Thermal and induced decompositions of *N*-alkoxycarbonyldihydropyridines: end product analysis and EPR spectra of azacyclohexadienyl radicals

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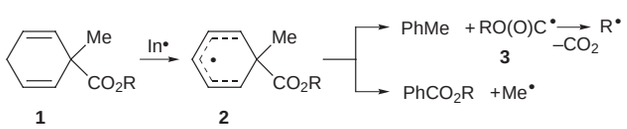
Hydrogen abstraction from *N*-alkoxycarbonyldihydropyridines generated azacyclohexadienyl radicals (pyridinyl radicals) which are characterised by EPR spectroscopy. In the presence of peroxide initiators, *N*-alkoxycarbonyl-1,2-dihydropyridines decomposed with production of pyridine, the corresponding alkyl formate, alkyl benzoate and alkanol being formed as the major products. Absence of cyclised products in experiments with substrates containing hex-5-enyl, pent-4-enyloxy *etc*. units demonstrates that radical production must be minor and that *N*-alkoxycarbonylazacyclohexadienyl radicals do not readily undergo β-scission of the exocyclic N–C bond. The most probable mechanism is a direct 1,2-elimination of formate. The alcohols which accompanied the other products are probably formed by hydrolysis of the formates and benzoates. Analogous chemistry is displayed by *N*-alkoxycarbonyl-1,4-dihydropyridines at higher temperatures where 1,4-elimination of formate is too rapid for homolytic radical production to compete.

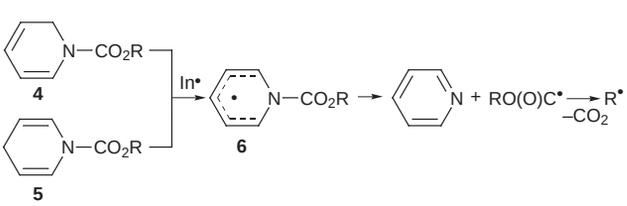
Introduction

Hydrogen abstraction from esters of 1-methylcyclohexa-2,5-diene-1-carboxylic acid **1** and 2-methyl-2,5-dihydrofuran-2-carboxylic acid, prepared by Birch reduction and alkylation of benzoic and furoic acid respectively, afforded cyclohexadienyl **2** and 2,5-dihydrofuranyl radicals.[1,2] The intermediate cyclohexadienyl radicals mainly underwent β-scission above *ca*. 80 °C to produce toluene and alkoxycarbonyl radicals **3**. Benzyl-, *tert*-, *sec*-, and to a lesser extent primary-alkoxycarbonyl radicals, subsequently extruded CO_2 to generate the corresponding alkyl radicals which could be trapped with moderate efficiency by halogen donors or alkenes. However, loss of a methyl radical to afford an alkyl benzoate was a significant competing β-scission (Scheme 1).



Scheme 1

Analogous radical-induced decomposition sequences could be envisaged for *N*-alkoxycarbonyl-substituted 1,2- (**4**) and 1,4-dihydropyridines (**5**) involving intermediate azacyclohexadienyl radicals **6**, (pyridinyl radicals) for which extrusion of alkoxycarbonyl radicals would be facilitated by aromatisation to produce pyridine (Scheme 2). With these precursors there is only



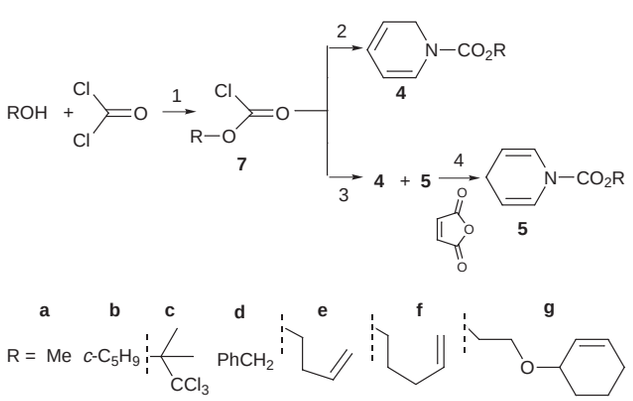
Scheme 2

one possible β-scission of the delocalised radicals **6**, and hence **4** and **5** appeared to be potentially cleaner sources of alkyl radicals than esters **1**. However, several electrocyclic reactions, such as a 1,2-elimination or a Diels–Alder cycloaddition of **4** with an added alkene, were potential competing non-radical processes. To evaluate the usefulness of dihydropyridines as radical sources in spectroscopic and preparative work, and to elucidate their main modes of reaction, several series were made and their thermal and radical induced decompositions were examined.

Results and discussion

Preparation of *N*-alkoxycarbonyldihydropyridines

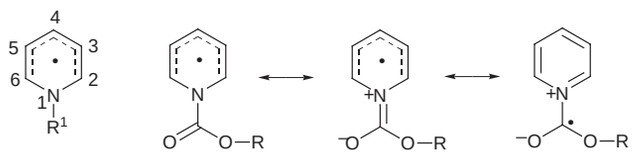
N-Alkoxycarbonyl-1,2-dihydropyridines **4** were prepared in good yields by treating pyridine with sodium borohydride and the appropriate chloroformate in methanol at −78 °C (Scheme 3).[3] *N*-Methoxycarbonyl- and *N*-benzyloxycarbonyl-



Scheme 3 *Reagents and conditions*: 1, quinoline, diethyl ether, PhMe, 0 °C, 24 h; 2, pyridine, $NaBH_4$, diethyl ether, MeOH, −78 °C, 2 h; 3, pyridine, $NaBH_4$, THF, −10 °C, 2 h; 4, CH_2Cl_2, reflux, 37 h

1,2-dihydropyridines, prepared in this way have previously been used in the synthesis of (±)-aminoarabinose and (±)-aminoaltrose derivatives *via* a double dihydroxylation reaction[4] and in a synthesis of *cis*-hydroisoquinoline.[5] Non-commercial chloroformates were prepared by treating the corresponding alcohol with phosgene in toluene.[6] The ^1H NMR spectra of the 1,2-dihydropyridines were in good agreement with the general structure **4**, though analysis by ^1H and ^{13}C NMR gave evidence for the presence of 1,4-dihydropyridines in small quantities

Table 1 EPR data for azacyclohexadienyl radicals (pyridinyl radicals)[a]



8 **6A** **6B** **6C**

Radical	*T*/K	N	H^4	$H^{2,6}$	$H^{3,5}$	H^{other}	Ref.
8, $R^1 = H$	308	5.85	11.62	5.91	0.97	3.47 (1 H)	9
8, $R^1 = CH_3$	233	5.35	11.18	5.77	0.92	6.78 (3 H)	10
8, $R^1 = SiMe_3$	383	4.20	11.55	6.26	1.38	—	11
6a, $R = CH_3$	260	1.30	12.00	7.65	1.95	0.45 (3 H)	*b*
6b, R = *c*-C_5H_9	250	1.26	11.74	7.52	1.90	0.38 (1 H)	*b*
6c, $R = C_4H_6Cl_3$	250	0.95	11.85	7.75	2.00	—	*b*
6d, $R = PhCH_2$	260	1.18	11.70	7.60	1.93	0.37 (2 H)	*b*
6e, $R = C_4H_7$	260	1.25	11.77	7.65	1.90	0.38 (2 H)	*b*
6f, $R = C_5H_9$	260	1.37	11.80	7.52	1.97	0.27 (2 H)	*b*
6g, $R = C_8H_{13}O$	250	1.20	11.93	7.73	1.90	0.37 (2 H)	*b*

[a] Hfs in G (10 G = 1 mT), all *g*-factors 2.003 ± 0.001. [b] This work.

