# Acid-Catalyzed Rearrangements of Some Bicyclic δ-Hydroxy-α,β-enones

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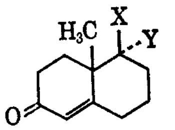
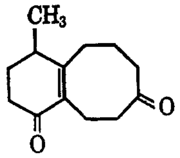
The enone alcohols Ia–e have been found to rearrange when treated with *p*-toluenesulfonic acid. While the epimeric vinyl alcohols Ia and Ib undergo rearrangement to give compounds II and III, their ethynyl precursors Ic and Id furnish compound V. The structures assigned are based on spectroscopic evidence. The parent alcohol Ie is found to give 4-methyl-*ar*-1-tetralol IX in addition to a compound believed to have structure VIII. A plausible mechanism is discussed to account for the products isolated.

We have previously reported[1] that the epimeric alcohols Ia and Ib undergo a ring enlargement to II when treated with base. We wish to report now on the chemical behavior of the same alcohols as well as the related compounds Ic, Id, and Ie when treated with *p*-toluenesulfonic acid (PTS).

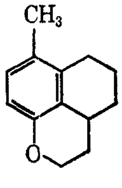




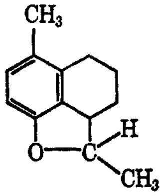
Ia, $X = OH;\ Y = CH{=}CH_2$
b, $X = CH{=}CH_2;\ Y = OH$
c, $X = OH;\ Y = C{\equiv}CH$
d, $X = C{\equiv}CH;\ Y = OH$
e, $X = OH, Y = H$

II

The vinyl alcohol Ia, when refluxed with 0.5–1 equiv of PTS in benzene solution, furnishes after chromatography over acid-washed alumina two crystalline compounds, one, mp 58–59°, in 11% yield and found to be identical with authentic II, and another, mp 79–80° (III), in *ca.* 25% yield. The latter has the formula $C_{13}H_{16}O$ as indicated by analysis and is devoid of infrared absorptions for carbonyl and hydroxyl groups. It has infrared absorptions, however, at 6.28 (aromatic) and 7.97 μ (O–C stretching) and ultraviolet absorptions at 283–286 mμ (log ε 3.29). The nmr spectrum[2] shows doublets for two adjacent aromatic protons with centers at $\tau$ 3.15 and 3.57, respectively, a sharp peak for an aromatic methyl at $\tau$ 7.98, multiplets for *three* benzylic protons in the range $\tau$ 7.1 to 7.6 and for two protons on carbon-bound oxygen ($-OCH_2-$) at $\tau$ 5.6 to 6.2, in addition to peaks for alicyclic methylene protons. Although the ultraviolet and infrared evidence fit for either of the structures III and IV, it is clear that the nmr evidence is consistent only with



III

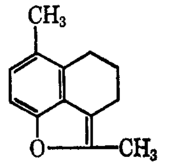


IV

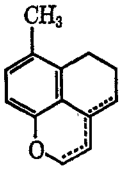
structure III for the compound in question. Treatment of the epimer Ib likewise with PTS also furnishes compounds II and III in 10 and 25% yields, respectively.

The epimeric ethynyl alcohols Ic and Id when treated similarly with PTS (1 equiv) furnish, after recovery of *ca.* 10% of the starting material, 40–45% yield (based on unrecovered starting material) of a colorless crystalline solid (V), mp 34–35°. This material has the formula $C_{13}H_{14}O$ as indicated by analysis and has infrared absorptions at 6.1, 6.15, 6.225, and 7.975 μ with no absorption either for carbonyl or hydroxyl which were present in the starting materials. The ultraviolet absorption maxima are at 224 mμ (log ε 4.22 and 258 mμ (log ε 4.09). The nmr spectrum shows doublets centered at $\tau$ 3.08 and 3.27 for two adjacent aromatic protons, multiplets for four benzylic and allylic protons in the range $\tau$ 7.28 to 7.57, a slightly split singlet at $\tau$ 7.72 for an aromatic $-CH_3$, a sharp signal[3] at $\tau$ 7.8 for a vinyl $-CH_3$, and multiplets in the region $\tau$ 7.8 to 8.3 for two alicyclic methylene protons. There is no absorption for either a vinyl proton or proton α to an ether oxygen.

