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Strategies of synthesis based on dihydrobenzenes

G S R SUBBA RAO* and K PRAMOD
Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India

Abstract. 1-Methoxycyclohexa-1,4-dienes are readily available from the metal-ammonia-alcohol reduction of aromatic ethers. The use of these dihydrocompounds in the synthesis of a variety of natural products is reviewed.

Keywords. Dihydrobenzenes; synthesis; methoxycyclohexa dienes; selective reactions.

1. Introduction

Reductions of substituted benzenes with alkali metal, alcohol in liquid ammonia, or similar reagents (Birch and Subba Rao 1972) yield with ease a unique set of substituted cyclohexa-1,4-dienes. They have unconjugated double bonds specifically oriented in relation to substituent positions. They act as sources of a further set of unique oriented conjugated dienes, particularly those carrying a 1-OR group. The positions of the hydrogens added in the initial reductions and consequently of the two unconjugated double bonds depend on the nature and position of the substituents. Reduction occurs 1,4- with CO_2H, $SiMe_3$, or in some cases –COR and 2,5- with alkyl, OMe, NR_2 and similar substituents.

A number of uses of cyclohexa-1,4-dienes have been described in the literature, with particular emphasis on the favourable properties conferred by alkoxyl groups. The 1-alkoxycyclohexa-1,4-diene series was originally investigated (Birch 1974, 1975) in order to synthesise analogues of steroid hormones (Birch 1950; Djerassi *et al* 1954).

The methoxycyclohexadienes are synthetically useful in many ways because of their valuable and unique structural features which comprise: (i) The directed enol-ether double bond, which has many synthetic equivalents; the ability to make distinctions, direct and indirect, between the reactivity of an enol ether bond and the other present. (ii) The diene system and its reactions in the form of unconjugated, and conjugated, with the effects of alkoxyl group on transformations of products. The reactions of dienes as unconjugated include the ability to form a regiospecific carbanion formation without the presence of anion stabilizing groups or aided by groups such as CO_2R and Ph, while the conjugated dienes are useful in the Diels-Alder and Alder-Rickert reactions.

Because of their structural versatality and easy availability, the methoxycyclohexadienes have been a favourite choice as starting materials in synthetic organic Chemistry. In this review, it is proposed to discuss some of our own recent work involving the strategies of synthesis of a number of natural products using methoxycyclohexa dienes as starting materials. The reductions of aromatic systems with metal-ammonia or related reagents will not be discussed except to note that the method makes

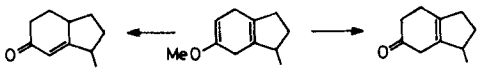
* To whom all correspondence should be addressed.

available many derivatives with specifically oriented unsaturation and has virtually displaced the high pressure catalytic reduction of aromatic systems for synthetic purpose.

2. Selective reactions on One double bond and the consequences

The more electron rich enol-ether double bond reacts preferentially with electrophilic reagents. Proton additions to an enol-ether double bond afford the β,γ-unsaturated cyclohexenone without effecting the other double bond or α,β-unsaturated cyclohexenone with the isomerization of the other double bond depending on the reaction conditions. These processes are very well known. An example is the conversion of the diene (1) to (2) or (1) to (3) which were required (Pramod and Subba Rao, Unpublished) as important intermediates in some of our synthetic projects.

Chart 1

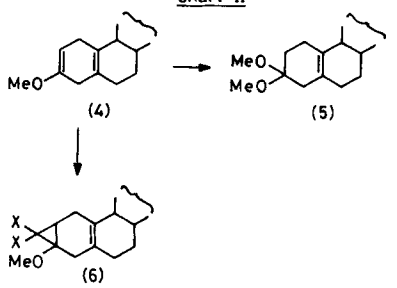


(3) (1) (2)

The enol-ether converted readily into a ketal by the action of an alcohol and a trace of acid without affecting the other double bond (Birch *et al* 1964), which can be used to protect the carbonyl equivalent and reactions can be carried out on the remaining double bond. An example is the conversion of (4) to (5) which was employed (Birch *et al* 1964) as a general method for introduction of angular methyl groups.

