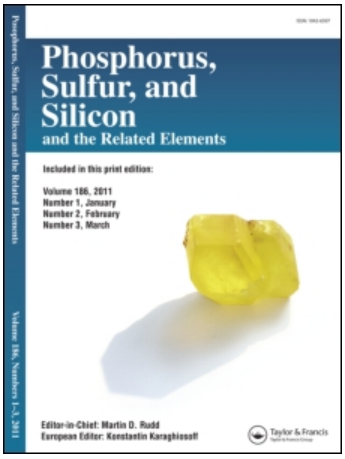

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CH 3 SO 3 H/P 2 O 5 (4:1) As An Efficient Reagent for the One-Pot Synthesis of Acylaryl Methane Sulfonates of Phenolic

B. Kaboudin[a]
[a] Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, Iran

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CH_3SO_3H/P_2O_5 (4:1) AS AN EFFICIENT REAGENT FOR THE ONE-POT SYNTHESIS OF ACYLARYL METHANE SULFONATES OF PHENOLIC

B. Kaboudin
Institute for Advanced Studies in Basic Sciences (IASBS), Gava Zang, Zanjan, Iran

Methansulfonic acid/di-phosphorus pentoxide (4:1) was found to be an efficient reagent for one-pot synthesis of acylaryl methane sulfonates of phenolic esters via Fries rearrangement. This method is easy, rapid, and high-yielding reactions for the synthesis of acylaryl methane sulfonates.

Keywords: Acylaryl methane sulfonates; di-phosphorus pentoxide; Fries rearrangement; methansulfonic acid

Acylaryl methane sulfonates have many industrial applications such as pesticides, insecticides, acaricides,[1,2] photosensitizers, and photoinitiator systems for radical and cationic polymerization.[3] These compounds have been prepared by reaction of hydroxyaryl ketones with methanesulfonyl chloride in the presence of a base.[2] The Fries reaction, used for the preparation of aryl ketones from phenolic esters, is one of the most useful rearrangements in aromatic chemistry.[4,5] Conducted thermally in the presence of Friedel-Crafts catalysts or photochemically by irradiation with UV light, reactions typically give mixtures of *ortho*- and *para*-substituted products.[6,7] Recently we found that the Fries rearrangement of phenolic esters in the presence of MAPO (methanesulfonic acid/phosphorus oxychloride),[8] gave acylaryl methane sulfonates products with good yields. This article reports the one-pot synthesis of acylaryl methane sulfonates via Fries rearrangement of phenolic esters in the presence of a mixture of CH_3SO_3H/P_2O_5 (4:1) as an efficient reagent. CH_3SO_3H/P_2O_5 first came to our attention when Eaton's reagent[9] (CH_3SO_3H/P_2O_5 with 10:1 ratio) (PPMA) was considered as a

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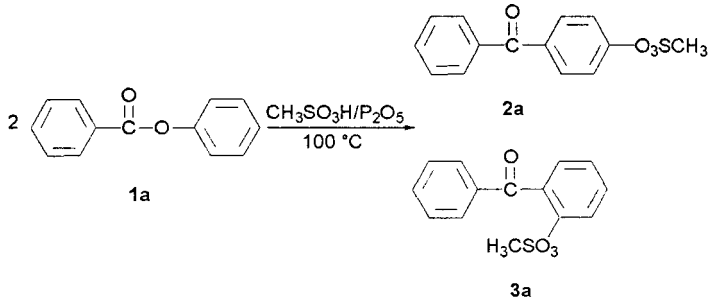
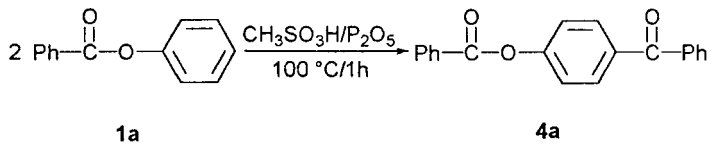
Address correspondence to B. Kaboudin, Institute for Advanced Studies in Basic Sciences, Gava Zang, Zanjan, 45195-159, Iran. E-mail: kaboudin@iasbs.ac.ir



SCHEME 1

suitable alternative to polyphosphoric acid. The Fries rearrangement of phenyl benzoate (**1a**) in the presence of this reagent (10:1), gave 4-benzoylphenyl methane sulfonate (**2a**) and 2-benzoylphenyl methane sulfonate (**3a**) in a 9:1 ratio (Scheme 1) in 35% yield. We speculated that improved yields of acylaryl methane sulfonates would be obtained by increasing the amount of P_2O_5 present (Table I).

