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REVELATION OF PENTACYCLO $(6.2.1.0^{2,7}.0^{4,10}.0^{5,9})$ UNDECANE $\rightleftharpoons$ OXA-BIRD CAGE EQUILIBRIUM BY ^{13}CMR SPECTROSCOPY : FRAGMENTATION OF CAGED POLYCYCLIC SYSTEMS WITH LEAD TETRAACETATE

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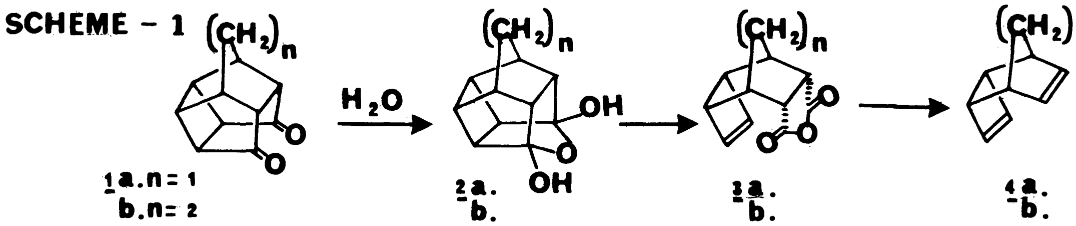
Summary: ^{13}Cmr evidence is presented to show the existence of pentacyclo $(6.2.1.0^{2,7}.0^{4,10}.0^{5,9})$ undecane $\rightleftharpoons$ oxa bird cage equilibrium in the parent system 1a. Preparation of some interesting polycyclic compounds via the lead tetracetate fragmentation of polycyclic ketones 1a, 1b and 10 is described.

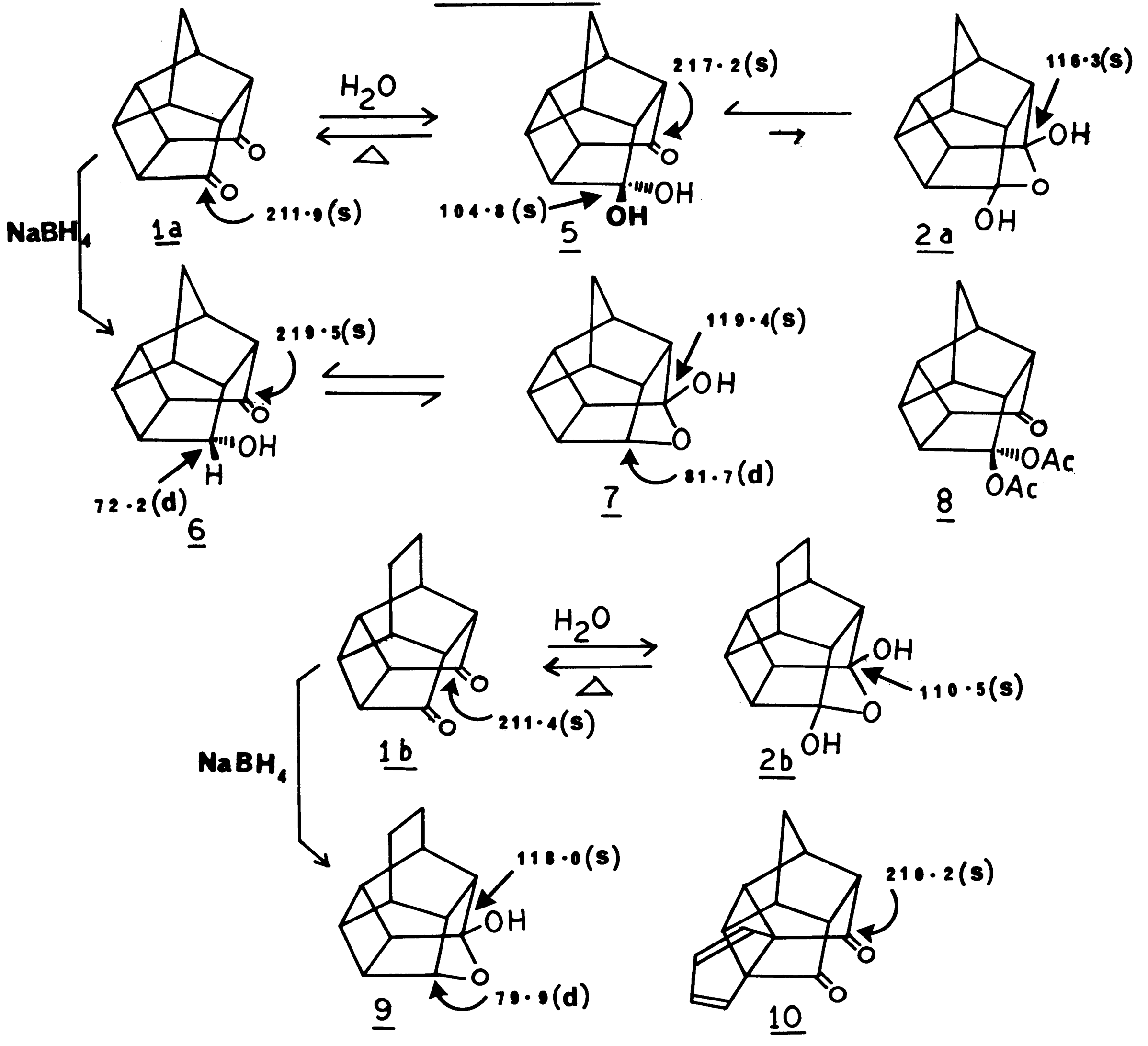
Conceptually, the sequence depicted in Scheme 1 should provide a non-conventional but purposeful alternate route to cubyl caged systems and their fused cyclobutene precursors. The key features of the scheme are the ready availability[2] of the starting diones 1a-b, the propensity[2] of the proximate carbonyl groups towards transannular hydration (1⟶2) and the well established precedence[3] for the contemplated fragmentation (2⟶3) with lead tetraacetate (LTA). In this letter, we report on the ^{13}cmr data which reveals the structure of hydrates derived from diones 1a, 1b, 10 and delineate the structures of several interesting and useful products derived from them.

