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Diels–Alder Cycloadditions of Vinyl- and Propenyl-allene to Methyl Vinyl Ketone

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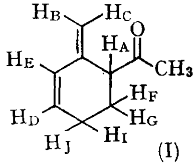
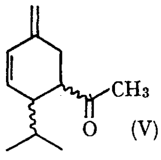
DIELS–ALDER reactions[1] involving vinylallenes have been little studied, especially from the mechanistic point of view.[2,3] Accordingly, information on directional effects on such [4 + 2] cycloadditions is particularly pertinent.

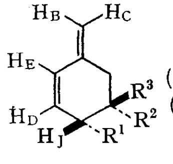
The interaction of equimolar quantities of vinylallene[4] and methyl vinyl ketone for 3 hr. at 100°, in a sealed tube gave two isomeric 1 : 1 adducts, in a 60% overall yield. Separation was effected by v.p.c., on a 9-foot-long Carbowax column at 135°. Structure (I) was assigned to the minor isomer (30%), and structure (II) to the major isomer (70%), on the basis of their spectral characteristics (Table), and their aromatisation to *o*- and *m*-methylacetophenone respectively.†



(I)



(V)



(II) $R^1=R^2=H$, $R^3=CO{\cdot}CH_3$
(III) $R^1=CH_3{}^A$, $R^2=H_I$, $R^3=CO{\cdot}CH_3{}^B$
(IV) $R^1=CH_3{}^A$, $R^2=CO{\cdot}CH_3{}^B$, $R^3=H_I$

A mixture of 40% *cis*- and 60% *trans*-propenylallene reacted with methyl vinyl ketone under the same conditions as previously used. Reaction occurred with the *trans*-isomer only. Undoubtedly the *cis*-isomer was unreactive because it is predominantly in the transoid conformation.[5] A 1 : 1 adduct was obtained (50% overall yield). On separation by v.p.c., it was found that only one positional isomer had been formed, comprising the pair of diastereoisomers (III) and (IV). The major compound (III) (75%), which is the kinetic product, was found to have the methyl and acetyl groups *cis*, whereas the minor compound (IV) (25%) had the *trans*-arrangement. Both structures were substantiated by spectral data (Table) and by their degradation to 2,5-dimethylacetophenone. The 2-acetyl derivative corresponding to (I) was not obtained, and no [2 + 2] cycloaddition products could be isolated. Under basic conditions (NaOH/MeOH), diastereoisomer (III) isomerised to (IV), [75% of (IV) and 25% of (III)] showing it to be the thermodynamic product. The same equilibrium was established starting from either diastereoisomer.

The surprising result that the more hindered products are obtained can be ascribed to electronic effects. In propenylallene, the inductive and hyperconjugative effects will render the central carbon of the allenic diene electron-rich. In the methyl vinyl ketone, on the other hand, the terminal vinylic carbon is electron-deficient because of carbonyl polarisation. Consequently, compound (III) is obtained as the kinetic product,

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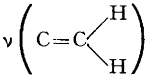
† Identified by their u.v. and n.m.r. spectra and their dinitrophenylhydrazone derivatives.

TABLE

	i.r.		u.v.	n.m.r.
Compound	$\nu_{C=O}$ (cm.$^{-1}$)	 $\nu\left(\mathrm{C{=}C}\lt^{\mathrm{H}}_{\mathrm{H}}\right)$ (cm.$^{-1}$)	λ_{max}[mμ(ϵ)](EtOH)	δ in p.p.m.; J in c./sec.
(I)	1720	890	230 (15,500)	H_E : q (δ 6·15; $J_{H_EH_D}$ 11; $J_{H_EH_C}$ 1·5) H_D : sext. (δ 5·79; $J_{H_DH_J} = J_{H_DH_I} = 3$) H_C : s[a] (δ 5); H_B : s[a] (δ 4·86); H_A : t (δ 3·19; $J_{H_AH_F} \sim J_{H_AH_G} = 4{\cdot}5$)
(II)	1710	880	231 (17,700)	H_E : q (δ 6·12); H_D : sext. (δ 5·75) H_B, H_C : s[a] (δ 4·8); CH_3 : s (δ 2·1)
(III)	1705	877	233 (17,800)	H_E : d (δ 6·1; $J_{H_GH_F}$ 10) H_D : q (δ 5·77; $J_{H_DH_J}$ 5) H_B, H_C : s[a] (δ 4·83); CH_{3B} : s (δ 2·1) CH_{3A} : d (δ 0·87; $J \sim 7$)
(IV)	1705	880	233 (12,800)	H_E : q (δ 6·1; $J_{H_EH_D}$ 10; $J_{H_EH_J} \sim 2$); H_D : m (δ 5·57); H_BH_C : s[a] (δ 4·82); CH_{3B} : s (δ 2·13); CH_{3A} : d (δ 0·98; $J \sim 7$)

s = singlet; t = triplet; q = quartet; sext. = sextuplet; m = multiplet.

[a] Slightly broadened singlet (the coupling between two geminal vinylic protons is known to be small).[8] The coupling of H_B and H_C with H_D and H_E is very small or equal to zero as shown by 100 MHz decoupling experiments.

according to the Alder "*endo*" rule [6] and the Woodward–Hoffmann rules[7] for concerted [4 + 2] cycloadditions.[1,5] It is interesting to note that the terminal bond of the allenic system—taken as a substituent—appears to have little effect on product orientation.

Finally, we would stress the synthetic applicability of these [4 + 2] cycloaddition reactions involving derivatives of vinylallene. Compounds such as (V), which possess the phelandrene skeleton, could be easily obtained, for example, by interaction of 2-methylbutenylallene and methyl vinyl ketone.

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