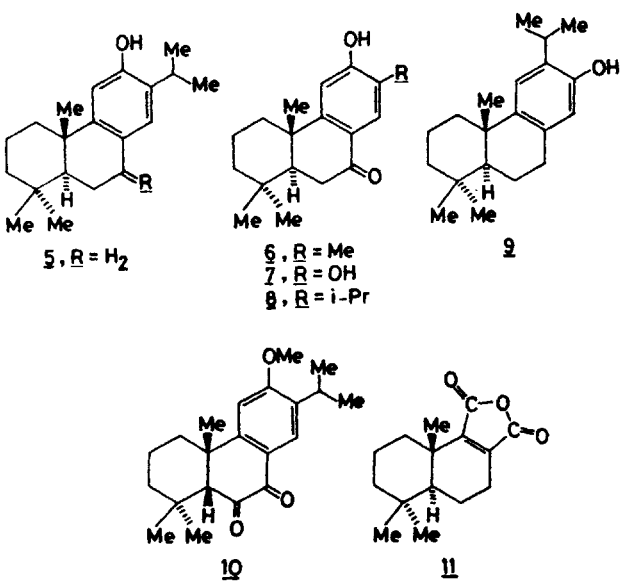
Entry	Cyclohexanol/ olefin	Yield (%)	Products *trans* + *cis*	Ratio of *trans/cis*
1	**1a**	93	**3a+4a**	99:1
2	**2a**	99	**3a+4a**	100:0
3	**1b**	95	**3b+4b**	100:0
4	**2b**	99	**3b+4b**	100:0
5	**1c**	93	**3c+4c**	99:1
6	**2c**	95	**3c+4c**	99:1
7	**1d**	83	**3d+4d**	42:58
8	**2d**	95	**3d+4d**	34:66
9	**1h**	82	**3h+4h**	53:47
10	**2h**	95	**3h+4h**	31:69
11	**1i**	90	**3i+4i**	99:1
12	**2i**	95	**3i+4i**	99:1
13	**1j**	92	**3j+4j**	99:1
14	**2j**	94	**3j+4j**	99:1



a : $R^1 = R^3 = R^4 = H, R^2 = OMe$
b : $R^1 = R^2 = R^3 = H, R^4 = OMe$
c : $R^1 = R^2 = R^3 = R^4 = H$
d : $R^1 = R^2 = R^4 = H, R^3 = OMe$
h : $R^1 = R^4 = H, R^2 = R^3 = OMe$
i : $R^1 = R^4 = OMe, R^2 = R^3 = H$
j : $R^1 = R^3 = H, R^2 = R^4 = OMe$

Structures 1-4

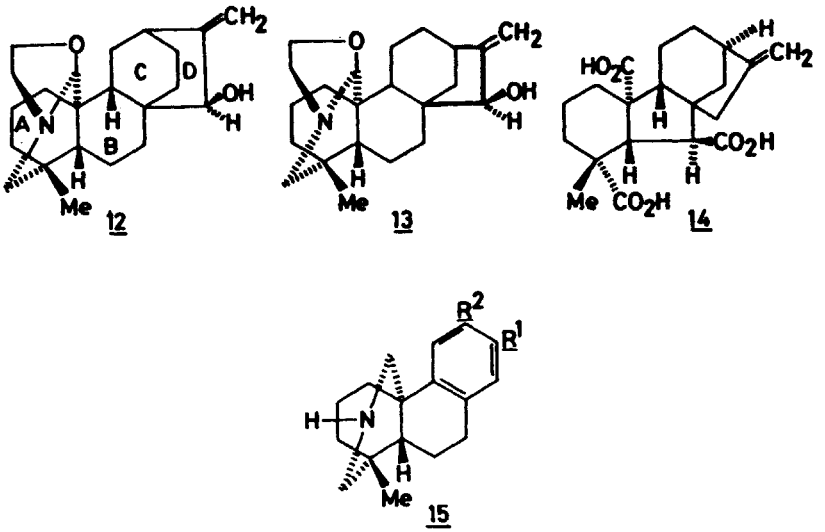
nucleus, lead clearly to the respective *trans*-products **3a-c, i, j**, even in higher purity and yields compared to that from the respective cyclohexanols **1a-c, i, j**. In contrast, the cyclization of the cyclohexanol substrates **1d, h** and the olefin **2d, h**, that incorporate an electron donating methoxy substituent, *para* to the site of electrophilic attack on the aromatic ring, including the disubstituted aromatic precursors, generate predominating or substantial amounts of the corresponding *cis* isomers **4d, h** along with the *trans*-isomers **3d, h**. It is important to note that olefins **2d** and **2h** (Table 1, entries 8 and 10) gave more of the *cis*-products compared to that from the cyclizations of the respective cyclohexanols **1d** and **1h** (entries 7 and 9). It is clearly evident that it is the *location of the electron donating aromatic substituent with respect to the site of electrophilic attack* that governs the 'reactivity' of the aromatic ring in the open chain substrates. The mechanisms of these cyclialkylation reactions are still not very clear. Recently Nasipuri[11] has advanced a rationalization of these and the related stereochemical results. Based upon our work on stereiochemical clarification remarkably simple and general stereoselective syntheses have been designed for *trans*-A/B-ring-C-aromatic diterpenoids, for example, (±)-ferruginol[12] (**5**), (±)-nimbiol[7] (**6**), (±)-nimbidiol[7] (**7**), (±)-sugiol[13] (**8**), (±)-sempervirol[13] (**9**), as well as the *cis*-diterpenoid (±)-xanthopherol[13] (**10**). A simple synthesis of the naturally occurring sesquiterpene (±)-winterin[14] (**11**) has also achieved through degradation of an easily accessible tricyclic intermediate by cyclialkylation method.



