Transformations of Ethoxycarbonyl-substituted But-3-enyl and Cyclopropylmethyl Radicals: Characterisation by E.S.R. Spectroscopy

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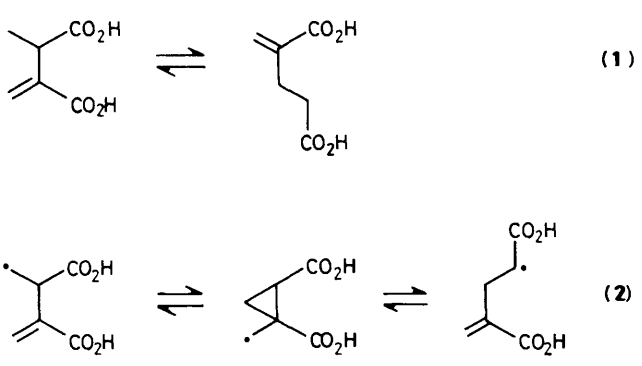
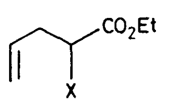
Ethoxycarbonyl-substituted but-3-enyl and cyclopropylmethyl radicals were generated from the corresponding halides by treatment with tributyltin and triethylsilyl radicals in cyclopropane solution; the radicals were characterised by e.s.r. spectroscopy and the rearrangement at −40 °C of the 3-ethoxycarbonylbut-1-enyl radical to the 1-ethoxycarbonylbut-1-enyl radical was demonstrated.

The adenosylcobalamin-dependent enzyme α-methyleneglutarate mutase catalyses the interconversion of 2-methylenepentane-1,5-dioic acid (α-methyleneglutarate) with 2-methyl-3-methylenebutane-1,4-dioic acid [equation (1)].[1–3] We concluded from model studies of but-3-enyl- and cyclopropylmethyl-cobaloximes that organocobalt intermediates were not plausible for this reaction.[4] Rather, it was inferred that carboxy-substituted but-3-enyl and cyclopropylmethyl radicals were intermediates in the enzymic reaction [equation (2)].

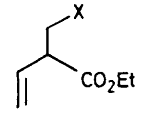
In contrast, Dowd and co-workers[5] have recently re-iterated their belief, based on studies of the chemistry of certain



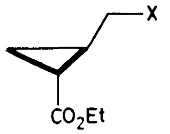
Scheme 1



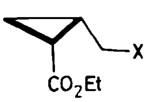
(1)



(2)



(3)



(4)

a; X = Br
b; X = free electron
c; X = Co(dmgH)$_2$py (dmgH = monoanion of dimethylglyoxime; py = pyridine)

