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Note

Applications of oxidative and reductive methodologies on coumarinyl ketones

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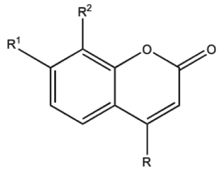
The higher degree of chemoselctivitiy and regioselectivity recorded during the selenium dioxide oxidation of various coumarinyl ketones **1-7** affords the corresponding coumarinyl **α**-di carbonyl compounds **1a-7a** and **5b** in which the compound **2a** has been isolated as an unexpected product and also the sodium borohydride reduction of coumarinyl ketones **1-14** affords the desired coumarinyl carbinols **1c-3c**, **5c**, **7c-9c**, **11**c and **13c** and 5-keto-6-hydroxy-cinnamic acid derivatives **4d**, **6d**, **10d**, **12d** and **14d** as unexpected products in minor amounts.

Keywords: Assorted, Chemoselectivity, Derivatives, Epoxides, Oxidation, Reduction, Unusual

Coumarins, a diversified family of compounds present in remarkable amount in nature[1,2] enjoy enormous research interests due to their extensive applications in pharmaceutical, and perfumery industries[3,4]. Due to such unique manifestation, the synthesis of coumarins with various substitution at position 8 and 4 have got wide attention[5,6] even today. A systematic investigations were carried out on various coumarins bearing carbonyl groups by employing Grignard Reaction[7,8], Reformatsky Reaction[9,10] and Wittig Reaction[11]. Keeping in mind that there are few comprehensive reports[12] on the applications on the oxidation using selenium dioxide[13] and reduction using sodium borohydride on coumarind[14,15]. Thus selenium dioxide and sodium borohydride reagents may be judiciously selected as the most useful and effective reagents for the assessment of their chemoselctivity and regioselectivity nature on coumarinyl ketones 1-14 (Fig. 1). Such studies may in turn develop a new synthetic strategy to build up assorted type of side chains in basic coumarin moiety.To assess the reactivities and chemoseltive nature of selenium dioxide for oxidation and sodium borohydride for reduction, we have selected 8-alkanoylketones and 8-benzoylketones for studies. It has been observed that varieties of notable selectivity along with some unusual products originating from selenium dioxide oxidation and sodium borohydride reduction on coumarinyl ketones which will be presented in this paper.



1 R=Me, R^1=-OMe, R^2=-COMe
2 R=H, R^1=-OMe, R^2=-COMe
3 R=Me, R^1=-OMe, R^2=-COEt
4 R=H, R^1=-OMe, R^2=-COEt

1a R=Me, R^1=-OMe, R^2=-COCHO
2a R=H, R^1=-OMe, R^2=-COCH$_2$OH
3a R=Me, R^1=-OMe, R^2=-COCOMe
4a R=H, R^1=-OMe, R^2=-COCOMe
4b R=H, R^1=-COCOCH$_2$OH

5 R=Me, R^1=-OMe, R^2=-COPr^n
6 R=H, R^1=-OMe, R^2=-COPr^n
7 R=Me, R^1=-OMe, R^2=-COPh
8 R=H, R^1=-OMe, R^2=-COPh
9 R=Me, R^1=-OH, R^2=-COMe

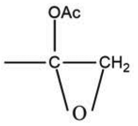
5a R=Me, R^1=-OMe, R^2=-COCOEt
5b R=CHO, R^1=-OMe, R^2=-COCOEt
6a R=H, R^1=-OMe, R^2=-COCOEt
7a R=CHO, R^1=-OMe, R^2=-COPh

10 R=H, R^1=-OH, R^2=-COMe
11 R=Me, R^1=-OH, R^2=-COEt
12 R=H, R^1=-OH, R^2=-COEt
13 R=Me, R^1=-OH, R^2=- COPr^n
14 R=H, R^1=-OH, R^2=- COPr^n

