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Al-NiCl$_2$.6H$_2$O-THF : A New, Mild and Neutral System for Selective Reduction of Organic Functional Groups

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Abstract : A mild and neutral reducing system consisting of Al-NiCl$_2$.6H$_2$O-THF has been developed and reacted with a series of organic compounds containing different functional groups in order to evaluate its synthetic utility. It was observed that this system very efficiently reduces the α-enones to the saturated ketones, aromatic aldehydes and ketones to the corresponding alcohols, nitriles and nitroarenes to amines, acid anhydrides and acid chlorides to aldehydes, disulphides to thiols and epoxides to the corresponding alcohols. On the other hand isolated double bonds, carboxylic acids, esters, lactones, primary, benzyl and allyl halides, aliphatic aldehydes and ketones and aliphatic nitro compounds were found to remain inert to this system. Furthermore, the reducing properties of Al-NiCl$_2$.6H$_2$O in several other organic solvents were also studied.

Although a host of reagents are available in the literature for reduction of organic functional groups; the development of mild, neutral and selective reducing systems still attract a great deal of attention of the organic chemists. In recent years, reagents based on aluminium find wide application in organic chemistry because of their ready availability, easy handling and low cost. In two earlier communications[1,2] we described the utility of the system consisting of Al-NiCl$_2$.6H$_2$O-THF for selective reduction of α-enones and nitroarenes under mild and neutral conditions. During the course of these investigations we observed some interesting reducing properties of this system which prompted us to take up a systematic study of the reduction of a series of selected organic compounds containing various functional groups, the results of which are delineated in this article.

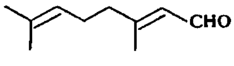
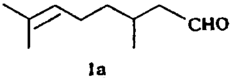
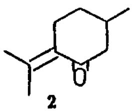
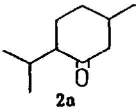
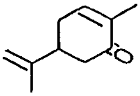
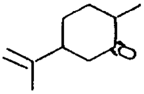
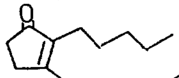
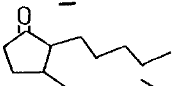
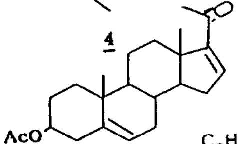
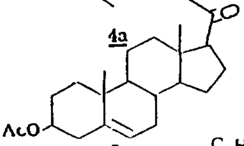
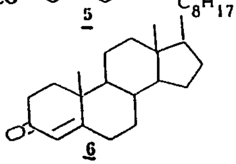
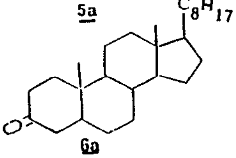
RESULTS & DISCUSSION

Moist $NiCl_2.6H_2O$ readily reacts with aluminium powder exothermically as such or in the presence of organic solvents such as THF, MeOH, EtOH, $CHCl_3$, Et_2O etc. with the formation of a black spongy mass. In this reducing system the substrate is taken in THF and poured into a solid mixture of metallic aluminium powder and nickel chloride hexahydrate. A vigorous exothermic reaction takes place which subsides automatically after some time (about ten minutes). Dilution followed by filtration of the reaction mixture constitute the simple work-up.

Reduction of α-enones

Selective reduction of the double bond of the α-enones without affecting the carbonyl is an important transformation in organic chemistry.

Table I: Reduction of the double bond of α-enone with $Al-NiCl_2.6H_2O$ in different solvent

α-enone	Reaction time(min)	Product[a]	Solvent	Yield[b] (%)
 1	10	 1a	THF Ether Methanol Toluene DMF	80 80 75 70 60
 2	10	 2a	THF Ether Methanol Toluene DMF	75 80 70 72 59
 3	15	 3a	THF Ether Methanol Toluene DMF	68 70 72 65 50
 4	10	 4a	THF Ether Methanol Toluene DMF	84 76 80 75 60
 5	5	 5a	THF Ether Methanol Toluene DMF	92 90 85 75 70
 6	5	 6a	THF Ether Methanol Toluene DMF	95 92 90 85 76

a, Products are characterised by IR,NMR and MS and by Direct comparison with authentic compounds.

b, Yield refers to the yield of pure isolated products of > 98% purity.

