

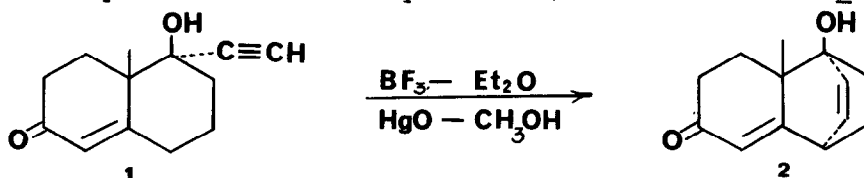
AN UNUSUAL TRANSANNULAR REACTION IN AN EIGHT-ATOM RING DURING HYDRATION
OF AN ACETYLENIC COMPOUND

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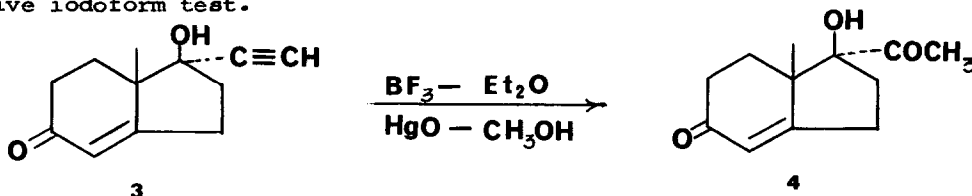
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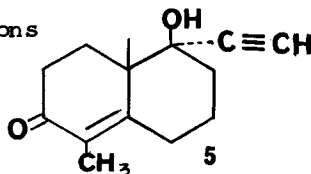
An attempted hydration of the ethynyl alcohol 1 with Nieuwland's catalyst (BF_3 -etherate \rightarrow HgO -Methanol) has previously been reported¹ from our laboratory to furnish the bicyclo(2.2.2)octane derivative 2.



In contrast, the ethynyl alcohol 3 has been reported² to give the product of normal hydration 4 as evidenced by its spectral properties and positive iodoform test.



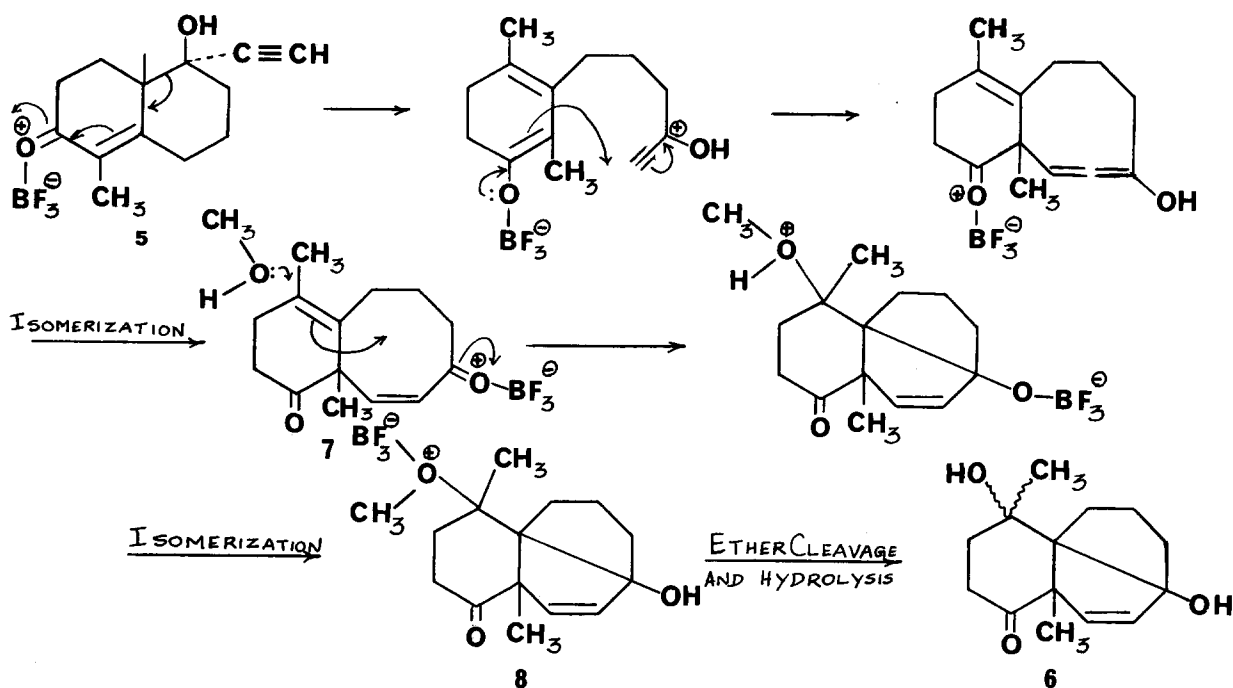
It was of interest therefore to study the behaviour of the ethynyl alcohol 5 under similar conditions