Structures 5-11

α-Diazoketone Mediated Carbon-Carbon Bond Formations

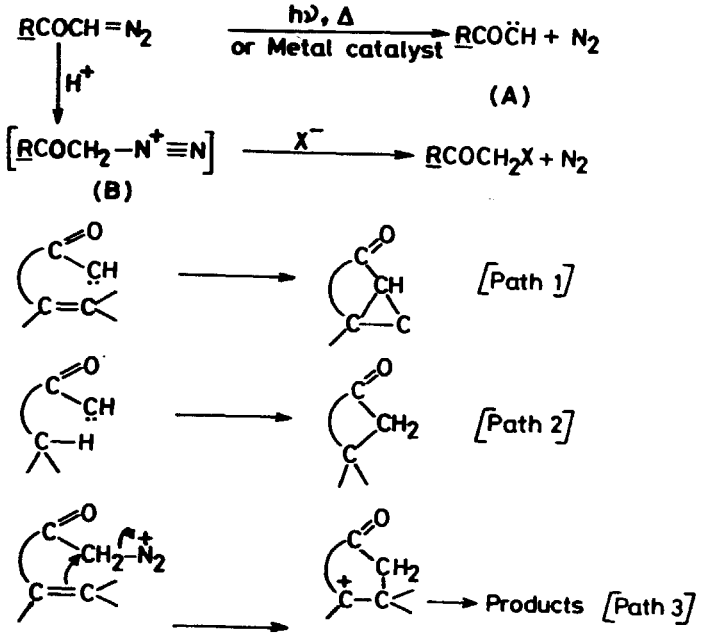
In the early seventies a great deal to attention was paid towards the synthesis of the complex diterpenoid alkaloids such as atisine (**12**) and veatchine (**13**) along with biogenetically related C_{20}-gibberellins, such as GA_{15} (**14**). A tetracyclic



Structures 12-15

synthon **15** (R = OMe) containing ring A, B and C followed by elaboration of the bridged-ring system D through aromatic moiety was utilized by Nagata *et al.* in their elegant total syntheses of (±)-atisine[15] (12), (±)-veatchine[16] (13), and (±)-gibberellin A_{15} (14)[17]. Being well aware of the difficulty that usually attends the construction of the congested functionalized quarternary carbon centres, as present in these compounds, it was clear that intramolecular carbon-carbon bond formation through reactive intermediates available from α-diazocarbonyl compounds: α-keto carbenes (or α-ketocarbenoids) (*A*) and α-diazonium ketones (*B*) (Scheme 1) held enormous potential in the area of such complex polycyclic molecules.

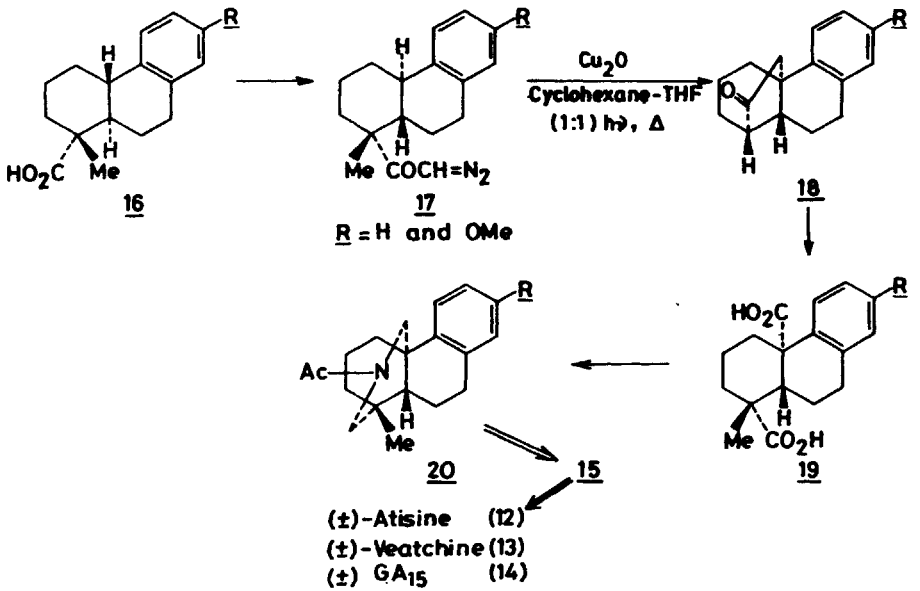
The principal reactive intermediates available from α-diazocarbonyl compounds, the ketocarbenes (*A*), generated by decomposition of the substrates by thermal, photochemical or metal catalysis process, can undergo two major classes of reactions: (*a*) addition to either C=C double bond in a second molecule (intermolecular addition) or to an appropriately situated olefinic group in the same molecule leading to a cyclization reaction (path 1), (*b*) insertion into C−H bond of a second molecule or within the same molecule (path 2) (Scheme 1). The third major class of reaction undergone by α-dizoketone is through α-diazonium ketone (*B*) which undergoes nucleophilic substitution with displacement of nitrogen (Scheme 1) in an intramolecular reaction; an appropriately situated olefin or aromatic ring can act as the nucleophile leading to a cyclization reaction (path 3) of great synthetic utility. A detailed discussion of extensive work carried out in our laboratories on these reactions is beyond the scope of the present lecture, which however, been reviewed earlier.[18] I will try to highlight only key aspects of some of these interesting chemistry within the context of our aforementioned targeted diterpenoids.



