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THERMAL AND SILVER ION CATALYZED ISOMERIZATION OF THE 1,1′-BISHOMOCUBANE SYSTEM: PREPARATION OF A NEW $C_{10}H_{10}$ ISOMER[1]

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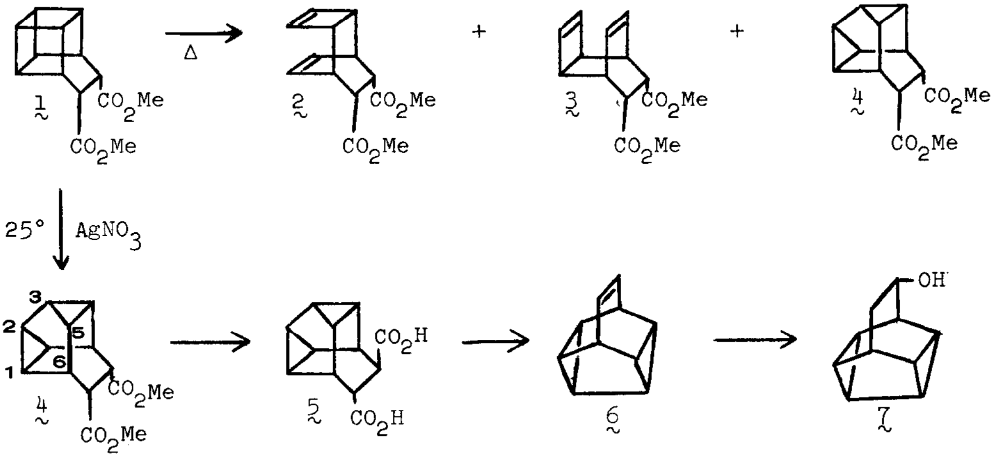
Study of the thermal induced reactions of diester 1[3,4] has shown that at 275° in an evacuated tube there is formed, in addition to dienes 2 and 3,[4] varying amounts (0-10%) of dimethyl cis-pentacyclo$[4.4.0.0^{2,10}.0^{3,5}.0^{4,9}]$decane-7,8-dicarboxylate 4, m.p. 104°: ir($CHCl_3$) 1735 cm^{-1}; mass spectrum, m/e 248. When the thermolysis was carried out at 235° under one atmosphere pressure of nitrogen, the yield of the two dienes fell to 0-30% and the formation of the new pentacyclic isomer increased to 70-100%. In analogy with the



1,1′-bishomocubane system, the <u>cis</u>-diester upon saponification yielded a <u>trans</u>-diacid 5, m.p. 218°. Treatment of 5 with $Pb(OAc)_4$ gave a new $C_{10}H_{10}$ olefin 6, m.p. 60°: ir($CHCl_3$) 3050, 2960, 1595 cm^{-1} ; mass spectrum m/e 130.

The rearrangement of 1 to 4 can also be effected at room temperature by using silver(I) as the catalyst. Stirring diester 1 with an aqueous methanolic solution of silver nitrate for three days produced 4 in quantitative yield. Also, simple filtration of an ether solution of 1 slowly through a column of silica gel impregnated with 10% $AgNO_3$ brought about the rearrangement.

The idea of using silver nitrate for the isomerization of diester 1 came from examination of the publication of Furstoss and Lehn[5] which reported the synthesis of several 1,1′-bishomocubane derivatives. Comparison of reported physical and spectral properties with those reported for our new diester 4, obtained by thermal rearrangement showed that they had unknowingly made the same new pentacyclic compound. Their synthetic scheme was identical to that used by earlier workers[3,4] except they purified their material by silver nitrate silica gel chromatography. The structures of all the pentacyclic compounds in their paper should be corrected.

