the axial and equatorial alcohols resulting from the $LiAlH_4$ reduction. The infrared spectrum showed hydroxyl stretching but no carbonyl stretching. Since both the coprostan-4α-ol and the coprostan-4β-ol would yield the same ketone, coprostan-4-one, upon oxidation, the alcohol mixture was not separated or purified any further.

The crude alcohol mixture (1.4 g, 3.2 mmol) was dissolved in 300 ml of acetone and oxidized at 19-21° by adding 1.6 ml of 8 *N* chromic acid reagent dropwise during 45 min. The solution was allowed to stand for 3 hr, and then was poured into water. The precipitate was collected and taken up in $CHCl_3$. The chloroform layer was washed and dried, and the solvent was evaporated *in vacuo*. The product was recrystallized from acetone, yield of 1.2 g, mp and mmp with authentic sample (mp 108°) 106°.

**Equilibration of the Ketones.** Standard solutions of the ketones were prepared by use of a Mettler H20 T balance and calibrated graduated flasks. Solutions were kept in a thermostat at 25° throughout. The ORD curves for the pure ketones were recorded for solutions in 95% ethanol (previously distilled off NaOEt to remove traces of aldehydes), in a jacketed 1-cm quartz cell at 26.3-26.4°. Solutions of the ketones were made up in the same way, except that 0.1 *M* KOH in ethanol or about 0.1 *M* HCl in ethanol were used instead of ethanol. Equilibrations were allowed to proceed at 25° under nitrogen. Concentrations were chosen to give the greatest possible amplitude on the recording chart on the 1° scale (about 60 mg in 10 ml for 5α-cholestan-4-one; about 20-30 mg in 10 ml for the less soluble 5β-cholestan-4-one). ORD curves were measured for the equilibrating solution after 3 hr for the base-catalyzed equilibrations, and after 7 days for the acid-catalyzed equilibrations. The amplitude of the Cotton effect and the magnitude of the rotation at 267 and 307.5 nm was recorded in each case, and the percentage of 5β-cholestan-4-one in the equilibrium mixture was calculated in the usual manner.[24]

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(2) This work was supported in part by Grant No. AM-14042 from the National Institutes of Health, and was taken in part from the Ph.D. dissertation of G. L. Wang, Wayne State University, 1968. Inquiries should be directed to the University of Georgia.
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(42) The ORD machine was equilibrated at 26.3-26.4°. This temperature difference would give a change of about 0.1% in the mole fraction of 5α-cholestan-4-one at equilibrium, which is small compared to other variations in the data.
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# Chemistry of Some Tricyclic Cyclopropyl Halides

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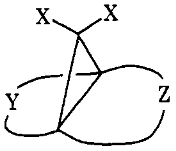
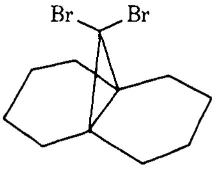
The silver ion assisted methanolysis of **2**, **3**, and **4** has been studied. Both rates and products are reported. Comments are made as to the effect of neighboring sites of unsaturation on relative reactivities. The effect of complexed silver ion on reactivity is also discussed.

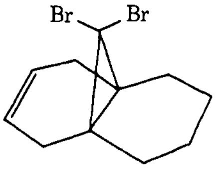
The chemistry of cyclopropyl systems of the general type **1** has been the subject of several recent studies.[2-7] Herein we report on the chemistry of systems of this type, namely, the silver ion assisted solvolysis of **2**, **3**, and **4**. Our immediate goal was to ascertain the reaction pathways available to systems in which the normal disrotatory mode of ring opening is apparently prohibited under solvolytic conditions. We were also interested in the role played by neighboring sites of unsaturation, as well as the effect of complexed silver ion on the rate of solvolysis of 3 and 4.