^{1}H NMR studies on the Fries rearrangement of **1a** at different temperatures showed that at the beginning of the reaction, 4-benzoyloxybenzophenone (**4a**) is the major product in the presence of MAPO.[8] In a similar experiment, when compound **1a** was added to a mixture of CH_3SO_3H/P_2O_5 (4:1) and stirred for 1 h at 100°C, compound **4a** was formed in 78% yield (Scheme 2).



1a **4a**

SCHEME 2

These results may be explained by considering the initial formation of **4a**, which undergoes decomposition leading to **2a**. I examined Fries rearrangement of phenyl benzoate using this reagent in the presence of solvent. Phenyl benzoate (**1a**) was treated with CH_3SO_3H/P_2O_5 in the presence of 1,2-dichloroethane at 80°C for 6 h, afford **4a** as the major product in an 84% yield (isolated yield, based on 2 mmol phenolic ester that has been used as starting material). Similar results were obtained in the presence of other solvents such as nitrobenzene and chlorobenzene.

The same process was successfully extended to other acyloxyarene derivatives as summarized in Table II. The Fries rearrangement of

TABLE I Progress of Fries Rearrangement of Ester **1a** in the presence of CH_3SO_3H/P_2O_5

Ratio of CH_3SO_3H to P_2O_5	Time (hrs)	Yields[a] (%)	Ratio of **2a/3a**
10:1	3	35	9:1
9:1	3	48	9:1
8:1	3	58	9:1
7:1	3	70	9:1
6:1	3	79	9.5:0.5
5:1	3	83	9.5:0.5
4:1	3	86	9.5:0.5
3:1	3	86	9.5:0.5

[a]Isolated yields.

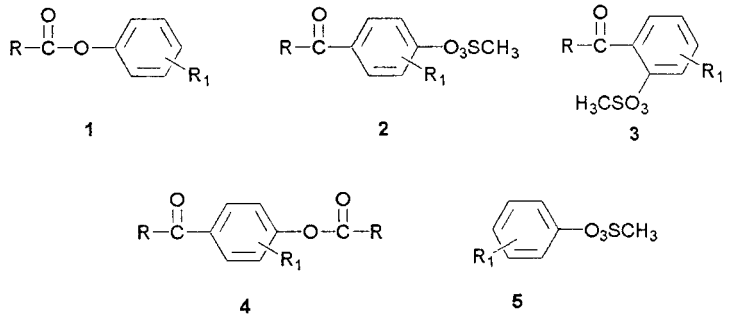
m-tolyl benzoates (**1b–e**) with this reagent afforded the desired products in 76–89% yields. The results in Table II clearly show that the reaction seems to be faster when the aryloxy part of the ester carries electron-donating groups; *p*-acylaryl methane sulfonates were formed selectively. The reaction of *o*-substituted phenolic esters (**1f–g**) in the presence of CH_3SO_3H/P_2O_5 (4:1) gave *p*-acylaryl methane sulfonates as major products. *m*-Nitro and *m*-fluoro phenyl benzoate (**1h**, **1i**) with CH_3SO_3H/P_2O_5 (4:1), gave the mesylated phenol (*m*-nitro and *m*-fluoro) (**5h**, **5i**) and the Fries rearrangement did not occur. These results

TABLE II Fries Rearrangement of Acyloxyarene (1) Derivatives in the Presence of CH_3SO_3H/P_2O_5 (4:1) at 100°C

