Initiation of radical cyclisation reactions using dimanganese decacarbonyl. A flexible approach to preparing 5-membered rings

Bruce C. Gilbert,[a] Wilhelm Kalz,[a] Chris I. Lindsay,[b] P. Terry McGrail,[b] Andrew F. Parsons*[a] and David T. E. Whittaker[a]

[a] *Department of Chemistry, University of York, Heslington, York, UK YO10 5DD*
[b] *ICI Technology, PO Box 90, Wilton, Middlesbrough, Cleveland, UK TS90 8JE*

Received (in Cambridge, UK) 31st January 2000, Accepted 28th February 2000
Published on the Web 31st March 2000

Photolysis of dimanganese decacarbonyl [$Mn_2(CO)_{10}$] using visible light produces the manganese pentacarbonyl radical [$^{\bullet}Mn(CO)_5$] which reacts with organohalides to form carbon-centred radicals. Efficient halogen-atom abstraction occurs with allylic or benzylic halides or polyhalogenated precursors bearing a weak carbon–halogen bond. Steric interactions are also important and primary halides generally react much faster with $^{\bullet}Mn(CO)_5$ than secondary or tertiary halides. The carbon-centred radicals can undergo efficient dimerisation or, in the presence of an acceptor double bond, cyclisation to form 5-membered rings. Cyclisation of terminal alkenes leads to primary radicals, which can then react by iodine- or bromine-atom transfer or, on addition of propan-2-ol, hydrogen-atom transfer. Hydroxylamines can also be formed when cyclisation reactions are carried out in the presence of TEMPO. These high-yielding cyclisation–trapping reactions are initiated under mild reaction conditions and the manganese halide by-products [of type $XMn(CO)_5$] can be easily separated from products by a simple DBU work-up procedure.

Introduction

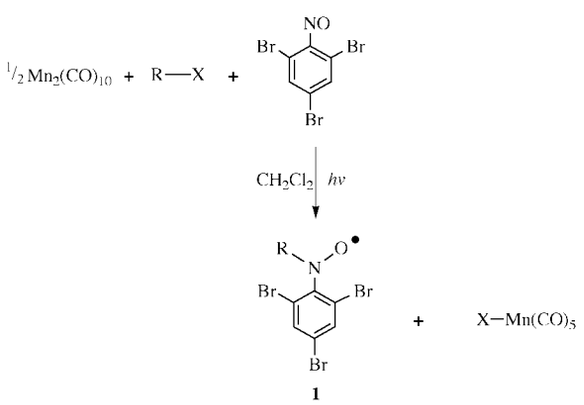
Free-radical reactions, particularly cyclisations,[1] have been extensively studied over the past twenty years and the most common method of initiation involves reaction of halide (or related thiophenyl, thiocarbonyl or phenyl selenide) precursors with tributyltin hydride. However, this method is far from ideal and the toxicity and difficulty of removing tin-containing by-products has led to the development of alternative reagents for radical generation.[2] Notable examples include tris(trimethylsilyl)silane,[3] cobaloximes,[4] manganese(III) acetate[5] and samarium(II) iodide[6] but the use of tributyltin hydride, which provides a flexible and mild method of radical generation, still dominates. This has restricted the use of radical chemistry, particularly in the pharmaceutical and fine chemical industries, which is unfortunate because radical reactions offer a number of advantages over ionic reactions (*e.g.* no solvation, ability to assemble hindered centres, flexible tandem and cascade sequences, and mild, neutral reaction conditions).

As part of a programme to develop alternative and more versatile free-radical initiators we investigated the use of dimanganese decacarbonyl [$Mn_2(CO)_{10}$] in synthesis. Photolysis of this dimer is known to lead to either decarbonylation to give $Mn_2(CO)_9$, or homolysis of the weak manganese–manganese bond (≈150 kJ mol^{-1}) to give the manganese pentacarbonyl radical [$^{\bullet}Mn(CO)_5$].[7] This manganese-centred radical is also known to abstract halogen atoms from a limited range of organohalides (*e.g.* CBr_4, $CHBr_3$, $C_6H_5CH_2Br$, CH_2Br_2 and CCl_4) and the rate constants for halogen-atom transfer (determined by flash photolysis techniques) have been shown to vary from 10^3 (for CH_2Br_2) to 10^9 (CBr_4) dm^3 mol^{-1} s^{-1} at 21 °C.[8] Surprisingly, the generation of radicals using $Mn_2(CO)_{10}$ has found very limited application in synthesis (chiefly in hydrogenolysis and oligomerisation reactions)[9] but the ability to generate carbon-centred radicals, under mild reaction conditions, suggests that $Mn_2(CO)_{10}$ could be utilised in a variety of carbon–carbon bond forming reactions.

Results and discussion

EPR spectroscopy studies

Initial experiments employed EPR spectroscopy in an attempt to detect the formation of any carbon-centered radicals produced on photolysis (λ > 400 nm) of $Mn_2(CO)_{10}$ in the presence of a variety of organohalides. *In situ* photolysis of $Mn_2(CO)_{10}$ in the presence of the organohalide and a spin trap, 2,4,6-tribromonitrosobenzene (TBNB), allowed the detection of organic radical spin adducts **1** formed on halogen atom abstraction (Scheme 1). These are characterised[10] by nitrogen and



1

Scheme 1

β-hydrogen splittings given in Table 1 and a *g*-value of 2.0066 (±0.0001). Reaction of a variety of alkyl and aryl chlorides, bromides or iodides in this way demonstrated that carbon-centred radicals could only be formed from precursors bearing a weak carbon–halogen bond (typically <310 kJ mol^{-1}). Thus, carbon-centred radicals were trapped when using CCl_4, CH_2=CH–CH_2Br, $PhCH_2Br$, $BrCCl_3$, CH_3I, ICH_2CONH_2 or $CH_3CH(I)CH_3$ but not for CH_2=CH–CH_2Cl, EtBr or CH_3-$C(Br)CH_3$ (Table 1). Typical results were as follows. On

DOI: 10.1039/b000835o

Table 1 EPR hyperfine splitting constants (a/gauss ± 0.1) of aminoxyl radicals generated by photolysis of halides and $Mn_2(CO)_{10}$ in the presence of TBNB

Spin adduct **1**, R	a(N)/G	$a(^{\beta}H)$/G
CH_3	13.1	11.9 (3H)
CCl_3	13.1	—
CH_2–CH=CH_2 [a]	13.3	10.6 (2H)
CH_2Ph [b]	13.1	9.8 (2H)
CH_2CONH_2	13.4	9.7 (2H)
$CH(CH_3)_2$	13.1	7.6 (1H)

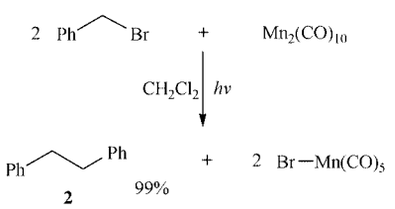
[a] Also generated from an *O*-allyl xanthate [CH_2=$CHCH_2OC$(S)SMe]. [b] Also generated from *S*-benzyl xanthates [RO(S)SBn, R = ethyl or allyl].

photolysis, a very strong ten-line signal attributed to spin-trapping of the $^{\bullet}Mn(CO)_5$ radical was initially observed[7] and, after irradiation, this rapidly diminished leaving a signal corresponding to the appropriate organic spin-adduct. Thus, in experiments for the benzyl radical, for example, the spin-adduct signal was detected as a 1:1:1 triplet, due to splitting from nitrogen [a(N) = 13.1 G], and with further splitting into a triplet due to the presence of two β-hydrogens [$a(^{\beta}H)$ = 9.8 G], as expected for successful trapping of $PhCH_2^{\bullet}$. As primary radicals were more easily formed than secondary radicals (*e.g.* $PhCHBrCH_3$ did not react) and tertiary radicals could only be generated from iodides such as Me_3C–I, which can also undergo direct photolysis,† steric effects are evidently important for radical generation.

Similar selectivities were observed on photolysis of the same organohalides with (the considerably more expensive) $Re_2(CO)_{10}$. Reaction of $Mn_2(CO)_{10}$ with other functional groups was also briefly explored. Although no organic radicals were trapped from corresponding reactions of phenyl sulfides (PhSR), photolysis of $Mn_2(CO)_{10}$ with xanthates [ROC(S)SR[1]] led to the formation of spin-adducts (Table 1). Thus, photolysis of $Mn_2(CO)_{10}$ with EtOC(S)SBn or CH_2=$CHCH_2OC$(S)SBn produced benzyl radicals evidently derived from cleavage of the C–S bond. Cleavage of the C–O bond was observed from xanthates bearing an SMe rather than SBn group; thus reaction of $Mn_2(CO)_{10}$ with CH_2=$CHCH_2OC$(S)SMe produces allyl rather than (less stable) methyl radicals.

