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CONFORMATIONS OF 3-CARENE AND 2-CARENE. THEIR CONFORMATIONAL PREFERENCE AND THE REACTIVITY OF THE DOUBLE BOND.

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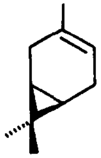
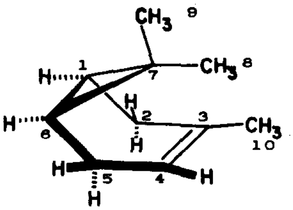
3-Carene (I) can exist in two conformations, boat form (II) and inverted boat form (III). A cursory examination of Dreiding models reveals that the boat form (II) is more crowded and hence unfavorable while the inverted boat form (III) is less crowded and hence favored. So also 2-carene (IV) can exist in two conformations, partial boat form (V) and partial inverted boat form (VI).

According to the anisotropic effects[1] of the double bond, hydrogen atoms lying in the positive cone are diamagnetically shifted upfield and those lying in the negative cone are shifted downfield. The magnitude of these shifts increases towards the symmetrical axis of the region and also towards the electrical center (see diagram, VII.)

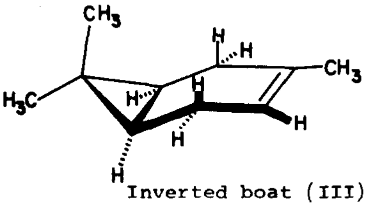
Table 1 shows that 8-methyl group in 2-carene is within 2.8 to 3.2 Å of the center of the double bond and that the angle to the symmetry axis is between 20 and 50°. Hence this methyl group is subjected to diamagnetic shielding to a



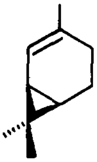
3-Carene (I)



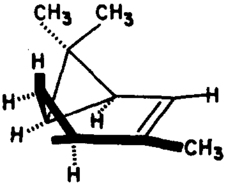
Boat (II)



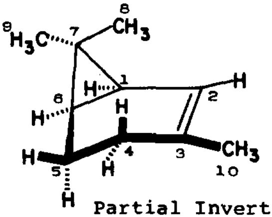
Inverted boat (III)



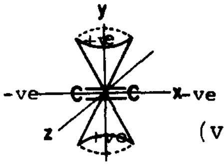
2-Carene (IV)



Partial Boat (V)



Partial Inverted Boat (VI)



(VII)

lesser degree than the 8-methyl of 3-carene when in the boat conformation (II). The inverted boat conformation of 3-carene (III) has both methyl groups far removed from the double bond and hence they should not be affected by the anisotropic effects of the double bond. The chemical shift difference between these two methyl groups should be the same as for carane, about 2 cps. On the other hand, if a 50:50 mixture of the two conformations exists, as assumed by Gollnick[2], the chemical shift difference between the 8- and 9-methyl groups should approach that observed for 2-carene. The fact that the chemical shift difference between 8- and 9-methyl groups of 3-carene, see Table 2, is larger than in 2-carene indicates that 3-carene exists preferentially in the boat conformation.

TABLE 1

Distances and Angles from the Center of the Double Bond to 8-Methyl and 9-Methyl in 3- and 2-Carenes

	3-Carene			2-Carene		
	Boat	Planar	Inverted boat	Partial boat	Planar	Partial Inverted boat
D_1	2.2 Å	3.2 Å	3.8 Å	3.2 Å	3.0 Å	2.8 Å
α_1	0°	30°	63°	22°	30°	50°
α_2	0°	0°	0°	20°	10°	-14°
D_2	4.7 Å	5.0 Å	5.2 Å	4.7 Å	4.4 Å	4.5 Å
α_3	4.8 Å	66°	104°	62°	50°	55°
α_4	0°	0°	0°	66°	48°	65°

D_1 = Distance between center of the double bond and 8-methyl
D_2 = Distance between center of the double bond and 9-methyl
α_1 = Angle between Y-axis and 8-methyl when viewed along X-axis.
α_2 = Angle between Y-axis and 8-methyl when viewed along Z-axis.
α_3 = Angle between Y-axis and 9-methyl when viewed along X-axis.
α_4 = Angle between Y-axis and 9-methyl when viewed along Z-axis.

TABLE 2

Chemical Shift of 8-Methyl and 9-Methyl in 3- and 2-Carenes.

Name	Chemical shift (δ) in cps from TMS.		Difference in (δ) of 8-Methyl and 9-Methyl in cps.
	8-Methyl	9-Methyl	
3-carene	48	64	16
2-carene	52	63.5	11.5

This is further confirmed by studying the NMR spectra of 3-carene at various temperatures (see Table 3). At room temperature, 27°, the free energy differences (ΔF) and the conformational equilibrium constant (K) between boat (II) and inverted boat (III) amount to -1.48 kcal./mole and 11.5 respectively.

TABLE 3

Variation of Chemical Shift Difference in cps between 8-Methyl and 9-Methyl with Temperature and the Per Cent of Boat Conformation in 3-Carene.

Temp., °C	-60	-40	-20	0	40	60	100	120	160
$\Delta\nu$	17	16.8	16.6	16.3	15.6	15.4	14.8	14.6	13.4
% Boat[a]	100	98.6	97.3	95.3	90.6	89.3	85.3	84.0	76.0

[a] Based on Eliel's equation[3] assuming $\Delta\nu_{boat}$ = 17 cps, $\Delta\nu_{inverted\ boat}$ = 2 cps (The present data does not permit accurate evaluation of $\Delta\nu_b$ and $\Delta\nu_{ib}$).

A possible explanation for the stability of the boat conformation of 3-carene may be rationalized as follows. In the inverted boat form the hydrogen atoms of 8-methyl will have a severe non-bonded interaction between bow and stern β-hydrogen atoms (at C_2 and C_5), the separation distance being 1.2 Å. The cyclopropane protons also are eclipsed with the α-hydrogens at C_2 and C_5, whereas in the boat form these interactions are absent.

In the partial boat conformation (V) of 2-carene the π-orbitals of the double bond make an angle of 15° with the electronic system lying in the plane of the cyclopropane ring. In the partial inverted boat form (VI) the corresponding angle is zero, thereby allowing the molecule to achieve maximum overlap. However, at the same time, in conformation (VI), the separation between the 8-methyl and the 3 β-H is only 0.2 Å, and this severe non-bonded interaction makes the conformation unfavorable.

In the epoxidation reaction it is believed that the conformational effects in the ground state are transmitted quantitatively to the transition state.[5] Since the top side of the molecule in 3-carene is shielded by the gem-dimethyl group, the approach of the reagent both in hydroboration[6] and epoxidation,[7,8] both of which involve cis addition with a cyclic transition state, should proceed from the bottom side of the molecule. In the transition state of both epoxidation and hydroboration of 3-carene, the 4-H and 10-methyl will tend to go above the plane of the double bond as the reagent approaches from the bottom side. In the boat form (II) there will be a severe interaction in the transition state between the 8-methyl, 4H and 10-methyl groups. These interactions are absent in the inverted boat form. In both conformations of 2-carene interactions will not be as severe as they are in this boat conformation of 3-carene. So, if the boat form is stable, 2-carene (IV) should hydroborate or epoxidise faster than 3-carene (I), whereas if the inverted boat form is more stable, 3-carene (I) should react faster. Experimentally 2-carene hydroborates and epoxidizes faster than 3-carene, thereby supporting our assignments.

That the increase in rate of hydroboration is not due to an increase in the nucleophilicity of the double bond in 2-carene is indicated by comparing the rate of hydroboration of styrene and allylbenzene. Here, the non-conjugated double bond of allylbenzene reacts faster.

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