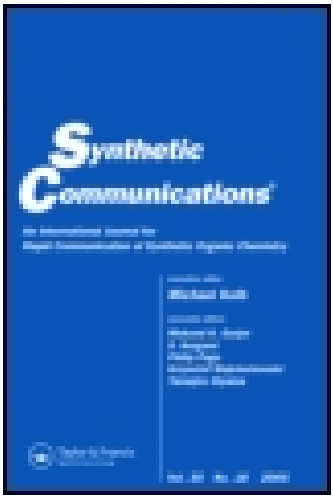

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Dry Reaction Under Microwave: Condensation of Sulfones with Aldehydes on KF-Alumina

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DRY REACTION UNDER MICROWAVE: CONDENSATION OF SULFONES WITH ALDEHYDES ON KF-ALUMINA

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Abstract: Ethyl phenylsulfonylacetate(**1**), phenylsulfonylacetonitrile(**2**) and phenylsulfonylacetophenone (**3**) were condensated with aldehydes (**a-d**) into unsaturated sulfone without solvent in the presence of KF on alumina under microwave irradiation.

Sulfones are useful intermediates in organic synthesis [1],arylsulfonyl group in particular can stabilize adjacent carbanions [2] and may easily be removed in a reductive way [1]. Unsaturated arylsulfones have been used in many synthetic reactions [3] such as conjugate additions and cycloadditions. A few synthetic methods were reported for these compounds [4].

Knoevenagel condensation of arylsulfonylalkanes with aldehydes is the method of choice for the synthesis of unsaturated arylsulfones. Deprotonation of phenylsulfonylalkanes generally involve strong bases [2] such as butyllithium, LDA or sodium hydride. Although potassium fluoride on alumina can be used as strong base for the deprotonation of phenylmethylsulfone [5], the deprotanation can greatly be easier by the presence of an adjacent electronwithdrawing group such as ester, nitrile or ketone.

We reported herein the dry condensation of ethyl phenylsulfonylacetate (**1**),

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Table I: Condensation of arylsufones (**1-3**) with arylcarboxaldehydes under microwave irradiation (280W,4 mn).

yield of condensation (%)

$C_6H_5\ SO_2\text{-}CH_2\text{-}Z$ \ aldehyde	a	b	c	d
Z= $COOC_2H_5$ (1)	58	64	55	50
Z=CN (2)	76	82	65	88
Z=COC_6H_5 (3)	78	68	74	60

aldehyde:

a) benzaldehyde

b) 3,4-methylenedioxy-benzaldehyde

c) 4-methoxybenzaldehyde

d) 3-nitrobenzaldehyde

phenylsulfonylacetonitrile (**2**) and phenylsulfonylacetophenone (**3**) with arylcarboxyaldehydes adsorbed on KF-alumina, under microwave irradiation.

Reaction: Condensation of arylsulfones with arylcarboxaldehydes under microwave irradiation on KF-alumina:

$$C_6H_5\ SO_2\text{-}CH_2\text{-}Z + \text{Ar-CHO} \xrightarrow[\text{microwave}\ 280W,\ 5\ mn]{KF\text{-}Al_2O_3} C_6H_5\ SO_2\text{-}\underset{\displaystyle Z}{\underset{|}{C}}{=}CH\text{-Ar}$$

Z= $COOC_2H_5$ (1) CN (2) COC_6H_5 (3)

Using the condensation under microwave irradiation, unsaturated functionalized sulfones were obtained in good yield (see Table I). This method is convenient and allows quick the preparation of functionalized unsaturated arylsulfones, useful as Diels-Adler or Michael substrats.

EXPERIMENTAL

Ethyl phenylsulfonylacetate (**1**), phenylsulfonylacetonitrile (**2**) and phenylsulfonylacetophenone (**3**) were prepared by alkylation of sodium phenylsulfinate on alumina under microwave irradiation [6].

General procedure

To a solution of sulfone (**1** or **2** or **3**) (5 mmol) in the minimum of dichloromethane, aldehyde (**a-d**) (5 mmol) and potasium fluoride on alumina (3 g) were added. The solvent was evaporated in vacuo with a rotary evaporator. The resulting solid was placed in a open Pyrex Elernmeyer flask (25 ml) and was irradiated in a microwave oven (280 W, 5 mm).

The product formed was extracted with dichloromethane (30 ml X 4) and filtered on Celite. After evaporation of the solvent, the product was purified by preparative thin layer chromatography (cyclohexane/ethyl acetate= 9/1 on silica and crystallized.

Ethyl α-phenylsulfonyl cinnamate (1 a).

Pale yellow solid ; Mp 54° (AcOEt), lit.[7] Mp 50° (AcOEt) ; PMR ($CDCl_3$) δ : 1.15 (t, 3H CH_3), 4.20 (q, 2H, CH_2O), 7.10-8.05 (m, 11H, 10H arom. and 1H, CH=C) ; IR (nujol) 1730 (ν C=O), 1610, 1600, ν C=C), 1350, 1150 (ν SO_2) ; UV (EtOH) λmax (log ε) : 318 (4.18), 232 (3.98).

Ethyl (3,4 dioxymethylene) α-phenylsulfonylcinnamate (1b).

Yellow solid : Mp 108° (EtOH), lit. [9] 110° ; PMR ($CDCl_3$) δ : 1.10 (t, 3H, CH_3), 4.15 (q, 2H, CH_2O), 6.15 (s, 2H, OCH_2O), 6.80-8.20 (m, 9H, 8H arom and 1H, CH=C) ; IR (nujol) : 1725 (ν C=O), 1620, 1600 (ν C=C), 1340 ; 1155 (ν SO_2) ; UV (EtOH) λ (log ε) ; 334 (4.22), 236 (4.01).