Preliminary dimerisation reactions

Having established the prerequisites for the formation of carbon-centred radicals, this method of initiation was then applied to the synthesis of a variety of dimers derived from radical (homo- and cross-) coupling reactions.[11] For example, benzyl bromide (1 equivalent) was photolysed with $Mn_2(CO)_{10}$ (0.5 equivalents) in dichloromethane to give 1,2-diphenylethane **2** in 99% yield (Scheme 2).[11] Complete removal of the by-

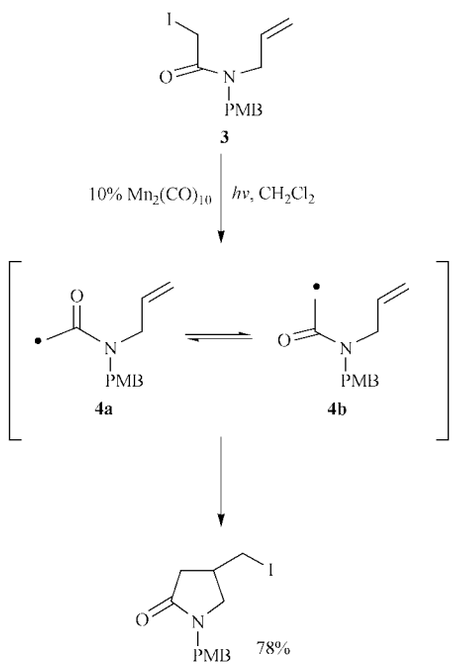


Scheme 2

product $BrMn(CO)_5$ (which can trail down a silica column) was achieved by a simple work-up procedure involving reaction of the crude reaction mixture with DBU (2 equiv.).‡ This method has been found to aid the removal of tin by-products[12] and reaction of DBU with $BrMn(CO)_5$ was found[11] to result in ligand exchange (rather than bromide displacement as observed for R_3SnBr) giving a complex which is retained by the silica column (along with any excess DBU). The dimerisation reaction could also be carried out in alternative solvents (to dichloromethane) and **2** was isolated in 61 or 82% yield when using ethyl acetate or methanol, respectively. However, attempted dimerisation of benzyl bromide using $Mn_2(CO)_{10}$ and thermolysis (in dichloromethane or methanol) or sonolysis (in dichloromethane), rather than photolysis, proved ineffective and only starting material was indicated on TLC analysis.

Atom transfer cyclisations

The novel use of $Mn_2(CO)_{10}$ as an initiator for atom transfer cyclisations was then investigated using iodoethanamide **3** (Scheme 3).[13] Irradiation of **3** (1 equivalent) with 0.1 equiv-



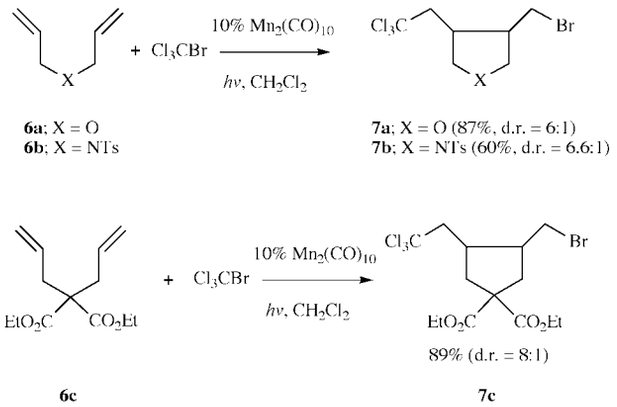
Scheme 3

alents of $Mn_2(CO)_{10}$ in dichloromethane for 1 h, afforded the desired iodo-pyrrolidinone **5** in 78% yield after column chromatography. This resulted from cyclisation of carbamoylmethyl radical **4b** to give a cyclic primary radical, which abstracts an iodine atom from another molecule of starting material **3**. Unlike related reactions employing Sn_2Bu_6, the presence of excess initiator [*e.g.* 0.5 equivalents of $Mn_2(CO)_{10}$] does not significantly alter the yield of the desired product **5**. Once formed, the primary iodide does not undergo fast iodine-atom abstraction with the $^{\bullet}Mn(CO)_5$ radical. This was supported by our finding that irradiation of a mixture of 1-iodohexane and $Mn_2(CO)_{10}$ over 4 h produced no radical coupling and the starting iodide was recovered in 77% yield. The efficient cyclisation of **3** at room temperature is noteworthy as reactions of this type are generally carried out at higher temperature[14] to increase the rate of rotation of the amide bond to convert *syn*-radicals **4a** to *anti*-radicals **4b** (which can then cyclise). As the lamp did not (significantly) increase the temperature of the reaction solution, the use of a bulky *N*-protecting group (which is known[14] to increase the proportion of the *anti*-amide conformer) was therefore effective in promoting efficient cyclisation.

Related bromine-atom abstraction reactions could also be effected on photolysis of $Mn_2(CO)_{10}$ and $BrCCl_3$ in the presence

† Spin adducts were observed on irradiation of alkyl iodides in the absence of $Mn_2(CO)_{10}$, although the signals were weaker than those observed for reactions using $Mn_2(CO)_{10}$.

‡ The use of alternative nitrogen bases (including triethylamine, pyridine or imidazole) was less effective.



Scheme 4

of a 1,6-diene (Scheme 4). The $^{\bullet}Mn(CO)_5$ radical selectively abstracts the bromine atom from $BrCCl_3$ to give the electrophilic $^{\bullet}CCl_3$ radical. This can add to an electron-rich double bond of diene **6a–c** to give a secondary radical which is able to undergo a 5-*exo-trig* cyclisation reaction. The resultant primary radical can abstract a bromine atom from $BrCCl_3$ to continue the chain reaction, leading to cyclic halides **7a–c** in 60–89% yield.§ These yields are similar, or compare favourably, to those obtained using related methods of initiation (*e.g.* Ru^{II} or Rh^{III} catalysts,[15] SmI_2[16] or AIBN–CCl_4[17]). The *cis*-diastereomers of **7a–c** were formed predominantly (as indicated by NMR spectroscopy) and this is expected for 5-*exo-trig* cyclisations of this type, which proceed *via* a chair-like transition state.[18]

Hydrogen atom transfer

Photolysis of iodide **3** with $Mn_2(CO)_{10}$ in the presence of a hydrogen-atom donor was then investigated (Scheme 5, Table 2). It was envisaged that radical cyclisation of **4b** could be followed by trapping the cyclic primary radical with a hydrogen atom from propan-2-ol, which contains a relatively weak H–C(OH)Me_2 bond (≈380 kJ mol^{-1}). This would produce pyrrolidinone **8** together with secondary radical **9**. Both iodine-atom transfer to give **5** and (simple) reduction of the carbamoylmethyl radical **4ab** to give **10** were expected to compete with this process. Indeed, initial experiments using propan-2-ol as the solvent and varying the concentration of **3** were disappointing as only iodine-atom transfer and simple reduction were observed (entries 1 and 2, Table 2). The higher the concentration of propan-2-ol, the greater the yield of simple reduction. However, when the reaction was carried out in dichloromethane, using 5 equivalents of propan-2-ol, and iodide **3** added dropwise to the reaction mixture over 2 h, the desired product **8** was isolated in 20% yield (entry 3, Table 2). Increasing the addition time, lowering the concentration and reducing the number of equivalents of propan-2-ol produced a further increase in the yield of **8**, to a maximum of 54% (entry 5, Table 2). This compares favourably with related tributyltin hydride-mediated cyclisations, which have been shown to produce pyrrolidinones with similar *N*-protecting groups (to **8**) in 12–54% yield.[19] The $Mn_2(CO)_{10}$–propan-2-ol reactions also led to dimerisation of secondary radical **9** to produce pinacol (as indicated by TLC) although no products derived from cross-coupling of **9** with, for example, **4ab** were isolated. Attempts to increase the yield of **8** by using an alternative hydrogen-atom donor, and reacting **3** with cyclohexa-1,4-diene (under similar conditions to the propan-2-ol reactions) were unsuccessful. For example, slow addition (5 h) of **3** to a solution of cyclohexa-1,4-diene (1.1 equivalents) gave ethanamide **10** in 14% yield and pyrrolidinone **8** in 30% yield (at 0.07 mol dm^{-3}).

Interestingly, whereas efficient cyclisation of **3** to give **8** required slow addition of iodide **3** to propan-2-ol, trichloroamide **11** underwent cyclisation to give **13** in a comparable yield (53% *versus* 54%) even when **11** was added in one portion (Scheme 6). The slower rate of simple reduction presumably reflects the greater stability of the intermediate dichlorocarbamoylmethyl radical **12** (compared to the carbamoylmethyl radical **4ab**) and/or the faster rate of cyclisation (onto the electron-rich double bond).

