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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

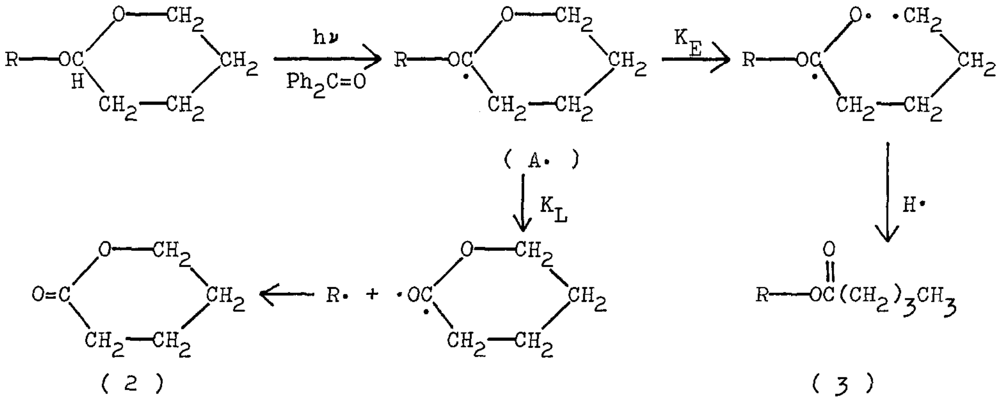
Table Irradiation of Cyclic Acetals at Room Temperature

	Acetals						Products		
	B.P.	C,(%)		H,(%)		NMR (τ)	Yield,(%)[a]		
R	°C(mm/Hg)	Found	Calcd	Found	Calcd	C_I-H	Lactone	Ester	K_L/K_E[b]
Methyl	53.0(63)	6I.84	62.04	I0.37	I0.4I	5.69	38.8	2.4	I6
Ethyl	40.5(35)	64.34	64.58	I0.72	I0.84	5.46	28.0	2.0	I4
n-Propyl	73.5(37)	66.79	66.63	II.26	II.I8	5.46	3I.6	—	
iso-Propyl	65.0(38)	67.07	66.63	II.20	II.I8	5.36	3I.6	—	
n-Butyl	83.0(30)	68.22	68.3I	II.54	II.47	5.46	27.5	I.6	I7
iso-Butyl	80.0(30)	68.48	68.3I	II.56	II.47	5.47	22.5	2.9	8
sec-Butyl	75.5(43)	68.34	68.3I	II.52	II.47	5.35	59.4	2.5	24
t-Butyl	73.0(33)	68.44	68.3I	II.43	II.47	5.23	75.8	<I.0	>76
n-Amyl	I05.0(33)	69.49	69.72	II.83	II.70	5.47	28.0	—	
Cyclohexyl	I86.0(I)	7I.22	7I.69	I0.98	I0.94	5.30	27.0	—	
Benzyl	II8.0(4)	74.65	74.97	8.36	8.39	5.35	57.0	<I.0	>57

[a] Based on the amount of acetals decomposed.

[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-β-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

I) E. S. Huyser, J. Org. Chem., 25, I820 (I960)

2) T. J. Wallace and R. J. Gritter, J. Org. Chem., 27, 3067 (I962). Cyclic ether free radicals $O\overset{CH}{\cdot}(CH_2)_n$ have been reported to be relatively unstable at elevated temperatures and tend to undergo decyclization of the ether ring.