NMR (60 MHz, $CDCl_3$) δ 1.31 (d, 3 H, J = 6.4 Hz), 1.4–1.9 (m, 4 H), 2.0–2.5 (m, 2 H), 4.5–5.1 (m, 1 H), 6.51 (t, 1 H, J = 5.6 Hz); MS, m/e 220, 218 (M^+).

A solution of **5b** (153 mg, 0.70 mmol), diethyl phosphonate (194 mg, 1.40 mmol), and triethylamine (283 mg, 2.80 mmol) was stirred at 80 °C for 3 h. Ether (20 mL) was added to the resultant mixture. The separated white deposit (Et_3N·HBr) was filtered off and washed with ether (2 × 10 mL). The filtrate and ethereal washings were concentrated and flash chromatographed, eluting with 10% EtOAc–hexane to give 59 mg (60%) of **6b** as a colorless oil and 25 mg (26%) of **7b**. **6b**: IR (neat) 1730, 1660 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.37 (d, 3 H, J = 6.4 Hz), 1.5–1.9 (m, 2 H), 2.0–2.6 (m, 2 H), 3.1–3.3 (m, 2 H), 4.5–5.0 (m, 1 H), 5.53 (dt, 1 H, J = 11.0, 3.8 Hz), 5.73 (dtt, 1 H, J = 11.0, 7.1, 1.9 Hz); MS, m/e 140 (M^+). Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.35; H, 8.90.

Thus obtained β,γ-unsaturated lactone **6b** (59 mg, 0.42 mmol) was treated with 6 N KOH in methanol (0.84 mL) and water (0.41 mL) at room temperature for 1 h. Water (2 mL) was added to the resultant mixture, which was extracted with ether (3 × 5 mL). The aqueous layer was adjusted to pH 2 with concentrated HCl and extracted with ether (3 × 5 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated to give 57 mg of the product **8**, which was pure by TLC (R_f 0.47, EtOAc): IR (neat) 3400 (broad), 1720 cm^{-1} (no peak assigned to the trans isomer); ^1H NMR (90 MHz, $CDCl_3$) δ 1.21 (d, 3 H, J = 6.3 Hz), 1.52 (q, 2 H, J = 6.3 Hz), 2.0–2.3 (m, 2 H), 3.0–3.2 (m, 2 H), 3.84 (sextet, 1 H, J = 6.3 Hz), 5.4–5.8 (m, 2 H), 6.16 (broad s, 2 H); MS, m/e 158 (M^+).

The dimerization of **8** was carried out according to the reported method[2a] to give **9** in 50% yield: IR (neat) 1730, 1660 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.23 (d, 6 H, J = 6.3 Hz), 1.4–1.8 (m, 4 H), 1.9–2.3 (m, 4 H), 2.9–3.2 (m, 4 H), 4.7–5.2 (m, 2 H), 5.3–5.8 (m, 4 H); high-resolution MS calcd for $C_{16}H_{24}O_4$ 280.1673, found 280.1689.

To a solution of **9** (33 mg, 0.12 mmol) in CH_2Cl_2 (2.5 mL) was added MCPBA (78 mg) at 0 °C. Stirring was continued at 0 °C for 0.5 h and at room temperature for 3 h. Ether (30 mL) was added to the mixture, which was washed with ice-cooled 5% $NaHCO_3$ (20 mL), 2% NaOH (10 mL), and brine. The organic phase was dried over $MgSO_4$ and concentrated to give 30 mg of a white solid (no olefinic proton in ^1H NMR). Butyllithium (43 μL, 0.069 mmol) was added to a solution of diisopropylamine (13 μL, 0.092 mmol) in THF (0.37 mL) at −78 °C. The resulting solution was stirred at 0 °C for 0.5 h. The white solid obtained above (7.2 mg, theoretically 0.023 mmol) in THF (0.18 mL) was added dropwise at −78 °C over 15 min. The mixture was stirred at the same temperature for 1 h and quenched with acetic acid (14 μL). After warming up to room temperature, brine (3 mL) was added to the mixture, which was extracted with ether (3 × 5 mL). The combined organic layers were washed with 5% $NaHCO_3$ (3 mL) and brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on a silica gel column eluting with 40% EtOAc–hexane to give **10** (3.7 mg, 50% based on **9**): IR (neat) 3400 (broad), 1715, 1650, 980 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.25 (broad d, 6 H), 1.4–2.0 (m, 8 H), 4.0–4.6 (m, 2 H), 4.7–5.3 (m, 2 H), 5.98 (d, 2 H, J = 15.6 Hz), 6.83 (dd, 2 H, J = 15.6, 5.1 Hz).