(<5%). However, this was not considered to be a problem because both isomers would give the same delocalised radical **6** when treated with an initiator. An attempt was made to purify **4a** by column chromatography to a condition suitable for microanalysis, but this was unsuccessful as the compound rapidly decolourised. Thus, the 1,2-dihydropyridines were isolated without additional purification and stored in the freezer under nitrogen prior to use.

When the reductive acyloxylation of pyridine was carried out at −10 °C in THF a mixture of dihydropyridines containing mainly the 1,4-isomer **5** was obtained. Pure 1,4-dihydropyridines were isolated by refluxing the mixture with excess maleic anhydride, followed by removal of the Diels–Alder adduct of **4** with aqueous alkali.

EPR spectroscopic studies of *N*-alkoxycarbonyl-1,2-dihydropyridines

Hydrogen abstraction from the dihydropyridines by photochemically generated *tert*-butoxyl radicals was investigated by EPR spectroscopy. Degassed solutions of individual dihydropyridines in neat di-*tert*-butyl peroxide (sometimes diluted in *tert*-butylbenzene) were photolysed in the resonant cavity of an EPR spectrometer. Under these conditions all of the dihydropyridines produced intense, well-resolved EPR spectra at *ca.* 250 K which were analysed with the aid of computer simulations.[7] For example, Fig. 1 top panel, illustrates the radical derived from the *tert*-alkyl substituted-dihydropyridine **4c** and the lower spectrum resulted from the pentenyloxy-dihydropyridine **4f**. The derived EPR parameters are listed in Table 1.

Azacyclohexadienyl radicals have previously been generated by photoreduction of substituted pyridines, from pyridinium salts, and by thermolysis of dimers. EPR spectra have been documented for a good range of C-substituted examples,[8] but only a few N-substituted species, all with electron-releasing substituents, have been reported. A short selection of hyperfine splittings (hfs) are included in Table 1 for comparison. The hfs patterns are similar for all the radicals, the main differences being the slightly larger hfs from the ring hydrogens of the present set of *N*-alkoxycarbonyl substituted radicals and the substantially smaller N-hfs. These differences can probably be attributed to the influence of the carbamate group which will enable structures such as **6B** and particularly **6C** to make significant contributions to the ground states of the radicals. A noteworthy feature of the spectra from radicals **6a**–**g** was the observation of long range hfs from hydrogens of the alkoxycarbonyl substituents. This is consistent with a significant

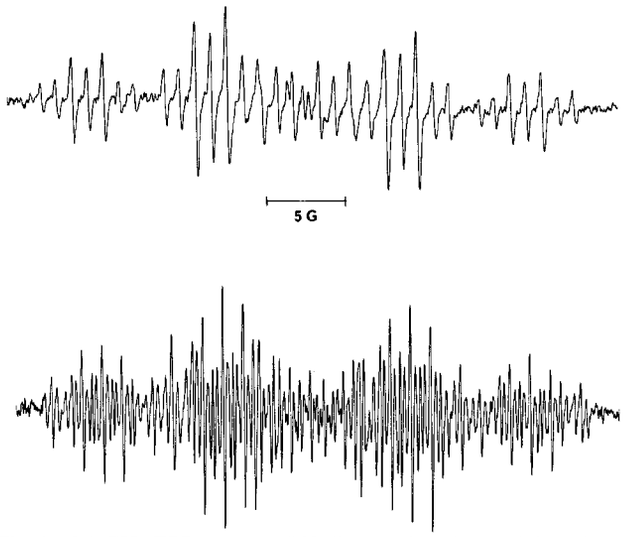


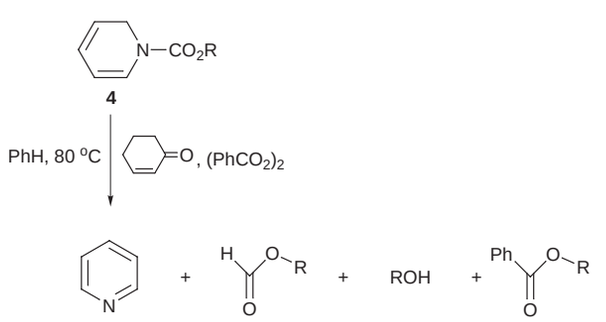
Fig. 1 9.1 GHz EPR spectra of *N*-alkoxycarbonylazacyclohexadienyl radicals in di-*tert*-butyl peroxide solution at 250 K. Upper spectrum: 2,2,2-trichloro-1,1-dimethylethyl-substituted radical **6c**. Lower spectrum: pent-4-enyl-substituted radical **6f**.

contribution from the resonance structure **6C**, which delocalises spin density outside the pyridine ring.

The ease of observation of the azacyclohexadienyl radicals, and the good quality of the spectra, is evidence that *tert*-butoxyl radicals efficiently abstract hydrogen at low temperatures. Spectra weakened significantly when the temperature of the cavity was raised, but were otherwise unchanged. For most of the dihydropyridines, spectra were too weak for detection above *ca.* 340 K, but in no case was the spectrum of an alkyl radical $R^{\bullet}$, from decarboxylative fragmentation of **6**, observed. Even strongly stabilised radicals ($R = PhCH_2$, CMe_2CCl_3) were not detected. Thus, under EPR conditions, fragmentation of radicals **6** must be slow, or non-existent. Previous EPR studies of the analogous cyclohexadienyl radicals **2** had also shown that their fragmentation could not be spectroscopically detected under EPR conditions, although product studies demonstrated that fragmentation did occur well at higher temperatures.[2] Thus, the negative EPR evidence for the dihydropyridines needed to be supplemented by more definitive results from product analyses of reactions under more vigorous conditions.

