SUMMARY

The research work being reported in this thesis has been divided into six chapters :-

CHAPTER-I

This chapter comprises a short review on the action of N–bromosuccinimide on triterpenoids and steroids. It has been divided into four sections **A, B, C, D**.

Section A deals with a short review on the action of N-bromosuccinimide on triterpenoids and steroids.

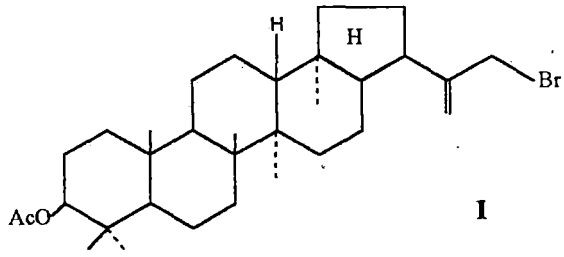
Section B deals with a short review on bromine and NBS oxidation of saturated hydrocarbon friedelane.

Section C deals with a short review on oxidation of allylic methylene to carbonyl group.

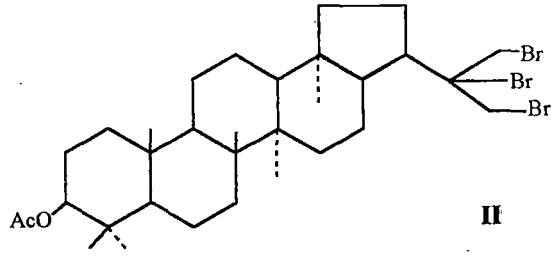
Section D deals with a short review on bromination and dehydrobromination.

CHAPTER-II

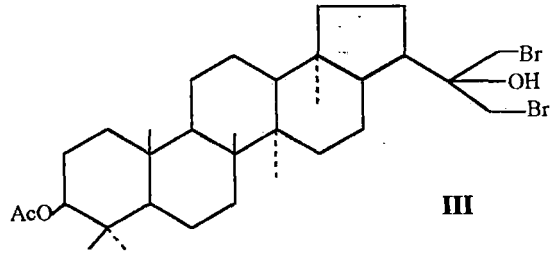
This chapter deals with the result and discussion of the reaction of NBS with moretenyl acetate in presence of dimethyl sulphoxide. Compounds **(I)**, **(II)**, **(III)**, **(IV)** and **(V)** have been isolated and characterized.



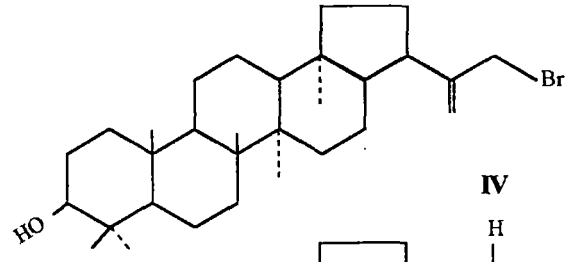
I



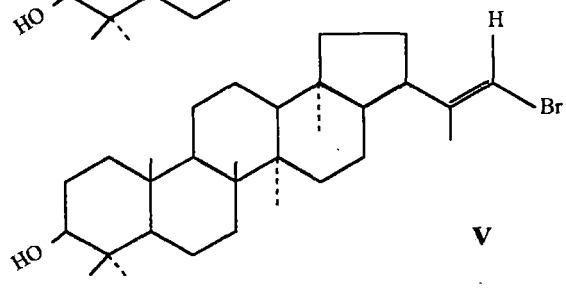
II



III



IV



V

Mass spectrum value M^+ (548, 546) and independent analysis established the molecular formula of the compound (**I**) as $C_{32}H_{51}O_2Br$ m.p. 224 - 3°. The compound in its IR spectrum showed peaks at 1720, 1245 cm^{-1} which indicated the presence of methylenic double bond. The compound gave positive Beilstein test for halogen. TNM test for the compound was positive that indicated the presence of olefinic double bond. The compound in its ^1H NMR spectrum showed peaks at δ 0.69, 0.76, 0.84, 0.94, 0.97, 1.25, 2.03, 4.1, 4.45 and 4.9 - 5.9 ppm. The six values δ (0.69 - 1.25) represented six tertiary methyls on saturated carbon. The peak at δ 2.03 ppm indicated the presence of acetoxy methyl at C -3. The proton geminal to acetoxy group appeared at δ 4.45 ppm as triplet. The peak at δ 4.1 ppm. that appeared as AB quartet indicated two protons of methylene group containing bromine atom. The peaks in the region δ 5.9 and 4.9 ppm. indicated the existence of two olefinic protons. The structure (**I**) has been proposed for compound with molecular formula $C_{32}H_{51}O_2Br$.

