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Triphenylphosphine-Mediated Synthesis of Methyl 2-Aroyloxypropenoates from 2-Aroyl-2-methoxycarbonyloxiranes

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Abstract: A new synthesis of several 2-aroyloxypropenoic acid methyl esters **5** by the reaction of 2-aroyl-2-methoxycarbonyloxiranes **2** with triphenylphosphine in tetrahydrofuran has been described.

Keywords: 2-Aroyl-2-methoxycarbonyloxirane, Baylis–Hillman adduct, methyl 2-aroyloxypropenoate, triphenylphosphine

The captodative alkene 2-aroyloxypropenoic acid methyl esters have been shown to be highly reactive and regioselective in Diels–Alder reactions.[1] Radical homopolymerization of some captodative substituted methyl 2-acyloxypropenoates was studied kinetically by azo initiators and was found to give a polymer with excellent optical properties.[2] The captodative olefin methyl 2-acyloxypropenoates were prepared mainly by reaction of methyl pyruvate with an acyl chloride in the presence of triethylamine.[1a,3]

The Baylis–Hillman reaction[4] is a powerful carbon–carbon bond-forming method for installing β-hydroxy-α-methylenecarbonyl units, which are extremely versatile building blocks in organic synthesis.[5] It is known that the reaction of Baylis–Hillman adducts with silica gel–supported sodium hypochlorite is an efficient procedure for the synthesis of acyloxiranes.[6] We envisioned that deoxygenation of acyloxiranes with a suitable

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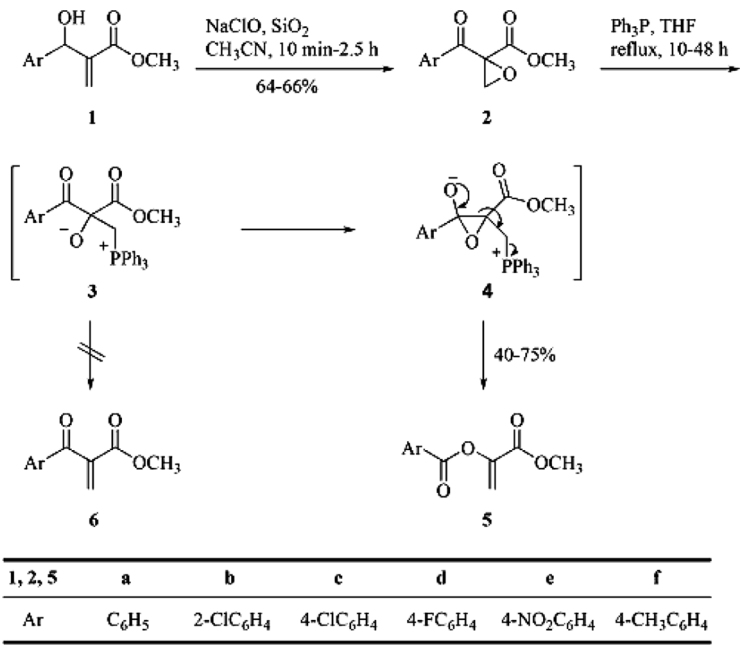
Table 1. Methyl 2-benzoyloxypropenoate **5a** synthesis in various reaction conditions

Entry	Reagem	Solvent	Time (h)[a]	Yield (%)
1	Ph_3P	Benzene	72	20
2	Ph_3P	Toluene	72	14
3	Ph_3P	Xylene	48	Trace
4	$(EtO)_3P$	Benzene	120	13
5	Bu_3P	Benzene	120	Trace
6	Ph_3P	THF	36	46
7	Ph_3P	Dioxane	24	25
8	Ph_3P	CH_3CN	4	23
9	Ph_3P	CH_2C1_2	72	23

[a]Reflux temperature.

phosphine reagent, originally discovered by Wittig,[7] might lead to the α-methylene-β-oxo esters, which are not easy to obtain.

Various reaction media were first scrutinized in a test reaction of benzoyloxirane **2a** with triphenylphosphine, tributylphosphine, or triethylphosphite (Table 1). The expected α-methylene-β-oxo ester **6a**



1, 2, 5	a	b	c	d	e	f
Ar	C_6H_5	2-ClC_6H_4	4-ClC_6H_4	4-FC_6H_4	4-$NO_2C_6H_4$	4-$CH_3C_6H_4$

Scheme 1. Synthesis of methyl 2-aroyloxypropenoates.