Thermal and induced reactions of *N*-alkoxycarbonyl-1,2-dihydropyridines

1,2-Dihydropyridines **4a**–**d** were individually dissolved in benzene and refluxed for an appropriate period of time (*ca.* 24 h) in the presence of an initiator, usually dibenzoyl peroxide, and cyclohexenone. For the methyl-substituted compound **4a** the only identifiable product was pyridine, but for the others (**4b**–**d**), pyridine, the corresponding formate **9**, alcohol **10** and alkyl benzoate **11** were obtained in the yields shown in Scheme 4. In



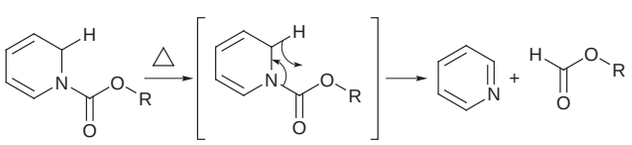
Scheme 4

addition, minor amounts of benzoic acid and biphenyl were identified, but in no case was any of the corresponding adduct (3-alkylcyclohexanone) detected. Careful search was made for the Diels–Alder adducts of each 1,2-dihydropyridine with cyclohexenone, but none were detected. The observed products might possibly be accounted for by fragmentation of radical **6** to produce pyridine and alkoxycarbonyl radicals [RO(O)C$^{\bullet}$], as indicated in Scheme 2. The RO(O)C$^{\bullet}$ radical could then abstract hydrogen to yield formates **9** or couple with a phenyl radical (from the initiator) to afford the benzoates **11**. Under some reaction conditions alkoxycarbonyl radicals can undergo α-scission with formation of an alkoxyl radical and carbon monoxide [reaction (1)].[12,13] Hydrogen abstraction by RO$^{\bullet}$

$$R^{\bullet} + CO_2 \longleftarrow RO(O)C^{\bullet} \longrightarrow RO^{\bullet} + CO \qquad (1)$$

would then explain the formation of the alcohols **10**. However, this mechanism is unconvincing because RO$^{\bullet}$ formation cannot compete with CO_2 loss and production of R$^{\bullet}$ when this latter radical is stabilised. Thus ROH formation would *not* be expected from reactions of **4c**,**d** (R = CMe_2CCl_3, $PhCH_2$), contrary to observation. Furthermore, any R$^{\bullet}$ generated from **4b**–**d** should have led to some adduct formation with the electron deficient cyclohexenone. Hence, the product analysis results did not support the production of either R$^{\bullet}$ or RO$^{\bullet}$ from **4**.

To shed additional light on the mechanism, the benzyl derivative **4d** was investigated in greater detail. More benzyl benzoate was produced when the initial quantity of dibenzoyl peroxide was increased, as would be expected if the Ph and/or $PhCO_2$ segments of **11d** were derived from the initiator. Furthermore, when the reaction was carried out in C_6D_6 no deuterium incorporation into **11d** (or into $PhCO_2H$) was detected (<10%). Hence, addition of benzyloxycarbonyl radicals to the solvent to produce cyclohexadienyl radicals, which were subsequently oxidised to **11d**, can be excluded. Benzyl alcohol (**10d**) was always obtained (2 to 20%) irrespective of reaction conditions. Most importantly, when **4d** was refluxed in benzene, in the absence of initiator or cyclohexenone, pyridine and formate **9d** were formed as by far the major products in a ratio of *ca*. 1.5 to 1.0. This latter result is most simply explained in terms of a direct thermal β-elimination of formate from the 1,2-dihydropyridine (see **12**, Scheme 5). In agreement with this, it was found that the



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Scheme 5

cyclopentyl compound **4b** also gave almost exclusively pyridine and cyclopentyl formate on refluxing in benzene.

To test for the involvement of alkoxycarbonyl, alkoxyl and alkyl radicals in the formation of ROH and benzoates **11**, 1,2-dihydropyridines designed to yield radicals capable of intramolecular cyclisations were investigated. Thus, but-3-enyloxycarbonyl radicals, if generated from **4e**, were expected to ring close to afford the corresponding γ- or δ-lactone.[14,15] Similarly, the pentenyloxycarbonyl radical from **4f** could cyclise to the corresponding lactone or lose CO with formation of the pentenyloxyl radical, which is known to cyclise rapidly, mainly in the *exo*-mode, to afford 2-methyltetrahydrofuran.[16,17] If cyclohexenyloxyethyl radicals were generated during the induced decomposition of **4g**, rapid 5-*exo* cyclisation to yield 7-oxabicyclo[4.3.0]nonane can be anticipated.

Each dihydropyridine (**4e**–**g**) was refluxed in benzene

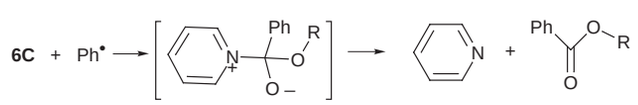
Table 2 Product yields[a] from reactions of *N*-alkoxycarbonyl-1,2-dihydropyridines and dibenzoyl peroxide in benzene at 80 °C

Substrate	Pyridine[b]	HCO_2R	ROH	$PhCO_2R$
4e	nd	6	*c*	11
4f	nd	22	[20]	4
4g	nd	15	19	[5]

[a] Isolated yields as mol%, except for those in square brackets which were estimated either by GC or from the ^{1}H NMR spectra. [b] Substantial amounts of pyridine were formed in each case but yields were not determined (nd) due to its volatility. [c] Not detected.

together with dibenzoyl peroxide until TLC showed consumption of the majority of the substrate. Reaction mixtures were examined by GC–MS and NMR and the main components were isolated by column chromatography. The main products and their yields are shown in Table 2; because of their volatility, the isolated yields of pyridine, alcohols and formates should be treated as lower limits. Table 2 shows that the product spectrum was similar to that observed with **4b**–**d**. Comparisons of the retention times and mass spectra of authentic samples of 2-methyltetrahydrofuran, tetrahydropyran and 7-oxabicyclo[4.3.0]nonane[18] with the GC–MS data of the product mixtures indicated that these cyclised products were not formed in detectable amounts (≤2%). Similarly, MS and NMR evidence showed that lactones were not formed in the reactions of **4e** or **4f**. The fact that 2-methyltetrahydrofuran (or THP) was undetectable in the reaction of **4f** is strong evidence that alkoxyl radicals RO$^{\bullet}$ are not intermediates in these reactions of 1,2-dihydropyridines. It is probable therefore that the alcohols are formed by a non-radical route which is most likely hydrolysis of the formate and benzoate esters. Although the conditions are non-aqueous, pyridine builds up during the course of the reaction and this could well catalyse the hydrolysis. Alternatively, benzoic acid (derived from the initiator) could act as a proton source.

