STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 8. CONDENSATION OF

cis-1,2,4a,5,8,8a-HEXAHYDRO-4a,7-DIMETHYL-4-VINYL-NAPHTHALEN WITH CITRACONIC ANHYDRIDE

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The diene condensations of 1-vinylcyclohexene with citraconic anhydride [1] and with dimethyl mesaconate [2] have made it possible to study some of the stereochemical transformations of bicyclic ortho-dicarboxylic acids and to make some interesting inferences relating to the dependence of their reactivities on their spatial structures. With the object of making a further study of the stereochemistry of cyclic compounds we have investigated the condensation of cis-1,2,4a,5,8,8a-hexahydro-4a,7-dimethyl-4-vinyl-naphthalene (I) [3] with citraconic anhydride. When a mixture of these components (70-80% excess of diene) was heated at 100° for ten hours, a 30% yield was obtained of a mixture of four stereoisomeric crystalline anhydrides (II); a, b, c, and d) which were separated by fractional crystallization.

These isomeric anhydrides were isolated in the proportions 15:16:2:1, and when they were hydrolyzed with 5% caustic soda solution, the corresponding individual crystalline stereoisomeric cis acids (III); a, b, c, and d) were obtained.

The proportions in which the crystalline isomers are formed in the diene synthesis were found to vary somewhat with temperature, and at 20° (10 days) very little of the isomer (IIe) was obtained. When reaction was at room temperature for one day and then at 100° for 10 hours, the amounts of the isomers (IIC) and (IID) were increased appreciably, though the isomers (IIA) and (IIB) were always the main reaction products.

The identity of the ring structure present in the isomeric dicarboxylic acids (III); a, b, c, and d), was proved by dehydrogenation over palladized charcoal (5% Pd) at 340-350°. The only product from all four isomers was 1,7-dimethylphenanthrene (IV), which was characterized as its picrate and styphnate. These results show that all four of the isomeric anhydrides (II) isolated in the synthesis described have the same phenanthrene skeleton and differ only in steric structure. These anhydrides were formed as a result of ortho addition; attempts to detect adducts formed by para addition in the products of the diene synthesis were not successful.

In accordance with the method of preparation (two-fold diene synthesis), for the anhydrides (II), which have five centers of asymmetry, the following four spatial configurations of the cis-cis series are possible:

![Diagram](https://example.com/diagram.png)
In view of the relative mildness of the condensation conditions (up to 100°), it may be considered that each of the four isomeric anhydrides isolated has a double bond in the normal position (C-9)-(C-11)* and that the two isomers formed in predominating amounts, (IIa) and (IIb), have spatial structures corresponding, according to molecular models, to endo addition. These suppositions were fully confirmed by a study of the chemical transformations of the isomers, so that their spatial configurations have been proved.

When the cis anhydride (IIa) was hydrogenated in benzene or acetic anhydride in presence of a platinum catalyst, only one molecular proportion of hydrogen was absorbed, with formation of the individual anhydride (V), which gave the corresponding acid (VI) when hydrolyzed. The same acid was formed when the cis acid (IIIa), obtained by hydrolysis of the anhydride (IIa), was hydrogenated. Treatment of the cis acid (IIIa) with an ether solution of diazomethane gave the corresponding diester (VII), m.p. 95°, and this again absorbed only one molecular proportion of hydrogen when hydrogenated in presence of a platinum catalyst, the individual diester (VIII), m.p. 85°, being formed. In accordance with its cis structure, the diester (VII) gave a good yield of the trans acid (IX) when isomerized with sodium methoxide, and this acid gave the trans diester (X) with diazomethane and the individual trans acid (XI), formed by absorption of one molecular proportion of hydrogen, when hydrogenated over a platinum catalyst.

* Steroid numbering.