

CHROMONES FROM ACYLSALICYLIC ACIDS

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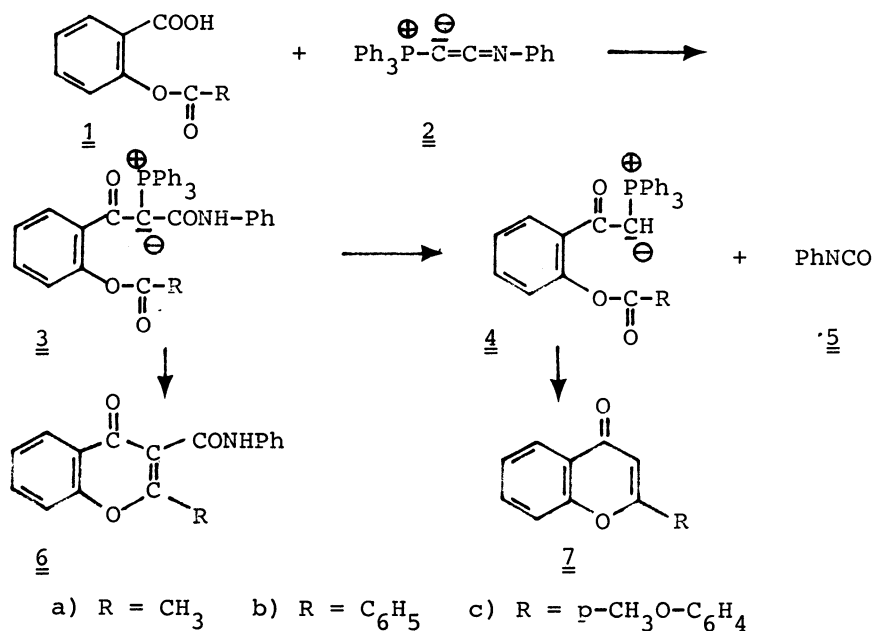
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Acylsalicylic acids 1 can be converted by reaction with N-Phenylketeniminylidene triphenylphosphorane 2 into chromones 6 or 7.

The OH-group of free carboxylic acids 1 can be substituted by the ylide function ¹⁾ when they are reacted with N-phenylketeniminylidene triphenylphosphorane 2. ²⁾ This reaction sequence allows the synthesis of chromones 6 and 7 starting from acylsalicylic acids 1.

Formula:



When acetylsalicylic acid 1 is converted with N-phenylketeniminylidene triphenylphosphorane 2 in acetic ester (30 min room temperature and subsequently 4h heating under reflux), the 3-(2-acetoxyphenyl)-3-oxo-2-(triphenylphosphoranylidene)-propanoic acid anilide 3a is formed ³⁾ [67% yield, colourless crystals, mp 150°C (dec.)]. When 3a is heated for 12h in toluene to which 5 volume percents

ethanol were added, then 2-methyl-4-oxo-4H-benzopyran-3-carboxanilide 6⁴) (45% yield, mp 128°C) as well as 2-methyl-4H-1-benzopyran-4-one 7a⁵) (37% yield, mp 70°C) can be isolated by chromatography with silica gel 60 (eluent diethyl ether). The reaction rate of the intra-molecular Wittig reaction with the ester carbonyl function of 3a, giving 6a, apparently is of the same order as the cleavage of phenyl isocyanate 5 (trapped by the alcohol present) and the formation of 4a, subsequently affording 7a via intramolecular estercarbonyl olefination. The reactants, 1b and 1c were reacted with 2 for 4 h in toluene (60°C), the 5 volume percents ethanol added and heated for 12 h under reflux. The compounds 7b (75% yield, mp 96°C⁶) and 7c (87% yield, mp 158°C⁷), respectively, were isolated. The formation of 6b and 6c could not be proven.

The course of an intramolecular Wittig reaction of acyl ylides with ester carbonyl groups, not found with open chain compounds, we deduce on entropic effects⁸).

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References

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