Elemental analysis and mass spectrum established the molecular formula of (**II**) as $C_{32}H_{51}O_2Br_3$ m.p. 241 - 2°, $[\alpha]_D$ + 32.14°. The compound gave negative T N M test but responded to positive Beilstein test. IR spectrum showed sharp peaks at 1725, 1245 cm^{-1} indicating the presence of C-3 acetoxy group (-0-$COCH_3$) in the compound. ^1H NMR spectrum of the compound showed a pair of AB quartets superimposed to each other in the region between δ 3.8 - 4.2 ppm. A plot of this region in COSY spectrum showed that this is a super imposition of two AB pairs resulting from two -CH_2 groups containing bromine atoms.

This was confirmed by adding C_6D_6 to the solution and reducing the spectrum.

The two groups were shifted differently and two separate AB pairs were seen at δ 3.89 (J = 16, 2HZ) and δ 4.04 (J = 20, 3HZ) ppm of unequal coupling constant. Peaks at δ 0.75, 0.84, 0.86, 0.87, 0.96 and 1.01 ppm clearly indicated the presence of six tertiary methyls in the compound. ^{13}CNMR spectrum of (**II**) showed the presence of 32 carbon atoms in the region δ 170- 15 ppm. APT showed seven quartets inclusive of acetoxy methyls, twelve triplets for 12 $>CH_2$ two of which were for the $-CH_2Br$ (δ38.86, 40.2 ppm) six doublets (δ 45 .8, 48.43, 50.17, 54.17, 55.17, 80.89), the one for methine carbon (δ 80.89) and seven singlets (δ 36.99, 37.76, 41.52, 41.76, 45.36, 76.05, 170.99) for tertiary carbons, the one at δ 76.05 ppm being for carbon bearing a bromine atom. On the basis of IR, ^{1}H NMR and ^{13}C NMR structure (**II**) has been proposed for compound $C_{32}H_{51}O_2Br_3$.

Analysis and molecular weight determination by mass spectrometry (M^+645, 643, 641) showed the molecular formula of the compound (**III**) to be $C_{32}H_{52}O_3Br_2$ m.p. 258-9°, $[\alpha]_D$ + 25°. The TNM test was negative for compound (**III**). The compound showed IR peaks at 3360cm^{-1} (-OH), 1730, 1250cm^{-1} (-$OCOCH_3$). ^{1}HNMR spectrum of the compound showed the presence of six tertiary methyls on saturated carbons at δ 0.72, 0.84, 0.85, 0.86, 0.94 and 0.98, acetoxy methyl at δ 2.06 and carbinol methine proton (C- 3) at δ 4.45 ppm. It showed a pair of AB quartets centred at δ 3.5 and 3.72 (J = 10HZ) ppm, two singlets a δ 3.48, 3.66 ppm. typical of a pair of - CH_2Br without restricted rotation and another set of non-resolvable peaks in the regions δ 3.42 - 3.56 ppm. pairs had free rotation. This interpretation is confirmed by ^{13}C NMR data of the compound.

The total number of protons was counted as four, an indication that - CH_2Br is in three different geometry in which one pair had restricted rotation whereas the ther two The compound (**III**) in its ^{13}C NMR spectrum showed three singlets around δ 74.0 ppm. for one carbon, showing that this carbon contains an oxygen function in three different environment. The - CH_2Br carbons appeared around δ 21 ppm. as a cluster of six peaks showing once again three isomeric - CH_2Br carbons. A three lined peak for triplet carbon at δ 38 ppm. was also observed showing that this carbon is also affected differently probably by its anisotropic effect of different stereomeric - CH_2Br group. Thus from spectral data structure (**III**) has been assigned for the compound $C_{32}H_{52}O_3Br_2$.

