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AN UNUSUAL REDUCTIVE CYCLIZATION

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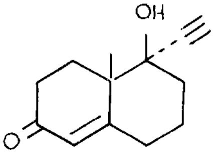
Summary Li-NH$_3$ reduction of 1α-Ethynyl-1β-hydroxy-6-oxo-8a-methyl-1,2,3,4,6,7,8,8a octahydronaphthalene 5 furnishes, in addition to reported products, the tricyclic compound 8.

Metal-ammonia reductions of the ketones 1 and 3 under controlled conditions are known[1] to give the cyclopropanes 2 and 4 respectively.

1 2

3 4

Birch reduction of the ethynyl carbinol 5 has been reported by Nazarov[2] to furnish the trans ethynyl carbinol 6. In repeating this experiment, we confirmed the formation of carbinol 6 as the predominant product; in addition, we obtained small amounts of the known trans vinyl carbinol 7 and another product 8 whose structure is the theme of this paper.



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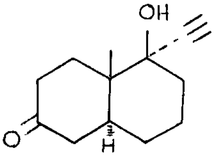

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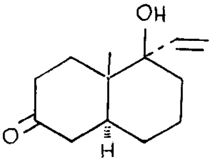

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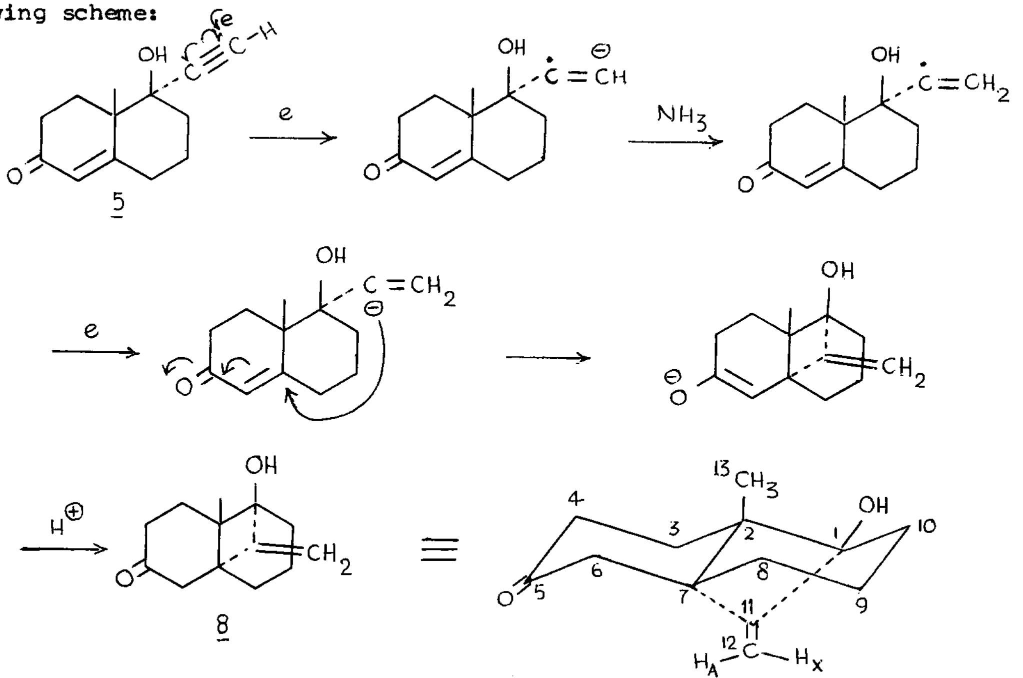
Lithium-ammonia reduction of the ethynyl carbinol 5 at -70°C furnished after workup, a solid (mp. 152-160°C) - obviously a mixture. Crystallization from ether yielded the trans carbinol 6 (mp. 160-162°C, 40%). The crystallization mother liquor was then chromatographed over silica gel. Elution with 5% ethylacetate-petrol gave in the earlier fractions a colourless crystalline solid (mp. 92°C, 4%) confirmed by comparison with an authentic sample as the reduced vinyl carbinol 7. Further elution gave a solid apparently homogeneous on TLC (40% ethylacetate - petrol) but with mp. 80-110°C. Multiple elution (5 times, 1:2 ether : petroleum ether) over silica gel plates revealed this to be a mixture of the trans carbinol 6 and another compound. Multiple elution over preparative plates gave a colourless crystalline solid (mp. 174-176°C, 4%, Found : C, 75.2; H, 8.4 $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.7%). This compound showed the following spectral properties : IR (KBr) : 3300 (broad, -OH), 1710 ($>$=O), 890 cm^{-1} ($>$=CH$_2$); NMR(CDCl$_3$/TMS) : δ 1.16 (s, 3H, -CH$_3$); 1.3-2.6 (m, 13H, -OH, methylene); 5.0, 4.83 (2s, 2H, H_A, H_X); ^{13}C NMR (CDCl$_3$) : δ 210.7 s (C-5); 159.4 s (C-11); 99.7 t (C-12); 81.1 s (C-1); 50.3 s (C-2); 18.0 s (C-7); 12.3 q (C-13). The six CH$_2$'s appeared as triplets between 17.1 - 43.2 ppm in the off-resonance decoupled spectrum. Also, the compound could not be obtained by treatment of the carbinol 6 with base (Li or KNH$_2$) in NH$_3$. The above evidence can be interpreted uniquely in favour of the tricyclic structure 8, among several possibilities. The transformation of 5 to 8 is best rationalized by the following scheme:

