Table III

added equiv of pyridine	chemical shift, Hz mercury-bound acetate	carbon-bound acetate
0	114.4	111.5
0.5	113.9	111.9
1.0	113.8	112.9
1.5	113.8	113.8
2.5	113.5	115.0
4	113.1	115.9
6	112.8	117.0
8	112.6	118.0
10	112.6	119.0

2930, and 2870 (m), 1755 (s), 1220 and 1165 (s) cm^{-1}; NMR (CCl_4) δ 2.3 (m, 4), 2.13 (s, 3) 1.97 (s, 3), 1.5 (m, 4), 0.9 (m, 6).

The compound was analyzed as its mercuri bromide **8a** which was prepared by washing a methylene chloride solution of **8b** with a saturated aqueous sodium bromide solution: mp 61–62 °C; IR (CCl_4) 2965, 2935, 1762 (s), 1215 and 1165 (s) cm^{-1}; NMR (CCl_4) δ 2.25 (q, 4, J = 7 Hz), 2.11 (s, 3), 1.5 (m, 4), 0.9 (m, 6).

Anal. Calcd for $C_{10}H_{17}BrHgO_2$: C, 26.70; H, 3.81. Found: C, 26.86; H, 3.75.

Reduction of Bis(*trans*-2-acetoxy-1-*n*-propylpent-1-enyl)mercury (17). To a solution of the mercurial 17 (0.27 g, 0.5 mmol) in 15 mL of acetic acid was added 0.2 g of zinc powder. After 15 min, 40 mL of methylene chloride and 200 mL of saturated sodium bicarbonate were added. The organic layer was dried ($MgSO_4$), and the methylene chloride solution was concentrated, affording 0.15 g (94%) of crude (*Z*)-4-acetoxy-4-octene. The major product (>95%) was isolated by preparative GLC (10% SE-30, 100 °C), affording 0.12 g (75%) of **18**.

Acetoxymercuration of 1,4-Butynediol Diacetate (9). To a stirred solution of 3.2 g (0.01 mol) of mercuric acetate in 30 mL of acetic acid and acetic anhydride (1:1 v/v) was added 1.72 g (0.01 mol) of **9**. After 72 h, the solvents were removed under reduced pressure with warming. The white crystalline residue was washed with pentane, affording 4.90 g (99%) of (*E*)-1,2,4-triacetoxy-3-(acetoxymercuri)-2-butene (**10**): mp 133–134 °C; IR (halocarbon) 2995 (m), 1750 (s) cm^{-1}; NMR (CH_2Cl_2) δ 4.7 (s, 4), 2.10 (s, 3), 2.00 (s, 3), 1.99 (s, 3), 1.92 (s, 3).

Anal. Calcd for $C_{12}H_{16}HgO_8$: C, 29.48; H, 3.29. Found: C, 29.44; H, 3.51.

(*E*)-2-Acetoxy-3-(acetoxymercuri)-1,4-dimethoxy-2-butene (11). To a stirred solution of 1.6 g (0.005 mol) of mercuric acetate in 20 mL of acetic acid was added 2 mL of acetic anhydride and 0.58 g (0.005 mol) of 1,4-butynediol dimethyl ether. After 16 h, the solvents were removed under reduced pressure. The residue was dissolved in 50 mL of methylene chloride, washed with 50 mL of water, dried ($MgSO_4$), and concentrated, affording 1.53 g (70%) of **11**: mp 79–80 °C; IR (CCl_4) 1770 cm^{-1}; NMR δ 3.95 (s, 2), 3.5 (m, 2), 3.45 (s, 3), 3.35 (s, 3), 2.15 (s, 3).

NMR Studies. To a solution of 0.25 g (0.5 mmol) of **2b** in 1 mL of methylene chloride were added increasing amounts of pyridine. Chemical shift values (in hertz) for the two acetate peaks were determined by using sidebanding techniques, and the data are summarized in the Table III. The solvents were removed at an aspirator affording 0.23 g of the original mercurial **2b**.

Acknowledgment. We gratefully acknowledge the National Institutes of Health (Grant No. ES 00761-08) for support of this work.

