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A Mild and Simple Procedure for the Reductive Cleavage of Acetals and Ketals

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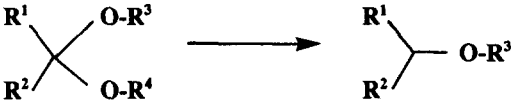
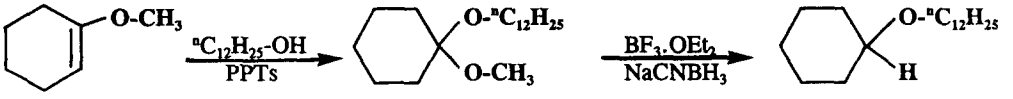
ABSTRACT: A convenient, mild and simple procedure, employing sodium cyanoborohydride in the presence of either catalytic or stoichiometric amount of boron trifluoride etherate in dry THF, for the reductive cleavage of the acetals and ketals is described.

The reductive cleavage of acetals and ketals to ethers (eq. 1) is a useful transformation in organic synthesis. Since the first report in 1951, on the reduction of a ketal when Doukas and Fontaine[1] showed that the spiroketal diosgenine could be reduced by lithium aluminium hydride in the presence of hydrogen chloride gas, a number of reagents have been developed[2] for the reductive cleavage of acetals and ketals (*via* ionic hydrogenation reaction), these include alanes, borane and haloboranes, trialkylsilanes in the presence of stoichiometric[3] or large excess of Bronsted or Lewis acids, etc. In our search for an alternative, mild and simple method for the reductive cleavage of acetals and ketals, we have investigated the use of sodium cyanoborohydride in the presence of boron trifluoride etherate.



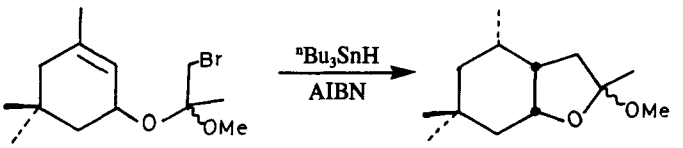
(eq. 1)

The use of sodium cyanoborohydride for the reductive cleavage of some acetals has been reported earlier using methanol as solvent in the presence of an excess of gaseous hydrogen chloride.[4] But irrespective of the starting acetals, only methyl ethers were obtained. We reasoned that the transacetalization preceded the reductive cleavage. We opted to investigate the use of sodium cyanoborohydride and boron trifluoride etherate in dry THF for developing a simple and convenient procedure for the reductive cleavage of acetals and ketals. To begin with the reaction was carried out on the ketal 1, obtained from 1-methoxycyclohexene and dodecanol. Treatment of the ketal 1 in dry THF in the presence of 0.25 equivalent of boron trifluoride etherate with sodium cyanoborohydride at room temperature for two hours, efficiently and cleanly, transformed it into dodecyloxycyclohexane (2),[5] in 97% yield, whose structure was



1 2

established from its spectral data. It is worth noting that a stoichiometric amount of $BF_3.OEt_2$ is not necessary for this transformation. For establishing the generality of this new and simple procedure, various (symmetrical and unsymmetrical) ketals and acetals **3**-**11**[6-10] were prepared using conventional procedures (see experimental section). The ketal **12** was obtained *via* the radical cyclisation reaction of the bromoacetal **13**.[11] The reductive cleavage of the acetals and ketals **3**-**12** with sodium cyanoborohydride and $BF_3.OEt_2$ in THF furnished the ethers **14**-**23**,[9-14] in good to excellent yields, and the results are summarised in the table 1. Quite expectedly cyclic ketals required either longer reaction times or increased amount of Lewis acid and we preferred the later option.



13 **12**

Experimental Section

IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^1H (90 MHz) and ^{13}C NMR (22.5 MHz) spectra in $CDCl_3$ were recorded on a JEOL FX-90Q spectrometer. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal tetramethylsilane (for ^1H) or central line (77.1 ppm) of $CDCl_3$ (for ^{13}C). In the ^{13}C NMR spectra off-resonance multiplicities, when recorded are given in parentheses. Low and high resolution mass measurements were carried out using a JEOL JMS-DX 303 GC-MS instrument using a direct inlet mode. Relative intensities of the ions are given in parentheses. Acme's silica gel (100-200 mesh) was used for column chromatography. 1-Methoxycyclohexene was prepared as per the reported procedure.[15]

General procedures for the preparation of ketals and acetals:

