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THE CONFORMATIONAL ANALYSIS AND THE REARRANGEMENTS OF (NORBORN-2-ENO)[d](3,6-DIHYDRO-1,2-DIOXINE)

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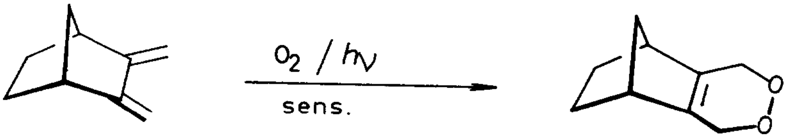
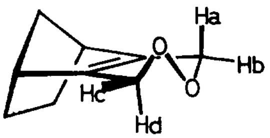
A recent communication of KONDO et al.[1] on the microwave and nmr studies of the structure and conformational isomerization of 3,6-dihydro-1,2-dioxine prompts us to disclose our results on the conformational analysis of the peroxide 1, as well as preliminary results on its thermal, photochemical, base, acid and Rh^I promoted rearrangements[2].



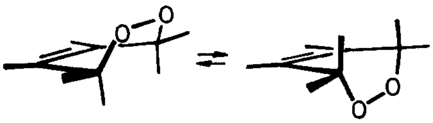
2 1

The diene 2 is highly reactive towards strong dienophiles[3]. As expected for a diene blocked in the s-cis conformation[4], 2 added $^1O_2$ (0.5 M in CCl_4, tetraphenylporphine, Pyrex vessel, Iodine 250 W lamp, -10°, O_2) rapidly, yielding the peroxide 1 (86%, after distillation). This 3,6-dihydro-1,2-dioxine is of special interest for at least 3 reasons: (1) distinction between the half-chair (C_1) and boat (C_s) conformations of the peroxide will be possible by ^{1}H-nmr, (2) variable temperature ^{13}C-nmr will allow an easy evaluation of the activation parameters of its ring inversion and (3) the stereochemistry of the thermal and photochemical peroxide → diepoxide rearrangement[1,5] can be established by product analysis.

The ^{1}H- and ^{13}C-nmr spectra of 1 at 30° were consistent either with the fast equilibrating half-chair conformers or with the degenerate or near-degenerate equilibrium of the boat conformers 1i and 1j. At -100°, the $^{13}C-\{^1H\}$-FT-nmr spectrum[6] showed splitting of all signals except



1(C_1)



1i (C_s) 1j (C_s)

δ_C = 46.7 ppm (C-7 of the norbornene substituent). This observation suggested the half-chair conformation, although it did not rule out a near 1:1 mixture of 1i:1j. Because of the bicyclic substituent, the methylene hydrogens ($H_{a,b,c,d}$) of 1 must show a ABCD pattern in the ^{1}H-nmr spectrum of a "blocked" half-chair conformation whereas the superposition of two symmetrical AA'BB' spectra should be observed for 1i ⇄ 1j. Low temperature ^{1}H-nmr (60 MHz, $CDCl_2/CHF_2Cl$, -103°) of 1 excluded the latter hypothesis and proved unambigously the half-chair conformation of the 3,6-dihydro-1,2-dioxine 1. Line-fitting of this spectrum with those simulated by the LOACN 4 method[7] for a ABCD spin system (long-range $J_{H,H}$ between the CH_2 protons of the peroxide 1 and the norbornene protons were neglected because they were smaller than the spectrum resolution) gave the ^{1}H-nmr characteristics of $H_{a,b,c,d}$ in 1 (see Table). A negative sign was attributed to $^2J_{H,H}$ between the geminal protons[8]. If the 3,6-dihydro-1,2-dioxine can be compared with (Z)-2-butene or cyclohexene derivatives[9], the homoallylic coupling constants $^5J_{H,H}$ enable distinction between the pseudo-axial ($H_{a,d}$) and pseudo-equatorial ($H_{b,c}$) hydrogens in 1[10].

Table : ^{1}H-nmr characteristics of the methylene $H_{a,b,c,d}$ in the peroxide 1 (60 MHz, -103°)

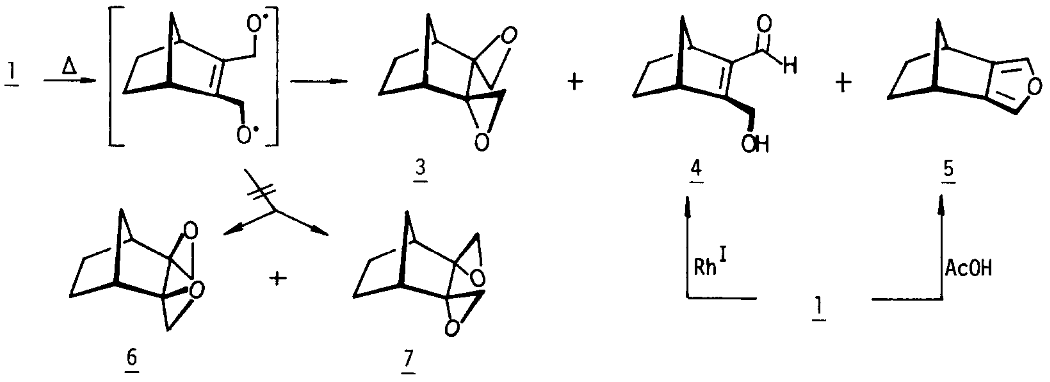
δ of H_a : 4.90 ; H_b: 4.04 ; H_c: 4.35 ; H_d: 4.64 ppm (δ_{TMS} = 0.0 ppm)