Ethyl (p-methoxy)-α-phenylsulfonylcinnamate (1 c).

Yellow solid ; Mp 104-106° (EtOH), lit. [8] 106-107° ; PMR ($CDCl_3$) δ : 1.20 (t, 3H, CH_3), 3.75 (s, 3H, OCH_3), 4.25 (q, 2H, CH_2O), 6.80-8.10 (m, 10H, 9H arom and ^{1}H, CH=C) ; IR (nujol) : 1725 (ν C=O), 1600, 1580 (νC=C), 1350, 1145 (ν SO_2) ; UV (EtOH) ; λmax (log ε) : 322 (4.35) 234 (4.20).

Ethyl (3-nitro)-α-phenylsulfonylcinnamate (1 d)

Orange solid ; Mp 156° (AcOH), lit. [9] Mp 154-155° ; PMR ($CDCl_3$) δ : 1.20 (t, 3H, CH_3), 4.30 (q, 2H, OCH_2), 6.90-8.10 (m, 10H, 9H arom. and 1H, CH=C) ; IR (nujol) 1720 (ν C=O) 1620, 1595 (ν C=C), 1345, 1150 (ν SO_2) ; UV (EtOH) λmax (log ε) : 346 (4.25), 245 (4.10).

α-(phenylsulfonyl) cinnamonitrile (2 a).

Yellow solid ; Mp 134° (EtOH), lit. [8] Mp 135-136° ; PMR ($CDCl_3$) δ : 6.90-8.10 (m, 11H, 10H arom. and 1H, CH=C) ; IR (nujol) : 2240 (ν C=N),

1610, 1590 (ν C=C), 1335, 1150 (ν SO_2) ; UV (EtOH) λmax (log ε) : 315 (4.4), 232 (4.1).

α-phenylsulfonyl (3,4-dioxymethylenecinnamonitrile) (2 b).
Yellow solid : Mp 170-172° (AcOH), lit. [8] Mp 170-171°; PMR($CDCl_3$) δ : 5.95 (S, 2H, OCH_2O), 6.95-8.05 (m, 9H, 8 Harom and 1H, CH=C) ; IR (nujol) : 2235 (ν C=N), 1620, 1595 (ν C=C), 1350, 1150 (ν SO_2) ; UV (EtOH) λmax (log ε) : 352 (4.39), 244 (4.11).

α- phenylsulfoxyl (4-methoxycinnamonitrile) (2c)
Yellow solid ; Mp 116° (EtOH), lit. [8] Mp 114.5-116° ; PMR ($CDCl_3$) δ : 3.8 (s, 3H, OCH_3), 6,8-8,0 (m, 10H, 9 Harom and 1H, CH=C) ; IR (nujol) : 2240 (ν C=N), 1615, 1580 (ν C=C), 1340, 1150 (ν SO_2) ; UV (EtOH) λmax (log ε) : 344 (4.54), 240 (4.12).

α-phenylsulfonyl (3-nitrocinnamonitrile) (2d)
Orange solid : Mp 152° (EtOH), lit. [9] Mp 149-150.5° ; IR (nujol) : 2240 (νC=N), 1620, 1575 (ν C=C), 1330, 1150 (ν SO_2) ; UV (EtOH) λmax (log ε) : 338 (4.12), 234 (4.15).

α-phenylsulfonyl chalcone (3a)
Orange solid ; Mp 136° (EtOH), lit. [9] Mp 137-138° ; PMR ($CDCl_3$) δ : 7,0-8,2 (m, Harom and CH=C) ; IR (nujol) : 1660 (ν C=O), 1595 (ν C=O), 1350, 1150 (ν SO_2) ; UV (EtOH) λmax (log ε) : 316 (4.43), 232 (3.95).

α-phenylsulfonyl (3,4-dioxymethylene chalcone) (3b)
Orange solid ; Mp 177-178° (dioxane), lit. [9] Mp 178-179° ; PMR ($CDCl_3$) δ : 5,9 (s, 2H, OCH_2O), 6,8-8,0 (m, 14H, 13 Harom and 1H, CH=C) ; IR (nujol) : 1670 , 1600 (ν C=O), 1330, 1150 (ν SO_2) ; UV (EtOH) λ max (log ε) : 328 (4.51), 236 (4.01).

α-phenylsulfonyl (4-methoxy chalcone) (3c)
Orange solid ; Mp 162° (EtOH), lit. [9] Mp 161-163° ; PMR ($CDCl_3$) δ : 3.7 (s, 3H, OCH_3), 7.0-8.1 (m, 15H, 14 Harom and 1H, CH=C) ; IR (nujol)

1665 (ν C=O), 1610, 1595 , 1345, 1150 (ν SO_2) ; UV (EtOH) λ max (logε) : 320 (4,5) 234 (4,1).

α-phenylsulfonyl (3-nitrochalcone) (3d)
Orange solid ; Mp 172° (EtOH), lit. [9] Mp 169-171° ; PMR ($CDCl_3$) δ : 7,1-8,1 (m, 15H,14 Harom and 1 H,CH=C) ; IR (nujol) : 1660 (ν C=O), 1605, 1585 (ν C=O), 1330, 1150 (ν SO_2) ; UV (EtOH) λmax (log ε) : 325 (4.39), 238 (4.15).

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