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POLARIZED KETENE DITHIOACETALS 63. STEREOSELECTIVE SYNTHESIS OF α-YLIDENE-γ-BUTYROLACTONES[1]

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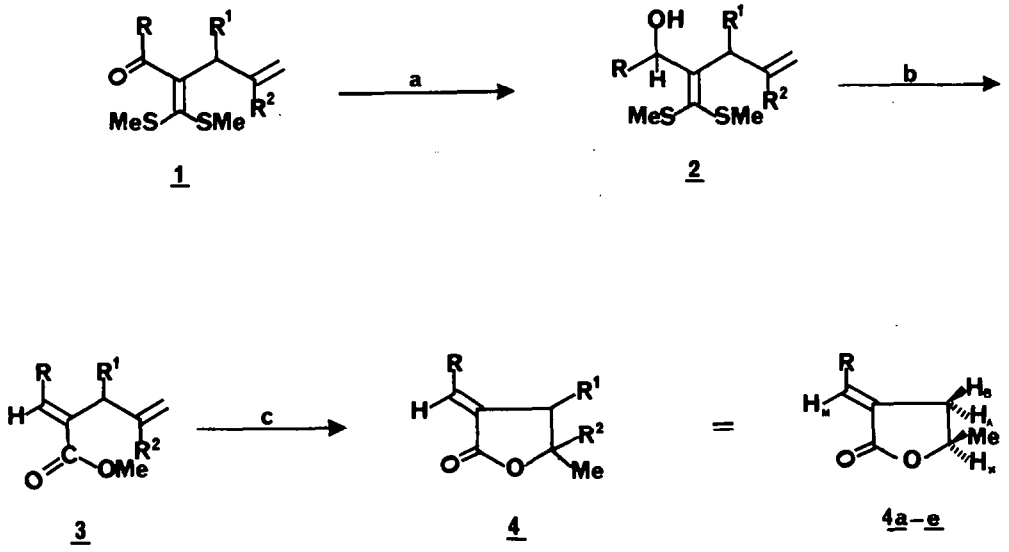
Abstract: A facile method for highly stereoselective synthesis of α-arylidene (4a-d, 4f-h and 4j) and α-ethylidene (4e,4i)-γ-butyrolactones has been developed by acid catalyzed lactonization of the corresponding α-ylidene-γ,δ-unsaturated esters 3a-j. The required esters 3a-j were obtained by regioselective reduction of the corresponding α-oxo-α-allyl (or substituted allyl) ketene dithioacetals 1a-j with sodium borohydride and subsequent boron-trifluoride etherate catalyzed methanolysis of the resultant carbinol acetals 2a-j. Treatment of α-acetylketene dithioacetals 1e and 1i with methylmagnesium iodide afforded the carbinol acetals 5b and 5c respectively which under above sequence of reactions yielded the corresponding α-isopropylidene-γ-butyrolactones 7a and 7b in good yields.

We have recently reported[2] a new general highly stereo- and regioselective method for α,β-unsaturated esters from the corresponding α-oxoketene dithioacetals, which can be derived from active methylene ketones in one pot reaction[3]. The method consists of 1,2-reduction of α-oxoketene dithioacetals with sodium borohydride to give the corresponding carbinol acetals in high yields, and subsequent borontrifluoride etherate catalyzed methanolysis to give the corresponding eneesters. The overall transformation is considered as homologation of active methylene ketones at α-position involving 1,3-carbonyl transposition. The method was further successfully extended for the synthesis of 5-aryl-2,4-pentadienoates[4] and 7-aryl-2,4,6-heptatrienoates[5] by employing the respective α-cinnamoyl and α-(5-aryl-2,4-pentadienoyl) ketene dithioacetals. In continuation of this work, we contemplated that the α-oxo-α-allyl/substituted allyl ketene dithioacetals of the general formula 1 should also yield under similar reaction sequence, the corresponding α-arylidene/alkylidene-γ,δ-unsaturated esters 3, which are useful precursors for α-arylidene/alkylidene γ-butyrolactones 4 (Scheme 1). We have thus realized these objectives and report our results in this paper.

