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Methanesulfonic Acid/Phosphorus Oxychloride (MAPO) as a New Efficient Reagent in the Fries Rearrangement

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Abstract: Methanesulfonic acid/phosphorus oxychloride (MAPO) was found to be a new efficient reagent in the Fries rearrangement of phenolic esters. Fries rearrangement of phenolic esters in the presence of MAPO, gave acylaryl methane sulfonates as major products.

The Fries reaction, used for the preparation of aryl ketones from phenolic esters, is one of the most important rearrangements in aromatic chemistry.[1,2] It consists of the rearrangement of a phenolic ester to *o*- and *p*-hydroxyaryl ketones, by heating with aluminum chloride[3] or other Lewis and protic acids;[4,5] however, treatment of the aluminum residue has sometimes led to environmental problems, and the drastic reaction conditions may promote some severe side-reactions. Results of the Fries rearrangement of acyloxybenzenes showed that in the most cases, mixtures of products are produced using $AlCl_3$,[6,7] $TiCl_4$,[8,9] PPA,[10] HF.[11] Recently we found that the Fries rearrangement of phenolic esters in the presence of methanesulfonic anhydride,[12] gave acylaryl methane sulfonates as major products which have many industrial applications such as pesticides, insecticides, acaricides,[13,14] photosensitizers and photoinitiator systems for radical and cationic polymerization.[15] These acylaryl methane sulfonates have been prepared by reaction of hydroxyaryl ketones with methanesulfonyl chloride in the presence of base.[14] This paper now reports the Fries rearrangement of acyloxybenzene derivatives in the presence of a mixture of methanesulfonic acid/phosphorus oxychloride ($CH_3SO_3H/POCl_3$) as a new efficient reagent for the one-pot synthesis of acylaryl methane sulfonates of phenolic esters. The Fries rearrangement of phenyl benzoate (**1a**), chosen as a model compound, was studied in the presence of MAPO, and the progress of the reaction was monitored by TLC. As described below, **1a** was treated with MAPO to give 4-benzoylphenyl methane sulfonate (**2a**) and 2-benzoylphenyl methane sulfonate (**3a**) in a 9:1 ratio (Scheme 1) in 91% yield. ^1H NMR studies on the Fries rearrangement of **1a** at different temperatures show that at the beginning of the reaction, 4-benzoyloxybenzophenone (**4a**) is the major product. In a separate experiment, when compound **4a** was added to a mixture of methanesulfonic acid/ phosphorus oxychloride and stirred for 4 h at 100°C, compound

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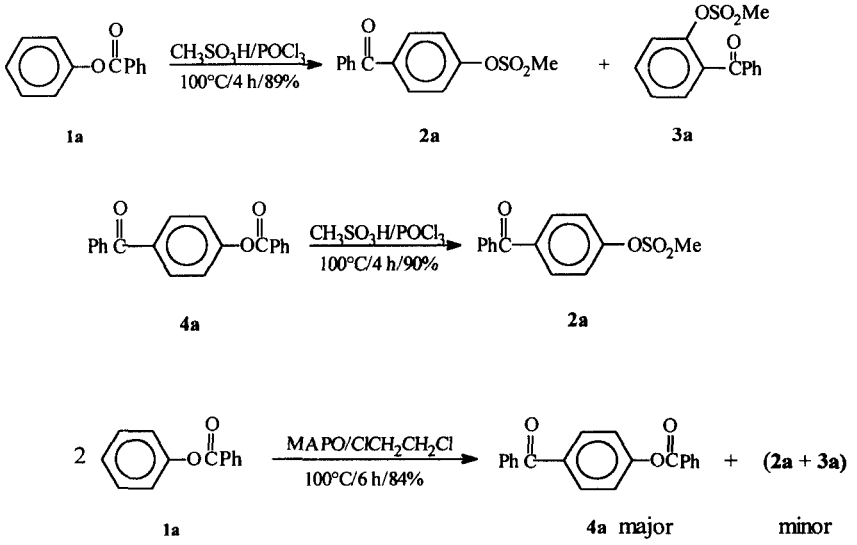
2a was formed in 90% yield. These results may be explained by considering the initial formation of **4a** which undergoes decomposition leading to **2b**. We then examined Fries rearrangement of phenyl benzoate using MAPO in the presence of solvent. Phenyl benzoate (**1a**) was treated with MAPO in the presence of 1,2-dichloroethane at 100°C for 6 h, to afford **4a** as the major product in an 84% yield (isolated yield, based on 2 mol phenolic ester that has been used as starting material). Similar results were obtained in the presence of other solvents such as nitrobenzene and chlorobenzene.



