As a result of a detailed study of the stereochemistry of the diene-synthesis reaction between 1-vinylcyclclohexene and maleic anhydride and the stereospecific transformations of the isomeric adducts formed, we obtained six of the eight theoretically possible geometric isomers of decahydro-1,2-naphthalenedicarboxylic acid [I], the configurations of which were proved rigorously. The other two isomers of this acid, having trans-syn-cis (I) and trans-syn-trans (II) configurations, could not be obtained by these methods; we did not succeed also in preparing them by the condensation of 1-(1-acetoxyvinyl)cyclohexane with maleic anhydride owing to the fact that this reaction proceeds in the direction contrary to that required by the rule of "maximum accumulation of unsaturation" [2] and gives an adduct of anti configuration.

However, an examination of molecular models showed that trans-syn-cis-decahydro-1,2-naphthalenedicarboxylic acid (I) should be quite stable, and its synthesis was very important for the confirmation of all the previously established steric laws. As will be seen from the configuration of this acid, in order to prepare it we had to find a route which would lead to a trans ring fusion with simultaneous preservation of the cis disposition of hydrogens at C-1, C-2, and C-8a. We succeeded in finding such a synthesis by studying the oxidation of the previously prepared anhydride of syn-cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid (III) [3] with peroxyacetic acid.

It was found that reaction of the syn-cis anhydride (III) with peroxyacetic acid in chloroform gave a good yield of a mixture of approximately equal amounts of the corresponding epoxide (IV) and the syn-cis 4-hydroxy γ-lactone acid (V), the latter being readily formed also by the hydrolysis of the epoxide (IV) with 5% sulfuric acid. The structure of the syn-cis 4-hydroxy γ-lactone acid (V) was proved by the fact that diazomethane converted it into the syn-cis 4-hydroxy γ-lactone ester (VI) which has a carbonyl absorption band in the infrared spectrum at 6.5 μ, characteristic for the γ-lactone ring. The presence of a secondary hydroxy group was confirmed by the formation of the corresponding acetic ester (VII) by boiling the hydroxy ester (VI) with acetyl chloride. The configuration of the 4-hydroxy γ-lactone acid (V) at C-1, C-2, C-4a, and C-8a follows quite obviously from the syn-cis configuration of the original anhydride (III) and the cis reaction of lactonization of the anhydride (IV) with participation of the axial carboxyl at C-1 and the epoxy ring. However, the configuration of the hydroxy group at C-4 is still not proved.
Oxidation of the syn-cis 4-hydroxy γ-lactone acid (V) with chromium trioxide in acetic acid gave a good yield of the syn-cis 4-oxo γ-lactone acid (VIII), which was converted by diazomethane into the corresponding oxo lactone ester (IX), formed also by the oxidation of the syn-cis 4-hydroxy γ-lactone ester (VI).

Thus, quite apart from the configuration of the epoxy ring and the 4-oxo group in the intermediaries (IV) and (V), we obtained the 4-oxo γ-lactone ester (VIII) and its ester (IX) with cis dispositions of the hydrogens at C-1, C-2, and C-8a which could serve as starting materials for a possible synthesis of trans-syn-cis-decahydro-1,2-naphthalenedicarboxylic acid (I).

For the preparation of this compound we made use of Clemmensen reduction of the oxo lactones (VIII) and (IX) because we might then expect that, in addition to removal of the oxo group, hydrogenolysis of the γ-lactone ring would occur with preservation of the original configuration. Similar reduction of a lactone ring has been observed recently in the catalytic hydrogenation of some simple oxo lactones [4], but this reaction has not been studied at all for polycyclic compounds. It was found that boiling of the syn-cis 4-oxo γ-lactone acid (VIII) with amalgamated zinc in a mixture of concentrated hydrochloric acid and methanol resulted in the reduction of the oxo group, esterification of the 2-carboxyl, and hydrogenolysis of the γ-lactone ring, the trans-syn-cis monoester (X) being obtained in good yield. The structure of this compound was proved unequivocally by the fact that it is formed also by similar reduction of the syn-cis 4-oxo γ-lactone ester (IX). Such hydrogenolysis of the γ-lactone ring occurs readily only in the case of oxo lactones, and the previously described lactones of decahydro-1,2-naphthalenedicarboxylic acid [5], which contain no oxo group, and the above-described 4-hydroxy γ-lactone acid were found to be incapable of such hydrogenolysis.

The configuration of the monoester (X) follows from the syn-cis configuration of the original 4-oxo γ-lactone acid (VIII) and the cis reaction of hydrogenolysis of the γ-lactone ring. This last circumstance does not give rise to doubt, since in this case Walden inversion at C-4a is impossible without conversion of a trans-decahydronaphthalene system into a cis-decahydronaphthalene system, which has never been observed to occur. In accordance with its structure and configuration, the monoester (X) should not undergo isomerization at the equatorial (stable) 2-methoxycarbonyl group and therefore should give by hydrolysis the expected trans-syn-cis-decahydro-1,2-naphthalenedicarboxylic acid (I), differing from the previously described six other isomers; this was confirmed experimentally.