Regioselective Allylation of Ketones under Neutral Conditions

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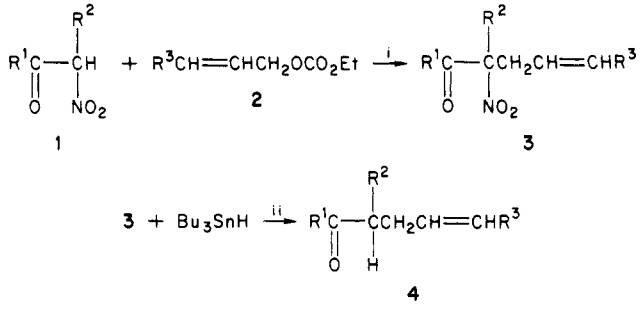
Regioselective allylation of ketones is an important process in organic synthesis and many methods have been devised for this purpose.[1] Among them, palladium-catalyzed allylation of β-keto esters or β-keto sulfones and subsequent removal of the ester or sulfonyl function has been used quite often owing to the high selectivity of these procedures.[2] In this note we report another selective method for the allylation of ketones. Our method consists of two key steps: allylation of α-nitro ketones (**1**) with allylic carbonates (**2**) in the presence of a palladium(0) catalyst[3] and subsequent denitration with Bu_3SnH.[4]



(i) $Pd(PPh_3)_4$ (5 mol %), THF, rt; (ii) AIBN (0.2 equiv), benzene, 80 °C, 2 h

Allylation was carried out by stirring a mixture of **1**, **2**, and $Pd(PPh_3)_4$ (5 mol %) in tetrahydrofuran (THF) at room temperature for 20 h. Allylated products (**3**) were obtained in 70–80% yields. Subsequent denitration was carried out by heating a mixture of **3**, tributylstannane (Bu_3SnH, 1.2 equiv), and azobis(isobutyronitrile) (AIBN, 0.2 equiv) in benzene at 80 °C for 2 h. The results are summarized in Table I. The requisite starting α-nitro ketones were prepared by acylation of nitroalkanes[5] or by oxidation of β-nitro alcohols.[6] Thus, the present method consist of genuinely simple procedures and required neither acidic nor basic conditions, so it affords some advantages over the conventional methods.[1]

Table I. Regioselective Allylation of Ketones

R^1	R^2	R^3	3, yield, %	4, yield, %
n-C_4H_9	Et	Ph	**3a**, 70	**4a**, 85
n-C_4H_9	Et	H	**3b**, 72	**4b**, 87
n-C_3H_7	n-C_3H_7	Ph	**3c**, 72	**4c**, 83
n-C_3H_7	n-C_3H_7	H	**3d**, 81	**4d**, 80
n-C_6H_{13}	Me	Ph	**3e**, 75	**4e**, 80
n-C_6H_{13}	Me	H	**3f**, 72	**4f**, 85

The present method can be applied to allylation of esters. Allylation of ethyl α-nitrobutyrate[3] and subsequent denitration gave the allylated product of ethyl butyrate.

Experimental Section

α-Nitro ketones (**1**) were prepared according to the literatures.[5,6]

Allylation of 1. General Procedure. To a stirred solution of **1** (0.01 mol) and **2** (0.01 mol) in THF (10 mL) under argon was added $Pd(PPh_3)_4$ (0.05 g) at room temperature. The resulting

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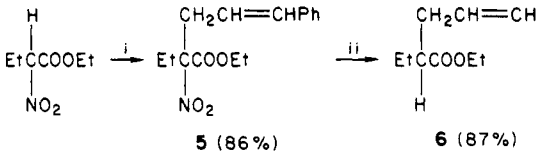

5 (86%) 6 (87%)

(i) $PhCH{=}CHCH_2OCO_2Et$, $Pd(PPh_3)_4$ (5 mol %), rt, 20 h; (ii) Bu_3SnH (1.2 equiv), AIBN (0.2 equiv), benzene, 80 °C, 2 h

mixture was stirred at room temperature for 20 h, and the mixture was filtered. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel/benzene–hexane) to give **3**.

3a: IR (neat) 1380, 1545, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.78–0.92 (m, 6 H), 1.05–1.70 (m, 4 H), 2.05–2.30 (m, 2 H), 2.42 (t, 2 H, J = 7 Hz), 2.98 (d, 2 H, J = 7 Hz), 5.70–6.02 (m, 1 H), 6.44 (d, 1 H, J = 17 Hz), 7.3 (m, 5 H). Anal. Calcd for $C_{17}H_{23}NO_3$: C, 70.56; H, 8.01; N, 4.84. Found: C, 70.84; H, 8.11; N, 4.84.