SCHEME - 1



Monohydration of 1a has been shown by Cookson et al.[2] to furnish dihydroxy-ether 2a, but more recently, Sasaki et al.[4] have shown that the hydrate derived from 1a has structure 5. The ^{13}cmr spectrum of the hydrate prepared by us from 1a exhibited resonances (Scheme 2) compatible with formulation 5. However, a careful analysis of the spectrum also revealed weak but discrete resonances at δ116.3, 54.4, 45.3, 43.3, 42.9 & 41.7 attributable to 2a. Thus, an equilibrium

SCHEME 2



^{13}Cmr chemical shifts were recorded at in $CDCl_3$ or $CDCl_3$+CD_3OD using a Bruker WH-90 spectrometer.

1a: δ 211.9(s), 54.8(d), 44.7(d), 43.9(d), 40.5(t), 38.9(d).

5: δ 217.2(s), 104.8(s), 55.7(d), 50.6(d), 46.8(d), 44.6(d), 43.5(d), 42.4(d), 41.5(d), 38.8(t), 36.4(d). The weak resonances of 2a are mentioned in text.

6+7: δ219.5(s), 119.4(s), 81.7(d), 72.2(d), 56.3(d), 55.0(d), 54.4(d), 50.0(d), 45.9(d), 45.3, 44.9, 44.8, 43.4(2C), 43.1, 42.2, 42.0, 41.7(2C), 40.7, 38.5(t), 37.0(d).

1b: δ 211.4(s), 48.2(d), 47.5(d), 35.6(d), 31.5(d), 16.7(t).

2b: δ 110.5(s), 48.7(d), 48.5(d), 37.0(d), 31.2(d), 17.2(t).