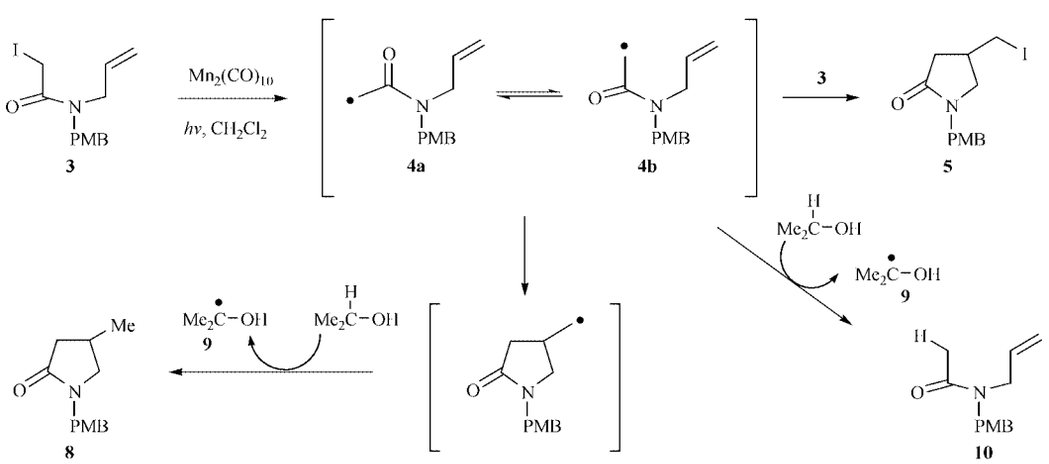
This method of initiation could also be applied to the preparation of pyrrolidine rings. Hence photolysis of allylic bromide **14** with $Mn_2(CO)_{10}$ and propan-2-ol produced disubstituted pyrrolidine **15** in 43% yield as a 1:1 mixture of diastereoisomers (Scheme 7). The formation of equal amounts of the *cis*- and *trans*-diastereoisomers may well reflect the stability of the allylic radical. This could lead to some reversibility of the radical cyclisation, resulting in the formation of a

Table 2 Reaction of **3** with $Mn_2(CO)_{10}$ in the presence of propan-2-ol

Entry	Concentration of **3**/mol dm^{-3}	Equivalents of propan-2-ol	Addition time/h[a]	Products (%) **5**	**10**	**8**
1	0.11	179	—	76	4	4
2	0.02	838	—	53	20	—
3	0.07	5[b]	2	27	16	20
4	0.07	2[b]	4	30	2	41
5	0.02	2[b]	6	—	8	54

[a] Dropwise addition of iodide **3** to a solution of $Mn_2(CO)_{10}$ and propan-2-ol. [b] Reactions carried out using a mixed dichloromethane–propan-2-ol solvent system.

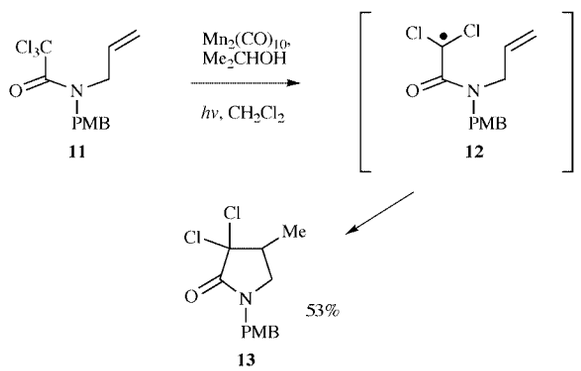
§ Control reactions were carried out to confirm that the cyclisations were initiated by $Mn_2(CO)_{10}$. Hence, irradiation of **6a–c** and $BrCCl_3$ [in the absence of $Mn_2(CO)_{10}$] only gave unreacted starting material.



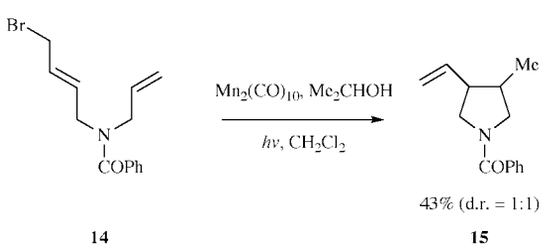
Scheme 5

Table 3 $Mn_2(CO)_{10}$ mediated cyclisations in the presence of TEMPO

Entry	Halide	X	Y	Z	TEMPO addition time/h	Products (yield, %)
1	**3**	I	H	H	0	**19** (61) + **20a** (18)
2	**3**	I	H	H	2	**19** (55) + **20a** (23)
3	**3**	I	H	H	3	**19** (11) + **20a** (74)
4	**3**	I	H	H	5	**19** (7) + **20a** (78)
5	**18**	Br	Br	Br	0	**20b** (72)
6	**11**	Cl	Cl	Cl	0	**20c** (65)
7	**11**	Cl	Cl	Cl	2	**20c** (74) + **13** (10)
8	**11**	Cl	Cl	Cl	5	**20c** (61) + **13** (18)



Scheme 6

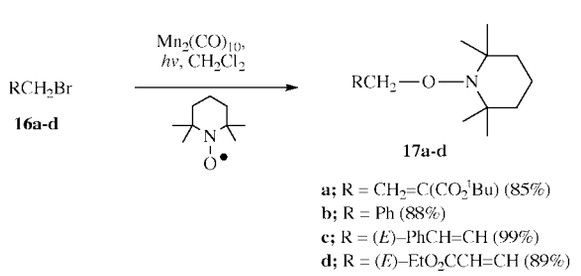


Scheme 7

significant yield of the thermodynamically more stable *trans*-isomer.[20]

Synthesis of hydroxylamines

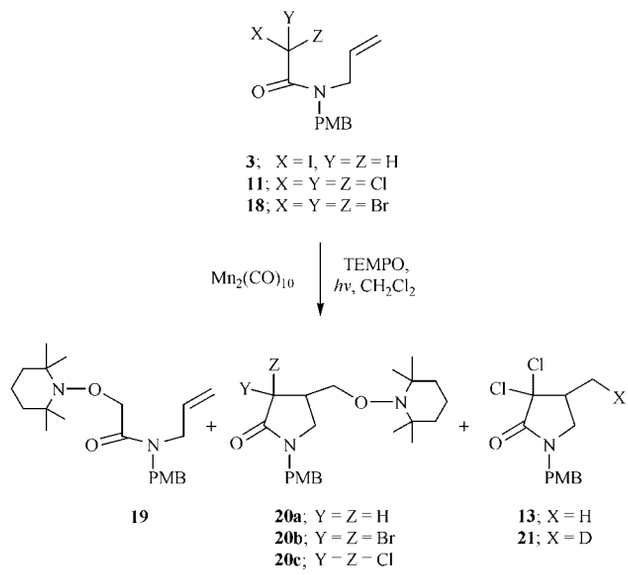
The possibility of $Mn_2(CO)_{10}$ promoted cyclisation followed by intermolecular trapping with tetramethylpiperidine oxide (TEMPO) was then explored. This would allow the formation of synthetically useful hydroxylamines which could, for example, be reduced (using zinc/acetic acid)[21] to alcohols or oxidised (using MCPBA)[22] to aldehydes. Model reactions using bromides **16a**–**d** established that this method could be used to efficiently produce hydroxylamines **17a**–**d**; these being derived from coupling of the primary radical intermediates with TEMPO (Scheme 8). The selective trapping of primary (rather than secondary) radicals to give **17c**,**d** is presumably due to



Scheme 8

steric effects, while the exclusive formation of the *E*-double bond hydroxylamines can be attributed to the greater stability of the intermediate *E*-allylic radicals.[23]

This work was followed by irradiation of iodoethanamide **3** and $Mn_2(CO)_{10}$ in the presence of 1.1 equivalents of TEMPO (Scheme 9, Table 3). Unfortunately, this resulted in predominant trapping of the carbamoylmethyl radical (**4ab**), prior to cyclisation, to give **19** in 61% yield (Table 3, entry 1). The desired pyrrolidinone **20a** was only isolated in 18% yield. However, when TEMPO was added slowly (over 5 h) to a mixture of iodide **3** and $Mn_2(CO)_{10}$, **20a** was isolated in an excellent 78% yield (Table 3, entry 4). Similar cyclisation yields were also obtained on reaction of the tribromo- and trichloroamides **18** and **11** to give pyrrolidinones **20b** and **20c**, respectively (Table 3, entries 5 and 6). It should be noted, however, that these cyclisation reactions did not require slow addition of TEMPO. Indeed, when TEMPO was added dropwise to **11** and $Mn_2(CO)_{10}$, the 4-methyl derivative **13** was also isolated in 10–18% yield (Table 3, entries 7 and 8). This suggested a competitive hydrogen-atom abstraction reaction involving the solvent dichloromethane. However, this is not the only hydrogen-atom donor because when the reaction was repeated in deuterated dichloromethane, a mixture of the deuterated product **21** [*m*/*z* 289 ($^{35,35}M + H^+$, 65%)] and the 4-methyl derivative **13** [*m*/*z* 288 ($^{35,35}M + H^+$, 55%)] were formed, as indicated by the mass spectrum (and the ^1H NMR spectrum) of the crude product.



Scheme 9

This work has demonstrated that photolysis of $Mn_2(CO)_{10}$ can efficiently initiate a number of radical reactions. A variety of 5-membered rings, for example, can be prepared on cyclisation of halide precursors followed by iodine-, bromine- or hydrogen-atom transfer, or reaction with TEMPO. Although the cost of $Mn_2(CO)_{10}$ may prohibit large scale synthesis, for

small scale preparations or for halogen-atom transfer reactions [using only a catalytic amount of $Mn_2(CO)_{10}$] this method has a number of advantages over existing methods. These include mild reaction conditions, clean and efficient cyclisation-trapping sequences and simple removal of manganese halide by-products (on DBU work-up).

