#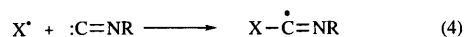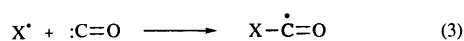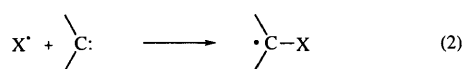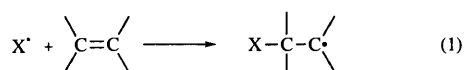 Radical addition to carbenoids. Chain reactions of α-diazo carbonyl compounds with triorganotin hydrides, tris(trimethylsilyl)silane and allyltributylstannane
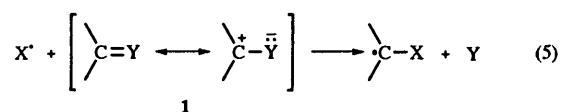
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α-Diazo ketones $RC(O)CH=N_2$ react with tributyltin hydride at 60 °C in benzene to give the corresponding α-stannyl ketones $RC(O)CH_2SnBu_3$, which exist in equilibrium with the stannyl enol ether tautomers $R(Bu_3SnO)C=CH_2$. The reactions are initiated by di-*tert*-butyl hyponitrite and follow a free-radical chain mechanism. Triphenyltin hydride and tris(trimethylsilyl)silane [$(TMS)_3SiH$] react similarly, the latter to yield the α-silyl ketone $RC(O)CH_2Si(TMS)_3$ which does not isomerise to the more stable silyl enol ether $R[(TMS)_3SiO]C=CH_2$ under the reaction conditions. This result indicates that $TMS_3Si^{\bullet}$ reacts at the α-carbon atom of the α-diazo ketone to give $R(CO)\overset{\bullet}{C}HSiTMS_3$, probably *via* an initial diazenyl radical adduct; triorganotin radicals are assumed to react in the same way. When the group R in the α-diazo ketone is but-3-enyl, the intermediate α-metalloalkyl radical undergoes 5-*exo*-cyclisation. Allyltributylstannane reacts with α-diazo ketones and with ethyl α-diazoacetate in refluxing benzene, in the presence of 2,2'-azo(2-methylpropionitrile) as initiator, to give butenyl ketones $RC(O)CH_2CH_2CH=CH_2$ and ethyl pent-4-enoate, respectively, after a hydrolytic work-up.

Radical addition to alkenes [reaction (1)] is very important and has been studied extensively from both mechanistic and synthetic standpoints. In contrast, the corresponding addition to a carbene [reaction (2)] has received almost no attention, although additions to the formally divalent carbon in carbon monoxide or in an isocyanide [reactions (3) and (4)] are well

$$X^{\bullet} + \overset{\backslash}{\underset{/}{C}}=C\overset{/}{\underset{\backslash}{}} \longrightarrow X-\overset{|}{\underset{|}{C}}-\overset{\bullet}{C}\overset{/}{\underset{\backslash}{}} \quad (1)$$

$$X^{\bullet} + \overset{\backslash}{\underset{/}{C}}: \longrightarrow \overset{\backslash}{\underset{/}{\bullet C}}-X \quad (2)$$

$$X^{\bullet} + :C=O \longrightarrow X-\overset{\bullet}{C}=O \quad (3)$$

$$X^{\bullet} + :C=NR \longrightarrow X-\overset{\bullet}{C}=NR \quad (4)$$

known. Reaction (2) is difficult to carry out in practice and would be of little use in organic synthesis. However, there are a large number of 'carbenoid' reagents of the general type **1** which could react to form carbon-centred radicals as shown in reaction (5). In principle, the group Y in **1** might be *inter alia* N_2,
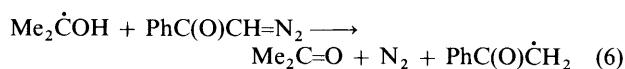
$$X^{\bullet} + \left[\overset{\backslash}{\underset{/}{C}}=Y \longleftrightarrow \overset{\backslash}{\underset{/}{C}}{}^{+}-\overset{..}{\overset{-}{Y}}\right] \longrightarrow \overset{\backslash}{\underset{/}{C}}-X + Y \quad (5)$$

1

CO, PZ_3, SZ_2, $S(O)Z_2$ or a transition metal moiety ML_n such as $Cr(CO)_5$,† and we have begun a programme of research to establish the scope of such radical–carbenoid reactions and of the related radical–nitrenoid reactions. The overall process shown in reaction (5) could be concerted or stepwise, proceeding *via* an unstable adduct radical.
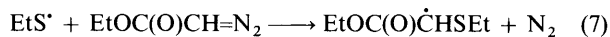
Diazo compounds of type **1** (Y = N_2) have a rich photochemistry and heterolytic chemistry, but only very few

examples of their reactions with radicals are known.[1–4] α-Diazo carbonyl compounds are key intermediates in a number of important synthetic transformations including the Arndt–Eistert homologation procedure, the photo-induced Wolff ring-contraction process and various C–H insertion and cyclopropanation reactions.[5–9] In the present paper we report a study of the radical-chain reactions of α-diazo ketones and of ethyl α-diazoacetate with triorganotin hydrides, with tris(trimethylsilyl)silane and with allyltributylstannane.