The addition of a dihalocarbene can be made selective for the enol-ether double bond and the resulting adducts (6) have several applications (Birch *et al* 1963, 1964; Birch and Keeton 1968)

Charf II



(4) (5) (6)

An enol-ether double bond is also susceptible to selective oxidative fission having the remaining *cis*- double bond untouched in the product. This type of procedure has been used to form synthetic precursors of cecropia hormone, losalocid-A and ionophore antibiotic A-23187 (Corey *et al* 1968; Nakata *et al* 1978). Making use of this method of selective oxidation of one of the double bonds, a very important C_7 synthon (7, 8) has been made (Pramod *et al* 1984) which served as a key intermediate in the synthesis of polyene natural products like, sex pheremones, vitamins A etc. Based on a similar strategy of cleaving one or two double bonds by ozonolysis, the anisole ring or

Chart III

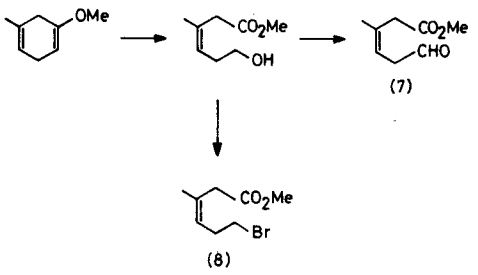
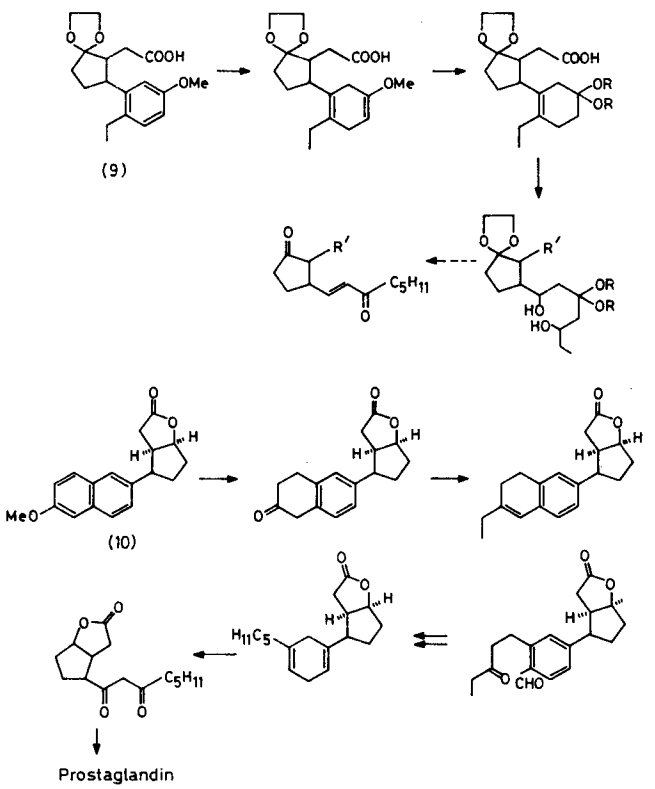


Chart IV



methoxynaphthalene group can act as a stored prostaglandin side chain following the sequence from (9) (Birch *et al* 1984b) and (10) (Ramanathan 1984) respectively.

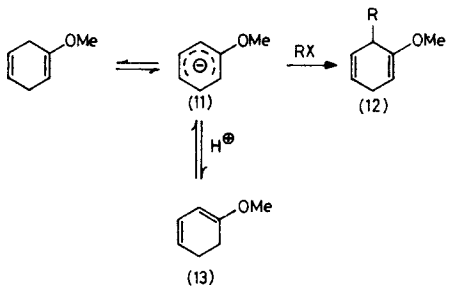
Both the double bonds can also be cleaved by ozonolysis, the first example being the conversion of 2,5-dihydro-m-xylene into acetylacetone (Birch 1944), thus leading to the synthesis of polyketides.

3. Reactions as a diene

(i) *Unconjugated*: An important reaction based on the cyclohexa-1,4-dienes is the

ability to loose a doubly allylic proton on treatment with base to give a regionally defined mesomeric C–5 anion (11). Presence of 1-methoxy and especially of 1,5-dimethoxy groups, has an acidifying effect (Birch 1947a, 1950) and the loss of proton is adjacent to –OMe only. Kinetically-controlled protonation or alkylation of U-shaped anions takes place principally or entirely at the central carbon (Birch 1947a, b; 1950). Reversible addditions lead (Birch 1947a, 1950) to equilibration resulting in the thermodynamically more stable diene. This was the first method of producing the 1,3-diene (12) (about 75%) in equilibrium with the 1,4-diene (11) (25%) using a small proportion of base. The conjugated diene yields with base the same anion as the unconjugated one. This idea was successfully exploited for the deconjugation of an α,β-unsaturated ketone via the enolate anions in the conversion of cholesta-4-enone into cholest-5-enone (Birch 1951).

Chart V



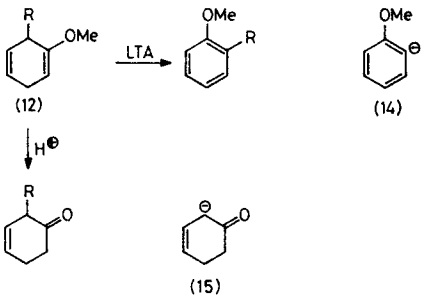
The most useful synthetic application so far involves the formation of a new carbon–carbon bond at the central position by alkylation (Birch 1947a, 1950; Pramod *et al* 1983), arylation (Pramod *et al* 1983) and Michael type reaction (Subba Rao *et al* 1980). Only one carbon–carbon bond can be formed, probably because of the reduced acidity due to substitution. This has the advantage of preventing over-reaction, but the disadvantage is that the quaternary carbon cannot be formed in this series. This type of alkylation leads to dienes which are difficult to obtain by any other methods. An exception is the 2,6-dimethoxybenzoic acid series, where –OMe directs the reductive alkylations into the 1-position even when substituted. However, such aromatic precursors are less readily available.