1



2



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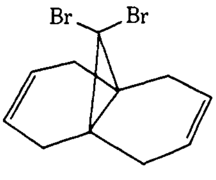
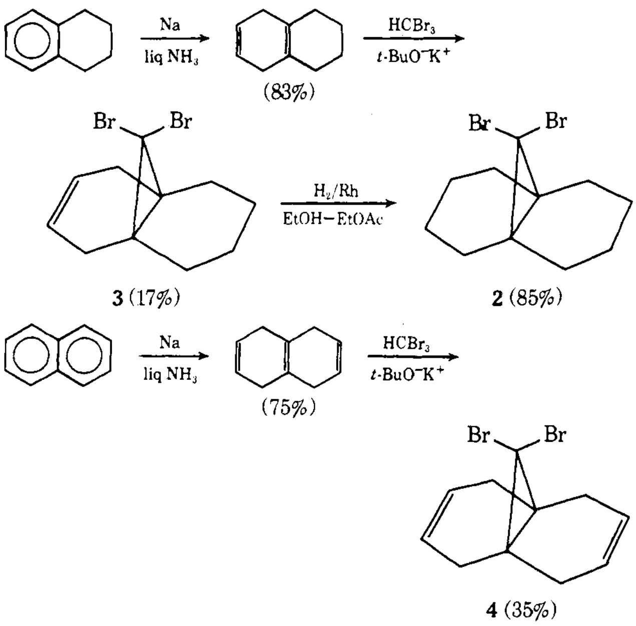


4

## Results

Synthesis of the compounds required for this investigation is outlined in Scheme I. Although the overall yield of 2 is only 12%, our method of synthesis is much less arduous than previously published procedures.[8,9]

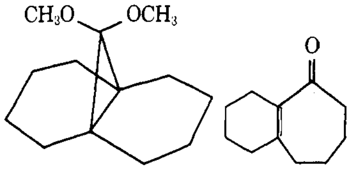
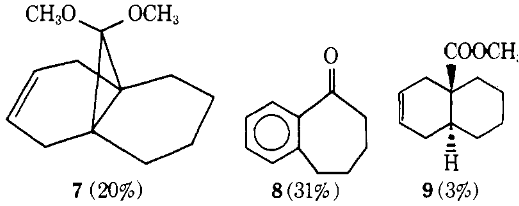
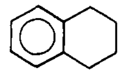
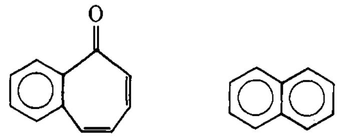
Scheme I



Product studies were carried out by reacting the compound in question with an excess of silver ion ($AgNO_3$) in methanol until all starting material had been consumed. An internal standard was added and the reaction mixture was analyzed *via* gas chromatography. The results obtained are contained in Table I.

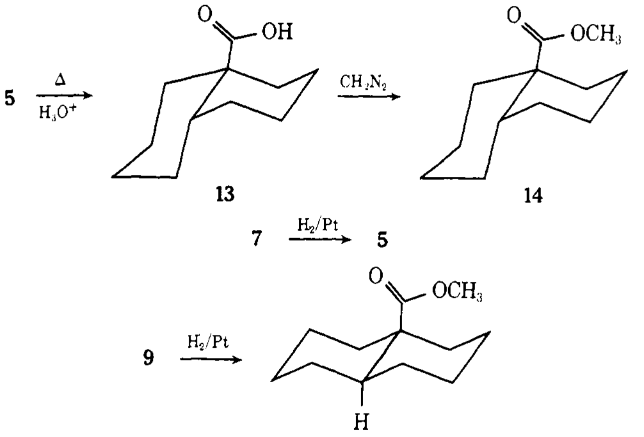
Compounds 8, 10, 11, and 12 were identified by comparison of their ir spectra with those of authentic materials.[11] The structure of 6 was assigned on the basis of spectral data and a correct elemental analysis.[6] Structures 5, 7, and 9 were assigned on the basis of the various chemical conversions outlined in Scheme II as well as spectral evidence.[12a] The infrared spectra of both 14 and 15 are identical with those of authentic materials.[12b]

**Table I**
**Products Obtained in the Silver Ion Assisted Solvolysis of 2, 3, and 4**

| Compd | Products |
|---|---|
| 2 |  5 (22%) 6 (43%) + others (~10%)[a] |
| 3 |  7 (20%) 8 (31%) 9 (3%)<br> 10 (7%) |
| 4 |  11 (2–5%) 12 (2–5%) |

[a] While these products were not rigorously identified, it is believed that they consist of a mixture of 14 and 15. This is based solely on infrared evidence.