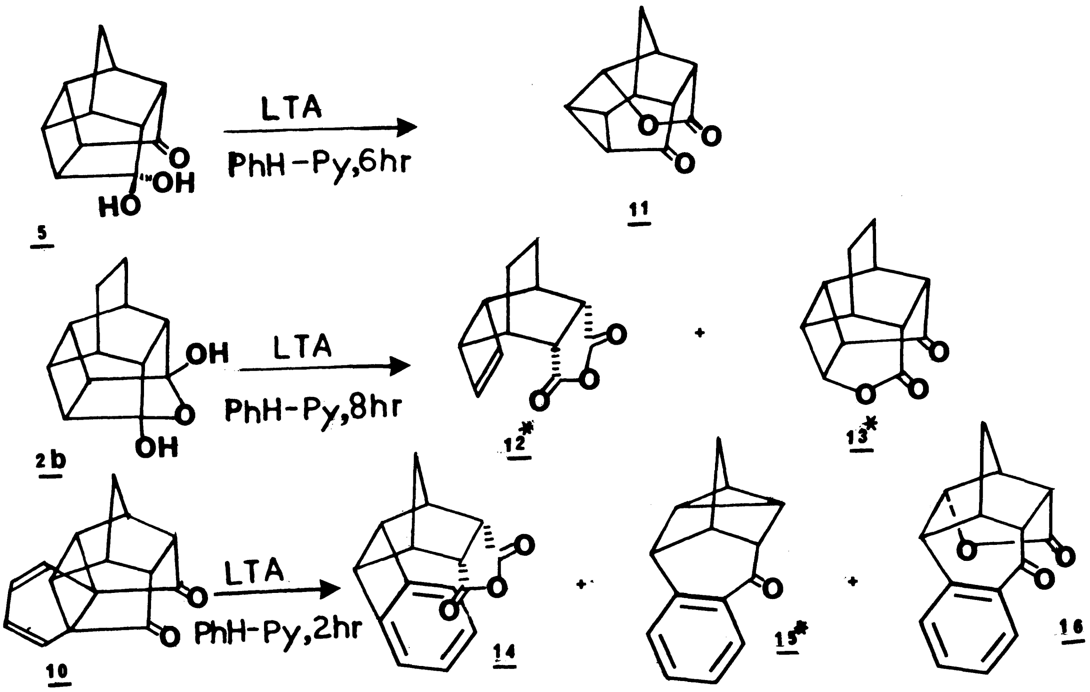
9: δ 118.0(s), 79.9(d), 47.9(d), 47.2(d), 45.7(d), 45.5(d), 37.7(d), 37.2(d), 32.7(d), 30.5(d), 17.6(t), 17.2(t).

10: δ 210.2(s), 124.8(d), 119.9(d), 54.6(d), 51.7(d), 50.2(s), 44.2(d), 39.0(t).

between the pentacyclic form 5 and the oxa-bird cage form 2a was indicated. Acetylation of 2a+5 with BF_3-Ac_2O, however, furnished only a single diacetate 8. To further probe the above equilibrium, ^{13}cmr spectrum of the known [2,4] 'ketol'6, mp.270°, prepared from 1a was examined. Surprisingly, 6 has been shown[2,4] to exist only in its open form. The ^{13}cmr spectrum of the 'ketol' showed a doubled set of signals due to 22 C's and characteristic resonances due to the presence of the open 6 and the cyclic hemi-acetal form 7 were discernible. Addition of few drops of CF_3COOH to the mixture of 6 and 7 caused the ^{13}cmr signals to coalesce and a spectrum showing 11 lines (δ 179.7, 76.3, 54.6, 52.6, 45.1, 43.9, 42.9, 42.6, 41.6, 40.6, 39.2) with positions between the original absorptions in 6 and 7 was observed. This spectrum seems to represent an average between 6 and 7 caused by fast interconversion in a dynamic equilibrium between the pentacyclic and the oxa-bird cage form. The ^{1}H nmr spectrum confirmed this contention and displayed two signals at δ 4.59 (t,J=5Hz) and δ 4.07 (t,J=4Hz) due to protons attached to carbon bearing oxygen in different environment. At room temp. the ratio of 6 and 7 was estimated (integration) to be 65:35.

Monohydration of dione 1b readily gave the transannular hydrate 2b, mp.252-3°, as reported[2] previously. Its structure was readily verified from its ^{13}cmr resonances. Similarly, ketol derived[2] from 1b, exclusively existed as the internal hemi-acetal 9. Lastly, the hexacyclic dione 10 did not furnish a clean hydrate that could be readily characterised by ^{13}cmr spectrum. The ^{13}cmr data for all compounds discussed above is summarised in Scheme 2 and off-resonance multiplicities are given in parenthesis. Conspicuous ^{13}cmr resonances that provide new and otherwise inaccessible clue to the existence of 6 $\rightleftharpoons$ 7 type equilibrium in the system 1a have been displayed on the structural formula.