Results and Discussions

Among the various α-allyl dithioacetals employed in the present investigation, 1a-d were already reported by us in connection with our base catalyzed rearrangement studies[6], and the remaining hitherto unknown 1e-j were prepared essentially by extending the same method. The β-oxodithioesters[7] which are common intermediates for all 1e-j were treated either with allyl bromide in the presence of base to give α- C-allyldithioesters followed by S-methylation to give 1e, or with methacrylyl chloride and crotyl bromide to give 1f-i and 1j respectively in 65-70% overall yield. These dithioacetals 1a-j were then subjected to further transformations. When 1a was treated with

sodium borohydride in refluxing ethanol, the corresponding carbinol acetal 2a was obtained in nearly quantitative yield. Subsequent methanolysis of 2a in the presence of borontrifluoride etherate gave the corresponding (E)-methyl-2-benzylidene-4-pentenoate 3a in 80% yield[8]. The ester 3a thus obtained was then heated with a mixture of phosphoric and formic acids (1:1), when the corresponding (E)-3-benzylidene-5-methyl-γ-butyrolactone (4a)[9] was obtained in 78% yield. The spectral and analytical data of 4a were in conformity with the structure assigned. Similarly, the dithioacetals 1b-d also yielded the corresponding (E)-dieneesters 3b-d (70-75%)[8], which were converted to the respective (E)-α-ylidene-γ-butyrolactones 4b-d[9] under identical conditions in 75-80% overall yields. When the α-isobutenyldithioacetals 1f-i and α-(1-methyl-2-propenyl) dithioacetal 1j were subjected to similar transformation, the corresponding diene esters 3f-j formed during the reaction could not be purified and were therefore subjected directly for cyclization under identical conditions to yield the corresponding 5,5-dimethyl-(4f-j) and 4,5-dimethyl-(4j)-α-ylidene-γ-butyrolactones in 76-81% overall yields (Scheme 1). Apparently, the lactone ring closure is accompanied with high stereoselectivity, since all the lactones were characterized as (E)-stereoisomers[9-12].



1 2 3 4 4a–e

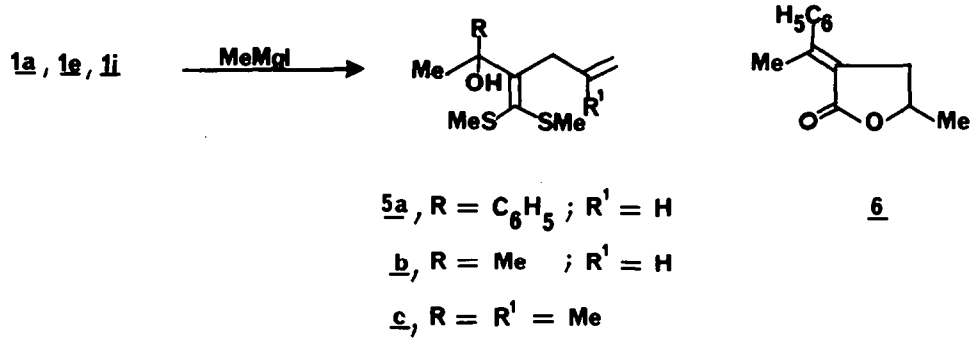
a. $NaBH_4/EtOH, \Delta$; b. $BF_3 \cdot Et_2O/MeOH, \Delta$; c. $H_3PO_4/HCO_2H, \Delta$.