There are a few isolated reports of radical reactions of α-diazo carbonyl and sulfonyl compounds which result in the elimination of nitrogen and the formation of carbon-centred radicals.[2,3] Horner and his co-workers have shown that α-hydroxyalkyl radicals react with α-diazo ketones to bring about overall hydrogen-atom transfer and loss of nitrogen [*e.g.* reaction (6)], although the initial homolytic addition was thought to take place at the terminal nitrogen atom of the α-diazo ketone.[3] A significant unpublished result cited by Ando[4] indicates that alkylthiyl radicals react readily with ethyl diazoacetate at 60 °C by addition to carbon, accompanied or followed by loss of nitrogen, as shown in reaction (7).
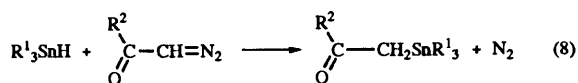
$$Me_2\overset{\bullet}{C}OH + PhC(O)CH=N_2 \longrightarrow$$
$$Me_2C=O + N_2 + PhC(O)\overset{\bullet}{C}H_2 \quad (6)$$

$$EtS^{\bullet} + EtOC(O)CH=N_2 \longrightarrow EtOC(O)\overset{\bullet}{C}HSEt + N_2 \quad (7)$$

The azido function $-N=N_2$ is isoelectronic with the $-CH=N_2$ group and we have used EPR spectroscopy to investigate radical reactions of (including addition to) alkyl and silyl azides.[10] Aliphatic azides are reduced to amino compounds by tributyltin hydride in what is probably a radical chain reaction[11] and, more recently, Kim and his co-workers[12–14] have exploited homolytic addition to alkyl azides in a synthetic context as a route to aminyl radicals.

Results and discussion

Nearly 40 years ago, Lesbre and Buisson[15] reported that trialkyltin hydrides react with α-diazo ketones according to

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† Organometallic carbenoids of the type exemplified by $ClCH_2Li$ might also react with X•, in this particular instance to give $X\overset{\bullet}{C}H_2$ and LiCl.

$$R^1_3SnH + \overset{R^2}{\underset{O}{C}}{-}CH{=}N_2 \longrightarrow \overset{R^2}{\underset{O}{C}}{-}CH_2SnR^1_3 + N_2 \qquad (8)$$

reaction (8) to form α-stannyl ketones. Ethyl α-diazoacetate and α-diazoacetonitrile reacted in a similar way. Apparently, the reactions occurred spontaneously above *ca.* 60 °C and the final products were isolated by distillation. Later work showed that α-stannyl ketones and the isomeric stannyl enol ethers interconvert very readily and the position of the metallotropic equilibrium varies markedly with the nature of the substituents, although for acyclic compounds the *C*-stannyl isomer is usually strongly favoured.[16–18] A number of subsequent reports have appeared of similar reactions of α-diazo carbonyl compounds with organo-tin, -germanium and -silicon hydrides.[19,20] These reactions often required the presence of copper powder as a catalyst, suggesting the possible involvement of carbenes/carbenoids, although the mechanisms were not well-defined. Most recently, α-silyl carbonyl compounds have been obtained in good yields from the reactions of α-diazo ketones or of α-diazo esters with triorganosilanes in the presence of rhodium(II) or copper(II) complexes as catalysts.[21] These reactions were presumed to be mediated by transition metal carbenoids and radical intermediates were not implicated.

We have now reinvestigated the reactions of organotin hydrides with α-diazo ketones (Scheme 1), in the absence of
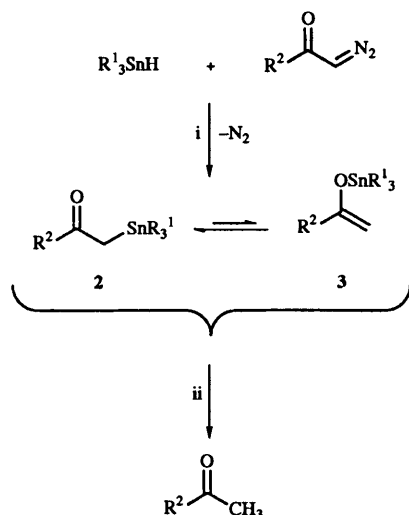
Scheme 1 *Reagents and conditions:* i, heat with initiator in benzene; ii, aqueous KF

transition metal catalysts, and have obtained clear evidence for the involvement of a radical chain mechanism. The α-diazo ketones 4–9 were prepared by treatment of the corresponding
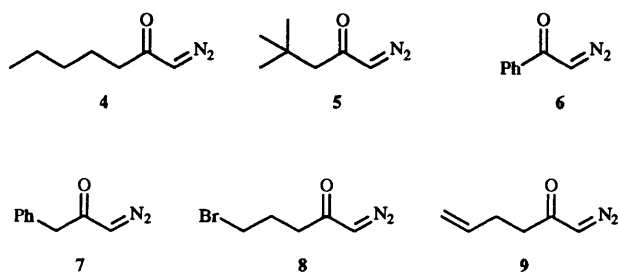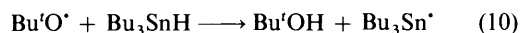

acid chlorides with diazomethane in diethyl ether, according to standard procedures;[22] ethyl α-diazoacetate 10 is readily available commercially.

A solution of 1-diazoheptan-2-one 4 (4.0 mmol) and tributyltin hydride (4.1 mmol) in benzene (6 cm³) was heated at

| 10 | 11 R = Me(CH₂)₃CH₂ | 16 |
	12 R = BuᵗCH₂	
	13 R = Ph	
	14 R = PhCH₂	
	15 R = BrCH₂CH₂CH₂	
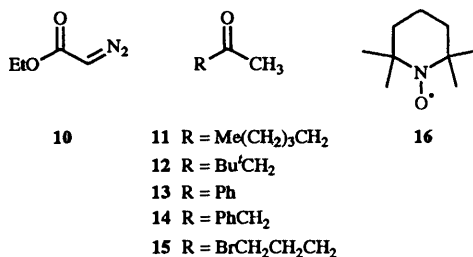
60 °C under nitrogen for 0.5 h. After treatment of the reaction mixture with aqueous potassium fluoride, GLC analysis (toluene internal standard) showed the presence of only a very small amount of heptan-2-one 11 (4% yield based on α-diazo ketone).‡ However, when the reaction was repeated in the presence of di-*tert*-butyl hyponitrite (TBHN, 0.2 mmol), which acts as a thermal source of *tert*-butoxyl radicals and thence of Bu₃Sn˙ [reactions (9) and (10)],§[23,24] heptan-2-one was

