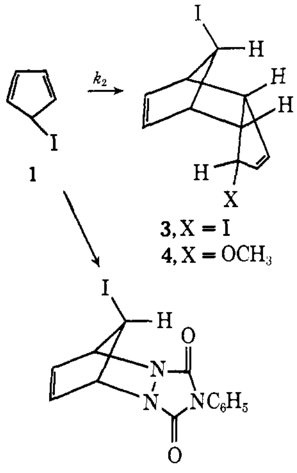
Communications to the Editor

Antiaromaticity in the Parent Cyclopentadienyl Cation. Reaction of 5-Iodocyclopentadiene with Silver Ion

Sir:

Although various derivatives of cyclopentadienyl cation have been prepared,[1] there is as yet no evidence about the properties of the parent cation, $C_5H_5^+$. The difficulty is in part due to the unavailability of suitable 5-substituted precursor cyclopentadienes. Such compounds tautomerize readily[2] to more stable vinyl-substituted cyclopentadienes, and substituents on position 5 of cyclopentadiene which carry unshared pairs increase the reactivity of the molecule in cycloaddition and dimerization reactions.[3] We now wish to report that it is possible to prepare a simple suitable precursor for the cyclopentadienyl cation, 5-iodocyclopentadiene (**1**). Attempted silver-assisted solvolysis of this compound reveals a striking unreactivity of the doubly allylic halogen, inconsistent with simple expectations but consistent with the proposition that cyclopentadienyl cation is antiaromatic (resonance destabilized).



1

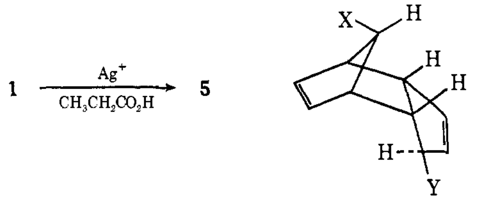
3, X = I

4, X = OCH_3

2

Solutions of **1** were prepared by slow addition of I_2 in CS_2 or CH_2Cl_2 to a suspension of a slight excess of thallium cyclopentadienide[4] at 0°, followed by filtration of the precipitated thallous iodide. Addition of *N*-phenyl-1,2,4-triazoline-3,5-dione to this solution afforded a 90% yield of adduct **2**.[5] In the nmr, **1** at 0° shows one proton at δ 5.54 and four protons at 6.54. On warming, **1** dimerized to **3**, and showed no tendency to tautomerize to any isomers of **1**. At $-15°$, the dimerization rate constant k_2 is 1.7×10^{-5} M^{-1} sec^{-1}; with an initial concentration of 2 M, 50% of **1** disappears in 8.5 hr. The structure of **3** is indicated by its nmr spectrum, with broad one-proton resonances at δ 3.85 and 4.46 for the 1-β proton and 8-anti proton, respectively. The Δ^5 hydrogens appear at δ 5.97 and the Δ^2 hydrogens appear as an AB quartet centered at δ 5.70 (J = 5.5 Hz). The other protons appear in the complex multiplets between δ 2.86 and 3.78. Although **3** is too reactive for easy isolation and purification, it is converted in methanol to the methoxy compound **4**,[5] which is easily handled.

In an attempt to generate the parent cyclopentadienyl cation as a solvolytic intermediate we have treated **1** with silver perchlorate in propionic acid at $-15°$. The product of this reaction is the dimeric propionate **5**, whose structure was confirmed by an unambiguous synthesis from the known[6] 8-*syn*-hydroxydicyclopentadiene (**6**). Thus, propionate **7**[5] was treated with selenium dioxide to give the hydroxypropionate **8**[5] which was esterified to give **5**, identical in all respects with the solvolysis product.