1c R=Me, R^1=-OMe, R^2=-CHOHMe
2c R=H, R^1=-OMe, R^2=-CHOHMe
3c R=Me, R^1=-OMe, R^2=-CHOHEt
5c R=Me, R^1=-OMe, R^2=-CHOHPr^n
7c R=Me, R^1=-OMe, R^2=-CHOHPh

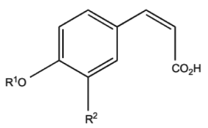
8c R=H, R^1=-OMe, R^2=-CHOHPh
9c R=Me, R^1=-OH, R^2=-CHOHMe
11c R=Me, R^1=-OH, R^2=-CHOHEt
13c R=Me, R^1=-OH, R^2=-CHOHPh
14c R=H, R^1=OH, R^2=-CHOHPr^n

1e R=Me, R^1=OMe, R^2=-CHOAcMe



2e R=H, R^1=OMe, R^2=

4e R=H, R^1=OMe, R^2=-COCOCH2OAc
7e R=Me, R^1=OMe, R^2=-CHOAcPh
9e R=Me, R^1=OAc, R^2=-CHOAcMe
11e R=Me, R^1=OAc, R^2=-CHOAcEt



4d R^1=Me, R^2=-COEt
6d R^1=Me, R^2=-COPr^n
7d R^1=Me, R^2=-COPh

Fig. 1 — Structure of the compounds

Table 1 — Physical characterization data and elemental analysis of the new compound

				Elemental Analysis (C and H)			
Compd	Mol. Formula	m.p/b.p (°C)	Yield (%)	Calcd (%)		Found (%)	
				C	H	C	H
1a	$C_{13}H_{10}O_5$	144	74	63.41	4.01	63.04	4.01
2a	$C_{12}H_{10}O_5$	171	70	61.54	4.27	61.3	4.2
3a	$C_{14}H_{12}O_5$	161	71	64.61	4.61	64.59	4.6
4a	$C_{13}H_{10}O_5$	181	72	63.38	4.06	63.28	4.01
4b	$C_{13}H_{10}O_6$	161	27	59.41	3.81	58.84	3.90
5a	$C_{15}H_{14}O_5$	157	40	65.67	5.1	65.67	5.09
5b	$C_{15}H_{12}O_6$	171	31	65.27	4.16	65.69	5.1
6a	$C_{14}H_{12}O_5$	172	60	64.61	4.16	64.58	4.14
7a	$C_{18}H_{12}O_5$	189	68	75.0	4.16	74.48	4.06
1c	$C_{13}H_{14}O_4$	135	75	66.65	6.02	66.61	6.00
2c	$C_{12}H_{12}O_4$	118	71	65.42	5.43	65.4	5.45
3c	$C_{14}H_{16}O_4$	123	73	67.78	6.45	67.75	6.33
5c	$C_{15}H_{18}O_4$	141	70	68.7	6.87	68.69	6.85
7c	$C_{18}H_{16}O_4$	188	70	72.99	5.44	72.99	5.41
8c	$C_{17}H_{14}O_4$	192	71	72.34	4.93	72.36	4.93
9c	$C_{12}H_{12}O_4$	138-139	74.80	65.42	5.45	65.45	5.44
11c	$C_{13}H_{14}O_4$	99-100	75	66.67	5.98	66.66	5.96
13c	$C_{16}H_{12}O_4$	176	73	71.64	4.47	71.62	4.45
4d	$C_{13}H_{14}O_5$	110	12	62.4	5.61	62.8	5.5
6d	$C_{14}H_{16}O_5$	118	15	63.63	6.06	63	6
7d	$C_{17}H_{14}O5$	148	21	68.48	4.2	68.8	4.5
1e	$C_{18}H_{16}O3$	188	78	65.21	5.84	65.17	5.8
2e	$C_{14}H_{12}O6$	184	77	60.86	4.84	61	4.28
4e	$C_{15}H_{12}O7$	168	72	59.21	5.94	59.1	5.91
7e	$C_{20}H_{18}O_5$	181	71	71	5.32	70.94	5.21
9e	$C_{16}H_{16}O_6$	144	70	63.15	5.26	63.04	5.2
11e	$C_{17}H_{18}O_6$	135	75	64.15	5.66	64	5.6

