

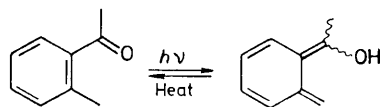
The Photochemical Enolization of an Aliphatic α,β -Unsaturated Ketone

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Summary Irradiation of 4-methylpent-3-en-2-one (**1**) in the presence of chlorotrimethylsilane yields the dienol silyl ether (*Z*)-4-methyl-2-trimethylsiloxy-penta-2,4-diene (**2b**); the trapping of a single dienol is shown to be consistent with a singlet excited state mechanism.

THE rather complex photophysics of ortho-alkyl-substituted aryl carbonyl compounds has been the subject of much study.¹ The primary photochemical act of these compounds is accepted as being an intramolecular hydrogen-abstraction reaction leading to the enol (Scheme). The corresponding reaction of aliphatic β -alkyl- α,β -unsaturated



carbonyl compounds has received far less attention, although the formation of dienols has been proposed on occasions.² Thus the apparent non-reactivity of 4-methylpent-3-en-2-one (**1**) under irradiation has been explained in terms of a thermally reversible photochemical enolization to give (**2a**) or (**3a**); deuterium incorporation into (**1**) when the irradiation is carried out in methan[²H]ol supports this.^{2a} Similarly, the photochemical deconjugation of α,β -unsaturated carbonyl compounds is thought to proceed through a dienol which reketonizes *via* α - rather than γ -protonation.^{2b} Barltrop and Wills have shown by quenching studies with *cis*- and *trans*-methyl but-2-enoate that the deconjugation reaction proceeds through a singlet or upper triplet excited state.^{2c}

Reported here are the results of a trapping experiment which confirms, for the first time directly, that irradiation of a simple aliphatic α,β -unsaturated carbonyl compound produces a dienol.† Furthermore, using the observed

† Following the completion of this work we became aware of a recent publication concerning the trapping of a photochemically produced trienol: C. P. Visser and H. Cerfontain, *Rec. Trav. Chim. Pays-Bas*, 1981, **100**, 153.