Experimental

IR spectra were recorded on an ATI Mattison Genesis FT IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL EX 270 or Bruker AMX 500 spectrometer. The ^{13}C spectra were assigned using DEPT experiments. Coupling constants (J) were recorded in hertz to the nearest 0.5 Hz. EPR spectra were recorded on a Bruker ESP_300 spectrometer. Mass spectra were recorded on a Fisons Instruments VG Analytical Autospec Spectrometer system. Thin layer chromatography (TLC) was performed on Merck aluminium-backed silica gel plates. Compounds were visualised under a UV lamp, using alkaline potassium permanganate solution and/or iodine. Column chromatography was performed using silica gel (Matrix Silica 60, 70–200 micron, Fisons or ICN flash silica 60, 32–63 microns). Irradiations with visible light (>400 nm) were carried out using an ICL 302 UV xenon lamp, 300 W. Petroleum ether refers to the fraction with bp 40–60 °C. $Mn_2(CO)_{10}$ and dienes **6a**, **6c** were purchased from Sigma–Aldrich Company Ltd. Halides **3**, **11** and **18** were prepared in an analogous manner to the corresponding *N*-benzyl derivatives.[24]

General procedure for EPR experiments

$Mn_2(CO)_{10}$ (0.02 g, 5×10^{-5} mol) or $Re_2(CO)_{10}$ (0.03 g, 5×10^{-5} mol) was added to a solution of the organohalide (0.04–0.12 g, 0.1 mol) and 2,4,6-tribromonitrosobenzene (3 mg, 1×10^{-5} mol) in dichloromethane (5 cm^3). A sample of this solution (*ca.* 1 cm^3) in a cylindrical quartz glass EPR tube was then irradiated *in situ* for 1–20 minutes and the spectra recorded during and after photolysis.

***N*-(4-Methoxybenzyl)-4-iodomethylpyrrolidin-2-one 5.** $Mn_2(CO)_{10}$ (0.11 g, 0.28 mmol) was added in one portion to a stirred solution of iodide **3** (1 g, 2.90 mmol) in dichloromethane (20 cm^3) under a nitrogen atmosphere. After photolysis for 1 h, DBU (0.17 g, 1.12 mmol) was added dropwise and the solution stirred for a further 1 h. The crude product was then adsorbed onto silica and column chromatography (diethyl ether–ethyl acetate, 1:1) gave **5** (0.78 g, 78%) as a pale yellow oil; R_f 0.3 (diethyl ether–ethyl acetate, 1:1); ν_{max} ($CHCl_3$) 2933 (m), 2245 (m), 1679 (s), 1612 (m), 1512 (s), 1443 (s), 1249 (s), 1179 (m), 1035 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.17 (2H, d, J = 9, aromatics), 6.86 (2H, d, J = 9, aromatics), 4.42 (1H, d, J = 14, NC*H*), 4.34 (1H, d, J = 14, NC*H*), 3.80 (3H, s, OCH_3), 3.39 (1H, dd, J = 11 and 8, NCH_AH$_B$), 3.23 (1H, dd, J = 10 and 5.5, ICH_AH$_B$), 3.14 (1H, dd, J = 11 and 7, NCH$_A$$H_B$), 2.96 (1H, dd, J = 10 and 6, ICH$_A$$H_B$), 2.69–2.55 (2H, m, C(O)CH_AH$_B$ and C*H*CH$_2$I), 2.22 (1H, dd, J = 18 and 8, C(O)CH$_A$$H_B$); δ_C (67.5 MHz, $CDCl_3$) 158.9 (*C*O, CH$_3$O*C*=C), 129.3 (*C*H=CCH$_2$), 128.0 (CH$_2$*C*=C), 113.9 (*C*H=COMe), 55.1 (O*C*H$_3$), 52.5 (N*C*H$_2$Ar), 45.7 (N*C*H$_2$CH), 38.5 (NCO*C*H$_2$), 33.6 (*C*HCH$_2$I), 9.6 (*C*H$_2$I); *m*/*z* (CI, NH_3) 346 (M + H$^+$, 53%), 306 (25), 236 (29), 220 (100) (Found: M + H$^+$, 346.0299. $C_{13}H_{16}INO_2$ requires for M + H$^+$, 346.0304).

***N*-(4-Methylphenylsulfonyl)-*N*,*N*-diallylamine 6b.** Triethylamine (2.29 g, 22.6 mmol) was added dropwise to a stirred solution of diallylamine (2 g, 20.6 mmol) in dichloromethane (20 cm^3) at 0 °C. After 0.5 h, 4-methylbenzenesulfonyl chloride (4.32 g, 22.6 mmol) in dichloromethane (20 cm^3) was added dropwise over 0.25 h, the solution was allowed to warm to rt and stirred overnight. The crude product was washed with water, brine, dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (petrol–diethyl ether, 6:4) gave **6b** (3.95 g, 76%) as a pale yellow oil; R_f 0.4 (petrol–diethyl ether, 6:4); ν_{max} ($CHCl_3$) 3034 (m), 2924 (w), 1599 (m), 1343 (br, s), 1160 (s), 1093 (s), 933 (s), 731 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.71 (2H, d, J = 8, aromatics), 7.29 (2H, d, J = 8, aromatics), 5.61 (2H, ddt, J = 17.5, 10 and 6.5, 2 × C*H*=CH$_2$), 5.18–5.11 (4H, m, 2 × CH=CH_2), 3.80 (4H, d, J = 6.5, 2 × NCH_2), 2.43 (3H, s, C=C–CH_3); δ_C (67.5 MHz, $CDCl_3$) 143.0 (CH=*C*–SO$_2$), 137.1 (CH=*C*–CH$_3$), 132.4 (*C*H=C–SO$_2$), 129.5 (*C*H=C–CH$_3$), 127.2 (2 × *C*H=CH$_2$), 119.0 (2 × CH=*C*H$_2$), 49.1 (2 × N*C*H$_2$), 21.2 (CH=C–*C*H$_3$); *m*/*z* (CI, NH_3) 252 (M + H$^+$, 100%), 224 (14), 96 (81) (Found: M + H$^+$, 252.1049. $C_{13}H_{17}NO_2S$ requires for M + H$^+$, 252.1058).

General procedure for bromine-atom transfer reactions using $BrCCl_3$

$Mn_2(CO)_{10}$ (0.11 g, 0.28 mmol) was added to a stirred solution of $BrCCl_3$ (0.51 g, 2.56 mmol) and diene **6a**–**c** (0.08–0.22 g, 0.86 mmol) in dichloromethane (20 cm^3) under an atmosphere of nitrogen. After photolysis for 2 h, DBU (0.17 g, 1.12 mmol) was added dropwise and the solution stirred for a further 1 h. The crude product was then adsorbed onto silica and column chromatography afforded products **7a**–**c** (60–89%), as colourless oils, as inseparable mixtures of diastereoisomers in the ratio 6–8:1 (as determined from the ^{1}H NMR spectrum).

***cis*- and *trans*-4-Bromomethyl-3-(2,2,2-trichloroethyl)tetrahydrofuran 7a.** Yield 87%; R_f 0.4 (petrol–diethyl ether, 8:2); ν_{max} ($CHCl_3$)[15] 2951 (br, m), 2871 (br, m), 2248 (w), 1058 (m), 789 (m), 740 (br, s) cm^{-1}; δ_H (270 MHz, $CDCl_3$)[15] (major *cis*-isomer) 4.16 (1H, apparent t, J = 8, OC*H*), 4.01–3.87 (2H, m, 2 × OC*H*), 3.68 (1H, apparent t, J = 8, OC*H*), 3.53 (1H, dd, J = 10.5 and 4, Cl$_3$C–CH_AH$_B$), 3.34 (1H, apparent t, J = 10, Cl$_3$C–CH$_A$$H_B$), 3.04 (1H, dd, J = 14 and 3, BrCH_AH$_B$), 2.96–2.71 (3H, m, BrCH$_A$$H_B$ and 2 × OCH$_2$C*H*); δ_C (67.5 MHz, $CDCl_3$) (major *cis*-isomer) 98.6 (*C*Cl$_3$), 71.8, 71.7 (2 × O*C*H$_2$), 52.7 (Br*C*H$_2$), 44.6, 40.5 (Cl$_3$CCH$_2$*C*H and BrCH$_2$*C*H), 31.1 (Cl$_3$*C*CH$_2$); *m*/*z* (CI, NH_3) 312 (^{79,35,35,35}M + NH_4^+, 22%), 215 (32), 200 (61), 179 (100), 106 (83), 56 (67) (Found: ^{79,35,35,35}M + NH_4^+, 311.9320. $C_7H_{10}BrCl_3O$ requires for ^{79,35,35,35}M + NH_4^+, 311.9324).

The presence of the (minor) *trans*-isomer was indicated by NMR spectroscopy: δ_H (270 MHz, $CDCl_3$) 4.29 (1H, dd, J = 9 and 7, Br*C*H$_A$H$_B$), 2.52–2.43 (2H, m, 2 × OCH$_2$C*H*); δ_C (67.5 MHz, $CDCl_3$) 98.3 (*C*Cl$_3$), 74.3 (2 × O*C*H$_2$), 58.2 (*C*H$_2$CCl$_3$), 47.7, 42.7 (BrCH$_2$*C*H and Cl$_3$CCH$_2$*C*H), 33.8 (*C*H$_2$Br).

