The Photolysis of Simple Acyclic 1,3-Dienes in Methanol

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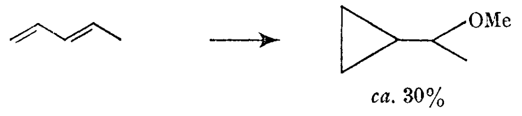
THE photoadditions of alcohols to conjugated, cyclic dienes held in a transoid conformation in the ground state have been extensively investigated.[1] Considerably less attention has been given to their acyclic counterparts,[1b,2] where both cisoid and transoid conformations are possible, although such reactions may be important synthetically.

We have irradiated all the mono- and di-methyl substituted buta-1,3-dienes in methanol. The products isolated are given in the Scheme; no other 1 : 1-adducts were present in yields >1%.

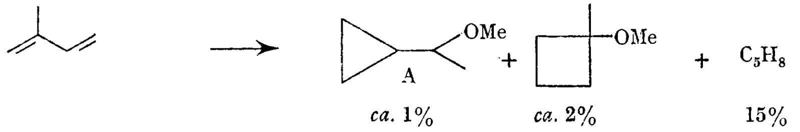
The dienes employed in steps (1), (3), and (7) were mixtures of geometric isomers. The irradiations were conducted in 0·5% or 1% solutions of the dienes, stirred and deoxygenated during the irradiations by bubbling a stream of dry oxygen-free nitrogen through them. The light source was a Hanovia 450 w medium-pressure mercury arc, filtered through quartz. Some of the products being photo-labile, the quoted yields are those obtained at small conversions, when the products absorb only a little of the light. These yields were calculated from plots of g.l.c. peak areas against irradiation time. Satisfactory analytical and spectroscopic data were obtained for all the products in the Scheme and the cyclopropyl ethers were identified by comparison with authentic samples prepared in this laboratory.

The cyclobutyl and cyclopropylcarbinyl ethers may be formed by addition of methanol to an intermediate bicyclobutane.[1,3] Bicyclobutane formation is known to accompany cyclobutene formation in non-polar solvents and in the vapour phase.[2,4] However, the allyl ethers are unlikely to be formed *via* a bicyclobutane, and their presence suggests a mechanism whereby the diene itself is protonated in an electronically-excited state or a vibrationally-excited ground state, to give a carbonium-ion intermediate.[5] A similar mechanism has been suggested for the photosensitised addition of methanol to olefins.[6]

Work is in progress on the mechanisms of these



(1)



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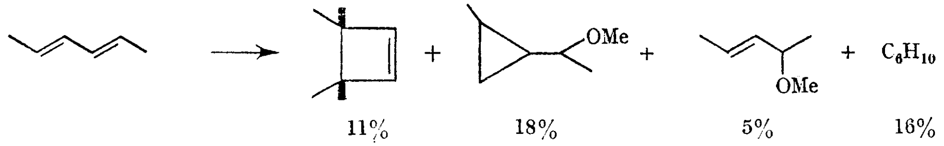

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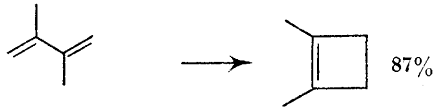

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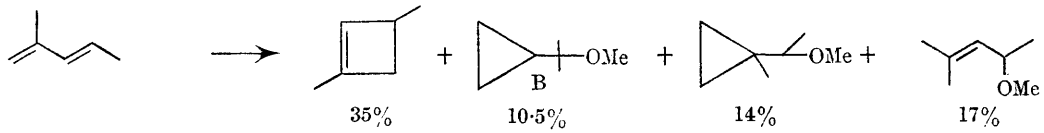

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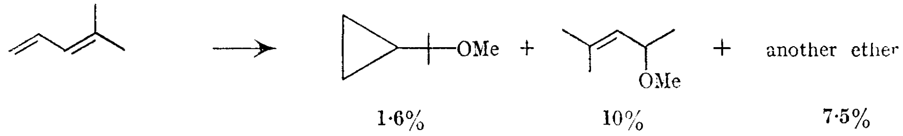

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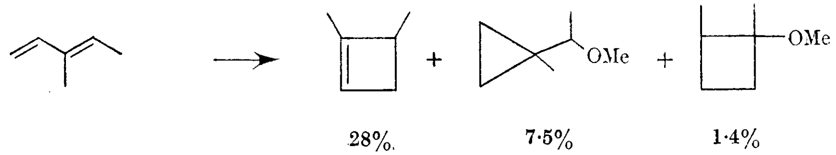

(7)

reactions but it is worth noting that when 3-methylpenta-1,3-diene was irradiated in pentane at room temperature and then treated with methanol, the same ethers were obtained as in scheme (7) and in similar proportions, suggesting the intervention of a bicyclobutane intermediate in this case. However, the cyclopropyl ethers A and B in schemes (2) and (5) can be directly formed neither from a bicyclobutane nor from a protonated excited state and clearly indicate the intervention of either a new mechanism or a molecular rearrangement.

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