1 – 4	R	R^1	R^2	1 – 4	R	R^1	R^2
a	C_6H_5	H	H	f	C_6H_5	H	Me
b	4-Cl C_6H_4	H	H	g	4-ClC_6H_4	H	Me
c	4-MeOC_6H_4	H	H	h	4-MeOC_6H_4	H	Me
d	4-MeC_6H_4	H	H	i	Me	H	Me
e	Me	H	H	j	4-ClC_6H_4	Me	H

Scheme 1

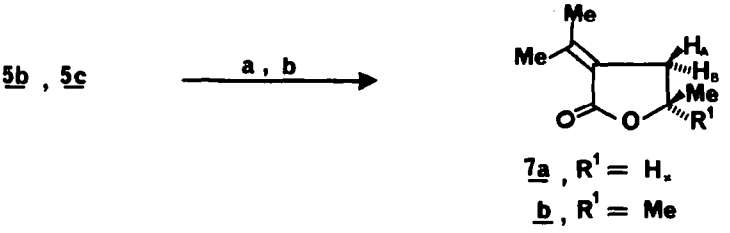
In order to further prove the generality and limitations of this transformation, we studied the reaction of 1a with methyl magnesium iodide[13] to give the carbinol 5a, which under similar reaction sequence by analogy with above results should afford the lactone 6. However, 5a, though obtained in good yield, failed to give any well defined product, when subjected to methanolysis. On the otherhand α-acetyl ketene dithioacetals 1e and 1i successfully met our expectations, and the carbinols 5b and 5c under above sequence of reactions yielded the corresponding α-isopropylidene-lactones 7a and 7b in good yields (Scheme 2).

In conclusion, the overall transformation provides a novel route for the synthesis of hitherto unknown α-ylidene-γ-butyrolactones. Synthetic methods for α-methylene/alkylidene-γ-butyrolactones have received considerable attention in recent years, in view of the varied biological activity exhibited by natural products containing this structural moiety[14]. A few of the α-arylidene-γ-butyrolactones have been used as intermediates in the synthesis of natural lignans[15,16]. It is pertinent to note that despite several approaches reported for the construction of α-methylene/alkylidene-γ-butyrolactones by lactonization of acyclic γ,δ-unsaturated acids[14], the corresponding parallel approach for α-arylidene-γ-butyrolactones from acyclic precursors is not reported earlier. The methods for such compounds usually involve α-arylidenation of preformed γ-butyrolactone ring[10,11,17]. The present lactone synthesis therefore, is an attractive alternative method for these class of compounds from functionalized acyclic precursors.



5a, R = C_6H_5 ; R^1 = H
b, R = Me ; R^1 = H
c, R = R^1 = Me

6



7a, R^1 = H_a
b, R^1 = Me

a. $BF_3 \cdot Et_2O/MeOH$, Δ ; b. H_3PO_4/HCO_2H, Δ.

Scheme 2

Experimental Section

Melting points were determined on a Thomas Hoover Apparatus and are uncorrected. The IR spectra were obtained on a Perkin Elmer 297 spectrophotometer. ^{1}H NMR spectra were recorded on Varian EM-390 and Bruker 250 MHz spectrometer and are reported in δ units down field from Me_4Si. Mass spectra were obtained on Jeol D-600 spectrometer.

The known ketene dithioacetals 1a-d,1j[18] and the unknown 1e-i were prepared according to earlier reported procedure[6].

3-Bis(methylthio)methylene-5-hexen-2-one(1e); yellow oil (65%); IR: ν_{max}(neat) 1660 cm^{-1}; ^{1}H NMR (CCl_4): 2.21(s,6H,SCH_3,CH_3); 2.29(s,3H,SCH_3); 3.22(d,2H,CH_2); 4.85-5.11(m,2H,=CH_2); 5.42-6.87(m,1H, -CH=CH_2); (Found: C,53.58; H,7.10; Calc. for $C_9H_{14}OS_2$; C,53.47, H,6.93%).

