

A NOVEL SYNTHESIS OF β -LACTONES

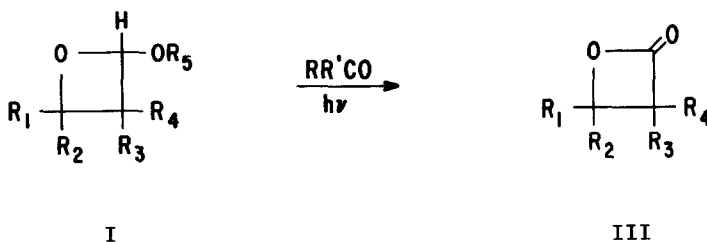
S. H. Schroeter

General Electric Research and Development Center

Schenectady, New York 12301

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The reaction of photoexcited carbonyl compounds R_1R_2CO with vinyl or enol ethers $R_3R_4C=CHOR_5$ leads to mixtures of 2- and 3-alkoxyoxetanes (I and II) as major products, the ratio of I to II depending largely on the nature of the substituents R_3-R_5 (1). The addition may proceed both via the singlet and the triplet state of the carbonyl compound, both types of addition give the same ratio of I:II (2). This ratio is generally found constant throughout the irradiation, provided that equimolar amounts of carbonyl compound and olefin or excess olefin are used. In the presence of excess carbonyl compound, however, the relative amount of I decreases with irradiation time. This change is due to attack of the 2-alkoxyoxetanes by the photoexcited carbonyl compound, a reaction which leads to the formation of β -lactones (III).



Irradiation of either 2-methoxy-, 2-ethoxy-, 2-n-propoxy- or 2-n-butoxy-3,3,4,4-tetramethyloxetane with acetone resulted in the formation of the same

product of mp 131°, tetramethyl- β -propiolactone. Structural assignment to the compound was based on its elemental analysis (Found: C, 65.63; H, 9.44), ir, nmr and mass spectra ($\nu_{\text{C=O}}$ at 1815 cm^{-1} , singlets at 8.51 and 8.70 τ , M^+ -CO ion at 112) and on its conversion to the known (3) 2,2,3-trimethyl-butane-1,3-diol by lithium aluminum hydride. The synthesis of this lactone can conveniently be carried out in a single step: Irradiation of either methyl or n-propyl β,β -dimethylvinyl ether (0.2 m) with acetone (1.0 m) in acetonitrile (250 ml) with a Hanovia 450 W mercury arc through Corex for 40 hours followed by evaporation of the solvent gave 37% (9.6 g) of the crystalline lactone (yield calcd for 0.2 mole of lactone) together with 29% of a 1:1-mixture of the corresponding isomeric oxetanes I and II. Irradiation of the same enol ethers with an equimolar or less than equimolar amount of acetone gives an oxetane ratio of I:II = 70:30 (1).

Similar irradiation of acetone with ethyl β,β -diethylvinyl ether gave a 31.5% yield of the corresponding lactone III, $\text{R}_1=\text{R}_2=\text{CH}_3$, $\text{R}_3=\text{R}_4=\text{C}_2\text{H}_5$ of bp 97° (14 mm) which was also obtained by irradiation of a mixture of the isomeric oxetanes I and II, $\text{R}_1=\text{R}_2=\text{CH}_3$, $\text{R}_3=\text{R}_4=\text{R}_5=\text{C}_2\text{H}_5$ with acetone (37% yield based on consumed oxetane) or benzophenone (28%). In all cases, the recovered oxetane mixtures were considerably enriched in the 3-alkoxy isomers. Photochemical dehydrogenation of 2-n-propoxy-3,3-dimethyl-1-oxaspiro[3.5]nonane with acetone gave 55% of 3,3-dimethyl-1-oxaspiro[3.5]nonane-2-one of mp 104-105°. Similarly, the lactone III, $\text{R}_1=\text{H}$, $\text{R}_2=\text{C}_2\text{H}_5$, $\text{R}_3=\text{R}_4=\text{C}_2\text{H}_5$ of bp 97° (13 mm) was obtained from irradiation of a mixture of the corresponding 2- and 3-methoxyoxetanes with acetone in 60% yield. Formation of β -lactones from 2-alkoxyoxetanes has been found to be quite general. Isolation of pure compounds, however, requires a proper selection of alkoxyoxetane and dehydrogenating agent in each case. In general, oxetanes or enol ethers with $\text{R}_5=\text{CH}_3$ were best suited for separation of oxetanes from lactones.

β -Lactone formation from 2-alkoxyoxetanes probably involves dehydrogenation at the C-2 carbon atom and decomposition of the resulting dialkoxy radical into an alkyl radical and the carbonyl compound (lactone). A similar mechanism has been proposed for free radical reactions of other acetals (4). Surprisingly, 2-alkoxyoxetane radicals do not undergo ring opening to give open chain carbonyl compounds as major products - as might have been expected on the basis of the known (5) free radical induced rearrangement of 2-methoxy-tetrahydropyran to methyl valerate.

References

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