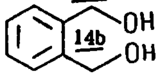
Quite a few number of reagents[3] are known to reduce the α-enone selectively but high cost of the reagents, stringent reaction conditions and poor selectivity of these procedures warrant the need for new and useful alternative procedures. We observed through entry 1 to 6 in Table 1 that with Al-NiCl$_2$.6H$_2$O in solvents like THF, diethyl ether, methanol, DMF etc. isolated double bond, carbonyl and ester function present elsewhere in the molecule is not effected.

Table 1 summarises the reduction results of α-enone chosen to determine the synthetic effectiveness of this reagent in diethyl ether, methanol, ethanol, toluene and dimethylformamide in addition to THF.

Reduction of carbonyl compounds with Al-NiCl$_2$.6H$_2$O-THF

Aliphatic cyclic and acyclic ketones, aliphatic aldehydes, carboxylic acids, esters and lactones were not reduced by this system even after prolonged exposure or excess use of the reagents. But when benzylaldehyde 8 was treated with this system for 10 minutes, it gave benzylalcohol 8a in

Table 2 : Reduction of carbonyl compounds with Al-NiCl$_2$.6H$_2$O-THF

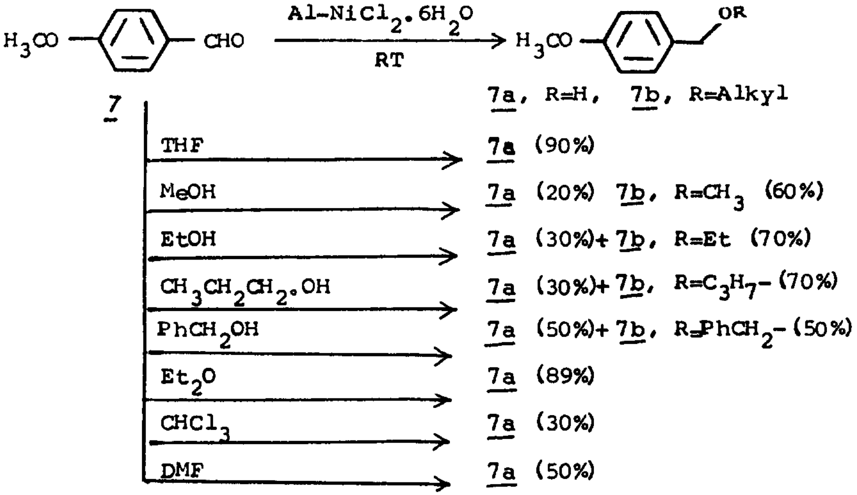
Substrate	Reaction time (min)	Product[a]	Yield[b] (%)
Benzaldehyde 8	10	Benzylalcohol 8a	92
Vanillin 9	10	Vanillylalcohol 9a	90
Acetophenone 10	10	Sec-phenethylalcohol 10a	75
m-Chlorobenzaldehyde 11	10	m-Chlorobenzyl alcohol 11a	80
o-Hydroxybenzaldehyde 12	10	o-Hydroxybenzyl alcohol 12a	85
Cinnamaldehyde 13	10	Cinnanyl alcohol 13a	60
Phthalic anhydride 14	10	Phthalaldehyde 14a	60
		 14b	20
α-Phenylbutiric anhydride 15	10	α-Phenylbutyraldehyde 15a	70
Benzoylchloride 16	10	Benzaldehyde 8	70
		Benzyl alcohol 8a	20
α-Phenylbutyroyl chloride 17	10	α-Phenylbutyraldehyde 17a	80
p-Chlorobenzoyl chloride 18	10	p-Chlorobenzaldehyde 18a	80
		p-Chlorobenzyl alcohol 18b	25

a, Products are characterized by IR, NMR, MS and by direct comparison with authentic materials.
b, Yields were determined by GLC

92% yield. Other examples or reduction of aromatic carbonyl groups are deleniated in Table 2. From Table 2 it is clear that ether, aromatic halide and even the double bond of the α-enone 13 was not affected in this reduction.