2-Bis(methylthio)methylene-1-phenyl-4-methyl-4-penten-1-one(1f); orange oil (68%); IR: ν_{max}(neat) 1665 cm^{-1}; ^{1}H NMR(CCl_4): 1.68(s,3H,CH_3); 2.0(s,3H,SCH_3); 2.31(s,3H,SCH_3); 3.38(s,2H,CH_2); 4.62(s, 2H,=CH_2); 7.35-7.89(s,5H,ArH); (Found: C,64.91, H,6.59, Calc. for $C_{15}H_{18}OS_2$: C,64.75; H,6.47%); m/z 278(35%,M^+); 263(100%).

2-Bis(methylthio)methylene-1-(4-chlorophenyl)-4-methyl-4-penten-1-one(1g); orange oil (69%); IR: ν_{max}(neat) 1660 cm^{-1}; ^{1}H NMR(CCl_4): 1.59(s,3H,CH_3); 2.03(s,3H,SCH_3); 2.32(s,3H,SCH_3); 3.35(s,2H, CH_2); 4.64(s,2H,=CH_2); 7.29-7.77(dd,A_2B_2,4H,ArH); (Found: C,57.78, H,5.59; Calc. for $C_{15}H_{17}ClOS_2$: C,57.60, H,5.44%); m/z 314,312(1%, 4%,M^+); 299,297(7%,17%).

2-Bis(methylthio)methylene-1-(4-methoxyphenyl)-4-methyl-4-penten-1-one(1h); orange oil(63%); IR: ν_{max}(neat) 1655 cm^{-1}; ^{1}H NMR(CCl_4): 1.70(s,3H,CH_3); 2.08(s,3H,SCH_3); 2.30(s,3H,SCH_3); 3.35(s,2H, CH_2); 3.81(s,3H,CH_3O); 4.64(s,2H,=CH_2); 6.78-7.79(dd,A_2B_2,4H,ArH); (Found: C,62.52, H,6.71; Calc. for $C_{16}H_{20}O_2S_2$: C,62.34; H,6.49%); m/z 308(7%,M^+); 293(29%).

3-Bis(methylthio)methylene-5-methyl-5-hexen-2-one(1i); orange oil (60%); IR: ν_{max}(neat) 1675 cm^{-1}; ^{1}H NMR(CCl_4): 1.65(s,3H,CH_3); 2.25(s,3H,SCH_3); 2.30(s,6H,SCH_3,CH_3CO); 3.16(s,2H,CH_2); 4.61(d,2H, =CH_2); (Found: C,55.68, H,7.60, Calc. for $C_{10}H_{16}OS_2$: C,55.55, H,7.41%).

General Procedure for Reduction of α-oxoketene dithioacetals (1a-j): The reduction of 1a with $NaBH_4$ is representative. To a solution of 1a (2.6g, 0.01 mol) in ethanol, 1.10g(0.03 mol) of $NaBH_4$ was added and the reaction mixture refluxed with stirring for 45 min. It was then poured into ice-cooled water (100 ml), extracted with chloroform (3x50 ml), the extract washed with water (100 ml), dried and evaporated to give carbinol (2.4g,92%) as light yellow oil. IR: ν_{max}(neat) 3200-3500 cm^{-1}. All the carbinols 2a-j thus obtained in nearly quantitative yields were used as such for subsequent methanolysis.

General Procedure for Methanolysis of Carbinolacetals (2a-j) to diene esters 3a-j.

Methanolysis of 2a is representative. To a solution of 2a(2.6g, 0.01 mol) in MeOH(30 ml) from previous reaction, 3 ml of $BF_3.Et_2O$ was added and the solution refluxed for 12-14 hr. The reaction mixture was cooled, poured into saturated sodium bicarbonate solution (75 ml), extracted with chloroform (3x50 ml), the combined extracts were washed with water (100 ml), dried (Na_2SO_4) and

evaporated to give the crude ester 3a, which was further purified by passing through silica gel column using hexane/ethylacetate(9:1) as eluent. The pure 3b-d could be obtained in this manner, however the esters 3e-j could not be purified for spectral and analytical data and were as such used for lactonization.

