

A facile synthesis of $\Delta^{7,9(11)}$ -steroidal dienes[†]

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Treatment of Δ^7 -steroids, dissolved in benzene, with sulfuryl chloride resulted in the formation of steroidal $\Delta^{7,9(11)}$ -in good yields.

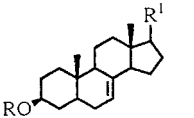
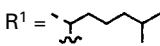
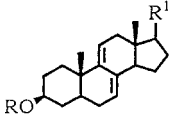
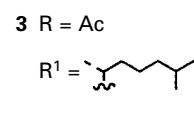
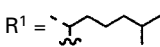
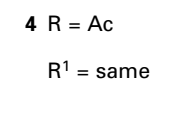
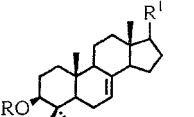
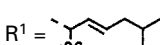
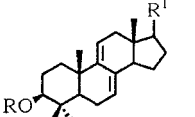
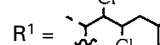
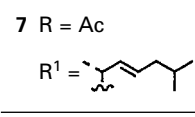
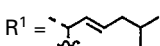
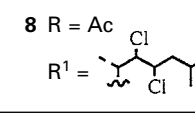
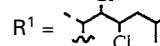
Steroids containing the $\Delta^{7,9(11)}$ -diene system are key intermediates in the chemical functionalization of carbons 7 and 11 in the steroid series.^{1–4} Previously, steroidal $\Delta^{7,9(11)}$ -dienes have been efficiently prepared from the corresponding Δ^7 -monoene by use of mercuric acetate.¹

In the course of our investigations, we required the protection of the Δ^5 -double bond of steroids as the dichloride through the use of sulfuryl chloride.^{5,6} While applying this approach to the protection of the Δ^7 -double bond, we have discovered that treatment of certain Δ^7 -steroids with sulfuryl chloride resulted in the formation of $\Delta^{7,9(11)}$ -dienes in good yields (Table 1).

Each product exhibited characteristic proton NMR signals at 5.35–5.37 and 5.46–5.46 for the olefinic hydrogens at carbons 7 and 11, respectively.^{7,11} Absence of the Δ^7 -proton signal at 5.14–5.16 indicated that the starting material was consumed in each case.^{7,11} These results were further confirmed by examination of the ¹³C NMR spectra.⁷ In addition, each product exhibited a characteristic UV spectrum for $\Delta^{7,9(11)}$ -steroidal dienes (λ_{\max} 242–246 nm, $\epsilon=10,000$ – $12,000$).^{4,8–10}

The reactions reported herein expand the scope of synthetic transformations known to be accomplished by sulfuryl chloride and offer a new and convenient method for the synthesis of steroidal $\Delta^{7,9(11)}$ -dienes.

Table 1 Synthesis of $\Delta^{7,9(11)}$ -steroidal dienes^a

Substrate	$\Delta^{7,9(11)}$ product	Yield (isolated) (%) ^b
 1 R = Bz R ¹ = 	 2 R = Bz R ¹ = same	78
 3 R = Ac R ¹ = 	 4 R = Ac R ¹ = same	75
 5 R = Bz R ¹ = 	 6 R = Bz R ¹ = 	76
 7 R = Ac R ¹ = 	 8 R = Ac R ¹ = 	74

^aThe reactions were carried out in benzene/pyridine.^bThe yield of isolated product.

The substrates (1,3,5 and 7) in Table 1 were reacted with 2.5 equiv. of sulfuryl chloride in benzene/pyridine for 2 h which resulted in the corresponding $\Delta^{7,9(11)}$ -dienes in good yields.

Experimental

Steroidal $\Delta^{7,9(11)}$ -dienes. general procedure: The Δ^7 -steroids exhibited in Table 1 (6.0 mmol) were dissolved in a mixture 37.5 ml of benzene and 3.5 ml pyridine and cooled to 0°C (solution solidifies). Sulfuryl chloride (2g;14.8 mmol) in 20 ml of dry benzene was slowly added, the temperature being kept below 2°C, when addition was complete, the mixture was stirred for an additional 2 h at 2°C. The mixture was then allowed to warm to 15°C and the product was extracted with ether, washed with water, sodium carbonate solution, and a saturated salt solution. The ether extract was dried with anhydrous Na₂SO₄, evaporated to dryness at reduced pressure, and the residue recrystallized from acetone-water to give the products shown in Table 1: m.p., **2**, 132–134°C (lit¹⁰ 132.5–133.5°C); m.p. **4**, 114–116°C (lit¹⁰ 114–115°C); m.p., **6**, 121–123°C; m.p., **8**, 112–114°C.

The structures of all isolated reaction products were characterized by m.p., IR, MS, ¹H and ¹³C NMR, and TLC and compared with data obtained from authentic $\Delta^{7,9(11)}$ steroidal dienes.^{1,7,11}

Received 22 March 2000; accepted 7 June 2000

Paper 00/246

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[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.