Solar light induced carbon–carbon bond formation *via* TiO_2 photocatalysis

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Solar light irradiation of a TiO_2 suspension in MeCN containing maleic anhydride and 4-methoxybenzyl(trimethyl)silane gives benzylated succinic acid (or anhydride) on a gram scale.

Irradiation of a semiconductor ($\lambda \geqslant \Delta E_{bg} = E_{cb} - E_{vb}$, see Scheme 1) causes charge separation. If a significant part of the solar emission is absorbed, methods for solar energy conversion based on this principle can be devised. Most of the research in this field makes use of titanium dioxide, an inexpensive, chemically stable and atoxic semiconductor which absorbs all of the UV component of the solar spectrum.[1–4] Photoelectrochemical solar cells have been devised and their efficiencies have been considerably improved over the years. However, solar light is diffuse, and electrical power produced in this way remains expensive.[5] The same holds for the production of fuels, *e.g.* hydrogen, which is also feasible using this principle.[5] On the other hand, the production of fine chemicals may be rewarding. We report here an example of the use of solar light for the most typical reaction of organic synthesis, carbon–carbon bond formation, *via* TiO_2 photocatalysis. The reaction considered is the radical alkylation of electron-withdrawing substituted olefins.

When planning a synthesis based on TiO_2 photocatalysis, the problem is to translate a *transient* charge separation (electron-hole recombination on the semiconductor surface takes place in *ca.* 30 ps)[6] into an irreversible and selective reaction. The system we used is outlined in eqns. (1)–(4). The solution

$$TiO_2(h^+, e^-) + R^1X + R^2Z \rightarrow TiO_2 + R^1X^{+\cdot} + R^2Z^{-\cdot} \quad (1)$$

$$R^1X^{+\cdot} + TiO_2(e^-) \rightarrow TiO_2 + R^1X \quad (2)$$

$$R^1X^{+\cdot} + R^2Z^{-\cdot} \rightarrow R^1X + R^2Z \quad (3)$$

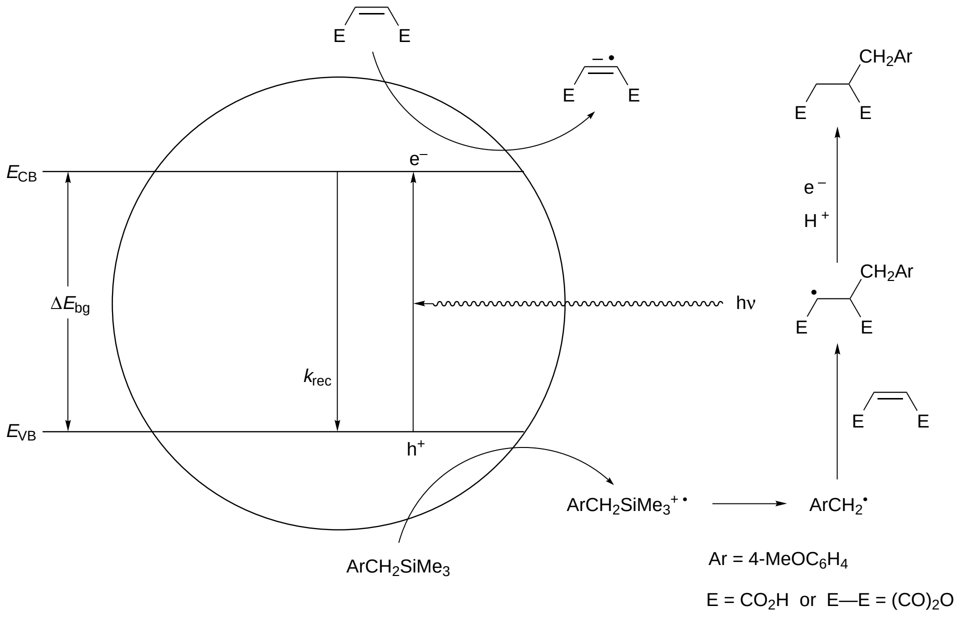
$$R^1X^{+\cdot} \rightarrow R^{\cdot} \rightarrow \text{Products} \quad (4)$$

must contain *both* a donor and an acceptor with the suitable redox potential [see eqn. (1)] since return electron transfer to the surface [*e.g.* eqn. (2)] would otherwise immediately quench the key intermediate. One of the radical ions should react rapidly in order to prevent back electron transfer after diffusion [eqn. (3)] from quenching the reaction. In our case, the reaction is cleavage of the radical cation leading to a radical, which is then trapped in the desired chemical reaction [eqn. (4)]. This implies that the radical anion should not fragment, because otherwise statistical radical coupling ($R^{1\cdot} + R^{2\cdot}$) would result, and that efficient trapping prevents dimerisation of $R^{1\cdot}$.