Scheme 1

The same process was successfully extended to other acyloxyarene derivatives as summarized in Table 1. The Fries rearrangement of *m*-tolyl benzoates (**1b-f**) with this reagent afforded the desired products in 73-85% yields. The results in Table 1 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 (**1g-h**) in the presence of MAPO, gave *p*-acylaryl methane sulfonates as major products. *m*-Nitro and *m*-fluoro phenyl benzoate (**1i, 1j**) with MAPO, gave the mesylated phenol (*m*-nitro and *m*-fluoro) and the Fries rearrangement did not occur. These results clearly indicate that electrophilic substitution did not occur because electron-withdrawing groups (*m*-nitro and *m*-fluoro) deactivate the aromatic ring. However, the Fries rearrangement of *m*-bromophenyl benzoate (**1k**) occurred in the presence of MAPO to give 4-benzoyl-3-bromophenyl methane sulfonate (**2k**) as the major product. *m*-Tolyl propanoate (**6a**) upon treatment with MAPO at 100°C, immediately produced the desired products (**7a**) in 67% yield. *m*-Nitrophenyl acetate (**6b**), with MAPO, gave **5a** as the major product. The action of MAPO on α-naphthyl benzoate leads to the desired Fries rearrangement product in 72% yield. The Fries rearrangement of the esters (**1b-n, 1k**) with MAPO in the presence of solvent, gave 4-aryloxy arylketone (**4**) as major product (**1i, 1j**, and **6b**, gave mesylated phenol).

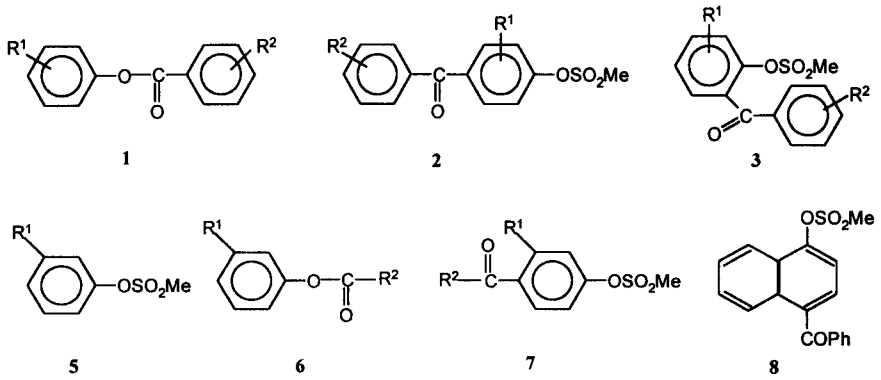


Table 1: The Fries Rearrangement of Acyloxyarene Derivatives in MAPO.

