# EPR Studies of the Addition of 1,1-Bis(alkoxycarbonyl)alkyl Radicals and Tris(ethoxycarbonyl)methyl Radicals to Alkenes and to Alkyl Isocyanides

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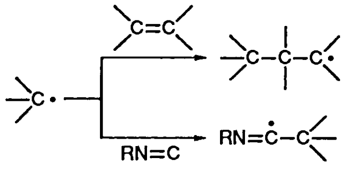
EPR spectroscopy has been used to monitor the addition of $R\dot{C}(CO_2Et)_2$ (R = H or Me) and of $^{\bullet}C(CO_2Et)_3$ to terminal alkenes, furan, MeNC and $Bu^tNC$ in cyclopropane solution at low temperatures. The radical addenda were generated by UV photolysis of di-*tert*-butyl peroxide in the presence of the corresponding malonate or triethyl methanetricarboxylate and trimethylamine–butylborane complex, which acts as a polarity reversal catalyst for hydrogen-atom abstraction from the electron-deficient α–C–H groups in the esters. For all acceptors, addition of each of the electrophilic α-alkoxycarbonyl(alkyl) radicals is more rapid than the corresponding addition of simple (nucleophilic) alkyl radicals, a result which is attributed to the importance of charge-transfer interactions in the transition states (polar effects). Relative rates of addition of $H\dot{C}(CO_2Et)_2$, $Me\dot{C}(CO_2Et)_2$ and $^{\bullet}C(CO_2Et)_3$ to $H_2C{=}CH_2$, $MeCH{=}CH_2$, $Me_2C{=}CH_2$ and $Me_3SiCH_2CH{=}CH_2$ are also governed mainly by polar effects. Approximate absolute rate constants for addition of $H\dot{C}(CO_2Et)_2$ and $^{\bullet}C(CO_2Et)_3$ to ethene at 221 K have been determined to be $7.3 \times 10^3$ and $1.4 \times 10^3$ $dm^3$ $mol^{-1}$ $s^{-1}$, respectively. The radical $H_2C{=}CH(CH_2)_3\dot{C}(CO_2Et)_2$ undergoes rapid 5-*exo*-cyclisation with a lower activation energy than that for corresponding cyclisation of the unsubstituted hex-5-enyl radical; this is attributed to the electrophilic nature of the radical centre in the former species. Addition of α-alkoxycarbonyl(alkyl) radicals to alkyl isocyanides occurs at the terminal carbon atom to give imidoyl radicals which are strongly bent at $C_\alpha$. Addition of $H\dot{C}(CO_2Et)_2$ to $Bu^tNC$ takes place 16 times faster than its addition to ethene at 220 K.

Addition of carbon-centred radicals to a coordinatively unsaturated carbon in a suitable acceptor molecule, especially an alkene, is an important synthetic tool for the formation of C–C bonds.[1,2] Such homolytic addition to alkenes [eqn. (1a)] is markedly influenced by polar factors[3–6] and simple alkyl radicals add only relatively slowly unless electron-withdrawing groups (EWGs) are attached to the C=C moiety.



(1a)

(1b)

Electrophilic carbon radicals, with one or more EWGs attached to $C_\alpha$, add more readily to simple alkenes[1,2] and there is much current interest in synthetic methods based on inter- and intra-molecular addition reactions of radicals of the type $R\dot{C}(EWG)_2$ (EWG = $CO_2R$ or CN, in particular).[1,2,7–13]

Although there have been a few mechanistic studies of the addition of 1,1-bis(alkoxycarbonyl)alkyl radicals $R^1\dot{C}(CO_2R^2)_2$ **1** to alkenes, using reaction kinetics and product analysis as probes,[1,14,15] there is still a need for more quantitative work.[9] In the present paper we describe the use of EPR spectroscopy to monitor the addition of the radicals **1** and $^{\bullet}C(CO_2Et)_3$ **2** to a number of alkenes, and to furan.

$R^1\dot{C}(CO_2R^2)_2$ **1**  $^{\bullet}C(CO_2Et)_3$ **2**

$$RN{=}C\!: \longleftrightarrow R\overset{+}{N}{\equiv}\overset{-}{C}\!:$$

**3a** **3b**

Addition of simple alkyl radicals to alkyl isocyanides to give imidoyl radicals[16–18] [eqn. (1b)] is a relatively slow process.[19–20] However, consideration of the contributing valence bond structure **3b** suggests that polar effects should favour the addition of more electrophilic carbon-centred radicals. Therefore, a second objective of this work was to investigate the reactions of the radicals **1** and **2** with alkyl isocyanides.

In order to monitor these elementary addition processes, it was necessary to generate the (alkoxycarbonyl)alkyl radicals efficiently in the presence of the acceptor molecules. *tert*-Butoxyl radicals may be produced readily by UV irradiation of di-*tert*-butyl peroxide (DTBP) [eqn. (2)], but these radicals are

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^{\bullet} \qquad (2)$$

electrophilic and abstract an α-hydrogen atom only slowly from malonates $R^1C(H)(CO_2R^2)_2$ or from $HC(CO_2Et)_3$, because of unfavourable polar effects.[21] However, this abstraction is efficiently promoted in the presence of trimethylamine–butylborane (TMBB),[21] which acts as a polarity reversal catalyst,[22,23] such that the slow single step (3) is replaced by the catalytic cycle of rapid reactions (4) and (5). This method of

$$Bu^tO^{\bullet} + R^1C(H)(CO_2R^2)_2 \xrightarrow{\text{slow}} Bu^tOH + R^1\dot{C}(CO_2R^2)_2 \qquad (3)$$

$$Bu^tO^{\bullet} + Me_3N{\rightarrow}BH_2Bu \xrightarrow{\text{fast}} Bu^tOH + Me_3N{\rightarrow}\dot{B}HBu \qquad (4)$$

$$Me_3N{\rightarrow}\dot{B}HBu + R^1C(H)(CO_2R^2)_2 \xrightarrow{\text{fast}} Me_3N{\rightarrow}BH_2Bu + R^1\dot{C}(CO_2R^2)_2 \qquad (5)$$