Registry No. 1, 501-65-5; (*Z*)-**2a**, 75721-25-4; (*E*)-**2a**, 82352-01-0; **2b**, 82352-02-1; (*E*)-**3**, 24647-07-2; (*Z*)-**3**, 13892-81-4; **5**, 928-49-4; **6**, 82352-03-2; **7**, 1942-45-6; **8a**, 82352-04-3; **8b**, 82352-05-4; **9**, 1573-17-7; **10**, 82352-06-5; **11**, 82352-07-6; **15**, 82352-08-7; **16**, 82352-09-8; **17**, 82352-10-1; **18**, 82352-11-2; benzil, 134-81-6; benzil dihydrazone, 4702-78-7; mercuric oxide, 21908-53-2; mercuric acetate, 1600-27-7; 1,4-butynediol dimethyl ether, 16356-02-8.

Mechanistic Aspects of the Silver(I)-Promoted Rearrangement of Cyclopropene Derivatives

Albert Padwa,*,† Thomas J. Blacklock, and Roman Loza

Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received February 11, 1982

The silver ion promoted isomerizations of several substituted cyclopropenes have been studied. The results of these studies have been compared to the rearrangements encountered on thermolysis and photolysis. Treatment of 1,3-diphenyl-2-methyl-3-benzylcyclopropene with silver ion afforded 1-phenyl-2-methyl-3-benzylindene as the exclusive product. In contrast, photolysis of this system gave rise to the isomeric 1-methyl-2-phenyl-3-benzylindene. The results obtained from the silver ion reduced reaction of 1-phenyl-2,3,3-trimethylcyclopropene indicates that the ring opening is not governed by the same electronic considerations that control its photochemical behavior. Placement of an allyl group on the C_3 position of the cyclopropene ring causes a different mode of behavior to occur on exposure to silver ion. These compounds give rise to bicyclo[3.1.0]hex-2-enes. The reaction proceeds with complete retention of stereochemistry about the π bond. A mechanism is proposed that involves preferential attack of the silver ion on the σ bond to give rise to an argentiocarbonium ion. Consistent with this mechanistic scheme were experiments in which the initially generated intermediate could be trapped with nucleophilic solvent. The regioselectivity of bond cleavage of an unsymmetrically substituted cyclopropene was found to be strongly dependent upon relative carbonium ion stabilities. An overall mechanistic picture is presented that provides a reasonable explanation of the processes that lead to each of the observed products.

The mechanism for the interconversion of the cyclopropene ring and the corresponding bond-cleaved species continues to be of both theoretical and experimental interest.[1-4] Recent calculations predict that the thermal ring opening of cyclopropene should proceed to a diradical planar intermediate which may subsequently decay to a vinylcarbene.[5] Despite the fact that the cyclopropene ring

---

† John Simon Guggenheim Memorial Fellow, 1981–1982.

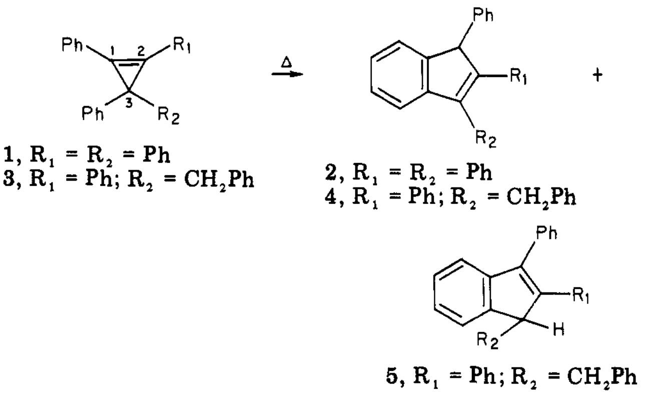
(1) Closs, G. L. *Adv. Alicyclic Chem.* **1966**, *1*, 53.
(2) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311.
(3) Padwa, A. *Acc. Chem. Res.* **1979**, *12*, 310.
(4) Schleyer, P. V. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

possesses a remarkably high strain energy (54 kcal/mol),[6] thermal reorganization of its derivatives requires elevated temperatures. For example, the formation of isomeric 2,4-heptadienes and 3-heptyne from the thermolysis of 1,3-diethylcyclopropene requires a temperature in excess of 160 °C.[7] The activation energy for the ring opening resides in the vicinity of 33 kcal/mol.[7] Another case of interest involves the thermal rearrangement of tetraphenylcyclopropene to 1,2,3-triphenylindene.[8] The reported activation energy of 40 kcal/mol for this reaction is surprisingly high. The 7-kcal difference between the above two systems suggests that phenyl groups affect the C–C single-bond energies in cyclopropenes in a strikingly different manner than that encountered with the related cyclopropane ring system.[9,10]