***cis*- and *trans*-1-(4-Methylphenylsulfonyl)-3-bromomethyl-4-(2,2,2-trichloroethyl)pyrrolidine 7b.** Yield 60%; R_f 0.3 (petrol–diethyl ether, 6:4); ν_{max} ($CHCl_3$) 2959 (br, m), 2250 (w), 1598 (w), 1347 (br, s), 1164 (br, s), 1092 (m), 1051 (m), 816 (m), 665 (m) cm^{-1}; δ_H (500 MHz, $CDCl_3$) (major *cis*-isomer) 7.69 (2H, d, J = 8, aromatics), 7.31 (2H, d, J = 8, aromatics), 3.62 (1H, dd, J = 10 and 7, NC*H*), 3.46–3.37 (2H, m, 2 × NC*H*), 3.29 (1H, dd, J = 10 and 4, BrC*H*), 3.18 (1H, dd, J = 10 and 8, NC*H*), 2.86 (1H, apparent t, J = 10, BrC*H*), 2.78 (1H, dd, J = 14.5 and 4, C*H*CCl$_3$), 2.68–2.60 (2H, m, 2 × CH$_2$C*H*), 2.50 (1H, dd, J = 14.5 and 7, C*H*CCl$_3$), 2.39 (3H, s, CCH_3); δ_C (67.5 MHz, $CDCl_3$) (major *cis*-isomer) 143.8 (*C*SO$_2$), 133.2 (*C*CH$_3$), 129.8 (CH$_3$C=*C*H), 127.2 (*C*H=CSO$_2$), 98.0 (*C*Cl$_3$), 52.5, 51.3 (2 × N*C*H$_2$), 44.1, 39.4 (2 × CH$_2$*C*H), 30.2 (Br*C*H$_2$), 21.4 (C*C*H$_3$); *m*/*z* (CI, NH_3) 448 (^{79,35,35,35}M + H$^+$, 50%), 406 (48), 370 (26), 252 (34), 214 (36), 139 (23) (Found: ^{79,35,35,35}M + H$^+$, 447.9302. $C_{14}H_{17}BrCl_3NO_2S$ requires for ^{79,35,35,35}M + H$^+$, 447.9307).

The presence of the (minor) *trans*-isomer was indicated by NMR spectroscopy: δ_H (500 MHz, $CDCl_3$) 3.78 (1H, dd, J = 18 and 10, NC*H*), 3.51 (1H, dd, J = 11.5 and 5, NC*H*), 3.14–3.04 (1H, m, NC*H*); δ_C (67.5 MHz, $CDCl_3$) 127.5 (SO$_2$C=*C*H), 52.4, 50.2 (2 × N*C*H$_2$), 43.8, 38.9 (2 × *C*HCH$_2$).

***cis*- and *trans*-Diethyl 3-bromomethyl-4-(2,2,2-trichloroethyl)-cyclopentane-1,1-dicarboxylate 7c.** Yield 89%; R_f 0.25 (petrol–diethyl ether, 9:1); ν_{max} ($CHCl_3$) 2984 (m), 1726 (br, s), 1445 (w), 1368 (w), 1264 (br, s), 1183 (s), 1112 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$)[15] (major *cis*-isomer) 4.21 (4H, q, J = 7, 2 × CO_2CH_2-CH_3), 3.51 (1H, dd, J = 10 and 6, $BrCH_AH_B$), 3.29 (1H, apparent t, J = 10, $BrCH_AH_B$), 2.96 (1H, dd, J = 19 and 5, Cl_3C–CH_AH_B), 2.80–2.52 and 2.42–2.32 (7H, m, Cl_3C–CH_AH_B, 2 × CCH_2CH and 2 × CH_2CH), 1.27 (6H, t, J = 7, 2 × CO_2-CH_2CH_3); δ_C (67.5 MHz, $CDCl_3$) (major *cis*-isomer) 171.9 (2 × *C*O), 98.9 (*C*Cl_3), 61.7 (2 × CH_3CH_2O), 58.0 (*C*CH_2CH), 54.0 (CH_2CCl_3), 44.5, 40.3 (*C*HCH_2Br and *C*HCH_2CCl_3), 38.9, 38.0 (2 × *C*CH_2CH), 33.2 (*C*H_2Br), 13.9 (2 × OCH_2CH_3); *m*/*z* (CI, NH_3) 437 ($^{79,35,35,35}M + H^+$, 53%), 410 (11), 190 (15), 173 (11) (Found: $^{79,35,35,35}M + H^+$, 436.9688. $C_{14}H_{20}BrCl_3O_4$ requires for $^{79,35,35,35}M + H^+$, 436.9689).

The presence of the (minor) *trans*-isomer was indicated by NMR spectroscopy: δ_H (270 MHz, $CDCl_3$) 3.60 (1H, dd, J = 10 and 4, $BrCH_AH_B$), 3.40 (1H, dd, J = 10 and 6.5, $BrCH_AH_B$); δ_C (67.5 MHz, $CDCl_3$) 172.1 (2 × *C*O), 61.7 (2 × CH_3CH_2O).

General procedure for photolysis of iodoethanamide 3 with $Mn_2(CO)_{10}$ and propan-2-ol in dichloromethane

A solution of iodide **3** (0.5 g, 1.45 mmol) in dichloromethane (5 cm^3) was added slowly (over 2 or 5 h) to a stirred solution of $Mn_2(CO)_{10}$ (0.28 g, 0.73 mmol) and propan-2-ol (2.90–11.0 mmol, 2–5 equivalents) in dichloromethane (15–75 cm^3) during continuous photolysis under an atmosphere of nitrogen. After the addition was complete, the solution was photolysed for a further 0.5 h, DBU (0.44 g, 2.9 mmol) was added dropwise and after 1 h, the crude product was adsorbed onto silica. Column chromatography afforded **5** (27–30%), **8** (20–54%) and **10** (2–16%) as colourless oils.

***N*-(4-Methoxybenzyl)-4-methylpyrrolidin-2-one 8.** R_f 0.4 (ethyl acetate); ν_{max} ($CHCl_3$) 2963 (m), 2244 (w), 1668 (s), 1612 (w), 1512 (m), 1443 (s), 1248 (s), 1177 (m), 1035 (m), 753 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.17 (2H, d, J = 9, aromatics), 6.86 (2H, d, J = 9, aromatics), 4.37 (2H, s, NCH_2), 3.80 (3H, s, OCH_3), 3.34 (1H, dd, J = 11 and 8, NCH_AH_B), 2.81 (1H, dd, J = 11 and 5.5, NCH_AH_B), 2.59 (1H, dd, J = 16 and 8, $C(O)CH_AH_B$), 2.48–2.29 (1H, m, $CHCH_3$), 2.06 (1H, dd, J = 16 and 5.5, $C(O)CH_AH_B$), 1.06 (3H, d, J = 7, $CHCH_3$); δ_C (67.5 MHz, $CDCl_3$) 158.9 (*C*O), 155.1 (CH_3OC=C), 129.5 (CH_2C=C), 129.4 (*C*H=CCH_2), 114.0 (*C*H=COMe), 55.2 (OCH_3), 54.8 (NCH_2Ar), 45.8 ($NCOCH_2$), 45.1 (NCH_2CH), 26.2 ($CHCH_3$), 15.2 (CH_3CH); *m*/*z* (EI) 219 (M^+, 82%), 188 (11), 176 (33), 146 (30), 121 (100), 78 (20) (Found: M^+, 219.1253. $C_{13}H_{17}NO_2$ requires for M^+, 219.1259).

***N*-Allyl-*N*-(4-methoxybenzyl)ethanamide 10.** R_f 0.75 (ethyl acetate); ν_{max} ($CHCl_3$) 2934 (m), 2243 (m), 1627 (s), 1434 (s), 1248 (s), 1177 (m), 1035 (m), 821 (m), 736 (s) cm^{-1}; δ_H (270 MHz, $CDCl_3$) (mixture of conformers) 7.18 and 7.09 (2H, 2 × d, J = 8, aromatics), 6.89 and 6.84 (2H, 2 × d, J = 9, aromatics), 5.82–5.66 (1H, m, C*H*=CH_2), 5.23–5.06 (2H, m, CH=CH_2), 4.52 and 4.44 (2H, 2 × s, NCH_2), 3.98 and 3.80 (2H, 2 × d, J = 6, NCH_2), 3.79 (3H, s, OCH_3), 2.14 and 2.16 (3H, 2 × s, $COCH_3$); δ_C (67.5 MHz, $CDCl_3$) (mixture of conformers) 159.4, 159.3 (*C*O), 133.4, 133.0 (*C*H=CCH_2), 128.0 (*C*H=CH_2), 117.8, 117.1 (CH=CH_2), 114.6, 114.2 (*C*H=COMe), 55.6 (OCH_3), 50.8, 50.1, 47.8 (2 × NCH_2), 22.1, 22.0 (CH_3CO); *m*/*z* (CI, NH_3) 220 (M + H^+, 100%), 178 (41), 136 (37), 121 (24) (Found: M + H^+, 220.1340. $C_{13}H_{17}NO_2$ requires for M + H^+, 220.1340).