**Table 1** EPR parameters for alkoxycarbonyl(alkyl) radicals in cyclopropane

| | | | Hyperfine splittings/G | | |
|---|---|---|---|---|---|
| Radical | $T$/K | $g$-Factor | $a(1H_\alpha)$ | $a(nH_\beta)$[a] | Others |
| $H\dot{C}(CO_2Et)_2$ | 179 | 2.0039 | 20.35 | — | — |
| $H\dot{C}(CO_2Bu^t)_2$ | 179 | 2.0039 | 20.32 | — | — |
| $H\dot{C}(CO_2SiMe_3)_2$ | 177 | 2.0039 | 20.08 | — | — |
| $Me\dot{C}(CO_2Et)_2$ | 183 | 2.0036 | — | 23.82 (3) | 0.89 ($4H_\delta$) |
| $Et\dot{C}(CO_2Et)_2$ | 246 | 2.0035 | — | 13.75 (2)[b] | 0.37 ($3H_\gamma$), 0.94 ($4H_\delta$) |
| $Bu\dot{C}(CO_2Et)_2$ | 184 | 2.0034 | — | 12.85 (2) | 0.40 ($1H_\gamma$),[c] 1.03 ($4H_\delta$) |
| $Bu^t\dot{C}(CO_2Et)_2$ | 243 | 2.0034 | — | — | 0.55 ($9H_\gamma$), 1.24 ($4H_\delta$) |
| $H_2C{=}CH(CH_2)_3\dot{C}(CO_2Et)_2$ | 187 | 2.0035 | — | 12.92 (2)[d] | 0.98 ($4H_\delta$)[e] |
| $^{\bullet}C(CO_2Et)_3$ | 197 | 2.0037 | — | — | 0.77 ($6H_\delta$) |

[a] Numbers of nuclei shown in parentheses. [b] $a(2H_\beta)$ = 12.85 G at 173 K. [c] Only one of the γ-protons gives rise to resolvable splitting. [d] $a(2H_\beta)$ = 13.31 G at 220 K.

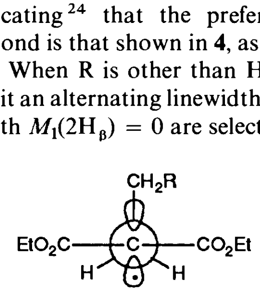
generation, which avoids possible complications arising from chain reactions and from the reactive by-products that might accompany the use of α-halogenomalonates, was adopted in this work.*

## Results and Discussion

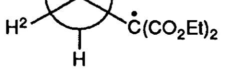
UV irradiation at 180–230 K of a cyclopropane solution containing DTBP (*ca.* 15% v/v), a malonate ester $R^1C(H)(CO_2R^2)_2$ (0.5–1 mol dm$^{-3}$) and TMBB (*ca.* 0.2 mol dm$^{-3}$) afforded the EPR spectrum of the corresponding radical **1**, as described previously.[21] In the absence of TMBB, hydrogen-atom abstraction by $Bu^tO^{\bullet}$ takes place unselectively. The tris(ethoxycarbonyl)methyl radical **2** was generated in the same way from triethyl methanetricarboxylate (0.3–0.4 mol dm$^{-3}$) at 220 K; this ester was not very soluble in cyclopropane at lower temperatures. The EPR parameters for the alkoxycarbonyl(alkyl) radicals are reported in Table 1 and the spectrum of $Et\dot{C}(CO_2Et)_2$ is shown in Fig. 1.

Radicals of the type $R^1\dot{C}(CO_2R^2)_2$ are transient when $R^1$ = H, Me or a primary alkyl group and their EPR spectra decay within the fall-time of the spectrometer (0.2 s) when photolysis is interrupted. In contrast, $Bu^t\dot{C}(CO_2Et)_2$ is a relatively persistent species, presumably because it cannot undergo disproportionation and the radical centre is sterically protected against dimerisation. This radical decayed with mixed first- and second-order kinetics; the half-life was *ca.* 7 s at 203 K.

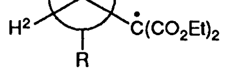
The values of $a(2H_\beta)$ for radicals of the type $RCH_2CH_2\dot{C}(CO_2Et)_2$ (R = H or alkyl) are appreciably smaller than the value for $CH_3\dot{C}(CO_2Et)_2$ and show positive temperature dependences, indicating[24] that the preferred conformation about the $C_\alpha$–$C_\beta$ bond is that shown in **4**, as would be expected on steric grounds. When R is other than H (see Table 1), the EPR spectra exhibit an alternating linewidth effect such that the lines associated with $M_I(2H_\beta) = 0$ are selectively broadened at low temperature. We attribute this lineshape effect to the existence of a hindered rotation about the $C_\beta$–$C_\gamma$ bond such that exchange involving the conformations **5a** and **5b** takes place on the EPR timescale. The existence of this lineshape effect requires that the conformations **5a** and **5b** must be significantly populated alongside the symmetrical conformation **5c**, which is presumably the most stable, and that the sum of the β-proton splittings for **5c** is similar to the sum for **5a**/**b**. An analogous situation exists for hindered rotation about the $C_\beta$–$C_\gamma$ bond in the butyl radical.[25]



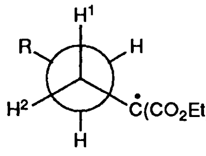
**4**



**5a**



**5b**



**5c**

Alongside each spectrum of **1** derived from the alkylmalonates, broader, less well-defined lines from a relatively persistent radical were observed. The persistent radical was barely detectable from $MeC(H)(CO_2Et)_2$, but was stronger when the *C*-alkyl group was larger than methyl. The persistent radicals appeared to be secondary reaction products which were not present immediately after the sample was first UV irradiated, suggesting that these species may be derived from a self-reaction product of **1**. Disproportionation of **1** would produce an alkylidenemalonate, to which the nucleophilic $Me_3N{\rightarrow}\dot{B}HBu$ would be expected to add very rapidly.

*Addition of* $H\dot{C}(CO_2R)_2$, $Me\dot{C}(CO_2Et)_2$ *and* $^{\bullet}C(CO_2Et)_3$ *to Alkenes.*—When these radicals were generated using polarity reversal catalysis (PRC) in the presence of an alkene, their EPR spectra were replaced by the corresponding substituted alkyl radical adduct (*e.g.* **6**), to an extent which increased with the concentration of alkene and with increasing temperature; it also depended on the nature of the alkene and of the addendum. In ethene solvent at *ca.* 180 K, the EPR spectrum of $H\dot{C}(CO_2Et)_2$ was detected alongside a strong spectrum of the adduct **6** [see Fig. 2(*a*)]. The small doublet splitting is absent in the

$$H(\dot{C}CO_2Et)_2 + CH_2{=}CH_2 \longrightarrow \underset{\mathbf{6}}{(EtO_2C)_2CHCH_2\dot{C}H_2} \quad (6)$$

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* Trimethylamine–methylborane was also used as a polarity reversal catalyst in some experiments, but this amine–borane is less soluble in hydrocarbons than is TMBB.

