CHAPTER I

Heterolytic Fragmentation Reactions - A Review

HETEROLYTIC FRAGMENTATION REACTIONS - A REVIEW

Abstract — A comprehensive literature survey of heterolytic fragmentation reactions from 1967 onwards to date is presented in this Chapter. The basic structural and stereoelectronic factors governing these reactions and more recent reports on olefin and alkyne forming reactions are reviewed.

HETEROLYTIC FRAGMENTATION REACTIONS - A REVIEW

1. INTRODUCTION

Heterolytic fragmentation reactions[1,2] are characterised by carbon-carbon bond cleavage in systems such as Y-C-C-C-X, where X is a normal nucleofuge[3] and Y is a heteroatom with p-electrons, to -C=C- and Y^+=C- moieties.

Such reactions have been extensively studied and frequently made use of in degradation, structure determinations, and syntheses. An excellent review on these fragmentation reactions reported upto 1967, has been published by Grob.[2] The basic structural and stereoelectronic factors governing these reactions and more recent reports (upto 1979) on olefin and alkyne forming reactions are reviewed in this Chapter.

2. STRUCTURAL FACTORS

The departure of the necleofuge X as X: in the system 1 leads to an electron deficient species 2 which can quench itself in more than one way (Eqn. 1). Fragmentation predominates in cases where the electrofuge $Y-C^+$ is stabilised by p-electrons on Y, i.e., oxygen, nitrogen or sulphur atoms or π-electrons from olefinic or aromatic systems. Therefore, typical electrofugal fragments are

carbonyl compounds, carbon dioxide, imonium, carbonium or acylium ions etc. The displacement of electrons from X to C in $Y-\overset{|}{C}^{+}$ (by inductive or conjugation effects) also promotes the release of unsaturated fragment 3. The latter, though usually olefinic, can also be an acetylene, an imine or a nitrile depending upon the structure of the starting material.

3. MECHANISM AND STEREOELECTRONIC REQUIREMENTS

Fragmentation reactions have been shown to take

place either by a two-step carbonium ion mechanism or by a synchronous mechanism. The course of the fragmentation reaction depends on the structure, configuration and conformation of the substrate.

3.1 The two-step Carbonium Ion Mechanism

The first step of this mechanism is the ionization of the substrate to form a free carbonium ion and the second step is the cleavage of the C — C bond(Eqn. 1). This mechanism becomes operative in cases where the tendency to ionize the substrate is great, e.g., when a tertiary and hence a particularly more stable carbonium ion is formed.

The support for this mechanism is provided by the solvolysis of 3-chloro-N,N-3-trimethylbutylamine(4) with 80% aq. ethanol which gives 38% of fragmentation product i.e., isobutene (3), 37% of the aminoolefins 6 and 7 (formed by elimination) and 22% of the alcohol 8a and the corresponding ethyl ether 8b (formed by substitution).

The formation of several products suggests the

(CH3)2N-CH2-CH2-C(CH3)2-Cl
4
(CH3)2N-CH2-CH2-C+(CH3)2
A
CH2 = C(CH3)2 + (CH3)2N=CH2
5
Fragmentation
38%
(CH3)2N-CH2-CH=C(CH3)2+
6
(CH3)2N-CH2-CH2-C(CH3)=CH2
7
Elimination
37%
(CH3)2N-CH2-CH2-C(CH3)2-OR
8a : R=H
8b R=C2H5
Substitution
22%

FIG. 1

9
A
(10a)
Fragmentation
62%
(10b)
Substitution
30%
(10c)
Elimination
6%

FIG. 2

formation of an intermediate γ-amino carbonium ion (A).

Another example of the two-step carbonium ion mechanism is provided by 3-(chlorodimethyl)quinuclidine(9) which reacts to give 62% of the fragmentation product (10a) together with 30% of the substitution product (10b) and 6% of the elimination product[5](10c) (FIG. 2).

3.2 The Synchronous Mechanism

In the one-step mechanism, the cleavage of C -C bond is accompanied by simultaneous loss of X^- ion from the α-carbon atom. Since five atomic centres of one molecule are involved in the transition state, it was expected that this mechanism would have rigorous structural and stereo-electronic requirements. That the synchronous mechanism operates only if both C -X bond and C -C bond are anti-periplanar to each other was indicated, when fragmentation was attempted with stereoisomers 11 and 12 of 3-chlorotropane. The 3-chloride(11), which satisfies the above condition, gave only the fragmentation product 13; whereas the 3 - chloride 12 furnished only substitution and elimination products[6] (FIG. 3).