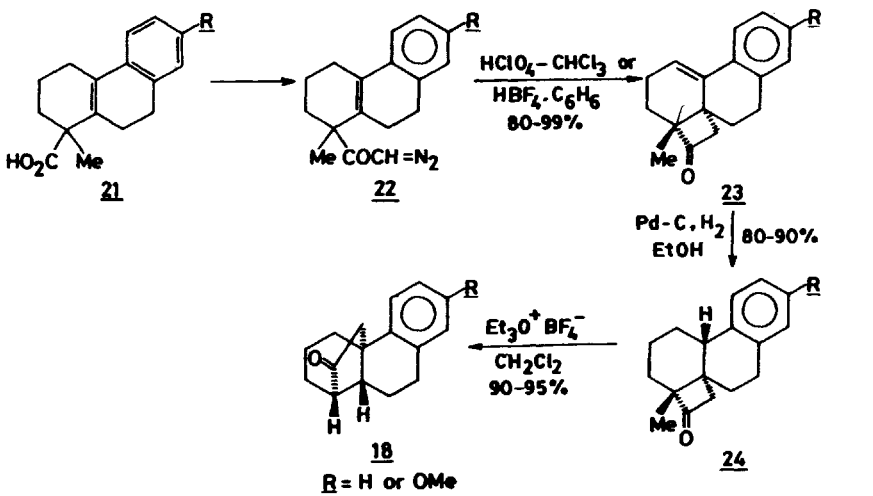
Scheme 1

Within a very short time we could achieve remarkably simple stereocontrolled syntheses of the racemic tetracyclic amines **15** (R=H or OMe) through the racemic 20-nor resin acids **16** (R=H and OMe), simple stereospecific syntheses of which were realized in our earlier works[19,20] on resin acids. This synthetic approach contains a novel method of angular alkylation at a classically nonreactive centre based upon a regioselective intramolecular α-oxo-carbenoid insertion across the benzylic C–H (at C-10) bond in the copper-catalyzed carbenoid decomposition of the easily accessible α-diazomethyl ketones **17** to the bridged tetracyclic ketones **18**. The ketones were converted in high yields to the respective dicarboxylic acids **19**, which were finally transformed to the tetracyclic amines **15** *via* the acetates **20** through a simple route as illustrated in Scheme 2. This sequence represents a highly efficient formal total synthesis[21,22] of racemic GA_{15}, atisine and veatchine. More recently we have introduced highly effective methods of intramolecular C–H insertion in diazoketone **17** to the respective bridged ketones **18** by using light-induced $Ni(acac)_2$[23] or 'activated CuO'[24] catalyzed reactions.

In spite of the successful functionalization in the hydrophenanthrene diazomethyl ketones, **17** an attempted oxocarbenoid insertion reaction of the α-diazomethyl ketone in the related hydrofluorene substrate failed to give any characterizable product. We started, therefore, to give adequate consideration to the prospect of developing an alternative and more controlled intramolecular alkylation route based within the broad and intricate carbocyclic frameworks of the readily available unsaturated acids, e.g., **21**[19,20]. Towards this goal a simple and highly efficient synthetic