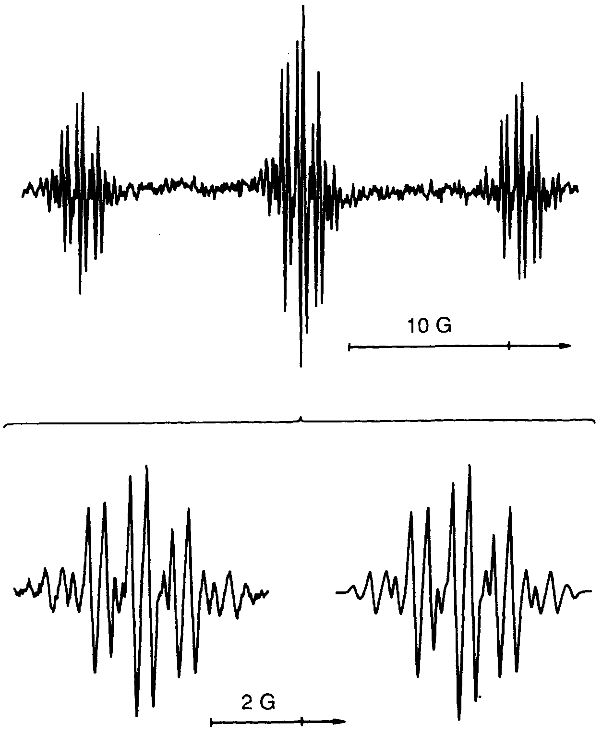

**Fig. 1** EPR spectrum of the radical $Et\dot{C}(CO_2Et)_2$ at 234 K, produced by UV irradiation of a cyclopropane solution containing DTBP, TMBB and diethyl ethylmalonate. The central multiplet at 246 K is shown expanded alongside its computer simulation obtained using the parameters given in Table 1.

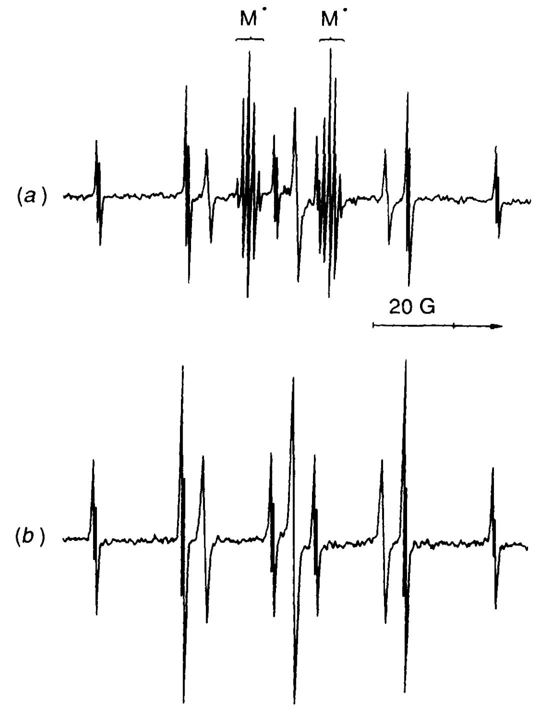

**Fig. 2** (*a*) EPR spectra of the radical $H\dot{C}(CO_2Et)_2$ ($M^{\bullet}$) and the adduct radical **6**, obtained during generation of the former radical in ethene solvent at 180 K. (*b*) Spectrum of **6** in cyclopropane at 183 K, obtained by bromine atom abstraction from diethyl 2-bromoethylmalonate using $Me_3N{\rightarrow}\dot{B}HBu$.

spectrum of the γ-deuterium-labelled radical generated from $D_2C(CO_2Et)_2$.*

Addition of $H\dot{C}(CO_2Et)_2$ to propene was more rapid, requiring a lower concentration of alkene for comparable quenching of the spectrum of the addendum; 2-methylpropene was a still more reactive acceptor. Addition to the electron-rich double bonds in ethyl vinyl ether and allyltrimethylsilane also took place readily.

Addition of $H\dot{C}(CO_2Bu^t)_2$, $H\dot{C}(CO_2SiMe_3)_2$, $Me\dot{C}(CO_2Et)_2$ and $^{\bullet}C(CO_2Et)_3$ to these alkenes was also investigated. The tris(ethoxycarbonyl)methyl radical **2** added readily, but the more sterically hindered, more stabilised and less electrophilic $Me\dot{C}(CO_2Et)_2$ showed no sign of addition to ethene (*ca.* 1.5 mol dm$^{-3}$) at 280 K. However, addition of this radical to propene was detected at 268 K. All addition reactions were highly regioselective and only adduct radicals formed by attachment to the unsubstituted end of the double bond were detected. The EPR parameters for all the adducts **6–20** are reported in Table 2.

Addition of $H\dot{C}(CO_2Et)_2$ to ethene was shown to be irreversible under the conditions of the EPR experiments. UV irradiation of a cyclopropane solution containing diethyl 2-bromoethylmalonate (0.6 mol dm$^{-3}$), DTBP (*ca.* 15% v/v) and triethylsilane (1.2 mol dm$^{-3}$) or TMBB (0.8 mol dm$^{-3}$), afforded a strong EPR spectrum of the radical **6** [eqn. (7); $M^{\bullet} = Et_3Si^{\bullet}$ or $Me_3N{\rightarrow}\dot{B}HBu$] and no signal from $H\dot{C}(CO_2Et)_2$ was observed up to 250 K [Fig. 2(*b*)].

$$(EtO_2C)_2CHCH_2CH_2Br + M^{\bullet} \longrightarrow (EtO_2C)_2CHCH_2\dot{C}H_2 + MBr \quad (7)$$

The conformational preferences of the adduct radicals can be inferred from the magnitudes and temperature dependences of the β-proton coupling constants.[24] Most of the adducts to ethene show values of $a(2H_\beta)$ fairly close to the value of $a(3H_\beta)$ in the ethyl radical (26.9 G), implying little conformational preference. Steric interaction between the addendum group and the α-methyl substituents in the 2-methylpropene adducts leads to a preference for the eclipsed conformation, as indicated by the small value of, and positive temperature coefficient for, $a(2H_\beta)$. Some adduct radical spectra showed selective line-broadening effects at low temperatures, probably because of hindered rotation about the $C_\beta$–$C_\gamma$ bond; in no case could spectra be obtained in the slow exchange region. Lineshape effects were particularly evident in the spectra of the 2-methylpropene adducts and the lines corresponding to $M_I(2H_\beta) = 0$ were severely broadened at low temperatures. Exact agreement between the experimental spectrum and its computer simulation, correct to second-order, could not be obtained for the propene adduct **10** at very low temperatures and we attribute this to the higher-order effects which become important when the difference between two coupling constants becomes comparable to the associated second-order shifts.[26]

Addition of $H\dot{C}(CO_2Et)_2$ and $^{\bullet}C(CO_2Et)_3$ to furan (1 mol dm$^{-3}$) also took place readily, but $Me\dot{C}(CO_2Et)_2$ again added much more sluggishly and the spectrum of the corresponding allylic adduct **23** was detectable only above *ca.* 270 K. The spectrum of the radical **21**, which exhibits strong chemically induced dynamic electron polarisation (CIDEP), is shown in Fig. 3 and the spectroscopic parameters for **21–23** are given in Table 3.