$$Bu^tON{=}NOBu^t \longrightarrow 2Bu^tO^\bullet + N_2 \qquad (9)$$

$$Bu^tO^\bullet + Bu_3SnH \longrightarrow Bu^tOH + Bu_3Sn^\bullet \qquad (10)$$

obtained in 90% yield. When the reaction was carried out in the absence of TBHN but in the presence of the nitroxide 16 (0.2 mmol),¶ the yield of ketone was only *ca.* 2%. Similar results were obtained in refluxing benzene solvent by using 2,2′-azo(2-methylpropionitrile) (AIBN, 0.2 mmol) as initiator. Thus, after heating for 2 h in the presence of AIBN the yield of heptan-2-one was 85%, while in its absence only a 32% yield was obtained; the results are summarised in Table 1. There was no detectable thermal decomposition of the diazo ketone 4 after it was heated alone in benzene under reflux for 2 h. These results indicate that the reaction of 4 with Bu₃SnH follows a free-radical chain mechanism, presumably mediated by Bu₃Sn˙, and suggest that some degree of self-initiation may occur at these reagent concentrations and with the ambient levels of illumination.‖

The corresponding ketones 12–15 were obtained, after hydrolytic work-up, when the α-diazo ketones 5–8 were treated with Bu₃SnH in the presence of TBHN at 60 °C and the results are included in Table 1. The α-diazo ketone 8 (entry 10) was examined in the hope that abstraction of the bromine atom would give the radical 17, which might undergo 5-*exo*-cyclisation to yield the diazenyl radical 18 followed by loss of nitrogen to give 19, which would go on to yield cyclopentanone.
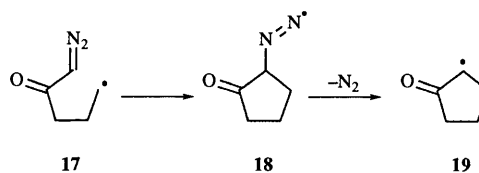
However, no trace of cyclopentanone was detected even when the tin hydride was added slowly using a syringe pump. The isolation of 5-bromopentan-2-one 15 implies that Bu₃Sn˙ reacts more rapidly with the diazo carbonyl function than it abstracts bromine from carbon. Attempts to repeat these experiments with the iodo analogue of 8 were frustrated because this α-diazo ketone proved too unstable to work with.

‡ Although all reactions involving diazo compounds were conducted in subdued light, no special efforts were made to exclude light completely.
§ The half-life of TBHN at 60 °C is *ca.* 55 min.[23]
¶ IUPAC prefer the term aminoxyl for R₂NO˙ radicals.
‖ It seems unlikely that the nitroxide 16, or any other commonly used radical scavenger, will be capable of completely inhibiting a radical chain reaction mediated by Bu₃SnH under these conditions.

Table 1 Reactions of α-diazo ketones with Bu₃SnH and with (TMS)₃SiH in benzene

Entry	α-Diazo ketone	R₃MH	Initiator/inhibitor[a]	T/°C	Reaction time/h	Products[b]
1	4	Bu₃SnH	None	60	0.5	11 (4)[c]
2	4	Bu₃SnH	TBHN (5)	60	0.5	11 (90)[c]
3	4	Bu₃SnH	16 (5)	60	0.5	11 (2)[c]
4	4	Bu₃SnH	AIBN (5)	Reflux	3	11 (85)[c]
5	4	Bu₃SnH	None	Reflux	3	11 (32)[c]
6	5	Bu₃SnH	TBHN (5)	60	0.5	12 (86)[c]
7	5	(TMS)₃SiH	TBHN (5)	60	2	25 (63)[d,e]
8	6	Bu₃SnH	TBHN (5)	60	0.5	13 (83)[c]
9	7	Bu₃SnH	TBHN (5)	60	0.5	14 (84)[c]
10	8	Bu₃SnH	TBHN (5)	60	0.5	15 (65)[d]
11	9	Bu₃SnH	TBHN (5)	60	5[f]	30 (80) + 31(6)
12	9	(TMS)₃SiH	TBHN (5)	60	5[f]	30 (71) + 31 (11)

[a] Amount (mol % based on α-diazo ketone) shown in parentheses. [b] Obtained after hydrolytic work-up with KF–H₂O or TBAF, as appropriate. Percentage yield, based on α-diazo ketone, shown in parentheses. [c] By GLC analysis. [d] Isolated yield. [e] The α-silyl ketone was isolated directly before treatment with TBAF. [f] Slow addition of R₃MH and part of the TBHN using a syringe pump.

In order to examine the initial products from the reactions of tin hydrides with α-diazo ketones (Scheme 1), the reaction of the α-diazo ketone 5 with triphenyltin hydride in perdeuteriobenzene was monitored by NMR spectroscopy. These reagents and the products (Scheme 2) give rise to simple ¹H NMR spectra in