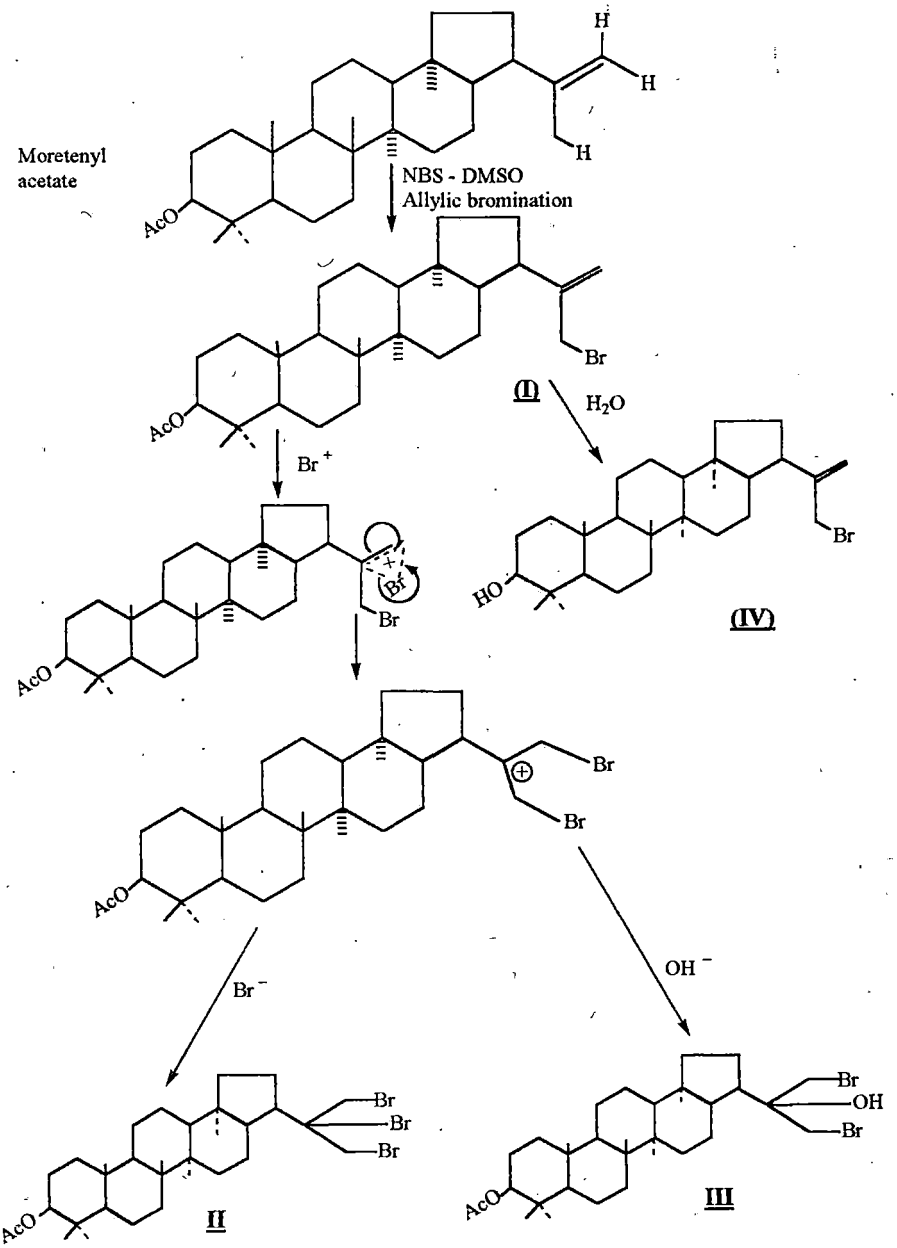
Elemental analysis and molecular weight determination by mass spectrometry (M^+ 506, 504) led to the molecular formula of (**IV**) as $C_{30}H_{49}OBr$. m.p. 238-9°. IR spectrum of the compound showed a characteristic peak at 3320 - 3286 cm^{-1} (-OH). 3040 - 60cm^{-1} (=CH_2) 1620 cm^{-1}. Thus the compound contains - OH group and a double bond. The compound is probably formed by allylic bromination and hydrolysis of acetoxy group at C - 3. From IR and mass spectra the compound $C_{30}H_{49}OBr$ has been assigned structure (**IV**).