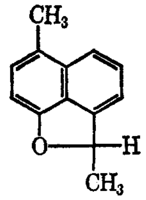
Although either of the structures V and VI can account as before for the ultraviolet and infrared data, it is apparent that the nmr data provide support now



V



VI



VII

for the benzofuran formulation V rather than for the benzopyran structure favored earlier for the product of rearrangement of Ia or Ib. The structure is further confirmed by smooth dehydrogenation (Pd–C) to compound VII: mp 48–49°; $\lambda_{max}^{EtOH}$ 317 mμ (log ε3 .81); $\lambda_{max}^{CHCl_3}$ 6.125 (w), 6.175 (w), 6.25 (m), and 7.975 (m) μ; and showing in the nmr spectrum multiplets in the range $\tau$ 2.40 to 3.67 for *five* aromatic protons, a quartet at $\tau$ 4.13 for *one* proton α to an ether oxygen, a slightly split singlet at $\tau$ 7.5 for an aromatic $-CH_3$, and a doublet at $\tau$ 8.4 for $>CHCH_3$. The position and intensity of the ultraviolet absorption maximum for VII are comparable with those reported[4] for the parent 4-methyl-1-naphthol: $\lambda_{max}^{C_6H_{12}}$ 312 mμ (log ε 3.6) and 318 mμ (log ε 3.51).

The parent secondary alcohol Ie also furnishes, when treated similarly with PTS, two isomeric crystalline compounds having the formula $C_{11}H_{14}O$: one, mp 88–

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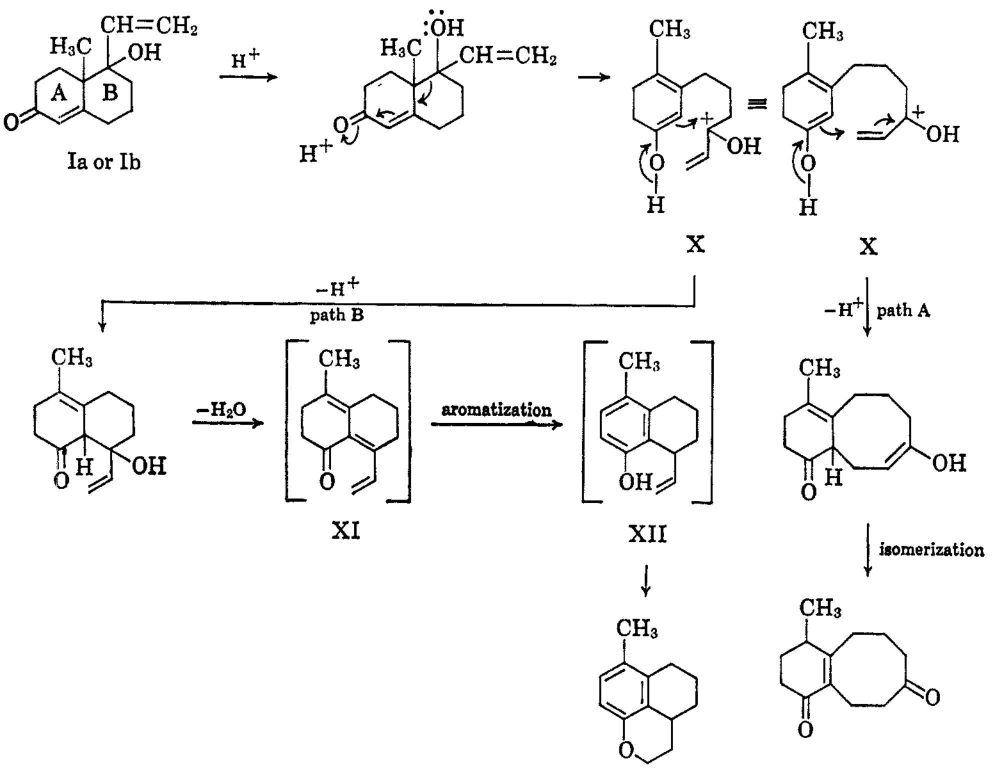
[1] S. Swaminathan, J. P. John, and S. Ramachandran, *Tetrahedron Letters*, 729 (1962).