Photolysis of trichloroamide 11 with $Mn_2(CO)_{10}$ and propan-2-ol

To a stirred solution of *N*-allyl *N*-(4-methoxybenzyl)-2,2,2-trichloroethanamide **11** (0.47 g, 1.45 mmol) in dry dichloromethane (75 cm^3) was added $Mn_2(CO)_{10}$ (0.28 g, 0.73 mmol) and propan-2-ol (0.17 g, 2.9 mmol) under an atmosphere of nitrogen. After photolysis for 3 h, DBU (0.89 g, 5.45 mmol) was added and the mixture stirred overnight. The solution was then adsorbed onto silica and column chromatography (petrol–diethyl ether, 1:1) afforded *3,3-dichloro-N-(4-methoxybenzyl)-4-methylpyrrolidin-2-one* **13** (0.22 g, 53%) as a white solid; mp 96 °C (Found: C, 54.0; H, 5.2; N, 4.8. $C_{13}H_{15}Cl_2NO_2$ requires C, 54.3; H, 5.3; N, 4.9%); R_f 0.25 (petrol–diethyl ether, 1:1); ν_{max} ($CHCl_3$) 2936 (m), 1723 (br, s), 1613 (m), 1513 (s), 1205 (br, s), 1177 (m), 823 (m), 748 (s) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.17 (2H, d, J = 9, aromatics), 6.86 (2H, d, J = 9, aromatics), 4.51 (1H, d, J = 14.5, NCH_AH_B), 4.38 (1H, d, J = 14.5, NCH_AH_B), 3.79 (3H, s, OCH_3), 3.21 (1H, dd, J = 10 and 7, NCH_AH_B), 2.88 (1H, dd, J = 10 and 7, NCH_AH_B), 2.78–2.70 (1H, m, NCH_2CH), 1.26 (3H, d, J = 6.5, CH_3CH); δ_C (67.5 MHz, $CDCl_3$) 166.6 (*C*O), 159.2 (CH_3OC=C), 129.3 (*C*H=CCH_2), 126.6 (CH_2C=C), 114.0 (*C*H=COMe), 87.2 (*C*Cl_2), 55.0 (OCH_3), 49.0 (NCH_2), 46.8 (NCH_2), 45.0 (*C*HCH_3), 11.5 ($CHCH_3$); *m*/*z* (CI, NH_3) 305 ($^{35,35}M + NH_4^+$, 29%), 288 ($^{35,35}M + H^+$, 34), 252 (100), 218 (23), 121 (64) (Found: $^{35,35}M + H^+$, 288.0559. $C_{13}H_{15}Cl_2NO_2$ requires for $^{35,35}M + H^+$, 288.0558).

(*E*)-*N*-Allyl-*N*-(4-bromobut-2-enyl)benzamide 14. Sodium hydride (0.33 g, 13.6 mmol) was added to a stirred solution of *N*-allylbenzamide[25] (2 g, 12.4 mmol) in *N*,*N*-dimethylformamide (100 cm^3). After stirring for 2 h, (*E*)-1,4-dibromobut-2-ene (7.8 g, 37.2 mmol) was added in one portion and the solution stirred overnight. The crude product was then washed with diethyl ether, brine, dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography (petrol–diethyl ether, 3:7) gave bromide **14** (1.04 g, 29%) as a pale yellow oil; R_f 0.3 (petrol–diethyl ether, 3:7); ν_{max} ($CHCl_3$) 3085 (s), 2245 (m), 1622 (br, s), 1453 (br, s), 1262 (s), 969 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) (mixture of conformers) 7.40–7.38 (5H, m, aromatics), 5.85–5.62 (3H, m, $BrCH_2CH$=C*H*CH_2 and NCH_2CH=C*H*), 5.26–5.17 (2H, m, NCH_2CH=CH_2), 4.13–3.84 (6H, m, $BrCH_2$ and 2 × NCH_2); δ_C (67.5 MHz, $CDCl_3$) (mixture of conformers) 171.7 (N*C*O), 135.2 (*C*=C), 134.3, 133.8, 132.4, 129.6, 128.1, 126.8 (6 × *C*H=C), 117.8 (CH=CH_2), 50.8, 49.1, 46.9, 45.3, 42.0 (2 × N*C*H_2), 32.2, 31.6 (Br*C*H_2CH); *m*/*z* (CI, NH_3) 294 ($^{79}M + H^+$, 62%), 250 (59), 216 (100), 174 (14), 110 (13) (Found: $^{79}M + H^+$, 294.0492. $C_{14}H_{16}BrNO$ requires for $^{79}M + H^+$, 294.0494).

***N*-Benzoyl-3-methyl-4-vinylpyrrolidine 15.** A solution of (*E*)-*N*-allyl-*N*-(4-bromobut-2-enyl)benzamide **14** (0.35 g, 1.20 mmol) in dichloromethane (5 cm^3) was added over 5 h to a stirred solution of $Mn_2(CO)_{10}$ (0.23 g, 0.6 mmol) and propan-2-ol (0.14 g, 2.4 mmol) in dry dichloromethane (75 cm^3), which was irradiated under an atmosphere of nitrogen. After the addition was complete, the mixture was photolysed for a further 1 h, DBU (0.89 g, 5.45 mmol) was added and the mixture stirred overnight. The crude product was adsorbed onto silica and column chromatography (petrol–diethyl ether, 3:7) afforded **15** (0.11 g, 43%) as a colourless oil as a 1:1 mixture of inseparable isomers; R_f 0.2 (petrol–diethyl ether, 3:7); ν_{max} ($CHCl_3$) 3055 (br, m), 2415 (w), 2253 (s), 1617 (br, s), 1432 (m), 896 (br, s), 735 (s), 655 (s) cm^{-1}; δ_H (270 MHz, $CDCl_3$) (mixture of isomers) 7.50–7.30 (5H, m, aromatics), 5.75–5.56 (1H, m, C*H*=CH_2), 5.21–5.09 (2H, m, CH=CH_2), 3.93–3.12 (4H, m, 2 × NCH_2), 2.37–2.30 (1H, m, C*H*–C=C), 2.04–1.89 (1H, m, C*H*CH_3), 1.08 and 0.89 (3H, 2 × d, J = 7, $CHCH_3$); δ_C (67.5 MHz, $CDCl_3$) (mixture of isomers) 164.3 (*C*ONH), 137.1, 136.5 (CH_2=*C*H), 136.7 (CO–*C*=C), 129.8, 128.2, 127.1 (3 × C*H*=C), 117.4, 117.1 (CH=*C*H_2), 56.6, 54.7 (NCH_2), 53.2, 51.4 (NCH_2), 51.3, 49.5 (C*H*–C=C), 39.6, 37.8 (*C*HCH_3), 15.4, 14.9 ($CHCH_3$); *m*/*z* (CI, NH_3) 216 (M + H^+, 100%), 105 (6) (Found: M + H^+, 216.1382. $C_{14}H_{17}NO$ requires for M + H^+, 216.1388).

General procedure for synthesis of hydroxylamines 17a–d

$Mn_2(CO)_{10}$ (0.28 g, 0.73 mmol) was added to a stirred solution of the bromide **16a–d** (0.24–0.32 g, 1.45 mmol) and TEMPO (0.25 g, 1.59 mmol) in dry dichloromethane (20 cm^3) under an atmosphere of nitrogen. The solution was then photolysed for approximately 2 h and then DBU (0.44 g, 2.92 mmol) was added dropwise. After 1 h, the crude product was adsorbed onto silica and column chromatography afforded **17a–d** (85–99%) as colourless oils.

***tert*-Butyl 2-[(2,2,6,6-tetramethylpiperidin-1-yloxy)methyl]-acrylate 17a.** Yield 85%; R_f 0.5 (petrol–diethyl ether, 10:1); ν_{max} ($CHCl_3$) 2989 (s), 2947 (s), 1711 (br, s), 1493 (w), 1370 (m), 1257 (w), 1153 (s), 1059 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 6.11 (1H, s, C=C$H_A$$H_B$), 5.74 (1H, s, C=C$H_A$$H_B$), 4.38 (2H, s, C$H_2$ON), 2.67–1.18 (6H, m, C$H_2CH_2CH_2$), 1.42 ($CO_2$C(C$H_3$)$_3$), 1.10 (6H, s, 2 × NCC$H_3$), 1.05 (6H, s, 2 × NCC$H_3$); δ_C (67.5 MHz, $CDCl_3$) 165.2 (CO_2), 138.6 (C=CH_2), 124.0 (C=CH_2), 80.7 (CO_2C), 74.7 (NOCH_2), 59.8 (2 × NCCH$_3$), 39.6 (2 × NCCH_2), 32.8 (2 × NCCH$_3$), 28.0 (CO_2C(CH_3)$_3$), 20.2 (2 × NCCH_3), 17.0 ($CH_2CH_2CH_2$); *m/z* (CI, NH_3) 298 (M + H^+, 100%), 156 (34), 140 (11) (Found: M + H^+, 298.2375. $C_{17}H_{31}NO_3$ requires for M + H^+, 298.2382).