Table 2. Methyl 2-Aroyloxypropenoates **5a–f**

Entry	Substrate	Product	Time (h)	Yield (%)
1	**2a**	**5a**	36	46
2	**2b**	**5b**	10	40
3	**2c**	**5c**	17	47
4	**2d**	**5d**	48	75
5	**2e**	**5e**	10	58
6	**2f**	**5f**	20	43

was not produced at all. We found that the product was the known methyl 2-benzoyloxypropenoate **5a**[1a] and the use of triphenylphosphine in tetrahydrofuran (THF) solvent system was the best reaction condition to improve product yields (entry 6, Table 1). The optimized protocol for the aroyloxypropenoic acid methyl ester synthesis proved to be general, and a wide range of acyloxiranes were readily converted to the aroyloxy propenoate product in moderate to poor yields (Scheme 1, Table 2).

The conversion of **2** into **5** would appear to proceed in such a way that a nucleophilic attack of triphenylphosphine at the epoxide gives a betaine **3**, the resulting negative oxygen attacks carbonyl carbon to give another epoxide betaine **4**, and the electrons on the negative oxygen reform the pi bond as the carbon–carbon bond cleaves and the triphenylphosphine leaves. Similar conversions are known, such as flash vacuum pyrolysis of indenone epoxide to isocoumarin[8] and acid treatment of 2,3-diphenyl-2,3-epoxyindanone to 3,4-diphenylisocoumarin.[9]

In summary, we have introduced a new synthesis of 2-aroyloxypropenoic acid methyl esters from the reaction of 2-aroyl-2-methoxycarbonyloxiranes, which are readily prepared from the Baylis–Hillman adducts with triphenylphosphine.

EXPERIMENTAL

Silica gel 60 (70–230 mesh ASTM) used for column chromatography was supplied by E. Merck. Analytical thin layer chromatography (TLC) was carried out on Merck silica-gel 60 F_{254} TLC plates. Melting points were taken using an Electrothermal melting-point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet Magna 550 Fourier transform (FTIR)-spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Gemini 300 spectrometer using $CDCl_3$. All chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS). Mass spectra (MS) were recorded on a Hewlett-Packard 5972A instrument operating at 70 eV.

The known Baylis–Hillman (BH) adducts **1a–f**[10] and oxiranes **2a, 2c, 2e**, and **2f**[6] were prepared according to the literature procedures.

2-(2-Chlorobenzoyl)-2-methoxycarbonyloxirane (2b)

Silica gel (10 g) was added to a stirred solution of BH adduct **1b** (2.27 g, 10 mmol) in acetonitrile (10 ml), and the mixture was treated with 10–13% sodium hypochlorite solution (40 ml). After stirring for 2.5 h, the mixture was extracted with diethyl ether (2×20 ml). The organic layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated in vacuo. The residue was purified by column chromatography to produce 1.54 g (64%) of **2b** as an yellow oil: IR (CH_2Cl_2) 1754, 1708 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.19 (d, $J = 6.4$ Hz, 1H), 3.47 (d, $J = 6.4$ Hz, 1H), 3.80 (s, 3H), 7.28–7.58 (m, 3H), 7.66–7.69 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 52.6, 53.2, 59.5, 126.9, 128.9, 130.6, 132.7, 133.2, 134.9, 166.8, 190.4; EIMS (%) 240 (1) [M^+], 205 (5), 141 (34), 139 (100), 113 (9), 111 (28), 75 (18). Anal. calcd. for $C_{11}H_9ClO_4$: C, 54.90; H, 3.77. Found: C, 54.72; H, 3.59.

2-(4-Fluorobenzoyl)-2-methoxycarbonyloxirane (2d)

Silica gel (10 g) was added to a stirred solution of BH adduct **1d** (2.10 g, 10 mmol) in acetonitrile (10 ml), and the mixture was treated with 10–13% sodium hypochlorite solution (40 ml). After stirring for 10 min, the mixture was extracted with diethyl ether (2×20 ml). The organic layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated in vacuo. The residue was purified by column chromatography to produce 1.48 g (66%) of **2d** as a white solid: mp 39–40°C; IR (KBr) 1763, 1692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.23 (d, $J = 6.1$ Hz, 1H), 3.41 (d, $J = 6.1$ Hz, 1H), 3.79 (s, 3H), 7.15–7.21 (m, 2H), 8.03–8.08 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 51.3, 53.4, 58.8, 116.1 (d, $J = 22.0$ Hz), 130.6, 131.9 (d, $J = 9.8$ Hz), 166.4 (d, $J = 258$ Hz), 167.5, 189.0; EIMS (%) 224 (1) [M^+], 123 (100), 95 (35), 75 (12). Anal. calcd. for $C_{11}H_9FO_4$: C, 58.93; H, 4.05. Found: C, 58.78; H, 4.25.