Experimental Section

Melting points and boiling points are uncorrected, IR spectra were recorded in KBr with Hitachi 270-30 data processor, ^1H NMR were recorded in $CDCl_3$ in JEOL FX 100 FT machine. Mass spectra was recorded in Finnigan MAT 1020C operating on 70ev. The products gave M^+ ion and fragmentation there of. ^{13}C NMR spectra were recorded in $CDCl_3$ in a Hitachi 400 MHz FT spectrometer.

Selenium dioxide oxidation of coumarinyl ketones (1-7) to the corresponding 1,2 dicarbonyl compounds (1a,3a-7a) and keto alcohol (2a)

The respective coumarinyl ketones (1-7) [4.2 m.mole] were taken in glacial acetic acid (60 ml) and selenium dioxide (7.2) m.mole) was added and the mixture were refluxed for 5hr and the mixtures were cooled and initially filtered through filter paper to remove bulk selenium metal, then the filtrates were passed through silica gel bed to remove the remaining selenium metal and were washed with acetic acid. All the acetic acid solution thus obtained were concentrated to 2 ml. To the concentrated solution chloroform (30) ml were added and were left overnight. The solid thus formed were filtered. Now solid products were crystallized from ethyl acetate and pet ether mixture afforded needle shaped crystalline solids (2a,1a-7a). (Mp/bp, yield shown in Table 1).

Sodium borohydride reduction of coumarinyl ketones (1-14) to the corresponding alcohols (1c-3c,5c,7c-9c,11c and 13c) and cinnamic acid derivatives (4d,6d and 7d)

The respective coumarinyl ketones (1-14) [1 m.mole]in different experiments were dissolved in methanol (20 ml) and sodium borohydride (2.5 m.mole)were added in portions till the effervescences stopped. The respective reaction mixtures were left overnight, decomposed with excess of cold water (150 ml) and acidified in cold conditions with 2% aqueous hydrochloric acid. The respective reaction mixtures were repeatedly extracted with chloroform and the combined organic extract were washed with brine solution. After drying over anhydrous sodium sulphate and evaporation of solvent an oily mass was obtained. The pure compounds (1c-3c,5c,7c-9c,11c,13c) were purified by column chromatography and recrystallization from alcohol. During borohydride reduction experiments of (4c, 6c, 7c) produced the crude products three spots in which one is starting material in TLC. The compounds were separated through column chromatography using ethyl acetate - pet ether as eluent. The first separated compound which was separated in different experiments starting material, second separated compounds are alcohols (4c,6c,7c) and the third products (4d,6d and 7d) separated from chromatography are cinnamic acid derivatives as light yellow solid. Finally all the corresponding products were crystallised using ethyl acetate and pet ether mixture. Melting points and percent yields (%) are given in the Table 1.

Preparation of acetate derivatives of the representative alcohols (2a,1c,7c,9c,11c)

The respective alcohols (2a,1c,7c,9c,11c) (9.67 m.mole) were acetylated with freshly distilled acetic anhydride (.01 mole) with few drops of dry pyridine in different experiments were heated on a water bath for 6 hr. Then the reaction mixtures (different experiment) were cooled, poured into crushed ice and were acidified with cold dil. aqueous hydrochloric acid. The solutions were extracted repeatedly with chloroform. The organic extracts were washed with cold dil. HCL, then with saturated sodium bicarbonate solution and again with saturated brine solution After drying organic layer over anhydrous sodium sulphate, the solvent were evaporated off. The crude products were obtained and crystallized from ethanol to obtain the corresponding acetate derivatives (1e,2e,7e,9e,11e). Melting point and % of yield given in Table 1).