Scheme II



15

Rate studies were carried out in 95% methanol using approximately a 20-fold excess of silver ion ($AgClO_4$). The standard ampoule technique was employed to determine pseudo-first-order rate constants ($k_1$) which were then converted to second-order rate constants ($k_2$) by dividing $k_1$ by the initial silver ion concentration. The results are contained in Table II.

## Discussion

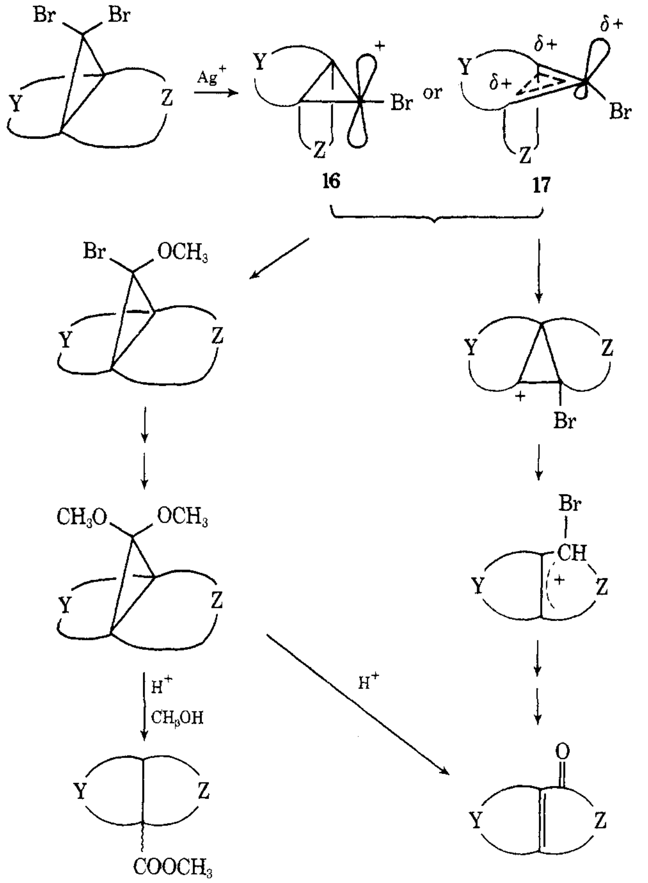
The majority of products obtained in this investigation can be rationalized as arising from a cyclopropyl cation (16) or a partially opened species (17)[13] (see Scheme III).

**Table II**
**Rate Constants and Activation Parameters of the Silver Ion Assisted Solvolysis of 2, 3, and 4**

| Compd | Temp, °C$^b$ | $k$, l. mol$^{-1}$ min$^{-1}$ | $\Delta H^*$, kcal mol$^{-1}$ | $\Delta S^*$, eu | $k^{25°}$ (rel) |
|---|---|---|---|---|---|
| **4** | 90.8 | $5.03 \times 10^{-3}$ (±0.01) | 30.3 | 5.7 | 1 |
| | 100.6 | $1.54 \times 10^{-2}$ (±0.01) | | | |
| | 25.0 | $4.18 \times 10^{-7\,a}$ | | | |
| **3** | 28.3 | $4.09 \times 10^{-2}$ (±0.18) | 18.0 | −13.2 | $7 \times 10^4$ |
| | 42.7 | $1.69 \times 10^{-1}$ (±0.05) | | | |
| | 25.0 | $2.90 \times 10^{-2\,a}$ | | | |
| **2** | 11.00 | $3.68 \times 10^{-1}$ (±0.09) | 12.9 | −23.3 | $3 \times 10^6$ |
| | 22.6 | $9.33 \times 10^{-1}$ (±0.12) | | | |
| | 25.0 | $1.12^a$ | | | |