Scheme 2

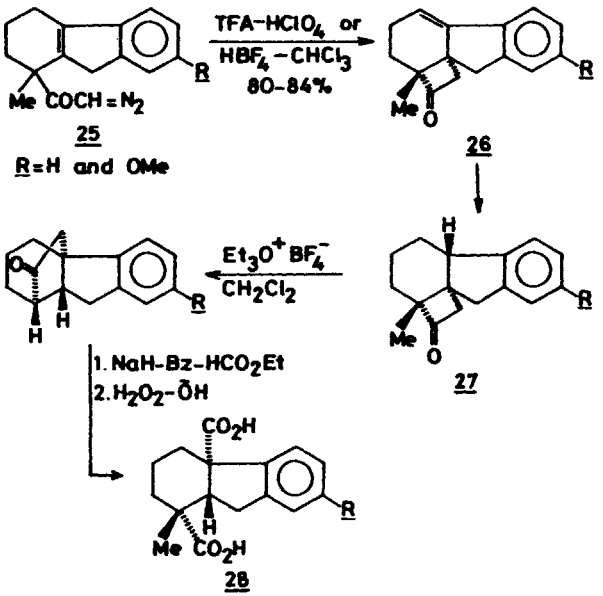


Scheme 3

route to the angularly fused cyclobutanones **23** by acid-catalyzed intramolecular C-alkylation reactions in the β,γ-unsaturated diazoketones **22**, was discovered in our laboratories in 1974[25]. The readily available styrenoid cyclobutanones **23** have been further transformed to the aforementioned key tetracyclic ketones **18** (Scheme 3) by a remarkable stereospecific rearrangement[26] of the respective stereoselectively hydrogenated cyclobutanones **24**.

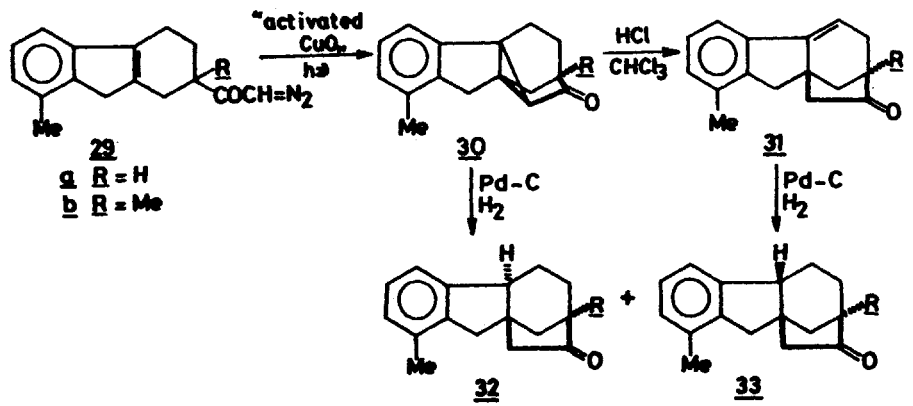
The mechanism of this novel rearrangement has been established[27] by specifically [$^2H_2$] labelled intermediates.

The β,γ-unsaturated α-diazomethyl ketones **25** also smoothly produced the respective styrenoid cyclobutanones **26** which were transformed through a similar sequence of reactions as used for the hydrophenanthrene derivatives, to the *trans*-hydrofluorene intermediates **28**[27], incorporating the C_4- and C_{10}-carboxylic acid groups of GA_{15} (**14**).



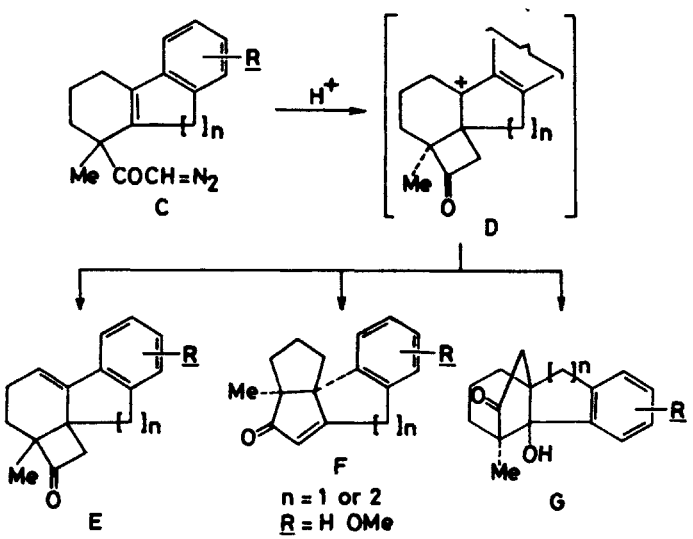
Scheme 4

As an example of the rapid construction[28] of bridged tetracyclic gibbane system by intramolecular keto-carbenoid addition reactions (*Scheme* 1, path 1), I would like to illustrate here (Scheme 5) the total syntheses of (±)-gibberone (**31*b***) and (±)-4-methyl-β,13α-dihydro-16-oxogibba-1,3,5, (10)-triene (**33a**), two degradation products of gibberellins.



Scheme 5

The intramolecular alkylation of diazomethyl ketones directed towards the synthesis of complex diterpenoids, not only provided a facile synthetic entry to a variety of complex polycyclic intermediates, but a few unusual rearrangements were also discovered during those studies. We have demonstrated that acid-catalyzed intramolecular alkylations of β, γ-unsaturated diazoketones *C* (Scheme 6) there is an overwhelming preference for the formation of the respective cyclobutanone cation *D* through the participation of π-bond in close proximity to the protonated diazocarbonyl centre, resulting each of the products *E*, *D* or *F* in excellent yields, depending upon the reaction conditions[29-32].