In dramatic contrast to the thermal results, we have found that exposure of dilute benzene solutions of 3-aryl-substituted cyclopropenes to catalytic amounts of silver perchlorate at room temperature results within minutes of quantitative conversion to an indene derivative.[11] The interaction of metal complexes, notably of silver(I) and rhodium(I), with strained carbocyclic compounds has been a subject of considerable interest in recent years.[12] These metals catalyze a variety of rearrangements that are often thermally disallowed according to the rules of "orbital symmetry conservation".[13] The course of the transition metal induced reaction has been found to depend on the nature of both the organic compound and the metal complex.[12] In this paper we describe some of the salient features associated with the silver-induced rearrangement of cyclopropene derivatives.[14]

Results

One of the more frequently encountered reactions of 3-aryl-substituted cyclopropenes involves rearrangement to indenes.[15,16] This reaction is formally analogous to the vinylcyclopropane–cyclopentene isomerization and has been proposed to proceed via an isoindene intermediate.[8] Recent MO calculations by Pincock and Boyd[17] provide a reasonable rationale to account for the high activation energy associated with the tetraphenylcyclopropene (1) pyrolysis. These workers found that the specific location of a vinyl or phenyl group on the cyclopropene has a remarkable effect on the barrier to ring opening. As expected on the basis of conjugate effects with the developing radical center, a vinyl group on C_3 of cyclopropene lowers (by 6.2 kcal/mol) the activation barrier for ring opening. A vinyl group at C_1 (C_1–C_3 cleavage) also decreases (by 2.5 kcal/mol) the barrier. In contrast, a vinyl group at C_1 (C_2–C_3 cleavage) is predicted to raise the barrier by 8.2 kcal/mol. In order to confirm these theoretical predictions, we decided to examine the thermolysis of 3-benzyl-1,2,3-triphenylcyclopropene (3) and compare its rate of rearrangement with that of 3-benzyl-2-methyl-1,3-diphenylcyclopropene (6).

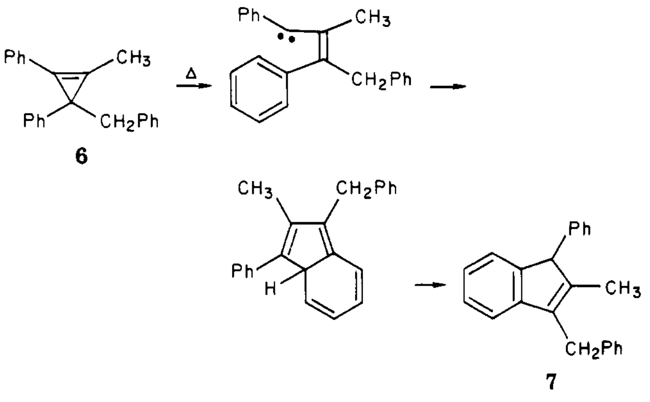


1, $R_1 = R_2 = Ph$
3, $R_1 = Ph; R_2 = CH_2Ph$

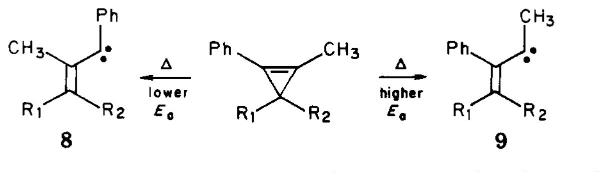
2, $R_1 = R_2 = Ph$
4, $R_1 = Ph; R_2 = CH_2Ph$

5, $R_1 = Ph; R_2 = CH_2Ph$

The thermolysis of 3 was carried out at 190 °C in xylene for 24 h. The two major products obtained (1:1 ratio) were assigned as 3-benzyl-1,2-diphenyl- (4) and 1-benzyl-2,3-diphenylindene (5). The structures of these indenes were confirmed by comparison with authentic samples prepared by treating 2,3-diphenylindanone and 3-benzyl-2-phenylindanone with the appropriate Grignard reagent, followed by dehydration of the resulting alcohols. A similar rearrangement was also found to occur with cyclopropene 6.



It is important to note here that the thermolysis of 6 gave 1-phenyl-2-methyl-3-benzylindene 7 as the exclusive regioisomer. The formation of indene 7 from 6 is perfectly consistent with the MINDO/3 calculations. The key feature of this system is the presence of the phenyl group on the double-bond carbon opposite the σ bond that is breaking, which causes a substantial increase in the activation barrier for bond cleavage. Apparently, cross-conjugated carbenes, such as 9, are less stable than linearly conjugated systems, like 8, and this is reflected in the energetics of ring opening.



