A facile synthetic route to complex polycyclic natural products through intramolecular alkylation with α-diazomethyl ketones

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Abstract. Some applications of the intramolecular alkylation of α-diazomethyl ketones through metal-catalysed addition and insertion reactions, and acid-catalysed olefinic and aryl participations, towards the synthesis of a variety of complex polycyclic natural products have been briefly reviewed with special emphasis on the results reported from the authors' laboratories. The possible mechanisms of the transition metal catalysed carbon-carbon bond forming reactions of carbenoids have been briefly discussed in the light of the recent literature.

Keywords. α-diazomethyl ketones; intramolecular alkylation; α-ketocarbenoids; metal-catalysed reactions; acid-catalysed reaction; polycyclic synthesis.

1. Introduction

The intramolecular reactions of α-diazo carbonyl compounds have received considerable attention as they lead to the construction of a variety of complex carbocyclic framework not easily accessible by conventional methodologies. The wide application of this intramolecular process is found in the total syntheses of gibberellins (Mander 1983), phytoecdysone (Tahara et al 1973), sirenin (Bhalerao et al 1970 and references therein), α-chamigrene (White et al 1974) and sabine (Vig et al 1969) as well as the synthesis of interesting compounds such as bullvalene (Doering et al 1967), twistane (Tichy 1972) and bridged annulenes (Vogel et al 1970; Vogel and Reel 1972).

Two principal reactive intermediates are available from α-diazo carbonyl compounds: α-ketocarbenes (or α-ketocarbenoids) (A) and α-diazonium ketones (B) (scheme 1). The ketocarbenes, generated by decomposition of α-diazo ketones 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 (intramolecular addition) or to an appropriately situated olefinic group in the same molecule leading to a cyclisation 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-diazo ketone 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 cyclisation reaction (path 3) of great synthetic utility. A detailed discussion of all these reactions is beyond the scope of this review.

A comprehensive account of these three aspects of the α-diazo ketone reactions was

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given by Burke and Grieco (1979). The acid catalysed reactions of α-diazoketones have been recently reviewed by Ghatak (1981) and Smith et al (1981). The present report includes the recent work in this area with special emphasis on the contributions made from authors' laboratories.

2. α-ketocarbenes or α-ketocarbonoids

Photochemical, catalytic or thermal conditions are employed for generation of ketocarbenes from α-diazoketones. Of these, catalytic (homogeneous or heterogeneous) conditions are most commonly used in synthetic organic chemistry. Until recently, all the reported catalytic decompositions were carried out under heterogeneous or homogeneous conditions with a variety of copper catalysts (Burke and Grieco 1979). Recently a few efficient and selective catalysts, for example copper(I) trifluoromethylsulphonate [CuTf] (Salomon and Kochi 1973) and some group 8 metals such as rhodium(II) (Anciaux et al 1980; Dowd et al 1982) and palladium(II) (Anciaux et al 1980; Smeets et al 1980) have been introduced for intermolecular cyclopropanation reactions of olefins with diazo compounds. Another significant development is the highly enantio-selective synthesis of cyclopropane derivatives involving carbenoid reactions between olefins and diazoalkanes catalysed by bis[(-)-camphorquinone-α-dioximato]cubalt(II) in excellent yields (Nakamura et al 1978). An efficient heterogeneous “activated CuO” catalyst was developed by Ghatak et al (1973) for intramolecular α-ketocarbonoid addition reaction in a number of γ, δ-unsaturated α-diazoketones under irradiation with tungsten lamp. Recently, Chakraborti et al
(1981) reported, for the first time, that \( \text{bis}[2,4\text{-pentanedionato} \text{Ni(II)}] \) \( \text{[Ni(acac)_2]} \) acts as a highly efficient homogeneous catalyst in these reactions. Only a single unsuccessful attempt at cyclopropanation using a nickel catalyst, nickelocene, has been recorded (Werner and Richards 1968).

