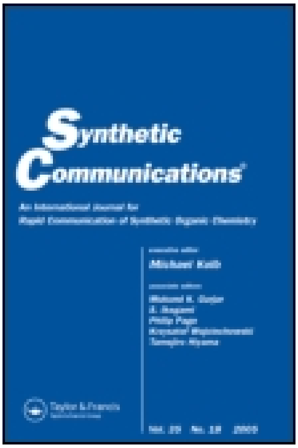

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# Perfluorocarbons as Novel Reaction Media for Photooxidation Reactions

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# PERFLUOROCARBONS AS NOVEL REACTION MEDIA FOR PHOTOOXIDATION REACTIONS

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ABSTRACT: Perfluorocarbons are excellent alternatives to chlorinated solvents as non-toxic, non-ozone-depleting, inert reaction media for photooxidation reactions. Essentially quantitative yields of peroxide products are obtained and the perfluorocarbon solvents are easily recovered and recycled.

Dye-sensitized photooxidation reactions[1,2,3,4] have been extensively studied by many investigators. When an aerated solution containing an alkene, diene or polyene and a sensitizer is irradiated with light that can be absorbed by the sensitizer, oxygen is introduced at a specific site in the substrate. A prime factor of

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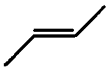
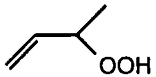
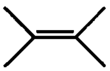
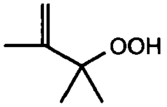
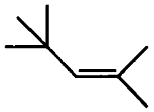
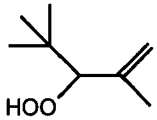
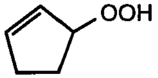
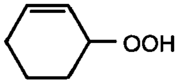
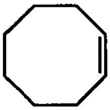
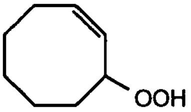
importance in these preparatively useful reactions is in the choice of solvent, which must be able to take up oxygen at a high rate in order to permit peroxide formation to occur. Chlorinated solvents are often used for singlet-oxygenation reactions. However, in response to the threat of global ozone depletion, their production will be phased out for all but a very limited number of essential uses. We were therefore interested in investigating alternative media for photooxidation reactions.

Perfluorocarbons have a unique combination of properties, in that they are chemically inert, dense liquids which are essentially immiscible with hydrocarbons as well as water. More importantly in the present context, they dissolve substantial amounts of oxygen and other gases ($CO_2$, $F_2$)[5,6]. This offers the prospect of interesting new uses in established synthetic procedures and some descriptions have already been made: perfluorocarbons have been used as immiscible reaction media for esterifications, transesterifications and polymerisations[7], flash photolysis[8], brominations[9] and fluorinations[10]. Fluorocarbon emulsions have also been reported to enhance photo-sensitized oxidation of histidine[11].

The high solubility of oxygen in perfluorocarbons in combination with the inertness of the solvent, suggested to us that these would be ideal media for known photooxidations[1], where no by-products arising from solvent would occur.

We now report that this has been realised in the case of tetraphenylporphine-sensitized photooxidation reactions of alkenes. Results for a representative series of reactions are shown in the table and in each case essentially quantitative conversion to a single product was observed. Isolation is then trivial by extraction with ether and the perfluorocarbon is simply recovered by separation. We envisage that further useful methodology will emerge involving perfluorocarbons in oxidation reactions.

**TABLE**

| **Entry** | **Reactant** | **Product**@ | **% Yield**<br>**(% conversion)** |
|---|---|---|---|
| **1** |  |  | 96<br>(100) |
| **2** |  |  | 98<br>(100) |
| **3** |  |  | 90<br>(100) |
| **4** |  |  | 95<br>(100) |
| **5** |  |  | 96<br>(100) |
| **6** |  |  | 80<br>(40) |

@ All products are known compounds and gave satisfactory $^{1}H$ n.m.r., $^{13}C$ n.m.r., and positive peroxide tests with acidic iron(II) thiocyanate. Conversions of starting alkenes were calculated from $^{1}H$ n.m.r. of crude reaction mixtures. Yields were obtained after purification by simple column chromatography ($SiO_2$, $CH_2Cl_2$).

## EXPERIMENTAL SECTION

A Hanovia medium vapour mercury lamp of U.V. output 125 W was used. $^1H$ and $^{13}C$ n.m.r. spectra were recorded at 200 MHz and 50 MHz respectively. Commercially available solvents and reagents were used without further purification. Various perfluorocarbons are available as the 'Flutec' range of products from BNFL Fluorocarbons Ltd.