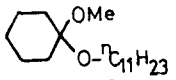
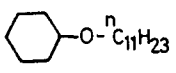
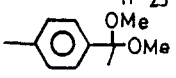
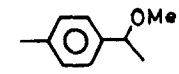
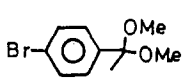
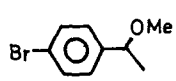
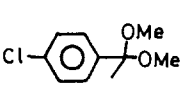
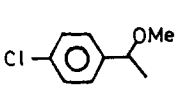
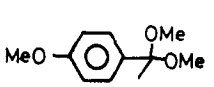
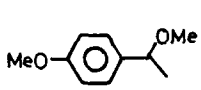
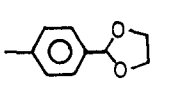
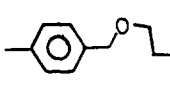
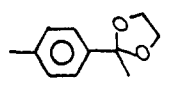
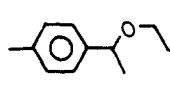
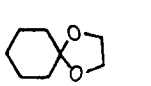
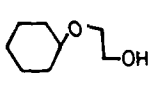
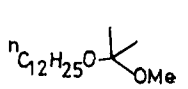
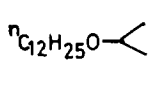
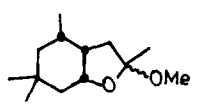
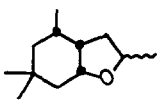
Method A: A solution of a ketone (1 gm), trimethyl orthoformate (2 ml) and a catalytic amount of PTSA in 5 ml of methanol was refluxed for 4-6 hr. The reaction mixture was cooled, treated with aqueous $NaHCO_3$ solution and extracted with ether. The ether extract was washed with brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by purification of the product through a small silica gel column using ethyl acetate-hexane (1:20) furnished the dimethyl ketals in 70-95% yield.

Method B: A solution of a ketone or aldehyde (1 gm), ethylene glycol (1.5 ml) and catalytic amount of PTSA in 20 ml of dry benzene was refluxed with a Dean-Stark water trap for $\approx$6 hr. Work-up and purification as described in method A furnished the cyclic ketals in 90% yield.

Method C: A solution of 1-methoxycyclohexene (or 2-methoxypropene, 2 mmol), an alcohol (2 mmol) and a catalytic amount of pyridinium p-toluenesulfonate in 5 ml of methylene chloride was magnetically stirred at room temperature for 12 hr. Work-up and purification as described in method A furnished the mixed ketals in $\approx$75% yield.

1-n-Dodecyloxy-1-methoxycyclohexane (1): Prepared from 2-methoxycyclohexene and dodecanol employing method C. IR (neat): ν_{max} 1450, 1150, 1150, 1095, 1050, 925 cm^{-1}; ^1H NMR: δ 3.36 (t, J=7.2 Hz, 2 H, O-CH_2), 3.20 (s, 3 H, O-CH_3), 1.30-1.82 (m, 30 H), 0.9 (distorted t, 3 H, terminal CH_3); Mass: m/z267 (M^+-OCH_3, 16), 131 (30), 113 (100), 99 (61); HRMS: m/z Calcd. for $C_{18}H_{35}O$ (M^+-OCH_3), 267.2688; Found, 267.2695.

***Table 1**: Reductive Cleavage of Ketals and Acetals*

entry	Ketal/Acetal		Product(s)	Time (hr)	% Yield[a]
(1)		**1** **2**		2.0	97
(2)		**3** **14**		2.0	97
(3)		**4** **15**		0.75	91
(4)		**5** **16**		3.5	59
(5)		**6** **17**		2.5	45
(6)		**7** **18**		3.0	52
(7)		**8** **19**		2.5 1.5	68 96[b]
(8)		**9** **20**		1.0 0.75	71 97[b]
(9)		**10** **21**		9.0 6.0	61 87[c]
(10)		**11** **22**		1.5	65
(11)		**12** **23**		1.5	96[c,d]

[a]Yields (unoptimised) refer to isolated and chromatographically pure products. [b]0.5 equiv. of $BF_3.OEt_2$ was used. [c]One equiv. of $BF_3.OEt_2$ was used. [d]Reaction was carried out at -10°C and the product was a 10:1 mixture of epimers.