The benzoate esters **11** could possibly be formed either by combination of a phenyl radical from the initiator with RO(O)C$^{\bullet}$ or by combination of PhC(O)O$^{\bullet}$ (from the initiator) with R$^{\bullet}$. However, the fact that no lactone was obtained on reaction of **4e**, no 7-oxabicyclo[4.3.0]nonane was obtained from **4g** and the general lack of adduct formation from **4a**–**d** and cyclohexenone, militates against the production of RO(O)C$^{\bullet}$ or R$^{\bullet}$ radicals from 1,2-dihydropyridines. Possibly the esters are formed directly from the azacyclohexadienyl radical **6** and a phenyl radical (see Scheme 6). In an attempt to encourage



Scheme 6

fragmentation of radicals **6**, neat 1,2-dihydropyridines **4f** and **4g** were heated with dibenzoyl peroxide at 140 °C, but even at this temperature the product range was similar and there was no evidence to suggest that alkyl radicals had been generated.

For comparison purposes the reaction of pent-4-enyl chloroformate with tributyltin hydride was also examined. Photolysis of a solution of this substrate and Bu_3SnH in C_6D_6 at 40 °C afforded pent-4-en-1-ol and pent-4-enyl formate, but no lactone or 2-methyltetrahydrofuran. Tributyltin hydride is known to react with acyl halides RC(O)Cl by a non-radical route to afford RC(O)H.[19,20] The absence of cyclised products is a strong indication that organotin hydride reductions of chloroformates proceed by a similar ionic route.

Reactions of *N*-benzyloxycarbonyl-1,4-dihydropyridine

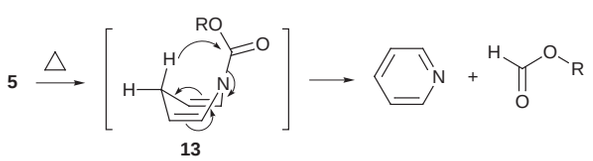
1,4-Dihydropyridines are incapable of the non-radical 1,2-elimination of formate depicted in Scheme 5 and might

Table 3 Product yields[a] from reactions of *N*-benzyloxycarbonyl-1,4-dihydropyridine **5d**

Other reactants	Conditions	*T*/°C	Pyridine	HCO_2CH_2Ph	$PhCH_2OH$	$PhCO_2CH_2Ph$
Cyclohexenone, $(PhCO_2)_2$	Reflux, PhH, 24 h	80	21	18	12	32
Cyclohexenone, $PhCO_3Bu^t$[b]	$EtCMe_2OH$, 48 h	104	5	2	3	0
Cyclohexenone, $(PhCO_2)_2$	Neat, 2 h	140	43	4	10	29
None[b]	Reflux, PhH, 72 h	80	~2	~2	~2	0

[a] Yields in mol% determined by ^{1}H NMR. Substantial amounts of $PhCO_2H$ were also formed in the reactions initiated with dibenzoyl peroxide. [b] Dihydropyridine consumption was small.

therefore be expected to generate alkoxycarbonyl radicals more readily than 1,2-dihydropyridines. To study this possibility, *N*-benzyloxycarbonyl-1,4-dihydropyridine **5d** was prepared as outlined in Scheme 3 and decomposed under several sets of reaction conditions (see Table 3). When **5d** was refluxed in benzene on its own very little reaction occurred and the majority could be recovered unchanged even after three days (entry 4). In the reaction induced by dibenzoyl peroxide at 80 °C in the presence of cyclohexenone (entry 1) the major products were again found to be pyridine, benzyl formate, benzyl alcohol and benzyl benzoate. No products incorporating cyclohexenone were detected. A reaction initiated with *tert*-butyl peroxybenzoate at 104 °C in 3-methylbutyl alcohol solvent resulted in low conversion of **5d**, but the same products (except benzyl benzoate) were observed. Even under forcing conditions at 140 °C no 3-benzylcyclohexanone was produced and the main products were as above. The formation of formate **9d** from **5d** was somewhat unexpected. However, it is probable that the quasi-axial boat conformer **13** of 1,4-dihydropyridine **5d** is easily accessible and hence the 1,4-elimination of formate with re-aromatisation, depicted in Scheme 7, is the major thermal reaction channel.



Scheme 7

Conclusions

tert-Butoxyl radicals readily abstract hydrogen from dihydropyridines at low temperatures to generate azacyclohexadienyl radicals. Dimer formation has been reported previously for azacyclohexadienyl radicals which had no substituents at C(4).[9–11] No dimers, or their oxidation products (diazabiphenyls), were found amongst the products in thermal or radical induced reactions of **4a**–**g**. The absence of products derived from azacyclohexadienyl radicals suggests that H-abstraction by C-centred radicals is a minor process at higher temperatures. In the presence or absence of peroxide initiators, *N*-alkoxycarbonyl-1,2-dihydropyridines decomposed with production of pyridine and the corresponding formate ester as the major initial products. Absence of cyclised products in experiments with substrates containing hex-5-enyl, pent-4-enyloxy *etc*. units demonstrated that radical production must be minor and that azacyclohexadienyl radicals do not readily undergo β-scission of the N–C bond. The most probable mechanism is therefore direct 1,2-elimination of formate. The alcohols which accompanied the other products were probably formed by hydrolysis of the formates, catalysed by pyridine and/or benzoic acid. Analogous chemistry was displayed by *N*-alkoxycarbonyl-1,4-dihydropyridines for which 1,4-elimination of formate was also too rapid for homolytic radical production to compete. Dihydropyridines provided no unequivocal evidence for radical decarboxylation and are not viable as radical precursors for preparative chain reactions.

Experimental

^{1}H NMR spectra were recorded at 200 or 300 MHz and ^{13}C NMR spectra at 75 MHz, in $CDCl_3$ solution with tetramethylsilane ($\delta_H = \delta_C = 0$) as reference. Coupling constants (J) are expressed in Hz. Ether refers to diethyl ether. Light petroleum refers to the fraction boiling in the range 40–60 °C. Mass spectra were obtained with 70 eV electron impact ionisation on a Kratos M25RF spectrometer. GC–MS analyses were run on a Finnigan Incos 50 quadrupole instrument coupled to a Hewlett Packard HP 5890 chromatograph fitted with a 25 m HP 17 capillary column (50% phenyl methyl silicone). For the calculation of yields from GC data, the detector response was calibrated with known amounts of authentic materials (or close analogues) and *n*-dodecane, or *n*-heptane was added as a standard. EPR spectra were obtained with Bruker ER 200D and Bruker EMX 10/12 spectrometers operating at 9.1 GHz with 100 kHz modulation. Samples of the substrate (*ca*. 40 mg) and di-*tert*-butyl peroxide (500 μl) or in *tert*-butylbenzene (0.5 cm^3) (occasionally cyclopropane) were degassed by bubbling nitrogen for 20 min and photolysed in the resonant cavity by light from a 500 W super pressure mercury arc lamp. EPR spectra were simulated with a program due originally to Heinzer.[7]

Methyl chloroformate, benzyl chloroformate and 2,2,2-trichloro-1,1-dimethylethyl chloroformate were purchased from Aldrich.

