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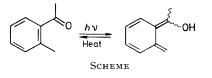
The Photochemical Enolization of an Aliphatic α,β -Unsaturated Ketone

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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-trimethylsiloxypenta-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 hydrogenabstraction reaction leading to the enol (Scheme). The corresponding reaction of aliphatic β -alkyl- α , β -unsaturated



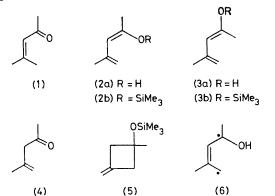
carbonyl compounds has received far less attention, although the formation of dienols has been proposed on occasions.² Thus the apparent non-reactivity of 4-methylpent-3-en-2-one (1) under irradiation has been explained in terms of a thermally reversible photochemical enolization to give (2a) or (3a); 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.

stereochemistry of the trapped dienol as a probe of the mechanism of the photoenolization reaction, it is shown that it apparently proceeds concertedly through a singlet excited state.

When 4-methylpent-3-en-2-one (1) was irradiated[‡] at room temperature in dimethylformamide containing imidazole and chlorotrimethylsilane,§ the only major initial product observed was (Z)-4-methyl-2-trimethylsiloxypenta-2,4-diene (2b) along with small amounts (<5%) of 4-methylpent-4en-2-one (4). At >ca. 60% conversion small amounts of (E)-4-methyl-2-trimethylsiloxypenta-2,4-diene (3b) and the cyclobutane (5) also appeared. The reaction was not observed in a parallel mixture kept in the dark for the period of the irradiation. The dienol ethers (2b) and (3b) were identified by comparison of their spectroscopic and chromatographic properties with those of authentic samples.3



Performing the irradiation in the absence of chlorotrimethylsilane resulted in complete conversion into the deconjugated enone (4); when the irradiation was carried out in benzene instead of dimethylformamide, and triethylamine was used as a base rather than imidazole, the only major reaction product was the cyclobutane (5).

If the photoenolization of enone (1) proceeded by way of a triplet excited state, it would be expected to yield a mixture of photoenols (2a) and (3a) owing to free rotation in the triplet biradical intermediate (6) prior to spin inversion and collapse to the dienols. Trapping of the dienols would then lead to (2b) and (3b). Alternatively, a reaction proceeding from the singlet excited state would yield a single dienol (2a) in an essentially concerted process.

Our results are compatible with a singlet process; in the initial stages of the reaction, mainly the dienol ether (2b) is formed, resulting from trapping of the singlet produced dienol (2a). Later formation of (3b) is presumably from triplet energy transfer to (2b) from triplet excited (1) or (4), the latter being derived from untrapped (2a). The cyclobutyl silyl ether (5) is derived from the corresponding alcohol produced by irradiation of (4).⁴

It would be possible for the same products to arise if a triplet reaction operated, either because collapse of the biradical (6) gives only (2a), or if only the dienol (2a) is trapped and not (3a). This seems unlikely as both the dienols are trapped when (1) is heated in dimethylformamide in the presence of chlorotrimethylsilane and imidazole and also because when the photochemical trapping reaction is performed in the presence of 4,4'-dimethoxybenzophenone such that the latter absorbs all light and all triplets are quenched by (1), both (2b) and (3b) are produced simultaneously (even at very low conversions) in the ratio 1.0:1.1. The efficiency of this trapping is, however, low, suggesting that the major pathway for decay of the triplet excited state of (1) is, perhaps, cis-trans isomerization rather than dienol formation.

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‡ Irradiations were performed using a medium-pressure mercury lamp filtered through Pyrex to avoid direct excitation of the diene products.

§ Enone concentration 0.07 m; 10 equiv. of imidazole and 5 equiv. of trimethylsilyl chloride.

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