3b: IR (neat) 1380, 1540, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.80–1.00 (m, 6 H), 1.10–1.70 (m, 4 H), 2.02–2.30 (m, 2 H), 2.41 (t, 2 H, J = 8 Hz), 2.84 (d, 2 H, J = 8 Hz), 4.98–5.20 (m, 2 H), 5.30–5.70 (m, 1 H). Anal. Calcd for $C_{11}H_{19}NO_3$: C, 61.95; H, 8.98; N, 6.57. Found: C, 61.88; H, 9.12; N, 6.38.

3c: IR (neat) 1370, 1538, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.80–1.01 (m, 6 H), 1.10–1.80 (m, 4 H), 2.02–2.28 (m, 2 H), 2.40 (t, 2 H, J = 7 Hz), 2.98 (d, 2 H, J = 7 Hz), 5.65–6.00 (m, 1 H), 6.42 (d, 1 H, J = 17 Hz), 7.5 (m, 5 H). Anal. Calcd for $C_{17}H_{23}NO_3$: C, 70.56; H, 8.10; N, 4.84. Found: C, 70.56; B, 8.14; N, 4.74.

3d: IR (neat) 1380, 1545, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.80–1.05 (m, 6 H), 1.10–1.80 (m, 4 H), 1.96–2.20 (m, 2 H), 2.40 (t, 2 H, J = 7 Hz), 2.80 (d, 2 H, J = 7 Hz), 5.00–5.22 (m, 2 H), 5.30–5.70 (m, 1 H). Anal. Calcd for $C_{11}H_{19}NO_3$: C, 61.95; H, 8.98; 6.57. Found: C, 62.25; H, 8.97; N, 6.47.

3e: IR (neat) 1370, 1545, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.78–0.92 (m, 3 H), 1.05–1.70 (m, 8 H), 1.60 (s, 3 H), 2.42 (t, 2 H, J = 7 Hz), 2.80–3.02 (m, 2 H), 5.80–6.05 (m, 1 H), 6.42 (d, 1 H, J = 17 Hz), 7.3 (m, 5 H). Anal. Calcd for $C_{18}H_{25}NO_3$: C, 71.25; H, 8.31; N, 4.62. Found: C, 70.96; H, 8.13; N, 4.93.

3f: IR (neat) 1380, 1545, 1720 cm^{-1}; NMR ($CDCl_3$) δ 0.78–1.00 (m, 3 H), 1.10–1.78 (m, 8 H), 1.66 (s, 3 H), 2.44 (t, 2 H, J = 7 Hz), 2.74–3.00 (m, 2 H), 5.0–5.22 (m, 2 H), 5.40–5.80 (m, 1 H). Anal. Calcd for $C_{12}H_{21}NO_3$: C, 63.41; H, 9.31; N, 6.16. Found: C, 63.41; H, 9.31; N, 6.12.

Allylation of ethyl α-nitrobutyrate[7] was carried out in the same way as allylation of **1**. Allylated product **5**[3] was obtained in 86% yield.

5: IR (neat) 1350, 1540, 1740 cm^{-1}; NMR ($CDCl_3$) δ 0.94 (t, 3 H, J = 7 Hz), 1.22 (t, 3 H, J = 7 Hz), 2.26 (t, 2 H, J = 7 Hz), 3.06 (d, 2 H, J = 8 Hz); 4.24 (q, 2 H, J = 7 Hz), 5.80–6.08 (m, 1 H), 6.50 (d, 1 H, J = 17 Hz), 7.3 (m, 5 H). Anal. Calcd for $C_16H_{19}NO_4$: C, 64.96; H, 6.91; N, 5.05. Found: C, 65.13; H, 6.97; N, 5.13.

Denitration of 3 and 5. A mixture of **3** or **5** (0.01 mol), Bu_3SnH (0.012 mol), and AIBN (0.002 mol) in benzene (5 mL) was heated at 80 °C for 2 h. The mixture was then subjected to column chromatography (silica gel/benzene–hexane) to give the denitrated product, **4** or **6**, respectively. Compounds **4a**, **4c**, **4e**, and **6** consisted of a single isomer and rearrangement product was not detected by NMR and GLC. When cinnamyl acetate was used, a small amount of allylic rearrangement product was formed (ca. 3%).[3]

4a: IR (neat) 1710 cm^{-1}; NMR ($CDCl_3$) δ 0.80–1.10 (m, 6 H), 1.10–1.80 (m, 6 H), 2.10–2.50 (m, 5 H), 5.90–6.18 (m, 1 H, 6.30 (d, 1 H, J = 17 Hz), 7.2 (m, 5 H); MS, m/e (M^+) calcd for $C_{17}H_{24}O$ 244.1828, found 244.1828.