1-Benzyloxy-2,2,6,6-tetramethylpiperidine 17b. Yield 88%; R_f 0.25 (petrol–dichloromethane, 10:1); ν_{max} ($CHCl_3$)[26] 2929 (s), 2876 (s), 1453 (m), 1363 (m), 1260 (w), 1132 (w), 1045 (m), 739 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$)[26] 7.55–7.31 (5H, m, aromatics), 4.97 (2H, s, NOCH_2), 1.79–1.42 (6H, m, 3 × CH_2), 1.39 (6H, s, 2 × CCH_3), 1.29 (6H, s, 2 × CCH_3); δ_C (67.5 MHz, $CDCl_3$) 138.3 (CH_2C=C), 128.2, 127.4, 127.3 (3 × CH=C), 78.7 (NOCH_2), 60.0 (2 × NCCH$_3$), 39.7 (2 × NCCH_2), 33.1 (2 × NCCH$_3$), 20.3 (2 × NCCH_3), 17.1 ($CH_2CH_2CH_2$); *m/z* (CI, NH_3) 248 (M + H^+, 100%), 156 (28), 142 (6) (Found: M + H^+, 248.2013. $C_{16}H_{25}NO$ requires for M + H^+, 248.2014).

(*E*)-1-Cinnamyloxy-2,2,6,6-tetramethylpiperidine 17c. Yield 99%; R_f 0.1 (petrol); ν_{max} ($CHCl_3$) 2980 (s), 2941 (s), 1493 (w), 1452 (m), 1362 (m), 1132 (m), 1028 (m), 956 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.30–7.08 (5H, m, aromatics), 6.49 (1H, d, *J* = 16, PhC*H*=CH), 6.18 (1H, dt, *J* = 16 and 5.5, PhCH=C*H*), 4.35 (2H, d, *J* = 5.5, NOCH_2), 1.43–1.17 (6H, m, 3 × CH_2), 1.12 (6H, s, 2 × CCH_3), 1.05 (6H, s, 2 × CCH_3); δ_C (67.5 MHz, $CDCl_3$) 137.4 (CH_2C=C), 130.4, 128.8, 127.8, 126.8, 125.9 (C*H*=C), 78.4 (NOCH_2), 60.1 (2 × NCCH$_3$), 40.0 (2 × NCCH_2), 33.4 (2 × NCCH$_3$), 20.6 (2 × NCCH_3), 17.5 ($CH_2CH_2CH_2$); *m/z* (CI, NH_3) 274 (M + H^+, 13%), 156 (100), 142 (22), 117 (28) (Found: M + H^+, 274.2170. $C_{18}H_{27}NO$ requires for M + H^+, 274.2171).

Ethyl (*E*)-4-(2,2,6,6-tetramethylpiperidin-1-yloxy)but-2-enoate 17d. Yield 89%; R_f 0.4 (petrol–diethyl ether, 4:1); ν_{max} ($CHCl_3$) 2942 (s), 1710 (br, s), 1659 (m), 1449 (m), 1367 (m), 1277 (s), 1182 (s), 1040 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 6.84 (1H, dt, *J* = 16 and 5.5, C*H*=CHCO$_2$Et), 6.03 (1H, dt, *J* = 16 and 2, CH=C*H*CO$_2$Et), 4.39 (2H, dd, *J* = 5.5 and 2, NOCH_2), 4.13 (2H, q, *J* = 7, OCH_2CH$_3$), 1.56–1.30 (6H, m, 3 × CH_2), 1.25 (3H, t, *J* = 7, CH_3CH$_2$O), 1.07 (12H, s, 4 × CCH_3); δ_C (67.5 MHz, $CDCl_3$) 166.5 (CO_2), 143.9 (*C*H=CHCO$_2$Et), 120.2 (CH=*C*HCO$_2$Et), 75.6 (NOCH_2), 60.2, 59.8 (2 × NCCH$_3$ and *C*H$_2$CH$_3$), 39.5 (2 × NCCH_2), 32.7 (2 × NCCH$_3$), 20.1 (2 × NCCH_3), 16.9 ($CH_2CH_2CH_2$), 14.2 (CH_2CH_3); *m/z* (CI, NH_3) 270 (M + H^+, 73%), 156 (100), 140 (16), 126 (8) (Found: M + H^+, 270.2068. $C_{15}H_{27}NO_3$ requires for M + H^+, 270.2069).

General procedure for cyclisations in the presence of TEMPO

A solution of TEMPO (0.25 g, 1.59 mmol) in dichloromethane (5 cm^3) was added slowly, or in one portion, to a stirred solution of $Mn_2(CO)_{10}$ (0.28 g, 0.73 mmol) and the organohalide **3**, **11**, **18** (0.47–0.60 g, 1.45 mmol) in dichloromethane (75 cm^3) during continuous photolysis under an atmosphere of nitrogen. After the addition was complete, the solution was photolysed for a further 1 h and DBU (0.44 g, 2.92 mmol) was added dropwise. After 1 h, the crude product was adsorbed onto silica and column chromatography afforded **19** (7–61%), **20a–c** (18–78%) and **13** (10–18%) as colourless oils.

***N*-Allyl-*N*-(4-methoxybenzyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethanamide 19.** R_f 0.4 (petrol–diethyl ether, 4:1); ν_{max} ($CHCl_3$) 2940 (s), 2246 (m), 1640 (br, s), 1247 (br, s), 1178 (m), 1037 (m), 991 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) (mixture of conformers) 7.19 and 7.13 (2H, 2 × d, *J* = 9, aromatics), 6.87 and 6.83 (2H, 2 × d, *J* = 9, aromatics), 5.80–5.70 (1H, m, C*H*=CH$_2$), 5.28–5.06 (2H, m, CH=CH_2), 4.58–4.50 (4H, m, NCH_2 and NOCH_2), 3.91 (1H, d, *J* = 6, NC$H_A$$H_B$), 3.83 (2H, d, *J* = 6, NCH$_A$$H_B$), 3.78 (3H, s, OC$H_3$), 1.62–1.23 (6H, m, C$H_2CH_2CH_2$), 1.18 (6H, s, 2 × CC$H_3$), 1.10 (6H, s, 2 × CC$H_3$); δ_C (67.5 MHz, $CDCl_3$) (mixture of conformers) 168.7, 168.5 (N*C*O), 158.9, 158.8 (O*C*=CH), 133.0, 132.6 (*C*H=CCH$_2$), 129.6, 129.3 (*C*H=CH$_2$), 128.3, 128.0 (CH=*C*CH$_2$), 117.3, 117.1 (CH=*C*H$_2$), 114.0, 113.8 (*C*H=COMe), 77.4 (NO*C*H$_2$), 59.9 (2 × N*C*CH$_3$), 55.1 (O*C*H$_3$), 48.0, 46.8, 46.7 (N*C*H$_2$), 39.6 (2 × NC*C*H$_2$), 32.8 (2 × NC*C*H$_3$), 20.2 (2 × NC*C*H$_3$), 16.9 ($CH_2CH_2CH_2$); *m/z* (CI, NH_3) 375 (M + H^+, 100%), 156 (20), 140 (16), 121 (27) (Found: M + H^+, 375.2653. $C_{22}H_{34}N_2O_3$ requires for M + H^+, 375.2648).

***N*-(4-Methoxybenzyl)-4-(2,2,6,6-tetramethylpiperidin-1-yloxymethyl)pyrrolidin-2-one 20a.** R_f 0.3 (diethyl ether); ν_{max} ($CHCl_3$) 2936 (s), 2246 (w), 1672 (br, s), 1512 (m), 1445 (br, m), 1299 (w), 1248 (s), 1037 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.19 (2H, d, *J* = 9, aromatics), 6.82 (2H, d, *J* = 9, aromatics), 4.42 (1H, d, *J* = 10, NC*H*), 4.35 (1H, d, *J* = 10, NC*H*), 3.79 (3H, s, OCH_3), 3.68 (2H, d, *J* = 6.0, OCH_2CH), 3.33 (1H, dd, *J* = 10 and 8, NC$H_A$$H_B$), 3.13 (1H, dd, *J* = 10 and 4.5, NCH$_A$$H_B$), 2.62–2.47 (2H, m, OCH$_2$C*H* and COC$H_A$$H_B$), 2.31 (1H, dd, *J* = 19 and 10, COCH$_A$$H_B$), 1.47–1.26 (6H, m, C$H_2CH_2CH_2$), 1.10 (6H, s, 2 × CC$H_3$), 1.03 (6H, s, 2 × CC$H_3$); δ_C (67.5 MHz, $CDCl_3$) 173.9 (N*C*O), 159.0 (O*C*=CH), 129.4 (*C*H=C), 128.5 (NCH$_2$*C*=CH), 113.8 (*C*H=C), 77.7 (NO*C*H$_2$), 59.8 (2 × N*C*CH$_3$), 55.2 (O*C*H$_3$), 49.2, 45.8 (2 × N*C*H$_2$), 39.5 (2 × NC*C*H$_2$), 34.3 (NCO*C*H$_2$), 33.0 (2 × NC*C*H$_3$), 30.5 (NCH$_2$-*C*H), 19.9 (2 × NC*C*H$_3$), 16.9 ($CH_2CH_2CH_2$); *m/z* (CI, NH_3) 375 (M + H^+, 100%), 126 (22), 121 (20) (Found: M + H^+, 375.2648. $C_{22}H_{34}N_2O_3$ requires for M + H^+, 375.2648).

