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THE STEREOSPECIFIC THERMAL RING ENLARGEMENT OF 1-VINYL CYCLOPROPANOLS INTO CYCLOBUTANONE DERIVATIVES

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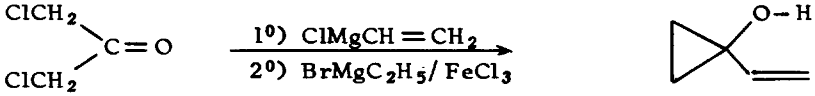
Recently, Wasserman et al. have reported the synthesis of 1-vinylcyclopropanol 1 from cyclopropanone hemiketal and vinylmagnesium bromide and the facile ring expansion from 1 into cyclobutanone derivatives occuring by the addition of a variety of electrophilic reagents (hydrogen bromide, perbenzoic acid, t-butyl hypochlorite ....) (1).

We report a simpler synthesis of vinylic cyclopropanols, their easy thermal ($\sim$100 °C) ring expansion into cyclobutanone derivatives and experimental data evidencing the mechanism of this rearrangement.



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Applying a known synthesis of 1-alkylcyclopropanols (2) we have carried out the addition of vinylic Grignard reagents (1 mole) to α, α'-dichloroacetone (1 mole), followed by the addition, in situ, of ethylmagnesium bromide (6 moles) in the presence of ferric chloride (0,07 mole) and hydrolysis by iced $H_2O + NH_4Cl$. From $ClMgCH=CH_2$, $BrMgC=C-(CH_2)_3$ (3), $LiC=CH-(CH_2)_4$ (4) we obtained the expected cyclopropanols, accompanied by the corresponding ethyl vinyl ketone of ring opening, readily eliminated by distillation :

- 1-vinylcyclopropanol 1 (b.p. 40 - 45°/ 28 mm ; y : 55%) (1) and two new alcohols
- 1-cyclopentenylcyclopropanol 2 (b.p. 35°/0,05 mm ; y : 55%) ; IR (CCl_4) 3615 cm^{-1} (free OH) 3530 cm^{-1} (π−H intramol. bond kept by dilution) and 3470 cm^{-1} (intermol. H−bond) ; NMR (CCl_4) δ 0,8 ppm (m, 4H), 2,10 ppm (m, 6H) and 5,55 ppm (m, 1H) ; Mass m/e 124 (M^+) : 30%, 67 ($C_5H_7^+$) : 100%
- 1-cyclohexenylcyclopropanol 3 (b.p. 45°/0,05 mm ; y : 60%) ; IR (CCl_4) 3615, 3530and 3470 cm^{-1} ; NMR (CCl_4) δ 0,8 ppm (m, 4H), 2,10 ppm (m, 8H) and 5,75 ppm (m, 1H) ; Mass m/e 138 (M^+) : 49%, 81 ($C_6H_9^+$) : 100%

On heating to 100° (liquid phase or g l p c) vinylcyclopropanols 1, 2 and 3 are, with nearly quantitative yield, converted into the known cyclobutanone derivatives 4, 5 and 6 respectively (5 – 8).

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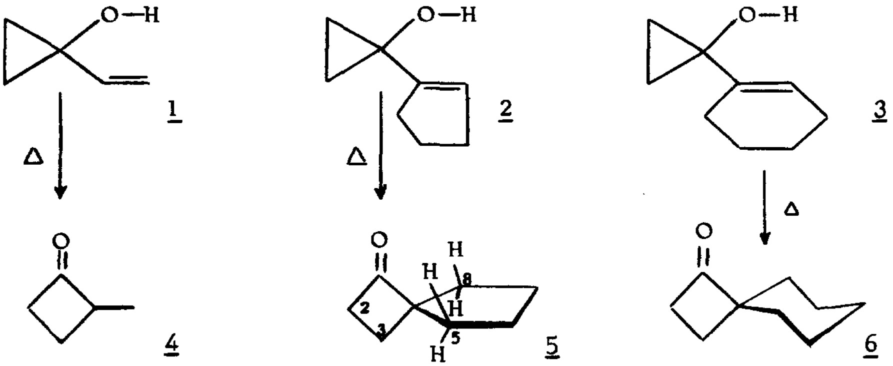
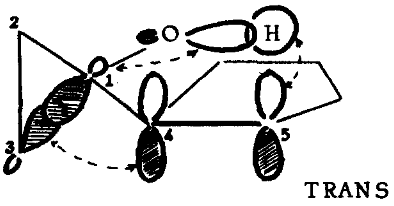
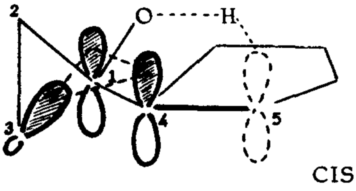


The stereochemistry and mechanism of such a thermal ring enlargement have been determined by the examination of the product obtained from a suitable deuterated derivative of cyclopropanol 2.