The products (12) of reductive alkylation have two types of synthetic equivalents according to their subsequent treatment. One is the aromatic anion (14) following the treatment with lead tetraacetate (LTA) which aromatizes the 1,4-diene quantitatively. The other is the equivalent of the enolate anion (15), following gentle acid hydrolysis. The alkylated dienes (12) themselves have direct synthetic uses in Alder-Rickert reaction as noted below.

Low acidities in the alkylcyclohexadiene series can be overcome by the attachment of a group to localise the anionic charge, such as carboxyl, even as the salt (Birch 1947a, 1950). Carboxyl has the advantage that it is possible to remove that group (Birch *et al* 1951) once the purpose is served.

The 2-methoxybenzoic acid series can undergo alkylation (Taber 1976; Birch and Slobbe 1977, Hook *et al* 1979; Bedri *et al* 1969) or Michael-type reactions (Subba Rao *et al* 1980). In –OMe series, synthetic use of –COOH group is unnecessary even though

Chart VI

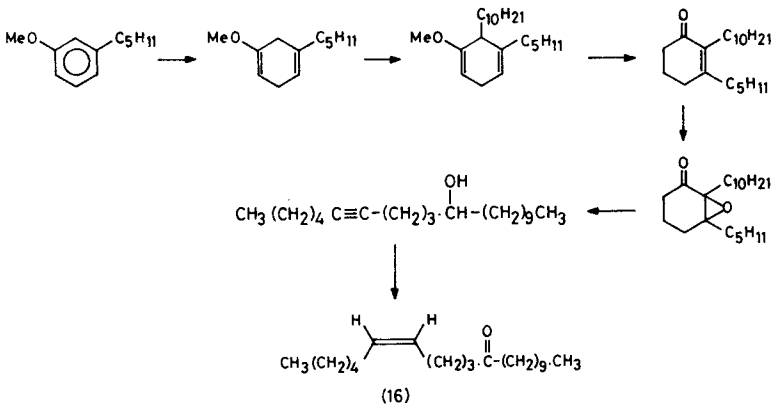


after acid hydrolysis it is readily lost from the resulting –keto acid and alkylation also proceeds efficiently. However, advantages arise if the $-CO_2H$ group is required to direct the course of reduction and alkylation, or if the diene is unusually non-acidic without it as in the 1,4-dimethoxy series.

Reductive methylations of 1- and 2-naphthoic acids were extensively studied (Sridhar 1959; Murthy 1981) and the products have been used as synthons for some natural products (Bedri *et al* 1969; Murthy 1981).

Based on these reactions of unconjugated dienes, 2-, 2,3-, and 2,4-substituted cyclohexenones are prepared (Pramod *et al* 1983) by the alkylation of mesomeric anions followed by acid hydrolysis. Some of the products obtained by this route were used for the efficient synthesis of the male sex attractant, heneicosa-6-ene-11-one (16) isolated (Smith *et al* 1975) from Douglas Fir Moth *Orgyia pseudosugata.*

Chart – VII



Reduction of 3-methoxy-4-methyl benzoic acid (17) with metal-ammonia solution followed by the Michael reaction of its anion with methyl crotonate and further synthetic manipulation resulted in the synthesis (Subba Rao and Ramanathan 1981) of (±) Acoric acid methyl ester (18) and its epimer.

Based on the methylation of the naphthoic acids and further transformations two key intermediates (19) and (20) for the synthesis of pentacyclic triterpenoids have been synthesized (Murthy and Subba Rao 1982) stereospecifically.