Preparation of cyclopentyl chloroformate 7b[6]

Cyclopentanol (15 g, 0.174 mol) and quinoline (22.5 g, 0.174 mol) dissolved in dry ether (50 cm^3) were added dropwise to a stirred mixture of phosgene (19 g, 0.192 mol) in toluene at 0 °C and the mixture was left stirring for 16–24 h. To the reaction mixture aqueous HCl (100 cm^3, 2 M) was added and the resulting layers were separated. The aqueous layer was extracted with ether (100 cm^3), the organic fractions were combined, dried ($MgSO_4$) and the solvents were evaporated and the chloroformate was purified by distillation.

Chloroformates **7e**–**g** were made in a similar manner with the appropriate alcohol.

Cyclopentyl chloroformate 7b. 7b was obtained as a clear, colourless liquid (82%), bp 56–58 °C/10–12 mmHg (lit.,[15] bp 69–71 °C/25 mmHg); δ_H 1.50–2.00 (8 H, m, methylene-H), 5.25–5.35 (1 H, m, *t*-H); δ_C(50 MHz) 23.4 (×2), 32.4 (×2), 86.4 (CH), 150.0 (CO).

But-3-enyl chloroformate 7e. 7e was obtained as a clear, colourless liquid (33%), bp 40–50 °C/10 mmHg; δ_H 2.41–2.56 (2 H, m, allylic-H), 4.33–4.42 (2 H, t, *J* 8.5, methylene-H), 5.10–5.26 (2 H, m, olefinic-H), 5.70–5.90 (1 H, m, olefinic-H); δ_C 32.8, 71.0, 118.6, 132.5, 151.2 (CO).

Pent-4-enyl chloroformate 7f. 7f was obtained as a clear, colourless liquid (61%), bp 56–58 °C/0.1 mmHg (Found: C, 48.48; H, 6.26. Calc. for $C_6H_9O_2Cl$: C, 48.50; H, 6.10%); δ_H 1.80–1.92 (2 H, quintet, *J* 6.9, methylene-H), 2.11–2.24 (2 H, q, *J* 7.1, allylic-H) 4.30–4.39 (2 H, t, *J* 6.6, methylene-H), 5.00–5.10 (2 H, m, olefinic-H), 5.70–5.85 (1 H, m, olefinic-H); δ_C 27.9, 30.0, 72.0, 116.5, 137.0, 151.1 (CO).

2-(Cyclohex-2-enyloxy)ethyl chloroformate 7g. 7g was obtained as a clear, colourless liquid (90%), bp 70–75 °C/0.1 mmHg (Found: C, 53.34; H, 6.64. Calc. for $C_9H_{13}O_3Cl$: C, 52.82; H, 6.40%); δ_H 1.45–2.15 (6 H, m, methylene-H), 3.72–

3.80 (2 H, q, *J* 4.4, 3-H), 3.85–4.00 (1 H, m, 4-H), 4.41–4.49 (2 H, t, *J* 4.8, 2-H), 5.70–5.97 (2 H, m, 5,6-H); δ_C 18.8 (8-C), 25.0, 27.9 (2 × 7,9-C), 64.8 (3-C), 71.0 (2-C), 73.3 (4-C), 126.9, 131.4 (2 × 5,6-C), 151.2 (1-C).

***N*-Methoxycarbonyl-1,2-dihydropyridine 4a**

Methyl chloroformate (5.95 g, 0.063 mol) in dry ether (10 cm^3) was added slowly to sodium borohydride (2.5 g, 0.066 mol) and pyridine (5 g, 0.063 mol) in Analar methanol (25 cm^3) at −78 °C under nitrogen. The mixture was left stirring for 1.5–2 h and then poured into ice–water (200 cm^3) and the product was extracted with ether (3 × 100 cm^3). The combined ethereal extracts were washed with H_2O (5 × 50 cm^3), dried ($MgSO_4$) and the solvent was evaporated to give the desired compound which was stored in the freezer.

Dihydropyridines **4b**–**g** were made in a similar manner with the appropriate chloroformate.

***N*-Methoxycarbonyl-1,2-dihydropyridine 4a. 4a** was obtained as a light yellow liquid (63%); δ_H 3.70–3.80 (3 H, m, methyl-H), 4.25–4.40 (2 H, m, allylic-H), 5.00–5.20 (1 H, m, olefinic-H), 5.35–5.60 (1 H, m, olefinic-H), 5.70–5.90 (1 H, m, olefinic-H), 6.55–6.80 (1 H, m, olefinic-H). Minor signals at 2.75–2.85 and 4.75–4.90 were also observed.

***N*-Cyclopentyloxycarbonyl-1,2-dihydropyridine 4b. 4b** was obtained as a light yellow liquid (74%); δ_H 1.50–2.00 (8 H, m, methylene-H), 4.25–4.40 (2 H, m, allylic-H), 5.00–5.20 (2 H, m; *t*–H and olefinic-H), 5.35–5.55 (1 H, m, olefinic-H), 5.75–5.85 (1 H, m, olefinic-H), 6.55–6.80 (1 H, m, olefinic-H); δ_C 23.6 (2 × 10,11-C), 32.4 (2 × 9,12-C), 43.4 (2-C), 79.0 (8-C), 104.4 (5-C), 119.1, 122.0, 125.9 (3 × 3,4,6-C), 150.0 (7-C); *m*/*z* 193 (M^+, 43%), 192 (15), 151 (16), 124 (50), 108 (10), 80 (91), 79 (26), 70 (53), 68 (56), 53 (34) (Found: M^+, 193.1100. $C_{11}H_{15}NO_2$ requires 193.1103).

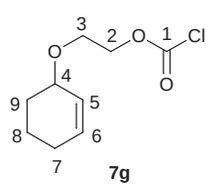
***N*-(1-Methyl-1-trichloromethylethoxycarbonyl)-1,2-dihydropyridine 4c. 4c** was obtained as a light yellow solid (91%); δ_H 1.90–2.00 (6 H, m, methyl-H), 4.30–4.45 (2 H, m, 2-H) 5.10–5.20 (1 H, m, olefinic-H), 5.45–5.60 (1 H, m, olefinic-H), 6.65–6.75 (1 H, m, olefinic-H), 5.75–5.95 (1 H, m, olefinic-H); δ_C 21.6 (2 × 11,12-C), 81.4 (9-C) 89.5 (8-C), 105.4 (5-C), 119.2, 122.1, 125.8 (3 × 3,4,6-C), 158.5 (7-C); *m*/*z* 285/283 (M^+, $^{37}Cl_3/^{35}Cl_3$, 10/10%), 163 (10), 161 (20), 159 (15), 125 (61), 124 (43), 123 (30), 108 (18), 80 (63), 79 (44), 59 (100) (Found: M^+, 282.9940. $C_{10}H_{12}{}^{35}Cl_3NO_2$ requires 282.9934).