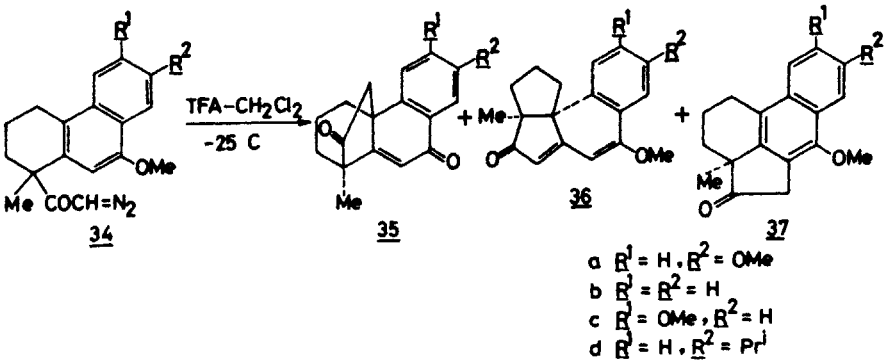


Scheme 6

The mechanisms of these rearrangements have been rationalized. In contrast to the β,γ-unsaturated diazoketones *C*, the acid-catalyzed reaction of 1-diazoacetyltetrahydrophenanthrene **34a** was reported to give both Ar_1-5 product **35a** and the rearrangement product **36a** from the Ar_1-4 intermediate, by Mukherjee and co-workers[33] from these laboratories. Recent reinvestigation[34] on the acid-catalyzed reaction of **34a** and the related diazoketone **34b-d** revealed that all the possible products **35a-d**, **36a-d** and **37a-d**, respectively arising from Ar_1-5, Ar_1-4 and aromatic ring alkylation are formed in each of these substrates. The ratio of the products, however, depends upon the position of substitution in ring-C.

Recently we have used stereospecific Ar_1-5 diazoketone cyclization for the construction of a spiro-cyclopentanone ring system incorporating *vicinal cis*-methyl groups towards the synthesis[35] of the complex carbocyclic systems of the indolic diterpene aflavinine.

The powerful approach for constructing complex carbocyclic skeleta by carbon-carbon bond formation through α-diazomethyl ketones, which was recognized very early in our research as summarized in this brief account, turned out to be an extremely important method for organic syntheses with the introduction of new catalysts and modifications in the recent years.[36]



Scheme 7

Radical Mediated Carbon-Carbon Bond Formation

In the last decade radical reaction have gained importance for the synthesis of complex carbocyclic and natural products.[37] The formation of the primary radical can result by reaction of halogens, phenylthio- and phenylselenium compounds with stannanes such as tri-*n*-butyltin hydride (TBTH). With only a few exceptions, 5-*exo-trig* radical cyclizations are generally preferred over 6-*endo-trig* ring closures in the intramolecular TBTH induced reactions in substituted hexenyl systems. The use of TBTH mediated aryl radical cyclization in the carbocyclic synthesis is considerably less wide spread than alkyl radical reaction. In 1990 an exclusive 6-*endo* aryl radical cyclization to an *exo*-methylene group leading to a condensed heterocyclic system was reported.[38] We envisaged that a TBTH induced aryl radical in a substrate such as I would readily undergo 6-*endo*-ring closure through the preferred attack[39] at the least substituted methylene centre *via* bridgehead radical **J** leading to exclusively or dominantly the respective *trans*-products **K** (Scheme 8), thus providing a simple general route to hexaanulated linear polycyclic systems.

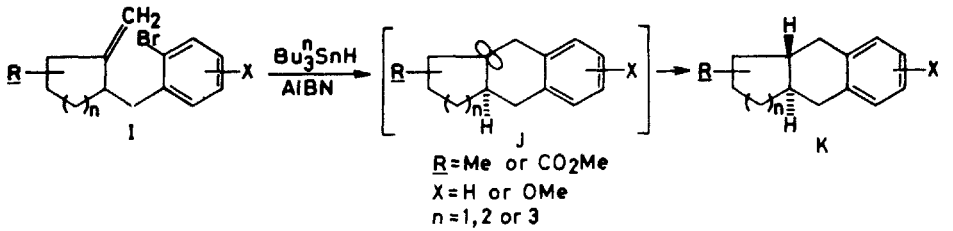
(*a*) 6-*endo-trig-Aryl radical cyclization*

The feasibility of our strategy was initially validated through implementation of an efficient and highly regioselective 6-*endo-trig*-aryl radical cyclization[40] leading to stereocontrolled synthesis of *trans*-octahydroanthracenes **41, 42** and **43** from the respective easily accessible 2-(*o*-bromoaryl)-1-methylenecyclohexanae **38, 39** and **40** (Scheme 9). While 2-*o*-bromobenzyl)-1-methylenecycloheptane **44** gave the *trans* product **45** exclusively, the radical cyclization of 2-(*o*-bromobenzyl)-1-methylenecyclopentane **46**, in contrast, produced a mixture of the *cis* and *trans*-hexahydro-1H-benz[f]indene **47** and **48** in a ratio of *ca* 2:1 (Scheme 9).

