Ene Reactions of Alkylallenes

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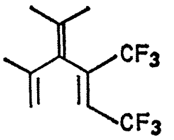
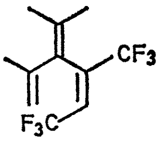
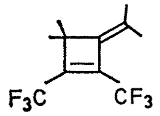
Summary Ene reactions between tetramethylallene and electron-deficient acetylenes lead to cross-conjugated trienes, possibly *via* a two-step reaction mechanism.

Two recent reports[1,2] describing ene reactions[3] between allenes and arynes or diaryl thioketones prompt us to communicate our own findings in this area. Treatment of tetramethylallene with electron-deficient acetylenes RC⋮CR (where R = CF_3 or CO_2Me) at 60—80° leads to smooth ene reactions in which the enophile becomes attached to the central carbon atom of the allene, and provides an unusually simple route to cross-conjugated trienes.

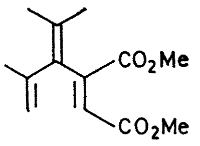

(I)

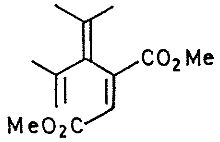

(II)


(III)

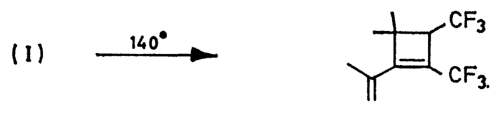
Thus, tetramethylallene and hexafluorobut-2-yne react at 80° to give a mixture of three isomeric 1:1 adducts in the ratio 78:8:11, which were separated by gas chromatography and identified spectroscopically as, respectively, the ene-adducts (I) and (II) and the cycloadduct (III). Both of the ene-adducts contained the $Me_2C:C(X)\cdot CMe:CH_2$ and the $:CH\cdot CF_3$ groupings, accompanied by a second $CF_3C:$ group; they must therefore be geometrical isomers. In the principal isomer (I), b.p. 152—153°, the F–F coupling (J_{FF} 10 Hz) is much stronger than in the minor isomer (II), b.p. 136°, for which $J_{FF} \leqslant 2$ Hz, indicating that (I) contains *cis*-CF_3 groups and (II) *trans*-CF_3 groups.[4] Furthermore, the low-field proton quartet of isomer (I) lies at τ 4·5 (J_{HF} 8·6 Hz), whereas that of isomer (II) resonates at τ 3·8 (J_{HF} 7·2 Hz) because, presumably, it is deshielded by the CF_3 group *cis* to it.

The corresponding reaction between tetramethylallene and dimethyl acetylenedicarboxylate is best carried out in benzene solution, to avoid rearrangement of the allene to 2,4-dimethylpenta-1,3-diene[5] and to minimise polymerisation of the product. At 60—65° a 40% yield of a mixture of two isomeric 1:1 adducts was obtained; in this case both are ene-adducts, formed in almost equimolar proportion and separable by spinning-band distillation. The higher-boiling adduct (IV) displays a low-field proton singlet at τ 4·3, whereas the corresponding resonance in the low-boiling isomer (V) appears to be relatively deshielded (τ 3·3), in agreement with the known tendency of a *cis*-CO_2R group to deshield a vinyl proton by *ca.* 1 p.p.m. relative to a *trans*-isomer.[6]


(IV)


(V)

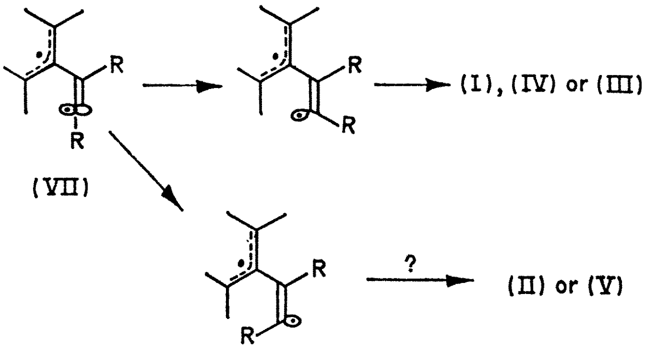
To our knowledge this is the first report of the formation of a *trans*-olefin by the ene reaction of an acetylene, although there are hints in earlier work that such isomers may have been formed.[7] A concerted mechanism may explain the formation of *cis*-adducts such as (I) and (IV), but appears to be less viable for *trans*-adducts (II) and (V), for which the orbitally required *anti–anti* geometry of approach[3] is highly hindered in these examples. We exclude the possibility that (I) and (IV) are formed first and then partially rearrange to (II) and (V), because we found by separate experiments that (IV) and (V) are not interconverted in refluxing benzene, and that (I) is unchanged at temperatures below 100°. After 48 h at 140°, however, (I) is almost completely converted into a fourth isomer, identified as the electrocyclic rearrangement product (VI).



(VI)

We further found, in a series of small-scale reactions between hexafluorobut-2-yne and tetramethylallene at four temperatures in the admittedly limited temperature range

80—140°, that the g.l.c.-determined product ratios (II)/(I + VI) and (III)/(I + VI) remained essentially constant.



This suggests that these three initial products (I), (II), and (III) do not arise by two or more competing pathways *via* significantly different transition states. In view of the generally accepted view that allene cycloadditions proceed *via* intermediate diradicals,[8] the experimental data seem rather to indicate that such a diradical (VII) is a common intermediate leading to all three types of product. Vinyl radicals are known to lose their stereochemical integrity,[9] so that (VII) can obviously adopt a *cis*-configuration favourable to the formation of either a cyclobutane, *e.g.*, (III), or a *cis*-adduct such as (I) and (IV). However, we are puzzled by one remaining problem: how does the diradical collapse to adducts such as (II) and (V), in which the groups R adopt a *trans*-geometry? Molecular models indicate that a *trans*-configuration in the diradical will make it difficult for a hydrogen atom to be captured intramolecularly.

A final conclusion regarding the mechanism must therefore await further investigation.

Ene reactions have also been achieved between tetramethylallene and (i) $CF_3{\cdot}C{\vdots}CH$, giving $CH_2{:}CMe{\cdot}C({:}CMe_2){\cdot}CH{:}CH{\cdot}CF_3$, (ii) $CF_3{\cdot}NO$, giving $CH_2{:}CMe{\cdot}C({:}CMe_2){\cdot}N(OH){\cdot}CF_3$, and (iii) $EtO_2C{\cdot}N{:}N{\cdot}CO_2Et$,[10] giving $CH_2{:}CMe{\cdot}C({:}CMe_2){\cdot}N(CO_2Et){\cdot}NH{\cdot}CO_2Et$, and between 1,1-dimethylallene and hexafluoroacetone, giving $CH_2{:}CMe{\cdot}C({:}CH_2){\cdot}C(OH)\,(CF_3)_2$.[11] Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds.

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