CH3
N
Cl
11
CH3
N
12
Cl
No fragmentation
CH2-CH=CH2
N
CH3
13

FIG. 3

CH3
CH3
N
OTs
14
CH3
CH3
N
OTs
CH3
CH3
N
OTs
15

FIG.4

This is further corroborated by the observation that cis-dimethylaminocyclohexyl p-toluene sulphonate (14) is solvolysed 39 times faster than its trans-isomer 15. Also the conversion in fragmentation is 99% in the former compared to 28% in the latter[7].(FIG. 4).

Similarly, Marshall and coworkers[8] have recently shown that the fragmentation of boronate esters 67 is highly stereoselective and shows no tendency to proceed via a free cation[8]. (see section 4.8).

4. ALKENE FORMING FRAGMENTATION REACTIONS

The cleavage of carbonium ions into smaller cationic fragments was recognized as early as 1933 as a possible secondary reaction of carbonium ions[1], but the reaction has gained importance comparatively recently. The reaction can be illustrated by the fragmentation of following systems:

4.1. Fragmentation of γ-branched Alcohols and Halides

When alkyl halides or alcohols with α and γ-branching are subjected to solvolysis, they undergo fragmentation to give an olefin and a carbonium ion. (Eqn. 2).

(Eqn. 2)

The carbonium ion then undergoes further elimination or substitution depending on the reaction conditions. As expected for a carbonium ion mechanism, these fragmentations occur to a greater extent for tertiary substrates; to a smaller extent for secondary substrates and essentially not at all for primary substrates (even with γ-branching), although they have been shown to occur in primary substrates when a very stable carbonium ion, eq. 16, could be expelled[9].

16

4.2. Fragmentation of γ-Hydroxy-Alcohols, Halides and Sulphonates. $\left[HO-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}-X\right]$

In many olefin-forming systems, the electron-donating part is a hydroxyl group or an alkoxide oxygen atom.

In these cases the electrofugal fragment is a carbonyl compound; for instance, the acid catalysed fragmentation of tetramethyl-2,4-pentandiol (17) into acetone and dimethyl-2-butene (18)[10]

17 18

In unsymmetrical 1,3-diols, the nucleofugal fragment is usually formed from the hydroxyl group on the more highly substituted C-atom, as is shown by the exclusive formation of benzaldehyde and 1,1-diphenylethylene when 1,1,3-triphenyl-1,3-propanediol(19) is heated with acid. This suggests that the fragmentation proceeds *via* the more stable carbonium ion 20[11].

19

Fragmentation can also occur *via* the decomposition of diazonium salts, e.g. 22, as in the deamination of γ-aminoalcohol (21) with nitrous acid[12]. The yields vary, and depend on the nature of substituents and stereochemical factors.

Similarly, γ-hydroxy-halides and tosylates are solvolysed under suitable conditions to undergo fragmentation to give olefins and carbonyl compounds. For instance, γ-hydroxy-tosylate (23) is cleaved to 24 when treated with strong base like potassium tertiary butoxide, the reactive species being the anion 23a[13] (FIG. 5). In such cases the fragmentation is also of preparative value, since it permits the stereospecific synthesis of medium-sized unsaturated rings that are otherwise difficult to obtain.

Similarly, γ-hydroxy-amino compounds 25 and 26

fragment to unsaturated aldehydes 27 and 28 by flash thermolysis[14].(FIG. 6).

4.3 Fragmentation of β-keto-Halides and tosylates

Aldehydes and ketones bearing a nucleofugal group in the β-position can be cleaved into acids and olefins by treatment with an alkali. (Eqn. 3).

X = Cl, OTs

This reaction is observed in particular when the usual 1,2-elimination of HX with the formation of the α,β-unsaturated carbonyl compound is difficult or prevented by structural factors. Thus, it has been shown that on treatment with sodium hydroxide, 29 or 30 breaks down via the adduct 31 into benzoic acid (32) and isobutene[15].

