

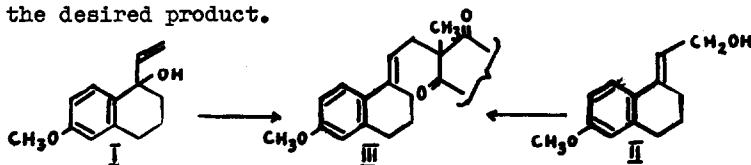
A REACTION OF 1-VINYL-1,2,3,4-TETRAHYDRONAPHTHALENE-1,6-DIOL
WITH CYCLIC 1,3-DIKETONES AND SYNTHESIS OF ESTRONE DERIVA-
TIVES.

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Previously it was shown^{1,2} that 6-methoxy-1-vinyltetra-
lol (I) and its isomer, primary carbinol (II) condense with
cyclic 1,3-diketones giving diketones of type (III). Here
the reaction of alkylation seems to take place. With cyclo-
hexane-1,3-dione we did not succeed however in preparing
the desired product.



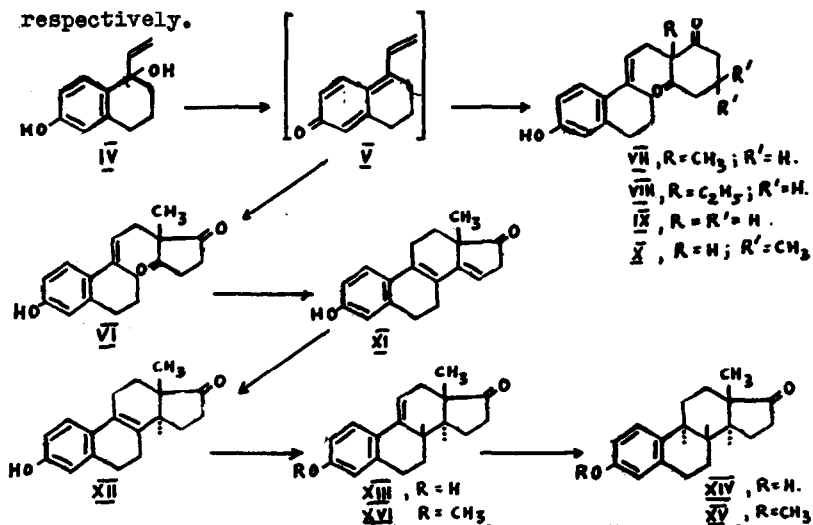
We have now established that 1-vinyl-1,2,3,4-tetrahydro-
naphthalene-1,6-diol (IV) readily reacts with cyclic 1,3-

¹ S.N. Ananchenko, V.Ye. Limanov, V.N. Leonov, V.M. Rzhizni-
kov, I. V. Torgov, *Tetrahedron*, **18**, 1355 (1962).

² S.N. Ananchenko, I.V. Torgov, *Tetrahedron Letters*, 1963,
No 23, 1553; A.V.Zakharichev, S.N. Ananchenko, I.V. Torgov,
Isv. Acad. Nauk SSSR, in press (1963); see also T.B.Windholz,
J.H.Fried, A.A.Patchett, *J. Org. Chem.*, **28**, 1091 (1963).

diketones including cyclohexane-1,3-dione and dimedone, provided the reaction is carried out in polar solvents in the presence of alkaline agents, i.e. using conditions of the Michael reaction. Possibly in this case diol (IV) partly isomerises (with elimination of water) into the intermediate trienone (V) which (itself or in the form of mesomeric ion) easily reacts with 1,3-diketones. Condensation of diol (IV) with 2-methylcyclopentane-1,3-dione in the presence of Triton B in tert.-butanol gives a good yield of $\Delta^{1,3,5(10),9(11)}_{-8,14}$ -secoestratetraen-3-ol-14,17-dione (VI), m.p. 124-126° (from CH₃OH), λ_{\max} (in alcohol) 215, 269 m μ (lg. 4.14, 4.15); infrared bands (in nujol): 1575, 1613, 1710, 1758, 3290 cm. A similar condensation of diol (IV) with 2-methylcyclohexane-1,3-dione yields the known $\Delta^{1,3,5(10),9(11)}_{-8,14}$ -seco-D-homoestratetraen-3-ol-14,17a-dione (VII)³, m.p. 134-135°; the corresponding homologue (VIII), m.p. 137-139°, λ_{\max} (in alcohol) 215, 266 m μ (lg 4.27, 4.26); infrared bands (in nujol): 1620, 1680, 1725, 3270 cm⁻¹, is formed from diol (IV) and 2-ethylcyclohexane-1,3-dione. Reaction of diol (IV) with cyclohexane-1,3-dione or dimedone affords $\Delta^{1,3,5(10),9(11)}_{-18,14}$ -seco-18-nor-D-homoestratetraen-3-ol-14,17a-dione (IX), m.p. 179-181° (from methanol-ethylacetate, 1:1); λ_{\max} (in alcohol) 230, 265 m μ (lg 3.9, 4.32); infrared bands (in nujol): 1515, 1588, 1602, 3117 cm⁻¹, and its 16,16-dimethyl homologue (X), m.p. 193-195° (from acetone); λ_{\max} (in alcohol) 227, 264 m μ (lg 3.9, 4.1); infrared bands (in nujol): 1510, 1589, 1601, 3098 cm⁻¹,

³A.V.Zakharichev, V.E. Limanov, S.N. Ananchenko, A.V. Platonova, I.V. Tongov, *Isv. Acad. Nauk SSSR, Otd. Chim.Nauk*, 1701 (1963).



Under the influence of hydrochloric acid in tetrahydrofuran diketophenol (VI) cyclises into the known $\Delta^{1,3,5(10),8,14}$ -estrapentaen-3-ol-17-one (XI)³, m.p. 216-218°, which on selective hydrogenation results in dl-8-dehydroestrone (XII), m.p. 251-254° (from CH_2OH); λ_{max} (in alcohol) 215, 276 m μ (lg 4.16, 4.14); infrared bands (in nujol) 1577, 1612, 1720, 3250 cm^{-1} . Exhaustive hydrogenation of (XI) gives dl-8-isoestrone. In the presence of hydrochloric acid⁴ in tetrahydrofuran ketophenol (XII) isomerises into dl-9(11)-dehydroestrone (XIII), m.p. 262-265°, λ_{max} (in alcohol) 264 m μ (lg 4.18). The hydrogenation of the latter leads to dl-estrone (XIV). dl-Estrone methyl ether (XV) has been prepared

⁴ D. Banés, J. Carol, *J. Biol. Chem.*, 204, 509 (1953)

by a similar procedure via dl-9(11)-dehydroestrone methyl ether (XVI), m.p. 151-153°, λ_{\max} (in alcohol) 263, 296 m μ (lg 4.29, 3.5).

Identification (and purity tests) of the products was carried out by means of thin layer binderless chromatography on Al₂O₃. For all products satisfactory elemental analyses were obtained.