Examination of the reaction kinetics of the thermal rearrangement of cyclopropenes 3 and 6 provides addi-

---

(5) Davis, J. H.; Goddard, W. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 4017. *Ibid.* **1977**, *99*, 2427.

(6) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395.

(7) York, E. J.; Dittman, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 2882. *Ibid.* **1973**, *95*, 5680.

(8) Battiste, M. A.; Halton, B.; Grubbs, R. H. *Chem. Commun.* **1967**, 907.

(9) Rodewald, L. B.; Depuy, C. H., *Tetrahedron Lett.* **1964**, 2951.

(10) Crawford, R. J.; Lynch, T. R. *Can. J. Chem.* **1968**, *46*, 1457.

(11) For a preliminary report, see Padwa, A.; Blacklock, T. J.; Loza, R. *J. Am. Chem. Soc.* **1981**, *103*, 2404.

(12) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461.

(13) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(14) There are a number of examples in the literature dealing with the transition metal promoted rearrangement of cyclopropenes. See (a) Stechl, H. H. *Chem. Ber.* **1964**, *97*, 2681. (b) Leftin, J. H.; Gil-av, G. *Tetrahedron Lett.* **1972**, 3367. (c) Shirafuji, T.; Yamamoto, Y.; Nozaki, N. *Ibid.* **1971**, 4713. (d) Weiss, R.; Schlier, F. C. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 811. (e) deWolf, W. H.; van Straten, J. W.; Bickelhaupt, F. *Tetrahedron Lett.* **1972**, 3509. (f) Weiss, R.; Andrae, S. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 150. *Ibid.*, **1973**, *12*, 152. (g) Landheer, I. J.; deWolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1974**, 2813. (h) Battiste, M. A.; Friedrich, L. E.; Fiato, R. A. *Ibid.* **1975**, 45. (i) Fiato, R. A.; Mushak, P.; Battiste, M. A. *J. Chem. Soc., Chem. Commun.* **1975**, 869. (j) Monahan, A. S.; Freilich, J. D.; Fong, J. J. *Tetrahedron Lett.* **1970**, 1865. (k) Walker, J. A.; Orchin, M. *Chem. Commun.* **1968**, 1239.

(15) Halton, B.; Kulig, M.; Battiste, M. A.; Perreten, J.; Gibson, D. M.; Griffin, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 2327.

(16) Dürr, H. *Justus Liebigs Ann. Chem.* **1969**, *723*, 103.

(17) Pincock, J. A.; Boyd, R. J. *Can. J. Chem.* **1977**, *55*, 2482.

Table I. First-Order Rate Constants and Arrhenius Parameters for the Rearrangement of Cyclopropenes 3 and 6

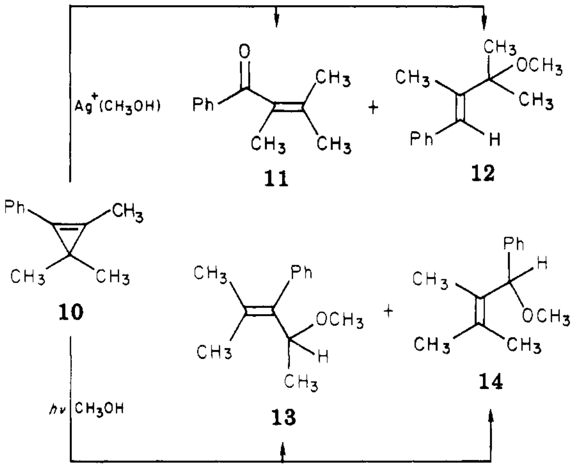
cyclopropene	temp, °C	$k \times 10^6$, s^{-1}	E_a[a]	$\Delta H^‡$	$\Delta G^‡$	$\Delta S^‡$
3	202	0.18				
3	212	0.55	38.8	38.2	41.1	−9.5
3	222	0.94				
6	170	1.42				
6	180	4.28	33.3	32.7	36.3	−11.8
6	190	7.26				

[a] Energy units are in kilocalories per mole. [b] Error limits in the reported rate constants are generally ±3%. [c] Arrhenius parameters were determined by plotting log K vs. $1/T$; the slope of the line = $-E_a/2.303R$. [d] $\Delta S^‡ = 4.576(\log A - 13.23)$ at 25 °C. [e] $\Delta G^‡ = \Delta H^‡ - T\Delta S^‡$. [f] $\Delta H^‡ = E_a - RT$.

