Short Communication

Use of convectional dynamic reactors for photochemical synthesis

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Contrary to classical synthesis some problems arise in photochemical synthesis when high concentrations of reactants are used.

(1) Self-quenching processes can become important.

(2) A "skin effect" with high optical densities can be observed.

(3) A third effect, correlated with the change in stoichiometry of the reaction, may be considered since dilution promotes the reaction of lowest order. For instance, in photopolymerization the products obtained in a diluted solution may have an average molecular weight lower than that of the products obtained in a concentrated solution.

For these reasons it seems useful in some cases to use low concentrations of starting material in photochemical synthesis. The use of a "poor solvent" and a convectional dynamic reactor can improve dramatically the yield of photochemical synthesis.

In such reactors the temperature difference provokes a continuous flow of solvent which dissolves small amounts of the starting material, thus keeping its concentration at a steady low value. In ideal cases the photochemical reaction may be almost complete and the photoproducts may precipitate. The chemical reaction, run at low concentration, may be almost complete. When the product is not eliminated through precipitation, this kind of reactor is nevertheless useful if the product does not undergo a secondary reaction. Several convectional photochemical reactors have been built in our laboratory. They should be adapted to each type of photoreaction according to physical states, to solubilities and to molecular extinction coefficients of the starting material and the photoproducts. We report here some examples of photochemical synthesis where the use of adapted convectional reactors gave good results.

Maleic anhydride (MA) gives rise to various photochemical reactions according to the solvent [1]. Carbon tetrachloride (CCl_4) is one of the few solvents leading to a quantitative photodimerization with a high quantum yield. The solubility of MA in CCl_4 is about 5×10^{-2} M at room temper-
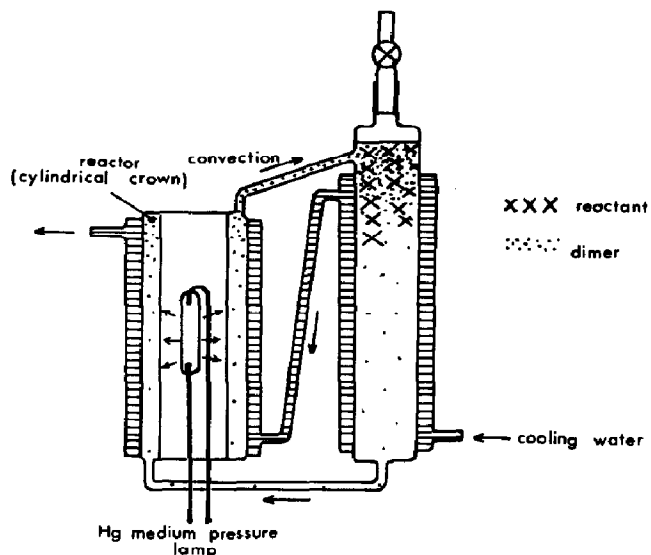
Fig. 1. A schematic diagram of a convectional reactor.

ature; therefore the photosynthesis of the dimer would require large quantities of solvent. The use of a convectional reactor (Fig. 1) permits us to reduce these quantities (starting from 8 - 9 g of MA and about 360 ml of CCl_4 we isolated 6 - 7 g of dimer after 12 h with our device equipped with a 250 W lamp).

The anhydride, which has a lower density than CCl_4, remains at the top of the reactor and acts as a filter for the insoluble dimer until the conversion reaches 60% - 80%. (In a classical static reactor the insoluble dimer would scatter the light from the beginning of the reaction and would thus lower the yield.)

A similar device made possible the isolation of several grams of the photoadduct MA–cyclohexane (I) (Scheme 1) using a small quantity of
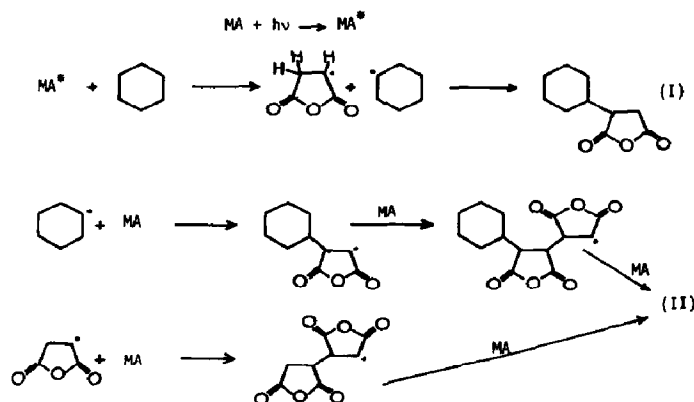
Scheme 1. Reactions of MA and cyclohexane.

cyclohexane in spite of the low solubility of MA in this solvent (10^{-2} M). The yield (about 16%) is limited by the formation of non-soluble oligomers (II). A classical reactor would give rise to only a very low concentration of (I).