Reduction of aromatic carbonyl compounds with Al-$NiCl_2.6H_2O$ in several other solvents were also studied. Interestingly, it was observed that when alcoholic solvents were used in place of THF the major isolable products of reduction were not the corresponding alcohols of the substrates but the corresponding ethers. When other solvents like diethyl ether, toluene, DMF, $CHCl_3$ etc. were used the products were only the corresponding alcohols albeit in low yields. As a typical example anisaldehyde was reduced with Al-$NiCl_2.6H_2O$ in various organic solvents and the results[4] are furnished in Scheme 1.

The possibility of a Cannizzaro type reaction in case of reduction of aromatic aldehyde is eliminated on the basis of the fact that in all the cases (Table 2) no trace of the corresponding acids were detected in the reaction mixture.



Scheme-1

Reduction of acid chlorides and acid anhydrides

Carboxylic acids such as benzoic acid, esters of carboxylic acids such as methyl benzoate, and lactones are resistant to this reducing system. However, acid anhydrides such as phthalic anhydride 14 and α-phenyl butyric anhydride 15 were reduced to the corresponding aldehydes in excellent yields (Table 2). In case of phthalic anhydride 14 the dialdehyde 14a produced initially are partially reduced to the corresponding diols 14b. Acid chlorides were also rapidly reduced to the corresponding aldehydes. Thus benzoyl chloride 16, α-phenyl butyroyl chloride 17 and p-chlorobenzoyl chloride 18 were converted into benzyldehyde 8, α-phenylbutyraldehyde 17a and p-chlorobenzaldehyde 18a in yields of 80%, 80% and 60% respectively. The low yield in case of benzoyl chloride 16 and p-chlorobenzaldehyde 18 is due to the fact that the aldehydes produced initially are partially converted into the corresponding alcohols 8a and 18b in 20% and 25% yields respectively. The reduction results of acid anhydrides and acid chlorides are summarised in Table 2.

Reduction of Nitroarenes

Reduction of nitroarenes to the corresponding amines could be achieved by a variety of reagents[5]. Reaction of nitroarenes with this system also gives the corresponding amines in excellent yield. Thus nitrobenzene 19 gave essentially pure aniline in 90% yield. It has been observed through substrates 20 to 27 in Table 3 that the presence of methyl, hydroxyl, amino-, nitro- and chloro substituent in any of the *ortho*, *meta* and *para* positions of the benzene ring do not have marked effect on the nature and yield of the products. In none of the cases mentioned in Table 3 formation of products other than the corresponding amines were observed.

Reduction of epoxides

Reduction of epoxides to the corresponding alcohols, is one of the fundamental reactions in organic synthesis and can be effected by a veriety of reducing agents.[6-21] However, preferential reduction of oxiranes in the presence of such easily reducible functionalities as carbonyl group is rare.[22-24] Our results of selective reduction of oxiranes using Al-NiCl$_2$ 6H$_2$O-THF are summarised in Table 4. From Table 4 it is evident that in the majority of the cases the ring opening of the oxiranes is taking place from the less hindered side of the epoxide giving the more substituted alcohols except in case of styrene oxide which gave 75% of 1-phenylethanol 37a and only 10% of 2-phenylethanol 37b. It is interesting to note that α,β-epoxy ketones such as 35 and 36 are not reduced by this system and the starting materials were recovered unchanged after work-up. The higher yields of 33a and 34a in case of epoxide 33 and 34 respectively indicate that the rate of reduction of epoxide is much faster than the rate of reduction of α-enones by this system.

