

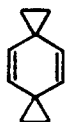
A TEST FOR CYCLIC CONJUGATION INVOLVING THE CYCLOPROPYL CARBINYL CATION

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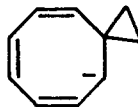
Cyclopropyl substitution strongly stabilizes carbonium ion centers, an interaction which has been intensively studied both experimentally¹ and theoretically². The interaction with carbanions^{3a} and double bonds^{3b} is much more limited. No significant spectral or chemical anomalies which could be the result of cyclic conjugation are apparent for 1^{4a} and a number of systems like it^{4b-d}, even though the ideal bisected geometry is ensured by the presence of spiro-fused cyclopropanes.^{3b} Two striking exceptions are compounds 2⁵ and 3⁶, both of which have strongly de-



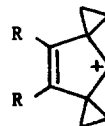
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3



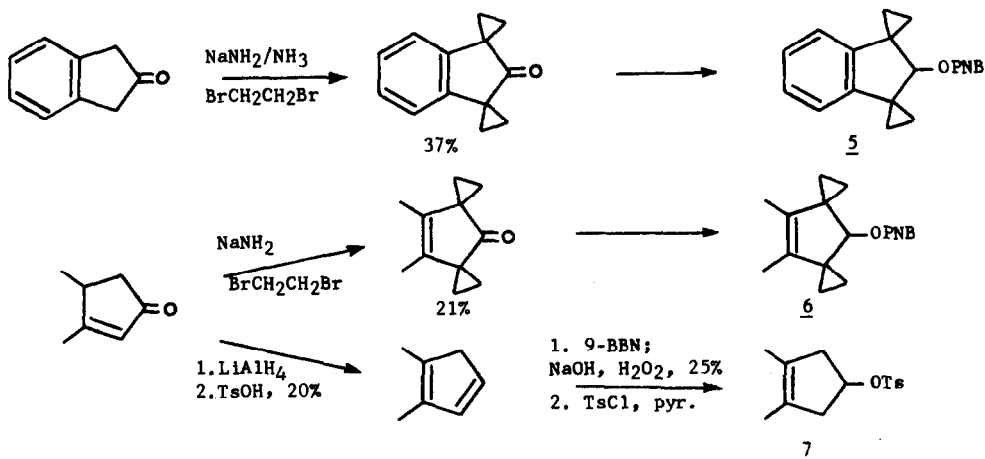
4 (a) R = benzo
(b) R = CH₃

shielded cyclopropane protons in the nmr spectrum, a phenomenon attributed to electron donation by cyclopropyl to the π -system. This observation suggests the intriguing possibility that a spiro-fused cyclopropane can act as a two-electron donor in a cyclic conjugated system.^{5,7} On this basis 1 is an eight-electron system, whereas 2 and 3 are six- and ten-electron potentially aromatic systems.

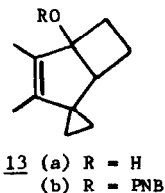
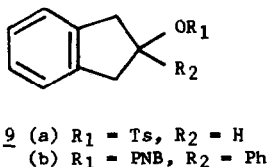
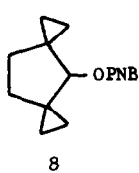
This paper describes experiments designed to test for cyclic conjugation involving interaction of a π -system with a bicyclic propylcarbinyl cation (4)⁸. Considered in terms of the above analysis, 4 could be anticipated to show unusual stability as a six-electron cation.

We have prepared the *p*-nitrobenzoates (PNB) 5 and 6, and the tosylate 7 as shown.⁹ The alkylation of 2-indanone and 3,4-dimethylcyclopent-2-enone^{10a} with dibromoethane was carried out using essentially the procedure of Newman, DeVries and Darlak.^{10b}

Table 1 lists the solvolysis rates of 5 and 6 in aqueous acetone, together with those of the model systems 7, 8,¹¹ 9a,¹² 9b, cyclopentyl tosylate (10)¹⁴, 1-phenylcyclopentyl *p*-nitroben-



zoate (11)¹⁵, and 1-phenylcyclopent-3-enyl *p*-nitrobenzoate (12).¹⁵ Compound 6 was studied in 90% acetone-water, since rates were too rapid to measure accurately in 80% acetone.



