

Enone-Benzene Rearrangement

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IT was found that six-membered $\alpha\beta$ -unsaturated ketones, when heated under reflux with an excess of trichloroacetic anhydride and catalytic amounts of toluene-*p*-sulphonic acid give benzene derivatives lacking the oxygen function. The $\alpha\beta$ -unsaturated ketones possessing a quaternary carbon atom undergo aromatization with carbon-carbon bond migration. The benzene derivatives were obtained in 10–50% yield and were accompanied

by other products, mainly the dienol trichloroacetates derived from the parent ketones.

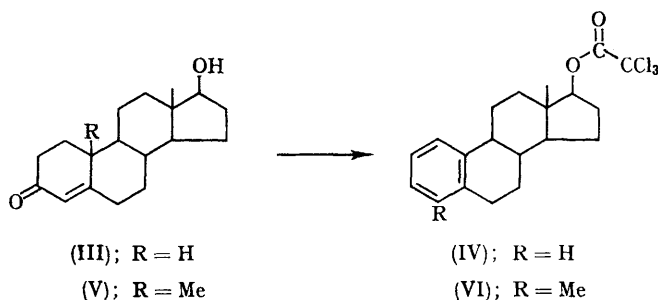
The reaction mixture was generally treated with sodium hydrogen carbonate solution and the products were isolated by extraction with ether and separated by chromatography or by distillation. Through this isolation most of the dienol trichloroacetates are converted back into the original $\alpha\beta$ -unsaturated ketones.

Thus 5,5-dimethylcyclohex-2-enone was converted into *o*-xylene, accompanied by small amounts of chloroxylene. None of the other isomeric xylenes could be found when the reaction products were separated by gas-liquid chromatography. 5-Isopropyl-2-methylcyclohex-2-enone under these conditions gave *p*-cymene. The latter was accompanied by 5-isopropyl-2-methylphenol and the corresponding trichloroacetate.

e.g. 17 β -hydroxy-19-norandrost-4-en-3-one (III) gave the œstra-1,3,5(10)-trien-17 β -yl trichloroacetate (IV)¹ and testosterone (V) led to the 4-methyl homologue (VI).¹

It is noteworthy that when trichloroacetic anhydride was replaced by trichloroacetic acid no aromatization of testosterone could be brought about.

A similar aromatization of 4-en-3-ones in



Similar enone-benzene rearrangements were observed also in condensed polycyclic six-membered $\alpha\beta$ -unsaturated ketones. Thus the bicyclic ketone (I) was smoothly converted by trichloroacetic anhydride and toluene-*p*-sulphonic acid into tetralin (II).

The steroidal 4-en-3-ones were similarly transformed into the ring A aromatic compounds;

steroids, using a mixture of acetyl bromide and α -bromopropionic acid and leading to the 4-methylœstra-1,3,5(10)-triene derivatives has been recently described by J. J. Panouse and his co-workers.²

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¹ It was identified by comparison with the known 17 β -alcohol. *Cf.*, M. J. Gentles, J. B. Moss, H. L. Herzog, and E. B. Hershberg *J. Amer. Chem. Soc.*, 1958, **80**, 3702; E. Caspi, P. K. Grover, N. Grover, E. J. Lynde and Th. Nussbaumer *J. Chem. Soc.*, 1962, 1710; E. Caspi, E. Cullen, and P. K. Grover *ibid.*, 1963, 212.

² J. Schmitt, J. J. Panouse, P. J. Cornu, A. Hallot, H. Pluchet, and P. Comoy, *Compt. rend.*, 1964, **259**, 1652.