A New Synthesis of Δ^2-Steroids

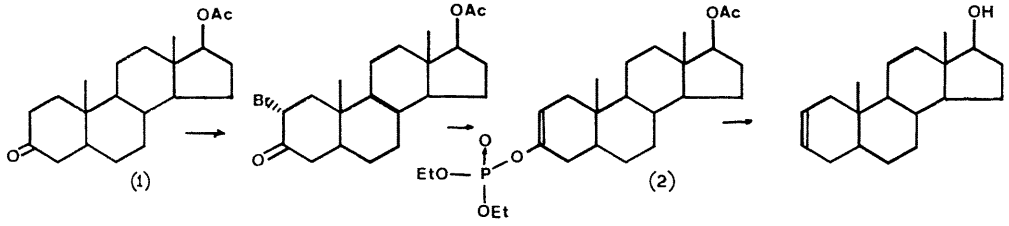
By MARCEL FETIZON,* MICHEL JURION, and NGUYEN TRONG ANH
(*Laboratoire de Stéréochimie, Faculté des Sciences, 91-Orsay, France*)

KENNER and Williams[1] showed that reduction of aryl diethyl phosphates with sodium or lithium in liquid ammonia gave arenes. We found that enol diethyl phosphates behave similarly to give ethylenic compounds in fair yield.

Enol diethyl phosphates are conveniently prepared from α-bromo-ketones *via* the Perkow reaction,[2] and their reduction provides a new preparation of ethylenic compounds from ketones. This reaction may be general, provided the synthesis of the enol phosphate is possible; this is so with α-bromocyclohexanones and α-bromo-aliphatic ketones, but not with α-bromocyclopentanones.[2] The reaction has been applied so far only to the preparation of Δ^2-steroids.

Bromination of dihydrotestosterone acetate (**1**) with phenyltrimethylammonium bromide gives the 2α-bromo-ketone (95%) which undergoes a Perkow reaction when heated for 3 hr. with freshly distilled triethylphosphite. The intermediate enol phosphate (**2**) [m.p. 90—91°, $[\alpha]_D$ + 38° ($CHCl_3$)] can be isolated in a 90—95% yield. A solution of crude (**2**) (3 g) in tetrahydrofuran (25 ml.) and dry t-butyl alcohol (25 ml.) added dropwise to a solution of lithium (2·5 g) in liquid ammonia (*ca.* 100 ml.) gave Δ^2-androstene-17β-ol [m.p. 163—164°, $[\alpha]_D$ + 57° ($CHCl_3$)] (1·5 g., 85%).

Similarly, Δ^2-cholestene (64%) was obtained from cholestan-3-one.



(*Received, December 10th,* 1968; *Com.* 1692.)

[1] G. W. Kenner and N. R. Williams, *J. Chem. Soc.*, 1955, **20**, 522.
[2] N. Perkow, K. Ullerich, and F. Meyer, *Naturwiss.*, 1952, **39**, 353; F. W. Lichtenthaler, *Chem. Rev.*, 1961, **61**, 608; B. A. Arbuzov, *Pure Appl. Chem.*, 1964, **9**, 307.
[3] A. Marquet, Thèse de Doctorat, Paris, 1961; A. Marquet, M. Dvolaitzky, H. B. Kagan, L. Mamlok, C. Ouannes, and J. Jacques, *Bull. Soc. Chim. France*, 1961, 1822.