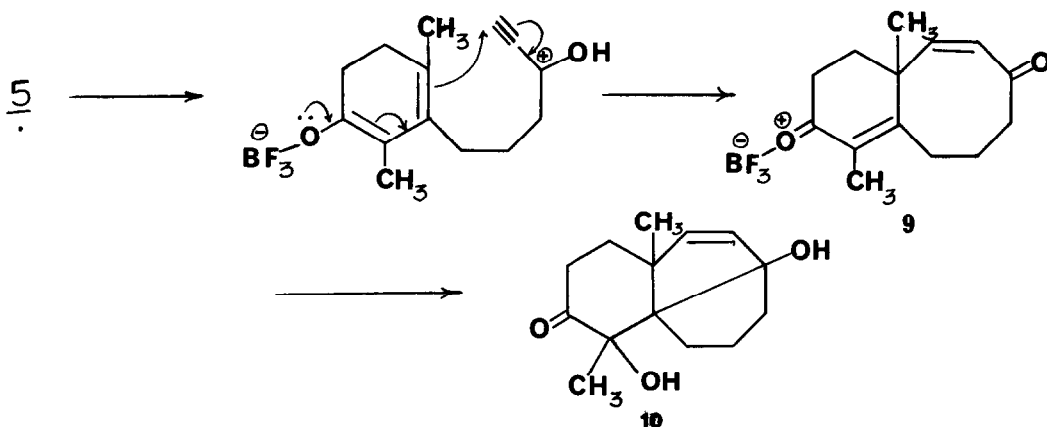
A solution of the ethynyl alcohol 5 (1 g) in methanol (4 ml) was stirred at 60°C for 30 minutes with Nieuwland's catalyst prepared from red mercuric oxide (0.45 g), boron-trifluoride etherate (1 ml) and methanol (1 ml). The mixture was cooled, poured into water, the resulting solution decanted from the sludge of mercury and extracted with methylene chloride. The extract was washed with water, dried and concentrated when solid (300 mg) was obtained; recrystallization from ethyl acetate gave

colourless crystals (200 mg) of compound 6 m.p. 244-245°C (d). Compound 6 analyzed for $C_{14}H_{20}O_3$ (m/e 236) and had $\lambda_{\text{max}}^{\text{EtOH}}$ 300 nm (ϵ 297); IR(KBr): split OH at 3400 and 3410 cm^{-1} ; conjugated carbonyl at 1690 cm^{-1} and >C=C< at 1640 cm^{-1} ; NMR CDCl_3 (TMS) δ values: 1.2 (s, CH_3 , 3H), 1.4 (s, CH_3 , 3H), 3.3 (s, OH, 2H exchanged completely with D_2O after 6 hr), 1.6-2.6 (broad multiplet, methylene protons, 10H) and a AB quartet centered at 5.3 and 5.66 (2 olefinic protons, 2H, $J = 9$ Hz).

The above data may be interpreted in terms of structure 6 formed through a ring enlargement of compound 5 followed by a transannular reaction as depicted below:



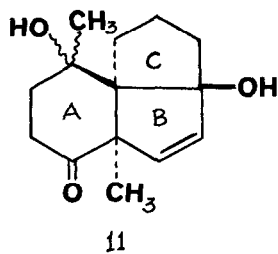
The postulated ring enlargement of the ethynyl alcohol 5 to the dione 7 is similar to acid catalyzed rearrangements⁴ of similar bicyclic δ -hydroxy- α,β -enones. The boron-trifluoride-ether complex 8 is invoked as the initial product of the transannular reaction since the reaction is carried out in methanol and since such complexes are known⁵ to undergo facile cleavage. In the case of complex 8, a hydrolytic cleavage may be expected to lead preferentially to the product 6. An alternative fragmentation and recombination can conceivably give the dione 9 instead of dione 7 and ultimately lead to the isomeric transannular product 10.



With a view to determine the course of the reaction, the known⁶ dione **7** was prepared by the base catalyzed rearrangement of the ethynyl alcohol **5** and treated with BF_3 -etherate in methanol at room temperature. The product obtained in 65% yield was identical (IR and mixed melting point) with the abnormal product of hydration of the ethynyl alcohol **5**, confirming structure **6** and also the intermediacy of the dione **7** in this abnormal hydration. The dione **7** was incidentally obtained in improved yield (80% based on recovered starting material) by treatment of the ethynyl alcohol **5** with 0.2% sodium methoxide overnight at room temperature followed by chromatographic separation. The UV and IR absorptions unequivocally confirmed that the structure of the product was **7** as reported⁶ and not **9** which may also result by a base catalyzed fragmentation and recombination of the ethynyl alcohol **5**.

The present case is a unique example of a Lewis-acid catalyzed ring enlargement followed by a transannular reaction, the latter process being a facile one in view of the favourable conformation which the eight-atom ring may assume during the reaction. A further point of strength towards this type of interaction is the 1,5-disposition of the carbonyl in the eight-membered ring and the attacking carbanionic species - a situation that is well known to favour transannular hydride shifts and rearrangements due to proximity effect.⁷ A closely related reaction in a medium-sized ring has been reported⁸ by Wharton.

The stereochemistry of the product **6** is probably best represented as in structure **11**. The cyclopentene ring must necessarily be planar. The ring fusion between rings B and C as well between A and B must be cis though the stereochemistry at C_1 is uncertain. The conformation and other stereochemical implications of the above tricyclic system are under study.



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