

## Effect of Electron Withdrawing Groups on Grignard Reaction With Unsaturated Carbonyl Compounds.

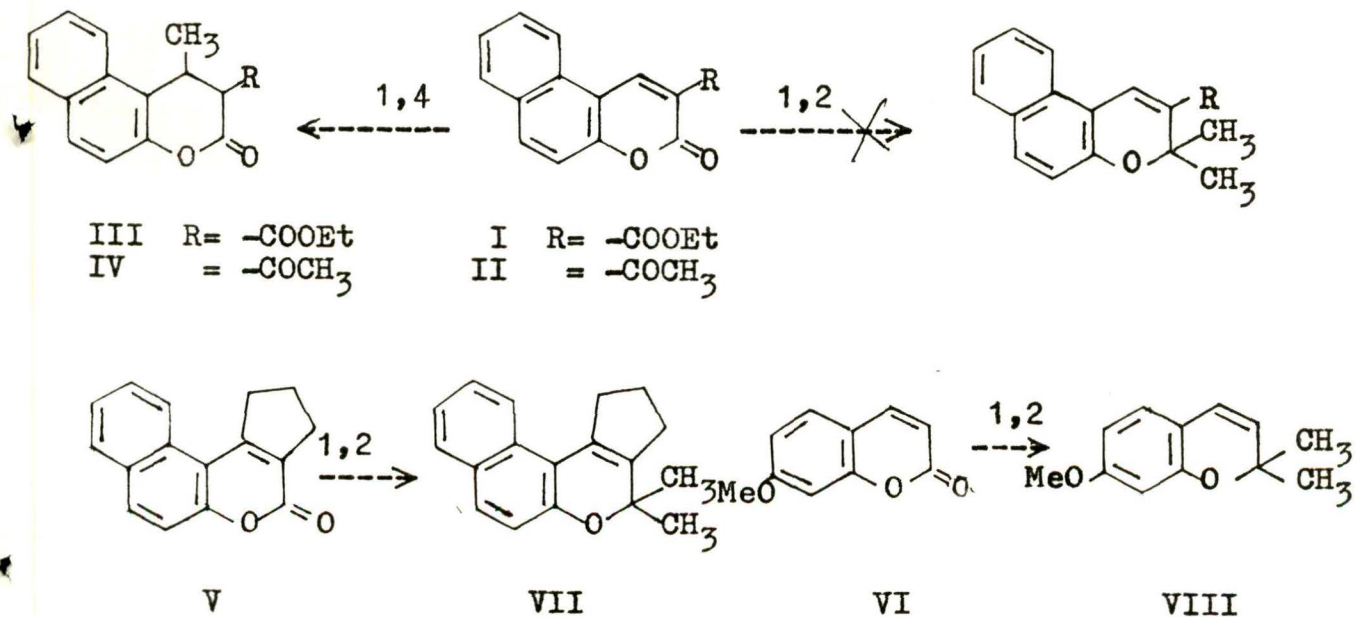
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**Abstract:** Addition of Grignard reagent to ethyl-[ 5,6 ] benzocoumarin 3-Carboxylate and 3-acetyl [ 5,6 ] benzocoumarin proceeds exclusively in the 1,4-fashion even in the absence of  $\text{Cu}^+$  ions.

It is well known that the mode of addition of Grignard reagents to unsaturated Carbonyl Compounds is influenced by  $\text{Cu}^+$  ions<sup>1</sup>. Whereas normal (1,2) addition takes place in the absence of  $\text{Cu}^+$  ions, conjugate addition takes place in their presence. We wish to report the unusual and exclusive 1,4 addition of the Grignard reagents to the coumarins ethyl[ 5,6 ]benzocoumarin-3-carboxylate (I) and 3-acetyl[ 5,6 ]benzocoumarin (II) in the absence of  $\text{Cu}^+$  ions. These compounds when reacted with methyl magnesium iodide according to the procedure of Cook and Wall<sup>2</sup> gave ethyl 4-methyl 3,4 dihydro[5,6]benzocoumarin-3-carboxylate (III) and 3-acetyl 4-methyl 3,4 dihydro[5,6]benzocoumarin (IV) respectively. The fact that Coumarins (V)<sup>3</sup> and (VI)<sup>4</sup> give normal addition products under the same conditions suggests that the electron withdrawing acetyl and ethoxy carbonyl groups at 3 position are responsible for this unusual behaviour. The structures of the adducts have been characterised by their spectra.



## Experimental:

A Solution of 2.5 mmol of the coumarins (I) and (II) in dry THF was added with stirring to a large excess (25 mmol) of methyl magnesium iodide in anhydrous ether under nitrogen atmosphere. Usual work-up gave the adducts (III) and (IV).