*Absolute Rate Constants for Addition of* $H\dot{C}(CO_2Et)_2$ *and* $^{\bullet}C(CO_2Et)_3$ *to Ethene.*—If the adduct radicals $A^{\bullet}$ are formed

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* In the absence of malonate, the amine–boryl radical $Me_3N{\rightarrow}\dot{B}HBu$ adds to ethene to give $Me_3N{\rightarrow}BH(Bu)CH_2\dot{C}H_2$. The β-protons are diastereotopic and the lines corresponding to $M_I(2H_\beta)$ were not observed at 180 K [$a(2H_\alpha)$ 20.48, $\bar{a}(2H_\beta)$ 22.22, $a(^{11}B)$ 17.40 G]. Corresponding addition to 2-methylpropene could not be detected, in accord with the dominance of polar factors in influencing the rate of addition of this highly nucleophilic amine–boryl radical.

**Table 2** EPR parameters for adduct radicals $(R^2O_2C)_2C(R^1)CH_2\dot{C}R^3R^4$ in cyclopropane

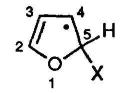
| | | | | | | | Hyperfine splittings[a]/G | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Structure | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $T$/K | $g$-Factor | $a(2H_\beta)$ | $a(R^1)$[c] | $a(R^3,R^4)$[c] | $da(2H_\beta)/dT$[b] (mG $K^{-1}$) |
| **6** | H | Et | H | H | 190 | 2.0026 | 27.25 | 0.70 (1) | 22.30 (2) | −14 |
| **7** | H | $Bu^t$ | | | 182 | 2.0026 | 28.09 | 0.70 (1) | 22.25 (2) | −22 |
| **8** | H | $Me_3Si$ | | | 180 | 2.0027 | 28.17 | 0.72 (1) | 22.35 (2) | −21 |
| **9** | $EtO_2C$ | Et | | | 220 | 2.0027 | 22.67 | — | 22.37 (2) | +5 |
| **10** | H | Et | H | Me | 187 | 2.0027 | 24.60 | 0.80 (1) | 21.95 (1), 25.10 (3) | −12 |
| **11** | $EtO_2C$ | Et | | | 220 | 2.0028 | 22.05 | — | 22.05 (1), 25.35 (3) | −3 |
| **12** | Me | Et | | | 270 | 2.0027 | 23.50 | — | 21.75 (1), 25.12 (3) | +4 |
| **13** | H | Et | Me | Me | 181 | 2.0026 | 15.68 | 1.05 (1) | 23.35 (6) | +10 |
| **14** | $EtO_2C$ | Et | | | 221 | 2.0028 | 14.00 | — | 23.00 (6) | +7 |
| **15** | Me | Et | | | 240 | 2.0026 | 13.18 | — | 23.30 (6) | +7 |
| **16**[d] | H | Et | H | EtO | 190 | 2.0032 | 15.30[e] | 1.05 (1) | 15.00 (1), 1.80 (2) | +10 |
| **17** | $EtO_2C$ | Et | | | 220 | 2.0032 | 13.85 | — | 15.33 (1), 2.00 (2) | +11 |
| **18** | H | Et | H | $Me_3SiCH_2$ | 218 | 2.0027 | 25.05[f] | 0.80 (1) | 20.85 (1), 17.50 (2)[f] | −22,[g] +10[h] |
| **19** | $EtO_2C$ | Et | | | 220 | 2.0027 | 23.35[f] | — | 20.80 (1), 17.50 (2)[f] | −16,[g] +13[h] |
| **20** | Me | Et | | | 254 | 2.0028 | 24.75[f] | — | 20.75 (1), 17.75 (2)[f] | |

[a] Corrected to second-order. [b] Average temperature dependence in the region of the stated temperature. [c] Numbers of equivalent protons shown in parentheses. [d] Central lines of the β-proton triplet broaden markedly below *ca.* 245 K. [e] $a(H_\alpha)$ is temperature dependent; 14.85 G at 221 K and 14.65 G at 260 K. [f] The assignments of $a(2H_\beta)$ are tentative. [g] Temperature coefficient for the larger β-proton splitting. [h] Temperature coefficient for the smaller β-proton splitting.

**Table 3** EPR parameters for the radicals **21**–**23** formed by addition to furan in cyclopropane

| | | | Hyperfine splittings/G | | | |
|---|---|---|---|---|---|---|
| Radical | $T$/K | $g$-Factor | $a$(5-H) | $a$(2,4-H)[a] | $a$(3-H) | $a$(1H)[b] |
| **21** | 185 | 2.0031 | 31.75 | 13.60 | 2.03 | 1.18 |
| **22** | 220 | 2.0031 | 34.02[c] | 13.60 | 2.00 | — |
| **23** | 286 | 2.0031 | 33.70 | 13.50 | 2.05 | — |

[a] The splittings from 2-H and 4-H indistinguishable within the linewidth. [b] Splitting from the α-proton of the malonate group, absent in experiments using $D_2C(CO_2Et)_2$. [c] 34.08 G at 260 K.