Spectroscopic data of synthesised compounds

^{1}H NMR ($CDCl_3$): δ **1a**: 2.41 (3H, s, 4-CH_3), 3.89 (3H, s, 7-OCH_3), 6.16 (1H, s, 3-H), 6.93 (1H, d, *J* = 8.7, 6-H), 7.63 (1H, d, *J* = 8.7, 5-H), 9.49 (8-O-COCHO); **2a**: 1.62 (2H,s, $COCH_2$), 3.87 (3H, s-, OCH_3) 6.24 (1H, d, *J*=8.8Hz,3-H), 6.80 (1H, s-, CH_2OH) 6.85 (1H, d, *J*=9Hz, 3-H), 7.35 (1H, s, *J* =9Hz, 5-H), 7.63 (1H, d, *J*=8.8Hz,4-H); **4b**: 7.53(1H, d, *J*=8Hz,4-H), 7.25 and 7.38 (each 1H, d, *J*=9Hz, 5-H, 6-H), 6.24 (1H, s, OH), 6.58 (1H, d, *J*=8Hz, 6-H), 3.89 (3H, s, OCH_3), 2.23 (2H, s, $COCH_2$); **1c**: 1.68 (3H,d, *J*= 6.6Hz, 8-CH(OH)CH_2), 2.43 (3H, broad s, 4-CH_3), 3.97 (3H, s, *J*=8.8Hz,3-H), 6.80 (1H, s, CH_2OH), 6.85 (1H, d, *J*=9Hz, 3-H), 7.35 (1H, s, *J* =9Hz, 5-H), 7.63 (1H, d, *J*=8.8Hz,4-H); **3c**: 1.12 (3H, t, *J*=7.2Hz, 8- CH(OH)CH_2CH_3), 1.81 (2H, dq, *J*=7.4 Hz and 7.2Hz, 8- CH(OH)CH_2CH_3), 2.42(3H, s, 4-CH_3), 3.91 (3H, s, 7-OCH_3), 3.95 (1H, broad s, 8-CH(OH)CH_2CH_3), 4.89 (1H, broad t, *J*=7.0 Hz, 8-CH(OH)CH_2CH_3), 6.15(1H, broad s, 3-H), 6.86 (1H, d, *J*=8.8 Hz,6-H), 7.38(1H, d, *J*=8.7Hz, 5-H); **5c:** 0.99 (3H, t, *J*=7.2Hz, 8- CH(OH)$CH_2CH_2CH_3$), 1.77 (2H, sextet, *J*=7.2Hz, 8- CH(OH)$CH_2CH_2CH_3$), 1.81 (2H,q, *J*=7.2Hz, 8- CH(OH)$CH_2CH_2CH_3$); **2e**: 2.02 (3H,s-, $OCOCH_3$), 3.08 (2H, s, CH_2 of epoxide), 3.85 (3H, s-, OCH_3), 6.27 (1H, d, *J*=8.8Hz, 3-H), 6.83 (1H, d, *J*=9 Hz, 6-H), 7.33 (1H, d, *J*=9Hz, 5-H), 7.68 (1H, d, *J*=8.8 Hz, 4-H); **4e**: 1.98 (3H, s-, $OCOCH_3$), 1.282(2H, s, 2' – CH_2), 6.82 (1H, d, *J*=9Hz, 3-H), 6.86 (1H, d, *J*=9Hz, 6-H), 7.33 (1H, d, *J*=9Hz, 5-H), 7.56 (1H, d, *J*=9Hz, 4-H).