1-n-Undecyloxy-1-methoxycyclohexane (3): Prepared from 2-methoxycyclohexene and undecanol employing method C. IR (neat): ν_{max} 1460, 1165, 1110, 1060, 930 cm^{-1}; ^1H NMR: δ 3.36 (t, J=7.2 Hz, 2 H, O-CH_2), 3.18 (s, 3 H, O-CH_3), 1.10-1.76 (m, 28 H), 0.9 (distorted t, 3 H, terminal CH_3); Mass: m/z 253 (M^+-OCH_3, 13%), 131 (30), 113 (100), 99 (40). HRMS: m/z Calcd. for $C_{17}H_{33}O$ (M^+-OCH_3), 253.2531; Found, 253.2538.

4-Methyl-(1,1-dimethoxyethyl)-benzene (4): Prepared from 4-methylacetophenone employing method A.[6] IR (neat): ν_{max} 1600, 1500, 1270, 1180, 1140, 1100, 1040, 870, 815 cm^{-1}; ^1H NMR: δ 7.16 and 7.38 (A_2B_2 q, J=9.0 Hz, 4 H, aromatic), 3.20 (s, 6 H, 2 x O-CH_3), 2.36 (s, 3 H, aromatic CH_3), 1.54 (s, 3 H, *tert*-

CH_3), Mass: m/z 180 (M^+, 2%), 165 (60), 150 (40), 149 (100), 119 (100), 91 (85); HRMS: m/z Calcd. for $C_{11}H_{16}O_2$, 180.1150, Found, 180.1094.

***4-Bromo-(1,1-dimethoxyethyl)-benzene (5)*:** Prepared from 4-bromoacetophenone employing method A.[6] IR (neat): ν_{max} 1585, 1480, 1265, 1190, 1145, 1095, 1040, 1010, 875, 825 cm^{-1}; ^1H NMR: δ 7.34 and 7.50 (A_2B_2 q, 4 H, J=9.3 Hz, aromatic), 3.18 (s, 6 H, 2 x O-CH_3), 1.52 (s, 3 H, *tert*-CH_3). Mass: m/z 246 (M^++2, 5), 244 (M^+, 5%), 231 & 229 (70), 218 & 216 (50), 217 & 215 (100), 185 & 183 (40), 134 (40), 89 (100); HRMS: m/z Calcd. for $C_9H_{10}O_2Br$ (M^+-CH_3), 228.9864; Found, 228.9835.

***4-Chloro-(1,1-dimethoxyethyl)-benzene (6)*:** Prepared from 4-chloroacetophenone employing method A.[7] IR (neat): ν_{max} 1485, 1155, 1085, 1040, 820 cm^{-1}; ^1H NMR: δ 7.24 and 7.46 (A_2B_2 q, J=9.3 Hz, 4 H, aromatic), 3.16 (s, 6 H, 2 x O-CH_3), 1.52 (s, 3 H, *tert*-CH_3).

***4-Methoxy-(1,1-dimethoxyethyl)-benzene (7)*:** Prepared from 4-methoxyacetophenone employing method A.[6] IR (neat): ν_{max} 1610, 1510, 1370, 1250, 1175, 1150, 1110, 1040, 875, 835 cm^{-1}; ^1H NMR: δ 6.86 and 7.42 (A_2B_2 q, J=8.5 Hz, aromatic), 3.82 (s, 3 H, aromatic O-CH_3), 3.20 (s, 6 H, 2 x O-CH_2), 1.54 (s, 3 H, *tert*-CH_3).

***2-(4-Methylphenyl)-dioxalane (8)*:** Prepared from 4-methylbenzaldehyde employing method B.[8] IR (neat): ν_{max} 1085, 935, 815 cm^{-1}; ^1H NMR: δ 7.18 and 7.38 (A_2B_2 q, J=9 Hz, 4 H, aromatic), 5.78 (s, 1 H, O-CH-C), 4.08 (m, 4 H, O-CH_2CH_2-O), 2.38 (s, 3 H, aromatic CH_3).

***2-Methyl-2-(4-Methylphenyl)-dioxalane (9)*:** Prepared from 4-methylacetophenone employing method B.[9] IR (neat): ν_{max} 1370, 1200, 1040, 820 cm^{-1}; ^1H NMR: δ 7.16 and 7.42 (A_2B_2 q, J=9 Hz, 4 H, aromatic), 3.5-4.25 (m, 4 H, O-CH_2CH_2-O), 2.36 (s, 3 H, aromatic CH_3), 1.66 (s, 3 H, *tert*-CH_3).

***1,1-Ethylenedioxycyclohexane (10)*:** Prepared from cyclohexanone employing method B.[10] IR (neat): ν_{max} 1450, 1365, 1105, 930 cm^{-1}; ^1H NMR: δ 3.88 (s, 4 H, O-CH_2CH_2-O), 1.2-2.4 (m, 10 H).