Chart VIII

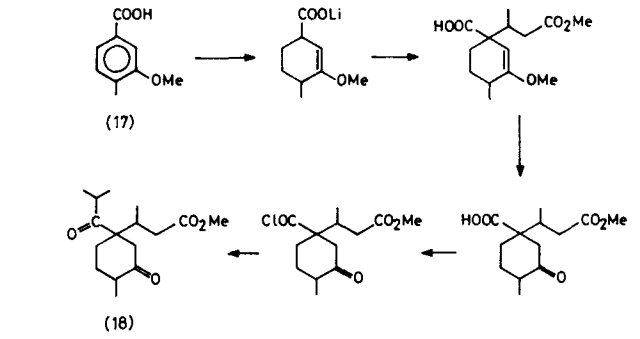
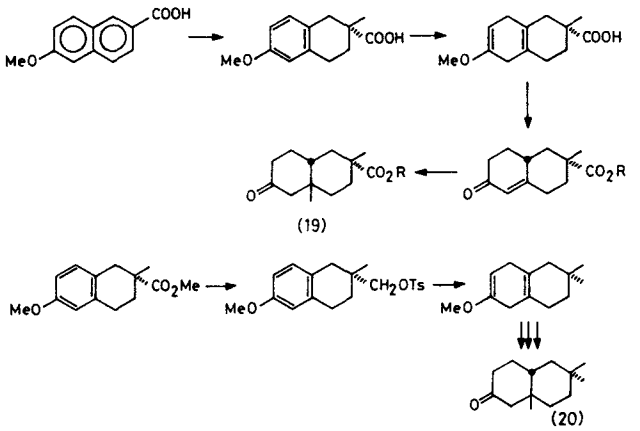


Chart IX



(ii) *Conjugated*: The most important reactions of the methoxycyclohexadienes are as components in various types of Diels-Alder reaction. These reactions are particularly important in forming six-membered rings by two carbon–carbon bonds. These reactions are insensitive to steric effects due to the substitution of the diene, enabling, for example, the production of quaternary carbon centres. There are now very well known rules of stereochemistry governing the lateral junction of two components (Diene and dienophile), for example, the configuration of the dienophile is retained, subject to certain orientation rules (Birch 1950).

Unlike of methoxycyclohexa-1,4-dienes, the alkylcyclohexa-1,4-dienes cannot be conjugated readily by charge transfer complexation or by high pressure to undergo Diels-Alder reactions *in situ*. Whereas 1-methoxycyclohexa-1,4-dienes can be readily used *in situ* for the reactions under high pressure (*i.e.* sealed tube reactions) or by catalytic amount of dichloromaleic anhydride for ready conjugation in the reaction mixture. This *in situ* process has the advantage that all the dienes present are positively used. However, the problem of conjugation of alkyl cyclohexa-1,4-dienes to the cyclohexa-1,3-dienes has been partially solved by the use of $(MeCN)_3Cr(CO)_3$ as catalyst (Birch and Day 1984).

The major synthetic advantage of using Diels-Alder reaction with cyclic dienes is that it generates bridged bicyclic globular products which are valuable synthetic inter-

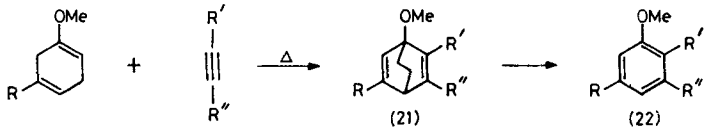
mediates. In cases where bridged ring has to be cleaved to get monocyclic products, two procedures can be envisaged: to break two carbon–carbon bonds simultaneously, obviously not those produced in the reaction, or to break one of the two new bonds specifically. The first requirement is met by the Alder-Rickert reaction, and the second by a fission based on the presence of a bridge head-OMe or an equivalent in retro-aldol fashion.

The importance of 1-methoxy group rests also on its ability to direct the regiochemistry of the addition. Whatever the substitution on the diene or the dienophile the activating group of the latter (CO_2Me, CN, COR etc.) is found adjacent to –OMe in the product. The easy availability of a very large number of substituted cyclohexa-1,4-dienes and their reduction alkylated products provide a range of cyclic dienes with wide orientation of substituents shows the importance of these dienes which are otherwise difficult to obtain for the Diels-Alder reaction.

(a) *The Alder-Rickert reaction for synthesis of aromatic compounds*

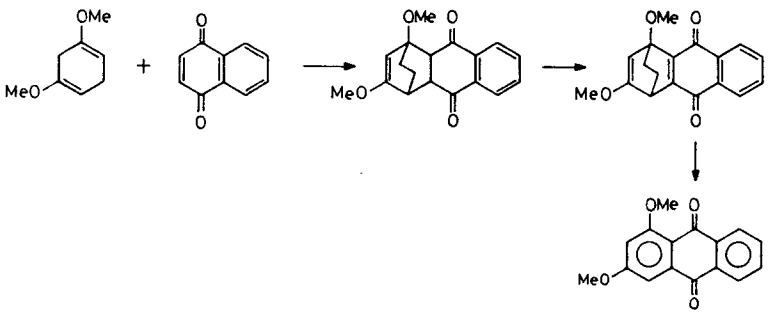
A typical Alder-Rickert reaction is shown in Chart X. The structural requirement for this reaction is a 2,5-C_2-bridge across a cyclohexa-1,4-diene (21) pyrolysis then, readily removes the ethano bridge as an olefin leaving a benzenoid ring (22). The nature of the bridge does not matter since it is lost. Diels-Alder reaction is the best source to get such unsaturated bridged ring structures by the addition of activated acetylenes with cyclohexa-1,3-dienes.