5, X = Y = $O_2CCH_2CH_3$

6, X = OH; Y = H

7, X = $O_2CCH_2CH_3$; Y = H

8, X = $O_2CCH_2CH_3$; Y = OH

Although **5** could have resulted from dimerization of a cyclopentadienyl propionate, the expected product of a silver-assisted solvolysis of **1**, rate studies show that a different mechanism is operating. The disappearance of **1** follows kinetics which are first order in [Ag^+] but second order in [**1**], k_3 = 1.2 sec^{-1} M^{-2}. (The only reproducible and reliable means of following this reaction involved quenching of the reaction mixture and treatment with *N*-phenyltriazolinedione to produce adduct **2**, which could be quantitatively estimated.) These results indicate that a complex of **1** with silver ion is reversibly formed and that the small amount of such a complex at equilibrium (saturation kinetics were not observed) reacts with another mole of **1** to produce a dimer. While the structure of this dimer cannot be established from these data it may well be dimer **3**, since under the solvolysis conditions **3** is rapidly converted to **5**. The mechanism of this conversion, more complicated than it appears at first sight, is the subject of the accompanying communication.[7]

It is apparent that the unobserved silver-assisted ionization of **1** to the cyclopentadienyl cation must be slower than the dimerization process we have just described. In order to put this into context, we have also examined the silver-assisted solvolysis of cyclo-

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[1] *E.g.*, R. Breslow, H. W. Chang, and W. A. Yager, *J. Amer. Chem. Soc.*, **85**, 2033 (1963); R. Breslow, R. Hill, and E. Wasserman, *ibid.*, **86**, 5349 (1964).

[2] V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

[3] H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967).

[4] E. J. Corey, U. Koelliker, and J. Neuffer, *ibid.*, **93**, 1489 (1971).

[5] Mass and nmr spectra were consistent with the assigned structure. In particular, nmr spectra of compounds **3–8** were uniquely interpretable in terms of both structure and stereochemistry, and could be distinguished from the nmr spectra of some authentically synthesized stereoisomers in this series.

[6] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[7] R. Breslow and J. M. Hoffman, *J. Amer. Chem. Soc.*, **94**, 2111 (1972).

pentyl iodide (**9**). In propionic acid at −15° with silver perchlorate, **9** solvolyzes with good second-order kinetics, first order in each component, k_2 = 59 sec^{-1} M^{-1}. The kinetics were followed by quenching and vpc assay, and the principal product was cyclopentyl propionate. (This rate was unaffected by the addition of **1**, confirming that the silver ion is not appreciably complexed by **1**.) The silver-assisted solvolysis of **9** in such a weakly nucleophilic solvent almost certainly goes through the cyclopentyl cation, and from the ratio of this second-order rate to the third-order rate for **1** at the 10^{-2} M concentrations used this solvolysis is at least 10^4 faster than the undetectable simple solvolysis of **1**. The limit can be expanded further, by following the disappearance of the chromophore of **1** at 285 nm, starting with a 6 × 10^{-4} M solution of **1** with 10^{-2} M $AgClO_4$. Even at this concentration the same third-order process involving dimerization of **1** was the only process detectable, so that the second-order ionization of **1** to its cation is not competitive in rate. This indicates that the simple silver-assisted ionization of **1** to its cation is at least 10^5 slower than the silver-assisted ionization of the saturated analog **9**.

The observation that a doubly allylic iodide such as **1** is inert to silver-assisted ionization compared with a saturated analog is of course contrary to simple classical expectations. Although **9** and **1** differ in conformational and inductive effects also, it seems an inescapable conclusion that the conjugation of a carbonium ion with two double bonds in the cyclopentadienyl cations has a net destabilizing effect on the carbonium ion. Thus, the cyclopentadienyl cation exhibits conjugative destabilization, and is antiaromatic.[8]

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[8] R. Breslow, *Chem. Eng. News*, 90 (June 28, 1965).