***N*-Benzyloxycarbonyl-1,2-dihydropyridine 4d. 4d** was obtained as a grey liquid (92%); δ_H 4.40 (2 H, s, benzyl-H), 5.15–5.30 (m, 3 H; 2 H, allylic-H and 1 H, olefinic-H), 5.40–5.60 (1 H, m, olefinic-H), 5.80–5.90 (1 H, m, olefinic-H), 6.70–6.87 (1 H, m, olefinic-H), 7.25–7.45 (5 H, m, arom-H); δ_C 43.6 (2-C), 67.8 (8-C), 104.9 (5-C), 119.2, 121.9, 125.5 (3 × 3,4,6-C), 128.1, 128.3, 128.5 (5 × arom-C), 136.5 (9-C), 161.6 (7-C); *m*/*z* 215 (M^+, 10%), 170 (15), 136 (8), 108 (13), 91 (100), 79 (21), 65 (11) (Found: M^+, 215.0956. $C_{13}H_{13}NO_2$ requires 215.0946). Minor signals at 44.1, 66.2 and 150.2 were also observed.

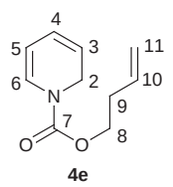
***N*-(But-3-enyloxycarbonyl)-1,2-dihydropyridine 4e. 4e** was obtained as a grey liquid (75%); δ_H 2.37–2.50 (2 H, m, 9-H), 4.19–4.27 (2 H, t, *J* 6.6, 8-H), 4.35–4.42 (2 H, m, 2-H), 5.12–5.23 (3 H, m; 2 H, 11-H and 1 H, olefinic-H), 5.44–5.60 (1 H, m, olefinic-H), 5.74–5.93 (2 H, m, olefinic-H), 5.63–5.83 (1 H, br d, olefinic-H); δ_C 33.3 (9-C), 43.5 (2-C), 65.1 (8-C), 104.8 (5-C), 117.4 (11-C), 119.2, 122.0, 125.7 (3 × 3,4,6-C), 134.0 (10-C), 150.0 (7-C); *m*/*z* 179 (M^+, 42%), 134 (18), 124 (23), 108 (7), 80 (69), 55 (100) (Found: M^+, 179.0941. $C_{10}H_{13}NO_2$ requires 179.0946).

***N*-(Pent-4-enyloxycarbonyl)-1,2-dihydropyridine 4f. 4f** was obtained as a grey liquid (76%); δ_H 1.68–1.84 (2 H, quintet, *J* 6.8, 9-H), 2.05–2.20 (2 H, q, *J* 7.1, 10-H), 4.12–4.20 (2 H, t, *J* 6.5, 8-H), 4.30–4.40 (2 H, m, 2-H), 4.95–5.20 (3 H, m; 2 H, 12-H and 1 H, olefinic-H), 5.40–5.60 (1 H, m, olefinic-H), 5.70–5.95 (2 H, m; 11-H and 1 H, olefinic-H), 6.50–6.85 (1 H, m, olefinic-H); δ_C 28.3, 30.0 (2 × 9,10-C), 44.0 (2-C), 65.9 (8-C), 105.0 (5-C), 115.9, 119.5, 122.1 (3 × 3,4,6-C), 126.0 (12-C), 138.2 (11-C), 161.3 (7-C); *m*/*z* 193 (M^+, 48%), 148 (7), 125 (62), 124 (68), 108 (10), 86 (21), 86 (21), 80 (100), 79 (49), 69 (71), 57 (56).

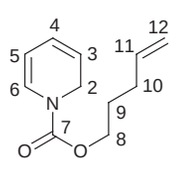
***N*-[2-(Cyclohex-2-enyloxy)ethylcarbonyl]-1,2-dihydropyridine 4g. 4g** was obtained as a grey liquid (77%); δ_H 1.50–2.20 (6 H, m, methylene 13,14,15-H), 3.60–3.80 (2 H, m, methylene 9-H), 3.80–3.95 (1 H, m, 10-H), 4.25–4.45 (4 H, m, methylene 2,8-H), 5.05–5.20 (1 H, m, olefinic-H), 5.40–5.60 (1 H, m, olefinic-H), 5.70–5.95 (3 H, m; 2 H, 11,12-H and 1 H, olefinic-H), 6.65–6.85 (1 H, m, olefinic-H); δ_C 19.5 (14-C), 25.5, 28.2 (2 × 13,15-C), 44.0 (2-C), 66.1, 66.3 (2 × 8,9-C), 73.5 (10-C), 105.0 (5-C), 119.1, 122.2, 126.0 (3 × 3,4,6-C), 127.9, 131.6 (2 × 11,12-C), 160.9 (7-C); *m*/*z* 249 (M^+, 5%), 168 (14), 124 (6), 99 (18), 97 (21), 81 (100), 80 (31), 79 (38), 73 (61) (Found: M^+, 249.1374. $C_{14}H_{19}NO_3$ requires 249.1365).



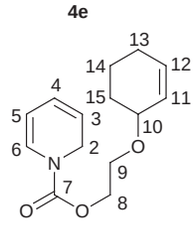
7g



4e



4f



4g

Radical initiated reaction of 1,2-dihydropyridine 4a with cyclohexenone

N-Methoxycarbonyl-1,2-dihydropyridine **4a** (0.4 g, 3 mmol) was dissolved in benzene (3 cm^3) and added to a mixture of benzene (7 cm^3), dibenzoyl peroxide (0.2 g, 50 wt%) and cyclohexenone (0.28 g, 3 mmol) under nitrogen. This mixture was refluxed under nitrogen for 3 days and analysis by GC–MS indicated that the main components were unreacted cyclohexenone and pyridine with no evidence for 3-methylcyclohexanone. The benzene was evaporated yielding a liquid (0.85 g) which was eluted through a column of silica gel using 30% ethyl acetate in light petroleum, but no products were isolated in pure form. The reaction yielded mainly unidentifiable polymeric material.