[2] The nmr spectra for the compounds reported in this paper were obtained in $CCl_4$ solution with a Varian Model A-60 spectrometer, using tetramethylsilane as internal standard.

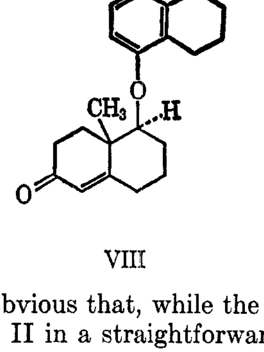
[3] These two assignments may perhaps be reversed; since, however, in the compound obtained by dehydrogenation of V, *viz.*, VII, the aromatic $-CH_3$ shows again as a slightly split singlet at $\tau$ 7.5, the above assignment has been preferred.

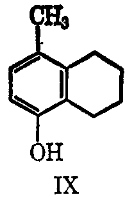
[4] T. L. Yarboro and C. Karr, Jr., *J. Org. Chem.*, **24**, 1141 (1959).

CHART I



89°, in 28% yield identified as 4-methyl-ar-1-tetralol[5,6] (IX) and another, mp 149–150°, in 12% yield. The latter has main infrared absorptions at 6.0 (conjugated carbonyl) and 6.15 μ (C═C) while $\lambda_{max}^{EtOH}$ is at 235 mμ.[7] The nmr spectrum reveals the compound to be dimeric and shows doublets centered at τ 3.2 and 3.6 for *two* adjacent aromatic protons, a singlet at τ 4.32 for $O{=}C{-}C\mathit{H}{=}C<$, a multiplet at τ 5.88 to 6.26 for a proton α to an ether oxygen, and sharp peaks at τ 7.88 for an aromatic $-CH_3$ and at τ 8.62 for a tertiary $-C\mathit{H}_3$. These data are consistent with structure VIII, though no further work has been done to confirm it.[7a]

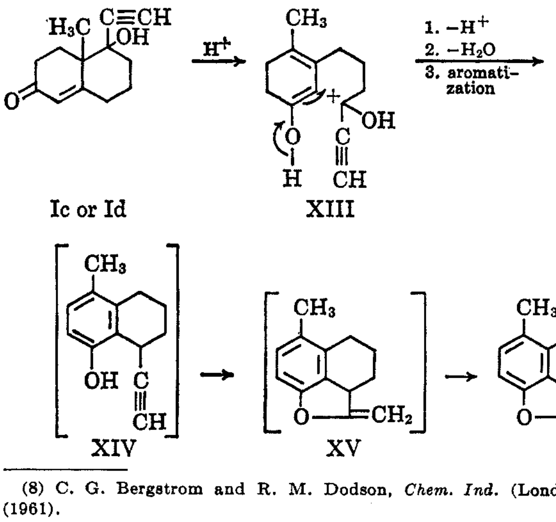

VIII


IX

It is obvious that, while the alcohols Ia and Ib rearrange to II in a straightforward manner when treated with base, their behavior with acid is more complicated. The mechanism in Chart I is suggested to account for the formation of the products isolated.