Substrate	R^1	R^2	Product(s)	Reaction Time	Yield[a]	Ratio 3:2
1a	H	H	**2a+3a**	4	89	1:9
1b	*m*-Me	H	**2b+3b**	2.5	85	3:7
1c	*m*-Me	*o*-Cl	**2c+3c**	4	82	2:8
1d	*m*-Me	*m*-Br	**2d+3d**	6	73	3:7
1e	*m*-Me	*p*-Cl	**2e+3e**	5.5	85	3:7
1f	*m*-Me	*p*-Me	**2f+3f**	1.5	85	3:7
1g	*o*-Cl	H	**2g**	6	83	-
1h	*o*-Me	H	**2h**	1	79	-
1i	*m*-NO_2	H	**5a**	6	90	-
1j	*m*-F	H	**5b**	3	85	-
1k	*m*-Br	H	**2k**	10	76	-
6a	Me	Et	**7a**	1	67	-
6b	NO_2	Me	**5a**	6	90	-
1-naphthyl benzoate			**8**	0.25	68	-

a) Yields refer to isolated yield

b) Ratio of **3:2** was calculated after separation by column chromatography.

In summary, methanesulfonic acid/phosphorus oxychloride (MAPO) has been shown to be an efficient reagent in the Fries rearrangement of acyloxybenzene derivatives to acylaryl methane sulfonates. The present method has the following advantages: a) the reagent is readily available; b) the procedure is simple; c) the reaction times are usually short ; d) work up is easy; e) a wide range of phenolic esters are rearranged by MAPO.

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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. Mass spectra (MS) were recorded on a Shimadzu GCMS-QP 1000 EX at 70 eV. UV spectra were determined on a PU 8700 instrument. 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 MAPO.

General Procedure- The acyloxybenzene derivative (1 mmol) was added to a mixture of methanesulfonic acid (1 mL) and phosphorus oxychloride (2 mL) at 100°C. The reaction mixture was stirred for the time reported in Table 1. The reaction mixture was poured into water, extracted with chloroform (2 x 25 mL), washed with sodium hydrogen carbonate solution (2 x 30 mL), dried ($CaCl_2$) filtered, and evaporated. The crude product was purified by simple filtration chromatography through a short plug of silica gel, eluting with *n*-hexane ethyl acetate (90:10). The solvent was evaporated. Ratio **3:2** (**1a-f**) was calculated after column chromatography with *n*-hexane ethyl acetate (90:10). Known compounds were characterized by comparison of their physical data with those prepared in accordance with literature procedures and the physical characteristics of new products are reported below.

4-Benzoylphenyl methane sulfonate (**2a**): White crystals, mp. 78-98°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). ^{1}H NMR ($CDCl_3$): δ 3.15 (s, 3H), 7.1-7.9 (m, 9H); UV (MeOH): λ 206(ε_{max} 19320), 254 nm (ε 18080). MS: *m/z* 276 (M^+, 3.5), 105 (12.7), 81 (18.4), 55 (57.4), 41(100).

Anal. Calcd for $C_{14}H_{12}O_4S$: C, 60.86; H, 4.38. Found: C, 60.71; H, 4.49.

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). ^{1}H NMR ($CDCl_3$): δ 2.3 (s, 3H), 3.10 (s, 3H), 7.0-7.75 (m, 8H); UV (MeOH): λ 209 (ε_{max} 11260), 252 (ε 9960). MS: *m/z* 290 (M^+, 0.4), 233 (35.9), 231 (100), 168 (23.9), 105 (76.7), 77 (85.5).

Anal. Calcd for $C_{15}H_{14}O_4S$: C, 62.05; H, 4.86. Found: C, 62.15; H, 4.75.

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). ^{1}H NMR ($CDCl_3$): δ 2.5 (s, 3H), 3.10 (s, 3H), 7-7.45 (m, 7H); UV (MeOH): λ 209 (ε_{max} 31680), 252 nm (ε 16480). MS: *m/z* 326 (M + 2, 21.4), 325 (M+1, 28.6), 324 (M+, 53.7), 323 (53.2), 289 (100, base peak), 211 (70.4), 182 (40.0), 135 (84.9).

Anal Calcd for $C_{15}H_{13}ClO_4S$: C, 55.47; H, 4.03. Found: C, 55.53; H, 4.15.

