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AN UNUSUAL BRIDGEHEAD SUBSTITUTION IN A POLYCYCLIC SYSTEM

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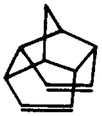
During concurrent studies directed towards an efficient synthesis[1] of homohypostrophene 1 and its logical precursor 2, we had the occasion to examine the dehydration of readily available[1d] lactol 3. The unexpected reaction encountered during the attempted acid catalysed dehydration of 3 is of sufficient interest to justify this brief report.



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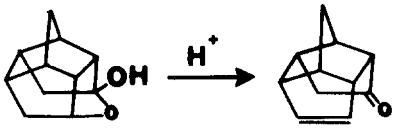

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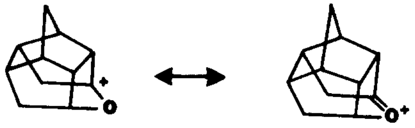
Reaction of readily available [1d] lactol 3 with p-toluenesuphonic acid in refluxing dry benzene was very sluggish and only trace amounts of a product exhibiting aromatic protons in the pmr spectrum was obtained. However, when the reaction was repeated in the presence of catalytic amounts of conc.H_2SO_4, a near quantitative yield of a crystalline product, mp 108-9° was obtained. The elemental analysis (M^+ 238, $C_{17}H_{18}O$) and pmr spectrum (δ 7-7.5, 5H, m) of the product clearly established the incorporation of a molecule of solvent during the reaction. The structure 4 for this product was deduced on the basis of pmr signal at δ 4.75 (1H, t, J=5Hz) due to a proton attached to ether oxygen and the signals at δ 83.4(d) and 93.9(s) in the cmr spectrum[2] due to carbon attached to oxygen and the carbon attached to both oxygen and an aromatic ring, respectively. When the lactol 3 was treated with naphthalene in the presence of catalytic amount of conc. H_2SO_4 in CH_2Cl_2 solvent, the corresponding addition product 5, mp 102° was obtained (50%).

The formation of 4 & 5 from 3 could be considered as arising through the intermediacy of bridgehead carbonium ion 6. However, this ion is unlikely to have much

4 R = C_6H_5

5 R = $C_{10}H_7$



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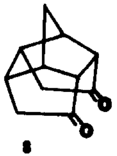

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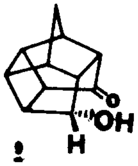

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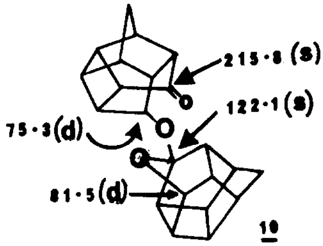

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stabilisation due to 7 because of unfavourable strain factors. Alternately, formation of 4 could be considered as proceeding *via* the attack of a ring opened hydroxy carbonium ion intermediate on benzene followed by recyclisation. In order to further explore this unusual substitution reaction the acid catalysed reactions of dione 8 and pentacyclic ketol[3] 9 were studied. While the dione 8 remained unchanged, the reaction of 9 adopted a different course.

Reaction of 9 with catalytic amount of conc. H_2SO_4 in refluxing benzene led to the isolation of a crystalline compound 10, mp 202-3°, in high yield, bearing an oxabirdcage skeleton. The dimeric nature of the product was evident from its mass spectrum (M^+ 334) and a doubled set of signals due to 22 carbons in the cmr spectrum. The structure of 10 was deduced from its ir spectrum: $\nu^{C=O}$ 1750 cm^{-1}, and pmr spectrum: δ 4.07 (1H, t, J = 4Hz) and 4.59 (1H, t, J = 5.5Hz) due to two protons attached to ether oxygen in different environment. Conclusive evidence for the structure of 10 was forthcoming from its cmr spectrum. The diagnostic cmr resonances are indicated on structure 10.

References and Notes:

1. (a) G.R. Underwood and B. Ramamoorthy, Tetrahedron Lett., 4125 (1970); (b) E.C.Smith and J.C. Barborak, J. Org. Chem., 41, 1433 (1976); (c) A.P. March and, T.C. Chou, J.D. Ekstrand and D. Van der Helm, J. Org. Chem., 41, 1438 (1976); (d) P.E. Eaton, L. Cassar, R.A. Hudson, D.R. Hwang, J. Org. Chem., 41, 1445 (1976).

2. Cmr spectra were recorded in $CDCl_3$ on a Brucker WH-90 spectrometer operating at 22.6464 Hz. Chemical shifts in ppm are with respect to internal TMS and off-resonance multiplicities are indicated in parenthesis.

3. We have observed that contrary to earlier reports[4,5], ketol 9 is in equilibrium with the oxa-birdcage system (unpublished results).

4. R.C. Cookson, E. Grundwell, R.R. Hill and J. Hudec, J. Chem. Soc., 3062 (1964).

5. T. Sasaki, S. Eguchi, T. Kiriyama and O. Hiroaki, Tetrahedran, 30, 2707 (1974).

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