Elemental analysis and mass spectrum value of compound (**V**) (M^+ 506, 504) led to its molecular formula as $C_{30}H_{49}OBr$, m.p. 206-8°. It gave positive TNM test and showed positive. Beilstein test for bromine. These observations indicated the presence of double bond and bromine it the molecule. ^1H NMR spectrum of the compound showed peaks at δ 0.64, 0.74, 0.88, 0.95, 1.52, 1.70 ppm. that indicated the presence of seven methyls as singlet. Of the seven methyls, one methyl appeared in the lower field at δ 1.70 ppm. The appearance of this methyl at δ1.70 ppm is due to its position on an olefinic carbon atom.

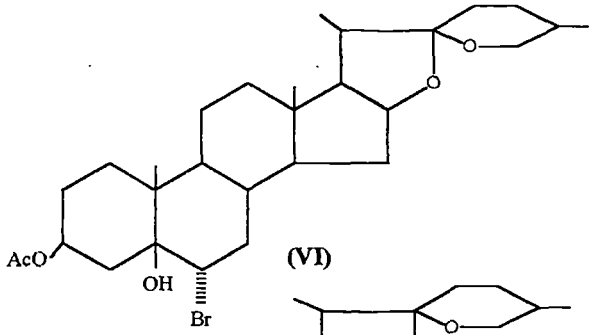
A vinyl proton appeared at δ 5.86 ppm. On the basis of these observations structure (**V**) has been assigned to compound $C_{30}H_{49}OBr$. This has most probably been formed by isomerisation followed by hydrolysis of the acetoxy group at C - 3.

The probable schematic mechanism of formation of **(I)**, **(II)**,**(III)**,**(IV)** is presented in the **Scheme A** below :-

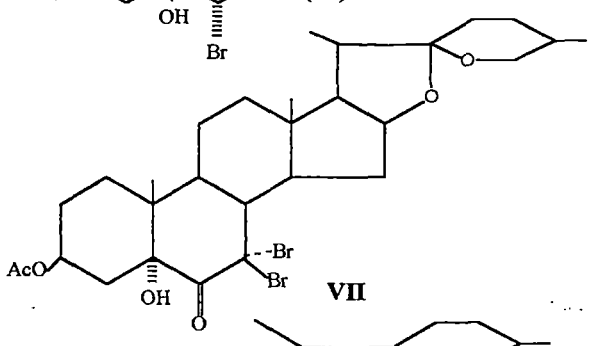
Scheme A



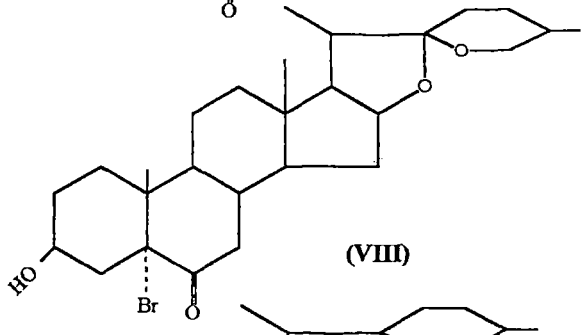
Chapter – III This chapter deals with the result and discussion of the reaction of NBS with diosgenin acetate in presence of dimethyl sulphoxide. Compound **(VI)**, **(VII)**, **(VIII)** and **IX** have been isolated and characterized.



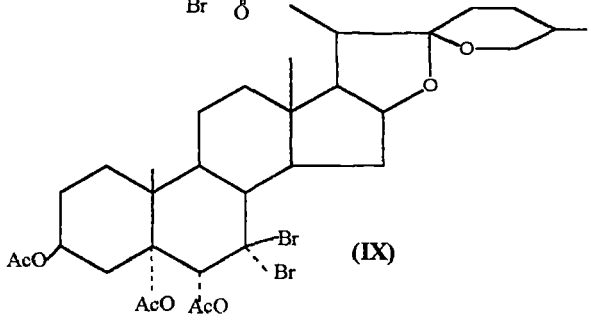
(VI)



VII



(VIII)



(IX)

Elemental analysis and mass spectrum established the molecular formula of **(VI)** as $C_{29}H_{45}O_5Br$. m.p. 230°C and $[\alpha]_D$ = 52.6°. The compound gave negative TNM test but gave positive Beilstein test for halogen. IR spectrum showed sharp peaks at 3350 cm^{-1} showing the presence of hydroxy group and at 1710 and 1240cm^{-1} indicating the presence of acetyl group in the compound.