4-(3-Bromobenzoyl)-3-methylphenyl methane sulfonate (**2d**) : White crystals, mp. 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). ^{1}H NMR ($CDCl_3$): δ 2.3 (s, 3H), 3.12 (s, 3H), 7.0-7.8 (m, 7H); UV (MeOH): λ 212 (ε_{max} 30440), 252 nm (ε = 14560). MS: *m/z*=370 (M + 2, 3.4), 369 (M + 1, 3.4), 368 (M^+, 3.4), 289 (33.3), 210 (23), 135 (35.6), 69 (42.4), 43 (100).

Anal. Calcd for $C_{15}H_{13}BrO_4S$: C, 48.79; H, 3.55. Found: C, 48.68; H, 3.76.

4-(4-Chlorobenzoyl)-3-methylphenyl methane sulfonate (**2e**) : Yellow viscous oil, R_f 0.75 (*n*-hexane/EtOAc 60:40); IR (neat): 1672 (C=O), 1605 (Ar), 1375 and 1190 cm^{-1} (S=O). ^{1}H NMR ($CDCl_3$): δ 2.3 (s, 3H), 3.14

(s, 3H), 7.0-7.7 (m, 7H); UV (MeOH): λ 208 (ε_{max} 23680), 264 nm (ε 20320); MS: *m/z* 326 (M + 2, 7.2), 325 (M + 1, 14.4), 324 (M^+, 19.8), 323 (31.6), 289 (100), 245 (31.9), 210 (42.2), 182 (26.6), 139 (63.9), 111 (96.6), 75 (43.7).

Anal.Calcd for $C_{15}H_{13}ClO_4S$: C, 55.47; H, 4.03. Found: C, 55.55; H, 4.14.

4-(4-Methylbenzoyl)-3-methylphenyl methane sulfonate (**2f**) : 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); UV (MeOH): λ 208 (ε_{max} 30200), 262 nm (ε 22760). MS: *m/z* 304 (M^+, 11.2), 303 (11.8), 289 (100), 225 (11.2), 210 (20.4), 154 (13.2), 119 (59.2), 91 (82.9), 65 (46.1).

Anal.Calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30. Found: C, 63.28; H, 5.31.

4-Benzoyl-2-chlorophenyl methane sulfonate (**2g**): 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); UV (MeOH): λ 206 (ε_{max} 23900), 254 nm (ε 11900). MS: *m/z* 310 (M^+, 34.3), 232 (28.6), 155 (37.0), 105 (100), 77 (87.3), 51 (45.3).

Anal.Calcd for $C_{14}H_{11}ClO_4S$: C, 54.11; H, 3.57. Found: C, 54.22; H, 3.68.

4-Benzoyl-2-methylphenyl methane sulfonate (**2h**): White crystals, mp. 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); UV (MeOH): λ 218 (ε_{max} 22020), 254 nm (ε 5300). MS: m/z 290 (M^+, 42.3), 264 (6.6), 213 (32.7), 183 (64.2), 155 (13), 135 (42.3), 123 (21.3), 105 (63.5), 77 (100).

Anal.Calcd for $C_{15}H_{14}O_4S$: C, 62.05; H, 4.86. Found: C, 62.11; H, 4.65.

4-Benzoyl-3-bromophenyl methane sulfonate (**2k**): Viscous oil, R_f 0.65 (*n*-hexane/EtOAc 60:40); IR (neat): 1680 (C=O), 1600 (Ar), 1375 and 1190 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 3.15 (s, 3H), 7.1-7.85 (m, 8H); UV (MeOH): λ 207 (ε_{max} 18120), 254 nm (ε 12320). MS: *m/z* 356 (M + 2, 16.5), 354 (M^+, 16.0), 279 (17.3), 277 (17), 201 (13.1), 199 (13.90), 149 (7.3), 105 (100), 77 (24.7).

Anal.Calcd for $C_{14}H_{11}BrO_4S$: C, 47.34; H,3.12. Found: C, 47.55; H, 3.18.

