

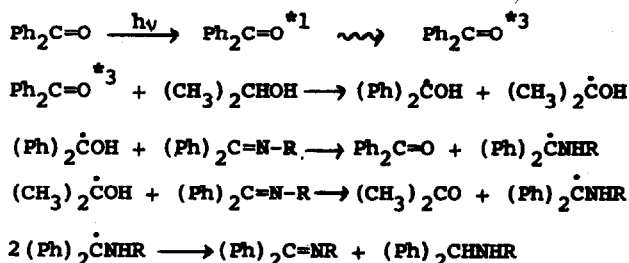
PHOTOCHEMICAL REDUCTION OF N-AROYLDIPHENYLKETIMINES

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Aryl imines have been shown to undergo reduction and reductive dimerization on irradiation in 2-propanol.<sup>1-5</sup> Although the reaction bears analogy to aryl ketone photoreduction, the available data indicate that the reaction is quite different mechanistically in that it appears not to involve the excited state of the imine as an intermediate in the reduction. The reaction has been shown to proceed via an  $\alpha$ -amino radical formed by hydrogen atom transfer to the imine from a ketyl radical. The ketyl radical is derived from carbonyl compounds present in starting material as an impurity, an added sensitizer, or as a photogenerated species (see Scheme I).



Scheme I

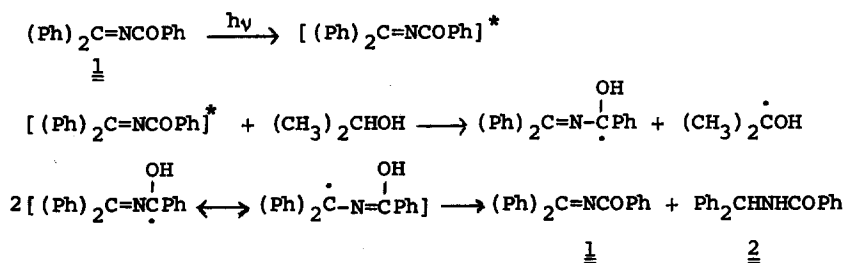
A number of related reports have appeared in the literature showing that reactions apparently involving sensitization by benzophenone in hydrogen donating solvents proceed, in fact, via formation of ketyl radicals.<sup>6-10</sup> The term "chemical sensitization" was suggested to distinguish between such cases and sensitization involving excitation-energy transfer.<sup>2</sup>

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Recently, Okada, Nozaki, Toshima and co-workers reported on the photo-reduction of N-benzoyldiphenylketimine (1) in propanol.<sup>11-13</sup> These workers suggested that the photoreduction of 1 proceeded via an electronically excited triplet state (i.e. intramolecular chemical sensitization), in contrast with other diarylimine photoreductions.



As part of an extended study of imine photochemistry, we have accumulated evidence which shows that the photoreduction of 1 does not involve an excited triplet state but rather is brought about by "chemical sensitization".

Irradiation of N-benzoyldiphenylketimine (0.1g) (1) in 2-propanol (125 ml) using an internal water-cooled mercury arc lamp (Hanovia, Type L-450W) equipped with a Pyrex Filter for 24 hr. afforded N-benzoylbenzhydramine (2) and acetone in quantitative yield. Similarly, N-p-methoxybenzoyldiphenylketimine (3) in 2-propanol was photoreduced to N-p-methoxybenzoylbenzhydramine (4). In agreement with the Japanese workers, we were unable to detect any dimeric material in the reaction mixture. The quantum yield for the photoreduction of 1 in 2-propanol is extremely low ( $\phi \text{ ca } 10^{-8}$ ) but increases substantially when benzophenone or acetophenone is used as a sensitizer ( $\phi \sim 2 \times 10^{-4}$ ). The quantum yield is also enhanced when a small amount of water is added to the reaction mixture. That the triplet state of the imine is not the active hydrogen-abstracting species is shown by the fact that benzophenone's phosphorescence is not appreciably quenched (EPA at 77° K) by the imine. High energy sensitizers such as triphenylene or triphenylamine, that do not themselves photoreduce in alcohol are ineffective as sensitizers. When an experiment was run using

benzophenone ketyl radicals, generated from the thermal decomposition of benzpinacol<sup>14</sup>, reduction of 1 to 2 (also 3 to 4) occurred. Similarly, thermal decomposition of di-t-butyl peroxide in 2-propanol in the presence of 1 afforded 2 in high yield. These observations when taken together suggest that the photoreduction of 1 does not involve the excited state of the imine but is brought about by one or more of the intermediates of the ketone photoreduction. The ability of piperylene and diphenyl disulfide to retard the formation of 2 (or 4) is perfectly consistent with the "chemical sensitization" scheme outlined above (Scheme I).

Another piece of data which supports the "chemical sensitization" mechanism for photoreduction is the photoreactivity of the N-p-methoxybenzoyldiphenylketimine (3) system. Introduction of substituent groups into the aromatic ring of aryl alkyl ketones is known to drastically alter the hydrogen abstracting ability of the carbonyl group. Electron releasing substituents increase the lifetime of the triplet state and also decrease the rate constant and quantum yield for abstraction.<sup>15,16</sup> The fact that both imines (1 and 3) show comparable reaction efficiencies is inconsistent with the intramolecular chemical sensitization path suggested by the Japanese workers.

Some comment is also in order concerning the low quantum efficiency of the ketone sensitized photoreductions. We have previously suggested that the lack of reactivity of the singlet excited state of the imine can be attributed to rotation about the  $\pi$ -bond in the excited state thereby allowing for dissipation of electronic energy.<sup>1</sup> We have recently found that photoisomerization about the C-N double bond can also be induced by triplet excitation.<sup>17</sup> This would suggest that if triplet energy transfer from benzophenone to 1 (or 3) occurred, it would be followed by a facile photoisomerization and thereby preclude hydrogen abstraction from the triplet state of the imine. Alternatively, if the hydrogen atom transfer from the ketyl radical to the imine were inefficient, a low quantum yield for photoreduction would result.

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