## ON THE QUESTION OF BISHOMOANTIAROMATICITY IN THE 7-NORBORNENYL ANION

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It has been recently reported[1] that the 7-norbornenyl anion (I) may possess bishomoantiaromatic character. anti-7-Cyanonorbornene (II) exchanged deuterium at the 7 position 1.4 times faster than 7-cyanonorbornane (III) while 3-cyanocyclopentene exchanged 10 times faster than cyanocyclopentane. Reasoning that the 10-fold rate difference in the cyclopentene system represented normal inductive effects, it was postulated that the lower relative rate in the norbornenyl system may be due to bishomoantiaromatic destabilization of the 7-norbornenyl anion formed during exchange.
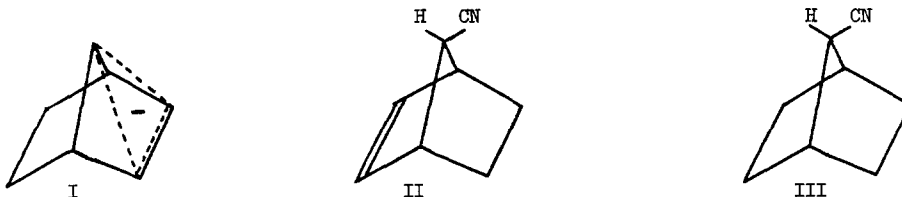
The indirect nature of this argument as well as the possibility of syn:anti isomerism led us to reinvestigate this question using the epimeric syn and anti-7-substituted norbornenes. Since bishomoantiaromatic interactions can only occur on the face syn to the double bond, there may be be a significant difference in the rates of exchange of syn and anti epimers.
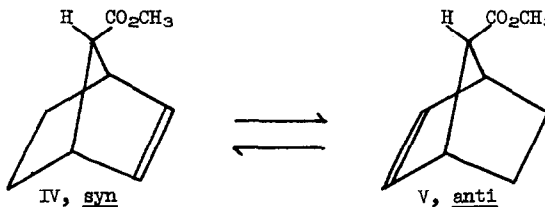
As models for strain and inductive effects, we have also measured the rate of isomerization of endo-5-carbomethoxynorbornene[3] (VI), endo-2-carbomethoxynorbornane (VIII), and cis-4-methyl carbomethoxycyclohexane (X). Rate data for exchange and isomerization, measured at 25° in 0.2 M NaOCH₃ in 10% (v:v) CH₃OD in hexamethylphosphoric triamide (HMPT), are summarized in Table 1.
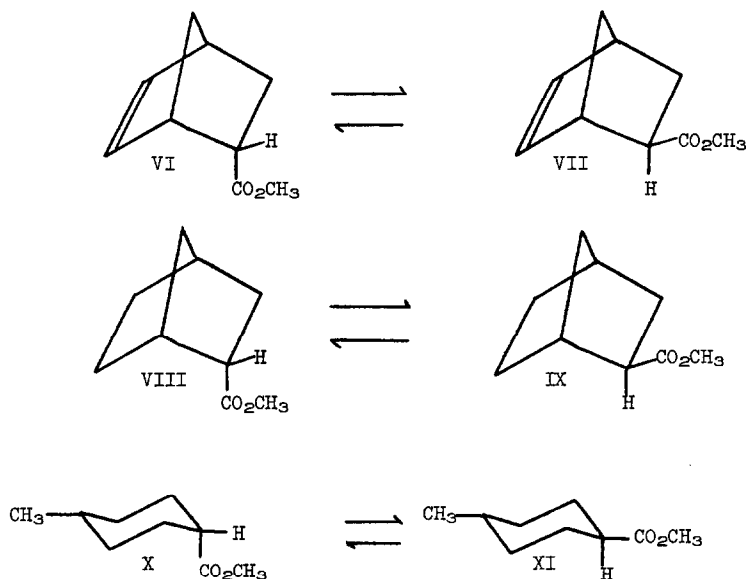
The data clearly show that there is very little difference in the rates of exchange or isomerization between IV and V, and thus no evidence for bishomoantiaromaticity.