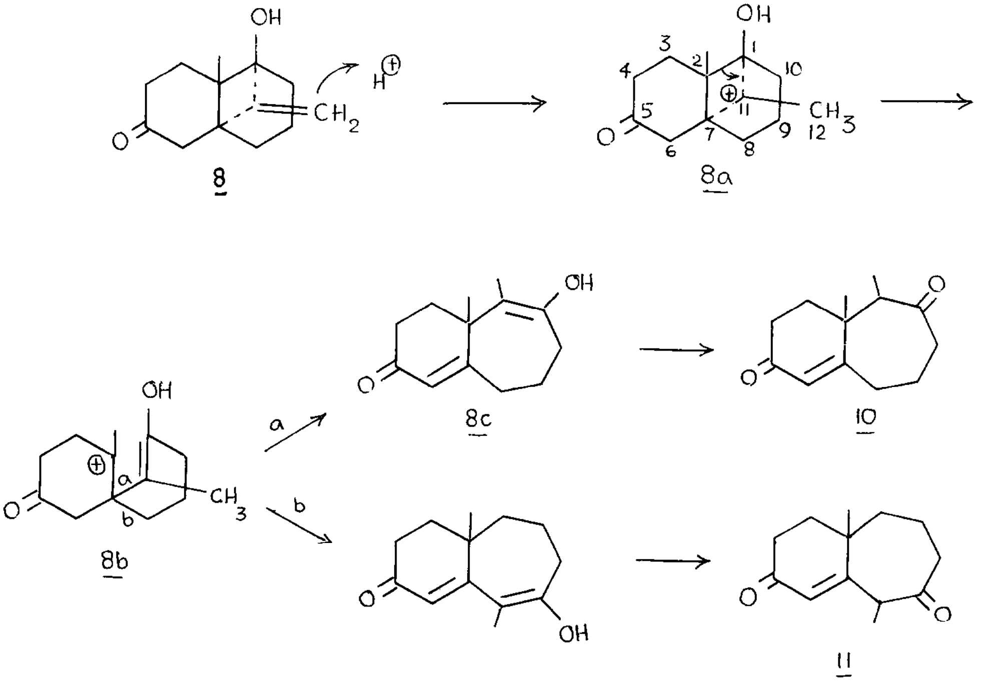


The C-C bond formation pictured above leading to a cyclobutane ring in compound 8 (1-hydroxy-2-methyl-11-methylene-tricyclo[5.3.1.0^{2,7}] undecan-5-one) is essentially an internal Michael addition involving a conjugated carbonyl system and a vinylic carbanion generated from an acetylenic moiety. Related transformations involving carbanion additions to unconjugated carbonyl groups have been reported by Stork[3,4] in metal/ammonia reductions of γ-ethynyl ketones. Compound 8 furnished on reaction with ozone a product 9; mp. 136-137°C (dec), 80%, Found : C, 61.73; H, 7.49 $C_{13}H_{18}O_5$ requires C, 61.41;