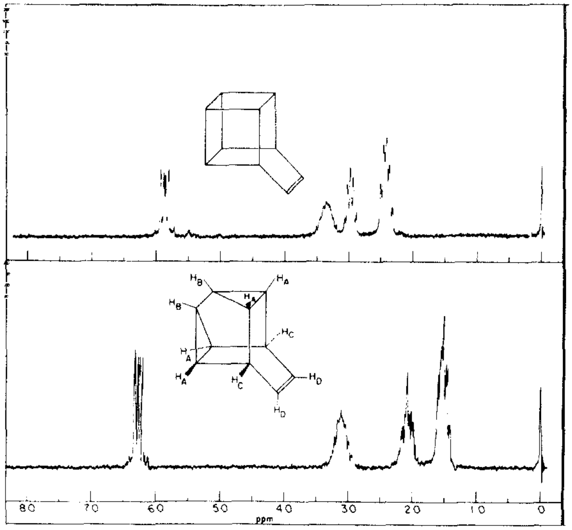


Fig. 1. 60 Mhz. nmr spectra

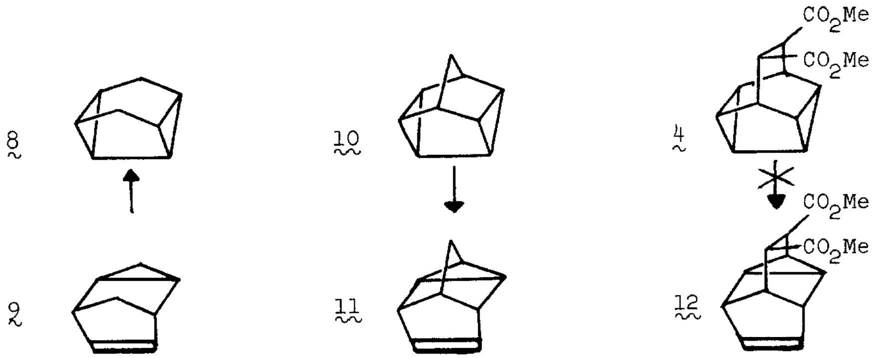
The structure of the pentacyclic system **4** was first conceived by evaluation of all possible two-bond cleavages and recombinations (hydride shifts excluded). Of all the structures generated in this manner, only **6** for the olefin contained the symmetry demanded by the nmr data. Fig. 1 compares the nmr spectra of 1,1′-bishomocubene with the new olefin **6**. Double resonance experiments gave results which were consistent with the assigned structure. Irradiation of resonance *A* in the spectrum of **6** reduced band *C* to a quartet, collapsed band *B* to a singlet, and left band *D* unchanged. Irradiation of band *C* caused band *D* to become a singlet, band *A* to become a doublet, and band *B* remained unchanged. When band *D* was irradiated, *C* became a quintet while *A* and *B* did not change.

The structure assignment was confirmed by X-ray structure determination. Olefin **6** was hydroborated to yield alcohol **7**, m.p. 129°, (identical with product from silver nitrate treatment of bishomocubanol) which, in turn, was converted to the 3-nitro-4-chlorobenzoate, m.p. 121°. All bond lengths and angles were the same as those found in the parent bicyclo[2.2.2]octane nucleus,[6] except that the C-1,C-6,C-5 bond angle was contracted to 105°. This angle change was reflected in the shortening of the C-2,C-3 bond to 1.49 A.

The conversion of **1** to **4** is essence transforms four cyclobutane rings into two cyclopropane and two cyclopentane rings, a favorable thermodynamic change. No other catalyst for this conversion besides silver has been found. Treatment of **1** with mineral acid or with mercuric, cuprous, zinc, iron, and rhodium compounds resulted in complete recovery of starting material.

Recently, the rhodium catalyzed interconversions of some related polycyclic hydrocarbons have been discussed in terms of thermodynamic stability.[7] Various rhodium catalysts isomerize **9** to the closed compound **8**. However, introduction of a methylene bridge into this ring system reverses the stability, i.e., **10** goes to **11** .

The new isomer **4** is the same as **10** except that it has a two carbon bridge in place of the methylene bridge. Catalysts such as silver nitrate or *tris-*



triphenylphosphine rhodium chloride did not effect further reaction of **4**. Thus, in line with the postulate of Katz and Cerefice,[7] the introduction of a two-carbon bridge into ring system **10** must cause **4** to be favored thermodynamically over its corresponding ring opened isomer **12**.[8]

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REFERENCES

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8. A similar thermodynamic argument can be used to rationalize the failure of 1,1′-bishomocubene to isomerize to olefin **6** with silver nitrate or rhodium catalysts. The introduction of two sp^2 centers into the two-carbon bridge must change the relative stabilities of the two olefins.