Scheme 2
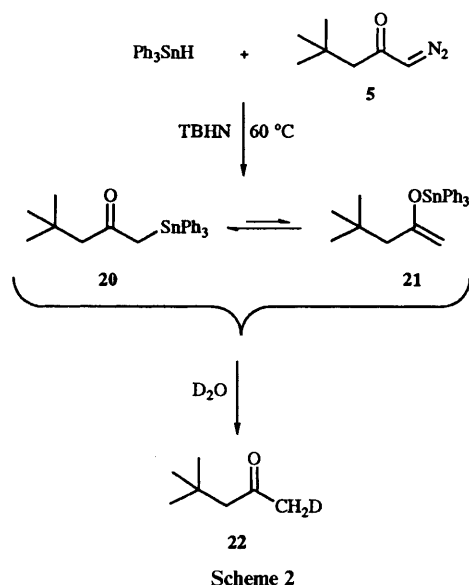
the regions of interest. When the α-diazo ketone (0.10 mmol) in C₆D₆ (0.6 cm³) was heated at 60 °C for 2 h, no change was evident in the ¹H NMR spectrum. In the presence of Ph₃SnH (0.10 mmol) no reaction was detectable after heating for 0.5 h. However, when TBHN (*ca.* 5 × 10⁻³ mmol) was also present, a rapid reaction took place and, after 15 min, the tin hydride had been consumed completely to give the α-stannyl ketone 20 as the major product, together with small amounts of the *O*-stannyl tautomer 21 ([20]:[21] *ca.* 95:5) and methyl neopentyl ketone 12. The compounds 20 and 21 were identified on the basis of their ¹H NMR spectra: 20 showed a characteristic singlet at δ 2.72, with tin satellites corresponding to J^{119}_{Sn} = 71.0 Hz and J^{117}_{Sn} = 68.0 Hz, arising from the α-CH₂Sn group, while 21 showed broad singlets at δ 3.66 and 3.81 arising from the terminal vinylic protons. After the reaction mixture had been shaken with excess D₂O for a few minutes, the spectra of 20 and 21 were replaced by the spectrum of [²H₁]methyl neopentyl ketone 22 ($^1J_{HD}$ = 2.12 Hz for the CH₂D group at δ 1.65). The small amount of methyl neopentyl ketone detected initially probably arises from hydrolysis of 20 and 21 by traces of adventitious water. Similar results were obtained from reactions of Bu₃SnH with 5, although now only the *C*-stannyl tautomer of the initial product was detectable.

The high rate of reaction of organotin radicals with the α-diazo carbonyl function was confirmed by treating an equimolar mixture of 1-bromobutane (0.10 mmol) and the α-diazo ketone 5 (0.10 mmol) with a slight deficiency of Ph₃SnH (0.09 mmol) in C₆D₆ (0.6 cm³) at 60 °C. The TBHN-initiated reaction was monitored by ¹H NMR spectroscopy, using methyl benzoate as an internal concentration standard. Essentially none of the alkyl bromide was consumed during 0.5 h, while all the tin hydride reacted with the α-diazo ketone.

There are two reasonable pathways for the reaction of R₃Sn with α-diazo carbonyl compounds and these are shown in Scheme 3.** The rate of interconversion of the radicals 23 and

**Scheme 3**
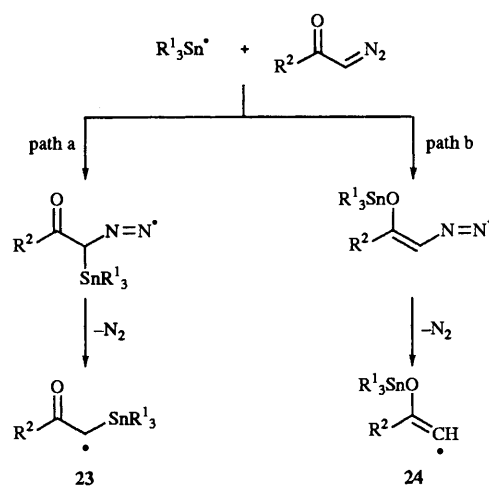
24 is not known, but it is unlikely to be sufficiently fast to compete with abstraction of hydrogen from R₃SnH by these radicals to give 2 and 3, respectively. However, since 2 and 3 themselves interconvert rapidly, the nature of the final product cannot be used as evidence for the initial site of attack by R₃Sn*.

Although α-silyl ketones are less stable than the corresponding isomeric silyl enol ethers,[16,25] the rate of interconversion of the two tautomers is much slower than for the tin analogues. The TBHN-initiated reaction of tris(trimethylsilyl)silane[26] [(TMS)₃SiH] with the α-diazo ketone 5 was carried out at 60 °C, using the same procedure as for the tin hydrides, to yield the α-silyl ketone 25 (Table 1, entry 7); the silyl enol ether 26 was


** Although addition of R₃Sn* to the terminal nitrogen atom of the C=N₂ group is also feasible, this mode of attack could lead to the observed products only by a circuitous route.
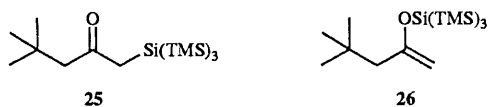
not detected. However, when a sample of **25** was heated in a sealed pyrex tube at 180 °C for 5 h,[27] isomerisation to **26** took place, accompanied by some decomposition. Since the less thermodynamically stable *C*-silyl isomer **25** is the product of the reaction between (TMS)$_3$SiH and **5**, it follows that attack of (TMS)$_3$Si$^\bullet$ on the α-diazo ketone takes place at carbon rather than at nitrogen. With the assumption that R$_3$Sn$^\bullet$ reacts in the same way (path a), the propagation stage of the chain process is shown generalised in Scheme 4 (M = Sn or Si).
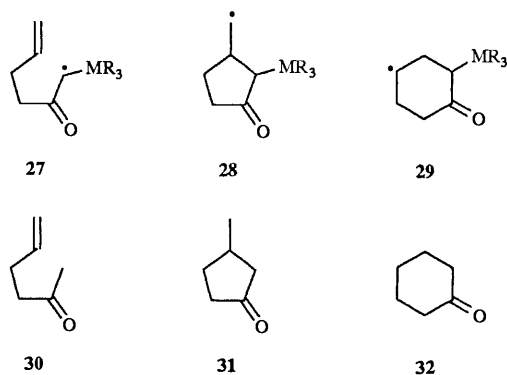
Scheme 4
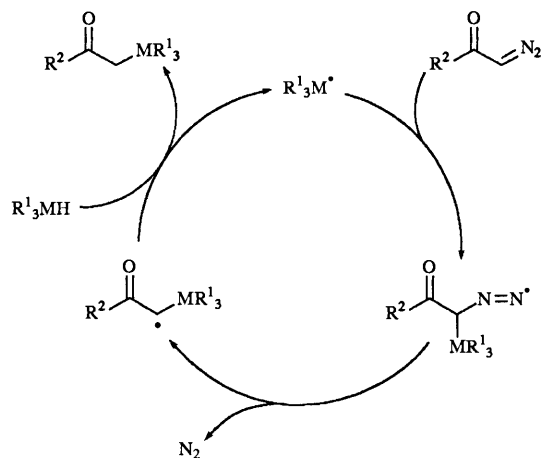
Triethylsilane[21] (even when present in large excess as the solvent) did not react with **5** under the conditions used for (TMS)$_3$SiH, presumably because the radical Bu^{t}CH$_2$C-(O)ĊHSiEt$_3$ does not abstract hydrogen from Et$_3$SiH sufficiently rapidly at 60 °C to maintain the chain.[28] We have reported that thiols promote the abstraction of hydrogen by alkyl radicals from simple triorganosilanes through the catalytic cycle of reactions (11) and (12),[28,29] but even in the