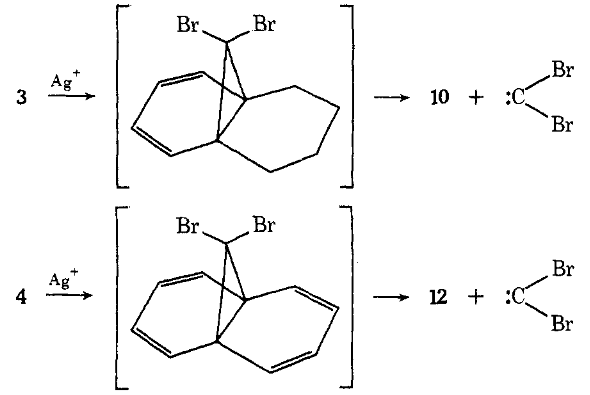
[a] This is an extrapolated value. [b] At least two runs were made at each temperature.

Scheme III

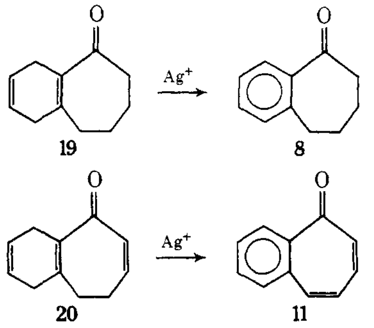


The origin of the aromatic compounds **10** and **12** finds precedence in the experiments reported by Vogel.[14] A possible mode of formation is outlined in Scheme IV.

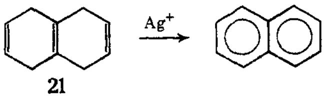
Scheme IV



It is surmised that **8** and **11** arise from a silver ion oxidation of **19** and **20**, respectively.

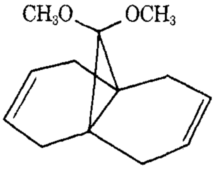


Calculations indicate that in the gas phase these reactions are thermodynamically feasible.[15,16] In addition we have also demonstrated that silver ion and a trace of nitric acid in either methanol or diglyme quantitatively converts triene **21** to naphthalene (eq 1).



(1)

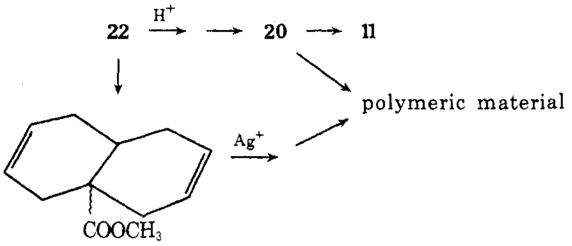
It is puzzling, at first glance, as to why such low yields of volatile products are obtained when **4** is solvolyzed. One must also offer an explanation for the absence of ketal **22**



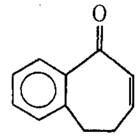
**22**

as a reaction product. While **2** and **3** are quite reactive at room temperature, **4** requires a temperature of ~100° for an extended period of time in order to react completely. We suggest that under these conditions (acid is produced as the reaction proceeds) **22** is unstable. Several reaction pathways available to **22** are illustrated in Scheme V.

Scheme V

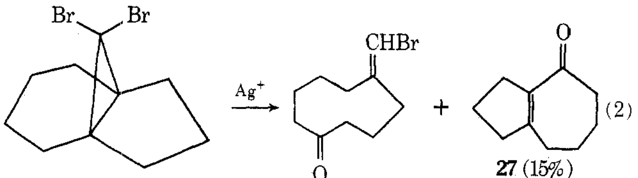


Buchanan has demonstrated that the ketone **23** is unstable at room temperature and rapidly polymerizes.[17] Thus if **23** is an intermediate in the formation of **11**, and **22** is unstable to the reaction conditions, one can readily explain the low yields of volatile material, as well as the absence of ketal **22**.