The ^1H NMR spectrum of the compound contained two doublets centered at δ 0.81 and 0.92 ppm each pair integrated for three protons with same coupling constant (J = 6.5 HZ) for two secondary methyls, two singlets at δ 0.72 and 1.0 ppm. for tertiary methyls. One sharp singlet at δ3.00 ppm was due to the hydroxy proton whereas a proton that appeared as doublet centered at δ 4.51 ppm. with J value of 14HZ and 5HZ must be due to an axially oriented proton having one axial and one equatorial neighboring protons. The singlet like peak at δ 5.3 ppm was considered to be due to C - 3 methine proton suggested that acetoxy group is axially oriented in the compound and this could be possible only if A/B ring juncture is assumed to be *cis* fused.

^{13}C NMR spectrum of the compound showed 29 peaks and showed presence of 5-CH_3 carbons, 10 - CH_2 carbons 9 - C - H and 5 - C - Br carbons as quartets, triplets, doublets and singlets respectively.

Mass spectrum of the compound showed molecular ion peak M^+ at 554. The other peaks appeared at *m/z* 537, 525, 519, 455, 395, 377, 345, 298, 281,267, 139 (base peak), 105, 95, 69 and 67.

The structure **(VI)** has been assigned to compound $C_{29}H_{45}O_5Br$.

Spectral analysis and molecular weight determination by mass spectroscopy showed the molecular formula of **(VII)** as $C_{29}H_{42}O_5Br_2$ m.p. 220°C. The compound responded to positive test for halogen. The IR spectrum of the compound showed peaks at 3350cm^{-1} for hydroxyl , 1700 cm-^{1} for six membered ketone and 1240cm^{-1} for acetate group.

^{1}H NMR spectrum of the compound showed the presence of a triplet at δ3.35 ppm. due to equatorial hydrogen at C - 26. A quartet at δ 4.41 ppm. indicated axial hydrogen at C - 26. A multiplet at δ 3.47 ppm. was attributed to the presence of an axial hydrogen at C - 16. A triplet appeared at δ 2.76 ppm, a heptet at δ 5.03 ppm, two sharp singlets at δ2.01 ppm and 2.27 ppm respectively.

The mass spectrum of compound showed molecular ion peak at M^+ 630.Other peaks appeared at *m/z* 615, 568, 566, 531, 488, 473, 458, 374, 341, 296, 139 (base peak), 115, 69 and 55.

Thus from spectral analysis the compound $C_{29}H_{42}O_5Br_2$ has been assigned structure (**VII**).

Elemental analysis established the molecular formula of **(VIII)** as $C_{27}H_{41}O_4Br$. m.p. 188°C. The compound gave positive Beilstein test for halogen. The IR spectrum of the compound showed a peak at 3400 - 3650 cm^{-1} indicating the presence of hydroxy group.

^{1}H NMR spectrum of compound showed the presence of two doublets centred at δ 0.77 and 0.95 ppm with J value of 6.5Hz. The peak at δ 3.76 ppm. that appeared as a broad hump with coupling at half height of 10Hz is due to 3α-H geminal to hydroxyl grouping. A triplet at δ 2.75 ppm. is attributed to axial hydrogen at C-8. A quartet and a triplet appeared at δ 4.46 ppm. and 3.37 ppm. The two double doublets appeared at δ 2.69 ppm. and 2.73 ppm.

The mass spectrum of the compound showed molecular ion peak at M^{+}509. The other peaks appeared at *m/z* 451, 430, 415, 413, 402, 371, 359, 316, 287, 140, 139.

From spectral analysis the compound $C_{27}H_{41}O_4Br$ has been assigned structure **(VIII).**

Elemental analysis showed the molecular formula of **(IX)** as $C_{33}H_{48}O_8Br_2$ m.p. 205 - 206°C. The compound gave a positive Beilstein test indicating the presence of halogen in the compound. IR spectra of the compound showed peaks at 1710, 1230 cm^{-1} indicating the presence of acetoxy group.