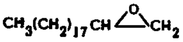
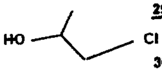
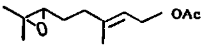
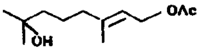
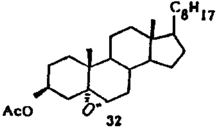
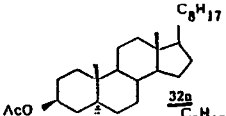
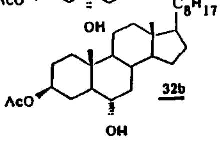
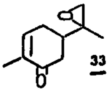
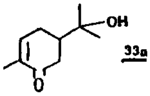
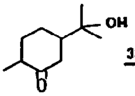
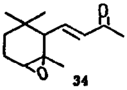
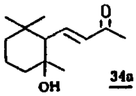
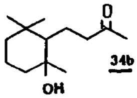
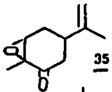
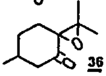
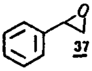
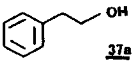
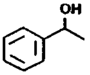
Table 3 : Reduction of aromatic nitro groups with Al-$NiCl_2 \cdot 6H_2O$ in different solvent

Substrate	Reaction time (min)	Product[a]	Solvent	Yield[b] (%)
C_6H_5-NO_2 19	10	$C_6H_5NH_2$ 19a	THF	90
			Ether	85
			Methanol	82
			Toluene	80
			DMF	70
p-$CH_3C_6H_4NO_2$ 20	10	p-$CH_3C_6H_4NH_2$ 20a	THF	95
			Ether	90
			Methanol	82
			Toluene	85
			DMF	72
o-$CH_3C_6H_4NO_2$ 21	10	o-$CH_3C_6H_4NH_2$ 21a	THF	80
			Ether	80
			Methanol	82
			Toluene	75
			DMF	75
p-$HOC_6H_4NO_2$ 22	10	p-$HOC_6H_4NH_2$ 22a	THF	85
			Ether	85
			Methanol	80
			Toluene	84
			DMF	75
p-$HOOCC_6H_4NO_2$ 23	10	p-$HOOCC_6H_4NH_2$ 23a	THF	80
			Ether	85
			Methanol	80
			Toluene	75
			DMF	70
p-$NH_2C_6H_4NO_2$ 24	10	p-$NH_2C_6H_4NH_2$ 24a	THF	90
			Ether	92
			Methanol	86
			Toluene	80
			DMF	70
p-$ClC_6H_4NO_2$ 25	10	p-$ClC_6H_4NH_2$ 25a	THF	85
			Ether	82
			Methanol	85
			Toluene	76
			DMF	72
m-Cl $C_6H_4NO_2$ 26	10	m-Cl $C_6H_4NH_2$ 26a	THF	90
			Ether	82
			Methanol	85
			Toluene	86
			DMF	79
6-Nitroquinolene 27	10	6-aminoquinolene 27a	THF	80
			Ether	82
			Methanol	75
			Toluene	70
			DMF	72

a, Products are characterised by direct comparison with commercially available authentic compounds and also by IR, NMR and MS.

b, Yields were determined by GLC.

Table 4 : Reduction of epoxides with Al-NiCl$_2$.6H$_2$O-THF

Epoxides	Reaction time (min)	Product[a]	Yield[b]
 $CH_3(CH_2)_{17}CH(O)CH_2$ 28	5	$CH_3(CH_2)_{17}CH(OH)CH_3$ 28a	80
Cyclohexene oxide 29	5	Cyclohexanol 29a	70[c]
Epichlorohydrin 30	10	 30a	75[c]
 31	5	 31a	82
 32	5	 32a	65
		 32b	10
 33	10	 33a	85
		 33b	5
 34	10	 34a	70
		 34b	5
 35	30	No reaction	
 36	30	No reaction	
 37	5	 37a	75[c]
		 37b	10[c]

a. Products are characterised by IR, NMR, MS and by direct comparison with authentic compounds.

b. Unless otherwise stated yield refers to the yield of pure isolated products.

c. Yields determined by GLC.