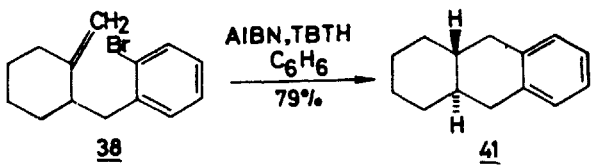
The detailed of this work has been published recently.[41].

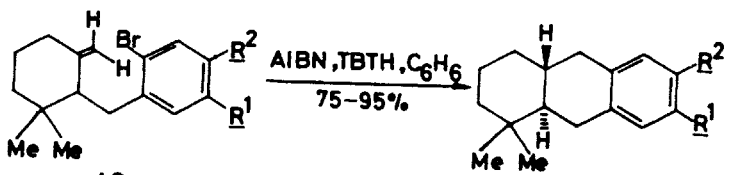
(*b*) 7-*endo-trig-Aryl radical cyclization*

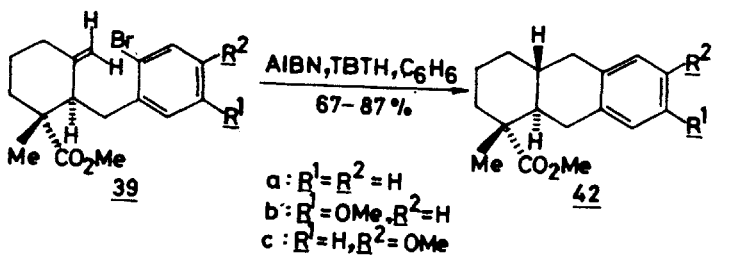
Although TBTH-induced free radical cyclization has been successfully used for the construction of macrocarbocycles, no definitive report existed for the for