TABLE I. RATES OF ISOMERIZATION AND EXCHANGE OF NORBORNENYL ESTERS

| Compound	k_2 iso x 10^4 $M^{-1}sec^{-1}$	k_2 ex x 10^4 $M^{-1}sec^{-1}$	K_{eq}[a]
IV	2.6 ± 0.1	5.0 ± 0.4	1.35
V	3.7 ± .05	6.2 ± 0.3	-
VI	69 ± 6.6	-	1.1
VII	62[b] ± 6	-	-
VIII	174 ± 4	-	-
IX	75[b] ± 1.7	-	2.3
X	651 ± 50	-	-
XI	176[b] ± 13	-	(3.7)[c]

a. K_{eq} is shown for the more stable isomer.
b. Rate calculated from rate constant of other isomer and equilibrium constant.
c. Equitorial/axial carbomethoxy by nmr.

Comparison of the rates of isomerization of VII and IX shows k_{VII}/k_{IX} = 0.83 indicating that

unsaturation effects are small in the norbornenyl system, and the observed[1] value of 1.4 for the 7-nitriles and 1.35 for the 7-esters probably reflects a combination of steric and inductive effects. Steric effects appear minor and readily understandable in terms of small rate accelerations due to relief of steric strain in the <u>endo</u> to <u>exo</u> isomerization of 2-carbomethoxynorbornane, but not in 2-carbomethoxynorbornene where the <u>endo</u> 5,6-H interactions are missing. Similar effects account for the rapid <u>cis</u> to <u>trans</u> isomerization of <u>cis</u>-4-methylcarbomethoxycyclohexane.

The ratios of the rates of isomerization and exchange of IV and V are ~2 and indicate that the reaction is proceeding via a "racemization" mechanism[4,5], in which an enolate (XII) is a probable intermediate. Enolate formation requires rehybridization of the α-carbon and angle compression effects at the reaction site would result in decreased π-overlap in the transition state leading to XII, and thus retard the rate of isomerization or exchange. Of several models for the
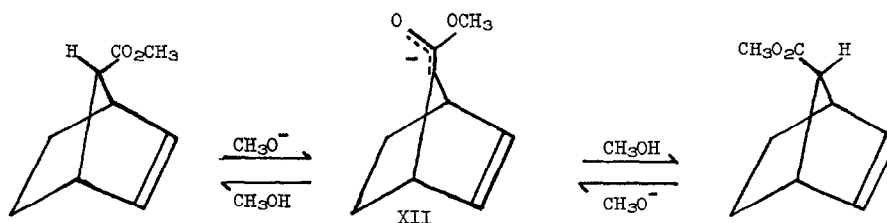
sp[3]-sp[2] rehybridization carbonyl stretching frequencies of ketones are the most readily available[6]. The rates measured in this work do correlate with carbonyl stretching frequency, and thus bond angle strain[7], as can be seen in Table II.

TABLE II. RATES OF ISOMERIZATION AT 25° <u>vs.</u> CARBONYL STRETCHING FREQUENCY

Compound	k_{iso} (rel)	C=O for ketone[5], cm^{-1}
IV	1	1780
V	1.4	
XIII	66	1750
IX	27	
VI	26	1745
VII	24	
X	251	1716
XI	46	

Since inductive and steric effects in these isomerizations are small, the dominant features appear to be best explained by a resistance to rehybridization induced by angle strain, without the need to consider bishomoantiaromatic destabilization.

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3. J Sauer and J. Kredel, Tetrahedron Lett., 731 (1966).

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5. In an isomerization reaction as opposed to a racemization, the K_{eq} need not be unity and limiting values for k_{ex}/k_{iso} for a limiting racemization reaction need not be two. Assuming a well-behaved reaction coordinate and Hammonds postulate it can be shown that the limiting value k_{ex}/k_{iso} for a racemization mechanism is $(1/K + 1)$. For the $A \rightarrow B$ isomerization with B as the more stable isomer, $K > 1$, and k_{ex}/k_{iso} for isomer A will then be less than the corresponding ratio for the other isomer.

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