H, 7.14%). This solid showed M^+ 254; IR (KBr) 3450 (-OH), 1700 ($>$=O), 1075, 1040 cm^{-1} ($-O-CH_2-O-$); NMR ($DMSO-d_6/CDCl_3/TMS$) : δ 1.15 (s, 3H); 3.2-1.2 (m, 13H); 4.8 (AB pair of doublets, 2H, J = 12 Hz); The mass spectrum and analysis confirmed the presence of three additional oxygen atoms. It is not certain, however, that the product 9 is an ozonide, since attempts to decompose it by treatment with dimethylsulfide, tetracyanoethylene, etc., failed. Since rearrangements are known[5] to take place during ozonisation, product 9 could be a rearrangement product. Work is in progress to determine its structure.

When the tricyclic compound 8 was refluxed with methanolic HCl and the mixture worked up, a viscous liquid (60%) was obtained having the following spectral characteristics : M^+ 206; IR ($CHCl_3$) : 1710 ($>$=O), 1665 (α, β -unsaturated carbonyl), 1615 cm^{-1} ($-\overset{|}{C}=\overset{|}{C}-$) ; NMR ($CCl_4/TMS$) : δ 1.04 (d, 3H, J = 7 Hz); 1.29 (s, 3H); 1.5-2.8 (m, 10H), 3.1 (q, 1H, J = 7 Hz); 5.62 (s, 1H). $UV\lambda^{EtOH}_{max}$ 238 nm (unchanged by addition of 0.1N alkali).

The NMR showed the disappearance of the exocyclic methylene group and the appearance of a $CH_3-\overset{|}{\underset{|}{C}}H$ moiety confirmed by decoupling experiments. Irradiation of the methyl doublet at δ 1.04 resulted in the collapse of the methine proton quartet at δ 3.1. The appearance of a new conjugated $>$C=O and a $CH_3-\overset{|}{\underset{|}{C}}H$ unit can be interpreted in favour of either structure 10 or 11 formed by an acid catalysed rearrangement as indicated below:



Since the UV absorption of the product is unaffected by the addition of alkali, the structure of the rearrangement product is best represented as 10. The formation of compound 10 is to be expected on mechanistic grounds since the migration of bond 'a' involves a favourable π -bond participation whereas the migration of bond 'b' involves a less favourable alkyl rearrangement[6].

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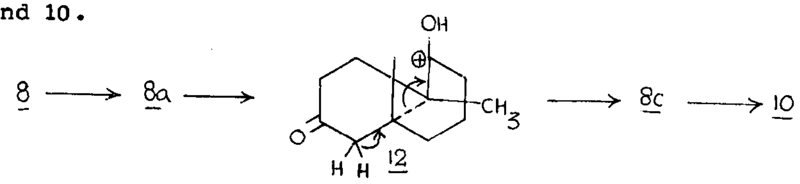
References

1. P.S.Venkataramani and W.Reusch, Tetrahedron Lett., 5283 (1968).
2. I.N.Nazarov and I.A.Gurvich, Zur. Obschi. Khim. USSR, 25, 956 (1955). [C.A. 50, 3351 (1956)].
3. G.Stork, R.K.Boeckmann, Jr., D.F.Taber, W.C.Still, J.Singh, J. Am. Chem. Soc., 101, 7107 (1979).
4. G.Stork, S.Malhotra, H.Thompson and M.Uchibayashi, J. Am. Chem. Soc., 87, 1148 (1965).
5. R.E.Erickson and G.D.Mercer, Ozone reactions with Organic compounds, Advances in Chemistry Series, 112, 114 (1972), American Chemical Society.
6. We are thankful to the referee for suggesting an alternative mechanism involving migration of the 1,2 bond to give the cyclopropane intermediate 12 followed by cleavage of the 7,11 bond to give the enol 8c and then compound 10.



The positive charge on C-1 in 12 may be expected to be stabilised by the -OH group. The intermediate 12 may also arise from 8b by a π bond participation.

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