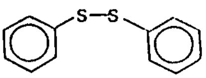
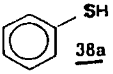
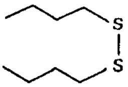
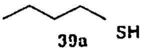
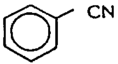
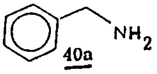
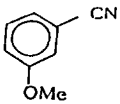
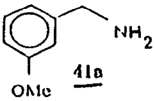
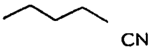
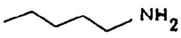
Reduction of miscellaneous organic compounds

Alkyl, allyl and benzyl halides are not reduced by this reagent and were recovered unchanged after the reaction. Similarly sulfoxides and sulfones were also inert to this system. Reduction of amides with this system was not clean. However, treatment of benzamide with Al-$NiCl_2 \cdot 6H_2O$-THF for ten minutes gave a complex mixture of products in which small amount of benzylalcohol was detected.

Disulphides upon treatment with the reagent gave thiols. Thus diphenyl disulphide 38 and dibutyl disulphide 39 were converted to thiophenol 38a and n-butyl marcaptan 39a in 95% and 90% yield respectively.

Nitriles were also cleanly reduced to the corresponding amines by this system. Reduction of benzonitrile 40 and m-methoxy benzonitrile 41 gave benzylamine 40a , m-methoxy aniline 41a in 90% and 85% yields respectively. Similarly n-butyro nitrile 42 gave n-pentyl amine in 70% yield.

Table 5 : Reduction of disulphides and Nitriles with Al-$NiCl_2 \cdot 6H_2O$-THF

Substrate	Reaction time (min)	Product[a]	Yield[b]
 38	5	 38a	95
 39	5	 39a	90
 40	10	 40a	90
 41	10	 41a	85
 42	10	 42a	70

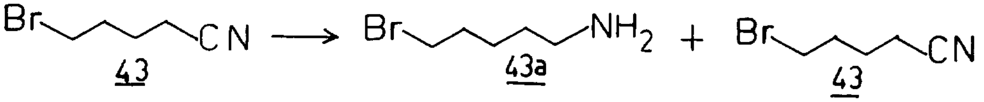
a, Products are characterised by IR, NMR, MS and by direct comparison with authentic compounds.

b, Yields were determined by GLC

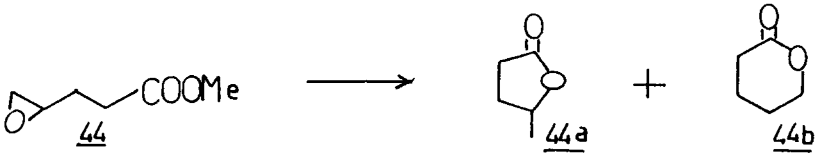
Selectivity

The systematic study on the reducing properties of the Al-NiCl$_2$·6H$_2$O-THF system described above indicate that this is a relatively mild reducing system than the hydride reducing agent like LiAlH$_4$, NaBH$_4$ etc. and therefore suggest the possibility of several selective reductions. As mentioned earlier, selective reduction of the double bond of an α,β-unsaturated carbonyl compound without affecting isolated double bonds, carbonyls and ester groups present elsewhere in the molecule is possible with this system. Similarly selective reduction of an epoxide is also possible in the presence of (i) carbonyl, (ii) acetate ester, (iii) halogen, (iv) isolated double bond and even (v) α-enone. It is noteworthy that in case of oxirane 34 the major product 34a was obtained in 70% yield which is indicative of the fact that the rate of reduction of epoxide ring with this system is even faster than the rate of reduction of α-enones.