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); UV (MeOH): λ 209 (ε_{max} 32700), 256 (ε 12300). MS: *m/z* 276 (M^+, 8.5), 105 (25.6), 52 (72.1), 41 (100).

Anal.Calcd for $C_{14}H_{12}O_4S$: C, 60.86; H, 4.38. Found: C, 60.96; H, 4.30.

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); UV (MeOH): λ 207 (ε_{max} 31200), 259 (ε 15600). MS: *m/z* 290 (M^+, 12), 231 (100), 213 (30.1), 155 (19.1), 105 (82), 77 (65.8).

Anal.Calcd for $C_{15}H_{14}O_4S$: C, 62.05; H, 4.86. Found: C, 62.15; H, 4.75.

2-(2-Chlorobenzoyl)-5-methylphenyl methane sulfonate (**3c**): White crystals, mp. 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); UV (MeOH): λ 211 (ε_{max} 39320), 259 nm (ε 22920). MS: *m/z* 326 (M+2, 10.3), 325 (M+1, 20.5), 324 M^+, 26.8), 289 (100), 245 (38.2), 211 63.2), 139 (24.5), 75 (53.4).

Anal. Calcd for $C_{15}H_{13}ClO_4S$: C, 55.47; H, 4.03. Found: C, 55.53; H, 4.15.

2-(3-Bromobenzoyl)-5-methylphenyl methane sulfonate (**3d**) : 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); UV (MeOH): λ 210 (ε_{max} 33440), 253 nm (ε 14240); MS: *m/z* 370 (M+2, 6.2), 368 (M^+, 6.2), 289 (100), 211 (72.6), 69 (48.5), 43 (80.3).

Anal. Calcd for $C_{15}H_{13}BrO_4S$: C, 48.79; H, 3.55. Found: C, 48.68; H, 3.76.

2-(4-Chlorobenzoyl)-5-methylphenyl methane sulfonate (**3e**) : White crystals, mp. 52°C (*n*-hexane/CH_2Cl_2). R_f 0.78 (*n*-hexane/EtOAc 60:40); IR (KBr): 1672 (C=O), 1618 (Ar), 1352 and 1185 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 2.54 (s, 3H), 3.06 (s, 3H), 7.1-7.8 (m, 7H); UV (MeOH): λ 206(ε_{max} 20120), 264 nm(ε 13320). MS: *m/z* 326 (M+2, 5.2), 325 (M+1, 11.2), 324 (M+, 15.3), 289 (100), 211(36), 139 (61.3), 111 (80.2), 75 (59.6).

Anal. Calcd for $C_{15}H_{13}ClO_4S$: C, 55.47; H, 4.03. Found: C, 55.55; H, 4.14.

2-(4-Methylbenzoyl)-5-methylphenyl methane sulfonate (**3f**): 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); UV (MeOH): λ 205 (ε_{max} 31800), 260 (ε 18600). MS: *m/z* 304 (M^+, 5.5), 289 (100), 211 (32), 91 (65.5).

Anal.Calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30. Found: C, 63.08; H, 5.36.

3-Nitrophenyl methane sulfonate (**5i**): White crystals, mp. 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); UV (MeOH): λ 206.7 (ε_{max} 18980), 254 nm (ε 11260). MS: *m/z* 217 (M^+, 8.5), 149 (11.2), 139 (35.3), 97 (19.0), 69 (57.2), 43 (100,).

Anal.Calcd for $C_7H_7NO_5S$: C, 38.71; H, 3.25; N, 6.49. Found: C, 38.60; H, 3.36; N, 6.57.

3-Fluorophenyl methane sulfonate (**5j**): 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); UV (MeOH): λ 206 nm (ε_{max} 8180); MS: *m/z* 190 (M^+, 2.5), 167 (33.5), 149 (100), 112 (17.5), 91 (21.0), 71 (47.4).

Anal.Calcd for $C_7H_7FO_3S$: C, 44.21; H, 3.71. Found: C, 44.33; H, 3.60.