Chart X



In cases of quinone as the dienophile, addition of quinone to a diene, followed by aromatization, or oxidation to quinone back provide the appropriate activation and elimination of the bridge as shown in the Chart XI.

Chart XI



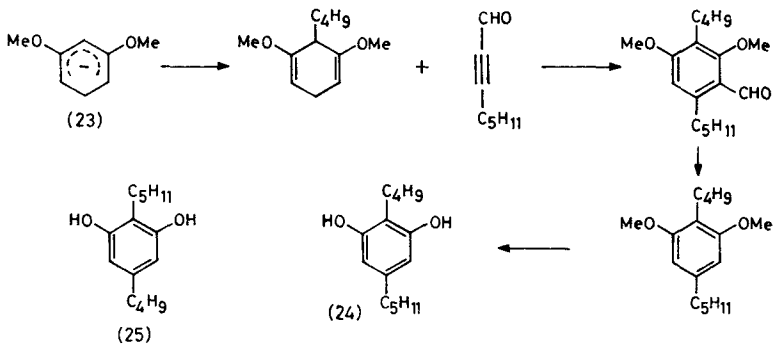
The presence of 1-methoxy on the diene has its own advantages, as pointed out earlier. The intermediate bicyclic adducts (21) from acetylenes can be isolated by carrying out the reaction at room temperature and 15 kbar pressure (Subba Rao and Ramanathan 1984; Subba Rao and Kanakam 1984). With this reaction many aromatic

polyketides derivatives with varying substituents unusual positions can be easily prepared. In this regard it is correct to say that the use of 1-methoxycyclohexadienes is equivalent to oriented addition of four carbons, carrying a possible variety of substituents, laterally to the two carbons of an acetylene to complete the aromatic skeleton.

The Alder-Rickert process in this series had initially given, by accident, several simple polyketide derivatives (Birch *et al* 1954). Later, using the similar strategy, mycophenolic acid (Birch and Wright 1969) a fungal product, and lasiodiplodin (Birch *et al* 1970) have been synthesised. Some other detailed examples are given below.

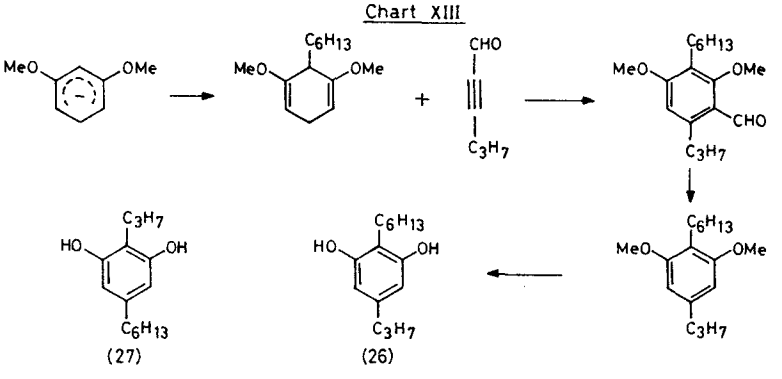
(1) *Stemphol* (24). This synthesis is an example of the use of an anion (23) as the basis of easy production of starting materials. The structure of the stemphol (24) was incompletely known when the synthetic work was carried out (C_4H_9 and C_5H_{11} interchangeable) and both isomers (24 and 25) were readily synthesised (Ramanathan *et al* 1984) and that shown being identical with authentic material.

Chart XII



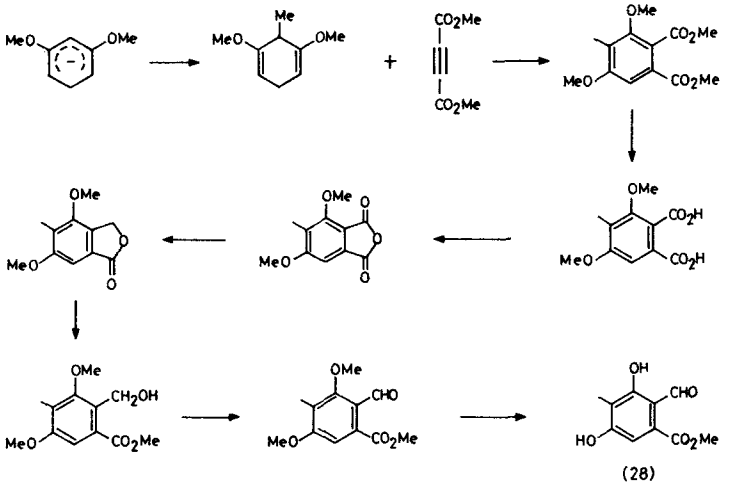
(2) *Antibiotic DB* 2073 (24). Similar to the synthesis of stemphol (24) and its isomer (25), starting with the mesomeric anion (23) the antibiotic 2073 (26) and its isomer (27) have been synthesised (Ramanathan *et al* 1984).