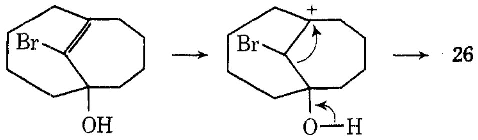


**23**

Recently, Reese reported on the silver ion assisted solvolysis of 10,10-dibromotricyclo[4.3.1.0$^{1,6}$]decane (**25**)[4] (see eq 2). The major product, **26**, can be explained as resulting from fragmentation of the protonated intermediate **29**.[18] No products of this type were obtained in the solvolysis of **2**, **3**, or **4**. This can be readily rationalized if one peruses the heats of reaction for the conversions contained in Table III.[19] As pointed out by Warner, the feasibility or net exothermicity of the conversion of a tricyclic cyclopropyl system to a bicyclic bridgehead olefin *via* a disrotatory ring opening depends on the magnitude of the strain energy inherent in the olefinic system in question as well as the exothermicity of the conversion listed in Table III.[3] For example, Warner calculates a strain energy of approximately 20 kcal in **31**. However, the exothermicity calculated in eq 4 is 29 kcal. Thus a net exothermicity of 9-10 kcal is calculated for the conversion of **30** to **31**.

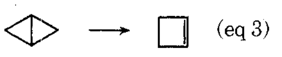
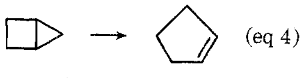
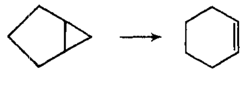
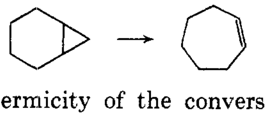


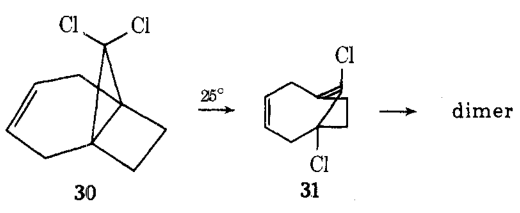
**25** **26** (50%) **27** (15%)



**28** **29**

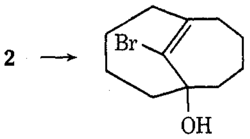
**Table III**
**Calculated Heats of Reaction for the Conversion of Several Bicyclic Systems to the Corresponding Monocyclic Olefin**

| Reaction | $\Delta H$, kcal mol$^{-1}$ |
|---|---|
|  (eq 3) | −14.50 |
|  (eq 4) | −29.10 |
|  | −10.10 |
|  | −2.20 |



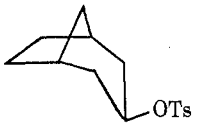
**30** **31**

Using a similar treatment one calculates the conversion of **25** to **28** to be endothermic by 9-10 kcal and the conversion of **2** to **32** to require an activation energy of approximately 20 kcal/mol$^{-1}$.[20a] Compounds **2**, **3**, and **4** therefore do not undergo reactions similar to **25** since lower energy reaction pathways are available.

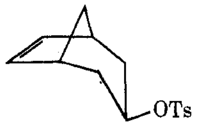


**32**

It now remains to explain the differences in relative rates observed in the solvolysis of **2**, **3**, and **4**. Le Bel has reported on the solvolytic behavior of the bicyclic tosylates **33** and **34**.[20b] It was found that **33** was three times more reactive than **34** at 25°. This corresponds to a difference in $\Delta G^*$ of 0.65 kcal/mol$^{-1}$. This difference can be ascribed solely to an inductive effect. The disposition of the double bond in **34** in relation to the leaving groups is similar to that found in **3**. However, the difference in $\Delta G^*$ between **2** and **3** is 2.10 kcal/mol$^{-1}$. The difference between these values [(2.10-0.65) = 1.45 kcal/mol$^{-1}$] is then a measure either of distabilization of the transition state in the ionization of **3** due to complexing of silver ion with the site of unsaturation[21] or relief of steric strain in the transition state in the ionization of **2** or some combination of these two factors. If the effect is completely inductive, then one would predict a difference in $\Delta G^*$ between **3** and **4** of 4.2 kcal/mol$^{-1}$ (*e.g.*, 2 × 2.1 kcal/mol$^{-1}$). This differs from the observed value by 2.4 kcal, a factor of ~60 in rate.[24]