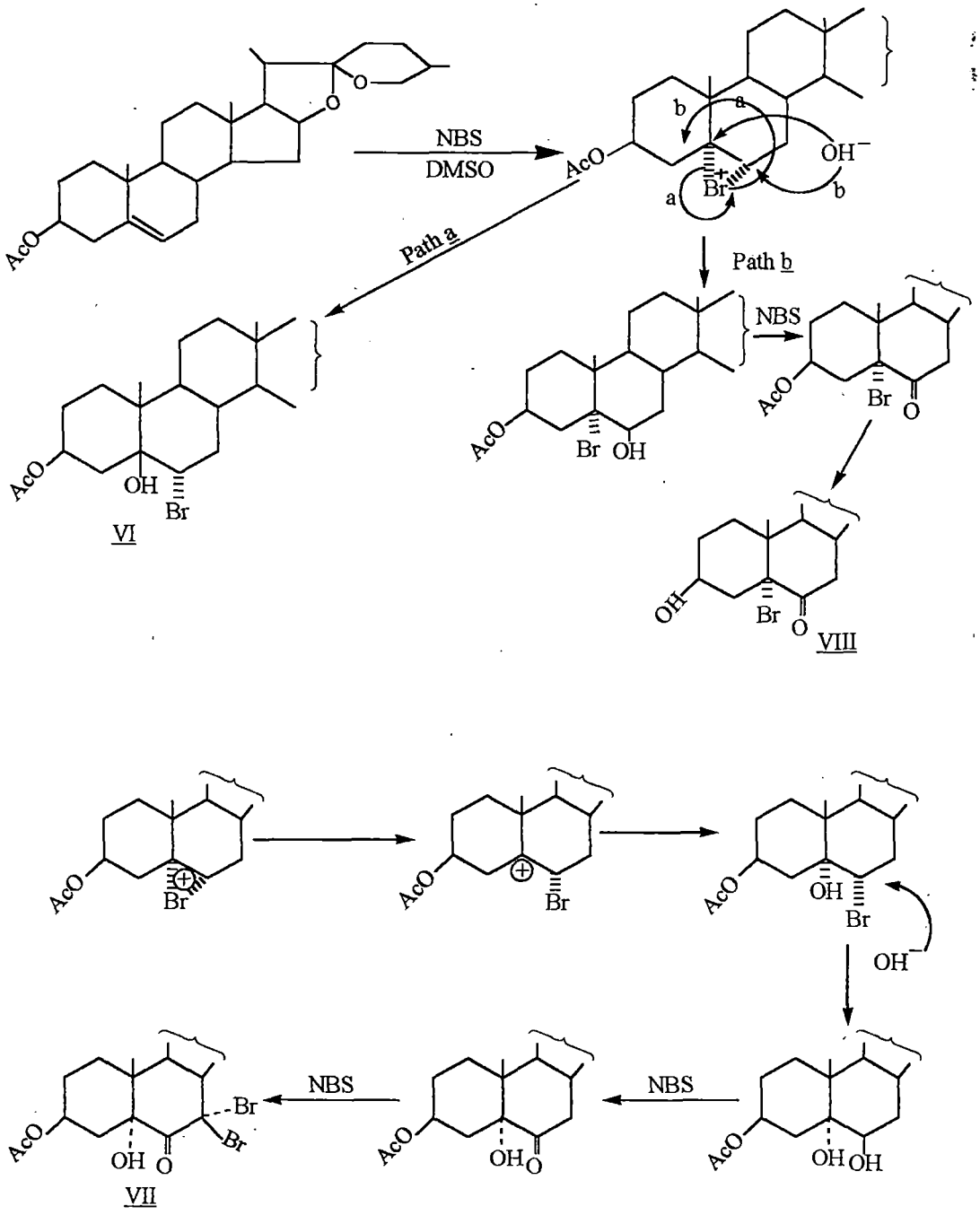
The ^{1}H NMR spectrum of the compound showed three sharp singlets at δ 2.08, 2.095 and 2.11 ppm. each one integrated for three protons indicating the presence of three acetate group in the compound. The heptet at δ 5.45 ppm. showed presence of 3α-protons. A singlet appeared at δ3.07 ppm.