The cleavage of ring B to form species X containing a protonated α,β-enone system in the side chain is essentially a retroaldol reaction of the type encountered[8] in the rearrangement of 9α-hydroxy-4-androstene-3,17-dione and evidently takes place to the exclusion of acid-catalyzed dehydration of Ia or Ib. Such a cleavage is suggested by the fact that similar yields and products are obtained from the two epimeric pairs Ia, Ib and Ic, Id and is further supported by the finding that material recovered from treatment of Ic with PTS is actually a mixture of the epimers Ic and Id. Both compounds II and III are probably formed from this common precursor—the former by an internal 1,4 addition (path A) and the latter by a 1,2 addition (path B) to the side-chain enone system. As for the rearrangements of the ethynyl alcohols Ic and Id, the species

CHART II



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[5] R. B. Woodward and T. Singh, *J. Am. Chem. Soc.*, **72**, 500 (1950).

[6] We are thankful to Professor Woodward for giving us an authentic sample of this compound.

[7] Based on the molecular formula $C_{22}H_{28}O_2$; log ε is 4.21.

[7a] NOTE ADDED IN PROOF.—This structure has since been confirmed in an independent study by M. Los and A. D. Mighell, *Tetrahedron*, **21**, 2297 (1965), which appeared while the present paper was in the process of publication.

[8] C. G. Bergstrom and R. M. Dodson, *Chem. Ind.* (London), 1530 (1961).

XIII (Chart II) analogous to X and similarly formed seems to undergo exclusively internal 1,2 addition at first and then cyclization probably *via* XIV and XV preferentially to the benzofuran V rather than to a benzopyran. Similar cyclizations have been reported in the literature.[9] An examination of models indicates that the stereochemistry of the double bond in XII would favor formation of the benzopyran III while the linear disposition of the triple bond in XIV would lead to the benzofuran V.

The conversion of Ie to the tetralol IX is probably analogous, involving initial cleavage of ring B followed by recyclization and aromatization. The isolation of the tetralol IX from Ie, however, does not help settle the question of whether aromatization of ring A precedes or follows formation of the heterocyclic ring in the rearrangements leading to III and V, especially since the phenolic intermediates XII and XIV have not been isolated by us, and steps indicated in path B (Chart I) represent only one possible sequence of events. It may be noted that the tetralol IX has previously been obtained[5] by a conventional dienone–phenol rearrangement, the mechanism for which has been established[10] to involve a spirocarbonium ion intermediate to the exclusion of an alternative mechanism involving cleavage of ring B. However, there seems to be no alternative to such a cleavage for the conversion of the enone Ie to the *ar*-tetralol IX.

## Experimental Section

**Rearrangement of 1α-Vinyl-1β-hydroxy-6-oxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene[1] (Ia) with PTS.**—A mixture of Ia (mp 77–78°, 10 g), PTS (5 g), and benzene (150 ml) was refluxed for 2 hr. The dark mixture was cooled, washed with water, dried ($MgSO_4$), and freed of solvent to furnish a liquid (10 g) which was chromatographed over acid-treated $Al_2O_3$. Elution with petroleum ether (bp 40–60°) gave III (2.2 g), which after two crystallizations from the same solvent had mp 79–80° (*Anal.* Calcd for $C_{13}H_{16}O$: C, 82.9; H, 8.6. Found: C, 82.8; H, 8.6.); $\lambda_{max}^{CHCl_3}$ 6.28 (s), 6.79 (s), 6.85 (w), 7.25 (w), 7.5 (w), and 7.9 (vs) $\mu$. Further elution with a petroleum ether–benzene mixture (9:1) gave an intermediate unidentified crude solid (0.4 g, mp 105–113°), while subsequent elution with 1:1 petroleum ether–benzene mixture gave II (1.1 g), mp 58–59° undepressed by an authentic sample and showing identical infrared absorptions.[1]

The epimer Ib[1] (mp 124–125°, 1 g) furnished, after a similar treatment and work-up, 100 mg of II and 220 mg of III.