$$R^\bullet + XSH \longrightarrow RH + XS^\bullet \tag{11}$$

$$XS^\bullet + Et_3SiH \longrightarrow XSH + Et_3Si^\bullet \tag{12}$$
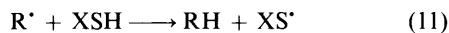
presence of 5 mol % of *tert*-dodecanethiol the α-diazo ketone **5** still failed to react. This is probably because the thiyl radical reacts[4] with **5** more rapidly than it abstracts hydrogen from triethylsilane.

The (TMS)$_3$Si group was readily removed from the α-silyl ketone **25** by treatment with tetrabutylammonium fluoride (TBAF) in moist tetrahydrofuran to give methyl neopentyl ketone, although **25** did not react readily with aqueous potassium fluoride.

Reactions of the unsaturated 1-diazohex-5-en-2-one **9** with organotin hydrides or with TMS$_3$SiH will proceed *via* the intermediate radical **27** which, in principle, could undergo cyclisation to give either **28** or **29**. After final work-up of the reaction mixtures using KF–H$_2$O or TBAF as appropriate, the ketones **30**–**32** should be produced. In order to increase the yield of cyclised products, the hydrides and TBHN were added slowly over 5 h to the reaction mixtures using a syringe pump. With Bu$_3$SnH (Table 1, entry 11), the ketones **30** (80%) and **31** (6%) were obtained, but no cyclohexanone **32** was detected. Carbon-centred radicals abstract hydrogen less readily from (TMS)$_3$SiH than from tin hydrides,[26] and with this silane under similar conditions (Table 1, entry 12), **30** (71%) and **31** (11%) were obtained; again no cyclohexanone was detected. These results indicate that radicals of the type **27** undergo 5-*exo*-

cyclisation to give **28** much more rapidly than they undergo 6-*endo*-cyclisation to give **29** and also that the cyclisation is a relatively slow process. In contrast, the unsaturated radical **33** is reported to undergo exclusively 6-*endo*-cyclisation to give **34**.[30–32] This was confirmed when 1-chlorohex-5-en-2-one **35**,
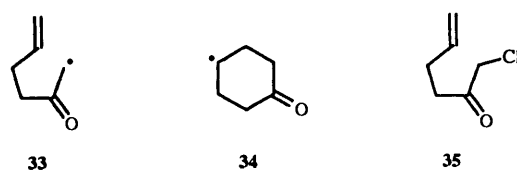
which was obtained as a by-product from the preparation of **9** when pent-4-enoyl chloride was treated with a small excess (1.5 equiv.) of diazomethane, was reduced with (TMS)$_3$SiH. Thus, the TBHN-initiated reaction of **35** with (TMS)$_3$SiH at 60 °C in benzene gave only hex-5-en-2-one **30** and cyclohexanone **32**, with no detectable yield of 3-methylcyclopentanone **31**. A rationalisation has been suggested by Curran[32] for this preference for *endo*-cyclisation when a carbonyl group is inside the ring which is formed and the reasons for the different behaviour of **27** and **33** are not obvious, although certainly steric effects could be important for **27** in which bulky Bu$_3$Sn or (TMS)$_3$Si groups are attached to the radical centre. Interestingly, α-stannylalkyl radicals also undergo 5-*exo*-cyclisation by intramolecular addition to carbonyl groups.[33]

In contrast to its reactions with tin hydrides and with (TMS)$_3$SiH, the unsaturated α-diazo ketone **9** reacted with Cl$_3$CBr in refluxing benzene, in the presence of dibenzoyl peroxide (BPO) initiator, to undergo addition across the double bond and form the α-diazo ketone **36**. Evidently the trichloromethyl radical adds to the C=C double bond in preference to attacking the C=N$_2$ group. The isolation of **36** in 85% yield and the absence of detectable amounts of cyclic products implies that the radical **37** abstracts bromine
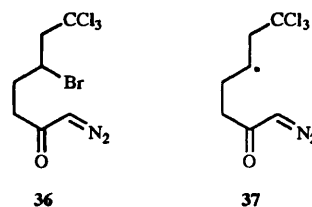
from Cl$_3$CBr faster than it undergoes 5-*exo*-cyclisation by intramolecular addition to the C=N$_2$ group.

Reactions with allyltributylstannane

Allyltributylstannane (ATBS) and substituted-allyl stannanes mediate a number of homolytic allylation reactions which are of considerable use in organic synthesis.[34,35] The key propagation step in these reactions involves addition to the allyl group followed by β-scission of the adduct radical to give Bu$_3$Sn$^\bullet$ [reaction (13)]. With this process in mind, we investigated the reactions of α-diazo ketones and of ethyl α-diazoacetate with

(13)
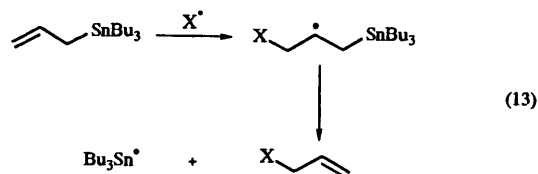
ATBS as a means of bringing about homolytic allylation at the α-carbon atom *via* the propagation sequence shown in Scheme 5.