3,3-Dibromo-*N*-(4-methoxybenzyl)-4-(2,2,6,6-tetramethylpiperidin-1-yloxymethyl)pyrrolidin-2-one 20b. Oil; R_f 0.4 (petrol–diethyl ether, 1:1); ν_{max} ($CHCl_3$) 2971 (s), 1711 (br, s), 1612 (w), 1513 (m), 1440 (br, w), 1249 (br, s), 1177 (m), 1036 (m) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.19 (2H, d, *J* = 8.5, aromatics), 6.88 (2H, d, *J* = 8.5, aromatics), 4.55 (1H, d, *J* = 15, NC$H_A$$H_B$), 4.35 (1H, d, *J* = 15, NCH$_A$$H_B$), 4.19 (1H, dd, *J* = 9.5 and 5, NC$H_A$$H_B$CH), 3.88 (1H, apparent t, *J* = 8.5, OC*H*), 3.81 (3H, s, OCH_3), 3.23 (1H, dd, *J* = 9.5 and 6.5, NCH$_A$$H_B$CH), 3.08–2.97 (2H, m, OC*H* and NCH$_2$C*H*), 1.55–1.17 (6H, m, CH_2CH_2CH_2), 1.08 (6H, s, 2 × CCH_3), 1.04 (6H, s 2 × CCH_3); δ_C (67.5 MHz, $CDCl_3$) 158.6 (N*C*O), 139.0 (O*C*=CH), 129.4 (*C*H=C), 127.1 (NCH$_2$*C*=CH), 114.1 (*C*H=C), 75.8 (NO*C*H$_2$), 60.0 (*C*Br$_2$), 59.7 (2 × N*C*CH$_3$), 55.1 (O*C*H$_3$), 50.0 (NCH$_2$-*C*H), 47.2, 46.4 (2 × N*C*H$_2$), 39.4 (2 × NC*C*H$_2$), 32.9 (2 × NC*C*H$_3$), 19.9 (2 × NC*C*H$_3$), 16.8 ($CH_2CH_2CH_2$); *m/z* (CI, NH_3) 531 (^{79,79}M + H^+, 16%), 158 (100), 142 (83), 126 (46) (Found: ^{79,79}M + H^+, 531.0860. $C_{22}H_{32}Br_2N_2O_2$ requires for ^{79,79}M + H^+, 531.0858).

3,3-Dichloro-*N*-(4-methoxybenzyl)-4-(2,2,6,6-tetramethylpiperidin-1-yloxymethyl)pyrrolidin-2-one 20c. R_f 0.5 (petrol–

diethyl ether, 1:1); ν_{max} ($CHCl_3$) 2932 (br, s), 1725 (br, s), 1612 (w), 1513 (m), 1440 (m), 1251 (s), 1178 (m), 828 (w) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 7.18 (2H, d, J = 8.5, aromatics), 6.88 (2H, d, J = 8.5, aromatics), 4.53 (1H, d, J = 14.5, NCH_AH_B), 4.39 (1H, d, J = 14.5, NCH_AH_B), 4.19 (1H, dd, J = 9 and 5, NCH_A-H_BCH), 3.88 (1H, t, J = 8, OCH_AH_B), 3.80 (3H, s, OCH_3), 3.35 (1H, dd, J = 9 and 5, NCH_AH_BCH), 3.10 (1H, t, J = 8, OCH_AH_B), 3.04–2.97 (1H, m, OCH_2CH), 1.45–1.13 (6H, m, $CH_2CH_2CH_2$), 1.07 (6H, s, 2 × CCH_3), 1.03 (6H, s, 2 × CCH_3); δ_C (67.5 MHz, $CDCl_3$) 166.3 (NCO), 159.3 (OC=CH), 129.4 (CH=C), 126.7 (NCH_2C=CH), 114.1 (CH=C), 84.0 (CCl_2), 73.6 ($NOCH_2$), 59.7 (2 × $NCCH_3$), 55.1 (OCH_3), 48.7 (NCH_2CH), 47.0, 46.3 (2 × NCH_2), 39.3 (2 × $NCCH_2$), 32.8 (2 × $NCCH_3$), 19.8 (2 × $NCCH_3$), 16.8 ($CH_2CH_2CH_2$); *m/z* (CI, NH_3) 443 ($^{35,35}M + H^+$, 100%), 409 (51), 126 (53), 121 (44) (Found: $^{35,35}M + H^+$, 443.1870. $C_{22}H_{32}Cl_2N_2O_2$ requires for $^{35,35}M + H^+$, 443.1868).

Acknowledgements

We thank ICI and The University of York for a University Studentship (to D. T. E. W.) and the EU (under the SOCRATES scheme) for funding (W. K.).

References

1 (*a*) B. Giese, B. Kopping, T. Göbel, J. Dickhaut, G. Thoma, K. J. Kulicke and F. Trach, *Org. React.*, 1996, **48**, 301; (*b*) F. Aldabbagh and W. R. Bowman, *Contemp. Org. Synth.*, 1997, 261; (*c*) W. R. Bowman, C. F. Bridge and P. Brookes, *J. Chem. Soc.*, *Perkin Trans. 1*, 2000, 1.
2 P. A. Baguley and J. C. Walton, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 3072.
3 M. Ballestri, C. Chatgilialoglu, K. B. Clark, D. Griller, B. Giese and B. Kopping, *J. Org. Chem.*, 1991, **56**, 678.
4 G. Pattenden, *Chem. Soc. Rev.*, 1988, **17**, 361.
5 B. B. Snider, *Chem. Rev.*, 1996, **96**, 339.
6 G. A. Molander and C. R. Harris, *Chem. Rev.*, 1996, **96**, 307.
7 (*a*) A. Hudson, M. F. Lappert and B. K. Nicholson, *J. Chem. Soc.*, *Dalton Trans.*, 1977, 551; (*b*) T. J. Meyer and J. V. Caspar, *Chem. Rev.*, 1985, **85**, 187.
8 R. S. Herrick, T. R. Herrinton, H. W. Walker and T. L. Brown, *Organometallics*, 1985, **4**, 42.
9 *Encyclopedia of Reagents for Organic Synthesis*, ed. L. A. Paquette, Wiley, Chichester, 1995, vol. 2, 1471.
10 (*a*) L. Grossi, S. Strazzari, B. C. Gilbert and A. C. Whitwood, *J. Org. Chem.*, 1998, **63**, 8366; (*b*) P. Smith, K. R. Maples and R. L. Lau, *Can. J. Chem.*, 1992, **70**, 116.
11 B. C. Gilbert, C. I. Lindsay, P. T. McGrail, A. F. Parsons and D. T. E. Whittaker, *Synth. Commun.*, 1999, **29**, 2711.
12 D. P. Curran and C.-T. Chang, *J. Org. Chem.*, 1989, **54**, 3140.
13 Part of this work has been published as a preliminary communication: B. C. Gilbert, W. Kalz, C. I. Lindsay, P. T. McGrail, A. F. Parsons and D. T. E. Whittaker, *Tetrahedron Lett.*, 1999, **40**, 6095.
14 (*a*) I. De Riggi, S. Gastaldi, J.-M. Surzur, M. P. Bertrand and A. Virgili, *J. Org. Chem.*, 1992, **57**, 6118; (*b*) G. Stork and R. Mah, *Heterocycles*, 1989, **28**, 723.
15 R. Grigg, J. Devlin, A. Ramasubbu, R. M. Scott and P. Stevenson, *J. Chem. Soc.*, *Perkin Trans. 1*, 1987, 1515.
16 S. Ma and X. Lu, *J. Chem. Soc.*, *Perkin Trans. 1*, 1990, 2031.
17 I. Lachaise, K. Nohair, M. Hakiki and J. Y. Nédélec, *Synth. Commun.*, 1995, **22**, 3529.
18 A. L. J. Beckwith and C. H. Schiesser, *Tetrahedron*, 1985, **41**, 3925.
19 (*a*) B. Cardillo, R. Galeazzi, G. Mobbili, M. Orena and M. Rossetti, *Heterocycles*, 1994, **38**, 2663; (*b*) T. Sato, Y. Wada, M. Nishimoto, H. Ishibashi and M. Ikeda, *J. Chem. Soc.*, *Perkin Trans. 1*, 1989, 879.
20 G. Stork and M. E. Reynolds, *J. Am. Chem. Soc.*, 1988, **110**, 6911.
21 (*a*) A. R. Howell and G. Pattenden, *J. Chem. Soc.*, *Perkin Trans. 1*, 1990, 2715; (*b*) J. L. Gage and B. P. Branchaud, *Tetrahedron Lett.*, 1997, **38**, 7007; (*c*) D. L. Boger and J. A. McKie, *J. Org. Chem.*, 1995, **60**, 1271; (*d*) D. L. Boger, R. M. Garbaccio and Q. Jin, *J. Org. Chem.*, 1997, **62**, 8875.
22 M. F. Semmelhack, C. R. Schmid and D. A. Cortés, *Tetrahedron Lett.*, 1986, **27**, 1119.
23 R. Sustmann and D. Brandes, *Chem. Ber.*, 1976, **109**, 354.
24 (*a*) M. Mori, N. Kanda, I. Oda and Y. Ban, *Tetrahedron*, 1985, **41**, 5465; (*b*) H. Nagashima, N. Ozaki, M. Ishii, K. Seki, M. Washiyama and K. Itoh, *J. Org. Chem.*, 1993, **58**, 464.
25 T. Taniguchi and K. Ogasawara, *Tetrahedron Lett.*, 1998, **39**, 4679.
26 J. E. Anderson, D. Casarini, J. E. T. Corrie and L. Lunazzi, *J. Chem. Soc.*, *Perkin Trans. 2*, 1993, 1299.