(E)-Methyl-2-benzylidene-4-pentenoate (3a); obtained as yellow viscous oil; 1.6g (79%); IR: ν_{max} (neat) 1710, 1630 cm^{-1}; ^1H NMR(CCl_4): 3.15(d,2H,CH_2); 3.67(s,3H,CH_3O); 4.80-5.85(m,2H,=CH_2); 5.74-6.11(m,1H,-CH=CH_2); 7.28(s,5H,ArH); 7.62(s,1H,ArCH=); (Found: C,77.41, H, 7.13; Calc. for $C_{13}H_{14}O_2$: C, 77.23; H, 6.93%); m/z 202 (31%, M^+).

(E)-Methyl-2-(4-chlorobenzylidene)-pentenoate (3b); yellow viscous oil; 1.8g (76%); IR: ν_{max}(neat) 1720, 1638 cm^{-1}; ^1H NMR(CCl_4): 3.09(s,2H,CH_2); 3.78(s,3H,CH_3O); 4.81-5.07(m,2H,=CH_2); 5.60-6.0(m, 1H,-CH=CH_2); 7.28(s,4H,ArH); 7.57(s,1H,ArCH=); (Found: C,65.74; H, 5.31; Calc. for $C_{13}H_{13}ClO_2$; C,65.96; H, 5.50%); m/z 236(31%,M^+).

(E)-Methyl-2-(4-methoxybenzylidene)-4-pentenoate (3c); yellow oil; 1.6g (70%); IR: ν_{max}(neat) 1712 1629 cm^{-1};^1H NMR;3.23(d,2H,CH_2); 3.72(s,3H,CH_3O); 4.92-5.20(m,2H,=CH_2); 5.71-6.18(m,1H,-CH=CH_2); 6.77-7.39(dd,A_2B_2,4H,ArH); 7.69(s,1H,ArCH=); (Found: C, 72.57; H, 7.14; Calc. for $C_{14}H_{16}O_3$: C, 72.41; H, 6.90%), m/z 232 (90%,M^+).

(E)-Methyl-2-(4-methylbenzylidene)-4-pentenoate (3d); yellow oil; 1.7g (75%); IR: ν_{max}(neat) 1715, 1626 cm^{-1}; ^1H NMR (CCl_4); 2.36(s,3H,CH_3); 3.21(d,2H,CH_2); 3.72(s,3H,CH_2); 3.72(s,3H,CH_3O); 4.92-5.21(m,2H,=CH_2); 5.71-6.18(m,-CH=CH_2); 7.10-7.30(dd,A_2B_2,4H,ArH), 7.69(s,1H,ArCH=); (Found: C, 77.60; H,7.33; Calc. for $C_{14}H_{16}O_2$: C, 77.78; H, 7.41%); m/z 216(29%,M^+).

General Procedure for α-Ylidene-γ-butyrolactones (4a-j); A mixture of diene ester 3a (2.0g, 0.01 mol), phosphoric acid (85%, 25 ml) and formic acid (98%, 25 ml) was heated with stirring at 90°C for 4 hr. The reaction mixture was then quenched with water (150 ml) and stirred at room temperature for 30 min, extracted with chloroform (3x50 ml) and the combined extracts washed successively with aqueous $NaHCO_3$ (10%, 100 ml),water (100 ml), dried (Na_2SO_4) and evaporated to give crude (E)-3-benzylidene-5-methyl-γ-butyrolactone (4a), which was further purfied by passing through silica gel column using hexane:ethyl acetate (9:1) as eluent, light yellow crystals ($CHCl_3$); yield 1.7g (88%); m.p. 48°C; IR: ν_{max}(KBr) 1740, 1640 cm^{-1}; ^1H NMR($CDCl_3$): 1.50(d,3H,CH_3, J=7Hz); 2.75(ddd,1H,H_B; J_{AB}=17.5 Hz; J_{BX} =5.5 Hz; J_{BM}=2.8Hz); 3.32(ddd,1H,H_A,J_{AB}=17.5 Hz; J_{AX}=7.7 Hz; J_{AM}=2.8 Hz); 4.23(br sext,1H,H_X); 7.28(s,5H,ArH); 7.40(t,1H,H_M, J=2.8 Hz); δ (C_6D_6) 0.91(d,3H,CH_3); 2.99(ddd,1H,H_B); 2.48(ddd,1H,H_A); 4.04(br sext, 1H,H_X); 7.11(s,5H,ArH); 7.63(t,1H, H_M); (Found: C, 76.79; H, 6.55; Calc. for $C_{12}H_{12}O_2$: C, 76.60; H, 6.38%); m/z 188(60%,M^+); 144(16%, M^+-44).