3-Methyl-4-propanoylphenyl methane sulfonate (**7a**): White crystals, mp. 38°C (*n*-hexane/CH_2Cl_2). R_f 0.75 (*n*-hexane/EtOAc 60:40); IR (KBr): 1700 (C=O), 1620 (Ar), 1375 and 1189 cm^{-1} (S=O). ^1H NMR ($CDCl_3$), δ 1.13 (t, 3H, J 8 Hz), 2.43 (s,3H), 2.9 (q, 2H, J 8 Hz), 3.22 (s, 3H), 7.08 (d, 1H, J 8Hz), 7.12 (s, 1H), 7.5 (d, 1H, J 8 Hz); UV (MeOH): λ 206(ε_{max} 26100), 243 nm (ε 9920). MS: *m/z* 242 (M^+, 2.4), 213 (88.0), 135 (100), 105 (12.8), 55 (48.0), 44 (96.8).

Anal.Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82. Found: C, 54.31; H, 5.93.

4-Benzoyl-1-naphthyl methane sulfonate (**8**): Viscous oil, R_f 0.70 (*n*-hexane/EtOAc 60:40); IR(neat): 1663 (C=O), 1600 (Ar), 1372 and 1183 cm^{-1} (S=O). ^1H NMR ($CDCl_3$): δ 3.20 (s, 3H), 7.3-8.25 (m, 11H); UV (MeOH): λ 218 (ε_{max} 42020), 248 nm (ε 17400). MS: *m/z* 326 (M^+, 34.7), 247 (100), 219 (19.9), 191 (33.4), 165 (10.7), 105 (46.4), 77 (66.9).

Anal.Calcd for $C_{18}H_{14}O_4S$: C, 66.24; H, 4.32. Found: C, 66.38; H, 4.43.

Reaction of 4-Benzoyloxybenzophenone (4a) with MAPO.

4-Benzoyloxybenzophenone **4a** (1 mmol) was added to a mixture of methanesulfonic acid (1 mL) and phosphorus oxychloride (2 mL) at 100°C and stirred for 4 h. The mixture was poured into water, extracted with chloroform (2 x 25 mL), washed with sodium hydrogen carbonate solution (2 x 30 mL), dried over calcium chloride and evaporated to give crude product **2a** in 90% yield.

Fries Rearrangement of Phenolic Esters with MAPO in the Presence of 1,2-dichloroethane.

The phenolic ester (1 mmol) was added to a mixture of methanesulfonic acid (1 mL) and phosphorus oxychloride (2 mL) in the presence of 1,2-dichloroethane (10 mL) at 100°C for 6 h. The reaction mixture was poured into water, extracted with chloroform (2 x 25 mL), washed with sodium hydrogen carbonate solution (2 x 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 ethyl acetate (90:10). The solvent was evaporated to give **4** in good yield (65-84%).

4-Benzoyloxybenzophenone (**4a**): White crystals (84%), mp. 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); UV (MeOH): λ_{max} 242 nm.

Anal. Calcd for $C_{20}H_{14}O_3$: C, 79.47 ; H, 4.63. Found: C,79.60 ; H, 4.51.

4-Benzoyloxy-2-methylbenzophenone (**4b**): White crystals (80%); m.p=90°C (*n*-Hexane/CH_2Cl_2); IR(KBr): 1760 (C=O), 1675 (C=O), 1600 cm^{-1}(Ar) ; ^1H NMR ($CDCl_3$), δ 2.3(s, 3H), 7.0-7.8 (m, 11H), 8.05 (dd, J 6, and 2Hz, 2H); UV (MeOH):λ_{max} 245 nm;

Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.75; H, 5.06. Found: C, 79.61; H, 5.01.