Radical initiated reaction of 1,2-dihydropyridine 4b with cyclohexenone

N-Cyclopentoxycarbonyl-1,2-dihydropyridine **4b** (0.68 g, 3.5 mmol) was added to a mixture of cyclohexenone (0.34 g, 3.5 mmol), *tert*-butyl peroxybenzoate (0.34 g, 50 wt%) and benzene (6 cm^3) under nitrogen. This mixture was refluxed for 3 days during which a further 0.34 g of initiator was added. A sample of the reaction mixture was submitted for GC–MS analysis which gave no evidence for the desired adduct, but detected cyclohexenone, cyclopentyl benzoate, cyclopentyl formate and three minor components which were not identified. The benzene was evaporated yielding a liquid (1.33 g) which was shown by ^1H NMR spectroscopy to contain unreacted cyclohexenone, pyridine and compounds bearing cyclopentyl fragments. The mixture was purified by column chromatography eluting with 30% ethyl acetate in light petroleum yielding a mixture (0.4 g) of cyclopentyl benzoate (0.31 g, 41%) and cyclopentyl formate (0.09 g, 23%); δ_H 1.50–2.10 (16 H, m; 8 H, methylene-H, cyclopentyl benzoate and 8 H, methylene-H, cyclopentyl formate), 5.00–5.10 (1 H, m, *t*-H, formate), 5.35–5.50 (1 H, m, *t*-H, benzoate), 7.35–7.60 (3 H, m, arom-H, benzoate), 8.00–8.10 (3 H, m; 2 H, arom-H, benzoate and 1 H, formyl-H,

formate); δ_C(50 MHz) 22.9 (2 × methylene-C, formate), 23.1 (2 × methylene-C, benzoate), 31.9 (2 × methylene-C, formate), 32.0 (2 × methylene-C, benzoate), 77.0 (1 × *t*-C, benzoate), 79.9 (1 × *t*-C formate), 127.5, 128.7, 130.2, 132.0, (6 × arom-C, benzoate), 153.8 (carbonyl-C, formate), 165.6 (carbonyl-C, benzoate); GC–MS *peak no. 413*, cyclopentyl formate, *m*/*z* 85 (4%), 69 (88), 57 (34), 41 (100), 27 (30), 18 (6); *peak no. 440*, cyclopentyl benzoate, 190 (M^+) (1), 173 (1), 140 (1), 134 (1), 123 (31), 105 (100), 77 (70), 68 (17), 51 (32), 41 (37), 27 (20), 18 (8).

Radical initiated reaction of 1,2-dihydropyridine 4c with cyclohexenone

N-(1-Methyl-1-trichloromethylethoxycarbonyl)-1,2-dihydropyridine (1.0 g, 3.5 mmol), cyclohexenone (0.34 g, 3.5 mmol) and dibenzoyl peroxide (0.1 g, 10 wt%), were refluxed in benzene (5 cm^3) for 2 days under nitrogen during which a further 0.2 g of initiator was added. A sample of the reaction mixture was submitted for GC–MS analysis; *m*/*z peak no. 195*, cyclohexenone; *peak no. 220*, 2,2,2-trichloro-1,1-dimethylethanol, 163 (2%), 161 (2), 127 (6), 125 (5), 77 (13), 59 (100), 43 (65), 31 (60); *peak no. 324*, identity was not confirmed, but probably the formate, 177 (2), 161 (4), 159 (4), 125 (8), 123 (11), 77 (27), 73 (100), 59 (41), 43 (79), 41 (25); *peak no. 566*, identity was not confirmed but probably the benzoate ester, 226 (1), 198 (3), 105 (100), 77 (76), 51 (47).

Radical initiated reaction of 1,2-dihydropyridine 4d with cyclohexenone

N-Benzyloxycarbonyl-1,2-dihydropyridine (1 g, 4.6 mmol), cyclohexenone (0.89 g, 9.3 mmol) and dibenzoyl peroxide (0.5 g, 50 wt%) were refluxed in benzene (5 cm^3) for 2 days under nitrogen. The benzene was evaporated yielding an oil (2.17 g) which was purified by column chromatography eluting with 30% ethyl acetate in light petroleum resulting in the isolation of benzyl benzoate (0.21 g, 21%), benzyl formate (0.19 g, 30%) and benzyl alcohol (0.13 g, 26%). Benzyl benzoate; δ_H 5.4 (2 H, s, benzyl-H), 7.4–7.7 (8 H, m, arom-H), 8.0–8.2 (2 H, m, arom-H); GC–MS *peak no. 527*, *m*/*z* 212 (M^+) (3%), 195 (1), 168 (1), 105 (100), 91 (68), 77 (63), 65 (29), 51 (50), 39 (24), 18 (9). Benzyl formate; δ_H 5.22 (2 H, s, benzyl-H), 7.32–7.50 (5 H, m, arom-H); *m*/*z* 136 (M^+) (24%), 108 (22), 107 (25), 91 (100), 79 (54), 77 (62), 65 (58), 51 (74), 39 (81), 29 (70), 18 (9).

Radical initiated reaction of 1,2-dihydropyridine 4e

N-(But-3-enyloxycarbonyl)-1,2-dihydropyridine **4e** (1 g, 5.6 mmol) and dibenzoyl peroxide (0.3 g, 30 wt%) were refluxed in benzene (5 cm^3) for 2 days under nitrogen. Analysis of the reaction mixture showed the formation of two main products; GC–MS *peak no. 352*, but-3-enyl formate, *m*/*z* 55 (100%), 54 (93), 39 (45), 29 (44), 27 (33), 18 (12); *peak no. 460*, but-3-enyl benzoate, 176 (M^+) (1), 105 (100), 77 (77), 54 (64), 51 (40), 39 (28), 17 (28). The benzene was evaporated yielding an oil which was purified by column chromatography eluting with 20% ethyl acetate in light petroleum to give a mixture (0.14 g) of but-3-enyl benzoate (0.11 g, 11%) and but-3-enyl formate (0.03 g, 6%); δ_H 2.40–2.65 (4 H, m, allylic-H, but-3-enyl benzoate and but-3-enyl formate), 4.13–4.27 (2 H, t, *J* 7.2, methylene-H, formate) 4.35–4.43 (2 H, t *J* 6.8, methylene-H, benzoate), 5.08–5.28 (4 H, m, olefinic-H, benzoate and formate), 5.80–6.00 (2 H, m, olefinic-H, benzoate and formate), 7.40–7.60 (3 H, m, arom-H, benzoate), 8.00–8.10 (3 H, m; 2 H, arom-H, benzoate and 1 H, formyl-H, formate). The remainder of the fractions gave poorly resolved ^{1}H NMR spectra and were considered to contain the products of polymerisation.

Radical initiated reaction of 1,2-dihydropyridine 4f

N-(Pent-4-enyloxycarbonyl)-1,2-dihydropyridine **4f** (2 g, 10.4 mmol) and dibenzoyl peroxide (0.05 g, 2.5 wt%) were refluxed in benzene (5 cm^3) for 3.5 days under nitrogen during which a further 0.2 g of initiator was added. The benzene was evaporated yielding a brown oil (1.89 g). This mixture was purified by column chromatography with 10% ethyl acetate in light petroleum yielding a mixture (0.32 g) of pent-4-enyl benzoate (0.07 g, 4%) and pent-4-enyl formate (0.25 g, 22%); δ_H 1.68–1.96 (4 H, m, methylene-H, pent-4-enyl benzoate and pent-4-enyl formate), 2.01–2.30 (4 H, m, methylene-H, benzoate and formate), 4.15–4.18 (2 H, *J* 6.5, methylene-H, formate), 4.30–4.37 (2 H, t *J* 7, methylene-H, benzoate), 4.95–5.18 (4 H, m, olefinic-H, benzoate and formate), 5.70–5.93 (2 H, m, olefinic-H, benzoate and formate), 7.38–7.60 (3 H, m, arom-H, benzoate), 8.00–8.10 (3 H, m; 2 H, arom-H, benzoate and 1 H, formyl-H, formate); δ_C(50 MHz) 28.3 (methylene-C, formate), 28.4 (methylene-C, benzoate), 30.3 (methylene-C, formate), 30.7 (methylene-C, benzoate), 64.8 (methylene-C, benzoate), 67.7 (methylene-C, formate), 115.9 (olefinic-C, formate), 116.1 (olefinic-C, benzoate), 137.7 (olefinic-C, formate), 137.9 (olefinic-C, benzoate), 155.8 (carbonyl-C, formate); GC–MS *peak no. 363*, pent-4-enyl formate, *m*/*z* 68 (62%), 67 (51), 41 (100), 39 (30), 29 (15), 18 (10); *peak no. 411*, pent-4-enyl benzoate, 123 (3), 105 (100), 77 (65), 68 (93), 51 (26), 41 (22), 39 (19), 28 (20), 18 (55).