**21**; X = $C(H)(CO_2Et)_2$
**22**; X = $C(CO_2Et)_3$
**23**; X = $C(Me)(CO_2Et)_2$

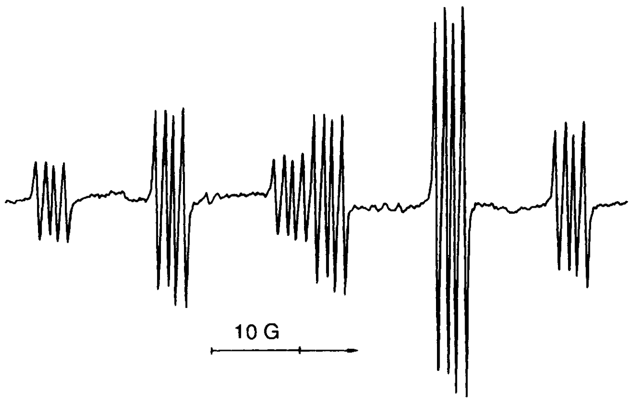


**Fig. 3** EPR spectrum of the radical **21** in cyclopropane at 184 K. The spectrum shows CIDEP effects such that the high-field triplet of multiplets associated with the $M_I - \frac{1}{2}$ state of 5-H are much more intense than those associated with the $M_I + \frac{1}{2}$ state (E/A polarisation).

and removed as shown in eqns. (8)–(10) and the assumption is made[27,28] that $2k_t^A = k_x$, then the steady-state radical concentrations during continuous generation of the addendum $X^\bullet$ will be given by eqn. (11).[4] Absolute radical concentrations were measured at 221 K and extrapolated to zero UV irradiation

$$X^\bullet + CH_2{=}CH_2 \xrightarrow{k_{add}} \underset{A^\bullet}{X{-}CH_2{-}\dot{C}H_2} \quad (8)$$

$$\left.\begin{array}{ll} A^\bullet + A^\bullet \xrightarrow{2k_t^A} & (9) \\ A^\bullet + X^\bullet \xrightarrow{k_x} & (10) \end{array}\right\} \text{Non-radical products}$$

$$(k_{add}/2k_t^A) = ([A^\bullet]/[CH_2{=}CH_2])([A^\bullet]/[X^\bullet] + 1) \quad (11)$$

time for initial ethene concentrations in the range 0.4–2.5 mol $dm^{-3}$. For $X^\bullet = H\dot{C}(CO_2Et)_2$ and $^\bullet C(CO_2Et)_3$, the values of $(k_{add}/2k_t^A)$ were $7.3 \pm 1.0 \times 10^{-7}$ and $1.4 \pm 0.3 \times 10^{-7}$, respectively.

Self-reactions of small and moderately sized alkyl radicals, which are not sterically protected at the radical centre, are diffusion controlled processes for which the rate constants will all be very similar in a given medium.[29] From rate constants in

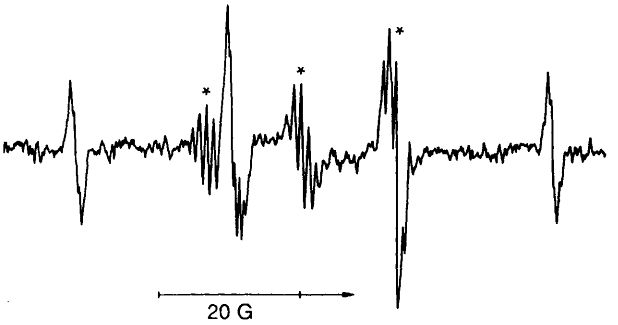


**Fig. 4** EPR spectrum of the radical **25** alongside that of the uncyclised radical **24** (multiplets marked with asterisks) in cyclopropane at 221 K

the literature for the self-reaction of *tert*-butyl radicals in alkanes[29] and for allyl radicals in propene–DTBP,[30] we estimate that, under our conditions, $2k_t^A$ will be *ca.* $1 \times 10^{10}$ dm$^3$ mol$^{-1}$ at 221 K for both of the primary alkyl radical adducts **6** and **9**. Using this value of $2k_t^A$, approximate rate constants for addition of $H\dot{C}(CO_2Et)_2$ and $^{\bullet}C(CO_2Et)_3$ to ethene at 221 K are $7.3 \times 10^3$ and $1.4 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively. If we take[5,31] the Arrhenius *A*-factor for these addition reactions to be $10^{7.5}$ dm$^3$ mol$^{-1}$ s$^{-1}$, the corresponding activation energies would be 15.4 and 18.4 kJ mol$^{-1}$, respectively. Both additions are appreciably more rapid than addition of the nucleophilic *tert*-butyl radical to ethene[31] ($k_{add} = 24$ s$^{-1}$ at 221 K) and the large difference is attributable mainly to polar effects.

Addition of $H\dot{C}(CO_2Et)_2$ to propene is 19 times faster than its addition to ethene at 221 K (see below) and thus the absolute rate constant for addition to propene is *ca.* $1.4 \times 10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$. This value is appreciably larger than the rate constant for addition of the less electrophilic $^{\bullet}CH_2CO_2Bu^t$ to butene ($5.6 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 221 K, extrapolated from data obtained at 296 K) determined by Beranek and Fischer,[6] again in accord with rate-controlling polar effects.

*Relative Rates of Addition to Alkenes.*—When an addendum radical X$^{\bullet}$ is generated continuously in the presence of two different alkenes B and C, the relative concentrations of adduct radicals under steady-state conditions will be given by eqn. (14), provided that the two adducts are removed by self- and cross-reactions which have equal (diffusion-controlled) rate constants.[4,27,28] Relative rate constants at 221 K were determined

$$X^{\bullet} + \text{alkene B} \xrightarrow{k_{add}^{B}} \text{adduct B}^{\bullet} \quad (12)$$

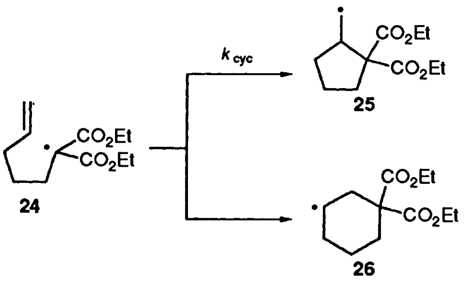
$$X^{\bullet} + \text{alkene C} \xrightarrow{k_{add}^{C}} \text{adduct C}^{\bullet} \quad (13)$$

$$(k_{add}^{B}/k_{add}^{C}) = [\text{adduct B}^{\bullet}][\text{alkene C}]/[\text{adduct C}^{\bullet}][\text{alkene B}] \quad (14)$$

by double integration and/or computer simulation of appropriate lines in the adduct EPR spectra for at least two different alkene concentration ratios, as described previously.[4,32] The results are given in Table 4.

Polar effects are evidently important in determining the relative rates of addition of the electrophilic radicals $H\dot{C}(CO_2Et)_2$ and $^{\bullet}C(CO_2Et)_3$, as is most clearly seen by comparing propene and allyltrimethylsilane when steric effects and reaction enthalpies will be similar. Addition of either radical to the electron-rich double bond in the silane ($E_i = 9.0$ eV) is much more rapid than its addition to propene ($E_i = 9.73$ eV). The rate differences are smaller for the less electrophilic and less reactive $Me\dot{C}(CO_2Et)_2$, although these data were obtained at higher temperature, which will also tend to compress the reactivities. A semi-quantitative investigation of the addition of $Me\dot{C}(CO_2Et)_2$ to propene at 275 K indicated that the rate constant was *ca.* $8 \times 10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$.