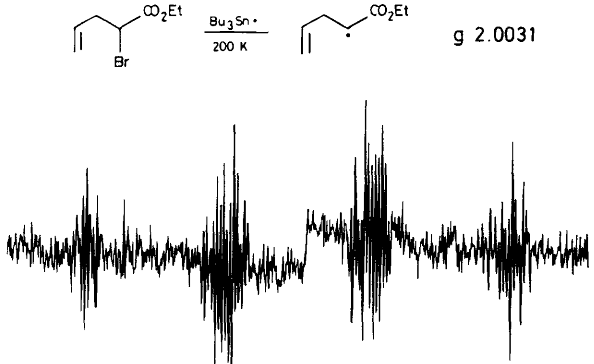


Figure 1

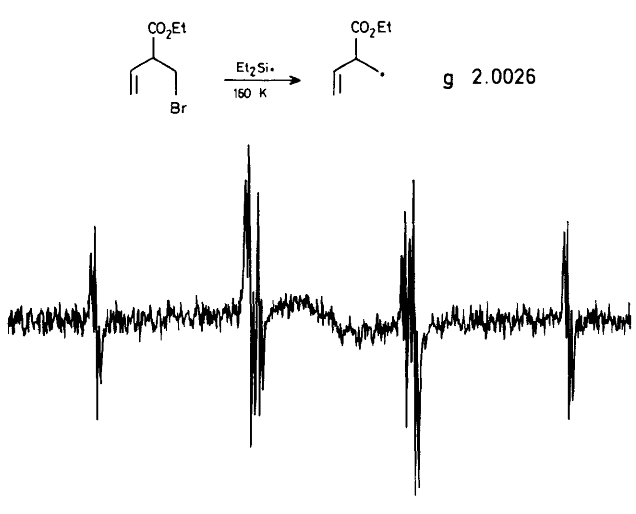


Figure 2

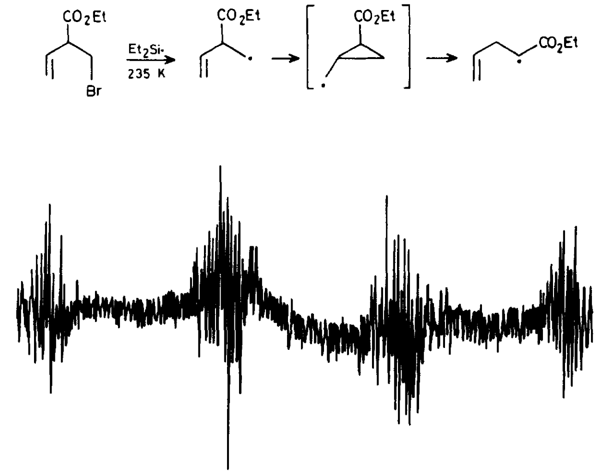


Figure 3

alkylcobalamins, that the α-methyleneglutarate mutase reaction proceeds *via* organocorrinoid intermediates. To complement model studies with organocobalt compounds we have attempted to prepare ethoxycarbonyl-substituted but-3-enyl and cyclopropylmethyl radicals from the corresponding halides (**1a**)—(**4a**) in order to characterise them by e.s.r. spectroscopy, and to study their interconversions.

Radicals were generated by irradiating, with ultraviolet light, solutions of the halides in cyclopropane containing either hexabutylditin, or a mixture of triethylsilane and di-t-butyl peroxide, initially at *ca.* 173 K. Under these conditions, halides (**1a**), (**3a**), and (**4a**)[4] all gave radical (**1b**) with a(H) 23.15, 22.0, 21.5, 1.63, 1.13, and 0.5 G, g 2.0031, at 200 K. The spectrum is shown in Figure 1; although it is surprising that the two β-hydrogen atoms should apparently be slightly non-equivalent, simulations in which a single value for a(2Hβ) were assumed were less satisfactory. The high g value is characteristic of an α-carbonylalkyl radical.

At 160 K, halide (**2a**)[4] gave radical (**2b**) with a(2Hα) 22.35, a(Hβ) 23.6, a(2H) 0.5 G, g 2.0026 (see Figure 2). When the solution of the radical (**2b**) was warmed, the spectrum began to change at 223 K, and at 235 K it showed the spectrum illustrated in Figure 3, which can be simulated as a 1 : 1 mixture of the radicals (**2b**) and (**1b**). At higher temperature, the spectrum was lost.† The rearrangement of (**2b**) to (**1b**) presumably occurs by ring-closure to (**3b**) and/or (**4b**), then ring re-opening.

The results described show the clean rearrangement of the 3-ethoxycarbonylbut-1-enyl radical (**2b**) to the 1-ethoxycar-

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† The radicals were also generated by γ-radiolysis of the halides in a CD$_3$OD matrix at 77 K.[6] Halides (**1a**) and (**2a**) gave the corresponding radicals (**1b**) and (**2b**), and halides (**3a**) and (**4a**) gave radical (**1b**) directly. However, if the matrix containing (**2b**) was allowed to warm up, the spectrum was lost before any transition to the spectrum of (**1b**) could be observed.

bonylbut-1-enyl (**1b**) at 223 K. This is thermodynamically favourable because the ester carbonyl of (**1b**) can stabilise the adjacent radical centre. The cyclopropylmethyl radicals (**3b**) and (**4b**) are both kinetically competent intermediates for the converson of (**2b**) into (**1b**).

In contrast to the rapid rearrangements observed with the free radicals (**1b**)—(**4b**), the corresponding cobaloximes (**1c**)—(**3c**) are thermally stable at room temperature[4] [*n.b.* (**4c**) has not been prepared]. This supports the postulated intermediacy of radicals [equation (2)], and not the corresponding organocorrinoids, in the α-methyleneglutarate mutase reaction [equation (1)].

Received, 2nd November 1987; Com. 1587

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