Mass spectroscopic studies: **3a:** 260 (1.0, $M^{\bullet+}$), 217 (100, $M^{\bullet+}$-$COCH_3$), 202 (6.2, $M^{\bullet+}$-$COCH_3$-CH_3), 189 (9.0, $M^{\bullet+}$-$COCH_3$-CO), 174 (20.2, $M^{\bullet+}$-$COCH_3$-CO-CH_3), 159 (2.62, M $M^{\bullet+}$-$COCH_3$-CO-CH_2O), 146 (10.2, $M^{\bullet+}$-$COCH_3$-CO-CH_3-CO), 131 (4.85, $M^{\bullet+}$-$COCH_3$-CO-CH_2O-CO), 118 (4.77, $M^{\bullet+}$-$COCH_3$-CO-CH_3-2CO), 103 (12.2, $M^{\bullet+}$-$COCH_3$-CO-CH_2O-2CO), 77 (8.01, $M^{\bullet+}$-$COCH_3$-CO-CH_2O-2CO-C_2H_2), 43 (87, CH_3-C≡O^+); **4a:** 246 (1.0, $M^{+\bullet}$), 203 (100, $M^{\bullet+}$-$COCH_3$), 188 (5.10, $M^{\bullet+}$-$COCH_3$-CH_3), 175 (8.50, $M^{\bullet+}$-$COCH_3$-CO), 160 (22.41, $M^{\bullet+}$-$COCH_3$-CO-CH_3), 145 (2.68, $M^{\bullet+}$-$COCH_3$-CO-CH_2O), 132 (8.13, $M^{\bullet+}$-$COCH_3$-CO-CH_3-CO), 117 (4.81, $M^{\bullet+}$-$COCH_3$-CO=CH_2O-CO), 104 (4.77, $M^{\bullet+}$-$COCH_3$-CO-CH_3-2CO), 89 (11.21, $M^{\bullet+}$-$COCH_3$-CO-CH_2O-2CO), 63 (7.96, $M^{\bullet+}$-$COCH_3$-CO-CH_2O-2CO-C_2H_2), 43 (83.5, CH_3-C≡O^+); **4b:** 262 (10, $M^{\bullet+}$), 232 (21, $M^{\bullet+}$-30), 231 (36, $M^{\bullet+}$-31), 203 (100, $M^{\bullet+}$-59), 175 (25, $M^{\bullet+}$-87), 160 (31, $M^{\bullet+}$-102), 145 (48, $M^{\bullet+}$-117), 104 (67, $M^{\bullet+}$-158), 89 (71, $M^{\bullet+}$-173); **5a:** 274 (63.2, $M^{\bullet+}$), 245 (5.2, $M^{\bullet+}$-29), 217 (100, $M^{\bullet+}$-C_2H_5CO), 202 (28.2, $M^{\bullet+}$-C_2H_5CO-CH_3), 189 (19.1, $M^{\bullet+}$-C_2H_5CO-CO), 161 ($M^{\bullet+}$-C_2H_2CO-2CO), 175 ($M^{\bullet+}$-C_2H_5CO-CO-CH_3+H^+).

Electron spray ionization: **4:** $[M-H]^+$at *m/z*247.90 $[M+Na]^+$at 269.09; **4a:** $[M-H]^+$ at *m/z* $[M+Na]^+$ at 246.1; **3a:** $[M-H]^+$ at *m/z* 261.1 $[M+Na]^+$ at 283.1; **6a:** $[M-H]^+$ at *m/z* 261.1 $[M+Na]^+$ at 283.1; **7a:** $[M-H]^+$ at *m/z* 309.1 $[M+Na]^+$ at 331.1; **11c:** $[M+H]^+$ at 235.10 $[M+Na]^+$ at 257.10; **3c:** $[M+H]^+$ at 263.3 $[M+Na]^+$ at 285.3; **8c:**

$[M+H]^+$ at 283.3 $[M+Na]^+$ at 295.3; **11e:** $[M+H]^+$ at 319.2 $[M+Na]^+$ at 341.12; **1e:** $[M+H]^+$ at 277.13 $[M+Na]^+$ at 299.13.

Results and Discussion

Considering the oxidation of various 8-alkanoyl ketones (1-6) and 8-benzoyl - ketone (7, 8) using selenium dioxide oxidation in acetic acid afforded 1,2 di carbonyl derivatives (1a, 3a-7a). The above results indicate that the oxidation take place at methyl or methylene carbon of carbonyl group without touching the lactone moiety of coumarins. Surprisingly 8-acetyl -7- methoxy-coumarin (2) on oxidation furnished 8-(1-keto-2-hydroxy propane)7-methoxy coumarin (2a) which on acetylation gave an epoxide(2e) as unusual products. In another oxidation 4-methyl-7-methoxy-8- benzoyl-coumarin (7) gave 4-formyl- 7-methoxy-8-benzoylcoumarin (7a).

