

CIS Δ^5 -OCTAHYDRO-1-NAPHTALENONES AND CIS Δ^5 -DECAHYDRO-1-NAPHTALENONES
(CIS-1-DECALONES) BY STEREOSELECTIVE INTRAMOLECULAR DIELS-ALDER REACTION.

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Intramolecular DIELS-ALDER reactions of requisite trienes led to
cis-1-decalones, via an endo intermediate state.

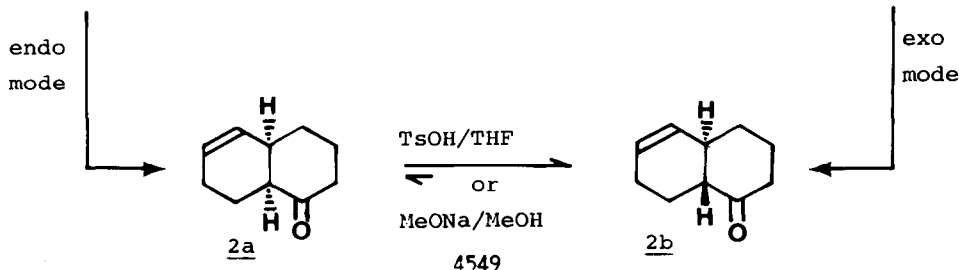
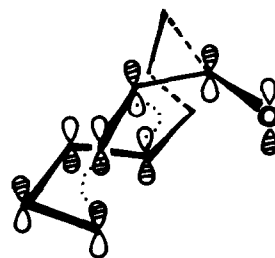
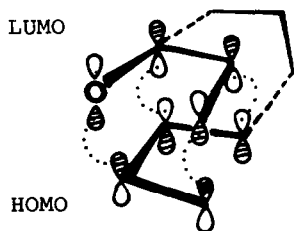
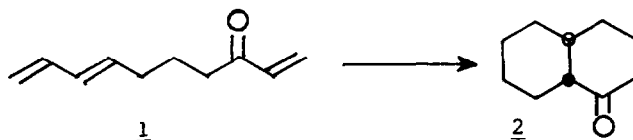
In connection with our synthetic work, we needed a method for the preparation of particular cis-1-decalones. Recent reports from the literature have demonstrated that the intramolecular variants of the DIELS-ALDER reaction offer a powerful method for the stereocontrolled synthesis of polycyclic structures (1).

Wishing to take advantage of this one-step construction of a bicyclic olefin, our interest was focused on the simultaneous formation of two 6-membered rings (2).

There are only few reported cases of such an intramolecular [4+2] addition which generate a simple octalone system, and 1 was mentioned to give 2 with the trans ring junction (3a).

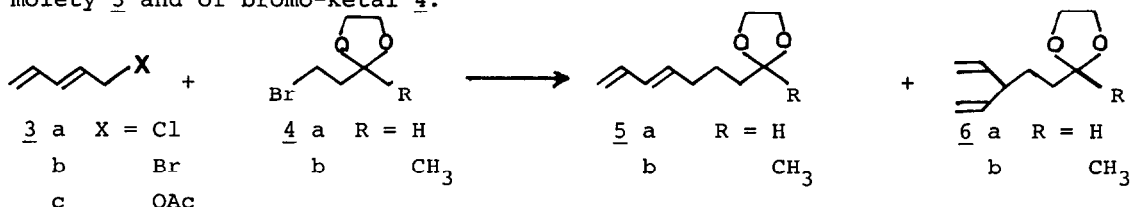
The stereochemical features of this type of reaction should be consequences

of a highly ordered transition state. Two requisite cis-coplanar arrangements of 1 lead to annelated products and both are strain-free.



The maximum orbital overlap lowers the energy of the endo transition state relative to that of the exo mode. Despite a previous report (3a), the cis-octalone 2a should be the one obtained under kinetically controlled conditions. Since 2a epimerized to 2b, we have carried out as mild as possible a synthesis of triene 1 to avoid loss of this selectivity by the formation of the thermodynamically controlled product 2b.

Our approach to the synthesis of 1 involves the union of a pentadienyl moiety 3 and of bromo-ketal 4.



From all the combinations investigated, including some copper catalysts (CuI or Li₂CuCl₄), the best results were obtained from :

- Condensation of the GRIGNARD reagent of 4a with a solution of 3a in THF at 0°C (78 % of a mixture 5a : 8.5/6a : 1.5).