$^2J_{a,b} = -15.8$; $^2J_{c,d} = -16.4$; $^5J_{a,d} = 3.6$; $^5J_{a,c} = 2.3$; $^5J_{b,d} = 2.05$; $^5J_{b,c} = 0.92$ Hz

Kinetic parameters for the half-chair inversion of 1 were determined by line-shape analysis[12] of the $^{13}C-\{^1H\}$-FT-nmr spectrum (15.08 MHz). At low temperature, the signal of the methylene carbons C-3,6 of the peroxide (δ_C = 69.7 ppm[6]) was split into 2 lines separated by 23.8 Hz; coalescence occurred between -72° and -70°. Measurements at 15 different temperatures were made between -88.3° (4.2 s^{-1}) and -51.4° (580 s^{-1})[11]. An Arrhenius plot of the rate constants thus obtained permitted determination of the activation parameters E_a and logA used to calculate the Eyring parameters at T_m = 200 K, $\Delta H^{\ddagger} = 10.2 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = 2.5 \pm 1$ e.u.(standard deviations). These data are similar to those reported for 3,6-dihydro-1,2-dioxine[1] and for 3,3,5-trimethyl-3,6-dihydro-1,2-dioxine[13]. Our $\Delta S^{\ddagger}$ is consistent with a transition state having either a half-boat or a boat conformation.

Thermal isomerization of 1 (degassed cyclohexane or pentane, 130°, 6 h) yielded the trans-diepoxide 3 (major; isolated yield: 57 - 70%) together with some γ-hydroxy-α,β-unsaturated aldehyde 4 (< 15%) and the furan 5 (∿ 1%)[6]. None of the cis-diepoxides 6 or 7 could be detected (vpc, tlc, nmr). Similar product mixtures 3 + 4 + 5 were formed in the photolysis of 1 (quartz, 2537 Å Hg lamp, pentane or acetone, -10°). The high-selectivity of the isomerization 1 → 3 can be rationalized by invoking stereoelectronic control and/or electronic repulsion between the oxygen atoms during the homolysis of the O-O bond and closure to the diepoxide 3.

In presence of CsF in DMF [14] (40°, 3 h), 1 was isomerized to 4 in moderate yield (60%). Better yields (75%) of 4 were obtained by promoting the rearrangement 1 → 4 with $Rh_2(CO)_4Cl_2$ (0.01 M) in $CHCl_3$ (1 M of 1, 20°, 10 - 12 h). This isomerization was not due to acidic impurities[15] as it was found that added K_2CO_3 did not stop the reaction. The diepoxide 3 was stable in presence of $Rh_2(CO)_4Cl_2$ or AcOH (25°). ^{1}H-, ^{13}C-nmr and IR spectra were consistent with the s-trans conformation of the α,β-unsaturated aldehyde 4. The labile aldehyde 4 decomposed upon heating (polymerization, isomerization). In presence of acids, it yielded the furan 5, which was best obtained by heating 1 in AcOH (80°, 2 h, 60% isolated yield), 4 being an intermediate in the acid promoted water elimination 1 → 5 + H_2O [11,16].



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6) Characteristics of:

1: colourless oil, ^{1}H-nmr(CCl$_4$, 30^{o}): 4.4(m,4H), 2.9(bs,2H), 0.9-1.9(m,6H); ^{13}C-nmr(CDCl$_3$, 30^{o}): 137(s), 69.7(t,144), 46.7(t,135), 42.5(d,146), 26(t,135); MS(70 eV): 152(20), 136(37), 120(29), 105(24), 95(35), 92(100), 91(62).

3: colourless oil, ^{1}H-nmr(CD$_3$COOD): 2.94(d,1H;5.2), 2.84(d,1H;4.6), 2.75(d,1H;5.2), 2.63 (d,1H;4.6), 2.4-1.3(m,8H); ^{13}C-nmr(CDCl$_3$): 67.7(s), 67.(s), 49.5(t,175), 46.5(t,175), 43.5(d,149), 41.8(d,148), 36.2(t,135), 26.2(t,135), 23.8(t,135); MS(70 eV): 152(2), 124(10), 107(13), 94(67), 93(80), 91(33), 79(100).

4: colourless oil, ^{1}H-nmr(CDCl$_3$): 10.1(s,1H), 4.7(s,2H), 3.6(bs,1H), 3.4(m,1H), 3.1(m,1H), 2.-1.7(m,2H), 1.6-1.(m,6H); IR(CH$_2$Cl$_2$): 3620, 3460, 2880, 1660, 1615 cm^{-1}; UV(ether): 250 nm(ε, 6600); UV(isooctane); 249, 280(sh); UV(ethanol): 256 nm. ^{13}C-nmr(CDCl$_3$): 188.3(d,175), 167.6(s), 142.7(s), 58.7(t,142), 45.8(d,147), 45.5(t,135), 40.1(d,150), 25.4(t,135), 24.7(t,135); 2.4-dinitrophenylhydrazone, m.p.: 175-176^{o}.

5: colourless oil, ^{1}H-nmr(CDCl$_3$): 7.(s,2H), 3.3(m,2H), 2.-1.1(m,6H); ^{13}C-nmr(CDCl$_3$): 134.8 (s), 129.6.(d, 202), 50.6(t,132), 36.8(d,150), 28.6(t,135); MS(70 eV): 134(87); 91(100).

All compounds gave satisfactory microanalyses.

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10) Distinction between the exo and endo methylene protons of the peroxide 1 is difficult. It was suggested by the use of LIS reagents [11].

11) Details will be given in a full paper.

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