With the nature of hydrates from the caged ketones 1a & 1b established, their reactions with LTA were investigated. Reaction of 5 with LTA gave the rearranged lactone 11, mp.280° (80%)[5,6]. The transannular hydrate 2b gave two products 12 and 13 in 25% and 20% yield. Finally the hexacyclic dione 10[8] with LTA gave a mixture of 14[9], 15 and 16[9] in 65%, 15% and 10% yield. Since anhydride moiety can be readily transformed to an olefin through a variety of reagents, the reactions described here provide ready access to tricyclo ($4.2.2.0^{2,5}$) deca-3,7-diene and 3,4-benzotricyclo ($4.2.1.0^{2,5}$) nona-3,7-diene ring systems.



*<u>12</u>,mp.199°,$C_{12}H_{12}O_3$,ir(KBr):1780,1840,1860 cm^{-1}(anhydride);pmr(.90MHz,$CDCl_3$): δ6.13(2H,s,olefinic),2.64(2H,br ring CH),2.07(2H,m,ring CH),2.95(2H,t,J=2Hz, ring CH),1.71(4H,t,J=1Hz,$-CH_2-CH_2$);cmr(22.64MHz,$CDCl_3$):δ174.7(2c,s,$-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}$), 142.7(2C,d,cyclobutene sp2),45.4(2C,d),42.4(2C,d),31.5(2C,d),24.2(2C,t,$-CH_2-CH_2$).
*<u>13</u>,mp.274-6°,$C_{12}H_{12}O_3$,ir(KBr):1735,1750 cm^{-1}(lactone and carbonyl);pmr(90MHz, $CDCl_3-CD_3OD$):δ4.83(1H,dt,J_1=3Hz,J_2=10Hz),3.63(1H,m),3.03(4H,m),2.27(1H,br),2.07 (1H,br),1.76(4H,m);cmr(22.64MHz,$CDCl_3-CD_3OD$):δ210.8(1C,s,$-\overset{O}{\overset{\|}{\underline{C}}}-$),171.9(1C,s,$-\overset{O}{\overset{\|}{\underline{C}}}-O$), 77.3(1C,d,H-<u>C</u>-O),53.4(1C,d),46.6(1C,d),39.8(1C,d),34.4(1C,d),33.9(1C,d), ,31.7 (1C,d),29.6(1C,d),19.6(1C,t),16.7(1C,t)[7].
*<u>15</u>,mp.43-5°,$C_{14}H_{12}O$,uv:λ_{max}^{MeOH} 249,214nm;ir(KBr):1675(Carbonyl),720,730 cm^{-1} (aromatic);pmr(60MHz,$CDCl_3$):δ7.1-8.1(4H,m,Ar),2.83(1H,s),2.7(1H,t,J=1Hz), 2.43(1H,br),1.7(4H,brs),1.45(1H,m).

References and Notes:

1. Department of Chemistry, Indian Institute of Technology, Kanpur.
2. R.C. Cookson, E. Crundwell, R.R. Hill and J. Hudec, J.Chem.Soc.,3062 (1964).
3. For a seminal example, see, R.B. Woodward, T. Fukunuga and R.C. Kelly, J. Am. Chem. Soc., <u>86</u>, 3162 (1964).
4. T. Sasaki, S. Eguchi, T. Kiriyama and O. Hiroaki, Tetrahedron, <u>30</u>, 2707 (1974).
5. Yields are based on the recovered starting materials. Various products were isolated by column chromatography on SiO_2 gel.
6. G. Mehta, V.K. Singh and H. Duddeck, Tetrahedron Letts., 1223 (1978).
7. On the basis of the spectral data we cannot rigorously rule out the alternate regioisomeric lactone structure.
8. A.S. Kushner, Tetrahedron Letts., 3275 (1971).
9. Spectral data for these compounds, obtained during some other studies, have been reported elsewhere, G. Mehta and V.K. Singh, submitted for publication.

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