**General procedure for singlet oxygenation reactions**.- Alkene (100 mmol) and 5,10,15,20-tetraphenyl-21H,23H-porphine (10 mg) dissolved in pyridine (10 ml), was suspended in perfluorooctane [Flutec PP3, $d_4^{25}$ 1.83 kg/l, b.p. 102 °C] or in perfluorohexane [Flutec PP1, $d_4^{25}$ 1.68 kg/l, b.p. 57 °C] (300 ml). This heterogeneous mixture was placed in a Pyrex immersion cell apparatus equipped with a medium vapour mercury lamp and oxygen gas was bubbled through as the mixture was stirred vigorously. The system was irradiated for approx. 5 hrs, after which the pyridine and fluorocarbon layers were separated, fluorocarbon layer extracted with ether (3 x 15 ml), and then ethereal extracts and pyridine layer were combined. After washing with 2M HCl (2 x 20 ml), the extracts were dried ($MgSO_4$) and concentrated (reduced pressure distillation). Purification was achieved by simple column chromatography ($SiO_2$, $CH_2Cl_2$) and pure products gave positive peroxide tests with acidic iron(II) thiocyanate and $^1H$ n.m.r. and $^{13}C$ n.m.r. spectra consistent with previously reported data[1].

3-Methylbut-1-en-3-yl hydroperoxide 1: TLC: $R_f = 0.51$ ($CH_2Cl_2$). $^1H$ ($CDCl_3$): 1.21 (d, J=6.59 Hz, 3H, $CH_3$), 4.44 (quin, J=6.59 Hz, 1H, CHOOH), 5.16-5.29 (m, 2H, $CH_2$=CH), 5.71-5.85 (m, 1H, $CH_2$=**CH**), 8.02 (br s, **OOH**). $^{13}$C ($CDCl_3$): 17.93 ($CH_3$), 82.33 (**C**OOH), 117.76 (**C**$H_2$=CH), 137.92 ($CH_2$=**C**H).

2,3-Dimethylbut-1-en-3-yl hydroperoxide **2**: TLC: $R_f$ = 0.49 ($CH_2Cl_2$). $^1$H ($CDCl_3$): 1.34 (s, 6H), 1.79 (s, 3H), 4.93 (m, 1H, unsat), 4.97 (m, 1H, unsat), 8.10 (br s, OO**H**). $^{13}$C ($CDCl_3$): 18.62 ($CH_2$=C**C**$H_3$), 23.82 (2C), 84.10 (**C**OOH), 111.69 (**C**$H_2$=C), 148.06 ($CH_2$=**C**).

2,4,4-Trimethyl-pent-1-en-3-yl hydroperoxide 3: TLC: $R_f$ = 0.50 ($CH_2Cl_2$). $^1$H ($CDCl_3$): 0.94 (s, 9H, $^t$Bu), 1.07 (s, 3H), 4.07 (s, 1H, C**H**OOH), 5.00 (m, 1H, unsat), 5.25 (m, 1H, unsat), 7.99 (br s, OO**H**). $^{13}$C ($CDCl_3$): 21.11, 26.87 (3C, $^t$Bu), 31.09 ($Me_3$**C**), 96.04 (**C**OOH), 114.57 (**C**$H_2$=C), 143.32 ($CH_2$=**C**).

Cyclopent-1-en-3-yl hydroperoxide **4**: TLC: $R_f$ = 0.51 ($CH_2Cl_2$). $^1$H ($CDCl_3$): 1.80-2.60 (m, 4H), 5.17 (m, 1H, C**H**OOH), 5.80 (m, 1H, unsat), 6.28 (m, 1H, unsat), 8.52 (br s, 1H, OO**H**). $^{13}$C ($CDCl_3$): 27.81, 31.15, 90.95 (**C**OOH), 127.92 (unsat C), 139.23 (unsat C).

Cyclohex-1-en-3-yl hydroperoxide **5**: TLC: $R_f$ = 0.48 ($CH_2Cl_2$). $^1$H ($CDCl_3$): 1.20-2.00 (m, 6H), 4.40 (m, 1H, C**H**OOH), 5.4 (m, 1H, unsat), 5.9 (m, 1H, unsat), 8.70 (br s, 1H, OO**H**). $^{13}$C ($CDCl_3$): 18.85, 25.77, 26.84, 78.77 (**C**OOH), 124.68 (unsat C), 134.60 (unsat C).

Cyclooct-1-en-3-yl hydroperoxide **6**: TLC: $R_f$ = 0.48 ($CH_2Cl_2$). $^1$H ($CDCl_3$): 1.44-1.55 (m, 8H), 4.90(m, 1H, C**H**OOH), 2.10 (br s, OO**H**), 5.61-5.66 (m, 2H, unsat). $^{13}$C ($CDCl_3$): 25.32, 26.02, 26.56, 29.08, 38.46, 83.03 (**C**OOH), 131.55 (unsat C), 141.57 (unsat C).

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