**33**



**34**

If, on the other hand, the difference in rate was due to relief of steric strain plus the normal inductive effect of two uncomplexed double bonds, one calculates a difference in $\Delta G^*$ between **3** and **4** of 2.75 kcal/mol$^{-1}$ [1.45 + (2)(0.65)] which differs from the observed value by 3.9 kcal/mol$^{-1}$, a factor of ~750 in rate. The former explanation thus seems more palatable. Perhaps the deviation between the observed and calculated rates for **4** (a factor of 20-60) is a result of the conformation of the system which allows for a more stable silver-olefin complex and more efficient electron withdrawal by silver ion.

It should also be noted that rate and product studies indicate no participation by double bond in either **3** or **4**.

## Experimental Section[25]

**1,2,3,4,5,8-Hexahydronaphthalene.** The procedure of Hückel and Worffel was employed with the exception that the reaction was carried out at −33°.[26] A yield of 67 g (83%) of material was obtained. An nmr spectrum of the product exhibited absorption at 5.45 (singlet, 2 protons), 2.40 (singlet, 4 protons), and 1.22-2.05 ppm (multiplet, 8 protons).

**11,11-Dibromotricyclo[4.4.1.0$^{1,6}$]undec-3-ene (3).** Compound **3** was synthesized according to previously published procedures.[10] It was obtained in a 17% yield. Its properties were identical with those reported.[10]

**1,4,5,8-Tetrahydronaphthalene.** The material was prepared in a 75% yield according to the method of Hückel and Schlee, mp 53-55° (lit. mp 53°).[27] An nmr spectrum of the compound exhibited absorption at 5.54 (singlet, 4 protons) and 2.44 ppm (singlet, 8 protons).

**11,11-Dibromotricyclo[4.4.1.0$^{1,6}$]undecane (2).** Compound **3** was reduced catalytically at atmospheric pressure [hydrogen, 5% rhodium on alumina, ethyl acetate-ethanol (1:1)] to afford **2** in an 85% yield. Its properties were identical with those previously reported.[6]

**Silver Ion Assisted Methanolysis of 3.** Compound **3** (1 g, 3.26 mmol) and silver nitrate (2 g, 12.5 mmol) were dissolved in 100 ml of methanol and refluxed for 2 hr. The reaction mixture was filtered to remove silver bromide, and water (150 ml) was added to the filtrate. The aqueous layer was extracted with 3 × 25 ml portions of pentane. The pentane extracts were combined and dried, and solvent was removed to afford 0.85 g of a yellow oil which was subjected to vpc analysis on a 2 ft × 0.25 in. 5% Carbowax 20M column. Four major components (**7**–**10**) were shown to be present. They were all collected. Both compounds **10** and **8** were identified by comparison of their infrared and nmr spectra with spectra of authentic materials. An nmr spectrum of compound **7** exhibited absorption at 0.90–2.56 (complex absorption, 12 protons), 3.17 and 3.24 (two singlets, 6 protons), and 5.34 ppm (broad singlet, two protons). Compound **9** exhibited infrared absorption at 3010, 1720, and 1615 $cm^{-1}$. In runs in which yields were determined an internal standard (biphenyl) was added directly to the reaction mixture after all starting material had been consumed. The reaction mixture was subjected to vpc analysis without further work-up (see text for a tabulation of yields).

