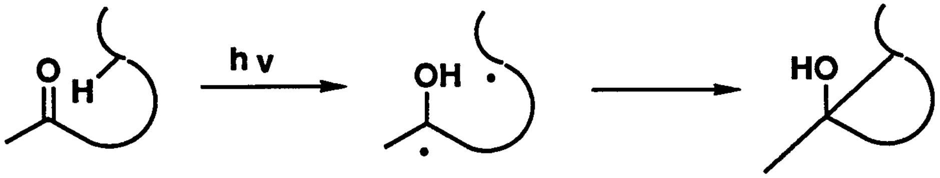
THE YANG REACTION

Peter J. Wagner
Michigan State University



I would like to suggest that a certain type of photochemical reaction be named the Yang reaction after its discoverers, N. C. and D. H. Yang of the University of Chicago. The reaction in question is any conversion of ketones or aldehydes to cyclic alcohols that proceeds mechanistically by intramolecular hydrogen abstraction followed by coupling of a biradical, including 1,4-biradicals.

The Yang Reaction:

My purpose in making this suggestion is not merely to honor one of the pioneers of modern organic photochemistry but to end some confusing and inaccurate attributions that I may have inadvertently promoted. I have already made this suggestion in a recent review of photogenerated hydrogen transfers[1] and at the 1991 Gordon Conference, so I am happy that the Editor of this newsletter asked me to expand upon my thoughts. Let me begin with some history.

As most readers know, Norrish was a pioneer in studying the photochemistry of ketones in the 1930's. He discovered two main *cleavage* reactions that to this day bear his name. First he found the ubiquitous α-cleavage that produces acyl and alkyl radicals. Later he found that ketones with alkyl chains bearing γ C-H bonds cleave to methyl ketones and alkenes. He named this process the Norrish Type II reaction to distinguish it from the other, type I reaction[2], but did not identify its mechanism. In fact, by the time I became a photochemist, the mechanism of the Norrish Type II photoelimination was still uncertain, with photochemistry textbook writers favoring either a concerted process[3] or a biradical process[4], while acknowledging the likelihood of the alternative.

In 1958 the Yangs reported that both 2-pentanone and 2-octanone undergo not only "type II" photoelimination in cyclohexane but also cyclobutanol formation; they compared this cyclization mechanistically to the corresponding bimolecular photoreduction of actone[5]. This was the first report of the photocyclization of a ketone to an alcohol and, as N. C. indicated in various talks, provided the first compelling evidence that a biradical could be formed by intramolecular hydrogen abstraction. At the same time N. C. found that cyclodecanone photocyclizes to 1-hydroxydecalin[6]. This result showed that rings containing more than four atoms were accessible by such photocyclizations and by inference that internal hydrogen transfer can occur from carbons other than γ.

The mechanistic uncertainty of the "type II" reaction and the probability that it involved radical-like reactivity attracted my attention in 1964; and soon N. C. and I were working independently on the reaction. By 1971 we had accumulated enough results to fully characterize the intermediacy of a 1,4-biradical, especially in the triplet reaction, and I wrote an *Accounts* article summarizing these results[7]. Here is where I may have created a nomenclature problem. Since we had been focusing on mechanistic concerns about the type II photoelimination and had concluded that a biradical intermediate is formed and then undergoes competitive cyclization, cleavage, and disproportionation, I thought that I should emphasize mechanistic harmony by lumping them together as "the type II photoprocesses". At that time only a few high yield photocyclizations of ketones to alcohols were known, so combining two formally quite different reactions under a single name seemed innocent enough.

Over the next two decades there have been reported many examples of δ- and more remote hydrogen abstraction, including attack on para-attached alkyl tails of benzophenone, all of which produce cyclic alcohols and none of which have anything to do with the Norrish type II elimination reaction. Likewise, many examples emerged of γ-hydrogen abstractions that result in high yields of substituted cyclobutanols with little or no accompanying elimination. Two years ago I undertook the task of reviewing hydrogen abstraction by excited ketones and was pleased to discover a good number of synthetic uses of these Yang reactions[1]. To my amazement and chagrin, however, the authors of many recent papers were calling these reactions examples of either a "Norrish type II process" or a "Barton reaction", even when they occur *via* hydrogen transfers other than 1,5 and thus do not involve the 1,4-biradicals that are responsible for the authentic Norrish type II reaction. Now Norrish, besides being a pioneer, was perceptive enough to realize that quantum yields for the type I radical cleavage are depressed in solution by solvent cage induced recombination, but he never found the cyclobutanols that accompany his name reaction. Barton has invented a large number of highly useful free radical reactions, including his name reaction based on intramolecular hydrogen abstraction by alkoxy radicals, and he actually studied one example of a remote hydrogen abstraction by an excited ketone[8]. However, when I asked him last summer, he replied that it was entirely inappropriate and unwarranted to extend his name reaction to the photochemical analogs.

There are some who question the necessity of name reactions. Nonetheless, organic chemists find them invaluable for identifying and distinguishing the many different reactions that, nameless, would appear to clutter rather than enliven our field. Used correctly, they should recognize the person who actually discovered a reaction. In this case, Yang discovered the first examples and also suggested and identified the general mechanism for photoinduced cyclization of ketones to alcohols. Association of his name with what has developed into a synthetically useful reaction is thus doubly appropriate.

REFERENCES:

1. Wagner, P. J. and Park, B.-S., *Org. Phtochem.*, **1991**, 11, 227.
2. Norrish, R. G. W. and Appleyard, M. E. S., *J. Chem. Soc.*, **1934**, 874; Norrish R. G. W., *Trans. Farraday Soc.*, **1937**, *33*, 1521.
3. Calvert, J. G. and Pitts, J. N. "Photochemistry", Wiley, New York, 1966.
4. Turro, N. J. "Molecular Photochemistry", W. A. Benjamin, Inc., New York, 1965
5. Yang, N. C. and Yang, D. H., *J. Am. Chem. Soc.*, **1958**, *80*, 2913.
6. Barnard, M. and Yang, N. C. *Proc. Chem. Soc., London*, **1958**, 302.
7. Wagner, P. J., *Acc. Chem. Res.*, **1971**, *4*, 168.
8. Barton, D. H. R., Magnus, P. D., Okugun, J. I., *J. Chem. Soc. Perkin 1*, **1972**, 1103.