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A STEREOSELECTIVE SYNTHESIS OF TRISUBSTITUTED OLEFINS

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Since the structure of the insect juvenile hormone was published (1), several stereoselective syntheses of trisubstituted olefins have been reported (2-7). We have investigated the stereochemistry of the pyrolysis products of allyl acetoacetates (Carroll reaction) and have found it to be a good alternative method for producing trisubstituted olefins of known geometry.

The allyl acetoacetates were pyrolyzed in diphenyl ether at 220° (8) and the results are given in Table I. Good stereoselectivity was achieved when the steric requirements of the two non-vinyl groups attached to the carbinyl carbon were very different. If the methyl group is moved from the vinyl carbon to the carbinyl carbon, the reaction is no longer stereoselective (compare III and V). The Carroll reaction has generally been considered to be nonstereoselective because most of the compounds investigated were of the latter type, although surprisingly high selectivity was reported in one case (10). The pyrolysis of I has been noted to give <u>trans</u>-II (11,12).

By mechanism, the Carroll reaction is closely related to the Claisen rearrangement (10), the stereochemistry of which had been studied extensively (13-15). The transition states of these reactions have chair, cyclohexane-like conformations and the known stability of an equatorial methyl group over an axial methyl was given as the reason for the predominant production of <u>trans</u>-olefins. The same reasoning was invoked for the assignment of a <u>trans</u> configuration to trisubstituted olefins in the syntheses of sinensal (16) and dendrolasin (17). Compound V would give a <u>gem</u>-disubstituted chair, cyclohexane-like transition state with very little conformational preference.

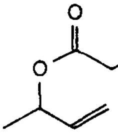
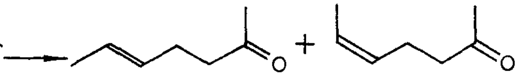
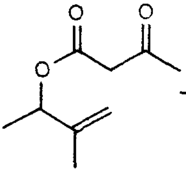
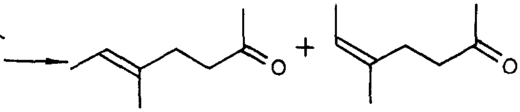
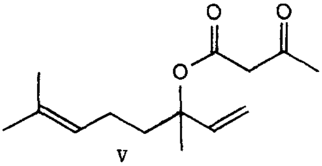
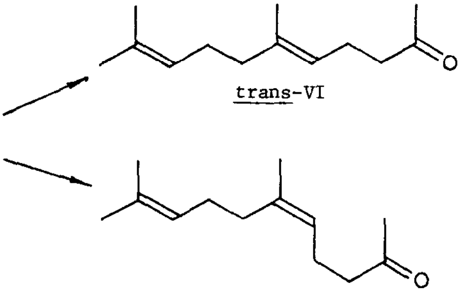
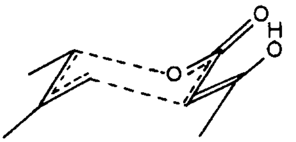
Reactant	Products	trans: cis	Total Yield
 I	 trans-II cis-II	97:3	76%
 III	 trans-IV cis-IV	93:7	85%
 V	 trans-VI cis-VI	54:46	67%

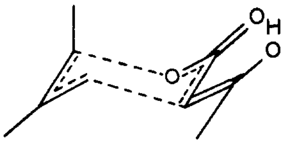
TABLE I

Proofs of Structure	
trans-II	Semicarbazone, mp 102-105 ($MeOH-H_2O$), lit. (8), mp 104.5-105.5; IR, 980 cm^{-1}.
cis-II	$C_7H_{12}O$ (Mass Spec.)
trans-IV	Semicarbazone, mp 121-123 ($MeOH-H_2O$); C, H by combustion; NMR, τ 8.44 (C-5 Me) (9).
cis-IV	$C_8H_{14}O$ (Mass Spec.); NMR, τ 8.38 (q; J, 1.5 Hz; C-5 Me).
trans- and cis-VI	Identical retention times on glc with commercial mixture of VI (K&K Laboratories) (19).

The difference in the heats of formation between axial and equatorial methylcyclohexanes is given as 1.8 kcal/mole, while ΔS is assumed to be zero (18). If we take this value to be the $\Delta\Delta F^{\ddagger}$ of the two conformers, VII and VIII, of the transition state leading to the products, cis- and trans-IV, we would expect, for a reaction carried out at 220°, a trans:cis ratio of 86:14. We would further expect this to be a high estimate because the two half-bonds lead to an elongated chair, with lessened skew and non bonded interactions. It is interesting that the actual ratios for compounds I and III (Table I) show a greater selectivity than is explainable by conformational argument only. The higher selectivity of compound I over compound III is probably due to product control.



VII



VIII

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