

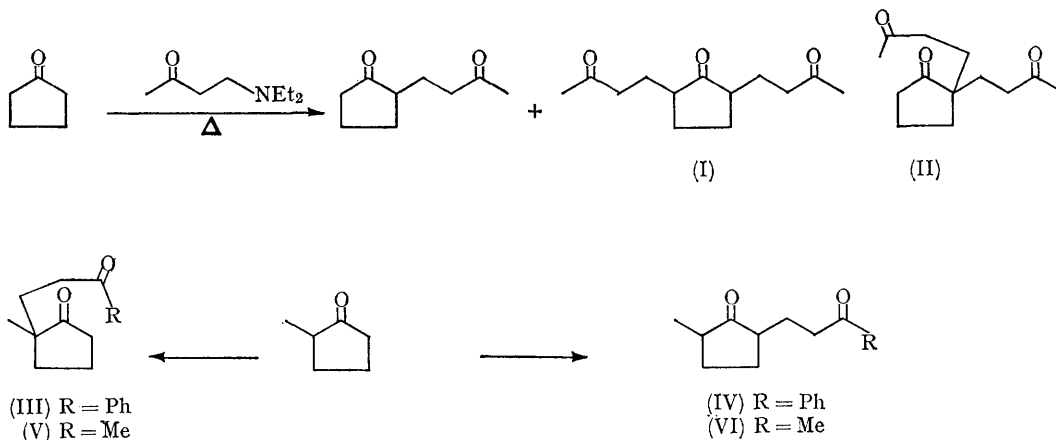
Orientation Control in the Michael Reaction

By G. L. BUCHANAN and G. W. McLAY

(Chemistry Department, University of Glasgow)

In a recent publication,¹ it has been noted that when the Michael addition of methyl vinyl ketone to cyclopentanone is carried out in the absence of strong base,² *i.e.*, by heating the related Mannich base in an excess of cyclopentanone, the di-addition by-product which is formed in low yield,

cm.⁻¹] in which the methyl signal appears as a doublet at τ 8.93 (J 7.0 c./sec.) and which is therefore formulated as (IV). Similar results accrue from experiments with methyl vinyl ketone and 4-dimethylaminobutan-2-one. In the presence of potassium hydroxide the former yields (V)⁵



has the 2,5-orientation (I), rather than the 2,2-orientation (II) normally encountered in the base-catalysed reaction.³ This observation prompts us to record our own experience of abnormal orientation.

When phenyl vinyl ketone is condensed with 2-methylcyclopentanone in the presence of potassium hydroxide,⁴ the product [m.p. 40—42°; ν_{CO} (CCl₄) 1736, 1689 cm.⁻¹] shows a sharp singlet (τ 8.98) for the methyl group, in the n.m.r. spectrum, as expected for structure (III).⁵ However, when β -dimethylaminopropiophenone is heated in 2-methylcyclopentanone, the main product (76%) is an isomer⁵ [m.p. 68—70°; ν_{CO} (CCl₄) 1739, 1692

[ν_{CO} (CCl₄) 1736, 1720 cm.⁻¹] showing a singlet methyl signal (τ 9.03) whilst the latter, on thermal decomposition in 2-methylcyclopentanone affords (VI)⁵ [ν_{CO} (CCl₄) 1739, 1723 cm.⁻¹] in which the methyl signal (τ 8.94) appears as a doublet (J 6.0 c./sec.).

It appears likely that the orientation effect described above will prove to be general,⁶ and that orientation in the Michael reaction can be controlled by choice of experimental conditions. The mechanism of the process is also of interest and will be discussed in a later communication.

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¹ H. O. House, B. M. Trost, R. W. Magin, R. G. Carlson, R. W. Franck, and G. H. Rasmusson, *J. Org. Chem.*, 1965, **30**, 2513.

² N. S. Gill, K. B. James, F. Lions, and K. T. Potts, *J. Amer. Chem. Soc.*, 1952, **74**, 4923.

³ E. D. Bergmann, D. Ginsburg, and R. Pappo, "Organic Reactions", R. Wiley and Sons, 1959, Vol. 10, p. 179.

⁴ N. C. Ross and R. Levine, *J. Org. Chem.*, 1964, **29**, 2341.

⁵ Satisfactory analysis figures obtained.

⁶ H. L. Brown and G. L. Buchanan, unpublished work.