2.1 Mechanism

From extensive mechanistic studies based upon mostly the intermolecular cyclopropanation reactions using a variety of homogeneous metal catalysts it has been postulated (Burke and Grieco 1979; Salomon and Kochi 1973; Anciaux et al 1980; Wulfman 1976) that two competitive pathways, one originating from the metal-olefin coordination as the key factor and the other, a bimolecular process with metal-carbenoid species attacking uncomplexed olefins are operative in these reactions. The influence of various catalysts on the regioselectivity of cyclopropanations to dienes and trienes was studied in detail by Anciaux et al (1980, 1983). From their studies, it is revealed that rhodium catalysts are extremely efficient for cyclopropanations of any kind of alkene, the electron rich double bond being regioselectively cyclopropanated. In contrast, palladium catalysts cyclopropanate the less substituted double bond regioselectively whereas copper catalysts exhibit borderline cases. Based on these results, two fundamental mechanistic pathways have been forwarded: a carbenoid mechanism as shown in scheme 2 and a co-ordination mechanism as shown in scheme 3 (where \( M = \) metal complex; \( S = \) unsaturated substrate, and \( P = \) products). Rhodium(II) carboxylates act exclusively according to scheme 2, while palladium carboxylates probably react according to scheme 3. Copper catalysts generally display a carbenoid (scheme 2) type of behaviour, with the exception of some complexes carrying weak ligands notably copper triflates where the contribution from the mechanism of scheme 3 becomes important.

2.2 Intramolecular ketocarbenoid addition to olefin

The ketocarbene addition to a suitably situated olefin within the same molecule has led to the synthesis of several natural products containing cyclopropyl ring. A brief account of the syntheses of such compounds will be found in the article by Burke and Grieco (1979).

\[ \text{Scheme - II} \]

\[
\begin{align*}
M + N_{2,\text{CHR}} & \rightarrow [M=\text{CHR}]_2 \\
& \xrightarrow{\text{N}_2} P + M
\end{align*}
\]

\[ \text{Scheme - III} \]

\[
\begin{align*}
M + S &= MS \\
MS + N_{2,\text{CHR}} & \xrightarrow{\text{N}_2} [\text{CHR}]_2 \\
& \xrightarrow{\text{N}_2,\text{CHR}} M + P
\end{align*}
\]
The cyclopropyl ketone resulting from intramolecular cyclisation of an olefinic ketocarbonoid can be cleaved by hydrogenolysis or protonolysis. This strategy has been extensively explored by Dasgupta et al (1969), Chakraborty et al (1972) and Ghatak and Roy (1981) for the synthesis of a number of bicyclo[3.2.1]octane derivatives (3) and (4) from the diazoketones (1) as depicted in scheme 4. Ghatak and Chakraborty (1979) extended this route for the total syntheses of (+)-gibberone (7b) and (±)-4-methyl-9β,13α-dihydro-16-oxogibba-1,3,5(10)-triene (9a), two degradation products of gibberellins. It is interesting to note that hydrogenolysis of the cyclopropyl ketones (6) produced exclusively C-9αx epimer whereas reduction of (7) produced mixture of 9αx and 9αβ epimers leading to the synthesis of C-9 epimeric gibbane synthons.

The conformational effect of a 1β-methyl substituent on the courses of intramolecular oxocarbonoid addition in the diazoketones (10) and on the stereoselectivities of catalytic hydrogenation of the derived pentacyclic ketones (11a & 11b) and tetracyclic ketones (12a & 12b) was evaluated by Ghatak et al (1974). The substituent effect of the aromatic ring in oxocarbonoid addition as well as in the stereoselectivities of catalytic hydrogenation of the cyclopropyl ketone and the gibbane was studied in detail by Ranu et al (1982).