Chart XIII



(3) 3,5-*Dihydroxy*-2-*formyl*-4-*methylbenzoate* (28). Sassa and Miura (1973) have isolated a root growth stimulant as metabolite from fungus. This root growth stimulant has been synthesised (Murthy 1981) by the strategy involving the reductive alkylation and Alder-Rickert reaction.

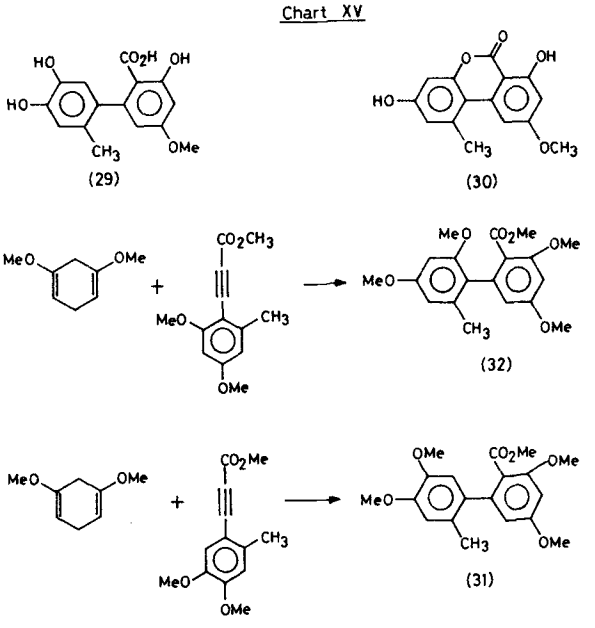
Chart XIV



(28)

(4) *Altenusin* (29) *and Alternariol* (30). Altenusin (29) (Rosett *et al* 1957) and alternariol (30) (Rarstrick *et al* 1953) the fungal metabolites having 6-arylresorcylate skeleton, are known to possess antibacterial activity. Synthesis (Kanakam and Subba Rao 1984) of tetramethyl altenusin (31) and tetramethyl alternariol (32) was accomplished by this strategy.

Chart XV



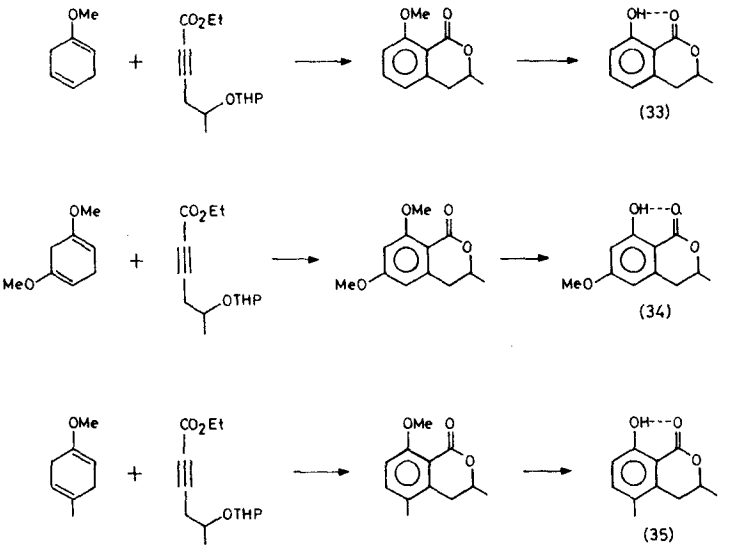
(29) (30)

(32)

(31)

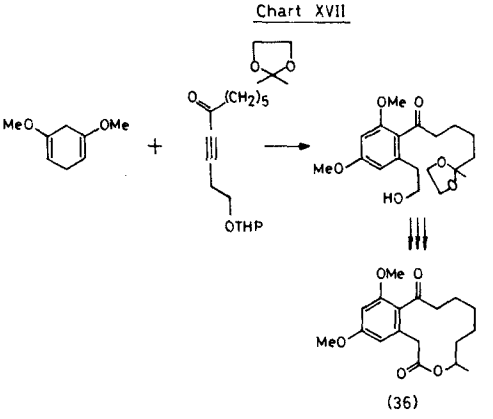
(5) *Mellein* (33), *6-Methoxymellein* (34) *and 5-Methylmellein* (35). Based on the Alder-Rickert reaction, the isocoumarin natural products mellein, 6-methoxymellein and 5-methylmellein have been synthesised (Mani and Subba Rao 1984).

