Tetrahedron Letters,Vol.30,No.29,pp 3833-3834,1989   0040-4039/89 \$3.00 + .00
Printed in Great Britain   Maxwell Pergamon Macmillan plc

METAL HYDRIDE PROMOTED [1,3] SIGMATROPIC REARRANGEMENT

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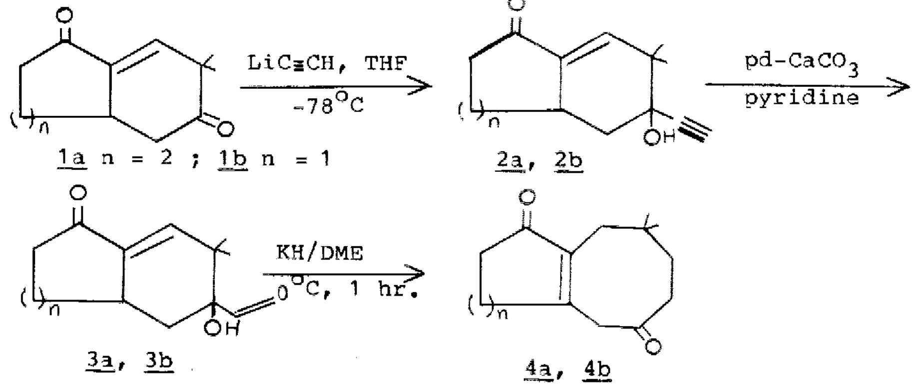
Summary : The divinyl carbinols 3a and 3b furnished the bicyclic diones 4a & 4b respectively on treatment with base via [1,3] sigmatropic rearrangement

Several examples of base catalysed oxy-Cope rearrangement in bicyclic systems have been reported from our laboratory.[1] In this communication, we report the synthesis and metalhydride promoted rearrangement of the bicyclic diones 1a & 1b.

Treatment of 7,7-dimethyl-$\overset{8}{\Delta}$-octalin-1,6-dione 1a[2] and 6,6-dimethyl-$\overset{8}{\Delta}$-heptalin-1,5-dione 1b with lithium acetylide in liquid ammonia at -78°C afforded the ethynyl carbinols 2a and 2b respectively in 65% yield while 2a was obtained as a colourless crystalline solid (mp. 182°C) 2b was obtained as a viscous liquid. Partial hydrogenation of the carbinols 2a and 2b in pyridine in the presence of pd/$CaCO_3$ gave the vinyl carbinols 3a as yellow solid (mp 111°C) and 3b as viscous liquid in excellent yields. No attempt has been made to assign the stereochemistry for the vinyl groups in 3a & 3b. Treatment of 3a and 3b with potassium hydride on 1,2-dimethoxyethane at 0°C for an hour followed by work up and chromatography over silica gel (10% ethyl acetate - petrol) afforded 4a and 4b respectively as liquids in 45% yield. The structure of 4a & 4b were confirmed by IR, H-^{1}NMR ^{13}C-NMR and UV absorptions.[3].



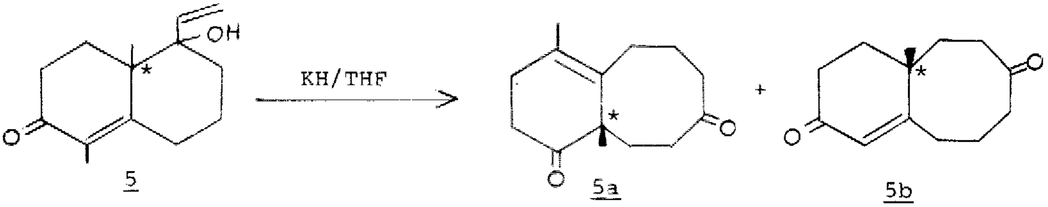
1a n = 2 ; 1b n = 1

2a, 2b

3a, 3b

4a, 4b

Two mechanisms can be visualized for the formation of the products 4a & 4b i) a fragmentation and recombination mechanism ii) concerted [1,3] sigmatropic rearrangement. It is reasonable to assume the operation of later mechanism in both from a point of view of conformational factors and observation made earlier during the rearrangement of the optically active vinyl carbinol 5[4].



It is envisaged that the ring-enlarged products 4a & 4b may serve as very good synthons towards the synthesis of sesquiterpenes like pentalenolactone and capnellene.[5]

Acknowledgement : G.S. acknowledges the awardof JRF by UGC (SAP) India.

References and notes

1. C.Seshu Sekhara Rao, G. Kumar, K. Rajagopalan and S.Swaminathan Tetrahedron 2195 (1986).

2. W.L.Meyer, M.J.Brannon, A. Merritt and D. Seebach, Tetrahedron Letters, 13, 1449-1452 (1986).

3. ^{13}C NMR data for 4a :- 218(s), 199.2(s), 169.41(s), 133.19(s) 43.20(s), 41.42(t), 33.24(t), 32.40(t), 34.37(t), 31.91(t), 29.60(t), 21.51(t), 18.6(q) and 16.1(q).

   ^{13}C NMR data for 4b :- 213.53(s), 197.34(s), 163.33(s), 134.19(s), 46.73(s), 40.42(t), 34.37(t), 33.20(t), 32.81(t), 29.30(t), 23.51(t), 18.1(q), and 17.14(q).

4. R.Uma, K. Rajagopalan and S.Swaminathan, Tetrahedron 42, 2757 (1986). The carbinol 5 was found to undergo concerted rearrangement in the presence of KH & THF yielding products 5a & 5b arising by a (3,3) and (1,3) pathways and significantly both the products were found to be optically active.

5. a. Murata, J., Ohtsuka. T., Shirahama, H., Matsumoto, T. Tet. Lett. 4313 (1981).

   b. Huguet, J., Karpf, M. Dreiding, A.S., Helv. Chim. Acta. 65, 2413 (1982).

(Received in UK 7 June 1989)