

Benzopyran derivatives

R 0350

16- 147

Trifluoromethanesulfonic Acid Mediated Friedel—Crafts Reaction of (E)-3-Aryl-2-(diethoxyphosphoryl)acrylic Acids with Electron-Rich Hydroxyarenes. A Convenient Approach to α -Methylene- δ -valerolactones. — Generally, TfOH is found to be the more efficient agent in the preparation of the trans-coumarin skeleton, present in natural products and pharmaceutical substances. In the case of substrate (XIV), however, only MesOH causes the desired transformation (during several weeks). The process is completely regio- and stereoselective, which is especially of interest in the case of dihydroxynaphthalenes such as (X). Horner—Wadsworth—Emmons olefination of the products allows the facile preparation of α -methylene- δ -valerolactones. — (KRAWCZYK*, H.; ALBRECHT, L.; WOJCIECHOWSKI, J.; WOLF, W. M.; Tetrahedron 63 (2007) 51, 12583-12594; Inst. Org. Chem., Tech. Univ., PL-90-924 Lodz, Pol.; Eng.) — Lindner

B): 2 equiv. TfOH, CH₂Cl₂, 25°C

c 94%

C): THF, 25°C, [90 min]

R1 Poe HOO
$$=$$
 R1 Poe HOO $=$ R1 Poe Excess (IV) $=$ R2 Tmp Poe Excess (IV) $=$ R1 Poe Excess (IV) $=$ R2 Tmp Poe Excess (IV) $=$ R1 Poe Excess (IV) $=$ R1 Poe Excess (IV) $=$ R2 Tmp Poe Excess (IV) $=$ R1 Poe $=$ R2 Tmp Poe Excess (IV) $=$ R1 Poe $=$ R2 Tmp Poe $=$ R3 Poe $=$ R4 Poe $=$ R4 Poe $=$ R5 Poe $=$ R6 Poe $=$ R6 Poe $=$ R6 Poe $=$ R7 Poe $=$ R6 Poe $=$ R7 Poe $=$ R7 Poe $=$ R8 Poe $=$ R9 Poe $=$ R8 Poe $=$ R9 Poe $=$ R8 Poe $=$ R9 Poe $=$ R9



$$\begin{array}{c} (XI). \ A) \\ O \longrightarrow OH \\ \hline [-> a] [34 \ d] \\ [-> b] [58 \ d] \end{array} \begin{array}{c} O \longrightarrow Ar^2 \\ O \longrightarrow OO \\ OO \end{array} \begin{array}{c} Ar^2 \\ C \longrightarrow OO \\ OO \end{array} \begin{array}{c} Ar^2 \\ C \longrightarrow OO \\ OO \end{array} \begin{array}{c} Ar^2 \\ C \longrightarrow OO \\ OO \end{array} \begin{array}{c} Ar^2 \\ C \longrightarrow OO \\ OO \end{array} \begin{array}{c} Ar^2 \\ C \longrightarrow OO \\ OO \end{array} \begin{array}{c} Ar^2 \\ C \longrightarrow OO \\ OO \bigcirc OO \\ OO \bigcirc OO \end{array}$$