THE PHOTOCHEMICAL CONVERSION OF CYCLIC ACETALS TO A LACTONE AND ESTERS

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We wish to report a photochemically benzophenone-initiated conversion of cyclic acetals (I) to a lactone (2) and esters (3).

The procedure involves the irradiation of acetals (I/20 mol per liter) in benzene (IO ml) with benzophenone (I/20 mol per liter) at room temperature for 8 hours. The resultant lactone and esters were identified with authentic samples by means of GLC retention times and IR spectra. Experimental data are summarized

Table Irradiation of Cyclic Acetals at Room Temperature

Acetals					Products			
B.P.	← C,(%)→		∕──H,(%)~		NMR	Yield,(%) ^a		
°C(mm/Hg)	Found	Calcd	Found	Calcd	С ₁ -Н	Lactone	Ester	K _L ∕K _E ^b
53.0(63)	61.84	62.04	10.37	I0.4I	5.69	38.8	2.4	16
40 .5(35)	64.34	64.58	I0.72	IO.84	5.46	28.0	2.0	I4
73.5(37)	66.79	66.63	II.26	II.I8	5.46	31.6		
65.0(38)	67.07	66.63	II.20	II.18	5.36	31.6		
83.0(30)	68.22	68 .3 I	II.54	II.47	5.46	27.5	I.6	17
80.0(30)	68.48	68 . 3I	II.56	II.47	5.47	22.5	2.9	8
75.5(43)	68.34	68 .3 I	II.52	II.47	5.35	59.4	2.5	24
73.0(33)	68.44	68 .3 I	II.43	II.47	5.23	75.8	<1.0	>76
105.0(33)	69.49	69.72	II.83	II.70	5.47	28.0		
I86.0(I)	7I.22	7I . 69	10.98	IO.94	5.30	27.0		
II8.0(4)	74.65	74.97	8.36	8.39	5.35	57.0	<1.0	> 57
	B.P. °C(mm/Hg) 53.0(63) 40.5(35) 73.5(37) 65.0(38) 83.0(30) 80.0(30) 75.5(43) 73.0(33) 105.0(33) 186.0(1) 118.0(4)	Ac B.P. –C, °C(mm/Hg) Found 53.0(63) 61.84 40.5(35) 64.34 73.5(37) 66.79 65.0(38) 67.07 83.0(30) 68.22 80.0(30) 68.48 75.5(43) 68.34 73.0(33) 68.44 105.0(33) 69.49 186.0(1) 71.22 118.0(4) 74.65	Acetals B.P. C.(%) °C(mm/Hg) Found Calcd 53.0(63) 61.84 62.04 40.5(35) 64.34 64.58 73.5(37) 66.79 66.63 65.0(38) 67.07 66.63 83.0(30) 68.22 68.31 75.5(43) 68.34 68.31 73.0(33) 68.44 68.31 105.0(35) 69.49 69.72 186.0(1) 71.22 71.69 I18.0(4) 74.65 74.97	Acetals B.P. -C,(%)- -H, °C(mm/Hg) Found Calcd Found 53.0(63) 61.84 62.04 10.37 40.5(35) 64.34 64.58 10.72 73.5(37) 66.79 66.63 11.26 65.0(38) 67.07 66.63 11.20 83.0(30) 68.22 68.31 11.54 80.0(30) 68.48 68.31 11.52 73.0(33) 68.44 68.31 11.52 73.0(33) 69.49 69.72 11.83 105.0(33) 69.49 69.72 11.83 186.0(1) 71.22 71.69 10.98 118.0(4) 74.65 74.97 8.36	Acetals B.P. C,(%) H,(%) °C(mm/Hg) Found Calcd Found Calcd 53.0(63) 61.84 62.04 I0.37 I0.41 40.5(35) 64.34 64.58 I0.72 I0.84 73.5(37) 66.79 66.63 II.26 II.18 65.0(38) 67.07 66.63 II.20 II.18 83.0(30) 68.22 68.31 II.54 II.47 80.0(30) 68.48 68.31 II.52 II.47 75.5(43) 68.34 68.31 II.52 II.47 73.0(33) 68.44 68.31 II.43 II.47 I05.0(35) 69.49 69.72 II.83 II.70 I86.0(1) 71.22 71.69 I0.98 I0.94 II8.0(4) 74.65 74.97 8.36 8.39	AcetalsB.P. $-C, (\%)$ $-H, (\%)$ NMR (7)°C(mm/Hg)FoundCalcdFoundCalcd C_1 -H53.0(63)61.8462.0410.3710.415.6940.5(35)64.3464.5810.7210.845.4673.5(37)66.7966.6311.2611.185.3665.0(38)67.0766.6311.2011.185.3683.0(30)68.2268.3111.5411.475.4680.0(30)68.4868.3111.5611.475.4775.5(43)68.3468.3111.5211.475.23105.0(33)69.4969.7211.8311.705.47186.0(1)71.2271.6910.9810.945.30118.0(4)74.6574.978.368.395.35	AcetalsPrB.P. $-C$, (%) $-H$, (%)NMR (7)Yiel°C(mm/Hg)FoundCalcdFoundCalcd C_1 Lactone53.0(63)61.8462.0410.3710.415.6938.840.5(35)64.3464.5810.7210.845.4628.073.5(37)66.7966.6311.2611.185.4631.665.0(38)67.0766.6311.2011.185.3631.683.0(30)68.2268.3111.5411.475.4627.580.0(30)68.4868.3111.5211.475.4722.575.5(43)68.3468.3111.5211.475.2375.8105.0(33)69.4969.7211.8311.705.4728.0186.0(1)71.2271.6910.9810.945.3027.0118.0(4)74.6574.978.368.395.3557.0	Products-Products-B.P. $-C, (\%)$ NMR (T) Yield, (\%) ^a °C(mm/Hg)FoundCalcdFoundCalcdC _I -HJactoneEster53.0(63)61.8462.0410.3710.415.6938.82.440.5(35)64.3464.5810.7210.845.4628.02.073.5(37)66.7966.6311.2611.185.4631.665.0(38)67.0766.6311.2011.185.3631.683.0(30)68.2268.3111.5411.475.4627.51.680.0(30)68.4868.3111.5211.475.3559.42.573.0(33)68.4468.3111.4311.475.2375.8<1.0