29 X = Cl

30 X = $N(CH_3)_3I^-$

31

32

This is an example of a compound that becomes fragmentable only after an active electrofugal group has been formed by the addition of a nucleophile.

Attempted reduction of 4-methyl-3-oxo-bicyclo[2,2,2]-octyl-1-tosylate (33) with Lithium Aluminium Hydride(LAH) results in its fragmentation to 4-methylene cyclohexane derivative (35), (reduced further to the corresponding alcohol) formed via. anion (34) which is an intermediate in the reduction[16].(FIG. 7).

Similarly, attempted dehydrohalogenation of γ-iodo-keto ester (36) with methanolic sodium methoxide results in its fragmentation to the olefinic diester (37) and on

FIG. 5

FIG. 6

FIG. 7

similar treatment of the bromoester 38 with NaCN in HMPA forms an olefinic ester 39[17]. (In both cases, the product arises from a nucleophile-induced fragmentation). (FIG. 8).

In the same way, keto-tosylate (40) fragments into 41 on treatment with a base[18], via the intermediate 40a[17] (Fig. 9).

4.4. Fragmentation of γ-Amino-Halides and Sulphonate $[NH_2-C-C-C-X]$

The most thoroughly studied fragmentation reactions include those of γ-amino halides and sulphonates. The γ-dialkyl amino halides undergo fragmentation when heated with water to give an olefin and an imonium salt which under the reaction conditions is hydrolysed to an aldehyde or a ketone (Eqn. 4).

$$R_2N-C-C-C-X \xrightarrow[\triangle]{H_2O} -C=C- + R_2\overset{+}{N}=C- \longrightarrow R\dot{N}H_2 + -C=O \qquad \text{(Eqn. 4)}$$

$X = Cl, OTS$.

36 X=I

38 X=Br

37

39

FIG. 8

40

41

FIG. 9

42

43

44

FIG. 10

The solvolysis of N-(3-chloro-3-methylbutyl) dimethyl amine(4) in 80% aqueous ethanol leads to the fragmentation product isobutylene in about 38% yield[4] (FIG.1).

Under solvolytic conditions, cyclic γ-amino halides such as 4-chloro-1-methylpiperidine (42)[19], 4-bromoquinitelidine (43)[20], as well as N-methyl-5-tosyloxy-trans-deca-hydroquinoline(44)[21], undergo quantitative fragmentation to imonium salts or their hydrolysis products, i.e. amino olefins, aldehydes, and ketones(FIG-10).

γ-Dialkylamino-alcohols do not give fragmentation products since for ionization the —OH group must be converted to $-\overset{+}{O}H_2$, and this would convert $-NR_2$ to $-\overset{+}{N}R_2H$ which does not have the unshared pair of electrons to form the double bond with the carbon atom.

4.5 Fragmentation of β-Haloimines

[-N=C-C-C-X]

Imines containing nucleofugal group in the β-position also become fragmentable after addition of a nucleophile. Thus the 3H-indole derivative(45) reacts with sodium hydroxide to form the unsaturated

nine-membered lactam 46[22] (FIG-11).

Similarly, β-hydroxyaldimine (47) undergoes fragmentation with the formation of cyclohexylformamide and α-methylstyrene 48[23].

47 48

4.6 Fragmentation of [-C-C-C-C-X] Systems

This class includes fragmentations induced by the formation of a carbanionic centre on the δ-carbon atom. The cleavage of 1,4-halides by zinc, or an alkali metal possibly follows this path[24]. In the reaction of cis and trans- 1,4-dibromocyclohexane (49) with zinc, 1,5-hexadiene is exclusively formed (FIG 12).

45

46

FIG.11

49

FIG.12

50

51

FIG.13

Another example is provided by the fragmentation of trans-8-bromocamphor hydrazone (50) to limonene (51) in the Wolff-Kishner reduction[25] (FIG 13).

Marshall and co-workers[26] reported a similar fragmentation of a malonyl tosylate 52 which on treatment with excess sodium t-butoxide afforded the unsaturated ester (53) (FIG 14).

Similarly, 1,3-dithiane (54), when treated with a base, fragments to (55)[27]. In this fragmentation, a 1,3-dithiane anion helps to stabilize the electrofugal group (FIG 15).

