The Multiplicity of the Photo-Fries Rearrangement

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Summary The triphenylmethane-sensitized photolysis of aryl benzoates is a singlet rather than triplet state reaction not quenched by naphthalene.

WITH the help of CIDNP we have shown that the direct Photo-Fries reaction of *p*-tolyl *p*-chlorobenzoate (**1**) is a singlet process.[1] Opposite polarizations are expected in the triphenylmethane-sensitized and naphthalene-quenched photolysis of (**1**) if triplet state precursors are involved.[2] The Figure shows the CIDNP effects of (**1**) during photolysis with an unfiltered 1000W Hg arc directly in the Varian HA-100-D n.m.r. spectrometer. In MeOH alone the *p*-methyl groups of the Fries-ester (**1**) and *o*-product (**2**) are *E* (emission) polarized but those of *p*-cresol (**3**) *A* (enhanced absorption) polarized. In the presence of triphenylmethane identical polarization patterns are observed. If effective triplet sensitization had taken place[2] reversal of the phases or at least changes in the relative amplitudes should have resulted. Since triphenylmethane absorbs about half of the incident light with no discernible rate decrease of the photolysis, and gives the same product distribution, triphenylmethane must be promoting some singlet rather than triplet sensitization in addition to the direct singlet state process.[1] In view of the fact that the polarizations in the presence of triphenylmethane (upper centre spectrum), are about as intense as in the direct photolysis (upper left-hand spectrum), the singlet-sensitized process must be about as efficient as the direct process, because the sensitizer absorbs about half the incident light intensity.[2]

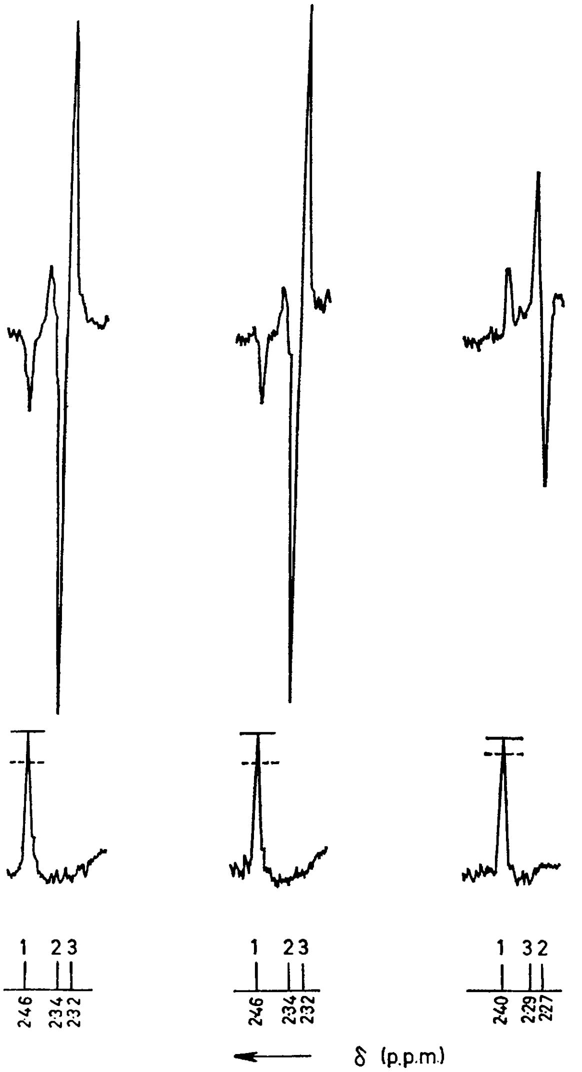

FIGURE. CIDNP effects during (upper spectra) the photolysis of 0·025M (**1**) in MeOH alone (left), with 0·05M triphenylmethane (centre) and with 0·5 M naphthalene (right). Lower spectra were taken before (solid bar) and after (broken bar) photolysis. The *p*-methyl assignments of (**1**), (**2**), and (**3**) in p.p.m. relative to Me_4Si (stick diagrams) were made with authentic materials.

In the presence of 0·5M naphthalene the polarizations are considerably lower (upper right-hand spectrum), but the photolysis rate is also reduced (lower right-hand spectrum). If triplet quenching by naphthalene had been significant,[2] the contributions to the polarizations from triplet precursors would be reduced and effectively stronger polarizations from singlet precursors should have been observed. Inspection of the upper right-hand spectrum shows the contrary, since apparently all the polarizations are reversed. One could conclude that CIDNP effects from triplet precursors are seen, so that naphthalene is acting as a singlet quencher in the photolysis of (**1**). This would explain the reduced photolysis of (**1**) and the apparent net triplet precursor polarizations. However, measurement of the normal n.m.r. absorptions in the presence of 0·5M naphthalene (lower right-hand spectrum), shows that the positions of the *p*-methyl resonances of the compounds (**2**) and (**3**) are reversed. Thus, the same phases of the polarizations as in the absence of naphthalene (upper left-hand spectrum), are observed, but of weaker intensities. The latter is due to partial absorption of the incident light by naphthalene, which decreases the rate of singlet excited state production of (**1**), accounting for the residual absorption (the first peak in the upper right-hand spectrum of the Figure is not enhanced absorption; but partial cancellation of the normal absorption by polarized emission) of the *p*-methyl resonance of (**1**). As expected, at lower naphthalene concentrations (*ca.* 0·10M) a similar polarized spectrum is observed, except that the intensities are stronger since naphthalene absorbs less light. The *p*-methyl resonance of (**1**) now appears weakly emissive due to increased singlet excited state production. Thus, triplet quenching of the Photo-Fries process by naphthalene is ineffective.[2] Yet, preliminary results confirm[3] that the related Photo-Claisen rearrangement can be triplet-sensitized by benzophenone.[4]

Of significance is the small *A* polarization at 2·39 p.p.m. assigned to *meta*-product, constituting another case of divergent singlet–triplet behaviour of radical pairs.[5]

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