Substrate	R	R^1	Product(s)	Reaction time (h)	Yields[a] (%)	Ratio of products
1a	Ph-	H	**2a/3a**	5	86	95/5
1a	Ph-	H	**2a/3a/4a**	1	87	5/5/90
1b	Ph-	*m*-Me	**2b/3b**	2.5	86	95/5
1c	*o*-ClC_6H_4-	*m*-Me	**2c/3c**	6	76	92/8
1d	*p*-MeC_6H_4-	*m*-Me	**2d/3d**	1.5	89	90/10
1e	*m*-BrC_6H_4-	*m*-Me	**2e/3e**	8	78	90/10
1f	Ph-	*o*-Cl	**2f**	8	76	—
1g	Ph-	*o*-Me	**2g**	1	86	—
1h	Ph-	*m*-NO_2	**5g**	6	90	—
1i	Ph-	*m*-F	**5i**	6	90	—
1j	$PhCH_2$	*m*-Me	—	1[b]	—	—
1k	Me-	*m*-Me	—	1[b]	—	—
1l	Me	*m*-NO_2	**5l**	1	90	—

[a]Isolated yields.
[b]Unknown products were produced.

clearly indicate that electrophilic substitution did not occur because electron-withdrawing groups (*m*-nitro and *m*-fluoro) deactivate the aromatic ring. *m*-Tolyl-phenylethanoate (**1j**) and *m*-tolyl etanoate (**1k**) upon treatment with CH_3SO_3H/P_2O_5 at 100°C, gave unknown products at 100°C after 1 h. *m*-Nitrophenyl acetate (**1l**), with CH_3SO_3H/P_2O_5, gave **5l** as the major product (Scheme 3).



SCHEME 3

In summary, methanesulfonic acid/phosphorus pentoxide (4:1) has been shown to be an efficient reagent in the Fries rearrangement of acyloxybenzene derivatives to acylarylmethane sulfonates.

EXPERIMENTAL

Chemicals were purchased from Fluka and Merck chemical companies. IR spectra were recorded on Perkin Elmer 781 spectrometer. ^{1}H-NMR spectra were obtained on a Bruker Avance DPX 250 MHz and a Hitachi, R-2413, 60 MHz spectrophotometers. All melting points were obtained by a Buchi 510 and are uncorrected. The purity of the substrates was determined by TLC on silica gel polygram SIL 6/UV 254 plates.

Fries Rearrangement of Acyloxybenzene Derivatives in the Presence of Methanesulfonic Acid/Phosphorus Pentoxide (4:1)

General Procedure

The acyloxybenzene derivative (0.003 mmol) was added to a 2 mL of mixture of methanesulfonic acid and phosphorus pentoxide (4:1 w/w) at 100°C. The reaction mixture was stirred for the time period reported in Table I. The reaction mixture was poured into water, extracted with chloroform (2 × 25 mL), washed with sodium hydrogen carbonate solution (2 × 30 mL), dried ($CaCl_2$), filtered, and evaporated. The crude

product was isolated in a pure state by simple filtration chromatography through a short plug of silica gel with *n*-hexane-ethylacetate (90:10). The solvent was evaporated. Known compounds were characterized by comparison of their physical data with those prepared in accordance with literature procedures.[8]

4-Benzoylphenyl methane sulfonate (2a): White crystals, m.p. 78–79°C (*n*-hexane/CH_2Cl_2). R_f 0.66 (*n*-hexane/EtOAc 60:40); IR (KBr): 1655 (C=O), 1600 (Ar), 1375 and 1175 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 3.15 (s, 3H), 7.1–7.9 (m, 9H).

4-Benzoyl-3-methylphenyl methane sulfonate (2b): Viscous oil, R_f 0.69 (*n*-hexane/EtOAc 60:40); IR (neat): 1668 (C=O), 1603 (Ar), 1372 and 1185 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 2.3 (s, 3H), 3.10 (s, 3H), 7.0–7.75 (m, 8H).

4-(2-Chlorobenzoyl)-3-methylphenyl methane sulfonate (2c): Viscous oil, R_f 0.68 (*n*-hexane/EtOAc 60:40); IR (neat): 1678 (C=O), 1608 (Ar), 1372 and 1185 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 2.5 (s, 3H), 3.10 (s, 3H), 7–7.45 (m, 7H).

4-(4-Methylbenzoyl)-3-methylphenyl methane sulfonate (2d): Viscous oil, R_f 0.74 (*n*-hexane/EtOAc 60:40); IR (neat): 1663 (C=O), 1608 (Ar), 1370 and 1182 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 2.25 (s, 3H), 2.35 (s, 3H), 3.15 (s, 3H), 6.95–7.6 (m, 7H).