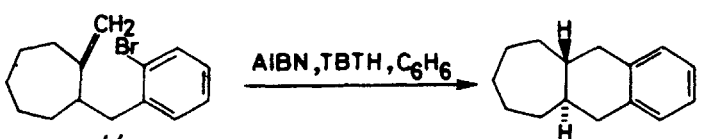


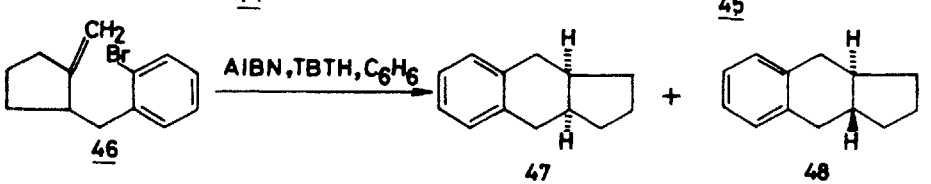
Scheme 8







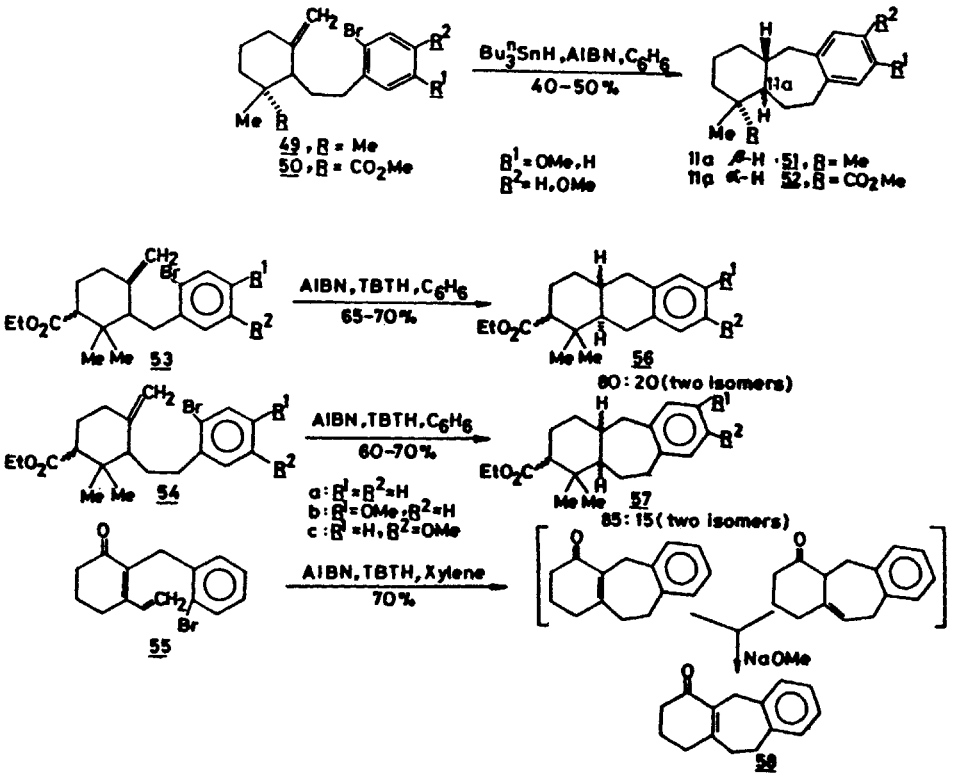




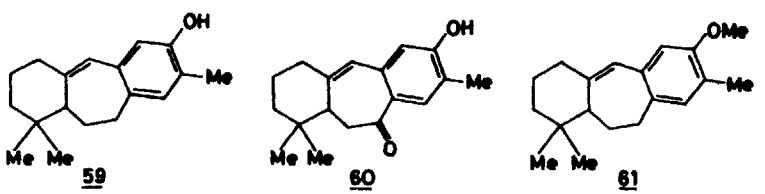
Scheme 9

mation of seven-membered carbocycles under such reaction conditions. We reported[42] in 1993 that the strategy outlined in Scheme 10 can be successfully employed in cycloheptene ring annulation leading to a simple route to partially reduced dibenzo[a,d]cycloheptenes, by 7-*endo-trig*-aryl radical cyclization of the substrates such as **49** and **50** to **51** and **52**, respectively, in 40-50% yields. The 7-*endo-trig* radical cyclization has been further extended[43] to a number of substrates **53, 54** and **55** leading to the respective linear products **56, 57** and **58**.

This new cycloheptene annulation by aryl radical mediated carbon-carbon bond formation appears quite attractive for the synthesis of the recently isolated cytotoxic rearranged 9(10→20)-*abeo*-dinorditerpenoids deoxofaveline (**59**), faveline methyl ether (**60**) and faveline (**62**), the racemates of which have been synthesised very recently by a non-radical method from our laboratories.[44]

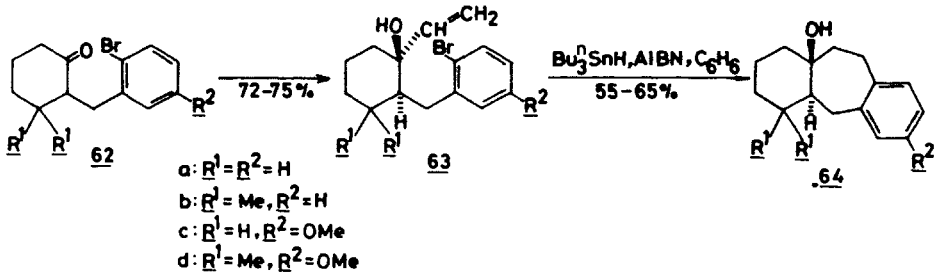


Scheme 10



Structures 59-61

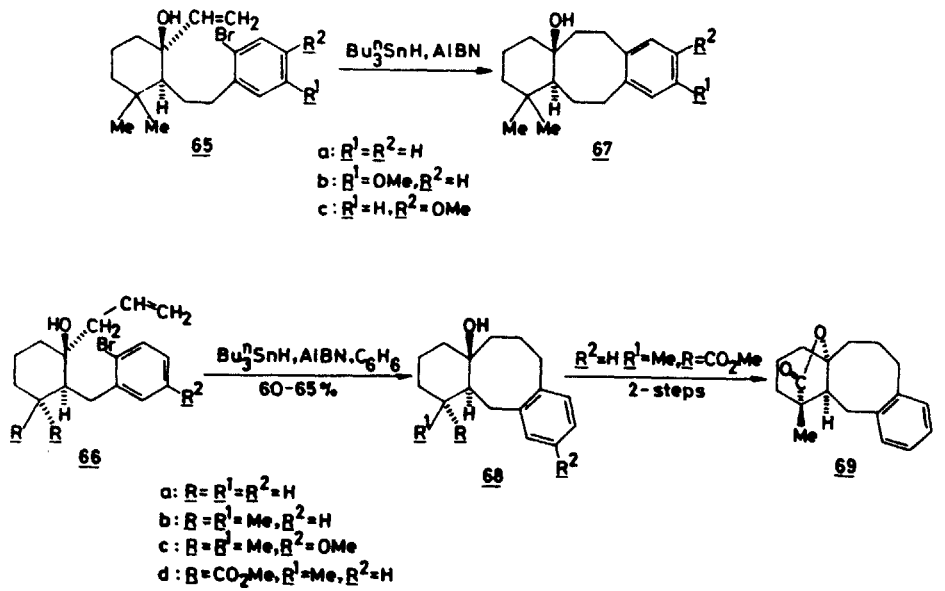
Finally, the scope of the 7-*endo-trig*-aryl radical cyclization has further been extended[42] to the easily accessible vinylcyclohexanols **63** through the ketones **62** leading to the respective tricyclic alcohols **64** in very good yields (Scheme 11).



Scheme 11

(*c*) 8-*endo-trig-Aryl radical cyclization*

Renewed recent interest in the synthesis of difficulty accessible eight-membered carbocycles[45] has been stimulated by the potent pharmacological activity exhibited by a variety of naturally occurring compounds incorporating this medium ring structure. Further to our successful implementations of six- and seven-membered ring annulations, we have now realized, for the first time, the highly regioselective 8-*endo-trig*-aryl radical cyclizations[46] of the vinylcyclohexanols **65** and allylcyclohexanols **66** to the respective decahydrodibenzo[a,e]- and [a,d]-cyclooctenols **67** and **68** in good to very good yields (Scheme 12).