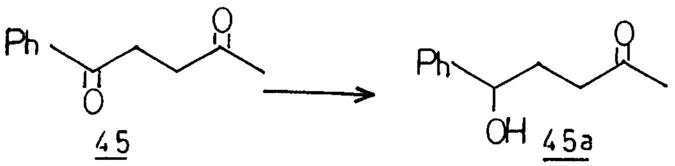
Similarly, the inertness of organic halides towards this reagent allows the selective reduction of a nitrile in the presence of a halide group. Reaction of 5-Bromovaleronitrile 43 with Al-NiCl$_2$.6H$_2$O-THF gave 80% yield of compound 43a



One important aspect of this reagent is that it is capable of selectively reducing an epoxide in the presence of an ester. Reaction of 4,5-oxidomethyl pentanoate 44 upon treatment with this reagent gave after work and treatment with p-TsOH, γ-valerolactone 44a and δ-valerolactone 44b in 80% and 15% yield respectively.



Selective reduction of aromatic carbonyl compounds in the presence of aliphatic carbonyl by this reagent is well demonstrated by the reduction of 1-phenyl pentane-1, 4-dione 45 to compound 45a in 80% yield.



As for the mechanism of this reduction no clear-cut statement can be made at this stage but based on the following noteworthy observations electron transfer cannot be dismissed as part of the mechanism. It is presumably involved in the dissolving metal reductions which do show the same regioselectivity (e.g. in case of oxirane reduction) as described in this paper. Anhydrous $NiCl_2$ does not react with aluminium powder but addition of a few drops of water to this system initiates a vigorous exothermic reaction and evolution of H_2 and formation of black precipitate which probably is Ni (O).[25] The hydrogen might be produced by aluminium with HCl generated from hydrolysis of $NiCl_2$.[26] Ni (O) has a strongtendency to lose electrons to go to its oxidation states and thereby makes the system a reducing one. The fact that both p-anisylalcohol and p-anisaldehyde give p-methoxy methylbenzoate[27] upon treatment with $Al-NiCl_2.6H_2O$ in MeOH suggest that reductions of aromatic aldehydes directly to their ethers take place via the alcohol stage and probably through a aluminium alkoxide intermediate. The most plausible reason for selectivity shown by this reagent towards different functional groups could be due to the fact that the potential needed to transfer an electron from Ni (O) to different functional groups is different.

Conclusions

The study described above confirms the versatility of $Al-NiCl_2.6H_2O$-THF as an useful, mild and simple reducing system. The reagent is mild and therefore selective in many cases. This reagent also reacts under neutral conditions and therefore useful when acid or base sensitive groups are present in the molecules. In this method the short reaction time is an added advantage. Besides the high yield of the reduced products and easy work-up procedure makes it an useful alternative to the existing methods.

EXPERIMENTAL

Melting points were determined in a kofler block and are uncorrected. G.C. analysis of the reaction mixture were performed on a varian 3700 9C gas chromatograph using carbowax 20M columns. For TLC silicagel G (E. Merck India) was used. All the solvents were purified and dried before use. Most of the starting materials utilized in this study were either commercially available or prepared as per standard literature procedure and were purified before use. All the reactions were carried out under nitrogen atmosphere.

General procedure for reduction of different functional groups with Al-NiCl$_2$.6H$_2$O in THF

To a freshly mixed solid mixture of aluminium powder (10 m mol) and nickel chloride hexahydrate (15 m mol) is added a solution of the substrate (0.3 m mol) in freshly distilled THF. A vigorous exothermic reaction takes place after a few seconds which subsides after 10 minutes. When TLC of the reaction mixture showed disappearance of the starting material the reaction mixture is diluted with THF (100 ml) and filtered. Evaporation of the filtrate gave the reduced products which are purified further by chromatography.

General procedure for reduction of different functional groups with Al-NiCl$_2$.6H$_2$O in organic solvents other than THF.