4-(3-Bromobenzoyl)-3-methylphenyl methane sulfonate (2e): White crystals, m.p. 84°C (*n*-hexane/CH_2Cl_2). R_f 0.73 (*n*-hexane/EtOAc 60:40); IR (KBr): 1678 (C=O), 1605 (Ar), 1368 and 1188 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 2.3 (s, 3H), 3.12 (s, 3H), 7.0–7.8 (m, 7H).

4-Benzoyl-2-chlorophenyl methane sulfonate (2f): Viscous oil, R_f 0.75 (*n*-hexane/EtOAc 60:40); IR (neat): 1670 (C=O), 1600 (Ar), 1383 and 1180 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 3.20 (s, 3H), 7–8.1 (m, 8H).

4-Benzoyl-2-methylphenyl methane sulfonate (2g): White crystals, m.p. 57°C (*n*-hexane/CH_2Cl_2). R_f 0.80 (*n*-hexane/EtOAc 60:40); IR (neat): 1675 (C=O), 1600 (Ar), 1388 and 1170 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 2.35 (s, 3H), 3.20 (s, 3H), 7.1–7.80 (m, 8H).

2-Benzoylphenyl methane sulfonate (3a): Viscous oil, R_f 0.89 (*n*-hexane/EtOAc 60:40); IR (neat): 1673 (C=O), 1610 (Ar), 1373 and 1180 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 3.2 (s, 3H), 7.2–7.8 (m, 9H).

2-Benzoyl-5-methylphenyl methane sulfonate (3b): Viscous oil, R_f 0.86 (*n*-hexane/EtOAc 60:40); IR (neat): 1670 (C=O), 1615 (Ar), 1370 and 1183 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 2.45 (s, 3H), 3.2 (s, 3H), 7.2–7.75 (m, 8H).

2-(2-Chlorobenzoyl)-5-methylphenyl methane sulfonate (3c): White crystals, m.p. 64°C (*n*-hexane/CH_2Cl_2). R_f 0.71 (*n*-hexane/EtOAc 60:40); IR (KBr): 1670 (C=O), 1610 (Ar), 1370 and 1180 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 2.52 (s, 3H), 3.11 (s, 3H), 7.2–7.9 (m, 7H).

2-(4-Methylbenzoyl)-5-methylphenyl methane sulfonate (3d): Viscous oil, R_f 0.88 (*n*-hexane/EtOAc 60:40); IR (neat): 1668 (C=O), 1612 (Ar), 1370 and 1180 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 2.2 (s, 3H), 2.28 (s, 3H), 3.1 (s, 3H), 7.1–7.65 (m, 7H).

2-(3-Bromobenzoyl)-5-methylphenyl methane sulfonate (3e): Orange viscous oil, R_f 0.76 (*n*-hexane/EtOAc 60:40); IR (neat): 1675 (C=O), 1615 (Ar), 1370 and 1185 cm^{-1} (S=O). ^1H NMR ($CDCl_3$), δ 2.5 (s, 3H), 3.06 (s, 3H), 7.0–7.98 (m, 7H).

3-Nitrophenyl methane sulfonate (5g): White crystals, m.p. 60°C (*n*-hexane/CH_2Cl_2). R_f 0.58 (*n*-hexane/EtOAc 60:40); IR (KBr): 1600 (Ar), 1530 (N=O), 1375, 1175 cm^{-1} (S=O). ^1H NMR ($CDCl_3$), δ 3.15 (s, 3H), 7.4–8.3 (m, 4H).

3-Fluorophenyl methane sulfonate (5i): Red viscous oil, R_f 0.78 (*n*-hexane/EtOAc 60:40). IR (neat): 1610 (Ar), 1375 and 1190 cm^{-1} (S=O). ^1H NMR ($CDCl_3$), δ 3.15 (s, 3H), 6.8–7.4 (m, 4H).

4-Benzoyloxybenzophenone (4a): White crystals, m.p. 83°C (*n*-hexane/EtOAc 90:10). IR (KBr): 1760 (C=O), 1675 (C=O), 1600 cm^{-1} (Ar). ^1H NMR ($CDCl_3$): 7.0–7.8 (m, 11H), 8.05 (dd, *J* 6 and 2Hz, 2H).

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