*Cyclisation of the* 1,1-*Bis*(*ethoxycarbonyl*)*hex*-5-*enyl Radical.*—The title radical **24** was generated from diethyl pent-4-enylmalonate under conditions of PRC using TMBB (see Table 1) and its cyclisation was monitored by EPR spectroscopy between 190 and 250 K (see Fig. 4). Persistent radicals (see above) were not detected at temperatures sufficiently high for significant concentrations of the cyclised radical **25** to be present along with **24**. Only 5-*exo*-cyclisation of **24** to **25** [$a(2H_\alpha)$ 22.13, $a(1H_\beta)$ 23.25 and $a(4H_{\gamma/\delta})$ 0.55 G at 225 K] was detected and no spectrum attributable to the more stable **26** was observed up to 270 K, at which temperature **24** was no longer detectable. These results are in accord with the cyclisation occurring irreversibly under our conditions, as expected.[7] From product isolation experiments,[7] carried out under conditions of kinetic control, it is known that the relative rates of 5-*exo*- and 6-*endo*-cyclisation of the dimethyl ester analogue of **24** are in the ratio 89:11 at 358 K. Assuming that the rate difference is wholly attributable to the difference in activation energies, this ratio would become *ca.* 94:6 at 270 K, consistent with our inability to detect **26** in the temperature range 190–270 K.



(15a)

(15b)

The rate constant for 5-*exo*-cyclisation of **24** was determined relative to that ($2k_t$) for self-reaction of **25** using eqn. (16), which is derived by assuming that the rate constant for (diffusion-controlled) reaction between **24** and **25** is equal to $2k_t$.[33]

$$(k_{cyc}/2k_t) = [\mathbf{25}]([\mathbf{25}]/[\mathbf{24}] + 1) \quad (16)$$

The results gave a good fit to the Arrhenius rate expression shown in eqn. (17), in which $\theta = 2.303RT$. If we take $2k_t$ to be the same as that for self-reaction of the cyclopentylmethyl

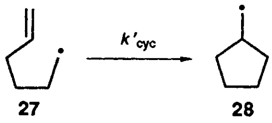
$$\log_{10}[(k_{cyc}/2k_t)/\text{mol dm}^{-3}] = -(2.56 \pm 0.20) - (16.42 \pm 1.50)/\theta \quad (17)$$

radical **28** in cyclopropane, which is given by eqn. (18),[34] then we obtain the rate expression (19). The rate constant ($k'_{cyc}$) for

$$\log_{10}(2k_t/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 11.85 - 7.1/\theta \quad (18)$$

$$\log_{10}(k_{cyc}/\text{s}^{-1}) = (9.3 \pm 0.3) - (23.5 \pm 2.0)/\theta \quad (19)$$

5-*exo*-cyclisation of the unsubstituted hex-5-enyl radical **27** to give **28** is given by eqn. (21).[33–35]



(20)

$$\log_{10}(k'_{cyc}/\text{s}^{-1}) = (10.35 \pm 0.35) - (28.29 \pm 1.89)/\theta \quad (21)$$

**Table 4** Relative rates of addition of alkoxycarbonyl(alkyl) radicals to alkenes in cyclopropane at 220 K

| | Relative rate of addition | | | |
|---|---|---|---|---|
| Alkene | $H\dot{C}(CO_2Et)_2$ | $^{\bullet}C(CO_2Et)_3$ | $Me\dot{C}(CO_2Et)_2$[a] | Alkene ionisation energy/eV[b] |
| $H_2C{=}CH_2$[c] | (1) | (1) | — | 10.51 |
| $MeCH{=}CH_2$ | 19 | 18 | (1) | 9.73 |
| $Me_2C{=}CH_2$ | 261 | 281 | 4.6 | 9.24 |
| $Me_3SiCH_2CH{=}CH_2$ | 444 | 900 | 5.4 | 9.0[d] |

[a] Relative rates at 275 K. [b] Data from G. Bieri, F. Burger, E. Heilbronner and J. P. Maier, *Helv. Chim. Acta*, 1977, **60**, 2213 unless noted otherwise. [c] Molar reactivities are reported; in ethene the two ends of the double bond are equally reactive. [d] U. Weidner and A. Schweig, *J. Organomet. Chem.*, 1972, **39**, 261.

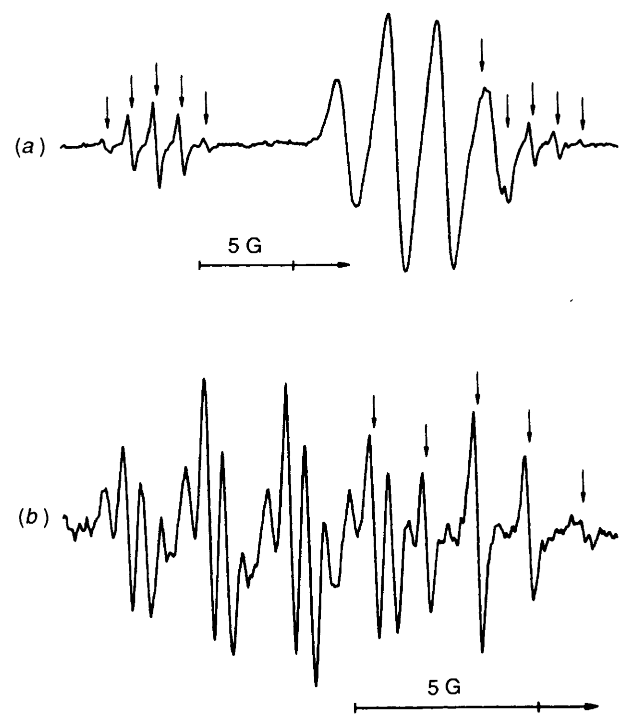
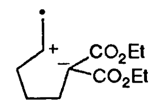


**Fig. 5** EPR spectra in cyclopropane at 173 K of (*a*) $Bu^tN{=}\dot{C}C(H)(CO_2Et)_2$ and (*b*) $MeN{=}\dot{C}C(H)(CO_2Et)_2$. Lines originating from $H\dot{C}(CO_2Et)_2$ are marked with arrows.

At 200 K the rate constants for cyclisation of **24** and **27** are similar ($1.5 \times 10^3$ s$^{-1}$ and $9.2 \times 10^2$ s$^{-1}$, respectively), even though cyclisation of **24** is presumably less exothermic and the radical centre in **24** is more crowded than that in **27**. The lower activation energy for cyclisation of **24** is probably a polar effect, reflecting charge-transfer stabilisation of the transition state as indicated in structure **29**. The lower *A*-factor for cyclisation of **24** may reflect a less flexible transition structure, because of steric effects and the probable requirement for fairly rigid orientation of the $CO_2Et$ groups.



