Photoinduced Intramolecular Hydrogen Abstraction in 1,1-Dideuterio-2-phenyl-2-*o*-tolylethylene[1]

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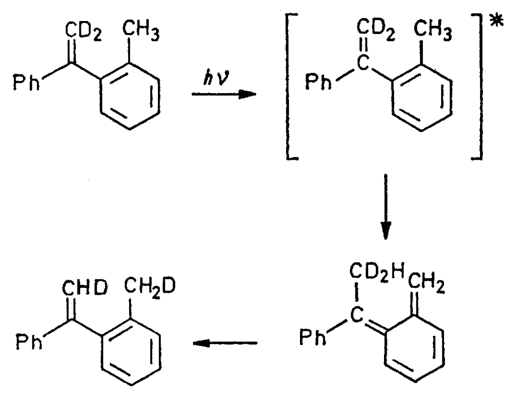
Summary The title compound has been shown to undergo a photoinduced internal exchange of vinyl deuterium and methyl hydrogen; it is suggested that the *n*,π* and reactive 1,1-diphenylethylene excited states may have significant structural similarity.

Recent reports on the photoreduction of 1,1-diphenylethylene (DPE) by propan-2-ol,[2] photocycloaddition of DPE to isobutene,[3] and photoaddition of DPE to benzene[4] have pointed out the similarities in the chemistry of the benzophenone and DPE reactive excited states. To demonstrate further the analogy between the *n*,π* and DPE excited states, we have investigated the possibility of *intra*molecular hydrogen abstraction in a DPE system, using an approach somewhat similar to the deuterium incorporation studies successfully employed on the *n*,π* systems *o*-methylbenzophenone[5] and *o*-nitrotoluene.[6]

1,1-Dideuterio-2-phenyl-2-*o*-tolylethylene was synthesized from triphenyl[$^2H_3$]methylphosphonium bromide and *o*-methylbenzophenone and isolated in 58% yield, b.p. 105° at 1·5 mmHg; ν_{max} 6·28 and 7·29 μm; δ 2·05 (s, 3H) and 7·24 (m, 9H). Integration of two barely detectable singlets at δ 5·20 and 5·78 showed the presence of 0·26 vinyl hydrogens corresponding to 87% deuteriation at the vinyl positions, with mass spectral analysis indicating 77·6% [$^2H_2$], 19·7% [$^2H_1$], and 2·8% [$^2H_0$]. Irradiation of a 5·7 × 10^{-3}M solution in methanol for 4·5 h using 2537 Å light, followed by evaporation, molecular distillation, and preparative g.l.c. gave an internally exchanged 2-phenyl-2-*o*-tolylethylene:† ν_{max} 11·1 μm (out-of-plane vinyl hydro-



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† G.l.c. analysis using an internal standard demonstrated a 48% loss of starting material during photolysis; no new volatile products were detected by g.l.c.

gen bending); δ 2·05 (s, 2·33H), 5·20 (s, $0{\cdot}33_5$H), 5·76 (s, $0{\cdot}33_5$H), and 7·24 (m,9H); *i.e.* 24% of the vinyl deuterium has exchanged into the methyl group. The reaction may be visualized as an excited-state‡ internal hydrogen abstraction to give an *o*-quinoidal structure followed by a ground state (orbital symmetry allowed) 1,5-hydrogen shift.

The analogy between DPE and benzophenone has already been suggested, the DPE excited state being visualized as a 1,2-diradical, and the radical reactivity of C-1 attributed to delocalization into the aromatic system of the electron on C-2.[2] We extend the similarity between the DPE (singlet or triplet) excited state and the n,π^* excited state by emphasizing that the excited olefin would be expected to twist rapidly to an orthogonal structure[7] (an expectation consistent with hydrogen abstraction from the coplanar methyl group). Interaction between the electrons on C-1 and C-2 is thus minimized by their orthogonal relationship as well as the extensive delocalization of the C-2 electron, with both factors combining to create a C-1 radical analogous to the lone non-bonding electron in an n,π^* state.

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‡ The DPE triplet has been implicated for intermolecular abstraction[2] but a singlet reaction cannot be discounted in the present system.

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