This strategy of the synthesis of bicyclo[3.2.1]octane through oxocarbonoid addition reaction has been extended to several other diazoketones e.g. (15) by Ghatak et al (1976) for the synthesis of intermediates (16-18) towards B-seco-gibberellins. A stereospecific synthetic route to a tetracyclic bridged-ring ketone (21) related to the B-homophylloloclade system was developed (Ghatak and Ray 1977) through the cyclopropyl ketone (20) from the diazoketone (19). Extension of this strategy to the diazoketone (22) has led (Roy et al 1980) to the synthesis of bicyclo[2.2.2]octane derivative (23), an important intermediate toward the synthesis of atisine.
Intramolecular alkylation of α-diazoethyl ketones

Scheme V

\[ (10) \xrightarrow{\text{HCl-x}} (11) \]
\[ (12) \xrightarrow{\text{H}_2, \text{Pd-C, ETOH}} (13) \]
\[ \text{a: } n = 1 \]
\[ \text{b: } n = 2 \]

Scheme VI

\[ (12) \xrightarrow{\text{Et}_2\text{O, } \text{CHCl}_3} (15) \]
\[ (16) \xrightarrow{\text{H}_2, \text{Pd-C, ETOH}} (17) \]
\[ \text{activated } \text{CuO} \]
\[ \text{50\%} \]
\[ (19) \xrightarrow{\text{HCl-x}} (20) \]
\[ \text{93\%} \]
\[ (22) \xrightarrow{\text{H}_2, \text{Pd-C, ETOH}} (23) \]
\[ \text{90\%} \]

A similar strategy was extensively used by Beames and Mander (1969), Beames et al (1972) and Mander et al (1974) for the construction of bicyclo[3.2.1]octane and bicyclo[2.2.2]octane derivatives.

An interesting application (Stork and Gregson 1969) of the intramolecular olefinic
ketocarbenoid addition reaction is found in Lewis acid-catalysed cleavage of the cyclopropyl ketone (25) derived from (24) with simultaneous participation of a suitably situated olefin or aromatic ring leading to cyclisation (scheme 7).

The intramolecular addition reactions of carbenoids derived from mixed diazomalonate have been applied for the synthesis of prostanoid intermediate (Corey and Fuchs 1972), α-methylene γ-butyro lactones (Ziegler et al 1974), spiro lactone and spiro ketone (Clark and Heathcock 1975). Recently, Hudlicky et al (1983) applied this strategy to synthesise bicyclic cyclopentene lactones (27) from the diazomalonate (26).

2.3 Intramolecular insertion of α-ketocarbenoids into C–H bond

Although relatively less explored, the intramolecular C–H insertion of α-diazo carbonyl compounds has made possible many important and otherwise difficult synthetic transformations. In a geometrically rigid system intramolecular C–H insertion is a highly favoured process.

The first example of intramolecular C–H insertion leading to cyclisation was observed (Greuter et al 1958) during decomposition of 21-diazo-5α-pregn-20-one (28) in refluxing toluene in the presence of Cu(I) oxide (scheme 8).

An intramolecular angular alkylation was achieved (Ghatak and Chakrabarty 1972, 1976) through regioselective α-keto carbenoid insertion into tertiary C–H bond of the diazoketones (29) in presence of Cu(II) sulphate or preferentially with Cu(I) oxide. The light induced Ni(acac)₂ catalysed reaction of (29) leads to (30) in excellent yield (Chakraborty et al 1984). The bridged cyclopentanones (30) were further transformed to the bridged-acylamines (32) through the respective dicarboxylic acids (31) as illustrated in scheme 8. This sequence represents a highly efficient formal stereospecific total synthesis of dl-atisine, dl-veatchine and gibberellin-A₁₅ (scheme 8). Ghatak et al (1976a) extended the C–H insertion reaction to the diastereoisomeric diazoketones (33) and (34) for the syntheses of the bridged-ketones (35) and (36), respectively (scheme 10).

In a systematic study of competitive intramolecular C–H insertion reactions of some substituted cyclohexane derivatives (Chakrabarty et al 1975; Chakraborty et al 1984), it
is revealed that insertion into Me–C–H bond in (37e) leading to the bridged bicyclo[3.2.1]octanone (39g) is marginally favoured to that Ph–C–H bond resulting in the regioisomeric ketone (38e). Also intramolecular competition in (37a) and (37b) strongly favours insertion into the tertiary benzylic C–H bond leading to mostly (38a) and (38b) rather the secondary ones leading to the respective regioisomers (39a) and (39b). The homogeneous catalyst, Ni(acac)₂ is found to be the most effective for these insertions compared to the other catalysts studied such as, Cu₂O, CuSO₄, Pd(acac)₂ and Co(acac)₂.