**29**

*Radical Addition to Alkyl Isocyanides.*—When $H\dot{C}(CO_2Et)_2$ was generated from diethyl malonate, using polarity reversal catalysis as before, in the presence of *tert*-butyl isocyanide (*ca.* 1.2 mol dm$^{-3}$) at 180 K, overlapping EPR spectra of the addendum and the imidoyl radical **30** were observed [see Fig. 5(*a*)]. *tert*-Butoxyl radicals react with amine–alkylboranes very rapidly[21] and no competing addition[19] to the isocyanide to give $Bu^tN{=}\dot{C}OBu^t$ was detected when $[Bu^tNC]/[TMBB]$ was *ca.* 4.

$$H\dot{C}(CO_2Et)_2 + Bu^tNC \xrightarrow{k_{22}} \underset{\textbf{30}}{Bu^tN{=}\dot{C}C(H)(CO_2Et)_2} \qquad (22)$$

The spectrum of **30** appears as a 1:2:2:1 quartet because the $^{14}N$ and β-proton splittings are almost equal, and this was confirmed by experiments with $D_2C(CO_2Et)_2$. The concentration ratio $[\textbf{30}]:[H\dot{C}(CO_2Et)_2]$ increased with increasing temperature and the spectrum of the imidoyl radical decayed within the fall-time of the spectrometer (0.2 s) when UV photolysis was interrupted.

Similar addition took place to methyl isocyanide and the spectrum of the imidoyl adduct is shown in Fig. 5(*b*); the spectroscopic parameters for all the imidoyl radicals are collected in Table 5. Addition of $Me\dot{C}(CO_2Et)_2$ to $Bu^tNC$ (*ca.* 1.2 mol dm$^{-3}$) was slower than addition of $H\dot{C}(CO_2Et)_2$ and an imidoyl adduct was detected only above *ca.* 260 K. Steric, polar and enthalpic factors are presumably responsible for this difference. The EPR spectrum of the more electrophilic $^{\bullet}C(CO_2Et)_3$ was almost completely replaced by that of the corresponding imidoyl adduct in the presence of $Bu^tNC$ (1.2 mol dm$^{-3}$) at 230 K. This adduct radical is relatively persistent and its spectrum decayed with mixed first- and second-order kinetics when photolysis was interrupted (first half-life *ca.* 1.5 s at 200 K for an initial concentration of *ca.* $10^{-6}$ mol dm$^{-3}$). Because of this, it is not possible to make a semi-quantitative estimate of the rate of addition based on the relative concentrations of the adduct and $^{\bullet}C(CO_2Et)_3$.

Competition experiments were carried out to determine the relative rate of addition of $H\dot{C}(CO_2Et)_2$ to $Bu^tNC$ and to ethene. UV irradiation of a cyclopropane solution containing ethene (3.4 mol dm$^{-3}$), $Bu^tNC$ (0.70 mol dm$^{-3}$), diethyl malonate, DTBP and TMBB at 220 K afforded an EPR spectrum which showed the presence of both adducts, and computer simulation gave $[\textbf{30}]/[\textbf{6}] = 3.3$. Hence, the rate constant for addition to $Bu^tNC$ is about 16 times that for addition to ethene and thus $k_{22}$ is *ca.* $1 \times 10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 220 K. Addition of methyl radicals to $Bu^tNC$ was not detected by EPR spectroscopy,[19b] and clearly polar factors are very important in determining the rate of addition of carbon radicals to isocyanides.

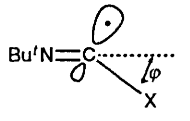
As judged from the relative concentrations of α-(ethoxycarbonyl)alkyl radicals and imidoyl adducts, addition to MeNC is significantly slower than corresponding addition to $Bu^tNC$ (in which the *N*-alkyl group is more bulky). In fact, addition of $Me\dot{C}(CO_2Et)_2$ to MeNC could not be detected up to 285 K and the difference between the isocyanides may be attributed to polar effects resulting from the greater nucleophilicity of $Bu^tNC$.[36]

Imidoyl radicals of the general type **31** are usually bent at $C_\alpha$ and the angle $\varphi$ increases as the electronegativity of the substituent increases.[19b] Using isotopically-enriched *tert*-butyl isocyanide (*ca.* 33 atom% $^{13}C_\alpha$), values of $a(^{13}C_\alpha)$ were measured for **31** in which X = $-C(H)(CO_2Et)_2$, $-C(Me)$-

Table 5 EPR parameters for imidoyl radicals $RN{=}\dot{C}X$ in cyclopropane

| | | | | Hyperfine splittings/G | | |
|---|---|---|---|---|---|---|
| R | –X | $T$/K | $g$-Factor | $a(N_\beta)$ | $a(^{13}C_\alpha)$ | Others |
| $Bu^t$ | $-C(H)(CO_2Et)_2$ | 180 | 2.0014 | 2.67[a] | 86.7 | 2.70[a] $(1H_\beta)$ |
| | $-C(D)(CO_2Et)_2$ | 180 | 2.0014 | 2.69 | | — |
| | $-C(CO_2Et)_3$ | 200 | 2.0014 | 3.00 | 92.8 | — |
| | $-C(Me)(CO_2Et)_2$ | 286 | 2.0014 | 2.50 | 85.3 | — |
| Me | $-C(H)(CO_2Et)_2$ | 180 | 2.0013 | 2.20 | | 2.35 $(1H_\beta)$, 0.51 $(3H_\alpha)$ |
| | $-C(CO_2Et)_3$ | 217 | 2.0014 | 2.53 | | 0.70 $(3H_\alpha)$ |

[a] At 212 K, $a(N_\beta) = 2.75$ G and $a(1H_\beta) = 3.35$ G.



31

$(CO_2Et)_2$ and $-C(CO_2Et)_3$ (see Table 5). These imidoyl radicals are evidently strongly bent at $C_\alpha$ and the extent of bending increases with the number of $CO_2Et$ groups attached to $C_\beta$, as expected from consideration of group electronegativities. The values of $a(^{13}C_\alpha)$ are larger than the value for $Bu^tN{=}\dot{C}SBu^t$ (76.0 G), but smaller than that for $Bu^tN{=}\dot{C}OBu^t$ (108.0 G).[19b]

In conclusion, these results indicate that the exploitation of polar effects to influence the rate of addition of carbon-centred radicals to isocyanides could provide a basis for useful procedures for chain extension and ring formation.[37] Similar principles might be applicable to radical addition to carbon monoxide.[38] Substituent effects which act to increase the nucleophilicity of the carbon atom in the NC function might be used to advantage.

