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TRANS-COPLANAR REARRANGEMENTS: THE SYNTHESIS OF TRANS- AND CIS-BICYCLO[7.1.0]DECAN-2-ONE

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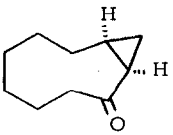
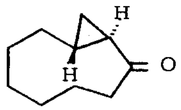
A variety of small rings containing bent bonds (2) have been synthesized primarily by ring contraction reactions that proceed in relatively poor yield (3-9). We wish to report the stereospecific synthesis of trans- and cis-bicyclo[7.1.0]decan-2-one in good yield from 1,2-cyclodecanedione (10, 11).

The photolysis of 1,2-cyclodecanedione proceeded as described (12) and gave 74% yield of 1-hydroxybicyclo[6.2.0]decan-10-one (I) whose ν_{max} 1800 cm^{-1} clearly indicated the presence of a four-membered cyclic ketone. The nature of the ring juncture in I had not been established (12). Reduction of I with lithium aluminum hydride or with aluminum isopropoxide gave two diols II and III, respectively. The diol II (62%), mp 153-5°, ν_{max}KBr 3250 cm^{-1}, insoluble in most organic solvents, M^+ = 170, base peak 98, was converted to the mono tosylate IV (79%), m.p. 82-3° dec., ν_{max}KBr 3400 cm^{-1}, nmr ($CDCl_3$) exhibited signals at δ = 1.00-2.30 (m, 15H) 2.41 (2, 3H), 2.51 (s, 1H, -OH), 4.50 (5, 1H), 7.51 (A_2B_2, 4H) by treatment with tosyl chloride in pyridine. The tosylate IV was converted to a ketone (88%), ν_{max}^{film} 3000, 1695 cm^{-1} as well as 1.634μ, ε = 0.43, in the near infrared (13) and M^+ 152.120 (152.1188 for $C_{10}H_{16}O$). The large ring cyclopropane-containing ketone was either V or VI. The ir and nmr spectra of an authentic sample of V were identical to the spectra of ketone obtained from rearrangement of IV (14, 15). The identity of the rearrangement product with V was confirmed by finding that the ir and nmr spectra of the alcohol, obtained from LAH reduction of the two samples were also identical.



V



VI

Consideration of established principles of stereoelectronic control in rearrangement reactions and of molecular models of the possible stereochemistries at the ring junctures in the diols II and III indicates that there are two combinations of stereochemistries consistent with the above observations. Either the ring juncture is *cis*, and II is a *trans*-diol while III is a *cis*-diol or the ring juncture is *trans*, and II is a *cis*-diol while III is a *trans*-diol.

The diol III (73%), m.p. 73-4°, ν_{max}^{KBr} 3200 cm^{-1} (very broad), nmr ($CDCl_3$) δ = 1.10-2.40 (m, 15H), 3.75 (s, 2H), 4.10 (broad, 2H, -OH) was readily converted to the mono tosylate VIII (92%), ν_{max}^{film} 3400 cm^{-1}, nmr ($CDCl_3$) δ = 1.1-2.3 (m, 15H), 2.41 (s, 3H), 3.05 (s, 1H-OH) which on passage through alumina (activity 3) gave a ketone (85%), ν_{max}^{film} 1695 cm^{-1}, 1.645μ, ϵ = 0.43, indicating large ring or open chain ketone and cyclopropane (13). The ketone was shown to be different from V by g.l.p.c. but gave an equilibrium mixture with V on treatment with potassium *t*-butoxide in toluene at 80° for 6 hours. Under the same conditions V gave the same mixture. The ketone must be the *trans* isomer, VI, with the ratio of *cis*:*trans* of 71:29 as determined by g.l.p.c. To establish whether the diol II or III was *cis*, both diols were treated with 2,2-dimethoxypropane (16). The diol III gave a volatile compound IX, (72%) which did not exhibit any hydroxyl in the infrared and whose nmr spectrum (CCl_4) had signals at δ = 1.23 (s, 3H), 1.48 (s, 3H), 1.3-2.2 (m, 15H), and 4.10 (m, 1H). The ketal IX gave a molecular ion M^+ 210 (relative abundance to the base peak at 41 of 17%) and M^+-15 (30%) indicating that the compound was not a dimer. The diol II was recovered in >90% from the reaction with 2,2-dimethoxypropane under the same conditions.

The assignment of the *cis* configuration for diol III in conjunction with the known stereospecificity of the rearrangement allows one to assign the stereochemistry of the ring juncture of the photoproduct I as *cis*. The stereochemistry of the remaining products in the reaction sequence then must be as shown in Chart I.

