Alkane Functionalisation on a Preparative Scale by Mercury Photosensitisation

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Alkanes can be functionalised on a multigram scale by mercury photosensitised cross-dimerisation with alcohols, ethers, and silanes.

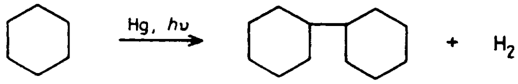
A variety of photochemical approaches[1—4] have been successfully applied to the problem of C–H activation.[5] Mercury photosensitised reactions of alkanes are well known;[6—8] some oxygenated compounds have also been studied.[9,10] The focus of attention has always been in the problems of kinetics and energy transfer and these reactions have not seen wide practical application because of the complexity of the apparatus previously employed, the small scale, and the apparent restriction to highly volatile substrates. We now find that these reactions do have synthetic utility when run in a 1.6 l quartz vessel in which *ca.* 50 ml of the substrate and a drop of mercury are refluxed under N_2 (1 atm) with simultaneous irradiation (254 nm) of the vapour phase.

The known photodimerisation reactions of equations (1) and (2) can be reproduced on a preparatively useful scale. The reactions can be carried out with conversions of 95—99%, and the products isolated in excellent chemical yields (90—95%) and quantum yields (*ca.* 0.25). In all the cases discussed, *ca.* 0.1 mol of dimers are formed per day under our conditions (Rayonet reactor, 4 × 8 W low-pressure mercury lamps), together with an equivalent amount of H_2. The chemistry can usefully be extended to high boiling substrates by operating under reflux conditions *in vacuo*; for example n-$C_{18}H_{38}$ at 200 °C gives a mixture of branched isomers of $C_{36}H_{74}$.

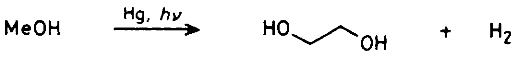
More importantly, cross-dimerisation is observed with alkanes and alcohols [equation (3)] to give the cross-dimer (**1**) as well as both of the possible homo-dimers. The three products have very different solubility properties and can be separated by simple solvent extractions, followed by distillation to give (**1**) in 30% yield. If the cyclohexane in equation (3) is replaced by methylcyclohexane, isomer (**2**) makes up 70% of the cross-dimers formed. In each case the dimers, being less volatile, stay in the liquid phase and further conversion is very slow. The selectivity is decided not only by the relative vapour pressures of the substrates but also by their chemical type; for example, C–H bonds α to the heteroatom are attacked in alcohols and ethers, and Si–H bonds in silanes, while for alkanes the selectivity is tertiary > secondary > primary.

Equation (4) is of particular interest in that hydrolysis of the cross-dimer gives the aldehyde, so that the overall reaction is equivalent to CO insertion into the alkane C–H bond. Silanes dimerise efficiently to the disilane and also cross-dimerise with alkanes [equation (5)].

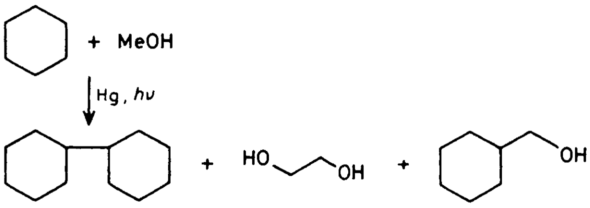
The generally accepted mechanism[6—8] involves H· abstraction from the alkane by the $^3P_1$ excited atomic state of mercury to give free R·. The mechanism may in fact be more complicated than this because any C_6H_{11}· formed in reaction (5) would be expected to abstract H· from the Et_3SiH to give



(1)

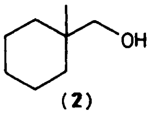


(2)

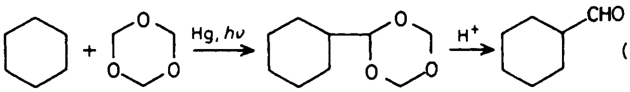


(3)

(1)

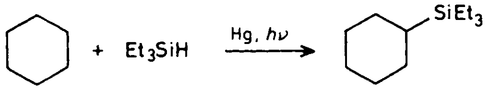


(2)



(4)

(+ homo-dimers)



(5)

(+ homo-dimers)

essentially only $Et_3Si-SiEt_3$ as the final product, given the much lower strength of an Si–H bond compared to a C–H bond; in fact, a near-statistical mixture of dimers is formed (disilane, 30%; alkane dimer, 40%; mixed dimer, 30%). Similarly, the dimerisation of $Bu^t_2CH_2$ gives up to 10% of the extremely hindered alkane $Bu^t_2CHCHBu^t_2$, even though the known $Bu^t_2CH\cdot$ radical does not dimerise.[11] Possibly, by analogy with recent matrix work on other metals,[3] intermediates with Hg–C bonds are involved. Unlike many systems that have been described, there is no measurable fall-off in rate even under conditions in which each Hg atom must cycle 10^4 times.

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References

1 M. L. H. Green, *Pure Appl. Chem.*, 1978, **50**, 27.
2 A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1983, **105**, 3929; J. K. Hoyano, A. D. McMaster, and W. A. G. Graham, *ibid.*, 1983, **105**, 7190; W. D. Jones and F. J. Feher, *ibid.*, 1984, **106**, 1650; M. J. Burk, R. H. Crabtree, and D. V. McGrath, *J. Chem. Soc., Chem. Commun.*, 1985, 1829.
3 W. E. Billups, M. M. Konarski, R. H. Hauge, and J. L. Margrave, *J. Am. Chem. Soc.*, 1980, **102**, 7393; G. A. Ozin and J. G. McCaffrey, *ibid.*, 1982, **104**, 7531.
4 R. F. Renneke and C. L. Hill, *J. Am. Chem. Soc.*, 1986, **108**, 3528.
5 R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245.
6 E. W. R. Steacie, *Chem. Rev.*, 1938, **22**, 311.
7 R. J. Cvetanovic, *Progr. React. Kinet.*, 1964, **2**, 77.
8 O. P. Strausz and H. E. Gunning, *J. Am. Chem. Soc.*, 1973, **95**, 746.
9 M. K. Phibbs and B. de B. Darwent, *J. Chem. Phys.*, 1950, **18**, 495.
10 R. A. Marcus, B. de B. Darwent, and E. W. R. Steacie, *J. Chem. Phys.*, 1948, **16**, 987.
11 K. U. Ingold, *J. Am. Chem. Soc.*, 1974, **96**, 2441.