A solution of the substrate (0.3 m mol) in an organic solvent (e.g. MeOH, EtOH, propanol, benzylalcohol, ether, chloroform and DMF) is added to a solid mixture of nickel chloride hexahydrate (15 m mol) and aluminium powder (10 m mol). A vigorous exothermic reaction takes place after a few seconds and subsides after about 10 minutes. When TLC of the reaction mixture showed disappearance of the starting material the reaction mixture is diluted with ether (100 ml) and filtered. Evaporation of the filtrate gave the reduced products which are purified by chromatography or by distillation.

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4 The NMR spectra were recorded either on a Varian T-60 or JEOL FX 90 instrument. Infra-red spectra were recorded on a PERKIN-ELMER 580 B spectrometer either in $CHCl_3$ solution or in KBr pellets. Mass spectra were recorded on a FINNIGAN MAT INCOS 50 GC MS instrument. Compound 7b ($R=CH_3$): ^1H NMR ($CDCl_3$), ppm: 6.9-6.0 (m, 3H, aromatic-H), 6.65 (br 1H, phenolic-OH), 4.92 (s, 2H, $-CH_2-OH$), 4.42 (s, 3H, OCH_3), 3.96 (s, 3H, $-\underline{OCH_3}$), IR (cm^{-1}): 1606, 1580, 1250, 1100, MS:m/z 164 (M^+), 7b ($R=CH_2-CH_3$): ^1H NMR ($CDCl_3$), ppm: 7.2-6.7 (m, 3H, aromatic-H), 4.2 (s, 2H, $-O-\underline{CH_2}-Ph$), 3.79 (s, 3H, OCH_3), 3.4 (q, J=7Hz, 2H, $-O-\underline{CH_2}-CH_3$) 1.25 (t, J=7Hz, 3H, $-O-CH_2\underline{CH_3}$), 1.25 (t, J=7Hz, 3H, $-O-CH_2-\underline{CH_3}$), IR (cm^{-1}): 2840, 1605, 1455, 1250, 1175 etc. MS:m/z 182 (M^+): 7b ($R=-CH_2-CH_2-CH_3$): ^1H NMR ($CDCl_3$) ppm: 7.2-6.6 (m, 3H, aromatic-H), 4.12 (s, 2H, $-O-\underline{CH_2}-Ph$), 3.5 (s, 3H, $-\underline{OCH_3}$), 3.2 (t, J=7Hz, 2H, $-O-CH_2-\underline{CH_3}$), 1.44 (m, J=7Hz, 2H, $-\underline{CH_2}-CH_3$), 0.8 (t, J=7Hz, 3H, $\underline{CH_3}-CH_2-O-$), IR (cm^{-1}): 2800, 1607, 1508, 1456, 1250, 1180, 1105, 830, MS:m/z 196 (M^+) 7b ($R=-CH_2-Ph$): ^1H NMR ($CDCl_3$) ppm: 7.2-6.6 (m, 8H, aromatic-H), 4.4 (s, 4H, $-O-\underline{CH_2}-Ph$), 3.7 (s, 3H, $-O-\underline{CH_3}$) IR (cm^{-1}): 2040, 1606, 1507, 1455, 1260, 1045 etc. MS:m/z 244 (M^+). 28a mp 55°C: ^1H NMR ($CDCl_3$) ppm: 3.97 (m, 2H, $-\underline{CH_2}-OH$), 3.8 (m, 1H, -OH), 1.22 (s, 4H, $-\underline{CH_2}-$),0.82 (t, J=5H_2, 3H, $-CH_3$), IR (cm^{-1}): 3400, 2950, 2860, 1490, 1080 etc. MS:m/z 298 (M^+), 280 (M^+-H_2O) etc. (On oxidation with Jones reagent in acetone gave 2-Eicosanone, mp 58°C). 31a : ^1H NMR ($CDCl_3$) ppm: 5.3 (m, $-C=\underline{CH}$), 4.5 (d, J=8Hz, 2H, $-\underline{CH_2}-OAc$), 3.7 (br, 1H, $-\underline{OH}$), 2.0 (s, 3H, $-\underline{OAc}$), 1.62 (br, 3H, $C=C-\underline{CH_3}$), 1.1 (s, 6H,$(CH)_2C((OH)C-)$; IR(cm^{-1}) 3450, 2960, 1740, 1440, 1370, 1235, 1030; MS:m/z 214 (M^+), 196 (M^+-H_2O), 155 ($M^+-O-COCH_3$), 154 ($M^+-H_2O-COCH_3$), 140, 137 etc. Analysis calculated for $C_{12}H_{22}O_3$: C: 67.26%, H 10.35%, found C 67.20%, H 10.4%. 33a: ^1H NMR ($CDCl_3$), ppm: 6.8 (m, 1H, $-\underline{CH}=C(CH_3)C$, 3.9 (br, 1H, $-\underline{CH}$), 2.4 (m, 4H, $-\underline{CH_2}-C(O)-$ and $C=CH-\underline{CH_2}-$,, 1.8 (s, 3H, $C=C(\underline{CH_3})-$), 1.16 (s, 6H, $-\underline{CH_3}$); IR (cm^{-1}) 3450, 2980, 1675, 1375, 1240, 1060; MS:m/z