Radical initiated reaction of 1,2-dihydropyridine 4g

N-[2-(Cyclohex-2-enyloxy)ethylcarbonyl]-1,2-dihydropyridine **4g** (2 g, 8.0 mol) and dibenzoyl peroxide (0.2 g, 10 wt%) were refluxed in benzene (5 cm^3) for 3 days under nitrogen. The benzene was evaporated and the resulting oil (2.42 g) was purified by column chromatography eluting with 40% light petroleum in ether. This resulted in the isolation of 3-(2-hydroxyethoxy)cyclohexene (0.22 g, 19%) and 2-(cyclohex-2-enyloxy)-ethyl formate (0.2 g, 15%). 3-(2-Hydroxyethoxy)cyclohexene: identical ^{1}H NMR and ^{13}C NMR spectra to those of authentic material.[18] 2-(Cyclohex-2-enyloxy)ethyl formate; δ_H(300 MHz) 1.42–2.10 (6 H, m, methylene-H), 3.62–3.80 (2 H, m, methylene-H), 3.84–3.94 (1 H, m, *t*-H), 4.21–4.35 (2 H, m, methylene-H), 5.65–5.92 (2 H, m, olefinic-H), 8.08 (1 H, s, formyl-H); δ_C 19.1, 25.1, 28.2 (3 × methylene C, cyclohexenyl ring), 63.6, 65.6 (2 × methylene C, ethyl chain), 73.4 (*t*-C), 127.4, 131.5 (2 × olefinic C), 161.3 (carbonyl-C); *m*/*z* 171 (MH^+, 5%), 137 (10), 123 (9), 97 (10), 81 (88), 72 (24) (Found: 171.1026. $C_9H_{15}O_3$ requires 171.1021).

Reaction of pent-4-enyl chloroformate 7f with Bu_3SnH

Pent-4-enyl chloroformate **7f** (0.2 g, 1.4 mmol) was dissolved in deuterated benzene (0.75 cm^3) in an NMR tube. To this, tributyltin hydride (0.2 g, 0.7 mmol) was added and the mixture was photolysed with a 125 W Hg lamp for 15 min at room temp. and at 40 °C for 2.5 h. A sample of the reaction mixture was analysed by GC–MS: *peak no. 159*, 5-chloropent-1-ene, *m*/*z* 106 (M^+) (2%), 104 (M^+) (6), 84 (16), 68 (38), 67 (55), 55 (98), 41 (100), 53 (26), 40 (63), 39 (84), 29 (30), 27 (76); *peak no. 202*, pent-4-en-1-ol, 68 (54), 67 (100), 53 (73), 41 (48), 39 (85), 31 (65), 29 (81), 27 (27); *peak no. 291*, pent-4-enyl chloroformate, 69 (13), 68 (48), 67 (95), 63 (30), 55 (22), 53 (36), 41 (100), 40 (31), 39 (84), 29 (30), 28 (25), 27 (55); *peak no. 619*, pent-4-enyl formate, 69 (17), 68 (48), 67 (42), 53 (11), 41 (100), 39 (28), 29 (15), 27 (11); *peak no. 843*, tributyltin chloride.

***N*-Benzyloxycarbonyl-1,4-dihydropyridine 5d**

Benzyl chloroformate **7d** (21.5 g, 0.126 mol) was added dropwise at −10 °C to a mixture of pyridine (10 g, 0.126 mol) and $NaBH_4$ (5 g, 0.133 mol) in dry THF (100 cm^3) under nitrogen. The mixture was stirred at this temperature for 2 h and poured onto ice–water (200 cm^3). The product was extracted with ether (3 × 100 cm^3), these extracts were combined, washed with H_2O (100 cm^3) and dried ($MgSO_4$). The solvent was evaporated to yield a mixture of the 1,4- and 1,2-dihydropyridines in a ratio of 1:0.65. The products were dissolved in dichloro-

methane (150 cm^3) to which maleic anhydride (20 g, 0.2 mol) was added and the mixture was refluxed for 2 days. The adduct was removed with NaOH (3 × 50 cm^3), the organic layer was dried ($MgSO_4$) and the solvent was evaporated to yield an orange liquid. This contained some benzyl chloride which was removed by stirring under low pressure (0.15 mmHg) for 10 h, yielding the title compound (7.1 g†); δ_H 2.80–2.88 (2 H, m, allylic-H), 4.79–5.02 (2 H, m, olefinic-H), 5.20 (2 H, s, benzylic-H), 6.66–6.87 (2 H, m, olefinic-H), 7.28–7.42 (5 H, m, arom-H); δ_C 21.9 (4-C), 67.3 (8-C), 123.4, 126.3 (2,3,5,6-C), 127.8, 128.0 (3 × arom-C) 141.1 (9-C), 160.3 (7-C); GC–MS *m*/*z* 215 (M^+) (3%), 170 (8), 91 (100), 80 (6), 65 (18), 51 (8), 39 (12).

Radical initiated reaction of 1,4-dihydropyridine 5d

N-Benzyloxy-1,4-dihydropyridine (1 g, 4.65 mmol), cyclohexenone (0.45 g, 4.7 mmol) and dibenzoyl peroxide (0.4 g, 40 wt%) were refluxed in benzene (5 cm^3) for 24 h under nitrogen. The benzene was evaporated yielding an oil which was shown by ^1H NMR to contain unreacted cyclohexenone, pyridine, benzoic acid, benzyl benzoate and the impurity from the starting material. The mixture was purified by column chromatography eluting with 30% ethyl acetate in light petroleum, yielding two compounds (0.32 g) one of which was benzyl benzoate (*ca*. 32%) and the other was the impurity present in the original 1,4-dihydropyridine.

Acknowledgements

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† This also contained an impurity which was not removed and the yield of the title compound was estimated to be *ca*. 16%.

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