The sequence of reactions described above provides a route to the difficult-to-obtain *trans*-bicyclo[7.1.0]decan-2-one ring system and illustrates the utility of *trans*-coplanar rearrangements. Similar routes, using 1-hydroxybicyclo[m.2.0]alkanones as starting materials for the synthesis of *cis*- and *trans*-bicyclo[n.1.0]alkanes (n=4, 5 and 6) are under investigation.

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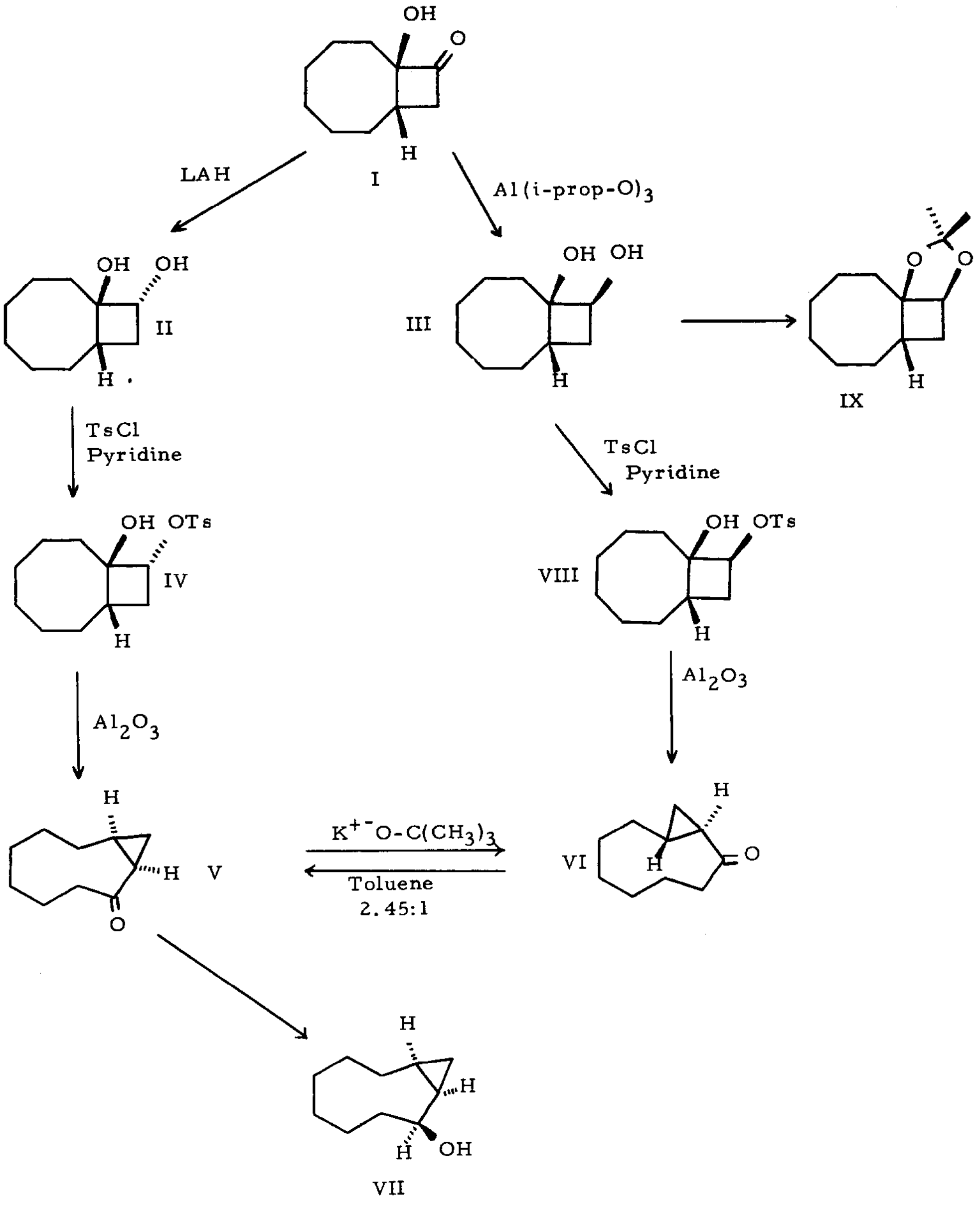
CHART I


OH
O
H
I
LAH
Al(i-prop-O)$_3$
OH OH
II
H
III
OH OH
H
O O
IX
H
TsCl
Pyridine
TsCl
Pyridine
OH OTs
IV
H
VIII
OH OTs
H
Al$_2$O$_3$
Al$_2$O$_3$
H
H
V
K$^+$ $^-$O-C(CH$_3$)$_3$
Toluene
2.45:1
O
VI
H
H
O
H
H
H
OH
VII

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