4b: IR (neat) 1710 cm^{-1}; NMR ($CDCl_3$) δ 0.80–1.10 (m, 6 H), 1.10–1.80 (m, 6 H), 2.10–2.55 (m, 5 H), 5.0–5.36 (m, 2 H), 5.40–5.80 (m, 1 H); MS, m/e (M^+) calcd for $C_{11}H_{20}O$ 168.1513, found 168.1517.

4c: IR (neat) 1710 cm^{-1}; NMR ($CDCl_3$) δ 0.80–1.10 (m, 6 H), 1.10–1.80 (m, 6 H), 2.20–2.70 (m, 5 H), 5.90–6.22 (m, 1 H), 6.35 (d, 1 H, J = 17 Hz), 7.2 (m, 5 H); MS, m/e (M^+) calcd for $C_{17}H_{24}O$ 244.1828, found 244.1823.

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4d: IR (neat) 1710 cm^{-1}; NMR ($CDCl_3$) δ 0.80–1.10 (m, 6 H), 1.10–1.80 (m, 6 H), 2.10–2.66 (m, 5 H), 5.0–5.30 (m, 2 H), 5.35–5.60 (m, 1 H); MS, m/e (M^+) calcd for $C_{11}H_{20}O$ 168.1513, found 168.1520.

4e: IR (neat) 1710 cm^{-1}; NMR ($CDCl_3$) δ 0.86 (t, 3 H, J = 7 Hz), 1.10–1.90 (m, 8 H), 2.20–2.75 (m, 8 H), 5.90–6.20 (m, 1 H), 6.30 (d, 1 H, J = 17 Hz), 7.3 (m, 5 H); MS, m/e (M^+) calcd for $C_{18}H_{26}O$ 270.1974, found 270.1982.

4f: IR (neat) 1710 cm^{-1}; NMR ($CDCl_3$) δ 0.85 (t, 3 H, J = 7 Hz), 1.10–1.90 (m, 8 H), 2.14–2.70 (m, 8 H), 5.02–5.30 (m, 2 H), 5.35–5.65 (m, 1 H); MS, m/e (M^+) calcd for $C_{12}H_{22}O$ 194.1669, found 194.1668.

6: IR (neat) 1730 cm^{-1}; NMR ($CDCl_3$) δ 0.80–1.02 (t, 3 H, J = 7 Hz), 1.08–1.32 (m, 3 H), 1.42–1.80 (m, 2 H), 2.20–2.62 (m, 3 H), 4.10 (q, 2 H, J = 7 Hz), 5.98–6.48 (m, 2 H), 7.2 (m, 5 H); MS, m/e (M^+) calcd for $C_{15}H_{20}O_2$ 232.1464, found 232.1475.

Registry No. 1 (R^1 = OEt, R^2 = Et) 2531-81-9; **19**, 83483-16-3; **1c**, 55601-75-7; **1e**, 85199-51-5; **2a**, 86537-61-3; **2b**, 1469-70-1; **3a**, 102492-82-0; **3b**, 102492-83-1; **3c**, 102492-84-2; **3d**, 102492-85-3; **3e**, 102492-86-4; **3f**, 102492-87-5; **4a**, 102492-88-6; **4b**, 102492-89-7; **4c**, 102492-90-0; **4d**, 102492-91-1; **4e**, 102492-92-2; **4f**, 102492-93-3; **5**, 79918-53-9; **6**, 102492-94-4.

Directed Ortho-Lithiation of Alkyl Arenesulfonates

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The well-documented, directed ortho-lithiation reaction has been utilized to prepare a wide variety of substituted aromatics. This reaction involves deprotonation ortho to heteroatom functions such as amides, sulfones, amines, sulfonamides, and many others.[1] The reactive anion thus formed can then be trapped by electrophiles. Recently Figuly and Martin reported the ortho-metalation of lithium arenesulfonates (**1a**).[2] The anion generated in this sequence could be reacted with a variety of electrophiles to furnish ortho-substituted arenesulfonic acids. The sulfonic acid functionality could be removed to afford substituted aromatic derivatives. The products of this procedure are lithium salts of sulfonic acids. The authors found these products difficult to separate from the starting material using standard manipulations such as chromatography. Some products were inseparable without prior chemical modification to remove the sulfonic acid group. In addition, Russian workers reported the polylithiation of both lithium arenesulfonates and alkyl arenesulfonates.[3] These lithiations were done in diethyl ether with up to a tenfold excess of *n*-butyllithium. Under these conditions the sequence is heterogeneous and products arising from polylithiation–alkylation predominate.

In this note, the ortho-metalation of alkyl arenesulfonates **1b–d** is reported as summarized in Table I. These examples demonstrate (1) that metalation is facile and (2) that the organolithium reagent can be trapped by

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