***n-Dodecyl 2-methoxyprop-2-yl ether (11)*:** Prepared from 2-methoxypropene and dodecanol employing method C. IR (neat): ν_{max} 1460, 1380, 1370, 1210, 1180, 1150, 1070, 1050, 845 cm^{-1}; ^1H NMR: δ 3.38 (t, J=7.2 Hz, 2 H, O-CH_2), 3.20 (s, 3 H, O-CH_3), 1.0-2.0 (m, 26 H), 0.88 (distorted t, 3 H, terminal CH_3).

***Typical experimental procedure for reductive cleavage*:** To a magnetically stirred solution of ketal or acetal (1 mmol) and $BF_3.OEt_2$ (0.03 ml, 0.25 mmol) in dry THF (2 ml) was added sodium cyanoborohydride (100 mg, 1.5 mmol) and the reaction mixture was stirred at room temperature. After the completion of the reaction (monitored by TLC) saturated aqueous sodium bicarbonate solution (5 ml) was added to the reaction mixture and extracted with ether (2 x 5 ml). The ether extract was washed with brine and dried (Na_2SO_4). Evaporation of the solvent followed by purification over a silica gel (3 gm) column using hexane as eluent furnished the product.

***n-Dodecyloxycyclohexane (2)*:** Reductive cleavage of the ketal **1** (300 mg, 1 mmol) with $NaCNBH_3$ (100 mg,1.0 mmol) and $BF_3.OEt_2$ (0.03 ml, 0.25 mmol) for 2 hr furnished the ether **2** (260 mg, 97%) as an oil.[5] IR (neat): ν_{max} 1450, 1360, 1110 cm^{-1}; ^1H NMR: δ 3.32-3.52 (m, 3 H, O-CH and O-CH_2), 1.0-2.0 (m, 30 H), 0.88 ppm (distorted t, 3 H, terminal CH_3); ^{13}C NMR: δ 77.4 (d, O-CH), 68.0 (t, O-CH_2), 32.4 (t, 2 C), 31.9 (t), 30.2 (t), 29.6 (t, 5 C), 29.3 (t), 26.2 (t), 25.9 (t), 24.3 (t, 2 C), 22.7 (t) and 14.0 ppm (q, CH_3); m/z 268 (M^+, 8%), 100 (26), 98 (24), 83 (100); HRMS: m/z Calcd. for $C_{18}H_{36}O$, 268.2766; Found, 268.2752.

Cyclohexyl n-undecyl ether (14): Reductive cleavage of the ketal **3** (284 mg, 1 mmol) with $NaCNBH_3$ (100 mg, 1.5 mmol) and $BF_3.OEt_2$ (0.03 ml, 0.25 mmol) for 2 hr furnished the ether **14** (245 mg, 97%) as an oil. IR (neat): ν_{max} 1450, 1360, 1110 cm^{-1}; ^1H NMR: δ 3.2-3.6 (m, 3 H, O-CH & O-CH_2), 1.1-2.0 (m, 28 H), 0.9 (distorted t, terminal CH_3); ^{13}C NMR: δ 77.5 (d, O-CH), 68.1 (t, O-CH_2), 33.3 (t), 32.5 (t, 2 C), 32.0 (t), 30.3 (t), 29.7 (t, 3 C), 26.3 (t), 25.9 (t), 24.4 (t, 2 C), 23.0 (t), 22.8 (t), 14.1 (q); Mass: m/z 254 (M^+, 16%), 211 (10), 183 (17), 154 (15), 100 (35), 83 (100); HRMS: m/z Calcd. for $C_{17}H_{34}O$, 254.2610; Found, 254.2636.

1-(4-Methylphenyl)-ethyl methyl ether (15): The reductive cleavage of the dimethyl acetal **4** (90 mg,0.5 mmol) with $BF_3.OEt_2$ (0.02 ml, 0.16 mmol) and $NaCNBH_3$ (60 mg, 1.0 mmol) for 45 minutes furnished the ether **15** (68 mg, 91%) as an oil.[12] IR (neat): ν_{max} 1445, 1105, 1080, 810 cm^{-1}; ^1H NMR: δ 7.2 (s, 4 H, aromatic), 4.28 (q, J=7.2 Hz, 1 H, O-CH), 3.24 (s, 3 H, O-CH_3), 2.38 (s, 3 H, aromatic CH_3), 1.46 (d, J=7.2 Hz, 3 H, *sec* CH_3); Mass: m/z 150 (M^+, 10%), 149 (100), 135 (61), 119 (38), 91 (40).