The lactones 4a-d were similarly obtained from the esters 3a-d, while the other lactones 4e-j were prepared under identical conditions by utilizing crude esters 3e-j without purification.

(E)-3-(4-Chlorobenzylidene)-5-methyl-γ-butyrolactones (4b); light yellow crystals ($CHCl_3$); 2.0g (90%); m.p. 82°C; IR: ν_{max}(KBr) 1740, 1638 cm^{-1}; ^1H NMR ($CDCl_3$): 1.48(d,3H,CH_3, J=6.5 Hz); 2.77 (ddd,1H,H_B,J_{AB}=17.7 Hz,J_{BX}=5.4 Hz; J_{BM}=2.8 Hz); 3.36(ddd,1H,H_A,J_{AB}=17.7 Hz; J_{AX}=7.7 Hz; J_{AM}=2.8 Hz);

4.77(sext,1H,H_X); 7.41(s,4H,ArH); 7.49(t,1H,H_M,J=2.8 Hz); δ(C_6D_6): 0.92(d,3H,CH_3); 1.87(ddd,1H, H_B); 2.35(ddd,1H,H_A); 4.03(sext,1H,H_X); 6.82 and 7.13(dd,A_2B_2,4H,ArH); 7.53(t,1H,H_M); (Found: C, 64.96, H, 4.79; Calc. for $C_{12}H_{11}ClO_2$: C, 64.72; H, 4.94%); m/z 224, 222(17%, 15%,M^+); 188, 178 (4%,6%,M^+-44).

(E)-3-(4-Methoxybenzylidene)-5-methyl-γ-butyrolactone (4c); light yellow crystals ($CHCl_3$); 1.8g (82%); m.p. 76°C; IR: ν_{max}(KBr) 1740, 1650 cm^{-1}; ^1H NMR($CDCl_3$): 1.43(d,3H,CH_3,J=6.6 Hz); 2.76(ddd, 1H,H_B,J_{AB}=17.4 Hz; J_{BX}=5.5 Hz; J_{BM}=2.7 Hz); 3.35(ddd,1H,H_A,J_{AB}=17.4 Hz; J_{AX}=8 Hz; J_{AM}=2.7 Hz); 3.85 (s,3H,CH_3O); 4.74(sext,1H,H_X); 6.96 -7.47(dd,A_2B_2,4H,ArH); 7.50(t,1H,H_M,J=2.7 Hz); δ(C_6D_6); 0.95 (d,3H,CH_3); 2.03(ddd,1H,H_B); 2.53(ddd,1H,H_A); 3.31(s,3H,CH_3O); 4.06(sext,1H,H_X); 6.74 -7.14(dd, A_2B_2,4H,ArH); 7.67(t,1H,H_M); (Found: C, 71.70; H, 6.56; Calc. for $C_{13}H_{14}O_3$: C, 71.56; H, 6.42%); m/z 218(82%,M^+).