4.7 Fragmentation of β-Halocarboxylic Acids:

[HOOC-C-C-X]

Many β-halocarboxylic acids undergo decarboxylation to olefins when their salts are heated in solution. One of the earliest examples is the formation of styrene (57) from 3-bromo-3-phenyl propionic acid (56) in aqueous soda[28].

(56) X = Br 57

X = NH_2

Similarly, the β-amino acid 58 undergoes spontaneous decarboxylation to form α,β-unsaturated carbonyl compounds[29].

58 59

In principle, any carboxylic acid having a carbonium ion center in the β-position can undergo decarboxylation as is shown by the acid catalysed fragmentation of the α,β-and β,γ-unsaturated acids 60 and 61. In

both cases, the olefinic double bond is protonated to form the β-carbonium ion 62 , which fragments into olefin 48[30].

The same is true of the decarboxylation of salts of α,β-unsaturated acids such as 63 with bromine to bromoolefin (64) . The reaction presumably proceeds *via* a bromonium ion 63a[31] .

63 63a 64

4.8 Fragmentation of Homoallylic Tosylate:

Marshall and co-workers have demonstrated through a series of papers, the application of this fragmentation reaction for the synthesis of medium sized rings. Homoallylic sulphonates 65 on hydroboration give the boronate derivatives (66) which cleave on being refluxed with sodium hydroxide to the corresponding olefins.

52 53

FIG. 14

54 55

FIG 15

67 67a 68

FIG. 16

70 69 71

FIG. 17

Hydroboration of the unsaturated methanesulphonate(67) and subsequent hydrolysis of the monoalkyl borane with sodium hydroxide brought about the fragmentation to provide the diene 68 in 90% yield[32] (FIG 16). The above bicycloboronate ester (67a) undergoes the cleavage of the more substituted internal bond to cyclodecane system. This is in contrast to fragmentation of perdehydroquinolyl-tosylate 69 to cyclohexene derivative 71 which forms through the cleavage of an external bond. Marshall and co-workers[33] have later established that the fragmentation of perdehydroquinolyl tosylate (69) occurs through an internal cleavage to 70 which undergoes 'Cope rearrangement' to give the ultimate product 71(FIG 17).

Similarly acyclic 1,5-diene 73 has been obtained by fragmentation of cyclohexyl boric acid mesylate 72[28] (FIG 18).

5. ALKYNE FORMING FRAGMENTATIONS

These fragmentations are not as common as the olefin forming fragmentations, probably because in these cases the nucleofugal group is attached to an unsaturated C-atom, and therefore ionizes with difficulty. In general, α,β-unsaturated β-haloacids or carbonyl compounds fragment to the corresponding alkynes on treatment with a base.

5.1 Fragmentation of β-Halo acrylic acid Salts

$$[R-\underset{\underset{Br}{|}}{C}=C-CO_2^-]$$

Salts of β-haloacrylic acids are dehalocarboxylated on heating, to give acetylenic compounds. For instance, β-bromo cinnamic acid (74) decomposes into phenyl acetylene (75) on heating[34].

$$\underset{\underset{Br}{|}}{C_6H_5-C}=CH-COO \longrightarrow C_6H_5C\equiv CH + CO_2$$

74 75

5.2 Fragmentation of β-Halo-α,β-Unsaturated Carbonyl Compounds [C=C-C-R]

The β-halo-α,β-unsaturated carbonyl compounds become fragmentable only upon addition of a nucleophile. Thus, in the presence of aq NaOH, β-haloacrolein (76) decomposes into formic acid and alkyne (77).

76 77

5.3 Fragmentation of α,β-Epoxy Hydrazones:

Cyclic α,β-unsaturated ketones can be cleaved by treating their epoxytosylhydrazone derivatives with a base to give acetylenic ketones. The reaction was used to prepare ~~of~~ acetylenic aldehyde 79 from epoxycyclohexanone tosylhydrazone derivative (78)[34] (FIG.19).

OTs
CH3
H3C
CH3
CH3
H3C
CH3
72
73

FIG.18

NHTS
N
O
R
78
CH
C=O
R
79

N-N
Ph
O
80
C-CH3
CHO

FIG. 19

FIG. 20

Similarly hydrazone (80) prepared from epoxy ketone and ring substituted N-aminoaziridines undergo similar fragmentation when heated[35] (FIG 14).