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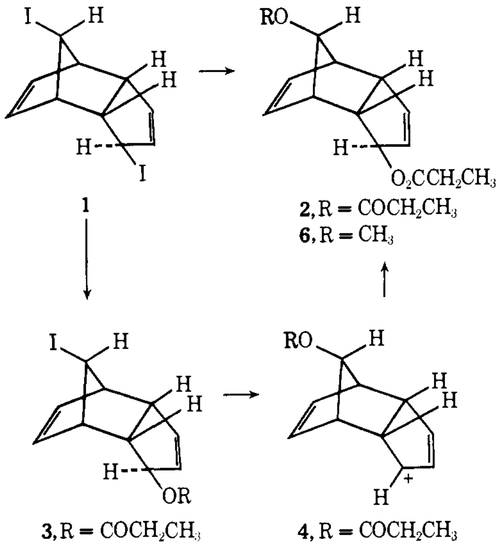
Solvolytic Cope Rearrangements

Sir:

In the preceding communication[1] we have reported a solvolytic study in which a dimer of cyclopentadienyl iodide (**1**) afforded a dimer of cyclopentadienyl propionate (**2**) on treatment with silver ion in propionic acid. Although at first sight this process may not seem remarkable, it was not expected that a *syn*-norbornenyl derivative would solvolyze with retention of configuration. Winstein[2] has solvolyzed simple *syn*-norbornenyl tosylate and finds that the exclusive product is a bicyclo[3.2.0]heptenol from migration of a methylene carbon trans to the leaving group. Various explanations could be advanced for the apparent retention of stereochemistry in the solvolysis of **1**, but a simple possibility is that **1** is actually undergoing a Cope rearrangement during its conversion to **2**. **1** would solvolyze rapidly to **3**, and if this underwent a Cope rearrangement on ionization of the 8-iodide the product would be the allylic cation **4**. This would then yield **2**.



1

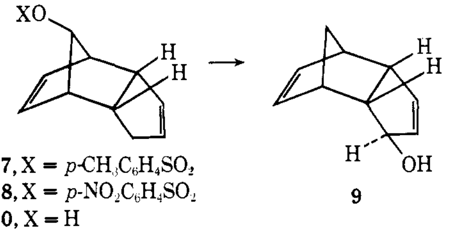
2, R = $COCH_2CH_3$
6, R = CH_3

3, R = $COCH_2CH_3$
5, R = CH_3

4, R = $COCH_2CH_3$

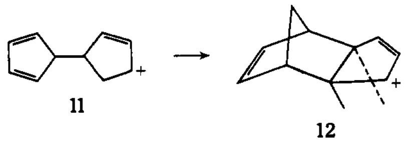
Our studies indicate that this is actually the mechanism involved. Thus, **1** undergoes methanolysis to **5**, as we have described;[1] when **5** is solvolyzed with silver ion in propionic acid it is converted to **6**, a compound in which the methoxyl group is now on the bridging carbon and the iodine has been replaced with rearrangement. The structure of **6** follows from the mass and nmr spectra. In particular, the C-1 proton is at δ 4.98, and the C-8 proton is at 3.52. This type of rearrangement is not restricted only to compounds **3** and **5**, since we find that tosylate **7** and nosylate **8** solvolyze at 95° in 2:1 dioxane–water containing 0.1 N $NaHCO_3$ to yield the (known[3]) rearranged alcohol **9**.

In principle, this conversion of **7** and **8** to **9** could involve Cope rearrangement of **7** or **8** followed by rapid solvolysis of the resulting allylic sulfonates related to **9**, but this is highly unlikely. The 8-syn alcohol **10**[3] rearranges to **9** only at considerably higher temperatures. Also, at 95° the solvolysis rate constant k_1 for **7** is 1.2 × 10^{-5} sec^{-1}, while the rate constant k_1 for compound **8** is 3.0 × 10^{-4} sec^{-1}; the nosylate reacts 25 times as fast as the tosylate, a rate enhancement typical of that reported[4] for solvolytic reactions. It is



7, X = p-$CH_3C_6H_4SO_2$
8, X = p-$NO_2C_6H_4SO_2$
10, X = H

9



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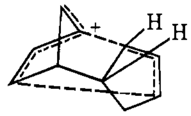
12



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[1] R. Breslow and J. M. Hoffman, *J. Amer. Chem. Soc.*, 94, 2110 (1972).

[2] S. Winstein and E. T. Stafford, *ibid.*, 79, 505 (1957).

[3] R. B. Woodward and T. J. Katz, *Tetrahedron*, 5, 70 (1959).