The mass spectrum of the compound showed peaks at *m/z* 674, 668, 658, 656, 632, 618, 616, 614, 596, 594, 578, 576, 556, 554, 537, 535, 527, 525, 522, 476, 454, 412 (base peak), 397, 298, 139, 115, 69

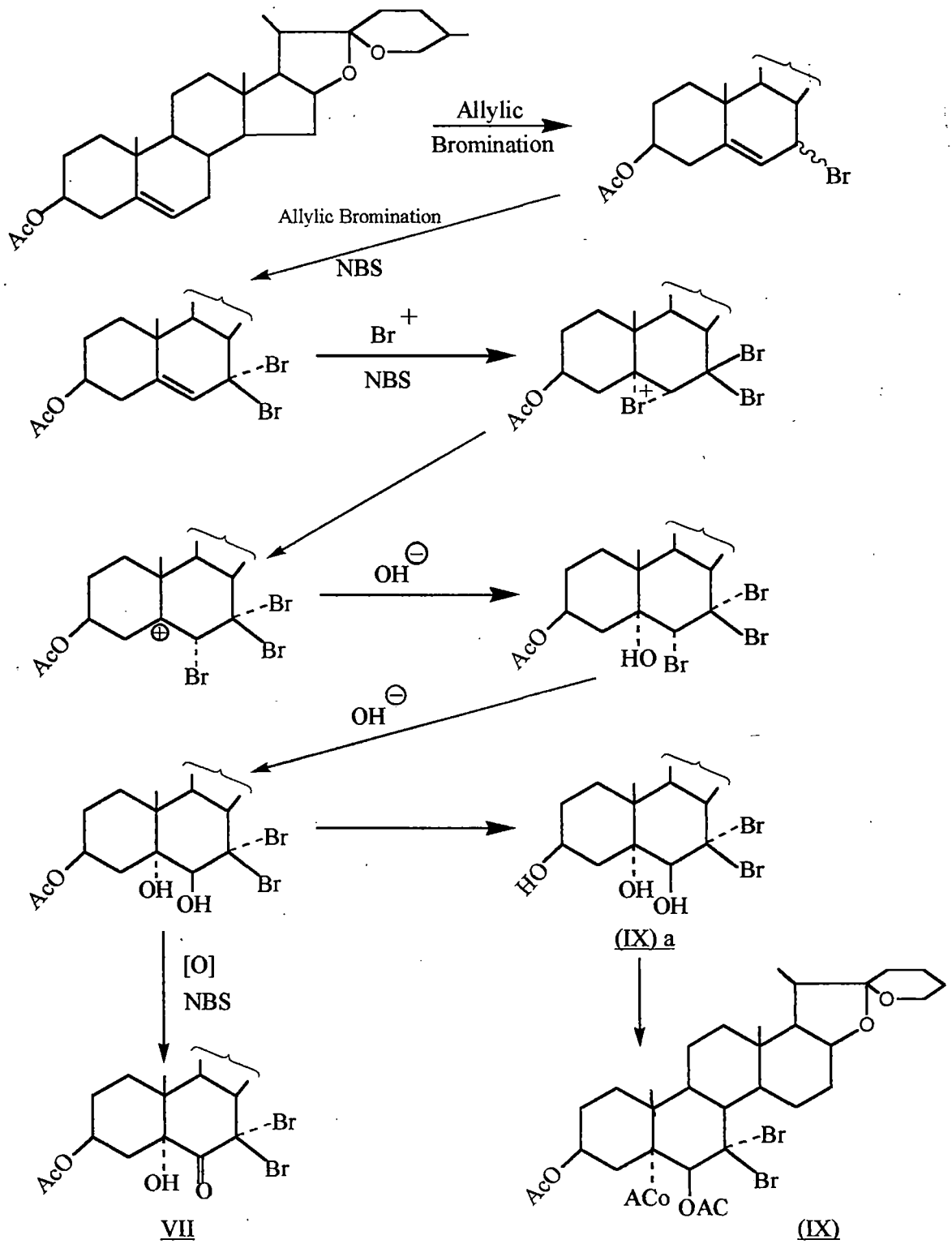
Thus from the spectral analysis compound $C_{33}H_{48}O_8Br_2$ has been assigned structure **(IX)**.

The probable schematic mechanism for formation of **VI, VII, VIII** and **IX** has been presented as in **Scheme B** and **Scheme C**.