In the present case, 4-methoxybenzyl(trimethyl)silane (see Scheme 1, E_{ox} 1.31 V *vs.* SCE in MeCN, *cf.* E_{vb} 2.2 V for TiO_2) functions as the fragmentable donor and either maleic acid or maleic anhydride (E_{red} −0.84 V, *cf.* E_{cb} −0.8 V) has the double role of electron acceptor and radical trap.

Thus, an MeCN solution (1 l) of the silane (3.88 g, 0.02 M) and maleic anhydride (2.16 g, 0.022 M) containing TiO_2 (1.4 g) (untreated Degussa P25 pigment) was pumped by means of a peristaltic pump through a refrigerated tube sitting in the focus of a parabolic mirror (surface exposed to the sun 0.2 m²), while maintaining a slow flux of nitrogen and keeping the temperature at 15 °C. This arrangement was sufficient for maintaining a uniform suspension of TiO_2 in the tube. After 10 h (July, Almeria, sunny day) of exposure to solar light, the suspension was filtered, the solvent evaporated and the residue recrystallized to give 2.86 g (65%) of 2-(4-methoxybenzyl)succinic anhydride. Minor products were 4,4′-bis(4-methoxy)bibenzyl and 2,3-bis(4-methoxybenzyl)succinic anhydride.

Monitoring the reaction by GC showed that it followed the expected zero-order kinetics, and reagent consumption and



Scheme 1

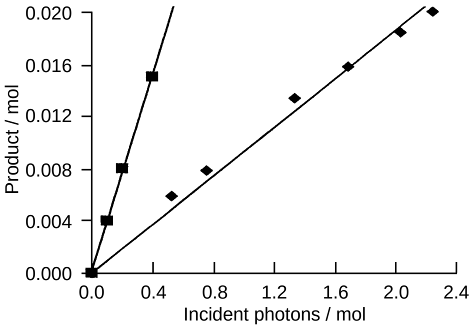


Fig. 1 Formation of (■) 4-Methoxybenzylsuccinic anhydride or (◆) acid *vs.* incident UV photons

product formation were proportional to the integrated incident flux‡ (Fig. 1). A similar reaction course and a similar yield of the benzylated succinic acid was obtained when maleic acid was used in the place of the anhydride, although this required 22 h exposure overall. Furthermore, the alkylation could be effected with other donors, *e.g.* 4-methoxyphenylacetic acid.

These reactions are initiated by hole/electron transfer to produce a pair of radical ions (see Scheme 1). The alkene radical anion is stable, while the silane radical cation fragments and gives the 4-methoxybenzyl radical. Under the present conditions this is mainly trapped by maleic anhydride (or acid), rather than coupling. The adduct radical is reduced by the persistent radical anion of the acceptor or by electron transfer at the semiconductor surface, and protonated by water present in MeCN to give the final products. Operation of a similar mechanism for photoinduced electron transfer initiated alkylation of unsatured acid derivatives had been previously demonstrated to occur when a soluble sensitizer was used (although in that case no benzylation was observed),[7] but has no precedent in photocatalysis.§ The change to a heterogeneous sensitiser simplifies the method, since introduction of other species into the solution is avoided, work-up is simpler and the semiconductor can be recovered.

Exploitation of solar light in this way is not efficient (at the present stage ‘apparent’¶ quantum yields are *ca.* 3% for the anhydride and 1% for the acid, see Fig. 1, and the literature shows that in general this quantity does not exceed 10% with TiO_2 sensitised reactions,[9] in part due to reflection). However, a good yield of alkylated products is obtained on a reasonable scale by this simple method, both solvent and semiconductor are easily recovered and reused, and little excess reagents or by-products remain. This may induce further exploration of heterogeneous photocatalysis for organic synthesis beyond the few cases that are known to date,[8,10] and lead to its use, along with homogeneous photoreactions,[11] for the exploitation of solar light.

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Notes and References

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‡ This was measured by means of a calibrated photometer (λ < 400 nm).

§ A 30% yield of dihydrofuranyldiphenylhydrazine (also on a gram scale) has been obtained by Kish *via* CdS photocatalysis from azobenzene and dihydrofuran; in that case, however, the key step is radical coupling (see ref. 8).

¶ Based on the total flux incident on the reflecting mirror surface exposed to the sun, 0.2 m^2) and the fact that this is concentrated on a Pyrex tube (∅ 3 cm, length 1 m), coaxial with the mirror, in which the solution flows. No account is taken of any loss by refraction or reflection.

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