^a Based on the amount of acetals decomposed.

 $^{\mathrm{b}}$ Relative ratios of cleavage in 2 ways from radical (A.).

in Table. The conversion of acetals to the lactone and esters may be accounted for by the following scheme.



The photoactivated benzophenone molecule plays a vital role in the initiation step, a hydrogen abstraction from the methine group bridging 2 oxygens. Consequently, the irradiation of acetals without benzophenone under the same conditions showed nearly no decomposition.

The following step is either the $exo-\beta$ -cleavage of radical (A.) to the lactone or the endo- β -cleavage to esters, respectively. In all of the photochemically benzophenone-initiated reactions in Table, the yields of the lactone (2) were far higher than those of esters (3), whereas an ester of high yield (40%) was obtained in the case of di-t-butyl peroxide-initiated reaction of a cyclic acetal (R=Methyl) at I30 °C.^I) The difference of experimental condition between 2 classes is remarkable and the effect of temperature will be studied.²)

A general examination of the data in Table indicates that the relatively higher yield of the lactone may be brought about by the resonance stability of radical R..

References

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2) T. J. Wallace and R. J. Gritter, <u>J. Org. Chem.</u>, <u>27</u>, 3067 (1962). Cyclic ether free radicals $O_{\underline{CH}}^{\underline{CH}}(CH_2)_n$ have been reported to be relatively unstable at elevated temperatures and tend to undergo decyclization of the ether ring.