Improvement of selectivity in the Fries rearrangement and direct acylation reactions by means of P_2O_5/SiO_2 under microwave irradiation in solvent-free media

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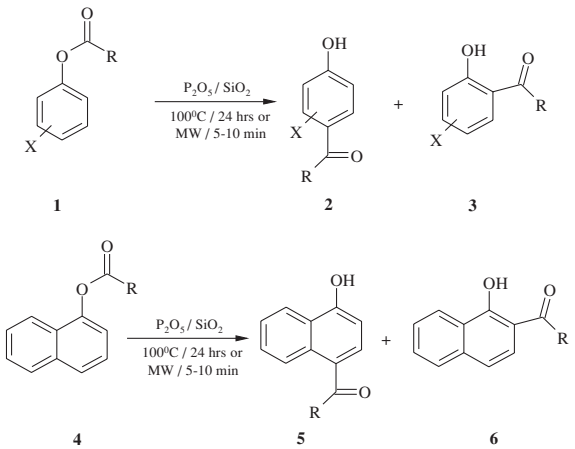
P_2O_5 / SiO_2 was found to be an efficient new reagent in the Fries rearrangement of acyloxy benzene or naphthalene derivatives and the direct acylation reactions of phenol and naphthol derivatives with carboxylic acids under microwave irradiation in solvent-free media.

Keywords: Fries rearrangement, direct acylation, microwave irradiation, phosphorous pentoxide

The Fries rearrangement is a synthetically useful reaction for the preparation of hydroxyaryl ketones not only in the laboratory but also in industrial processes.[5] New catalysts such as $Hf(OTf)_4$,[7] $Sc(OTf)_3$,[8] $ZrCl_4$,[9] montmorillonite clays[10] and methanesulfonic acid / phosphorus oxychloride[11] have been developed recently for this reaction. However, most of these catalysts suffer from serious drawbacks which include the use of hazardous and expensive or commercially unavailable reagents, long reaction times, low yields, drastic reaction conditions and tedious workup procedures. Earlier reports[16-19, 21] of the Fries rearrangement using microwave heating suffer from disadvantages such as lack of regioselectivity, versatility and the use of sealed tubes, which can cause hazards due to the high pressures built up causing explosion during reactions. Therefore, the development of a new catalyst, which promotes direct acylation or the Fries rearrangement cleanly and regioselectively, is required.

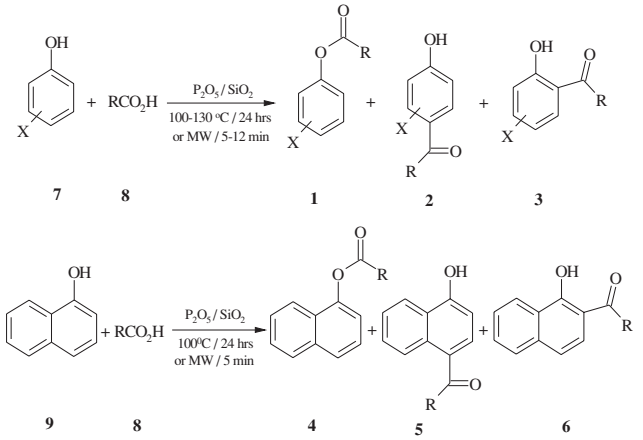
It appeared that Lewis acids supported on a solid phase could be good alternative reagent for this reaction involving solvent-free media.[22] Recently, we have reported that P_2O_5 / SiO_2 is an efficient medium for the esterification of phenols[23] and Beckmann-type rearrangement of ketones.[24] In this paper, we describe the Fries rearrangement of acyloxy benzene and naphthalene derivatives (Scheme 1) and also the direct acylation of phenol and naphthol derivatives with carboxylic acids (Scheme 2) using the P_2O_5 / SiO_2 reagent thermally or under microwave dielectric heating (MW) in solvent-free media.