38	R = Me(CH$_2$)$_3$CH$_2$	(68%)
39	R = Bu^{t}CH$_2$	(72%)
40	R = Ph	(75%)
41	R = PhCH$_2$	(70%)
42	R = H$_2$C=CHCH$_2$CH$_2$	(58%)
43	R = EtO	(82%)
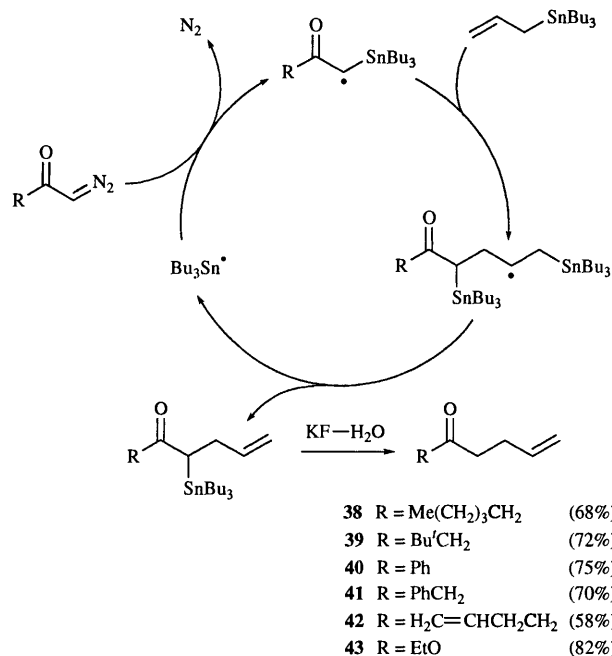
Scheme 5

The α-diazo carbonyl compound and two equivalents of ATBS, together with AIBN as initiator, were heated in benzene under reflux. Neither BPO nor TBHN (in benzene under reflux or at 60 °C, respectively) were satisfactory as initiators, perhaps because the radicals which they produce tend to abstract allylic hydrogen atoms rather than add to the C=C double bond or react with the C=N$_2$ group. This result emphasises once again the importance of the correct choice of initiator for the successful use of radical chain processes in organic synthesis.[28] The reaction mixtures were treated with aqueous KF to remove the Bu$_3$Sn group from the α-stannyl carbonyl compounds and the butenyl ketones **38–42** and ethyl pent-4-enoate **43** were purified chromatographically; the isolated yields are given in Scheme 5.

The reaction of ATBS with α-diazo carbonyl compounds thus provides a new radical-mediated method for allylation at carbon α to a carbonyl group under non-basic conditions.

Experimental

NMR spectra were recorded using a Varian VXR-400 instrument (400 MHz for ^{1}H). The solvent was CDCl$_3$, unless stated otherwise, and chemical shifts are reported relative to Me$_4$Si; *J* values are quoted in Hz. Mass spectra were obtained with VG 7070H or VG ZAB-2F instruments using electron impact or fast-atom bombardment ionisation. GLC analyses were carried out using a Pye-Unicam 304 chromatograph equipped with a flame-ionisation detector and a Hewlett-Packard model 3392A integrator. Column chromatography and TLC were carried out using Merck Kieselgel 60 (230–400 mesh) and Kieselgel 60 F$_{254}$ aluminium-backed pre-coated plates, respectively. All manipulations and reactions of air-sensitive

compounds were carried out under an atmosphere of dry argon or nitrogen and all extracts were dried over anhydrous MgSO$_4$. Petroleum refers to the fraction of bp 40–60 °C.

Materials

Benzene was heated under reflux over metallic sodium, then distilled and stored over 4 Å molecular sieves under argon. Tributyltin hydride (Aldrich or Lancaster Synthesis) was distilled and stored under argon. Triphenyltin hydride, allyltributylstannane and ethyl α-diazoacetate (all Aldrich) and tris(trimethylsilyl)silane (Fluka) were used as received. TBAF was used as a 1 mol dm^{-3} solution in moist tetrahydrofuran (THF) (Aldrich). TBHN was prepared by the reaction of sodium hyponitrite with *tert*-butyl bromide in the presence of zinc chloride, as described by Mendenhall;[24] it was recrystallised from methanol and stored at −18 °C. BPO (Aldrich) was dissolved in chloroform at room temperature, precipitated with an equal volume of methanol and the solid obtained was dried under reduced pressure at room temperature; AIBN (Merck-BDH) was recrystallised from dichloromethane–petroleum.

α-Diazo ketones

These were prepared by the reaction of the corresponding acyl chloride (10 mmol) with a solution of diazomethane in diethyl ether [prepared from *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide (Diazald, Aldrich, 45 mmol) at 0 °C, following the standard procedure].[22] The solvent was removed under reduced pressure and the resulting yellow α-diazo ketones **4–8** were sufficiently pure to be used directly. The α-diazo ketone **9** was purified by column chromatography.

1-Diazoheptan-2-one[36] **4.** Compound **4** was an oil (90–95%); δ_H 0.87 (3 H, t, *J* 7.02), 1.28 (4 H, m), 1.58 (2 H, m), 2.27 (2 H, t, *J* 7.30) and 5.24 (1 H, br s); δ_C 13.9, 22.4, 24.9, 31.4, 41.0, 54.2 and 195.4.

1-Diazo-4,4-dimethylpentan-2-one[37] **5.** Compound **5** was an oil (85–95%); δ_H 1.02 (9 H, s), 2.15 (2 H, br s) and 5.20 (1 H, br s); δ_C 29.8, 54.1, 55.7 and 194.3.

