PART-IV

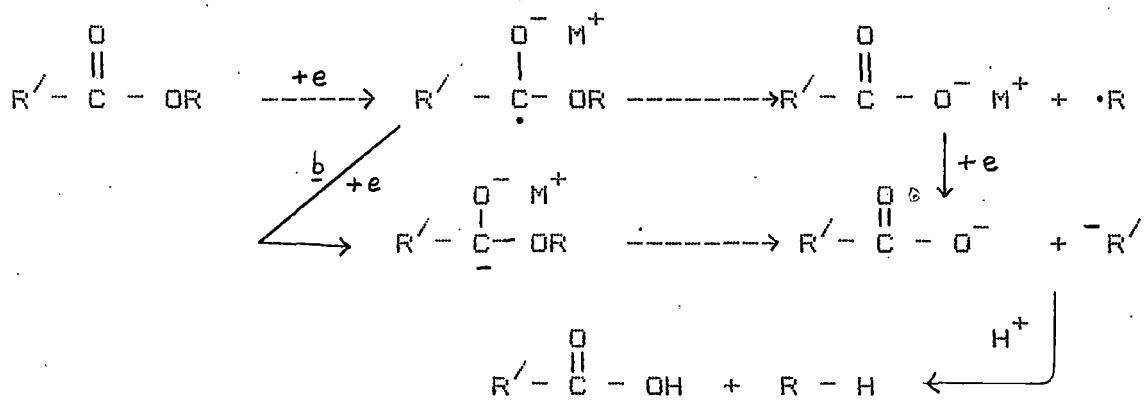
REDUCTIVE CLEAVAGE OF SEVEN MEMBERED LACTONE RING WITH LITHIUM IN ETHYLENEDIAMINE.

CHAPTER-I

A SHORT REVIEW OF LITHIUM ETHYLENEDIAMINE AS A REDUCING AGENT.

Reggel and co-workers[1] used Lithium(Li) Ethylenediamine (EDA) at 90-100°C as a potential reducing agent. Barton et al[2] showed that the esters of tertiary acids furnished acids on reduction with alkali metal amine. They proposed the mechanism as shown in scheme-I.

SCHEME-I



Likewise Sengupta et al[3] converted the C-17 carbomethoxy group of triterpenoids in to carboxylic acids on treatment with Li-EDA. Pradhan et al[4] performed a systematic study on the reduction of triterpenoids with Li-EDA and reported the wide applicability of this system in the reduction of ketones and aldehydes to alcohols, isopropenyl groups to isopropyl groups and esters of hindered acids to carboxylic acids, on a series of triterpenoids containing one or more of these functional groups as shown in the following table.

TABLE-I.

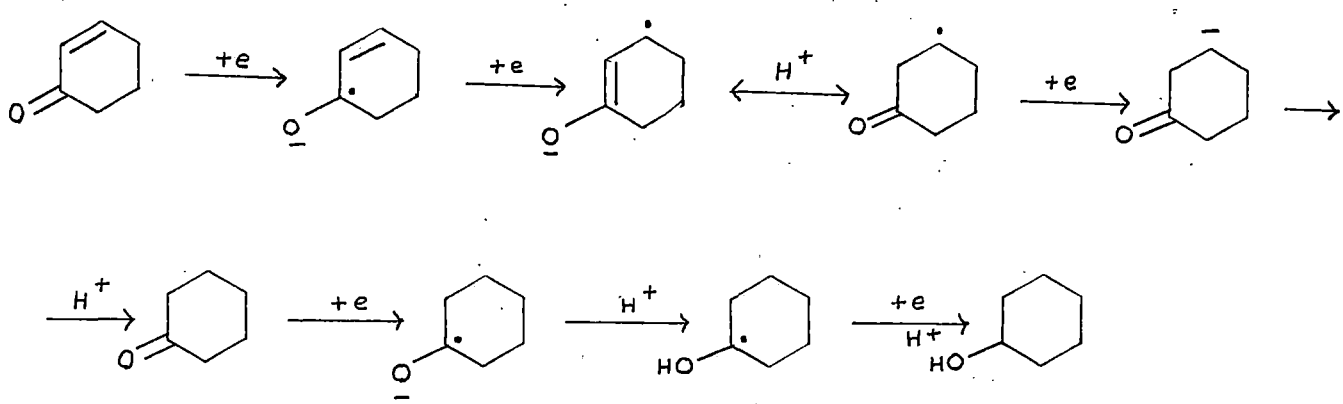
Reduction of ketones, aldehydes, isopropenyl group and esters of hindered carboxylic acids belonging to a series of triterpenoids.

ENTRY	TRITERPENOIDS	PRODUCTS	FUNCTIONAL GROUPS REDUCED
1.	*Lupanone*[6]	*Lupanol*[6]	C=O

2.	*Friedlin*[6]	*Friedelinol*[6]	C=O
3.	*Betulonic* aldehyde[6]	*Dihydrobetulin*[6] C=O,	CHO, $C=CH_2$
4.	*Oleanonic alhedyde*[6]	*Erythrodiol*[6]	C=O, CHO.
5.	*Lupeol*[6]	*Lupanol*[6]	$C=CH_2$
6.	*Moretenol*[7]	*Moretanol*[7]	$C=CH_2$
7.	*Lupenone*[6]	*Lupanol*[6]	$C=CH_2$, C=O,
8.	*Methyl aleuritolate*[9]	*Aleuritolic acid*[9]	COOMe.
9.	*Methyl trichadinate*[10]	*Trichadenic acid*[10]	COOMe
10.	*Methyl oleanonate*[8]	*Oleanolic acid*[8]	C=O, COOMe
11.	*Methyl Urosonate*[8]	*Ursolic acid*[8]	C=O, COOMe
12.	*Methyl betulonate*[6]	*Dihydrobetulinic acid*[6]	$C=CH_2$, CO, and COOMe.

