

OXIDATION OF FRIEDELIN 30, TO FRIEDELAN 3→4 OLIDE 32 BY META CHLORO-PERBENZOIC ACID.

This method has been discussed in the experimental section of part-III of this thesis.

REDUCTIVE CLEAVAGE OF FRIEDELIN 3→4 OLIDE 1 WITH LITHIUM ETHYLENE-DIAMINE.

About 1.0 g of compound 1 was dissolved in 150 ml. of dry ethylenediamine and lithium metal 1.0 g was added in small pieces at intervals. The mixture was then refluxed over heating mantle for 2 hours and it was allowed to cool. Then excess lithium metal was destroyed by adding solid NH_4Cl and acidified with (1:1) HCl. The compound was then extracted with ether, washed with water till neutral and ether layer was dried with anhydrous Na_2SO_4 . Finally the solvent was distilled off to yield a gummy mass (0.6 g) which was chromatographed over silica gel column.

TABLE-I

Eluent	Fraction of 50 ml each.	Residue on distillation.
1. petrol	1-3	nil.
2. petrol-benzene (4:1)	4-6	nil.
3. petrol-benzene (3:2)	7-10	nil.
4. petrol-benzene (1:4)	11-13	nil.
5. benzene	14-16	nil.
6. benzene-chloroform	17-22	solid (0.6)

further elution did not afford any compound more.

The fractions 17-22 were collected together and crystallised from CHCl_3 -petrol, M.P. $173-4^\circ\text{C}$. identified as 3,4 seco friedelan 3,4 diol 3.

ANALYSIS REPORT.

Found : C 79.6 H 9.8%
 Calculated for $C_{30}H_{54}O_2$: C 80.7 H 10.2%

IR (nujol) : ν_{max} 3350 cm^{-1} . (broad) (2X-OH)
 fig.1

Mass : m/e 446 (M^+), 428, 413, 402, 397,
 273, 219, 205, 191, 163, 123,
 109, 95 (100).

fig.2

1H NMR ($CDCl_3$) : 0.87, 0.92, 0.94, 0.97, 0.96
 (δ in ppm.) 1.05, 1.15 (7s.21H, 7Xt- CH_3)
 1.18 (d, J= 7 Hz. - C_4H-CH_3)
 3.6 (m, 2H+1H, - CH_2-OH , -CH-OH)

fig.3

OXIDATION OF SECO FRIEDELIN 3,4 DIOL 3 BY JONES REAGENT.

0.2 g of compound 3 was dissolved in acetone (20 ml.) and Jones reagent was added dropwise with constant shaking till a orange colour persisted. The mixture was then kept at room temperature for 1 hour and diluted with water when a white solid mass separated out, which was filtered using suction, washed with water and finally dried.

It was crystallised from $CHCl_3$ -MeOH, M.P.273-4°C, found to be identical with friedelan 3→4 olide 1.

OXIDATION OF FRIEDELAN 3-OXO, 27→15 OLIDE TO FRIEDELAN 3→4, 27→15 DI-OLIDE BY META CHLOROPERBENZOIC ACID IN CHLOROFORM.

This step is discussed in the experimental portion of part-III of this thesis.

REDUCTIVE CLEAVAGE OF FRIEDELAN 3→4, 27→15 DI-OLIDE WITH LITHIUM ETHYLENEDIAMINE.

The compound 2 (1.0 g) was dissolved in dry ethylenediamine and 1.0 g of lithium metal was added in small pieces at intervals. The mixture was stirred with a magnetic stirrer for 3 hours at room

temperature and after the reaction solid NH_4Cl was added to destroy excess Li-metal. The mixture was than cooled, acidified with (1:1) HCl and extracted with ether, washed with water, dried with anhydrous Na_2SO_4 and finally the solvent was distilled off to give a gummy mass (0.6 g) which was difficult to purify by chromatography. As the IR spectrum indicated absorption in the region $3200-3600\text{ cm}^{-1}$. it was than acetylated with acetic anhydride-pyridine mixture. The acetylated product was than chromatographed with solvents as shown in table-II.

TABLE-II
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Eluent	Fraction of 50 ml each.	Residue on distillation
1. petrol	1-5	nil
2. petrol-benzene (1:4)	6-10	nil
3. petrol-benzene (2:3)	11-15	solid, (0.7 g)

The fractions 11-15 were crystallised from CHCl_3 -MeOH to furnish white crystalline compound identified as seco friedelan 3,4 dio-acetoxy-27 \rightarrow 15 olide 4, *M.P.* 241-42°C.

ANALYSIS REPORT.
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Found : C 72.40 ; H 10.36%
Calculated for $\text{C}_{34}\text{H}_{54}\text{O}_6$: C 72.56 ; H 10.37%

IR (nujol) : ν_{max} 1260 and 1750 cm^{-1} .
(-CO-, -CH₃-CO-O-)
fig.4

Mass : m/e 558 (M⁺), 514, 498, 471 (100)
425, 411, 369, 341, 315, 269.
fig.5

¹H NMR (CDCl_3) : 0.84, 0.86, 0.94, 0.96, 1.00
(δ in ppm.) 1.16 (7s, 21H, 7Xt-CH₃)
1.14 (d, J= 7 Hz. -C₄H-CH₃)
2.02 and 2.05
(2s, 6H, 2X-O-CO-CH₃)
3.96 (m, -CH₂-OAc)
4.34 (t, 1H, -CO-O-CH-)
4.83 (AB_q, 1H, -C₄H-CH₃) fig.6

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