α-Diazoacetophenone[38] **6.** Compound **6** was a crystalline solid (92%), recrystallised from CH$_2$Cl$_2$–petroleum, mp 48 °C (lit.,[38] 47.8–48.3 °C); δ_H 5.92 (1 H, br s), 7.43 (2 H, m), 7.52 (1 H, m) and 7.75 (2 H, m); δ_C 54.1, 126.6, 128.6, 132.6, 136.6 and 186.3.

1-Diazo-3-phenylpropan-2-one[39] **7.** Compound **7** was an oil (92%); δ_H 3.61 (2 H, s), 5.12 (1 H, s) and 7.20–7.40 (5 H, m); δ_C 48.1, 54.8, 127.2, 128.8, 129.3, 134.5 and 192.8.

5-Bromo-1-diazopentan-2-one[40] **8.** Compound **8** was an oil (72%); δ_H 2.17 (2 H, m), 2.49 (2 H, t, *J* 6.45), 3.45 (2 H, t, *J* 6.37) and 5.28 (1 H, br s); δ_C 27.5, 33.1, 38.5, 54.7 and 193.2.

1-Diazohex-5-en-2-one[41] **9.** Compound **9** was an oil (74–85%); δ_H 2.38 (4 H, m), 4.99 (1 H, d, *J* 10.3), 5.06 (1 H, d, *J* 17.1), 5.23 (1 H, br s) and 5.81 (1 H, m); δ_C 28.9, 39.9, 54.4, 115.5, 136.7 and 194.2. This α-diazo ketone was obtained in high purity by column chromatography using petroleum–diethyl ether (5:1 v/v) eluent. When pent-4-enoyl chloride was treated with 1.5 equiv. of diazomethane in diethyl ether, 1-chlorohex-5-en-2-one[42] **35** was obtained along with **9**; the former was readily separated in a pure state by column chromatography using petroleum–diethyl ether (10:1 v/v) eluent; δ_H 2.37 (2 H, m), 2.69 (2 H, t, *J* 7.20), 4.07 (2 H, s), 5.02 (2 H, m) and 5.79 (1 H, m); δ_C 27.5, 38.8, 48.2, 115.8, 136.2 and 201.8.

Reactions of α-diazo ketones with tributyltin hydride

A solution of the α-diazo ketone (4.0 mmol), tributyltin hydride (4.1 mmol) and TBHN (0.2 mmol) in benzene (6.0 cm^3) was prepared in a flask equipped with a short reflux condenser, to the top of which was attached a one-piece unit comprising an inert-gas inlet, bubbler and an entry port closed with a self-sealing rubber cap. The mixture was stirred under nitrogen for 0.5 h in an oil bath which had been preheated to 60 °C. In some experiments a solution of the tin hydride (4.1 mmol) and TBHN

(0.16 mmol) in benzene (2 cm^3) was added slowly, using a syringe pump, to a solution of the α-diazoketone (4.0 mmol) and TBHN (0.04 mmol) in benzene (4 cm^3). The tin hydride solution was introduced to the reaction flask through a fine-bore PTFE tube which passed through a small hole in the rubber cap and down the condenser. After reaction, the mixture was allowed to cool, diluted with diethyl ether (20 cm^3), washed with saturated aqueous KF (10 cm^3), then with saturated brine and dried. The solvent was removed by evaporation and the residue was either subjected to column chromatography or, after addition of methyl benzoate as a concentration standard, was examined by NMR spectroscopy to determine the yields of products. Alternatively, toluene was added as internal standard and the reaction mixture was analysed by GLC. All products were identified by comparison with the authentic compounds and the results are summarised in Table 1. 5-Bromopentan-2-one[43] was isolated chromatographically as an oil; δ_H 2.02 (2 H, m), 2.11 (3 H, s), 2.55 (2 H, t, J 6.65) and 3.40 (2 H, t, J 6.56). In all reactions, the α-diazoketone was completely consumed, as judged by the absence of the characteristic NMR signal from the CH=N$_2$ group (δ 5.1–5.9).

4,4-Dimethyl-1-tris(trimethylsilyl)silyl-pentan-2-one 25. The reaction of the α-diazoketone 5 with (TMS)$_3$SiH, under the same conditions used with the tin hydride, but without the hydrolytic work-up, gave the α-silyl ketone as an oil after flash chromatography using petroleum–diethyl ether eluent (10:1 v/v); δ_H 0.20 (27 H, s), 1.01 (9 H, s), 2.21 (2 H, s) and 2.29 (2 H, s); δ_C 0.9, 28.5, 29.9, 31.3, 56.4 and 210.8; ν_{max}(liq. film)/cm^{-1} 2954, 1688, 1246 and 838; m/z (FAB) 359 (M$^+$ − H, 8%), 345 (45) and 73 (100) (Found: M$^+$ − H, 359.2085. C$_{16}$H$_{40}$OSi$_4$ requires M − H, 359.2078).

TBAF in moist THF (0.30 cm^3 of 1 mol dm^{-3}) was added to the α-silyl ketone 25 (100 mg) in THF (2 cm^3) and the mixture was stirred at room temperature for 1 h, then washed with saturated brine and dried. GLC analysis of the resulting solution showed that methyl neopentyl ketone 12 was formed in 92% yield.

4,4-Dimethyl-2-[tris(trimethylsilyl)siloxy]pent-1-ene 26. The α-silyl ketone 25 (20 mg) was heated at 150 °C under nitrogen in a sealed Pyrex tube for 8 h. Examination of the product by NMR spectroscopy showed that 55% of the silyl ketone had rearranged to the silyl enol ether 26. When the thermolysis was repeated at 180 °C for 8 h, 75% of the silyl ketone rearranged to the silyl enol ether which showed the following spectroscopic characteristics: δ_H(C$_6$D$_6$) 0.30 (27 H, s), 1.00 (9 H, s), 4.00 (1 H, br s) and 4.20 (1 H, br s); δ_C(C$_6$D$_6$) 0.6, 29.5, 30.2, 50.7, 89.8 and 162.3.