2`-Chloro-4-(2-chlorobenzoyloxy)-2-methylbenzophenone (**4c**): White crystals (78%); m.p=89°C (*n*-Hexane/CH_2Cl_2); IR(KBr): 1760 (C=O), 1675 (C=O), 1600 cm^{-1}(Ar) ; ^1H NMR ($CDCl_3$), δ 2.56(s, 3H), 6.85-7.6 (m, 9H), 8.05 (dd, J 6, and 2Hz, 2H); UV (MeOH):λ_{max} 240 nm;

Anal. Calcd for $C_{21}H_{14}Cl_2O_3$: C, 65.45; H, 3.64. Found: C, 65.3; H, 3.7.

3`-Bromo-4-(3-bromobenzoyloxy)-2-methylbenzophenone (**4d**): White crystals (75%); m.p=98°C (*n*-Hexane/CH_2Cl_2); IR(KBr): 1765 (C=O), 1670 (C=O), 1600 cm^{-1}(Ar) ; ^1H NMR ($CDCl_3$), δ 2.3(s, 3H), 7.0-8.3 (m, 11H). UV (MeOH):λ_{max} 243 nm;

Anal. Calcd for $C_{21}H_{14}Br_2O_3$: C, 53.16; H, 2.95. Found: C, 53.30; H, 2.80.

4`-Chloro-4-(4-chlorobenzoyloxy)-2-methylbenzophenone (**4e**): White crystals (76%); m.p=90°C (*n*-Hexane/CH_2Cl_2); IR(KBr): 1770 (C=O), 1665 (C=O), 1600 cm^{-1}(Ar) ; ^1H NMR ($CDCl_3$), δ 2.3 (s, 3H), 6.9-7.8 (m, 9H), 8.15 (d, J 12Hz, 2H). UV (MeOH):λ_{max} 246 nm;

Anal. Calcd for $C_{21}H_{14}Cl_2O_3$: C, 65.45; H, 3.64. Found: C, 65.36; H, 3.60.

4`-Methyl-4-(4-methylbenzoyloxy)-2-methylbenzophenone (**4f**): White crystals (81%): mp=76°C (*n*-Hexane/CH_2Cl_2); IR(KBr): 1760 (C=O), 1665 (C=O), 1600 cm^{-1}(Ar) ; ^1H NMR ($CDCl_3$), δ 2.3 (s, 3H), 2.4 (s, 6H), 6.9-8.2 (m, 11H). UV (MeOH):λ_{max} 239 nm;

Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.23; H, 5.81. Found: C, 80.38; H, 5.87.

4-Benzoyloxy-3-chloro benzophenone (**4g**): Viscous oil (71%); IR(neat): 1756 (C=O), 1673 (C=O), 1605 cm^{-1}(Ar). ^1H NMR ($CDCl_3$): 6.8-7.7 (m, 12H), 8.1 (d, J 6Hz, 1H); UV (MeOH): λ_{max} 241 nm.

Anal. Calcd for $C_{20}H_{13}ClO_3$: C, 71.32; H, 3.86. Found: C, 71.20; H, 3.93.

4-Benzoyloxy-3-methylbenzophenone (**4h**): Viscous oil (78%); IR (neat): 1760 (C=O), 1675 (C=O), 1600 cm^{-1}(Ar) ; ^1H NMR ($CDCl_3$), δ 2.35(s, 3H), 7.0-7.8 (m, 12H), 8.05 (d, J 6 Hz,1H); UV (MeOH):λ_{max} 245 nm;

Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.75; H, 5.06. Found: C, 79.65; H, 5.15.

4-Benzoyloxy-2-bromobenzophenone (**4k**): Viscous oil (65%); IR(neat): 1765 (C=O), 1670 (C=O), 1605 cm^{-1}(Ar). ^1H NMR ($CDCl_3$): 6.8-7.7 (m, 12H), 8.05 (d, J 6Hz, 1H); UV (MeOH): λ_{max} 246 nm.

Anal. Calcd for $C_{20}H_{13}BrO_3$: C, 62.99; H, 3.41. Found: C, 70.10; H, 3.33.

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