Tricyclic tosylhydrazone (81) on treatment with base fragments to monocyclic alkyne (82) and allene (83). The mechanisms for the formation of 82 and 83 have been proposed to implicate carbene intermediate 84[36] (FIG 20)

6 ALLYLIC ALCOHOL AND ALLYLIC HALIDE FORMING FRAGMENTATIONS

Sukh Dev and coworkers[38] reported a novel fragmentation reaction of homoallylic alcohols under conditions of electrophilic addition of chlorine or acid-catalysed ring opening of the corresponding epoxides. In generalised terms, this fragmentation can be depicted as shown in Eqn. 5.

Eqn. 5

The reaction differs from Grob fragmentation in producing halides or alcohols; instead of olefins and in appropriate cases, this can be of distinct value for synthetic operation.

Treatment of 85 and 86 with 1 mole equivalent of chlorine in presence of excess of lithium carbonate yields the fragmented product 87 . Similarly, exposure of epoxides (88) to a 0.5% $HClO_4$ in 90% aqueous dioxane furnished in almost quantitative yield, a mixture of epimeric alcohols (89) (FIG 21).

Likewise, the homoallylic alcohol 90 on an exposure to chlorine yields (90%), the expected chloroaldehyde (91) which was characterised by reduction (LAH) to the known α-campholenic alcohol 92[39] (FIG 22).

85 R_1=H, R_2= OH

86 R_1= OH, R_2=H

87

88

89

FIG. 21

90

91

92

FIG.22

The substrates investigated for this fragmentation are all based on bicyclo [2,2,1] heptane system ; more examples of this type of fragmentation and geometrical requirements of this reaction are discussed in the next Chapter.

7. APPLICATION OF FRAGMENTATION OF REACTIONS IN ORGANIC SYNTHESIS

The Grob fragmentation has been put to wide application and has been used for the synthesis of many natural products.

The key reaction in the sequence of the synthesis of caryophyllene (93) by Corey et al[40] is the base catalyzed fragmentation of tricyclic precursor A (FIG-23).

The synthesis of nootkatone 94[41] is based on acid catalyzed fragmentation of the intermediate A to a 4-substituted cyclohexenone, which undergoes ring closure in formic acid (FIG 24).

The total synthesis of Byssochlmic acid (95) involved the transformation of intermediate A to a substituted nine membered ring by formation of the oxime, followed by fragmentation with phosphorous-oxychloride pyridine at $0^{o}C$ to olefinic nitrile[42] (FIG. 25).

FIG. 23 : SYNTHESIS OF CARYOPHYLLENE (93)

FIG. 24 : SYNTHESIS OF NOOTKATONE (94)

De Mayo's approach to the synthesis of β-Himachalene (97) is based on his discovery that acetyl acetone undergoes photochemical cyclo addition with 2,2-ethylenedioxycyclohexene yielding an intermediate cyclobutanol , which can fragment to δ-diketone 96[43] (FIG-26).

Another synthesis of β-Himachalene 97 also involved the fragmentation of tricyclic sesquiterpene bromide 98[44] (FIG 27).

Similarly, ketone 99, an intermediate in a synthesis of Juvenile hormone[45], was obtained stereospecifically from the bicyclic compound 98 using two successive fragmentation steps. The geometry of the intermediates A and B is such as to allow easy fragmentation at each stage (FIG 28).

Sukh Dev and coworkers[46] reported the synthesis of sceolongifolene diol 100 , from hydroxyepoxide A utilizing the fragmentation reaction of homoallylic alcohols (FIG 29).

FIG 25: SYNTHESIS OF BYSSOCHLMIC ACID (95)

FIG. 26: SYNTHESIS OF β-HIMACHALENE (97)

FIG 27 SYNTHESIS OF β-HIMACHALENE (97)

FIG 28 : SYNTHESIS OF JUVENILE HORMONE

Sakakibara et al reported the one step synthesis of diterpenoid Leucothol-D 102[47] from Grunotoxine 101 by fragmentation with palladium acetate in methanol at room temperature (FIG 30).

FIG. 29 SYNTHESIS OF SECOLONGIFOLENEDIOL (100)

FIG 30. SYNTHESIS OF LEUCOTHOL-D (102)

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