Chart XVI



(6) *Curvularin* (36). This is a naturally-occurring macrolide and notable for its antifungal and antibiotic activity (Mirrington *et al* 1966; Mecapra and Scott 1964). This 12-membered macrocycle fused to aromatic ring has been synthesised recently (Wasserman *et al* 1981). Based on the Alder-Rickert reaction an easy and efficient synthesis of this molecule has been achieved (Mani and Subba Rao 1984).

Chart XVII

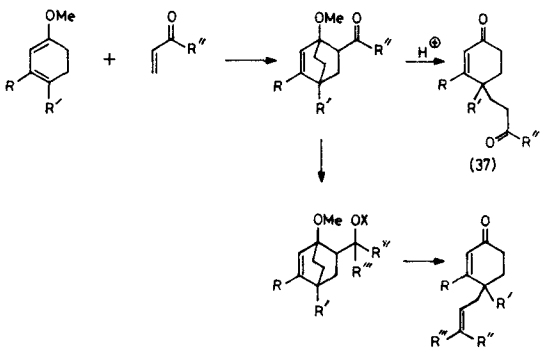


In addition to all the examples described above many derivatives of natural polyketide class compounds like resorcilates (Ramanathan 1984) and salicylates (Kanakam 1981) have been prepared in good yields.

(b) *Retro-Aldol type fissions*

More often in the organic synthesis, not only making new carbon–carbon bond is important but the cleavage of a carbon–carbon bond also plays a very crucial role. Eschenmoser fragmentation (Eschenmoser *et al* 1967) reaction is a classical example where acetylenic aldehydes are prepared from α,β-unsaturated cyclohexenones. The bicyclic-bridged systems with bridge head-OMe are readily prepared by Diels-Alder reaction of 1-methoxycyclohexadienes play an important role in the organic synthesis. The cleavage of one of the carbon–carbon bond formed in the above process yield very useful synthetic intermediates (37) as illustrated in Chart XVIII.

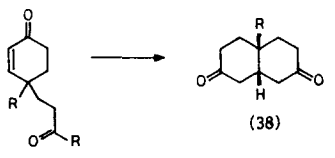
Chart XVIII



This cleavage process has been affected under mild conditions probably due to the release of the strain which accompanies the breakdown of the bridged ring system. Acid-catalysed ring opening involves a retro-aldol fission initiated by protonation of the carbonyl group adjacent to the bridgehead –OMe group. Appropriate carbonium ion for initiating ring fission can also arise from the ionisation of the C–O bond as a tosylate, or by the acid treatment on a tertiary alcohol. However, adducts from acrylic esters or nitrile do not undergo the reaction presumably because of lack of protonation of these groups.

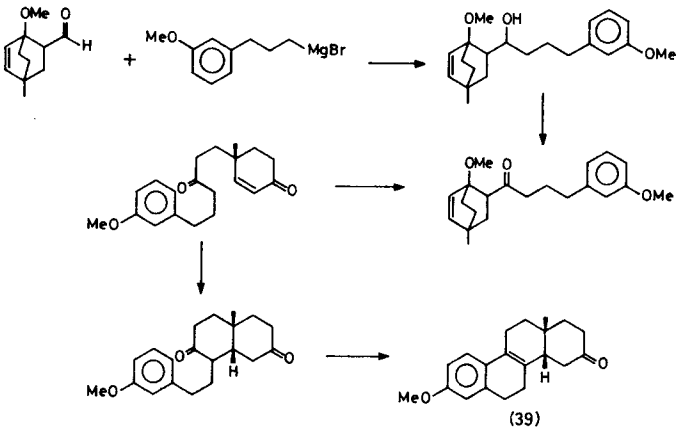
The products obtained by this type of fission, like compound (37) having reactive functions in their side chain undergo with suitable conditions, cyclisation with the cyclohexenone system to give *cis*-decalin system (38) (Birch *et al* 1964), stereospecifically in addition to some other products. Some other similar reaction of cyclisations were reported and their stereochemistry also elaborately discussed (Johnson *et al* 1964; House *et al* 1965).

Chart XIX



Based on this retro-aldol type fission, followed by cyclisation, a potential intermediate (39) for the synthesis of aromatic steroids has been achieved (Uma Sheriff and

Chart XX



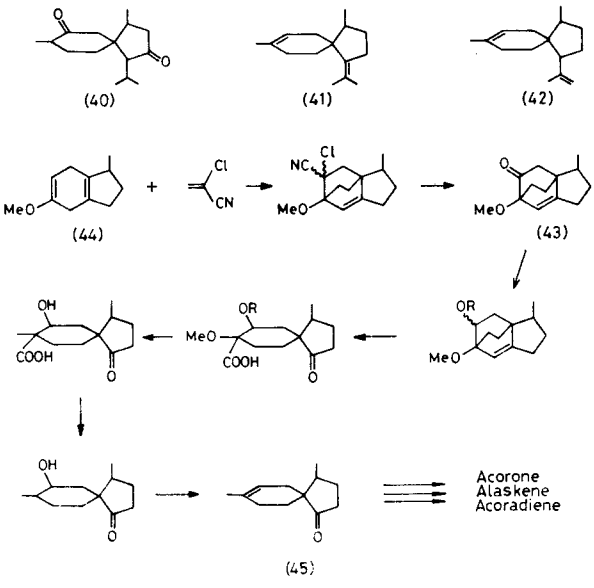
(39)

Subba Rao 1984). With this another new method of building aromatic steroid by AD → ABCD approach has been accomplished.

