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CONVERSION OF LACTONES TO THE HIGHER HOMOLOGOUS α, β-UNSATURATED LACTONES *VIA* HYPERVALENT IODINE OXIDATION OF 1-TRIMETHYLSILYLOXY-2-OXA[n.1.0] CYCLOALKANES

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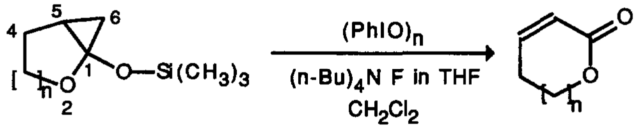
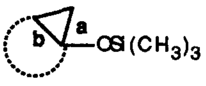
We report the ring expansion of lactones *via* oxidation of the derived trimethylsilyloxycyclopropanols to the higher homologous α, β-unsaturated lactones (**1a-d→2a-d**).



1a, n = 1; **1b**, n = 2;
1c, n = 3; **1d**, n = 9

2a-d, n = 1,2,3,9



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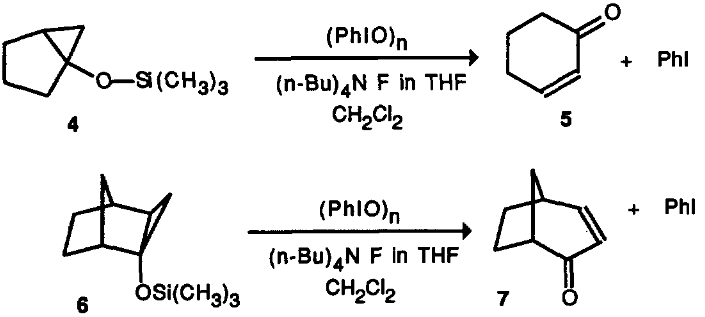
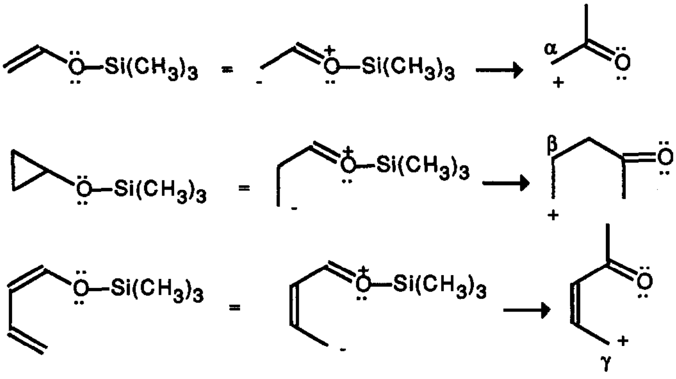
By way of background, similar reactions of 1-trimethylsilyloxybicyclo[n.1.0]alkanes derived from ketones (**3**) have been reported but the lactone system has not been transformed in this manner. Considering the general case studied for ketones and exemplified by **3**, bond cleavage in the sense of **b** yields the ring-expanded product and this has been observed using FeCl$_3$ to yield β-chloroketoneS.[2] Subsequent dehydrohalogenation using NaOAc yields the higher homologous α, β-unsaturated ketone. Also electrolysis proceeds *via* **b** bond cleavage.[3] Bond **a** cleavage occurs with ZnI$_2$,[4] base,[5] halogen,[6] Hg(OAc)$_2$,[7] AgBF$_4$[8] or Cu(BF$_4$)$_2$,[8] SnCl$_4$[9] and TiCl$_4$.[10]

