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SHORT LIVED INTERMEDIATES I. THE TYPE II PHOTOFRAGMENTATION OF THREO-AND ERYTHRO-1,2-DIMETHYLBUTYL ACETATE

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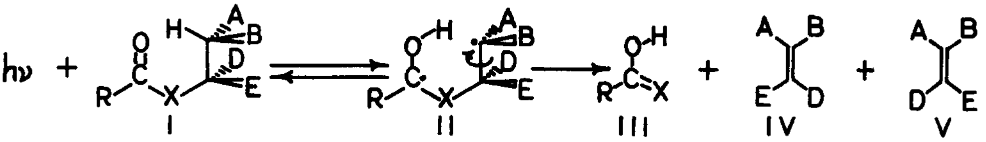
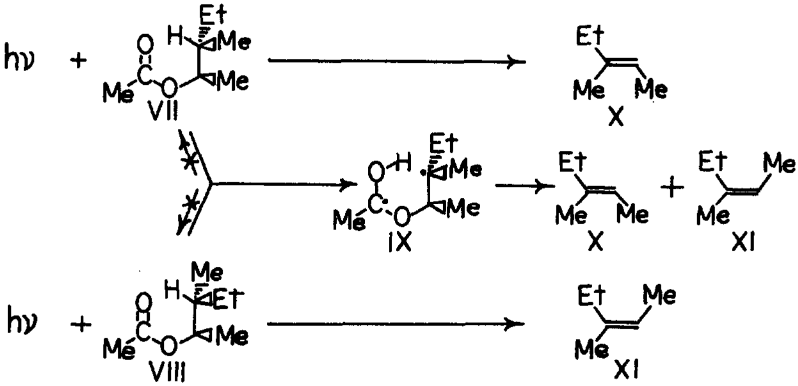
Considerable interest has recently centered around the Norrish Type II photofragmentation of carbonyl compounds, especially with respect to the nature of the fragmentation process (1). Evidence, such as solvent effects, kinetic isotope effects, and molecular orbital calculations, has been presented to support a two step mechanism incorporating a biradical intermediate (2,3,4). In hope of providing direct evidence to substantiate the existence of this intermediate and to establish the generality of this conclusion, a systematic study of Type II fragmentations in a variety of systems has been initiated. Molecules such as I were suitably constructed to reveal the existence of the postulated biradical, II, by rotation about a carbon-carbon bond before collapse of the biradical and formation of olefins IV and V. The initial results of these studies on the simple esters threo-1,2-dimethylbutyl acetate, VII, and erythro-1,2-dimethylbutyl acetate, VIII, are presented below.



An equimolar solution of esters VII and VIII was degassed in a quartz tube and photolyzed (5). Comparison of ir (gas phase), and nmr spectra and retention times on two columns of widely differing polarity with authentic samples provided evidence for the positive identification of the major hydrocarbon photoproducts: trans-3-methyl-2-pentene, X; cis-3-methyl-2-pentene, XI, and 3-methyl-1-pentene, XII.



Quantitative studies employed the photolysis (5) of 70 microliter samples of the pure esters (6) in sealed 4 mm i.d. quartz tubes. Spectroscopy grade dodecane and cyclohexane were used as internal standards to estimate the unreacted ester and photoproducts, respectively. Product analyses were performed on a gas chromatograph equipped with a flame ionization detector.

Photolysis of simple esters bearing a hydrogen on the β-carbon in the alkyl group is known to yield olefins by an intramolecular process (7). If only olefin X was obtained in the photolysis of the threo-ester VII and olefin XI from the erythro ester VIII, a completely concerted process would be indicated, vida supra; whereas, the same mixture of olefins from both isomeric esters would support stepwise mechanisms involving the same biradical intermediate. Since the isomeric 2-pentenes were found to be unstable with extended exposure to the reaction conditions, the conversion of ester to olefins was kept below 0.2%. The results (8), as shown below, clearly indicate considerable rotation about the C-1, C-2 bond before formation of the olefin products thus implicating a biradical intermediate such as IX, although complete equilibration of the intermediate has not occurred.

Table. Quantum yields of olefin formation in ester photolyses (8).

Ester	Φ_{cis}	Φ_{trans}	%cis
threo-1,2-Dimethylbutyl acetate	.034	.107	25
	.032	.107	23
erythro-1,2-Dimethylbutyl acetate	.047	.039	55
	.049	.043	53

Assuming an equilibrated biradical would give 39% cis-olefin, the average for the isomeric esters, it can be calculated that 39% and 25% of VII and VIII, respectively, fragmented in a stereospecific manner. There is ample precedence for a number of interpretations involving the biradical IX (1,4,7,10) including reaction from either a singlet or triplet state to give a biradical where fragmentation competes with rotation or simultaneous reaction from both singlet and triplet states via concerted and nonconcerted pathways, respectively. There is insufficient data to differentiate between these at this time.

The possibility of reversible hydrogen atom abstraction by biradical IX to regenerate the original or isomeric ester has been suggested to explain solvent effects on the quantum yields of ketone Type II fragmentations (2). Figure 1A shows the nmr spectrum of the methyl doublet in VII. Figure 1B shows the same doublet after decomposing 16.5% of the ester by photolysis and 1C the same position after adding 5% of isomeric ester VIII. The presence of the small methyl doublet from ester VIII, designated by arrows in 1C, demonstrates that less than 5% of ester VII could have isomerized under the reaction conditions without being detected indicating little if any decomposition of the biradical back to ester occurs in this system.

Further work to clarify the reactive state(s) leading to fragmentation and to extend this study to ketone and amide systems is now in progress.

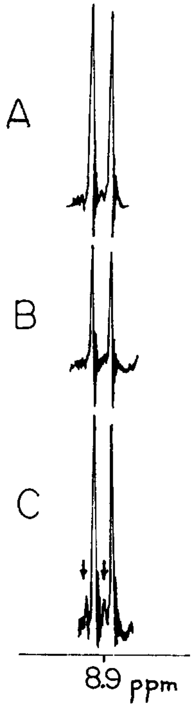


Figure 1. Nmr spectra of threo-1,2-dimethylbutyl acetate; (A) before photolyzing; (B) after photolyzing for 1115 min (16.5% decomposition) and; (C) after adding 5% erythro-1,2-dimethylbutyl acetate.

Acknowledgment

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5. All solutions were degassed a minimum of four times at $<10^{-3}$ mm in quartz tubes and photolyzed at room temperature in a merry-go-round apparatus surrounding a Hanovia 450 W medium pressure mercury lamp contained in a quartz water cooled jacket.
6. Prepared by hydroboration of trans-and cis-3-methyl-2-pentene and workup with basic hydrogen peroxide followed by esterification with acetyl chloride. After treatment with activated silica gel and purification by preparative gas chromatography, the samples were typically >99% pure by glpc and showed no anomalous absorptions in their uv spectra.
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8. Since simultaneous photolysis of γ-butyrolactone was used as the actinometer (9), the relative quantum yields are probably far more accurate than the absolute values.
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