**Rearrangement of 1α-Ethynyl-1β-hydroxy-6-oxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene[11] (Ic) with PTS.**—A mixture of Ic (mp 171–172°, 10 g), PTS (9 g), and chloroform (150 ml) was refluxed for 2 hr, and the dark mixture was worked up as before to furnish a crude liquid (9 g) with a pleasant smell. Trituration with a small amount of benzene–petroleum ether mixture and cooling gave solid (1 g), mp 150–160°, which was filtered off. Chromatographic purification of this material as described previously[11] showed it to be a mixture of the epimers Ic and Id. The filtrate was concentrated and the residual liquid was also chromatographed over acid-treated $Al_2O_3$. Elution with petroleum ether gave V (4 g): mp 34–35° (*Anal.* Calcd for $C_{13}H_{14}O$: C, 83.9; H, 7.5. Found: C, 83.6; H, 7.6.); $\lambda_{max}^{CHCl_3}$ 6.1 (w), 6.15 (w), 6.225 (w), 6.75 (w), 6.9 (s), 6.975 (s), and 7.975 (s) $\mu$. The epimer[11] Id (mp 184–185°) furnished the same yields of V under identical conditions.

Attempts to rearrange Ic under the same conditions but at room temperature were unsuccessful.

**Dehydrogenation of V.**—A mixture of V (700 mg) palladized carbon (5%, 300 mg) and *p*-cymene (20 ml) was refluxed for 9 hr in an atmosphere of $CO_2$, the catalyst was filtered, and the filtrate was freed of solvent. The residual liquid (500 mg) solidified and was recrystallized from petroleum ether to give colorless crystals of VII, mp 48–49°.

*Anal.* Calcd for $C_{13}H_{12}O$: C, 84.8; H, 6.5. Found: C, 85.3; H, 6.8.

**Rearrangement of 1β-Hydroxy-6-oxo-8a-methyl-1,2,3,4,6,7,8,-8a-octahydronaphthalene[12] (Ie) with PTS.**—A mixture of Ie hydrate (mp 57–58°, 5 g), PTS (5 g), and benzene (70 ml) was refluxed for 2 hr, and the mixture was worked up as before to furnish crude liquid (4.8 g) which was chromatographed as usual. Elution with a petroleum ether–benzene (3:2) mixture afforded VIII (0.5 g) which was twice recrystallized from petroleum ether: mp 149–150°.

*Anal.* Calcd for $C_{22}H_{28}O_2$: C, 81.5; H, 8.6. Found: C, 81.1; H, 8.7.

Subsequent elution with benzene afforded crude IX (1.1 g) purified by two further crystallizations from a petroleum ether–benzene mixture: mp and mmp (with an authentic sample) 88–89°; $\lambda_{max}^{EtOH}$ 280 m$\mu$ (log $\epsilon$ 3.21). Compound IX was also characterized by its acetyl derivative, mp 81–82° (lit.[5] mp 82°), and by dehydrogenation to 4-methyl-1-naphthol, mp 83–84° (lit.[13] mp 84–85°).

The starting material was recovered with no evidence of rearrangement when Ie (2 g) was stirred at room temperature with PTS (2 g, 1 equiv) in benzene (50 ml) for 9 hr. In another run employing 0.15 equiv of PTS and refluxing the reaction mixture for 12 hr. only 13% of IX was obtained. Attempts to effect rearrangement of Ie to IX using a mixture of acetic anhydride and sulfuric acid[5] furnished only tar.

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[9] R. A. Raphael, "Acetylenic Compounds in Organic Syntheses," Butterworth and Co. (Publishers) Ltd., London, 1955, p 170.

[10] N. L. Wendler, "Molecular Rearrangements," Vol. II, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 1028.

[11] M. S. Newman, S. Ramachandran, S. K. Sankarappa, and S. Swaminathan, *J. Org. Chem.*, **26**, 727 (1961).

[12] C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2680 (1960).

[13] R. E. Steiger, *Helv. Chim. Acta*, **13**, 180 (1930).