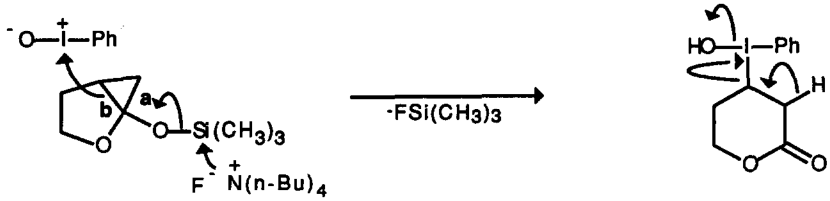
1-Trimethylsilyloxy-2-oxa or 1-trimethylsilyloxybicyclo[n.1.0]alkanes[11] were prepared by the reaction of the corresponding 1-trimethylsilyl enol ethers[12] with CH$_2$I$_2$/ Et$_2$Zn in cyclohexane. Treatment of 1-trimethylsilyloxy-2-oxa bicyclo[n.1.0]alkanes (**1a-d**; 0.01 mole) with iodosobenzene (0.01 mole) and (n-Bu)$_4$N·F (0.01 mole) in dichloromethane resulted in the direct formation of ring homologated α, β-unsaturated lactones (**2a-d**) in good yields (Table 1).[13] Similarly, 1-trimethylsilyloxy-bicyclo[3.1.0]hexane (**4**) and 1-trimethylsilyloxytricyclo [4.1.1^{2,5}. 0] octane (**6**), upon reaction with (PhIO)$_n$/(n-Bu)$_4$N·F, yielded 2-cyclohexen-1-one (**5**) and 2-oxobicyclo[3.2.1]oct-3-ene (**7**), respectively.



It has been well established that the hypervalent iodine oxidation of ketonic silyl enol ethers yields the product of α-functionalization,[14,15] while γ-functionalization occurs with 2-(trimethylsilyl)furan.[16] In a strictly formal sense, these reactions correspond to an umpolung of the enolate system, and homoenolate systems,[17] respectively, with the generation of the "synthetic equivalent" of an α, β and γ-carbonyl cation.



The reactions reported herein involve β-functionalization and concomitant elimination. A possible mechanistic pathway is the following:



This process corresponds to a bond cleavage and is the sole reaction route in the lactone series. The analogous oxidation in the ketonic series, with systems larger than 4, i.e. 1-trimethylsiloxy[n.1.0] cycloalkanes, where n = 4,5,6,7, does not proceed purely with a bond cleavage; b bond cleavage occurs to yield exocyclic substitution products. In summary, the valuable homologation-oxidation works excellently for lactones, but ketone homologation is not generally useful.

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Table.1 Ring Homologated α, β-Unsaturated Carbonyl Compounds from Oxidation of **1a-d**, **4** and **6** With $(PhIO)n/(n\text{-}Bu)_4N\cdot F$.

Reactant	Product	% Yield	b.p. [Lit]	IR (Neat; cm^{-1})	^{1}H-NMR ($CDCl_3$; δ)
1a[1]	**2a**	72	oil[3] [103°/ 10mm]	1724(C=O) 1624(C=C)	2.50(m,2H,CH=CHCH$_2$),4.44(t,2H,OCH$_2$), 6.05(m,1H,OCOCHCH), 7.10(m,1H, COCHCH).
1b[1]	**2b**	75	oil[2,4]	1720(C=O) 1626(C=C)	1.90(m,2H,OCH$_2$CH$_2$CH$_2$),2.60(m,2H,OCH$_2$-CH2CH$_2$CH=CH),4.33(t,2H,OCH$_2$CH$_2$),5.55(m, 1H,COCH=CH),6.45(m,1H,COCH=CH).
1c[1]	**2c**	62	oil[2,5]	1714(C=O) 1637(C=C)	1.70(m,2H,OCH$_2$CH$_2$CH$_2$),1.85(m,2H,OCH$_2$CH$_2$) 2.30(m,2H,CH$_2$CH=CH),4.40(t,2H,OCH$_2$), 5.16(dd,1H,COCH),6,26(m,1H,COCH=CH).
1d[1,6]	**2d**	78	oil[2,5]	1720(C=O) 1633(C=C)	1.12-1.72(m,16H,8xCH$_2$),2.30(m,2H,=CH$_2$), 4.2(t,2H,OCH$_2$),5.45(m,1H,COCH),6.12(m,1H, COCH=CH).
4[7]	**5**	72	oil[2] [168°C][8]	1686(C=O) 1616(C=C)	1.80-2.7(m,6H,3xCH$_2$),6.14(m,1H,COCH=CH), 7.15(m,1H,COCH=CH).
6[7]	**7**	73	oil[2] [94-99°/ 17mm][9]	1670(C=O) 1630(C=C)	1.20-2.30(m,6H,3xCH$_2$),3.00(m,2H,2xCH), 5.9(dd,1H,COCH=CH),7.35(m,1H,COCH=CH).