Pradhan et al[4b] proposed the mechanism as shown in scheme-II.

SCHEME-II



Lactones may be considered as intramolecular esters which are formed by condensation of hydroxy groups with carboxylic acid functions of the same molecule.Therefore it was envisaged that lactone oxygen might be cleaved from its point of attachment by the action of Li-EDA..This application of lithium - ethylenediamine on lactones obtained from the bark of *Gynocardia Odorata*,[5] for reductive cleavage of their lactone rings had been sucessful.[5] The results of several such reactions are shown in table-II.

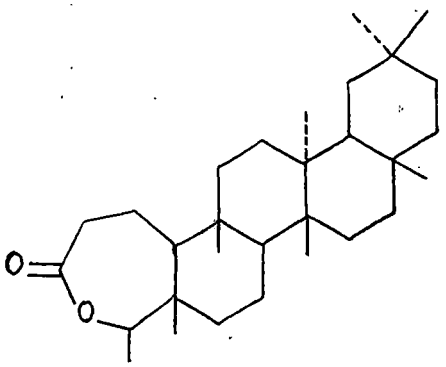
TABLE-II

Substrate lactones.	Product.	Yield.
1.3α-hydroxy friedelan 27→15α-olide.	3α-hydroxy friedelan 27-oic acid	80%
2.3α-acetoxy friedelan 27→15α-olide.	(a).Friedelan 27-oic acid.	40%
	(b).3α-hydroxy friedelan 27-oic acid.	40%
3.3-oxo-friedelan 27→15α-olide. (odolactone)	3α-hydroxy friedelan 27-oic acid	80%
4.Friedelan 27→16α -olide. (Iso-deoxyodolactone)	(a) Friedelan 27-oic acid.	20%
	(b) Friedelan 16α,27 -diol	60%
5. Friedelan 27→15α -olide. (Deoxyodolactone)	Friedelan 27-oic acid.	80%
6. 3β-acetoxy oleanan 18α-H,28→13β-olide.[8]	(a) Oleanan 18α-H,28 -oic acid.	40%
	(b) 3β-hydroxy oleanan-18α-H,28-oic acid.	40%
7. 3β-acetoxy oleanan 18α-H,28→19β-olide.[8]	(a) Oleanan 18α-H,28 -oic acid.	30%
	(b) 3β-acetoxy oleanan-18α-H,28-oic acid.	30%
	(c) Oleanan 18α-H,3β,19β, 28-triol.	15%

All the above products were characterised from their spectral data.

From the above observations it can be concluded that five membered lactones (1 to 7)on reductive cleavage with lithium-ethylene

diamine furnished the corresponding acids in all but one (7c) cases. So, presently the author was interested to see the effect of Lithium-ethylene diamine on seven membered lactone ring compounds and have chosen 3,4 seco-friedelan 3→4 olide 1 and 3,4 seco-friedelan 3→4, 27→15α di-olide 2 as the substrate.



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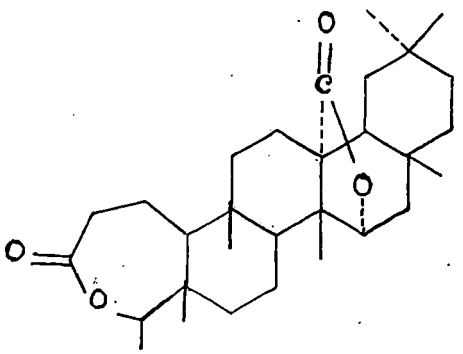

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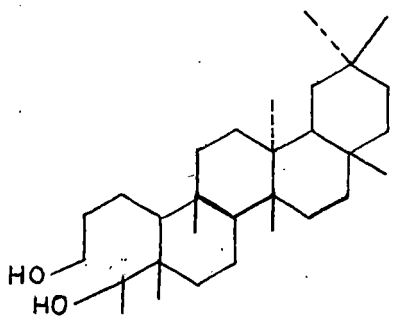
Both the compounds 1 and 2 on reduction with lithium ethylenediamine (the latter was carried out at room temperture to keep the five membered lactone moiety intact) produced diol exclusively.



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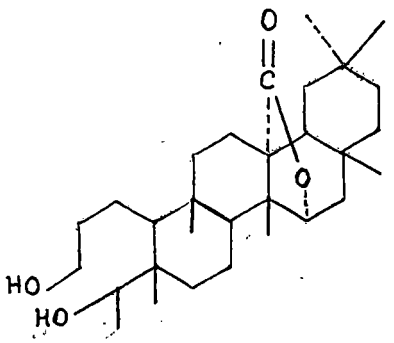

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The two diols 3 and 4 were identical with the products obtained from LAH reduction of compounds 1 and 2.