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Synthesis of 4'-Methoxy Flavone

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Abstract: Synthesis of 4'-methoxyflavone, first by the reaction of 4－methoxy acetophenone enamine with heptanedioyl chloride , then by dehydrogenation, is described.

Keywords: Enamine, heptanedioyl chloride, tetrahydroflavone, flavone, synthesis.

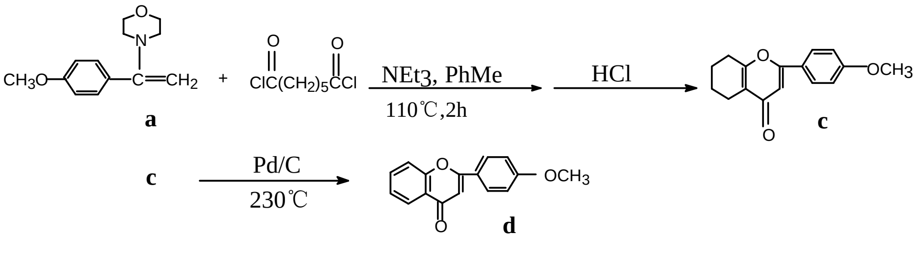
The flavones are obtained mainly from nature, secondly by biological synthesis. The chemical synthesis is carried out mostly by cyclization and condensation of o-hydroxyacetophenone[1,2,3], or by dehydrogenation of flavanones[4,5,6]. Here we report a new synthetic method of flavones by the reaction of enamine and heptanedioyl chloride.

Acylation of 2 mole enamine with 1 mole chloride of dicarboxylic acid has been used to prepare bis-(1,3-diketone) compound[7], but we discovered that 4'-methoxy-5,6,7,8-tetrahydroflavone prepared by reaction of 4-methoxy acetophenone enamine with heptanedioyl chloride in 80% can be easily transformed to 4'-methoxy flavone.

4'-Methoxy flavone was prepared *via* 3 steps, first by the reaction of 1 mole 4-methoxy acetophenone enamine with 1 mole heptanedioyl chloride dissolved in toluene in the presence of triethylamine at refluxing temperature for 2 hours, and then by hydrolysis with 3mol/L hydrochloric acid, finally by dehydrogenation with Pd/C catalyst in diphenyl ether under the normal pressure at about 230℃. The overall procedure is shown in **scheme 1.**

The structure of compound **c** and **d**, which have not been reported, were confirmed by elementary analysis, IR, and ^{1}H NMR spectra[8]. Moreover, the crystal structure of **c** was determined by a single-crystal X-ray diffraction to testify the new reaction and the compound **c.**

Scheme 1



4'-Methyl flavanone was also obtained with the same synthetic method.

Acknowledgment

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References and notes

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8. Spectroscopic data of compounds

c: pink crystal, m. p 149. 0-150. 0℃. IR (KBr, cm^{-1}) 3075(Ar-H), 1651(C=O), 1605(C=C) , 1173(C=C-O-C=C). ^{1}H NMR (CDCl$_3$, δ ppm) : 7. 00-7. 75(m, 4H, Ar-H), 6. 76(s, 1H, CH=), 3. 88(s, 3H, CH$_3$O), 2. 67-2. 70(t, 2H, CH$_2$), 2. 51-2. 54(t, 2H, CH$_2$), 1. 87-1. 90(m, 2H, CH$_2$), 1. 75-1. 78(m, 2H, CH$_2$).
Anal. for $C_{16}H_{16}O_3$: Calcd: C,74. 98; H, 6. 30; Found: C, 74. 88; H, 6. 29.
d: pale crystal, m. p 158. 0-159. 0℃. IR(KBr, cm^{-1}): 3047(Ar-H), 1648(C=O), 1514(C=C), 1127(C=C-O-C=C). ^{1}H NMR (CDCl$_3$, δ ppm): 7. 0-8. 0(m, 8H, Ar-H), 6. 78(s, 1H, CH=), 3. 85(s, 3H, CH$_3$O) .
Anal. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80; Found: C, 75.96; H, 4.79 .

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