General Procedure for the Synthesis of Methyl 2-Aroyloxypropenoates 5a–f

2-Aroyl-2-methoxycarbonyloxirane **2a–f** (1 mmol), PPh_3 (1 mmol), and THF (2 ml) were stirred at reflux temperature for the time indicated in

Table 2. After the reaction was completed, the reaction mixture was concentrated under reduced pressure. The resulting mixture was chromatographed on silica gel, eluting with hexane/EtOAc (8:1) to produce pure **5a–f**.

The physical and spectral data of **5a–f** prepared by this general method follow.

Methyl 2-Benzoyloxypropenoate (5a)[1a]

Yellow oil; yield 46%; IR (CH_2Cl_2) 1736, 1649 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 5.62 (d, $J = 1.8$ Hz, 1H), 6.17 (d, $J = 1.8$ Hz, 1H), 7.46–7.52 (m, 2H), 7.60–7.66 (m, 1H), 8.12–8.14 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 52.6, 114.3, 128.6, 128.8, 130.3, 133.8, 144.8, 162.0, 164.7; EIMS (%) 206 (1) [M^+], 175 (2), 105 (100), 77 (44).

Methyl 2-(2-Chlorobenzoyloxy)propenoate (5b)

Yellow oil; yield 40%; IR (CH_2Cl_2) 1737, 1649 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.84 (s, 3H), 5.65 (d, $J = 1.8$ Hz, 1H), 6.18 (d, $J = 1.8$ Hz, 1H), 7.34–7.40 (m, 1H), 7.48–7.52 (m, 2H), 8.02–8.05 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 52.7, 114.6, 126.7, 128.1, 131.3, 132.2, 133.5, 134.7, 144.5, 161.8, 163.1; EIMS (%) 240 (1) [M^+], 209 (2), 211 (1), 141 (33), 139 (100), 113 (9), 111 (26), 75 (19). Anal. calcd. for $C_{11}H_9ClO_4$: C, 54.90; H, 3.77. Found: C, 54.68; H, 3.57.

Methyl 2-(4-Chlorobenzoyloxy)propenoate (5c)[1a]

White solid; yield 47%; mp 38–39 °C; IR (KBr) 1736, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 5.63 (d, $J = 1.8$ Hz, 1H), 6.18 (d, $J = 1.8$ Hz, 1H), 7.45–7.48 (m, 2H), 8.05–8.08 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 52.7, 114.5, 127.0, 129.0, 131.6, 140.4, 144.6, 161.8, 163.8; EIMS (%) 240 (1) [M^+], 209 (3), 211 (1), 141 (44), 139 (100), 113 (13), 111 (41), 75 (26).

Methyl 2-(4-Fluorobenzoyloxy)propenoate (5d)

White solid; yield 75%; mp 53–54 °C; IR (KBr) 1739, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.82 (s, 3H), 5.63 (d, $J = 1.8$ Hz, 1H), 6.18 (d, $J = 1.8$ Hz, 1H), 7.13–7.20 (m, 2H), 8.13–8.17 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 52.7, 114.4, 115.8 (d, $J = 22.0$ Hz), 124.8, 132.9 (d, $J = 9.8$ Hz), 144.6,

161.9, 163.7, 166.3 (d, $J = 255$ Hz); EIMS (%) 224 (1) [M^+], 193 (2), 123 (100), 95 (33), 75 (13). Anal. calcd. for $C_{11}H_9FO_4$: C, 58.93; H, 4.05. Found: C, 58.72; H, 4.26.

Methyl 2-(4-Nitrobenzoyloxy)propenoate (5e)[1a]

White solid; yield 58%; mp 79–81 °C; IR (KBr) 1745, 1726, 1647, 1526, 1325 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.84 (s, 3H), 5.69 (d, $J = 1.8$ Hz, 1H), 6.23 (d, $J = 1.8$ Hz, 1H), 8.29–8.36 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 52.8, 114.9, 123.7, 131.4, 134.0, 144.4, 151.0, 161.5, 162.8; EIMS (%) 251 (1) [M^+], 220 (3), 150 (100), 120 (7), 104 (30), 92 (13), 76 (22).

Methyl 2-(4-Methylbenzoyloxy)propenoate (5f)

Yellow oil; yield 43%; IR (CH_2Cl_2) 1734, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.43 (s, 3H), 3.81 (s, 3H), 5.60 (d, $J = 1.8$ Hz, 1H), 6.15 (d, $J = 1.8$ Hz, 1H), 7.27–7.30 (m, 2H), 8.00–8.03 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.7, 52.6, 114.2, 125.8, 129.3, 130.3, 144.7, 144.8, 162.1, 164.7; EIMS (%) 220 (1) [M^+], 189 (2), 119 (100), 91 (37), 65 (15). Anal. calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.28; H, 5.25.

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