(E)-3-(4-Methylbenzylidene)-5-methyl-γ-butyrolactone (4d); light yellow crystals ($CHCl_3$); 1.6g (80%); m.p. 42°C; IR: ν_{max}(KBr) 1738, 1650 cm^{-1}; ^1H NMR($CDCl_3$): 1.35(d,3H,J=6.5 Hz,CH_3); 2.32(s, 3H,CH_3Ar); 2.68(ddd,1H,H_B,J_{AB}=17.5 Hz; J_{BX}=5.3 Hz; J_{BM}=3 Hz); 3.24(ddd,1H,H_A,J_{AB}=17.5 Hz;J_{AX}=7.8 Hz; J_{AM}=2.8 Hz; 4.60(sext,1H,H_X); 7.0-7.25(dd,A_2B_2,4H,ArH); 7.29(t,1H,H_M,J=2.8 Hz); δ (C_6D_6): 0.88(d,3H, CH_3); 1.97(ddd,1H,H_B); 2.08(s,3H,ArCH_3); 2.47(ddd,1H,H_A); 3.99(sext,1H,H_X); 6.94-7.05(dd,A_2B_2,4H, ArH); 7.69(t,1H,H_M): (Found: C, 76.98, H, 7.10; Calc. for $C_{13}H_{14}O_2$: C, 77.23; H, 6.93%); m/z 202 (53%,M^+); 130(100%).

(E)-3-Ethylidene-5-methyl-γ-butyrolactone (4e); light yellow oil; 1.0g (80%): IR: ν_{max}(neat) 1756, 1680 cm^{-1}; ^1H NMR($CDCl_3$); 1.35(d,3H,J=6 Hz,CH_3); 1.83(dt,3H,CH_3CH=; J=6.5 Hz, 2.8 Hz); 2.30(m,1H, H_B); 2.92(m,1H,H_A); 4.53(sext,1H,H_x); 6.63(m,1H,CH_3CH=); (Found: C, 66.90; H, 8.05; Calc. for $C_7H_{10}O_2$: C, 66.67, H, 7.94%); m/z 126(12%,M^+).

(E)-3-Benzylidene-5,5-dimethyl-γ-butyrolactone (4f); light yellow crystals ($CHCl_3$); 1.5g (76%); m.p. 47°C; IR: ν_{max}(KBr) 1744, 1658 cm^{-1}; ^1H NMR($CDCl_3$); 1.45(s,6H,CH_3); 3.0(d,2H,CH_2,J=2.8 Hz); 7.52(s,6H,ArH and ArCH=); (Found: C,77.10, H, 6.73; Calc. for $C_{13}H_{14}O_2$: C, 77.23, H, 6.93%); m/z 202(M^+); 187(19%,M^+-15).

(E)-3-(4-Chlorobenzylidene)-5,5-dimethyl-γ-butyrolactone (4g); light yellow crystals ($CHCl_3$); 1.90g (80%); m.p. 58°C; IR: ν_{max}(KBr): 1739, 1659 cm^{-1}; ^1H NMR(CCl_4): 1.45(s,6H,CH_3); 2.93(d,2H, CH_2,J=3 Hz); 7.35(s,4H,ArH); 7.40(t,1H,ArCH=, J=3 Hz); (Found: C, 66.12; H, 5.73; Calc. for $C_{13}H_{13}ClO_2$: C, 65.96; H, 5.50%); m/z 238, 236(7%,29%,M^+).

(E)-3-(4-Methoxybenzylidene)-5,5-dimethyl-γ-butyrolactone (4h); light yellow crystals ($CHCl_3$); 1.7g (75%); m.p. 52°C; IR: ν_{max}(KBr) 1730, 1643, 1602 cm^{-1}; ^1H NMR(CCl_4): 1.47(s,6H,CH_3); 2.92(d, 2H,CH_2,J=3 Hz); 3.55(s,3H,CH_3O); 6.90-7.40(dd,A_2B_2,4H,ArH); 7.45(t,1H,ArCH=, J=3 Hz); (Found: C, 72.58; H, 6.68; Calc. for $C_{14}H_{16}O_3$: C, 72.41; H, 6.90%); m/z 232(29%,M^+).