Scheme 1

When 3-methylphenyl acetate **1b** was heated at 100 °C in the presence of P_2O_5 / SiO_2 in solvent-free conditions, the *ortho*-product **3b** was obtained regioselectively in 70% yield. Whereas, this reaction under microwave irradiation for only 5 min, exclusively gave after work up, the *ortho*-directed product (Entry 4). Several further examples have been examined and compared with the conventional heating method. The completion of the reactions was monitored by TLC and by IR spectroscopy. In most cases, regioselectivity was improved and a single product derived from the *ortho*-shift of the acyl group was obtained (Table 1). Improvement of the conversion yield to 85–100 % and the high *ortho*-regioselectivity of these reactions under microwave irradiation provides an efficient and versatile procedure for isolation of *o*-hydroxyaryl ketones in 47–98 % isolated yield.

We then examined the P_2O_5 / SiO_2 reagent for direct acylation of phenol and naphthol derivatives. *m*–Cresol **7b** was treated with acetic acid in the presence of P_2O_5 / SiO_2 in solvent-free conditions at 100 ^{0}C for 24 h, to afford 2-acetyl-5-methylphenol **3b** as the major product in 80 % yield. Several examples of direct acylation reactions of phenol and naphthol derivatives with carboxylic acids are shown in Table 2. In every case, the reaction proceeded smoothly using equimolar amounts of carboxylic acids and phenols in the presence of P_2O_5 / SiO_2 in solvent-free conditions, to afford the corresponding hydroxyaryl ketones in good to high isolated yield (45–78%).



Scheme 2

The product distribution upon microwave irradiation of the mixture of substrates and reagent in solvent-free media are summarised in Table 2. In the case of reactive phenols with benzoic acid or aliphatic carboxylic acid the *ortho* product was obtained as the major product. Microwave irradiation improved the isolated yield from direct acylation up to 45–85 %.

Interesting differences in product distribution between the Fries rearrangement and the direct acylation reaction are clearly seen. Microwave irradiation improved the yield from Fries rearrangement especially in the case of benzoate esters (Entries

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Table 1 The Fries rearrangement of acyloxybenzene and naphthalene derivatives using P_2O_5 / SiO_2 in dry media under conventional or microwave heating

Entry	Reactant	R	X	Reaction conditions	Yield/% of products[a] [Isolated from major product][b]		
1	**1a**	CH_3	H	100 °C / 24 h	**1a** (2)	**2a** (38)	**3a** (60) [41]
2	**1a**	CH_3	H	MW / 5 min	**1a** (0)	**2a** (15)	**3a** (85) [74]
3	**1b**	CH_3	*m*-CH_3	100 °C / 24 h	**1b** (2)	**2b** (28)	**3b**(70) [59]
4	**1b**	CH_3	*m*-CH_3	MW / 5 min	**1b** (0)	**2b** (0)	**3b** (100) [95]
5	**1c**	CH_3	*p*-CH_3	100 °C / 24 h	**1c** (15)	–	**3c** (85) [78]
6	**1c**	CH_3	*p*-CH_3	MW / 5 min	**1c** (0)	–	**3c** (100) [98]
7	**1d**	Ph	*m*-CH_3	100 °C / 24 h	**1d** (32)	**2d** (12)	**3d** (56) [35]
8	**1d**	Ph	*m*-CH_3	MW / 5 min	**1d** (15)	**2d** (15)	**3d** (70) [61]
9	**1e**	Ph	*p*-CH_3	100 °C / 24 h	**1e** (100)	–	**3e** (0)
10	**1e**	Ph	*p*-CH_3	MW / 0.5 min	**1e** (95)	–	**3e** (5)
11	**1e**	Ph	*p*-CH_3	MW / 5 min	**1e** (10)	–	**3e** (90) [85]
12	**4a**	CH_3	–	100 °C / 24 h	**4a** (0)	**5a** (32)	**6a** (68) [43]
13	**4a**	CH_3	–	MW / 6 min	**4a** (0)	**5a** (15)	**6a** (85) [80]
14	**4b**	Ph	–	100 °C / 24 h	**4b** (27)	**5b** (23)	**6b** (50) [32]
15	**4b**	Ph	–	MW / 10 min	**4b** (5)	**5b** (5)	**6b** (90) [77]

[a]Yields calculated from ν_{CO} IR spectra of crude product in the carbonyl region.
[b]Isolated yield of pure product after column chromatography (CH_2Cl_2 / *n*- hexane).

