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NORRISH II FRAGMENTATION OF 3,4-DIPHENYLBUTYROPHENONE.
LOSS OF SPIN MEMORY IN A 1,4-BIRADICAL.

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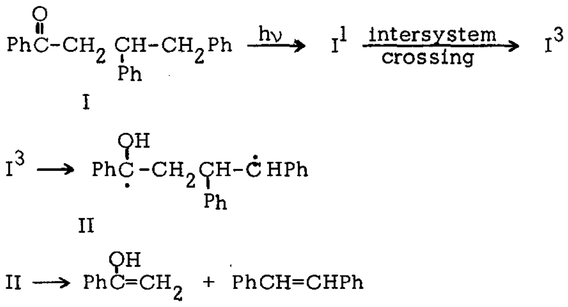
The Norrish II fragmentation of ketones is one of the most thoroughly investigated photochemical reactions (2,3). We have recently raised the question, in another context, of whether triplet excitation can be carried off in the products of a photochemical fragmentation (4). Our results for the title reaction indicate: (a) that the reaction, as expected (2,3), is best interpreted on the basis of a biradical intermediate, and (b) that the biradical intermediate must have lost essentially all memory of its triplet spin state by the time fragmentation occurs.



$$PhC(=O)-CH_2CH(Ph)-CH_2Ph \xrightarrow{h\nu} I^1 \xrightarrow[\text{crossing}]{\text{intersystem}} I^3$$

I

$$I^3 \longrightarrow Ph\dot{C}(OH)-CH_2CH(Ph)-\dot{C}HPh$$

II

$$II \longrightarrow PhC(OH)=CH_2 + PhCH=CHPh$$

The fragmentation of I (5) occurs on excitation at 3660Å in benzene to give ultimately an 80% yield of *cis* and *trans* stilbenes. No TLC spot was detected for starting material when the reaction mixture is analyzed at the end of the reaction. Acetophenone is formed simultaneously and in 1:1 ratio with the stilbenes. We presume, but have not shown, that the remaining 20% of the material is 1,2,3-triphenylcyclobutanol, formed by radical coupling of II, since cyclobutanol products are often found in Norrish II fragmentations (2,6). The reaction can be quenched with isoprene and is therefore presumably a triplet reaction.

Of particular interest is the *cis*-*trans* ratio of the stilbenes produced, since the extensive information available on the stilbene triplet (7) makes that ratio diagnostic for its presence in any reaction. The decay ratio of the stilbene triplet is 0.59 *cis*: 0.41 *trans* (7). Deviation from this ratio indicates nonintervention of stilbene triplets. On prolonged irradiation of I, the ratio of stilbenes approaches this decay ratio; however, this is clearly due to (the expected) energy transfer from starting material and/or acetophenone triplets (7). The crucial initial stilbene ratio is at least 40:1 trans, indicating at most 3-4% intervention of stilbene triplets. The 40:1 ratio adheres well to expectations based on steric considerations in biradical II, and we suspect that there is probably no intervention of stilbene triplet.

If this fragmentation reaction were concerted, one would expect that the triplet excitation, for reasons of conservation of spin, would be carried through to one of the products. Since the lower-energy triplet is undoubtedly stilbene and not acetophenone enol, nonintervention of stilbene triplets indirectly provides support for the intermediacy of biradical II.

Nonintervention of stilbene triplets similarly suggests that biradical II generates its products in their electronic ground states on fragmentation. It may well be that the exothermicity of going to ground state molecules provides the driving force for the fragmentation of II. This suggests that, in general, one should not expect to find electronically excited products in fragmentations unless their formation is very exothermic; we are currently examining this point in another system (4).

The quantum yield for total stilbene production is 0.084 ± .003 when I is 0.277 M in benzene. The quantum yield is almost independent of the extent of reaction out to 7% conversion; at 13%, it is 0.074 ± .005. Since the stilbenes should be excellent quenchers of the reaction, this fact suggests an unusually short lifetime for I^3, when compared to other Norrish II reactants (2,8). In fact, quenching by isoprene led to a linear Stern-Volmer plot with slope $k_Q\tau = 2.5 \pm 0.2\ M^{-1}$, corresponding to $\tau = 0.5 \pm 0.05$ nanoseconds if k_Q is taken as diffusion-controlled, $5 \times 10^9\ M^{-1}\ sec^{-1}$.

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