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CHROMONES FROM ACYLSALICYLIC ACIDS

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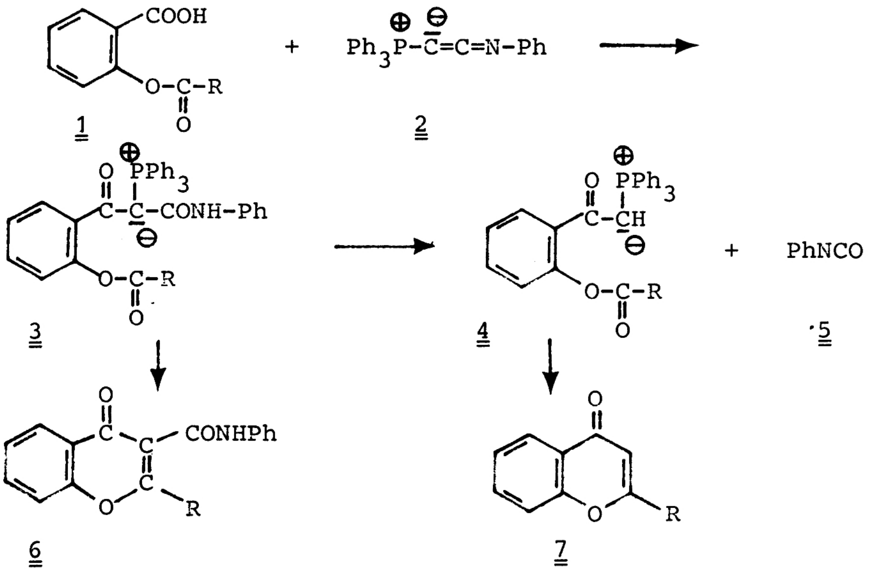
Acylsalicylic acids 1 can be converted by reaction with N-Phenylketeniminylidene triphenylphosphorane 2 into chromones 6 or 7.

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:



a) $R = CH_3$ b) $R = C_6H_5$ c) $R = p\text{-}CH_3O\text{-}C_6H_4$

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-4*H*-benzopyran-3-carboxanilide **6**4) (45% yield, mp 128°C) as well as 2-methyl-4*H*-1-benzopyran-4-one **7a**5) (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 been 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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