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ALLYLIC HYDROGEN EXCHANGE IN THE TRICYCLO[3.3.1.0^{2,4}]NON-6-ENE AND TETRACYCLO[4.4.0.0^{2,4}.0^{3,7}]DEC-8-ENE RING SYSTEMS[1]

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Studies of the rate of allylic hydrogen-deuterium exchange (KOtBu, DMSO-d_6) of bicyclo [3.2.1]oct-2-ene (1) and bicyclo[3.2.1]octa-2,6-diene (2) ($k_2/k_1 = 3 \times 10^4$)[2] and analysis of the nmr spectrum of the stable anion obtained by cleavage of 8-OCH_3 with sodium-potassium alloy[3] have provided evidence supporting an aromatic 6π electron bishomocyclopentadienyl structure (5) for the anionic intermediate generated. Since cyclopropane rings substituted β to the leaving group, and of suitable geometry, are, in some cases, even more effective than olefinic linkages at delocalization of positive charge,[4] we felt it would be of considerable interest to study the base catalyzed allylic hydrogen-deuterium exchange reactions of tricyclo[3.3.1.0^{2,4}]non-6-ene (3) and tetracyclo[4.4.0.0^{2,4}.0^{3,7}]dec-8-ene (4) in order to determine if proton abstraction would generate homoaromatic anions with a trishomocyclopentadienyl structure of the type illustrated in 6. Prompted by the recent report on the related cationic system, which demonstrates that there is no significant interaction of cyclopropane with the transannular allylic system, 9-OPNB solvolyzes at one-third the rate of 7-OPNB,[5] in contrast to 8-OPNB, which solvolyzes 235 times more slowly than 7-OPNB,[6] we report our work at this time in order to provide complementary data on the remaining anionic intermediate of the set.


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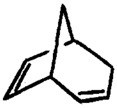
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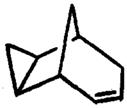
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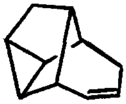
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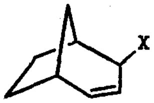
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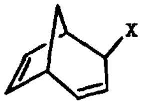
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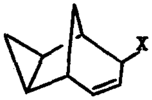
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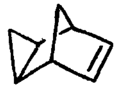
Addition of dibromocarbene to tricyclo[3.2.1.0^{2,4}]oct-6-ene (10) gave rearranged dibromide 11 in 37% yield (bp 78-80°, 0.1 mm). Reduction with $LiAlH_4$ yielded bromide 12 (40% yield bp 43-45°, 0.3 mm) and reaction with sodium in tetrahydrofuran-t-butyl alcohol produced alkene 3 (83 % yield), which was purified by preparative vpc before use. In a similar manner, addition of dibromocarbene to deltacyclene (13) gave a 36% yield of dibromide 14 (bp 99-102°, 0.15 mm). Subsequent reduction with $LiAlH_4$ yielded 47% of 15 (bp 73-75°, 0.24 mm), which was further reduced by reaction with sodium in tetrahydrofuran-t-butyl alcohol to 4 (76 % yield).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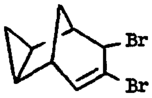

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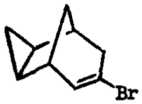

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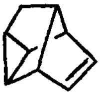
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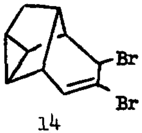

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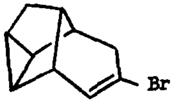

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The allylic hydrogen-deuterium exchange reactions were carried out in 0.90 M potassium t-butoxide in dimethylsulfoxide-d_6, following the disappearance of olefin by mass spectral analysis. The rate data obtained (Table I) demonstrate that there are no interactions of cyclopropane with the transannular allylic anion system derived from the parent hydrocarbons 3 or 4 to produce homoaromatic trishomocyclopentadienyl anions. This is reinforced by the fact that neutralization of the exchange reaction mixture (0.90 M potassium t-butoxide in dimethylsulfoxide at 155° for 15 hrs) produces only starting substrate 3 or 4. Thus, we find that the lack of interaction of cyclopropane with the allylic anionic systems in the intermediates derived from 3 and 4 is in harmony with the lack of interaction in the cationic system related to 3 and contrasts with the strong interaction of similarly positioned olefinic units in both cationic and anionic intermediates derived from 2.

Table I. Rates of Allylic Hydrogen Exchange in Dimethylsulfoxide-d_6 (0.90 M KOtBu) at 61°

alkene	$k(\sec^{-1})^{a}$	$k_{alkene}/k_{cyclohexene}$
2	1.6×10^{-3} [b] $(5.8 \times 10^{-3})^{c}$	1.6×10^{4}
cyclohexene	1.0×10^{-7} [b] $(6.7 \times 10^{-7})^{c}$	1.0
3	5×10^{-8} [d]	0.5
4	5×10^{-8} [d]	0.5

[a] From first order plots of d_o versus t.

[b] ± 20%

[c] Reference 2. Our values for 2 and cyclohexene are consistently lower than those of reference 2, but the ratio is in good agreement.

[d] ± 50%

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1. We express our appreciation for partial support of this work by a grant from the National Science Foundation.

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