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THE PHOTOCHEMICAL CONVERSION OF ACETALS TO CARBOXYLIC ESTERS

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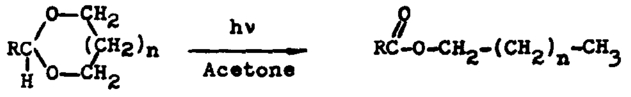
WE wish to report the photochemically acetone-initiated conversion of acetals to the corresponding carboxylic esters.[1]



n = 0 or 1

The procedure involves irradiation[2] of the acetal (3 g.) in a mixture of acetone (10 ml.) and t-butanol (90 ml.) at room temperature for 20-40 hours.

The resulting carboxylic esters were isolated by chromatography on alumina, and identified by comparison with authentic samples through the respective boiling points, infrared spectra, refractive indices and gas chromatographic retention times. Experimental data are summarized in Table I.

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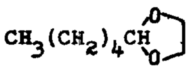
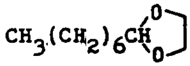
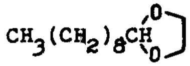
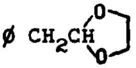
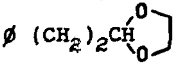
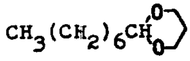
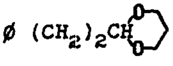
[1] The peroxide-induced conversion at elevated temperature of cyclic acetals of benzaldehyde to benzoic esters has been reported recently. [E.S. Huyser and Z. Garcia, *J. Org. Chem.*, *27*, 2716 (1962)].

[2] Hanau Q81 high pressure mercury vapor lamps were used as the radiation source.

Table I

Irradiation of Acetals at Room Temperature

Acetals[a]			Products	
	b.p. (34 mm)	n_D^{30}		% yield[b]
	89-90°	1.4224	Ethyl hexanoate	36[c]
	117-9°	1.4292	Ethyl octanoate	55[c]
	151-3°	1.4365	Ethyl decanoate	33[c]
	137-8°	1.5153	Ethyl phenyl-acetate	35[c]
	152-3°	1.5102	Ethyl hydrocinnamate	30[c] 52[d]
	133-5°	1.4356	Propyl octanoate	23[c]
	163-5°	1.5104	Propyl hydrocinnamate	14[c]

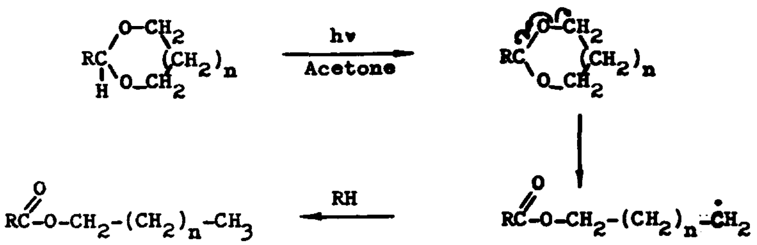
[a] All acetals gave correct analytical data for carbon and hydrogen.

[b] Based on total amount of acetal irradiated.

[c] Irradiated through Pyrex immersion tube.

[d] Irradiated through quartz immersion tube.

This conversion may be regarded as an isomerization by an intramolecular oxidation-reduction, for which the following mechanism may be suggested:



The photoactivated acetone molecule plays a vital role in the initiation step, which involves a hydrogen atom abstraction from the carbon attached to the two oxygen atoms. Consequently, irradiation of the acetals under the same experimental conditions, but in the absence of acetone, led to rather poor yields of the esters.

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