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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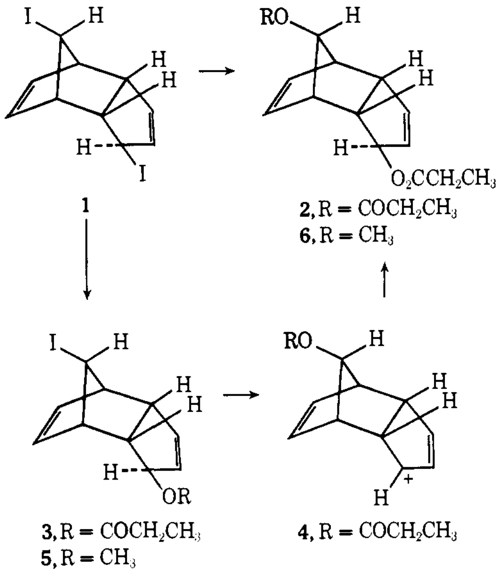
Solvolytic Cope Rearrangements

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

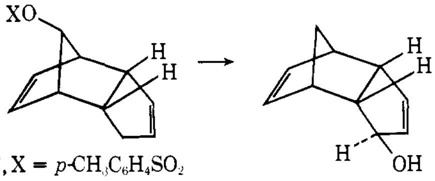
2, R = $COCH_2CH_3$
6, R = CH_3

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

4, R = $COCH_2CH_3$

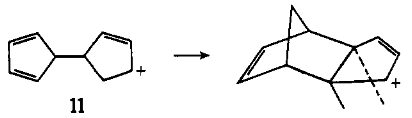
Our studies indicate that this is actually the mechanism involved. Thus, **1** undergoes methanolysis to **5**, as we have described;[1] when **5** is solvolyzed with silver ion in propionic acid it is converted to **6**, a compound in which the methoxyl group is now on the bridging carbon and the iodine 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



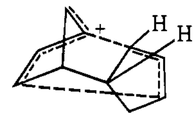
7, X = p-$CH_3C_6H_4SO_2$
8, X = p-$NO_2C_6H_4SO_2$
10, X = H

9



11

12



13

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thus apparent that the rate-limiting step involves loss of the sulfonate group, which would not be observed if there were rate-limiting Cope rearrangements to a highly reactive allylic sulfonate ester. Furthermore, the silver-assisted rearrangement of **3** or **5** occurs rapidly at −15°, while Cope rearrangement of **10** is rapid only above 140°.

The most attractive mechanism consistent with these data is that **3**, **5**, **7**, or **8** ionizes to carbonium ions in which Cope rearrangement to ions like **4** is then extremely rapid. An alternative path for the overall rearrangement involves solvolytic fragmentation of **3**, **5**, **7**, or **8** to an allylic cyclopentenyl cation bonded to a cyclopentadiene (**11**). Such a cation could then cyclize again to a cation like **4**. The major argument against this mechanism is that **11** could also have cyclized to **12**, the less-hindered exo isomer, and no product derived from this is detected in any of our solvolytic studies. If some special overlap is invoked in the cyclization of **11** to favor endo closing, the bonding (**13**) for the cyclization transition state would be similar to that in the Cope rearrangement transition state. Some slight participation of the double bond in the solvolyses is indicated by our finding that the solvolysis rate of nosylate **8** is 1.5 times the rate for its 2,3-dihydro analog; this would be consistent with either the fragmentation or the Cope rearrangement mechanism.

Although this is the first example of an apparent solvolytic Cope rearrangement, studies[3,5,6] on 8-ketones related to **10** indicate that they undergo relatively rapid Cope rearrangements and that these rearrangements are facilitated by protonation of the carbonyl oxygen. It is not surprising that these processes are facilitated by a conjugating carbonium ion as a substituent on a Cope rearrangement system: the six delocalized electrons of the Cope transition state can conjugate with the external carbonium ion much as the six electrons of a benzene ring stabilize (and *ipso facto* are stabilized by) the positive carbon in a benzylic cation. An alternate description is that the carbonium ion formed begins to fragment toward a structure like that of **11**, but the new bond then begins to form before the fragmentation is complete.

Acknowledgment. Support by the National Institutes of Health is gratefully acknowledged.

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Rapid Reaction of Representative Olefins with Monochloroborane Diethyl Etherate. A Simple, Convenient Synthesis of Dialkylchloroboranes and Dialkylborinic Acid Derivatives

Sir:

Monochloroborane diethyl etherate, conveniently prepared by the reaction of boron trichloride diethyl etherate with lithium borohydride in diethyl ether, readily hydroborates a variety of olefins at 0° to give the corresponding dialkylchloroboranes in excellent yields. The dialkylchloroboranes thus formed are easily isolated as such by distillation under reduced pressure. Alternately, they are readily converted into borinic acid esters *in situ* by treatment with alcohols. This provides a very simple and convenient general synthesis of dialkylchloroboranes and its derivatives *via* hydroboration.

The redistribution of trialkylboranes with boron trichloride and boric acid esters, generally at elevated temperatures, provides the basis for the methods generally used in the past for the synthesis of dialkylchloroboranes and dialkylborinic acid esters, respectively.[1,2] Unfortunately, these methods are often difficult to apply, especially for the synthesis of relatively large amounts required as synthetic intermediates. Recent developments[3–6] in our laboratory have established that these compounds are exceptionally valuable synthetic intermediates. Consequently, we sought a convenient synthesis of dialkylchloroboranes and dialkylborinates. Since hydroboration of olefins with BH_3 etherates provides an exceptionally simple synthesis of trialkylboranes,[7] it appeared that hydroboration by monochloroborane etherates[8] might provide an analogous simple route to dialkylchloroboranes.

Actually, studies of the hydroboration of olefins by monochloroborane, BH_2Cl, have already been reported.[9–11] These studies utilized BH_2Cl in tetrahydrofuran. In this solvent the reaction of olefins with BH_2Cl is very slow and incomplete. We undertook to overcome this difficulty by increasing the concentrations of the reactants and the reaction temperature. The reaction rates were greatly improved. However, analysis of the reaction products revealed that the reactions were not proceeding to the formation of the desired R_2BCl products, as had been assumed previously.[9]

For example, from 4 *M* 1-butene and 2 *M* BH_2Cl in THF at 0° (6 hr) there was obtained 35% *n*-Bu_3B, 20% *n*-Bu_2BCl, and 45% *n*-$BuBCl_2$. Similarly, at 25° (12 hr) 2 *M* 1-butene and 1 *M* BH_2Cl in THF yielded a product which analyzed for 60% *n*-Bu_3B, 10% *n*-Bu_2BCl, and 30% *n*-$BuBCl_2$. Under the same conditions *cis*-2-butene yielded 62% *sec*-Bu_3B, 1% *sec*-Bu_2BCl, and 37% *sec*-$BuBCl_2$.[12]

It occurred to us that the reason for this very low reactivity of BH_2Cl in THF could be the strong complexation of the reagent with the highly basic THF, rendering the boron atom much less reactive toward the olefin. The rate and relatively long reaction times could also be responsible for the observed complexity of the prod-

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