

## Deoxygenation of Some 3-Oxo-steroids by Chlorotrimethylsilane and Zinc

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5 $\alpha$ -Cholestan-3-one reacted with chlorotrimethylsilane and zinc dust in ether or tetrahydrofuran to give 5 $\alpha$ -cholest-2-ene. 17 $\beta$ -Acetoxy-5 $\alpha$ -androstan-3-one and methyl 3-oxo-5 $\beta$ -cholanate behaved similarly, but examples of 6-, 7-, 12-, 17-, and 20-oxo-steroids did not react. Diones containing a 3-oxo-group reacted selectively at the 3-position.

MOTHERWELL recently reported<sup>1</sup> that ketones can be deoxygenated to olefins by treatment with an excess of chlorotrimethylsilane and zinc in ether. Cyclohexanone, for example, gave cyclohexene in 72% yield when treated with the reagent for 18 h in ether at 25°. We report here the action of this reagent on some steroid ketones.

Deoxygenation also occurred when tetrahydrofuran was the solvent and use of this solvent at reflux temperature (65°) allowed a good yield to be obtained in 20 h. Under the latter conditions other 3-ketones and examples of 6-, 7-, 12-, 17-, and 20-ketones were treated with the reagent. 17 $\beta$ -Acetoxy-5 $\alpha$ -androstan-3-one gave 17 $\beta$ -acetoxy-5 $\alpha$ -andro-2-ene in 53% yield and

TABLE  
Reactions of oxo-steroids with chlorotrimethylsilane-zinc dust

Ketone	Conditions		Major product(s)	Yield (%) <sup>a</sup>	
	Solvent	Temp. (°C)			Time (h)
5 $\alpha$ -Cholestan-3-one	Et <sub>2</sub> O	21	72	} 5 $\alpha$ -Cholest-2-ene ca. 70 <sup>b</sup> ca. 50 <sup>b</sup>	
	Et <sub>2</sub> O	35	48		
	THF	21	96		
	THF	65	6		
	THF	65	20		
17 $\beta$ -Acetoxy-5 $\alpha$ -androstan-3-one	THF	65	20	} 17 $\beta$ -Acetoxy-5 $\alpha$ -andro-2-ene 53	
Methyl 3-oxo-5 $\beta$ -cholanate	THF	65	20		
3 $\beta$ -Acetoxy-5 $\alpha$ -cholestan-6-one	THF	65	20	} No reaction <sup>c</sup>	
3 $\beta$ -Acetoxy-5 $\alpha$ -cholestan-7-one	THF	65	20		
Hecogenin acetate <sup>d</sup>	THF	65	20		
Estrone methyl ether <sup>e</sup>	THF	65	20		
3 $\beta$ -Acetoxy-5 $\alpha$ -pregnan-20-one	THF	65	20		
5 $\alpha$ -Cholestane-3,6-dione	THF	40	120		} 5 $\alpha$ -Cholest-2-en-6-one 61
5 $\alpha$ -Cholestane-3,7-dione	THF	21	168		
Methyl 3,12-dioxo-5 $\beta$ -cholanate	THF	65	20		No reaction <sup>c</sup>
5 $\alpha$ -Androstane-3,17-dione	THF	21	216		5 $\alpha$ -Androst-2-en-17-one 60
5 $\alpha$ -Pregnane-3,20-dione	THF	65	20		5 $\alpha$ -Pregnan-2-en-20-one 67

<sup>a</sup> Of crystalline material unless indicated otherwise. <sup>b</sup> Estimated from <sup>1</sup>H n.m.r. spectrum of crude product. <sup>c</sup> In each case where no reaction occurred, <sup>1</sup>H n.m.r. and t.l.c. analysis of the crude product indicated that it was starting material. This was recrystallised (at least 70% recovered) and its identification confirmed by m.p., mixed m.p., and spectral data. <sup>d</sup> 12-ketone. <sup>e</sup> 17-ketone.

Our results are summarised in the Table. Treatment of 5 $\alpha$ -cholestan-3-one with the reagent in ether, the solvent used by Motherwell,<sup>1</sup> gave 5 $\alpha$ -cholest-2-ene (together with a small amount of 5 $\alpha$ -cholest-3-ene), but long reaction periods were required to obtain good

methyl 3-oxo-5 $\beta$ -cholanate gave a mixture of methyl 5 $\beta$ -chol-2- and -3-enates in 37% yield. None of the other substrates reacted. This suggested that diones containing a 3-oxo-group react selectively at this position,

<sup>1</sup> W. B. Motherwell, *J.C.S. Chem. Comm.*, 1973, 935.



$-7^\circ$ );  $5\alpha$ -cholestan-7-one (67%), m.p.  $111-113^\circ$  (lit.,<sup>15</sup>  $113.5-115^\circ$ ),  $[\alpha]_D^{23} -44^\circ$  (*c* 1.3) (lit.,<sup>15</sup>  $-47^\circ$ );  $5\alpha$ -androstan-17-one (80%), m.p.  $117-119^\circ$  (lit.,<sup>16</sup>  $120-121^\circ$ ),

<sup>15</sup> O. Wintersteiner and M. Moore, *J. Amer. Chem. Soc.*, 1950, **72**, 1923.

<sup>16</sup> L. Ruzicka and A. C. Muhr, *Helv. Chim. Acta*, 1944, **27**, 503.

$[\alpha]_D^{21} +87^\circ$  (*c* 1.0) (lit.,<sup>16</sup>  $+88^\circ$ ); and  $5\alpha$ -pregnan-20-one (78%), m.p.  $132-134^\circ$  (lit.,<sup>17</sup>  $136-137^\circ$ ),  $[\alpha]_D^{21} +96^\circ$  (lit.,<sup>17</sup>  $+100^\circ$ ).

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<sup>17</sup> J. Romo, M. Romero, C. Djerassi, and G. Rosenkranz, *J. Amer. Chem. Soc.*, 1951, **73**, 1528.

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