Table 2 2- Acylation reactions of phenols and α-naphthol using P_2O_5 / SiO_2 in dry media under conventional or microwave heating

Entry	Reactants	R	X	Reaction conditions	Yield/% of products[a] [Isolated from major product][b]		
1	**7a, 8a**	CH_3	H	100 °C / 24 h	**1a** (5)	**2a** (35)	**3a** (60) [45]
2	**7b, 8a**	CH_3	*m*-CH_3	100 °C / 24 h	**1b** (3)	**2b** (17)	**3b** (80) [72]
3	**7b, 8a**	CH_3	*m*-CH_3	MW / 10 min	**1b** (0)	**2b** (5)	**3b**(95) [85]
4	**7c, 8a**	CH_3	*p*-CH_3	100 °C / 24 h	**1c** (21)	–	**3c**(79) [70]
5	**7c, 8a**	CH_3	*p*-CH_3	MW / 10 min	**1c** (15)	–	**3c**(85) [80]
6	**7b, 8b**	Ph	*m*-CH_3	100 °C / 24 h	**1d** (20)	**2d** (48)	**3d** (32)
7	**7b, 8b**	Ph	*m*-CH_3	MW / 5 min	**1d** (0)	**2d** (75) [55]	**3d** (25)
8	**7b, 8b**	Ph	*m*-CH_3	MW / 10 min	**1d** (0)	**2d** (35)	**3d** (65) [49]
9	**7c, 8b**	Ph	*p*-CH_3	100 °C / 24 h	**1e** (95) [90]	–	**3e** (5)
10	**7c, 8b**	Ph	*p*-CH_3	MW / 12 min	**1e** (40)	–	**3e** (60) [47]
11	**7d, 8b**	Ph	*m*-OH	100 °C / 24 h	**1f** (20)	–	**3f** (80) [66]
12	**7d, 8a**	CH_3	*m*-OH	100 °C / 24 h	**1g** (30)	–	**3g** (70) [65]
13	**7a, 8b**	Ph	H	100 °C / 24 h	**1h** (85) [70]	**2h** (12)	**3h** (3)
14	**7a, 8b**	Ph	H	MW / 5 min	**1h** (0)	**2h** (80) [65]	**3h** (20)
15	**7b, 8c**	*i*-Pr	*m*-CH_3	100 °C / 24 h	**1i** (4)	**2i** (26)	**3i** (70) [52]
16	**9, 8a**	CH_3	–	100 °C / 24 h	**4a** (0)	**5a** (28)	**6a** (72) [65]
17	**9, 8a**	CH_3	–	MW / 5 min	**4a** (0)	**5a** (20)	**6a** (80) [68]
18	**9, 8b**	Ph	–	130 °C / 24 h	**4b** (7)	**5b** (29)	**6b** (64) [45]
19	**9, 8b**	Ph	–	MW / 6 min	**4b** (0)	**5b** (40)	**6b** (60) [45]
20	**9, 8c**	*i*-Pr	–	130 °C / 24 h	**4c** (0)	**5c** (20)	**6c** (80) [74]
21	**9, 8d**	*c*-Hexyl	–	130 °C / 24 h	**4d** (0)	**5d** (5)	**6d** (95) [78]

[a]Yields calculated from ν_{CO} IR spectra of crude product in the carbonyl region.
[b]Isolated yield of pure product after column chromatography (CH_2Cl_2 / *n*- hexane).

8, 11 and 15 from Table 1) and usually the *ortho*-product was obtained. Whereas, in direct benzoylation of phenol derivatives (Entries 7, 14 and 19 from Table 2) a mixture of products was obtained in which the *para*-product usually predominated. The major products in each case were isolated and characterised on the basis of their ^{1}H NMR and IR spectral analysis, and melting points were compared with literature data (Table 3).

P_2O_5 / SiO_2 is an efficient reagent in both the Fries rearrangement of acyloxybenzenes or naphthalene derivatives and the direct acylation reaction of phenol and naphthol derivatives with carboxylic acids. In conclusion, with the easily available reagent, mild solvent-free conditions, as well as easy operation, it is thought this work provides a useful method for selective preparation of *ortho* isomer of hydroxyaryl ketones from Fries rearrangement or direct acylation reactions under microwave irradiation.

Techniques used: TLC, m.p., IR and ^{1}H NMR.

References: 34

Tables: 3

Schemes: 2

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