Agosta and Wolff (1975), in their detailed study of the Cu-catalysed decomposition of the diazoketones (40) to the regioisomeric C–H insertion products (41) and (42), pointed out the three following structural effects in controlling the site of C–H insertion reaction: (a) the degree of substitution of the C–H bond into which insertion may occur (tertiary is preferred to secondary one), (b) the conformation of the cyclohexane ring,
(c) geminal substitution at the carbon bearing the diazocarbonyl group, as revealed from the composition of the products (scheme 10).

The conformational effect on the regiochemistry in intramolecular C-H insertion reactions was also demonstrated by Wenkert et al (1968) (scheme 10). In all the cases studied, formation of a five-membered ring is favored over the four-membered one.

An attempted Wolff rearrangement of the diazoketone (43) by Wenkert et al (1975) led to the isolation of C-H insertion product (44) in 22% yield. Similar C-H insertion under Wolff-rearrangement condition of the diazoketone (45) afforded a mixture of (46) and (47); the cyclobutanone (46) being the major product (Takahashi et al 1975). Very recently, a diterpene to steroid conversion has been reported (Wenkert et al 1982) by an intramolecular C-H ketocarbene insertion reaction of the diazoketone (48), derived from the virenescon B diacetate, to the tetracyclic keto-diacetate (49).

Scheme - X

Substituents

<table>
<thead>
<tr>
<th>R²</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>Me</td>
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</tr>
<tr>
<td>H</td>
<td>26</td>
</tr>
<tr>
<td>Me</td>
<td>51</td>
</tr>
<tr>
<td>Me</td>
<td>58</td>
</tr>
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</table>

Scheme - XI

<table>
<thead>
<tr>
<th>n</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(-)</td>
</tr>
<tr>
<td>2</td>
<td>19</td>
</tr>
<tr>
<td>3</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>72</td>
</tr>
</tbody>
</table>
3. Acid-catalysed carbon–carbon bond formation in α-diazoalkyl ketones through π-bond participation

The acid-catalysed cyclisation of diazomethyl ketones through π-participation of suitably situated olefinic bonds or aromatic groups has accumulated a great deal of interest as it provides a good method for carboxyclic ring annulation.

3.1 Carbon–carbon bond formation from γ,δ-unsaturated α-diazoalkyl ketones

A new cyclopentanone annelation reaction of great synthetic potential was developed by several groups for the introduction of a bicyclo[3.2.1]octanone or a bicyclo[2.2.1]heptanone moiety into a variety of carboxyclic systems by the acid-catalysed intramolecular electrophilic cyclisation of γδ-unsaturated α-diazoalkyl ketones. The first example of acid-catalysed intramolecular olefinic participation was reported by Erman and Stone (1971) in an elegant synthetic approach to the α-patchouline class of sesquiterpene by BF₃–Et₂O catalysed cyclisation of the diazoketones (50) to give the respective double bond isomeric cyclisation products (51) and (52) in moderate to good yields.

During the early seventies several efficient carbon–carbon bond formation reactions involving α-diazoalkyl ketones (1) (schemes 4) and (19) (scheme 6) have been studied independently (Chakrabortty et al 1972; Ghatak et al 1976; Ghatak and Ray 1977) for the construction of the tetracyclic intermediates (4) and (20A) (scheme 6) and a number of related compounds incorporating bicyclo[3.2.1]octanone bridged-ring systems towards the total synthesis of several complex diterpenoids. Mander and his co-workers (Mander et al 1974; Beames et al 1972) have independently developed similar cyclisation reactions of diazoketones leading to the tetracyclic ketones (4, n = 1
and 2; R$^1$ = H and Me; R$^2$ = H and Me) in much improved yield by using HBF$_4$ in nitromethane.