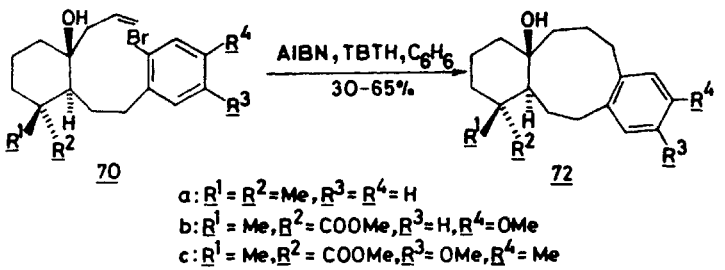


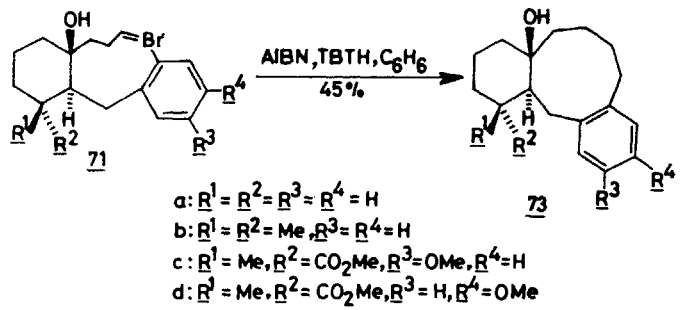
Scheme 12

The assigned stereostructure[47] of the lactone **69** has been confirmed by X-ray crystal structure determination.

(d) 9-endo-trig-Aryl radical cyclization

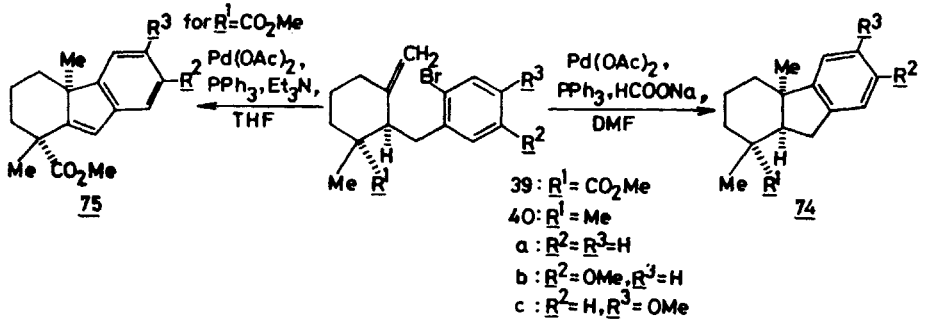
The investigations currently under progress in our laboratories have realized[48] regioselective 9-*endo-trig*-aryl radical cyclizations of the allyl and the butenyl-carbinols **70** and **71** to the respective decahydro-5H-dibenzo[a,d]- and -[a,c]cyclononenols **72** and **73** in moderate to good yields (Scheme 13).





Scheme 13

The unprecedented efficacy in the medium ring annulation, including seven-membered ring, by TBTH mediated exclusive 7-*endo*-, 8-*endo*- and 9-*endo-trig* aryl radical cyclizations by the appropriate choice of the terminal olefin, has opened up a new strategy in the construction of a large number of inaccessible condensed carbocyclic systems widely present in the bio-active natural products from the plant and the marine sources.



Scheme 14

Palladium-Catalyzed regio- and stereo-selective 5-endo-cyclization

As noted earlier (cf. Scheme 8), TBTH induced aryl radical reactions of the *exo*-olefins **39** and **40** result in the exclusive formation of the respective *trans*-octahydroanthracenes **41** and **42** through 6-*endo*-*trig*-mode. We were curious whether intramolecular Heck-type cyclization, extensively used in the recent years, could be viable to effect 5-*exo*-ring closures of these *exo*-olefins. As shown in Scheme 14, we have been able to implement[49] such a strategy by Pd(O)-induced cyclizations of the substrates **39** and **40** in the presence and absence of the hydride donors to the respective saturated *cis*-hydrofluorenes and the unsaturated hydrofluorenes in excellent yields.

Conclusion

In this brief account attempts have been made to emphasize the basis of improvements of known synthetic methodologies as well as the discovery of unknown reactions, through some selected examples in polycarbocyclic synthesis, carried out in our laboratories. As was mentioned at the outset, for a passionate synthetic chemist synthesis is much more than just achieving the targated goal it is indeed the expression of his intelligence, creativity and lead for the future.

Acknowledgement

I am indebted to my colleagues, whose names are listed in the references, for participation in the studies presented here. It is mostly their hard works, clear understanding and experimental skills that have proven decisive both in the formulation of the projects and their executions in the laboratory to a realizable conclusion. The financial supports from Science and Engineering Research Council/DST Scheme under Grant No. 23(3p-8)/81-STP/II and from CSIR, New Delhi through the Grant No. 02(368)/92/EMR-II are gratefully acknowledged.

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