5-Bromo-7,7,7-trichloro-1-diazoheptan-2-one 36. A solution of the unsaturated α-diazo ketone 9 (1.1 g, 8.9 mmol), bromotrichloromethane (1.76 g, 8.9 mmol) and BPO (110 mg, 0.45 mmol) in benzene (10 cm^3) was heated under reflux for 3 h. The solvent was removed under reduced pressure and the residue was subjected to column chromatography using petroleum–diethyl ether (5:1 v/v) eluent to give 36 (2.45 g, 85%) as an oil; δ_H 2.15 (1 H, m), 2.50 (1 H, m), 2.61 (2 H, m), 3.23 (1 H, dd, J 15.80 and 5.50), 3.48 (1 H, dd, J 15.80 and 5.00), 4.38 (1 H, m) and 5.31 (1 H, br s); δ_C 34.1, 38.3, 48.4, 54.9, 62.7, 96.8 and 192.8 (Found: C, 26.3; H, 2.6; N, 8.9. C$_7$H$_8$BrCl$_3$N$_2$O requires C, 26.1; H, 2.5; N, 8.7%).

Reactions with allyltributylstannane (ATBS)

A solution of the α-diazo carbonyl compound (4.0 mmol), ATBS (2.6 g, 8.0 mmol) and AIBN (33 mg, 0.20 mmol) in benzene (12 cm^3) was heated under reflux for 3 h. The reaction mixture was allowed to cool to room temperature, diluted with diethyl ether (20 cm^3) and shaken with saturated aqueous KF (10 cm^3). The organic layer was washed with saturated brine, dried and the solvent was removed under reduced pressure. Flash chromatography of the residue, using petroleum–diethyl ether (7:1 v/v) as eluent, gave the product as an oil; the yields

are shown in Scheme 5 and the analytical data are given below.

Dec-1-en-5-one[44] 38. δ_H 0.87 (3 H, t, J 7.21), 1.29 (4 H, m), 1.56 (2 H, m), 2.31 (2 H, m), 2.38 (2 H, t, J 7.54), 2.49 (2 H, t, J 7.58), 4.96 (1 H, dd, J 10.33 and 1.86), 5.15 (1 H, dd, J 17.13 and 1.86) and 5.79 (1 H, ddt, J 17.13, 10.33 and 7.10); δ_C 13.9, 22.4, 23.5, 27.8, 31.4, 41.7, 42.9, 115.1, 137.2 and 210.5; m/z (EI) 154 (M$^+$, 9%), 99 (100), 83 (44) and 71 (56) (Found: M$^+$, 154.1354. C$_{10}$H$_{18}$O requires M, 154.1358).

2,2-Dimethyloct-7-en-4-one[45] 39. δ_H 1.00 (9 H, s), 2.29 (4 H, m), 2.47 (2 H, t, J 7.30), 4.95 (1 H, dd, J 11.42 and 1.71), 5.01 (1 H, dd, J 17.18 and 1.71) and 5.79 (1 H, ddt, J 17.18, 11.42 and 7.30); δ_C 27.7, 29.8, 31.0, 44.1, 55.0, 115.1, 137.3 and 210.0; m/z (EI) 154 (M$^+$, 5%), 99 (100), 83 (67) and 71 (38) (Found: M$^+$, 154.1353. C$_{10}$H$_{18}$O requires M, 154.1358).

1-Phenylpent-4-en-1-one[46] 40. δ_H 2.50 (2 H, m), 3.08 (2 H, t, J 8.02), 5.01 (1 H, dd, J 10.11 and 1.34), 5.08 (1 H, dd, J 17.06 and 1.34), 5.90 (1 H, ddt, J 17.06, 10.11 and 8.02), 7.46 (2 H, t, J 7.86), 7.56 (1 H, m) and 7.96 (2 H, m); δ_C 28.2, 37.7, 115.3, 128.0, 128.6, 133.0, 136.9, 137.3 and 199.4; m/z (EI) 160 (M$^+$, 8%), 105 (100) and 77 (43) (Found: M$^+$, 160.0884. C$_{11}$H$_{12}$O requires M, 160.0888).

1-Phenylhex-5-en-2-one[47] 41. δ_H 2.32 (2 H, m), 2.57 (2 H, t, J 7.58), 3.70 (2 H, s), 4.96 (1 H, dd, J 10.25 and 1.69), 5.00 (1 H, dd, J 17.09 and 1.69), 5.78 (1 H, ddt, J 17.09, 10.25 and 6.71), 7.23 (2 H, m), 7.28 (1 H, m) and 7.35 (2 H, m); δ_C 27.6, 41.0, 50.2, 115.2, 126.9, 128.7, 129.3, 134.1, 136.9 and 207.4; m/z (EI) 174 (M$^+$, 4%), 91 (77) and 55 (100) (Found: M$^+$, 174.1036. C$_{12}$H$_{14}$O requires M, 174.1045).

Nona-1,8-dien-5-one[48] 42. δ_H 2.32 (4 H, m), 2.51 (4 H, t, J 7.01), 5.00 (4 H, m) and 5.79 (2 H, m); δ_C 27.7, 41.8, 115.2, 137.1 and 209.3.

Ethyl pent-4-enoate[49] 43. Compound 43 was identified by comparison of spectroscopic data with authentic material (Lancaster Synthesis); δ_H 1.24 (3 H, t, J 7.08), 2.38 (4 H, m), 4.13 (2 H, q, J 7.08), 5.02 (2 H, m) and 5.81 (1 H, m); δ_C 14.2, 28.8, 33.5, 60.3, 115.4, 136.7 and 173.1.

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