- Condensation of the GRIGNARD reagent of 4b with a boiling solution of 3b in THF (72 % of a mixture 5b : 7/6b : 3).

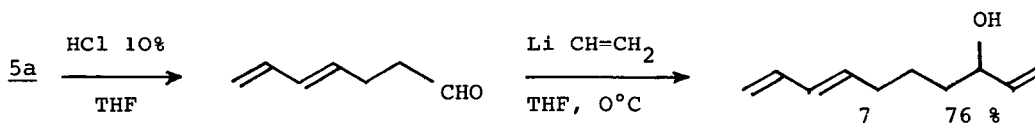
Diene 5b : IR cm⁻¹ = 3084, 1652, 1608, 1070, 903

NMR (δppm, CCl₄) : 5.35 to 6.66, m, 3H ; 5.00, m, 2H ; 3.86, s, 4H ; 2.10, m, 2H ; 1.50, t, 2H ; 1.23, s, 3H.

After chromatographic purification (SiO₂), diene 5a was deketalized and condensed with vinyl-lithium in THF, to yield triene carbinol 7.

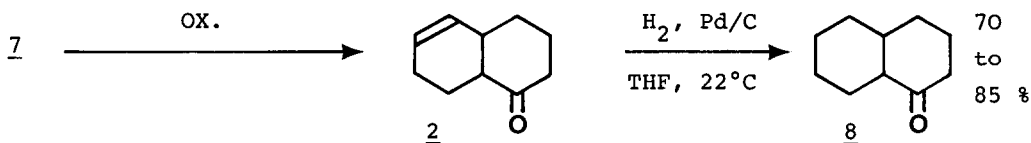
Triene 7 : IR cm⁻¹, CCl₄ = 3600, 3340, 3080, 1650, 1604, 924, 900.

NMR (δppm, CCl₄) : 5.91, m, 4H ; 5.12, m, 4H ; 4.02 d of t, 1H ; 3.08, s, 1H ; 2.10, m, 2H ; 1.10 to 1.70, m, 4H.



Oxidation of the vinyl carbinol moiety in triene ketone 1 directly produced the cis-fused octalone 2 *via* a smooth *in situ* intramolecular [4+2] cyclization.

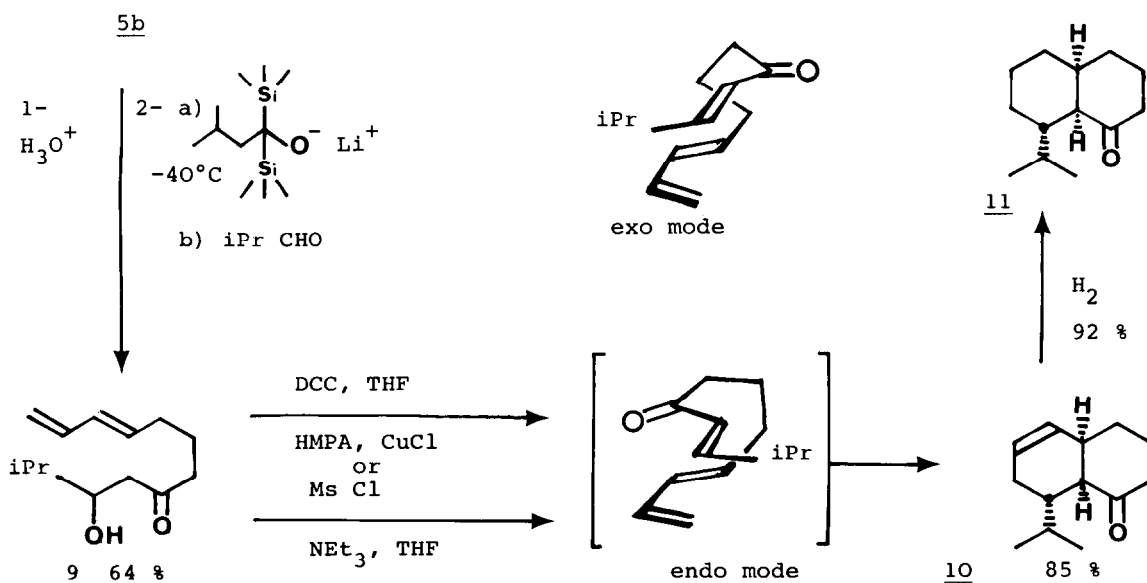
The stereochemical structure of 2 was established by chemical connection with the known, independently synthesized cis and trans-decahydro-1-naphtalones 8 (1-decalones) (4). We have found that the nature of the ring fusion was dependent on the crucial oxidation step :