The intramolecular alkylation reactions of unsaturated diazomethyl ketones have been further improved and extended in our laboratories for the preparation of a large number of $\Delta^9(11)$-gibbenes and related compounds as illustrated in scheme 14 (Ghatak and Chakraborti 1979; Ghatak et al. 1981; Ranu et al. 1982). The yield of the cyclised products has been substantially improved (70–95%) by using 70% perchloric acid-trifluoroacetic acid as catalyst in chloroform.

Hook et al. (1980) utilised the tetracyclic ester (54), prepared by cyclisation of the diazoketone (53) in a classic total synthesis of (+) gibberellic acid (55) (scheme 15).

The intramolecular cyclisation was also extended (Ghatak et al. 1976) for the synthesis of some important intermediates (18) for B-seco gibberellins through the diazomethyl ketones (15) (scheme 6). A similar cyclisation of the diazoketone (22) (Ghatak and Roy 1981) led to a tetracyclic intermediate incorporating the basic bicyclo[2.2.2]octanean skeletal structure of atisine diterpenoids (scheme 6).

In each of the above examples, acid-catalysed cyclisation reaction of $\gamma\delta$-unsaturated $\alpha$-diazoethyl ketones produced essentially a single annelated ketone arising through the initial electrophilic attack by the protonated diazo-carbonyl function to the electron rich centre. The absence of such polarisation in the double bond may result in a mixture of the possible regioisomeric cyclised ketones as evidenced (Ceccherelli et al. 1978) in the cyclisation of (56) to (57) and (58) in a 3:2 ratio (scheme 16). The steric environment
also seems to be important as it reflects in the regiospecific cyclisation of (59) to (60) (scheme 15). Similar lack of regioselectivity in the carbon–carbon bond formation has been observed in some relatively simple substituted monocyclic 𝛾Δ-unsaturated diazomethyl ketone (61) in this laboratory (Saha and Chakraborti unpublished work).

3.2 Acid-catalysed intramolecular C-alkylation in 𝛽Δ-unsaturated diazomethyl ketones

The acid-catalysed intramolecular cyclisation of 𝛽,𝛾-unsaturated 𝛼-diazomethyl ketones has led (Ghatak and Sanyal 1974) to introduce a highly efficient new synthesis of angularly fused cyclobutanones. The readily available styrenoid cyclobutanones (63) from the respective diazomethyl ketones (62), have been further transformed to the corresponding cyclopentanones (30) (scheme 17) by a remarkable stereospecific rearrangement (Ghatak 1976b) of the stereoselectively hydrogenated cyclobutanones
As mentioned earlier, the bridged cyclopentanones (Ghatak et al. 1978; Ghatak et al. 1980) are the key intermediates for the total synthesis of atisine, veatchine and gibberellin-\(\text{A}_{15}\).