(Figure 1)

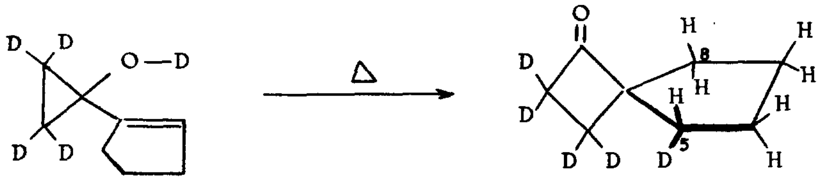


(Figure 2)

A thermally allowed 2a + 2a + 2s concerted process (9) would imply, from 2 to 5, a trans addition on the double bond ($H-C_5$ and C_3-C_4 bonding) (Figure 1). On the other hand, an intramolecular addition of the hydroxyl proton to the π-orbital of C_5 (intramol. π—H bond revealed by IR) would result in the formation of a positive charge at C_4. As it has been shown by Olah et al., (10) that delocalization occuring in such carbinyl cyclopropylcations prevents free rotation along C_1-C_4 axis, such a process would imply a cis addition (Figure 2). Finally, an intermolecular transfer of proton to C_5 and delocalized charge would probably lead to a cis + trans addition.

From O—deuterated cyclopropanol 2 trans addition would lead to a spirocyclobutanone with deuterium atom and carbonyl group syn relative to the cyclopentane ring of 5 but cis addition would lead to the anti isomer and cis + trans addition to the epimeric mixture.

In order to determine the stereochemistry of the reaction we prepared 5 d-labeled cyclopropanol 2' (mass spectrum M^+ : 129) from per-deutero- α, α'dichloroacetone (11) and hydrolysis of the reaction mixture by D_2O, and carried out the thermal rearrangement (sealed tube, 100^0) $2' \longrightarrow 5'$(M^+ : 129).



2'

5'

The NMR spectrum of spiro[3.4]octan-1-one 5 displays a triplet at δ (CCl_4) 2,80 ppm (2H of C_2, ^3J = 8,00 cps) and a multiplet at δ 1,75 ppm (10H, among which the triplet of protons at C_3 appears clearly). When coordinated with tris (dipivalomethano) Europium (Eu(dpm)$_3$/ketone 5 = 1/2) the two protons at C_5 and C_8 in syn position relative to the carbonyl group, then closer to the coordinated metal ion than the corresponding anti protons (12), are markedly shifted downfield ($\Delta\delta \simeq 3$ ppm) and assignments are made unambiguously.

The NMR spectrum of 5d-spiro [3.4] octan-1-one 5' displays a unique multiplet at δ (CCl_4) 1,75 ppm ; but when coordinated with Eu(dpm)$_3$, two multiplets are present at 4,70 ppm (2H) and 3,20 ppm (5H) respectively. The ratio 2/5 implies two protons with the syn configuration at C_5 and C_8 and therefore the anti configuration for the deuterium atom at C_5. Consequently the thermal ring enlargement $2' \longrightarrow 5'$ seems to involve an intramolecular stereospecific cis addition on the double bond (Figure 2).

In any case the thermal ring expansion of vinyl cyclopropanol, although stereospecific, does not involve a concerted valence reorganization under the control of orbital symmetry (13). This result should be compared to the closely related, but reverse ($C_4 \longrightarrow C_3$) thermal rearrangement of 2-bromocyclobutanone ketals into cyclopropanecarboxylic esters reported recently for which an allowed concerted valence reorganization was ruled out too (14).

It must also be emphasized that from the preparative point of view this thermal ring enlargement of 1-vinyl cyclopropanols into cyclobutanone derivatives appears highly competitive with the new spiroannelation techniques involving a sulfoximine cyclopropylylide (6), a diphenylsulfonium or triphenylphosphonium cyclopropylylide (7) or the reaction of 1,3-bis diazopropane with cycloalkanones (8).

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