## Spectral Data

Compound (III): M.P.: 96°C; IR: 1715, 1755  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  in  $\text{CDCl}_3$ : 6H aromatic  $\delta$  8-7.2, 1H d  $\delta$  4.27, 2H q  $\delta$  4.0, d  $\delta$  1.53, 3H t  $\delta$  0.97; MS: 284 ( $\text{M}^+$ , 17), 211(100), 168(32), 115(33).

Compound (IV): M.P.: 114°C; IR: 1715, 1762  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  in  $\text{CDCl}_3$ : 1H s  $\delta$  13.2, 6H aromatic  $\delta$  8-7.2, 1H q  $\delta$  4.4, 3H d  $\delta$  1.5; MS: 254 ( $\text{M}^+$ , 28), 221(31) 211(100), 197(50).

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## References:

- 1a. M.S. Kharasch and O. Reinmuth, Grignard Reactions of Nonmetallic Substances, Prentice Hall, Englewood Cliffs, N.J., p 196-239, (1954).
- b. S. Patai and Z. Rapport, in "The Chemistry of Alkanes", S. Patai Ed., Interscience Publishers, New York, p 550, (1964).
- c. J. Munch-Peterson, Bull. Soc. Chim. Fr., p471 (1966) and references cited there in.
- d. K. Thornburg, Organic Chemistry Seminar, University of Illinois, Urbana, Illinois, Jan 6, 1969.
2. C.E. Cook and M.E. Wall, J. Org. Chem., **33**, 2998-3000, (1968).
3. M. Basak, G.S.S. Murthi and M. Murthi, Unpublished work.
4. John Mann and Peter D. Kane, Tet. Lett., **26**, 4677-4680, (1985).

**175. Addition of Grignard Reagent to Ethyl [5,6] Benzocoumarin-3-Carboxylate.**

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**Key words :** *Benzocoumarin-3-Carboxylate*

Addition of Methyl Magnesium Iodide to Ethyl [5, 6] Benzocoumarin-3-carboxylate exclusively takes place in the 1, 4 fashion even in the absence of Cuprous iodide. The structurally similar 3, 4-cyclopenteno derivative gave 1, 2 adduct under identical conditions. The structures of the adducts have been established by spectral studies.

## ADDITION OF GRIGNARD REAGENT TO ETHYL [5,6] BENZOCOUMARIN-3-CARBOXYLATE.

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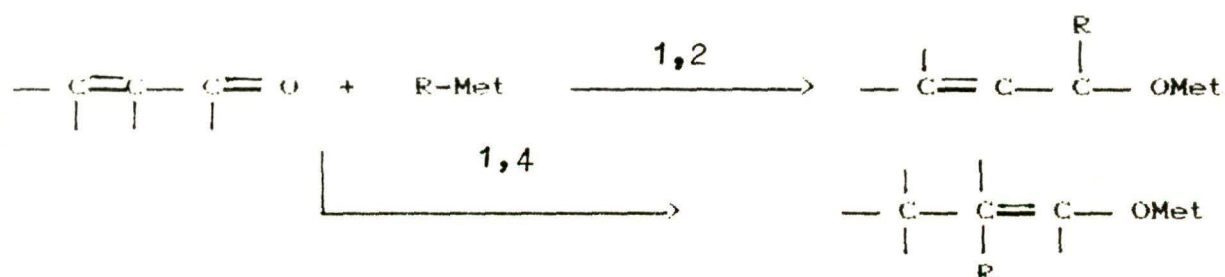
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ABSTRACT: ADDITION OF METHYL MAGNESIUM IODIDE TO ETHYL [5,6] BENZOCOUMARIN-3-CARBOXYLATE EXCLUSIVELY TAKES PLACE IN THE 1,4-FASHION EVEN IN THE ABSENCE OF CUPROUS IODIDE. THE STRUCTURALLY SIMILAR 3,4-CYCLOPENTO DERIVATIVE GAVE 1,2 ADDUCT UNDER IDENTICAL CONDITIONS. THE STRUCTURE OF THE ADDUCTS HAVE BEEN ESTABLISHED BY SPECTRAL STUDIES.

Addition of an organometallic reagent to an  $\alpha,\beta$ -unsaturated carbonyl compound occurs in one or both of two modes: attack at the carbonyl function products 1,2 adduct, whereas reaction with the entire conjugated system gives a 1,4 adduct.



Addition of Grignard reagents to  $\alpha,\beta$ -unsaturated carbonyl systems normally gives 1,2 adducts and in systems where the carbonyl group is sterically inaccessible the Grignard addition often gives 1,4 adducts