Regiospecific Control in the Formation of Cyclohexenes from Dienes. The Catalysed and Non-catalysed Reactions of Butadiene and 2,3-Dimethylbutadiene with Methyl Sorbate

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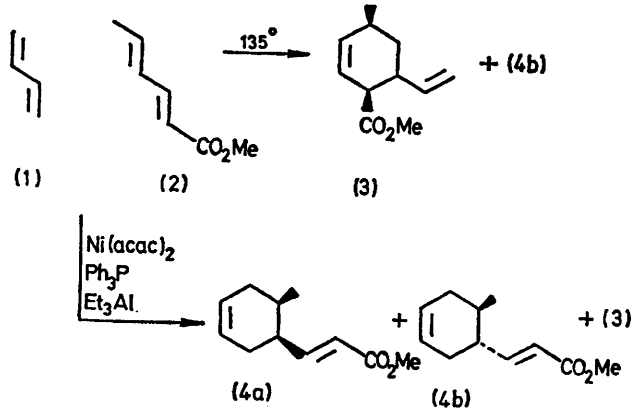
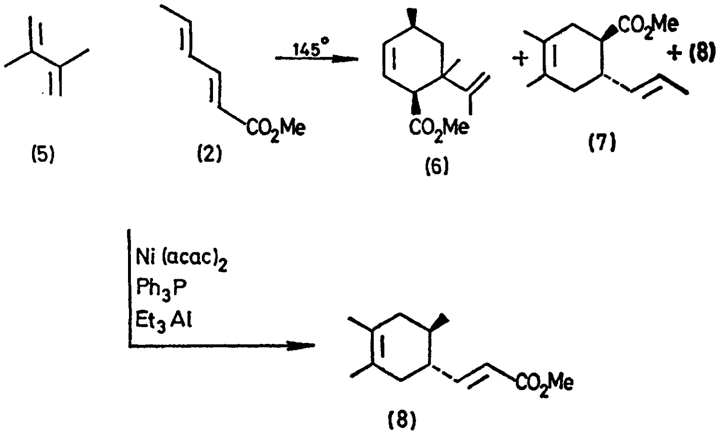
Summary The products derived from the reaction of methyl sorbate (**2**) with butadiene (**1**) and with 2,3-dimethylbutadiene (**5**) are altered by the presence of a nickel catalyst.

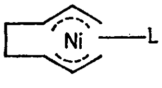
In the Diels–Alder reaction of butadiene (**1**) with methyl sorbate (**2**), the methyl sorbate behaves primarily as the diene component and the butadiene as the dienophile.[1] Thus, heating a 1:1 mixture of (**1**) and (**2**) at 125° gave, as the major products (60%),† (**3**)‡ and (**4b**) in the ratio *ca.* 20:1.§ When the reaction was carried out at 40° in the presence of a nickel catalyst $[Ni(acac)_2, Et_3Al, Ph_3P]$[2] using a 3:2 mixture of (**1**) and (**2**), the major products (90%)† were (**4a**) and (**4b**) (2:1),§ resulting from the apparent reaction of (**1**) as the diene and (**2**) as the dienophile.¶



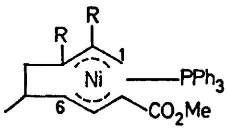
Heating 2,3-dimethylbutadiene (**5**) and (**2**) at 145°** gave a mixture (95%)† of three products. These were identified as (**6**)‡ (17%), (**7**) (42%), and (**8**) (37%).§ In this reaction (**5**) has behaved primarily as the diene and (**2**) as the dienophile.[1] There has been little selectivity between the two olefinic bonds of (**2**) in its reaction as the dienophile component. When the reaction of (**5**) and (**2**) was carried out in the presence of the nickel catalyst at 40°, the compound (**8**) was obtained as the major product (75%) of the reaction.† The only other products were derived from butadiene, which had been used to activate the catalyst. Compound (**8**) appeared to be one isomer, to which the *trans*-stereochemistry was assigned.§ The absence of *cis*-isomer corresponding to (**4a**) is presumably due to the steric requirements of the methyl groups in the transition state.



The presence of the nickel catalyst thus allows control of the cyclisation to give the product in which (**1**) or (**5**) acts as the 'diene' component, and in which the double bond in (**2**) that is remote from the methoxy-carbonyl group acts as the 'dienophile' component. Wilke[3] has suggested that the nickel-catalysed dimerisation of butadiene goes *via* an intermediate of type (**9**). A similar intermediate for the present reaction would be (**10**) and the ring closure would then have to occur preferentially between positions 1 and 6. Alternatively, catalysis and stereochemical control of a Diels–Alder type reaction may be occurring.[4]



(9)



(10) R=H, Me

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† Yields are based on recovered methyl sorbate.

‡ Mixture of two stereoisomers.

§ Satisfactory mass spectral and microanalytical results were obtained for all compounds. Structural and stereochemical assignments are based on the n.m.r. spectra and, where applicable, by consideration of the Alder '*cis*' rule. Product ratios are based on the n.m.r. spectra of the mixtures compared with those of the pure products.

¶ The ratio of (**4a**) to (**4b**) in the original mixture is probably greater, as the amount of (**4b**) in the mixture increases on heating.

** Similar results were obtained at 70°.

[1] For related findings with 1-cyanobuta-1,3-diene see H. R. Snyder and G. I. Poos, *J. Amer. Chem. Soc.*, 1949, **71**, 1057; 1950, **72**, 4096.

[2] W. Brenner, P. Heimbach, H. Hey, E. W. Muller, and G. Wilke, *Ann. Chem.*, 1969, **727**, 161.

[3] G. Wilke, *Angew. Chem. Internat. Edn.*, 1963, **2**, 105.

[4] See H. Wollweber, 'Houben-Weyl's Methoden der Organischen Chemie,' ed. E. Müller, 1970, Vol. 5/1C, 1072.