1-(4-Bromophenyl)-ethyl methyl ether (16): The reductive cleavage of the dimethyl acetal **5** (122 mg, 0.5 mmol) with $BF_3.OEt_2$ (0.02 ml, 0.16 mmol) and $NaCNBH_3$ (60 mg, 1.0 mmol) for 3.5 hr furnished the ether (68 mg, 59%) as an oil.[12] IR (neat): ν_{max} 1480, 1365, 1115, 1090, 1010, 825 cm^{-1}; ^1H NMR: δ 7.52 and 7.20 (A_2B_2 q, J=9 Hz, 4 H, aromatic), 4.28 (q, J=7.2 Hz, 1 H, O-CH), 3.26 (s, 3 H, O-CH_3), 1.44 (d, J=7.2 Hz, 3 H, *sec*-CH_3); Mass: m/z 216 (M^++2, 10%), 214 (M^+, 10), 201 & 199 (100), 185 & 183 (18), 104 (25); HRMS: m/z Calcd. for $C_9H_{11}OBr$, 214.0002. Found, 213.9998.

1-(4-Chlorophenyl)-ethyl methyl ether (17): The reductive cleavage of the dimethyl acetal **6** (100 mg, 0.5 mmol) with $BF_3.OEt_2$ (0.02 ml, 0.16 mmol) and $NaCNBH_3$ (60 mg, 1.0 mmol) for 2.5 hr furnished the ether **17** (38 mg, 45%) as an oil.[12] IR (neat): ν_{max} 1485, 1120, 1085, 1010, 820 cm^{-1}; ^1H NMR: δ 7.24 and 7.36 (A_2B_2 q, J=9 Hz, 4 H, aromatic), 4.3 (q, J=7.2 Hz, 1 H, O-CH), 3.26 (s, 3 H, O-CH_3), 1.46 (d, J=7.2 Hz, 3 H, *sec*-CH_3); Mass: m/z 170 (M^+, 7%), 171 (17), 169 (50), 157 (20), 155 (62), 141 (30), 139 (100), 113 (15), 111 (45).

1-(4-Methoxyphenyl)-ethyl methyl ether (18): The reductive cleavage of the dimethyl acetal **7** (98 mg, 0.5 mmol) with $BF_3.OEt_2$ (0.02 ml, 0.16 mmol) and $NaCNBH_3$ (60 mg, 1.0 mmol) for 3 hr furnished the ether **18** (43 mg, 52%) as an oil.[12] IR (neat): ν_{max} 1600, 1510, 1245, 1170, 1105, 1080, 1035, 835 cm^{-1}; ^1H NMR: δ 6.90 and 7.26 (A_2B_2 q, J=9 Hz, 4 H, aromatic), 4.26 (q, J=7.2 Hz, 1 H, O-CH), 3.84 (s, 3 H, aromatic O-CH_3), 3.20 (s, 3 H, O-CH_3), 1.46 (d, J=7.2 Hz, 3 H, *sec*-CH_3); Mass: m/z 166 (M^+, 10%), 151 (100), 135 (52), 91 (32); HRMS: m/z Calcd. for $C_{10}H_{14}O_2$, 166.0994; Found, 166.0977.

2-[(4-Methylphenyl)-methoxy]-ethanol (19): The reductive cleavage of the cyclic ketal **8** (164 mg, 1 mmol) with $BF_3.OEt_2$ (0.07 ml, 0.5 mmol) and $NaCNBH_3$ (100 mg, 1.5 mmol) for 1.5 hr furnished the alcohol **19** (112 mg, 96%) as an oil.[13] IR (neat): ν_{max} 3400 (O-H), 1240, 1110, 1070, 800 cm^{-1}; ^1H NMR: δ 7.22 (s, 4 H, aromatic), 4.56 (s, 2 H, Ar-CH_2-O), 3.5-3.9 (m, 4 H, O-CH_2CH_2-O), 2.4 (s, 3 H, aromatic CH_3), 2.12 (brs, 1 H, O-H); Mass: m/z 166 (M^+, 14%), 121 (17), 105 (100), 91 (17); HRMS: m/z Calcd. for $C_{10}H_{14}O_2$, 166.0994; Found, 166.0987.