The \(\beta,\gamma\)-unsaturated \(\alpha\)-diazomethyl ketones (65) incorporating a tetrahydrofluorene moiety, also produced the respective styrenoid cyclobutanones (66) which were transformed through a similar sequence of reactions (Ghatak et al. 1980) to the potential hydrofluorene intermediates (67) towards \(\text{C}_{20}\)-gibberellins (scheme 17).
This cyclobutanone annelation was utilised by Ceccherelli et al (1980) for the preparation of two 4,4-dimethyl-D-norsteroids. Hudlicky and Kutchan (1980) applied this method on the diazomethyl ketone (68) to the respective cyclobutanone (69) and finally to filifolone (70) (scheme 19). Smith et al (1975) and Smith and Dieter (1977) developed the acid-catalysed alkylation method to a few relatively flexible $\beta\gamma$-unsaturated $\alpha$-diazomethyl ketones e.g. (71) and (73) leading to the corresponding cyclopentenones (72) and (74) (scheme 19) as sole products. Extensive studies on the related cyclopentenone annulation reaction and its extension were reported by Smith et al (1981). After considerable experimentation, Ghatak et al (1981), discovered that it is not the structure of the substrate alone which controls the nature of the products in the acid-catalysed reactions of the $\beta\gamma$-unsaturated diazoketones such as (62) and (65) but that the choice of the acid catalyst and solvent is also critical. For example, the reactions of the diazoketones (62) and (65) in weakly polar solvents such as benzene, chloroform or methylene chloride in the presence of strong protic acids namely aq. HClO$_4$ (70%), aq. HBF$_4$ (48%), CF$_3$COOH or H$_2$SO$_4$ (98%) gave the respective unsaturated cyclobutanones (63) and (66) in good to excellent yields. In contrast, when the diazoketones (62) and (65) were subjected to cyclisations (Ghatak et al 1981; Satyanarayana et al 1982; Roy et al 1982) with aq. HBF$_4$ (48%) or BF$_3$·Et$_2$O in strongly polar solvent nitromethane, the respective rearranged bridged hydroxyketones (75, $n = 2$) were predominating product (ca 90%) (scheme 20). The hydroxycyclopentanones (75, $n = 2$) underwent facile rearrangement with p-TsOH or iodine in boiling benzene to afford the respective rearranged cyclopentenones (76, $n = 2$). In contrast, the hydrofluorene analogues (75, $n = 1$) under similar conditions did not produce the rearranged cyclopentenones (76, $n = 1$). These compounds, however, have been obtained in excellent yields (Satyanarayana et al 1981) by direct cyclisations of the diazoketones (62, $n = 1$) with p-TsOH in boiling benzene. The mechanistic pathways
for the formation of different products from the diazomethyl ketones (62) and (65) have been rationalised as depicted in scheme 20.

The alkylation rearrangement reaction has also been extended (Satyanarayana et al 1981) to the bicyclic diazoketone (77) leading to the bridged ketone (78) and the rearranged cyclopentenone (79) (scheme 20) in excellent yields. This mixture undergoes facile acid-catalysed rearrangement to (79). The lower homologous diazomethyl ketone (80) undergoes cyclisation-rearrangement to afford the angularly fused cyclopentenone (81) along with other minor products. This sequence appears extremely attractive for the synthesis of complex polycyclopentanoid sesqui- and sesterterpenes. A similar alkylation-rearrangement of a diazomethyl ketone has been exploited previously (Takano et al 1978) for the synthesis of an intermediate towards aspidosperma alkaloids.

3.3 Intramolecular alkylation of diazoketones through aryl participation

The elegant studies of Mander (1983) have elaborated the aryl participations in protonated diazomethyl carbonylalkylations as a viable method for bridged- and spiro-ring annelations, leading to an elegant synthesis (Lombardo et al 1980) of (±)-
gibberellin-A$_1$ (84) as depicted in scheme 22, starting from the diazoketone (82) through the aryl participated product (83).

Spiroannelation reactions have been extended by Bhattacharya and Sen (1979) for the synthesis of spirocyclobutanone and a few spirocyclopentanones.

Ring annelation by aryl participation has been successfully utilised by Sanyal et al (1978) and Mukherjee et al in these laboratories, for preparation of the spiro- and bridged-ketones (85), (86) and a number of related compounds as key intermediates towards the synthesis of sester- and sesquiterpenoids. Several tetracyclic skeletons e.g. (87), (88), (89), and (90) related to a number of diterpenes have been prepared in these laboratories (Maiti et al 1982, 1983; Maiti and Mukherjee 1984a, b) Basu et al 1981; Basu and Mukherjee 1984) through aryl participation (scheme 23).
4. Conclusions

The intramolecular alkylation of diazomethyl ketones provides a facile synthetic entry to a variety of complex polycyclic natural products incorporating functionalised quaternary carbon residues. With appropriate selection of the substrates and reaction condition it is possible to use such process for carbon–carbon bond formations involving a double bond, aromatic ring or even a classically inactive C–H bond. The most important advantage the present method offers, of course, is the fact that preparation of a large number of bridged-ring systems, the fabrication of which would otherwise require a long sequence of synthetic transformations, can be efficiently accomplished in a single operation by diazomethyl ketone alkylation reaction. Furthermore, it is quite obvious that this reaction has a wide scope for extension to other types of complex natural products.

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