**Catalytic Hydrogenation of 9.** Compound **9** was reduced at atmospheric pressure (hydrogen, $PtO_2$, ethanol). The usual work-up afforded a crude product which was subjected to vpc analysis. One major component (>90%) was in evidence. The material was collected and its infrared spectrum was measured; it was identical with that of compound **15**.

**Catalytic Hydrogenation of 7.** Compound **7** was reduced (hydrogen, $PtO_2$, ethanol) to afford material which had an infrared spectrum identical with that of **5**.

**Silver Ion Assisted Methanolysis of 4.** Compound **4** (5 g, 16.4 mmol), silver nitrate (11.2 g, 65.6 mmol), and 100 ml of methanol were placed in a high pressure apparatus and heated at 100° for 20 hr. The reaction was worked up in the usual manner to afford 1.2 g of crude material that was subjected to gas chromatographic analysis on the Carbowax column mentioned previously. Two volatile components were present and both were collected. The first to elute was identified as naphthalene (**12**) and the second was identified as benzotropone (**11**). In both cases the structures in question were assigned by comparison of infrared spectra with spectra of authentic materials. Yields were determined in the same manner as reported for the solvolysis of **3**.

**Silver ion Assisted Methanolysis of 2.** For complete experimental details see ref 6.

**Kinetic Procedures.** The standard ampoule technique was employed in all kinetic runs. All ampoules were wrapped in aluminum foil. Solvents were rigorously purified and used immediately after preparation. The concentration of silver ion (~20-fold excess in each case) was determined *via* titrametric methods. In all runs except the solvolysis of **2** at least six points were taken (four points in the case of **2** at 22.6°). Reactions were followed by determining (vpc) the amount of starting material remaining at a given time. Biphenyl was employed as the internal standard. All reactions were followed to 90% completion. Pseudo-first-order rate constants were determined using a least-squares computer program.

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**Registry No.**—**2**, 20564-71-0; **3**, 38760-88-2; **4**, 4578-96-5; **7**, 34201-85-9; **9**, 49744-92-5; 1,2,3,4,5,8-hexahydronaphthalene, 36231-13-7; 1,4,5,8-tetrahydronaphthalene, 493-04-9.

## References and Notes

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(11) We thank Professor G. L. Buchanan for supplying us with the infrared spectrum of **11**.
(12) (a) Although this does not constitute rigorous proof of the location of the double bond in either **7** or **9**, it does establish the structure of the carbon skeleton. Mechanistic considerations lead us to believe that our assignments as to the location of unsaturation in **7** and **9** are correct. (b) These spectra were graciously supplied to us by Professor F. D. Greene.
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(18) Professor Philip Warner has recently informed us of experiments in which he has trapped **28**, the precursor to **29**.
(19) Calculated from values obtained in ref 15 and 16.
(20) (a) This value is somewhat exaggerated since the strain energy in **31** would be expected to be a little larger than in **28** or **32**; (b) N. A. Le Bel and R. Maxwell, *J. Amer. Chem. Soc.*, **91**, 2307 (1969).
(21) It is well known that silver ion will complex with double bonds.[22] Dewar has depicted the bonding in the silver–olefin complex as a twofold interaction.[23] It consists of (a) an interaction between a bonding $\pi$ molecular orbital of the olefin and a vacant silver s orbital and (b) an interaction between the antibonding molecular orbital of the olefin and a filled silver d orbital of the appropriate symmetry.
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(24) If one corrects for the amount of silver ion consumed in both ionization and oxidation processes when calculating the rates for **3** and **4**, this factor reduces to ~20.
(25) Infrared spectra were determined with a Perkin-Elmer 457 recording spectrophotometer. The nmr spectra were measured at 60 Hz with an Hitachi Perkin-Elmer R20 spectrometer using tetramethylsilane as the internal reference. All spectra were measured in $CCl_4$ unless otherwise stated. A Hewlett-Packard 5750B gas chromatograph was used for all vpc analysis. All peak areas were integrated with a planimeter. Magnesium sulfate was employed as the drying agent. All reactions involving air- or moisture-sensitive compounds were carried out under a nitrogen atmosphere.
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