A Room Temperature Photochemical Dehydrogenation Catalyst

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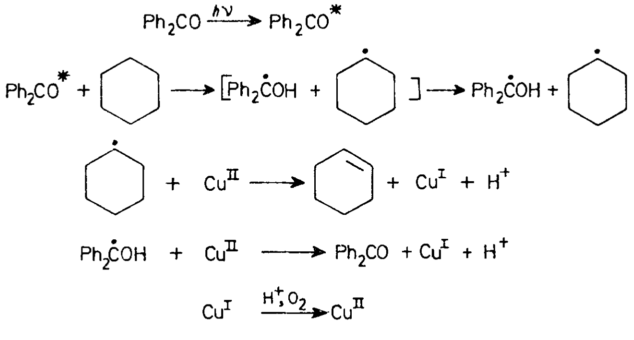
Summary The room temperature irradiation of solutions of benzophenone and copper(II) in a variety of hydrocarbon solvents results in the introduction of unsaturation into these hydrocarbons in a manner demonstrated to be catalytic in both benzophenone and copper(II).

Irradiation of benzophenone in alkane solvents efficiently produces alkyl radicals by hydrogen abstraction.[1] Copper(II) is equally noted for its ability to convert alkyl radicals cleanly into olefins and 2-hydroxy-2-propyl radicals into acetone.[2] We reasoned that alkanes (and related substrates) might therefore undergo photochemically initiated dehydrogenation with a homogeneous system comprising benzophenone and a copper(II) salt. Moreover the reaction might be catalytic by virtue of the $Ph_2\dot{C}OH$ radical being recycled back to benzophenone. This process has now been demonstrated. The conversion of cyclohexane into cyclohexene illustrates the catalytic cycle (Scheme).



Scheme

When a solution of benzophenone (3×10^{-2} M) and copper(II) pivalate (1×10^{-2} M) in cyclohexane was irradiated at room temperature under nitrogen in a Pyrex flask with near-u.v. light from a medium pressure mercury lamp (primarily excitation by the 365 nm band) the blue colour was steadily discharged from the solution. Progress of the reaction was recorded colorimetrically in the 600—700 nm region and when most of the copper(II) had been reduced to colourless copper(I) the lamp was switched off. Upon contacting the solution with air the blue colour was restored. This two-step process was repeated ten times, taking care to minimise the presence of residual oxygen in the solution prior to each irradiation cycle. A steady build up of cyclohexene in a yield of 90 ± 10%, based on copper(II) consumed, was evident by g.l.c. In contrast, when the cyclohexane was replaced by a relatively 'inert' solvent, such as benzene or acetic acid, the rates of decolourisation of these solutions were *ca.* 100 times slower. In other experiments in which such substrates as hexadecane, decahydronaphthalene, tetrahydronaphthalene, and stearic acid were dehydrogenated in benzene solution, the introduction of unsaturation into these substrates was confirmed by n.m.r. analysis of the products.

In experiments with low concentrations of benzophenone (5×10^{-4} M) in various solvents it was demonstrated by repetitive reduction and recycling of the copper(II) pivalate (5×10^{-3} M) that the ketone was being used catalytically. Preliminary turnover numbers for benzophenone in excess of 100 have been obtained for abstraction from cyclohexane, and for related abstractions from toluene (which gives bibenzyl) and propan-2-ol (which gives acetone). From arguments based upon the slow disappearance of benzophenone (observed at these very low ketone concentrations by a gradual rate deceleration) an upper limit for the non-trappable cage component[3] of the initially formed radical pair (detected in certain systems by C.I.D.N.P.[4]) of no more than 1% has been derived.

The combined effect of competitive light absorption and triplet quenching[5] was examined. Changes in the rate of generation of cyclohexyl radicals by benzophenone over a range of initial copper(II) concentrations were calculated from the observed changes in the corresponding rate of copper(II) reduction (assuming them to be related by a factor of two). At an overall copper concentration of 1×10^{-3} M, the rate of cyclohexyl radical production was *ca.* 80% of the extrapolated maximum rate (at zero copper concentration). From related experiments in propan-2-ol, a quantum yield of 0·8 is implied.

Traditional dehydrogenation catalysts[6] lack the mildness and selectivity possessed by enzymes.[7] Methods for introducing regioselectivity into non-catalytic oxidation reactions using benzophenone[8] and copper(II)[9] have been reported separately. The system described here may provide a basis for the extension of these techniques into catalysis.

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