Considering IR spectral data of newly synthesised compounds (Table 2) the notable structural information has been gathered. Since most of the oxidation products are 1,2-di ketones, a most remarkable change in IR spectral behaviour could be detected and all the IR absorption band recorded at 1705cm^{-1} to 1725cm^{-1} for 1,2 dicarbonyl group. A brief discussion on the available ^{1}H NMR spectral analysis of rationalizing various structural aspects of the oxidation products. The oxidation products (1a) and (7a) exhibit a sharp singlet at 9.49 for aldehyde proton of COCHO.It has been observed that absence of triplet and quadrate of signal at 1.20 and 2.86 for methyl and methylene proton and appearance of sharp singlet at 2.57 indicate the presence of $COOCH_3$ of compounds (3a and 4a).The most interesting features of the spectra of the compounds (5a and 5b) that the absence of sextet and triplet at □ 1.70 and 3.30 for 8-$COCH_2CH_2CH_3$ protons and appearance of a quartet signal at □3.0 for methylene protons of $COCOCH_2CH_3$.Considering ^{13}CNMR spectra of the oxidation products their structure can be unambiguously established. Appearance of chemical shift at around 197(4°, 8-$COCOCH_3$) and at 191(4° 8$COCOCH_3$). All the structure of the compounds (1a-7a) were fully established through IR, ^{1}H NMR, ^{13}C NMR and Mass Spectra. 2D COSY(□^{1} H vs. □H), HMBC, HMQC of some representative compounds are also are delineated in tabular form (Supplementary file, Table S2)

Table 2 — IR spectroscopic data of new compounds

Compd	IR spectroscopic data (cm^{-1})
1a	1740, 1726, 1710, 1600
2a	3480, 1722, 1698, 1601
3a	1740, 1725, 1715, 1600
4a	1735, 1725, 1705, 1598
4b	3458, 3190, 1705, 1600
4d	3490, 3185, 1705, 1695, 1598
5a	3410, 1725, 1705, 1602
5b	1740, 1720, 1698, 1601
6a	1740, 1715, 1605
6d	3500, 3190, 1720, 1692, 1605
7a	1720, 1685, 1600
7d	3470, 3185, 1708, 1695, 1598
1c	3528, 1728, 1602
2c	3530, 1730, 1600
3c	3530, 1730, 1601
5c	3535, 1735, 1602
7c	3498, 1740, 1620
8c	3510, 1742, 1612
9c	3295, 3180, 1728, 1610
11c	3280, 3190, 1730, 1601
13c	3280, 3190, 1734, 1615
1e	1745, 3190, 1734, 1615, 1625
2e	3050, 1730, 1705, 1695
4e	1740, 1725, 1625
7e	1730, 1690, 1602
9e	1740, 1725, 1625
11e	1740, 1720, 1680

Now in this part it needs to be enlighted that Sodium borohydride reduction may also be carried out in contrast to the reduction of selenium dioxide oxidation for the assessment of observed deviation if any in chemoselectivity and regioselectivity nature of coumarinyl Ketones (1-14). The selected coumarinyl Ketones (1-14) were allowed to react with sodium borohydride in excess quantity (1: 5 molar ratio) in methanol solvent at room temperature in different experiments. (vide experimental procedure). Usual work up followed by evaporation of solvent and crystallization of the crude products afforded the desired alcohols (1c-3c,5c, 7c-9c,11c and 13c).