	<u>Cis</u>	<u>Trans</u>
$\text{CrO}_3, \text{H}_2\text{SO}_4, \text{Et}_2\text{O}/\text{H}_2\text{O}, 0^\circ\text{C}, 1.5 \text{ h}$	6	4
$\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4, \text{Et}_2\text{O}/\text{H}_2\text{O}, 0^\circ\text{C}, 2 \text{ h}$	8	2
$\left[\text{C}_6\text{H}_5\text{NH} \right]^+ \cdot \text{Cr}_2\text{O}_7^{--}, \text{CH}_2\text{Cl}_2, 22^\circ\text{C}, 24 \text{ h}$	9	1
$\text{MnO}_2, \text{HCCl}_3, 22^\circ\text{C}, 5 \text{ days}$	1	9
$\text{MnO}_2, \text{HCCl}_3, 22^\circ\text{C}, \text{stopped at } 48 \text{ h}$	7	3
Active MnO_2 (5), $\text{HCCl}_3, 22^\circ\text{C}, 4 \text{ h}$	9.5	0.5

The observed stereoselectivity of this intramolecular DIELS-ALDER reaction is thus fully reconciled with the original prediction. Secondary orbital interactions play an important part in the stereoselectivity, and the reaction is kinetically controlled *via* the preferred endo-orientation of the carbonyl group.

In diene 5b, we have linked a substituted dienophile unit after deketalization *via* regioselective aldol condensation, followed by dehydration. Once again, the alkylidene-ketone directly cyclized into the pure *cis*-octalone 10.



10 : IR cm^{-1} : 1708

NMR (δ ppm, CCl_4) : 5.43, m, 2H ; 2.50, m, 1H (J = 2 Hz and 5 Hz) ;
2.30, m, 3H ; 1.97, m, 2H ; 1.73 broad s, 5H ; 1.60, m, 1H ; 1.04, d,
(J = 6 Hz), 3H ; 0.85 d (J = 6 Hz), 3H.

In this case, the preference for the endo transition state is enhanced by a steric repulsion present in the exo mode, between the newly introduced iPr- substituent and the diene.

In the stereochemistry assigned to 10 and 11, the isopropyl group lays in an equatorial position. Neither 10 nor 11 epimerize to the trans fused decalone system (with the iPr-group brought to an axial position) under the standard conditions used for the epimerization 2a \rightleftharpoons 2b.

To sum up, we have shown by this study that the stereospecific construction of Δ^5 -octahydro or decahydro-1-naphtalenones with a cis ring junction is possible in useful yields, *via* the intramolecular DIELS-ALDER reaction of appropriately functionalized precursors (6).

References and notes :

- 1 - For a review, see W. OPPOLZER, Angew. Chem. Int. Ed. Eng., 16, 10, (I977).
- 2 - S.R. WILSON, D.T. MAO, J. Amer. Chem. Soc., 100, 6289, (I978).
- 3 - a) W. OPPOLZER, R.L. SNOWDEN, Tetrahedron Letters, 4187, (I976).
b) O.P. VIG, I.R. TREHAN, N. MALIK, R. KUMAR, Ind. J. Chem., 16B, 449, (I978).
c) F. NÄF, R. DECORZANT, W. THOMMEN, Helv. Chim. Acta, 62, 114, (I979).
- 4 - Cis-1-decalone 8 was synthesized from 1-naphtol according to :
E.R. TALATY, G.A. RUSSEL, J. Amer. Chem. Soc., 87, 4867, (I965).
8 epimerizes easily under acidic catalysis in the trans epimer. Besides spectroscopic identification, the two epimers are very well separated by gas chromatography (20 % Carbowax column).
- 5 - A.J. FATIADI, Synthesis, 65, (I976).
- 6 - After the submission of this article, a report described the synthesis of (\pm)-torreyol, using the same speculations on intramolecular DIELS-ALDER reaction. D.F. TABER, B.P. GUNN, J. Amer. Chem. Soc., 101, 3992, (I979).

(Received in France 10 July 1979)