



anilinomagnesium bromide, which would be expected to cause fission of the enol-acetate by analogy with the reaction of anilinomagnesium bromide with esters (Hardy 1936). In fact, a 50 per cent. yield of III was obtained without difficulty. The reagent should be useful with molecules containing other active groups, and other ketones are now being examined. Attempts to prepare enamines by the action of piperidine in boiling benzene on I or II ( $R=COCH_3$ ) did not give the compounds of the desired structure, since the action of acid regenerated I together with what may be polymers. According to the results of Mannich and Kniss (1941) any 3-piperidinocholesta-3,5-diene should have given rise to III.\*

The Grignard reagent from magnesium (0.295 g; 3 mol), ethyl bromide and methylaniline (2.16 g; excess) in ether (25 c.c.) was cooled in ice and the enol-acetate (II,  $R=Ac$ ) (1.70 g) in a small volume of ether added. After 1 hr at room temperature hydrochloric acid (5 per cent.) was added, the ether layer separated and rapidly washed with dilute acetic acid (10 per cent.), water, saturated sodium bicarbonate solution, water, and then dried (sodium sulphate). After evaporation of the solvent the residue was twice crystallized from ethanol to give cholest-5-en-3-one (0.75 g), m.p. 122–124 °C,  $[\alpha]_D -2.2^\circ$  (in chloroform). It was further characterized by reduction with lithium aluminium hydride to cholesterol, m.p. 144–145 °C, undepressed by an authentic specimen, m.p. 147–148 °C,  $[\alpha]_D -39.5^\circ$  (in chloroform).

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### References

- BELLEAU, B., and GALLAGHER, T. F. (1951).—*J. Amer. Chem. Soc.* **73**: 4458.  
BIRCH, A. J. (1950).—*J. Chem. Soc.* **1950**: 2325.  
BIRCH, A. J., QUARTEY, J. A. K., and SMITH, H. (1952).—*J. Chem. Soc.* **1952**: 1768.  
CARDWELL, H. M. E., CORNFORTH, J. W., DUFF, S. R., HOLTERMAN, H., and ROBINSON, SIR R. (1951).—*Chem. & Ind. (Rev.)* 389.  
CARDWELL, H. M. E., CORNFORTH, J. W., DUFF, S. R., HOLTERMAN, H., and ROBINSON, SIR R. (1953).—*J. Chem. Soc.* **1953**: 361.  
DAUBEN, W. G., and EASTHAM, J. F. (1951).—*J. Amer. Chem. Soc.* **73**: 3260, 4463.  
HARDY, D. (1936).—*J. Chem. Soc.* **1936**: 398.  
HEYL, F. W., and HERR, M. E. (1953).—*J. Amer. Chem. Soc.* **75**: 1918.  
MANNICH, C., and KNISS, E. (1941).—*Ber. dtsch. chem. Ges.* **74**: 1629, 1637.  
WOODWARD, R. B., SONDHEIMER, F., TAUB, D., HEUSLER, K., and McLAMORE, W. M. (1951).—*J. Amer. Chem. Soc.* **73**: 2403.

\* *Note added in Proof.*—Since this work was completed Heyl and Herr (1953) have shown that a 3,5-dienamine can be prepared using pyrrolidine. We confirm this, but find the substance unexpectedly difficult to hydrolyse, and under conditions leading to hydrolysis only the 4-unsaturated ketone is obtained.