It should be mentioned that coumarinyl ketones (4,6,10,12 and 14) failed to record any reduction due to the absence of methyl group at position 4 of coumarin moiety which make the lactone moiety more reactive for nucleophile[7] than carbonyl group at position 8. The coumarinyl ketones (4,6,7) undergo basic hydrolysis during sodium borohydride reduction using methanol (presence of water) solvent at room temperature and afforded 2-hydroxy-3acetyl cinnamic acid derivatives (4d,6d, 7d) in minor amount. Thus here it can be explained by the interaction of the solvent environments[16] of the initial and transition state with the solvent co-sphere of the added substances should be understand the solvent effects on the reaction rate. The hydrolysis of coumarin derivatives by sodium borohydride in methanol (water impurity) takes place in one stage and lead to the rate determining step by the opening of lactone moiety and formation of salt of coumarinic acid. This type of chemoselctive reaction was reported in the literature[17]. The compounds (4d,6d,7d) show IR absorption band at around 3490cm-1 (s) for COOH group, 3190 cm^{-1} for phenolic OH group and the lactone moeity is absent. The phenolic OH proton in PMR shows sharp singlet at. 13.70 and unsaturated acid show 7.40 and 5.39 (each1H, d, *J*=13 Hz for 2'-H and 3'-H which indicates Z- configuration All the alcohols (2a,1c,7c,9c and 11c) were acetylated to the corresponding acetyl derivatives (1e,2e,7e,9e and 11e) respectively to assign the presence of alcoholic functionality. A brief discussion on the available IR NMR, Mass spectral data was given for rationalization of various structural aspects of compounds (1c-14c). Since 8-acyl/aroyl coumarinyl carbinol (1c-14c) failed to record any sharp stretching frequency of keto carbonyl group at ~1700cm^{-1} and appearance of broad IR band at 3500cm^{-1} indicate the formation of alcohols by the reduction of carbonyl group of coumarins. ^1H NMR spectral behaviour of sodium borohydride reduction products (1c- 3c,5c, 7c-9c,11c,13c,) and O-acetylated derivatives (1e,2e,7e,9e and 11e) demand brief discussion. It is interesting[18] to note that the genesis of diasterotopic methylene protons through the reduction of carbonyl compounds enjoying enantiotopic ketocarbonyl faces were firmly established by two quintet signal of H_a and H_b protons of 8-$CH(OAc)CH_aH_bCH_3$ respectively of compound (11 e). For providing rational arguments in order to confirm the structure of all new compounds ^{13}C NMR spectra were recorded along with plausible assignment and interpretation using noise decoupled technique and carbon absorption originating from their 1°,2°, 3°,4° were established using DEPT-135 pulse sequence technique[19,20]. For further structural proof 2D-COSY, HMBC and HMQC spectral analysis turn out to be essential and all the analyses have been carried out on some representative reduction products and O-acetylated derivatives and have been delineated in tabular form (Supplementary file, Table S3). Finally in order to establish the structure unambiguously mass spectroscopy studies[21] were undertaken in the electron impact (EI) mass spectrum and the electron spray ionisation has been utilised to detect the molecular ion which are detected at an *m/z* for the ion as $[M^+Na]^+$ (Supplementary file, Table S4).

Conclusion

The higher degree of chemoselctivities and regioselectivities are recorded through reduction and oxidation employing sodium borohydride and selenium dioxide respectively on various coumarinyl ketones as the substrate. It should be noted that both selenium dioxide and sodium borohydride record excellent chemoselctivitiy in order to convert coumarinyl Ketones to the corresponding coumarinyl 1,2-dicarbonyl compounds or coumarinyl carboxyaldehyde, coumarinyl carbinols keeping the coumarin lactone moiety untouched. It was noted that unexpected chemo-selctivities were recorded in forming carbonyl hydroxy ketone (2a), epoxide (2e) during SeO_2 oxidation and 5-keto-6-hydroxycinnamicacid derivatives (4d, 6d, 10d, 12d and 14d) during sodium borohydride reduction. Thus all the products isolated and identified could be unequivocally characterized as the outcome of the proposed study.

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

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N.B.: All new compounds gave expected UV, IR, NMR and Elemental Analysis data.

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