(E)-3-Ethylidene-5,5-dimethyl-γ-butyrolactone (4i); light yellow viscous oil; 1.0g (74%); IR: ν_{max} (neat) 1757 cm^{-1}; ^1H NMR(CCl_4): 1.40(s,6H,CH_3); 1.80(dt,J=6.5 and 2.5 Hz); 2.60(distorted quintet, J=2.5 Hz,2H,CH_2); 6.65(m,1H,CH_3CH=); (Found: C,68.72, H, 8.77, Calc. for $C_8H_{12}O_2$: C, 68.57, H,8.57%).

(E)-3-(4-Chlorobenzylidene)-4,5-dimethyl-γ-butyrolactone (4j); light yellow crystals ($CHCl_3$); 1.7g (70%); m.p. 79°C; IR: ν_{max}(KBr) 1745, 1657 cm^{-1}; ^1H NMR($CDCl_3$): 1.12(d,3H,CH_3,J=7 Hz); 1.40 (d,3H,CH_3,J=7 Hz); 3.48(quintet d,1H,H-4,J=7 Hz), 2.8 Hz); 4.55(quintet,1H,H-5,J=7 Hz); 7.29(t,1H, ArCH=,J=2.8 Hz); 7.49(A_2B_2,4H,ArH); (Found: C, 65.69, H, 5.72; Calc. for $C_{13}H_{13}ClO_2$: C, 65.96, H, 5.50%), m/z 238, 236(10%,31%,M^+).

Reaction of (1a),(1e) and (1j) with Methylmagnesium iodide; General Procedure: To an ice cold solution (-5°C-0°C) of methylmagnesium iodide [0.03 mol, prepared from magnesium turnings (0.72g, 0.03g atom) and methyl iodide (4.2g, 0.03 mol)] in dry ether (30 ml) a solution of 1a (2.6g,0.01 mol) in dry benzene (25 ml) was gradually added (5 min.) and the mixture stirred at room temperature for 30 min. The reaction mixture is then poured into satd. NH_4Cl solution (100 ml), extracted with ether (3x50 ml). The combined extracts were washed with water, dried (Na_2SO_4) and evaporated to give the carbinol acetal 5a (2.5g). The other carbinol acetals 5b and 5c were also obtained in the similar way in nearly quantitative yield and were subjected to methanolysis and lactonization according to the general procedure described for carbinols 2a-j.

3-Isopropylidene-5-methyl-γ-butyrolactone (6a) was obtained as light yellow viscous oil; 0.9g (68%); IR: ν_{max}(neat) 1750, 1660 cm^{-1}; ^1H NMR(CCl_4): 1.32(d,3H,CH_3,J=6.5 Hz); 1.80(t,3H,CH_3C=trans to CO,J=2.8 Hz); 2.28(t,3H,CH_3C= cis to CO,J=3 Hz); 2.42(m,1H,H_B); 2.70-3.18(m,1H,H_A); 4.45(br sext,1H,H_X); (Found: C,68.79, H, 8.82; Calc. for $C_8H_{12}O_2$: C, 68.57, H, 8.57%).

3-Isopropylidene-5,5-dimethyl-γ-butyrolactone (6b); light yellow viscous oil; 1.0g(65%); IR: ν_{max} (neat) 1741, 1666 cm^{-1}; ^1H NMR(CCl_4): 1.35(s,6H,5-CH_3); 1.75(brs,3H,CH_3C= trans to CO); 2.18(t,3H, CH_3C=cis to CO: J=2.8 Hz); 2.63(q,2H,CH_2,J=2.8 Hz); (Found: C,69.95, H,9.21: Calc. for $C_9H_{14}O_2$: C, 70.13; H,9.09%); m/z 154(58%,M^+).

References and Notes

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