168 (M$^+$), 150 (M$^+$-H$_2$O), 135 (M$^+$-H$_2$O-CH$_3$) etc. Analysis calculated for $C_{10}H_{16}O_2$, C 71.39%, H 9.59%, found C 71.42%, H 9.7%. 33b : ^{1}H NMR (CDCl$_3$) ppm: 3.92 (br, 1H, -OH), 2.42 (m, 3H, -CH$_2$-C(O)- and C(O)-CH. 1.22 (s, 6H, CH$_3$, 1.02 (d, J=17Hz, 1H, -CH$_3$) IR (cm^{-1}) 3450, 2980, 1720, 1375, 1240, 1060 etc. MS:m/z 170 (M$^+$), 152 (M$^+$ -H$_2$O), 134 etc. Analysis calculated for $C_{10}H_{18}O_2$, C 70.55%,H 10.66% found C 70.57%, H 10.68%. 33a: ^{1}H NMR (CDCl$_3$) ppm: 6.9 (dd, J=16 and 10Hz, 1H, -CH=C), 6.0 (d, J=16Hz, 1H, -C=CH-), 3.8 (m, 1H, OH), 2.2 (s, 3H (O)C-CH$_3$), (s, 3H, C(OH)CH$_3$), (s, 3H,C(OH)CH$_3$), 1.1 (s, 3H,CH$_3$), 0.89 (s, 3H,-CH$_3$), IR (cm^{-1}) 3400, 2960, 2880, 1680, 1640, 1070 etc. MS:m/z 210 (M$^+$), 192 (M$^+$-H$_2$O), 177 (M$^+$-H$_2$O-CH$_3$) etc. Analysis calculated for $C_{13}H_{22}O_2$, C 74.24%, H 10.54%, found C 74.31%, H 10.57%. 34b: ^{1}H NMR (CDCl$_3$), ppm: 3.72 (m, 1H, -OH), 2.2 (s, 3H, -C(O)-CH$_3$), 2.0 (m, 2H, -(O) C-CH$_2$), 1.3 (s, 3H, -C(OH)-CH$_3$), 1.1 (s, 3H, -CH$_3$), 0.9 (s, 3H, -CH$_3$), IR (cm^{-1}): 3400, 2960, 2880, 1725, 1640, 1370 etc. MS:m/z 212 (M$^+$), 194 (M$^+$-H$_2$O), 179 (M$^+$-H$_2$O-CH$_3$) etc. Analysis calculated for $C_{13}H_{24}O_2$, C 73.54%, H 11.54%, found C 73.51% H 11.42%.

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