## Experimental

EPR spectra were recorded during continuous UV irradiation of samples positioned in a standard variable temperature insert in the microwave cavity of a Varian E-109 or a Bruker ESP-300 spectrometer operating at 9.1–9.4 GHz. The light source was a 500 W mercury discharge lamp (Osram HBO 500 W/2) in an Oriel 1 KW housing equipped with an f0.7 Aspherab fused silica condensing lens. The slightly converging beam from this was focused using a fused silica lens (focal length 10 cm, diameter 7.5 cm) and directed onto the sample through a 3 cm pathlength water-cooled silica cell filled with an aqueous solution containing $NiSO_4{\cdot}7H_2O$ (0.38 mol $dm^{-3}$), $CoSO_4{\cdot}7H_2O$ (0.07 mol $dm^{-3}$) and sulfuric acid (0.04 mol $dm^{-3}$). The temperature of the sample during photolysis was determined, using the method described previously,[4] by careful measurement of the value of $a(H_\beta)$ for the isobutyl radical in cyclopropane. The temperature dependence of this splitting constant (in gauss) is given by eqn. (23). The heating effect at full light intensity varied between 5 and 7 K depending on conditions.

$$T/K = 2.703\,94\,a(H_\beta)^2 - 198.419\,a(H_\beta) + 3763.56 \quad (23)$$

Samples were prepared using a vacuum line and were sealed in evacuated Suprasil quartz tubes (2 or 3 mm i.d., 0.5 mm wall, depending on the dielectric properties of the contents).

The microwave frequency was measured using a frequency counter (Hewlett-Packard 5350B) and the magnetic field was measured using an NMR gaussmeter calibrated to account for the field difference between the sample and the NMR probe using the pyrene radical anion ($g$ 2.002 71) as standard.[39] Where necessary, second-order corrections[40] were applied to $g$-factors and hyperfine splittings.

Computer simulations of spectra were obtained using a modified version of ESRSPEC2,[41] extended to handle composite spectra from up to four radicals with different centres, second-order shifts for coupling to single nuclei with $I > \frac{1}{2}$, and lineshapes continuously variable between 100% Gaussian and 100% Lorentzian.

Relative radical concentrations were determined by double integration of appropriate lines in each spectrum and/or by computer simulation of the composite spectrum. On the timescale of most measurements, extrapolation of radical concentration ratios to zero photolysis time gave negligible corrections. The EPR spectra of some radicals exhibited CIDEP effects such that corresponding hyperfine lines to low- and high-field of the spectrum centre were of unequal intensity (E/A polarisation).[42] In those circumstances, relative radical concentrations were determined by taking the average intensity of corresponding low- and high-field lines.[42] Absolute radical concentrations were measured by comparison with the spectrum obtained from a standard solution of *N,N*-diphenyl-*N*-picrylhydrazyl in carbon tetrachloride, using the signal from a piece of synthetic ruby (fixed permanently inside the microwave cavity) as an internal standard.[4]

*Materials.*—NMR spectra ($CDCl_3$ solvent) were obtained with a Varian VXR-400 instrument (400 MHz for $^1H$), using tetramethylsilane as an internal standard ($^1H$) or $Et_2O{\rightarrow}BF_3$ as an external standard ($^{11}B$). $J$ values are in Hz.

Di-*tert*-butyl peroxide (98%, Aldrich) was passed down a column of basic alumina (activity 1) and distilled (b.p. 46–47 °C at 76 Torr) before use. Diethyl pent-4-enylmalonate[43] and methyl isocyanide[44] were prepared as described in the literature. Trimethylamine–butylborane (TMBB) was prepared using the method of Hawthorne,[45] with a slight modification as described below for trimethylamine–methylborane.

*Trimethylamine–Methylborane.*[22b,46]—Lithium aluminium hydride (13.7 g, 0.36 mol) was added to dry diethyl ether (250 $cm^3$) and the mixture was stirred under reflux for 1 h under argon. The resulting solution was cooled in an ice-bath, the reaction flask was equipped with a condenser containing solid $CO_2$–acetone slush, and trimethylamine (45 $cm^3$, 0.50 mol) was allowed to evaporate into the solution. The mixture was stirred and warmed under reflux during dropwise addition of trimethylboroxine (10.2 g, 0.08 mol; Aldrich) in ether (40 $cm^3$). After the addition was complete, the mixture was heated under reflux for 1.5 h, then cooled using an ice–salt bath during *cautious* dropwise addition of water (30.5 $cm^3$). Anhydrous $MgSO_4$ (*ca.* 20 g) was added and the mixture was left to stand at room temperature overnight. The mixture was filtered under argon, the filtrate was dried further ($MgSO_4$), ether was removed under reduced pressure and the residue was distilled to yield trimethylamine–methylborane (14.4 g, 70%), b.p. 60 °C at

16 Torr. $\delta_H$ −0.20 (br t, 3 H, MeB), 1.80 (q, 2.H, *J* 95, $BH_2$) and 2.52 (s, 9 H, MeN); $\delta_B$ −3.8 (t, *J* 95).

*Diethyl 2-Bromoethylmalonate.*[47]—Diethylcyclopropane-1,1-dicarboxylate (10.32 g, 0.055 mol; Aldrich) was weighed into a dry, argon-filled, two-necked, flat-bottomed flask containing a magnetic stirrer bar. One neck was connected through an air condenser to a bubbler and the other neck was fitted with a gas inlet tube through which either argon or dry HBr gas could be passed. The flask was immersed in a water bath (20 °C) and the contents stirred while HBr gas was bubbled slowly through the liquid. The weight gain was determined periodically after flushing out the flask with argon. When HBr (4.22 g, 0.052 mol) had been absorbed (5–10 min bubbling) analysis by $^1H$ NMR spectroscopy showed the presence only of residual cyclopropanedicarboxylate (5%) and diethyl 2-bromoethylmalonate (95%); $\delta_H$ 1.28 (t, 6 H, Me), 2.44 (q, 2 H, $CH_2CH$), 3.46 (t, 2 H, $CH_2Br$), 3.66 (t, 1 H, CH) and 4.22 (q, 4 H, $CH_2O$). This mixture was used without purification.

$^{13}C$-Labelled *tert*-butyl isocyanide was prepared according to the method of Nef,[19b,48] from *tert*-butyl iodide and labelled silver cyanide, itself prepared from $K^{13}CN$ (Aldrich; 99% atom% $^{13}C$) diluted with normal KCN. The remaining compounds used in this work were obtained commercially and were purified, if necessary, using standard methods.

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