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[1] **1a**, b.p.=26-28°C/0.05mm: **1b**; b.p= 36-38°C/0.05mm; **1c**. b.p.=42-44°C/0.06mm; **1d**. b.p.=66-69°c/0.05mm; **6**, b.p.=25°-28°C/0.05mm. [2] Products were purified by column chromatography using neutral alumina and hexane:dichloromethane as eluents (9:1). [3] L.J.Haynes and E.R.H.Jones, *J.Chem. Soc,* 954 (1946). [4] H.J.Reich, J.M.Renga and I.L.Reich, *J. Am. Chem. Soc.*, **97**,5434(1975). [5] Compounds showed satisfactory carbon and hydrogen analysis. [6] The macrolactone required for the synthesis of **1d** was prepared according to procedure developed by Bidd et al., I.Bidd, D.J.Kelly, P.M.Ottley, O.I.Paynter, D.J.Simmonds and M.C.Whiting, *J. Chem. Soc., Perkin Trans. I*, 1369 (1983). [7] S.Miyano, Y.Izumi, H.Fujii and H.Hashimoto, *Synthesis*, 700 (1977). [8] Aldrich Catalog 1988. [9] S.I.Murahashi, K.Okumura, T.Naota and S.Nagase, *J. Am. Chem. Soc.*, **104**, 2466 (1982).

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11. A 500 ml., three-necked flask, round bottomed flask equipped with a magnetic stirring bar, two pressure equalizing dropping funnels, and a reflux condenser bearing a nitrogen inlet at its top was purged with nitrogen and charged with cyclohexane (dry) 200 ml. To this is added 0.025 mole (2.56 ml) of Et_2Zn slowly drop wise. The contents are cooled to 0^oC. Diiodomethane (0.025 mole 6.7 g), and 1-trimethylsilyloxy-7-oxaheptane (0.020 mole 3.8 g) dissolved in 50 ml of dry cyclohexane was added slowly dropwise to the Et_2Zn solution under nitrogen at 0^oC (10-15 minutes). The contents were stirred under nitrogen for 1.5 hr, and then dry air was passed over the surface for 4 hour at 0^oC. White solid (ZnI_2) is appeared at this time. Cyclohexane (100 ml) is added and the contents are filtered & vacum dried. Reduced pressure distillation afforded 2.8 g (68%) of 1-trimethylsilyloxy-2-oxan[6.1.0]cyclononane (**1c**). b.p. = $42\text{-}44^oC/0.06$ mm.
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13. In a typical experiment, 1-trimethylsilyloxy-2-oxabicyclo[5.1.0]octane (**1b**, 1.00 g, 5.04 mmol) was dissolved in dichloromethane with stirring under nitrogen. The solution was cooled to 0^o and iodosobenzene (1.11 g, 5.04 mmol) was added to the cold solution followed by tetra-n-butylammonium fluoride in tetrahydrofuran (5.04 ml, 1.0 M, 5.04 mmol). The reaction mixture was allowed to warm to room temperature over one hour. The reaction slurry was stirred an additional 15 hours at room temperature. The resulting homogeneous mixture was washed with water (2 X 25 ml) and dried over anhydrous magnesium sulfate. Chromatography on silica and elution with hexane: dichloromethane (19 : 1) yielded the product.
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