2-[1-(4-Methylphenyl)-ethoxy]-ethanol (20): The reductive cleavage of the cyclic ketal **9** (178 mg, 1mmol) with $BF_3.OEt_2$ (0.07 ml, 0.5 mmol) and $NaCNBH_3$ (100 mg, 1.5 mmol) for 45 minutes furnished the alcohol **20** (175 mg, 97%) as an oil.[9] IR (neat): ν_{max} 3400 (O-H), 1510, 1450, 1110, 1060, 820 cm^{-1}; ^1H NMR: δ 7.20 (s, 4 H, aromatic), 4.44 (q, J=7.2 Hz, 1 H, Ar-CH-O), 3.4-3.9 (m, 4 H, O-CH_2CH_2-O),

2.36 (s, 3 H, aromatic CH_3), 2.10 (brs, 1 H, O-H), 1.46 (d, J=7.2 Hz, 3 H, *sec*-CH_3); Mass: m/z 180 (M^+, 9%), 165 (32), 121 (30), 119 (100), 91 (52); HRMS: m/z Calcd. for $C_{11}H_{16}O_2$, 180.1150; Found, 180.1159.

***2-Cyclohexyloxyethanol (21)*:** The reductive cleavage of the cyclic ketal **10** (142 mg, 1.0 mmol) with $BF_3.OEt_2$ (0.13 ml, 1.0 mmol) and $NaCNBH_3$ (100 mg, 1.5 mmol) for 6 hr furnished the alcohol **21** (125 mg, 87%) as an oil.[10] IR (neat): ν_{max} 3310 (O-H), 1445, 1110, 1060 cm^{-1}; ^1H NMR: δ 3.1-3.8 (m, 5 H, O-CH & O-CH_2CH_2-O), 1.0-2.5 (m, 10 H).

***n-Dodecyl isopropyl ether (22)*:** The reductive cleavage of the mixed acetal **11** (130 mg, 0.5 mmol) with $BF_3.OEt_2$ (0.02 ml, 0.16 mmol) and $NaCNBH_3$ (60 mg, 1 mmol) for 1.5 hr furnished the ether **22** (74 mg, 65%) as an oil.[14] IR (neat): ν_{max} 1455, 1370, 1360, 1140, 1125, 1080 cm^{-1}; ^1H NMR: δ 3.48 (sepset, 1 H, O-CH), 3.40 (t, J=7.2 Hz, 2 H, O-CH_2), 1.28 (brs, 20 H), 1.18 (d, J=7.2 Hz, 6 H, 2 x CH_3), 0.88 (distorted t, 3 H, terminal CH_3); ^{13}C NMR (67.89 MHz): δ 70.2 (O-CH), 67.2 (O-CH_2), 30.9, 29.2 (2 C), 28.6 (3 C), 28.3 (2 C), 25.2, 21.6, 21.1 (2 C), 13.0; Mass: m/z 213 (M^+-CH_3, 10%), 169 (12), 85 (25), 43 (100); HRMS: m/z Calcd. for $C_{14}H_{29}O$ (M^+-CH_3), 213.2219; Found, 213.2243.

***(2α and 2β),3aβ,4α,7aβ-2,4,6,6-Tetramethylperhydrobenzofurans (23)*:** The reductive cleavage of the ketal **12**[11] (85 mg, 0.4 mmol) at -10°C with $BF_3.OEt_2$ (0.05 ml, 0.4 mmol) and $NaCNBH_3$ (60 mg, 1 mmol) for 1.5 hr furnished the tetrahydrofuran **23** as a 10:1 mixture of diastereomers (70 mg, 96%) as an oil.[11] IR (neat): ν_{max} 1450, 1350, 750 cm^{-1}; ^1H NMR (400 MHz, for major 2α-isomer): δ 4.0-4.2 (m, 2 H), 2.3-2.4 (m, 1 H), 1.95-2.05 (m, 1 H), 1.35-1.80 (m, 3 H), 1.27 and 1.17 (d, J=6.2 Hz, 3 H, *sec*-CH_3), 0.95-1.10 (m, 3 H), 0.92 (d, J=6.6 Hz, 3 H, *sec*-CH_3), 0.89 (s, 3 H) and 0.85 (s, 3 H) (2 x *tert*-CH_3); ^{13}C NMR: δ 76.5, 75.0, 44.5, 43.8, 42.2, 41.6, 33.1, 32.0, 27.2, 24.4, 23.2, 20.3; Mass: m/z 182 (M^+, 15%), 181 (20), 167 (45), 123 (85), 111 (100), 95 (30).

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