Scheme B

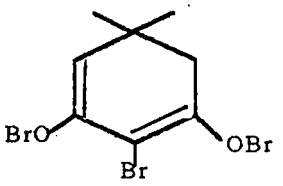


Scheme C


Allylic
Bromination
Allylic Bromination
NBS
Br +
NBS
OH
OH
[O]
NBS
(IX) a
(IX)
VII

Chapter IV

This chapter deals with the result and discussion of the reaction of NBS with dimedone in presence of dimethyl sulphoxide. Only a single product (**X**) was isolated and characterized.



X

Elemental analysis and mass spectrum established the molecular formula of (**X**) as $C_8H_9O_2Br_3$. The compound gave positive Beilstein test for halogen. The TNM test was positive indicating the presence of double bond in the compound.

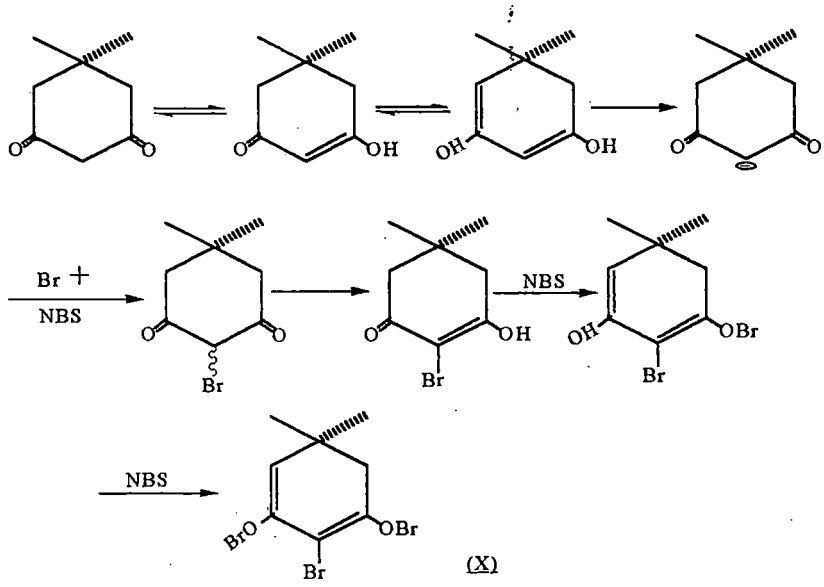
^1H NMR spectrum of the compound showed a singlet at δ 1.11 ppm. integrated for six protons. A doublet at δ 2.48 integrated for two protons showed a coupling constant of 10Hz is due to a geminal proton of methylene group and a singlet is due to an isolated olefinic bond.

^{13}C NMR of the compound showed the presence of a quartet at δ 28.03 ppm., a singlet at δ 32 ppm and another singlet at δ 101 ppm.

The mass spectrum of compound showed peaks at *m/z* 299, 218, 255, 203, 164, 162, 122, 83.

Thus from spectral analysis the compound $C_8H_9O_2Br_3$ has been assigned structure (**X**).

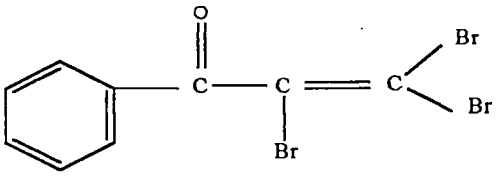
Scheme D



Chapter V

This chapter deals with the result and discussion of the reaction of NBS with benzoyl acetone in presence of dimethyl sulphoxide.

Only a single product compound(**XI**) was isolated and characterised.



XI

Elemental analysis established the molecular formula of (**XI**) as $C_9H_5OBr_3$. The compound gave positive Beilstein test for halogen. The TNM test was positive indicating the presence of double bond in the compound.

IR spectra of (**XI**) showed absorption at 1690cm^{-1}.

^1H NMR spectrum of the compound(**XI**) showed signals at δ 8.12, 7.62 and 7.48 ppm which was attributed to ortho, para and meta protons of benzene ring in the compound.

Mass spectrum of the compound (**XI**) showed molecular ion peak at M^+ 367. The other fragments appeared at *m/z* 262, 234, 218, 217, 188, 173, 172, 159, 146, 145, 122, 115, 106, 105 (base peak) 91, 77, 69, 65.

From spectral analysis compound $C_9H_5OBr_3$ has been assigned structure(**XI**).

The mechanism for the formation of compound (**XI**)can be drawn as in **Scheme E** below:-

Scheme E