Another type of photosynthetic reaction has been studied. The photoreduction of aromatic ketones (benzophenone, acetophenone, xanthone, dibenzosuberone, thioxanthone) by lactames (e.g. N-methyl-2-pyrrolidone (NMP)) and amides (N,N-diethylacetamide) leads to radicals, the cross-coupling of which yields adducts of synthetic interest [2] (Scheme 2). The
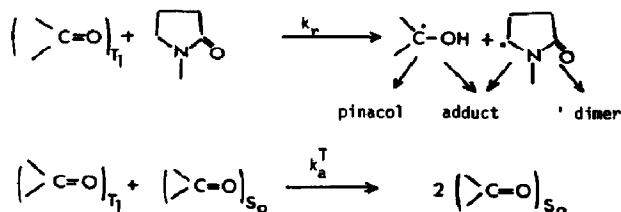
Scheme 2. The photoreduction of aromatic ketones by lactames and amides and self-quenching of the ketones.

photoreduction competes with self-quenching and it is desirable to keep the ratio

$$k_r[\text{lactame}]/k_a^T[\text{ketone}]$$

as high as possible.

The rate constants k_r and k_a^T can be measured from the phosphorescence quenching in CCl_4 solution. The values of k_r are 3.9×10^8 M^{-1} s^{-1} for xanthone–NMP and 4.4×10^7 M^{-1} s^{-1} for thioxanthone–NMP, but a very fast self-quenching is observed for these two ketones ($k_a^T = 8.1 \times 10^9$ M^{-1} s^{-1} for xanthone and $k_a^T = 0.97 \times 10^7$ M^{-1} s^{-1} for thioxanthone) [3, 4].
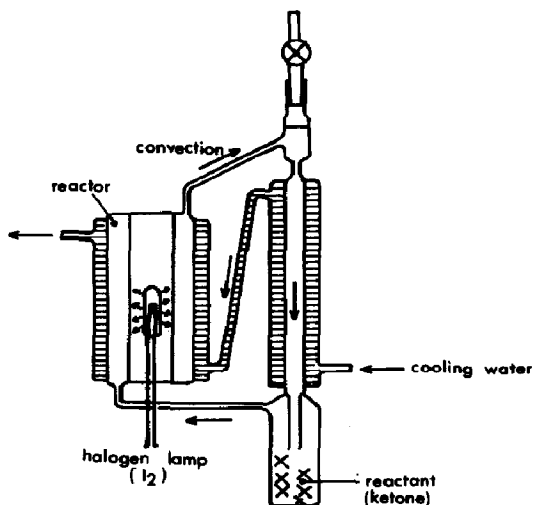
Fig. 2. A schematic diagram of a dynamic reactor.

The ratio of photoreduction to self-quenching is thus very unfavourable when equal concentrations of ketone and lactame are used (and no photoadduct has been isolated in a classical static reactor using benzene as solvent).

A low steady state concentration of the ketone can be obtained using a dynamic reactor (Fig. 2) and hexane as a "poor" solvent of the ketone (the solubility of xanthone and thioxanthone in hexane is around 5×10^{-3} M), thus improving the ratio of photoreduction to self-quenching. Under these conditions, with an initial concentration of NMP or N,N-diethylacetamide of 0.1 M, the photoreduction of xanthone and thioxanthone gives rise to the desired adducts with acceptable yields (Scheme 3).
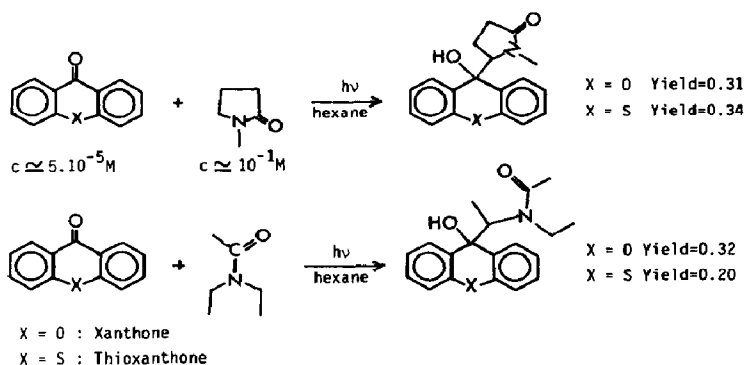
Scheme 3. Photoreduction of xanthone and thioxanthone.

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3 J.-P. Jeandrau, J.-C. Gramain and J. Lemaire, *J. Chem. Res.*, (1979) M2237, S186.
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