Compound 5 gave unrearranged alcohol as the major product (90%) together with traces of olefin. Compound 6, on the other hand, gave less than 5% unrearranged alcohol, the major products are the alcohol 13a (59%) and its *p*-nitrobenzoate 13b (23%). The structure of 13 was determined from its spectral¹⁶ and analytic data.

Table 1. Solvolysis Rates in Aqueous Acetone^{a,b} at 50° (kx10⁵)

	p-Nitrobenzoates						Tosylates			
	<u>5</u>	<u>6</u>	<u>8</u>	<u>9b</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>7</u>	<u>9a</u>	<u>10</u>
80% Acetone:	4.48		23.1	0.237	6.16 ^d	1.97 ^d		1.29	0.159	6.04
90% Acetone:		35.6	2.34 ^c				1.06			

a. Rates were determined titrimetrically, and are the average of at least two runs. b. Buffered with 1.1 eq of lutidine. c. Ref. 11. d. Ref. 15.

The solvolysis rates of 5 and 6 are 1/5.2 and 15.2 times that of the model system 8 in the appropriate solvent. Clearly no pronounced stabilization of 4 is indicated, a conclusion also

supported by the infrared carbonyl frequencies of the ketone precursors of 5 and 6, which are unchanged from that of the model system (ketone derived from 8, 1725 cm^{-1}).

A more detailed consideration of rate effects must take into consideration the rate retarding inductive effect of the benzo or olefin group. We have used as model systems the secondary tosylates 7, 9a and 10, and the tertiary *p*-nitrobenzoates 9b, 11 and 12 to evaluate inductive effects both in an unstabilized secondary cation and a highly stabilized benzyl cation. For the benzo system (5) the rate ratio of 9a/10 in 80% acetone is $1/38$,¹² whereas 9b/11 is $1/26$. Apparently the inductive effect does not vary markedly with carbonium ion stability, nor does solvent have a large influence.^{12,14} Applying this correction, a net acceleration of 5.0 to 7.3 can be attributed to cyclic conjugation in the transition state leading to 4a, which corresponds to 1.0-1.3 kcal/mol in free energy. Thus a real effect does seem to be present, but it is small compared to the cyclopropylcarbiny l stabilization itself.

The inductive correction for compound 6 is $1/4.7$ (rate ratio 7/10)^{14,17}, close to the factor of $1/3.1$ (rate ratio 12/11) found for the tertiary benzyl system lacking vinyl methyl substitution¹⁵ (both model systems were measured in 80% acetone). Application of the inductive correction leads to an acceleration of approximately 70 for 6. The larger effect compared to 5 is not unexpected since benzo should a priori be less capable of participating in cyclic conjugation than a double bond. However, the situation here is complicated by the observation that only rearranged products (13) are isolated.¹⁸ It is therefore conceivable that part of the acceleration is a consequence of participation during ionization. Roberts¹⁹ has shown that 1-phenylcyclopropylcarbiny l tosylate rearranges completely to 1-phenylcyclobutyl during solvolysis. The rate is only 1.02 times that of cyclopropylcarbiny l tosylate itself at 50° in 90% acetone. The phenyl substituted compound thus is anchimerically accelerated by no more than the normal phenyl inductive effect (5-10)²⁰.

The small magnitude of the stabilization detected for 4 by these solvolytic rate studies is consistent with other data on related systems. An electron diffraction study of 2 revealed no structural effects attributable to conjugative interaction between diene and cyclopropyl.²¹ The work of Semmelhack et al.²² indicates the absence of any large stabilizing effect in the spiro-[2.3]hexenyl anion (also a potential six-electron system), although adequate models are not available.

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