(c) *Other reactions based on Diels-Alder adducts of methoxycyclohexadienes*

Adducts form from methoxycyclohexadienes by Diels-Alder reaction have been extensively used in the organic synthesis. One of the recent examples is the synthesis of bazzanene, α and β-barbalenes and gymnomitral by Sho Ito (1980). The ease of formation of quaternary centres, presence of double bond and the substituent groups of diene and dienophile in the adduct, made them very potent synthons for many natural product synthesis. The presence of bridgehead methoxyl group may not be

Scheme XXI



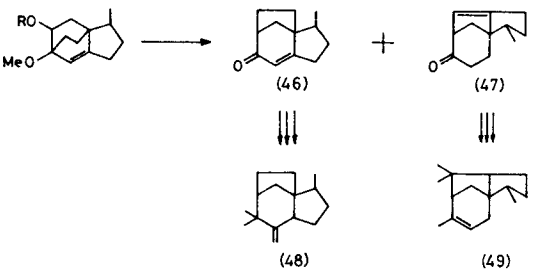
(45)

structurally essential in the product, but its presence in the diene orients the addition and increase the rate of addition. There are many natural products where (2.2.2)bicyclo system is apparent in their structures.

The presence of a double bond in the (2.2.2)bicyclo adduct makes these adducts to be as potent intermediates for the synthesis of spiro systems. Oxidative cleavage of the double bond in such systems yield spiro skeleton. This method has been successfully used (Pramod and Subba Rao 1984) in the synthesis of spiro (4·5) decane sesquiterpenes like Acorone (40), Alaskene (41) and Acoradiene (42). The adduct (43) which was prepared by the regioselective addition of ketone equivalent to methoxydiene (44) followed by hydrolysis has been used to prepare a key intermediate (45) for the synthesis of the spiro sesquiterpene natural products.

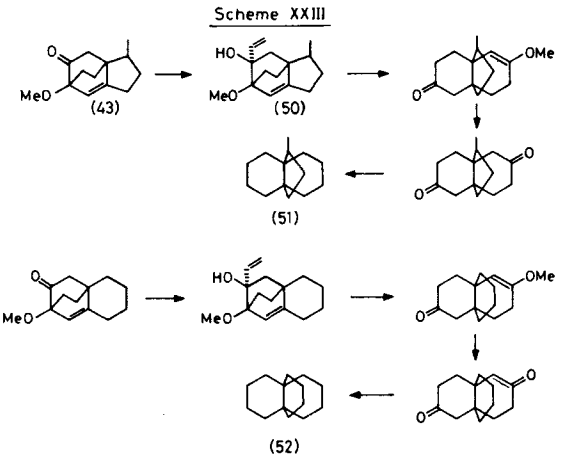
The bridgehead –OMe permits rearrangement of a (2.2.2)bicyclo system into a (3.2.1)-bicyclo system, presumably due to the release in the ring strain (Alfaro *et al* 1974). This rearrangement has been extended to zizaene (48) and cedrene (49) sesquiterpenes (Pramod and Subba Rao 1982; Pramod *et al* 1984) *via* their intermediates (46) and (47) respectively.

Scheme XXII



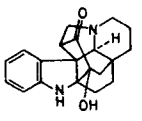
Using the adduct (43) a new and efficient synthesis (Pramod and Subba Rao 1982) of 11-methyl[4.4.3]propellane (51) has been prepared by the base catalysed rearrangement of the carbinol (50). Similarly the [4.4.4]propellane (52) has also been prepared.

Scheme XXIII

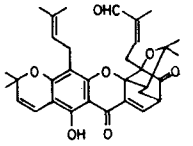


It is clear from the above discussion that cyclohexa-1,4-dienes are highly versatile building blocks whose further use in organic synthesis, particularly in the realm of naturally occurring substances, should prove of immense value. The technique of reductive alkylation followed by cycloaddition has been extended to the synthesis of natural products which contain the (2.2.2)-bicyclic system or its equivalents. Among these compounds the synthesis of kopsine (53), morellin (54) and aphidicolin (55) is in progress in our laboratory.

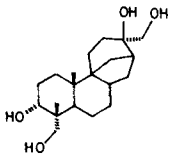
Chart XXIV



(53)



(54)



(55)

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