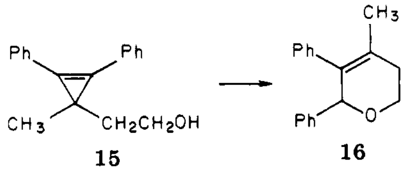
tional support for the above conclusion. Rates of rearrangement were determined in ampules sealed under vacuum. A trace of pyridine was added to inhibit acid-catalyzed ring opening. The rearrangement was followed by NMR, and good first-order dependence of the rate data was obtained, indicating that the reaction is a true unimolecular process. Rate constants for conversion of the cyclopropene to indene were measured at three temperatures over a 20 °C range. The activation parameters were determined by least-square analysis and are given in Table I. From the table it is seen that the isomerization of **6** proceeds at a rate approximately 10 times faster than that observed for **3**. While this rate difference is small, it is significant that opening of the triphenyl-substituted cyclopropene ring is occurring slower than that for the diphenylmethyl-substituted system. The activation energy for rearrangement of **3** (E_a = 39 kcal/mol) is essentially identical within experimental error with that measured by Battiste for tetraphenylcyclopropene.[8] Diphenylmethyl-substituted cyclopropene **6** undergoes rearrangement with an activation of 33 kcal/mol; this is 5.5 kcal less than that required for the rearrangement of **3**. A comparison of the effect of phenyl substitution on cyclopropane pyrolyses is worth mentioning here. 1,2-Diphenylcyclopropane undergoes stereoisomerization with an activation energy of 35 kcal/mol,[9] which suggests that each phenyl group lowers the barrier to ring cleavage by about 12–13 kcal/mol relative to 1,2-dimethylcyclopropane.[10] Clearly, the presence of a phenyl group on the C-1 position of a cyclopropene ring affects the C–C σ-bond cleavage in an unusual manner. The results, however, are perfectly consistent with the MINDO/3 calculations, which suggests that conjugation of the phenyl group with the developing double bond of the vinyl carbene (i.e., structure **9**) prevents stabilization of the carbene itself.

In dramatic contrast with the thermal results, exposure of dilute benzene solutions of **3** to catalytic amounts of silver perchlorate at room temperature resulted in the formation of indene **4** in quantitative yield. Treatment of an unsymmetrically substituted cyclopropene, such as **6**, with 2 mol % of silver perchlorate in benzene at room temperature afforded 1-phenyl-2-methyl-3-benzylindene (**7**) as the exclusive product. This result is similar to that encountered on thermolysis but differs from the well-established photochemical rearrangements[18,19] in that different carbon–carbon bonds are cleaved in the two processes.

In order to obtain a better understanding of the factors controlling the regiochemistry of the silver-induced rearrangement, we decided to investigate the isomerization of a system devoid of a phenyl group in the 3-position of the cyclopropene ring. Treatment of 1-phenyl-2,3,3-trimethylcyclopropene (**10**) with a slight excess of silver perchlorate in methanol for 1.5 h at 25 °C gave rise to a mixture of 2,3-dimethyl-1-phenyl-2-buten-1-one (**11**; 55%) and 3-methoxy-2,3-dimethyl-1-phenyl-1-butene (**12**; 45%). The structures of **11** and **12** were established by a comparison of their IR and NMR spectra with authentic samples. In contrast to the silver ion promoted reaction, the only products obtained from the irradiation of **10** in methanol are ethers **13** (78%) and **14** (9%). The distribution of products obtained from the irradiation of **10** corresponds to preferential bond b cleavage and is closely related to results encountered with 3-aryl- and 3-vinyl-substituted cyclopropenes.[18,19] It is clear from the above data that the silver-induced rearrangement of an unsymmetrical cyclopropene is not governed by the same electronic considerations that control its photochemical behavior.[18,19]



As a continuation of our investigations in this area, we became interested in determining whether the silver-induced reaction would also occur when the alcohol and the cyclopropene ring were constrained to be within the same molecule. In order to probe this possibility, we carried out a study dealing with the silver-induced reactions of several hydroxy-substituted cyclopropenes. The first compound investigated was 1-methyl-2,3-diphenyl-2-cyclopropene-2-ethanol (**15**). Treatment of **15** with an excess of silver perchlorate gave 5,6-dihydro-4-methyl-2,3-diphenyl-2*H*-pyran (**16**; 78%) as the exclusive product. The structure of **16** was readily established by examination of its characteristic NMR spectrum (CDCl$_3$, 60 MHz): δ 1.67 (*d*, *J* = 1 Hz, 3 H), 2.13 (*m*, 2 H), 3.85 (*m*, 2 H), 5.30 (*q*, *J* = 1



15 16

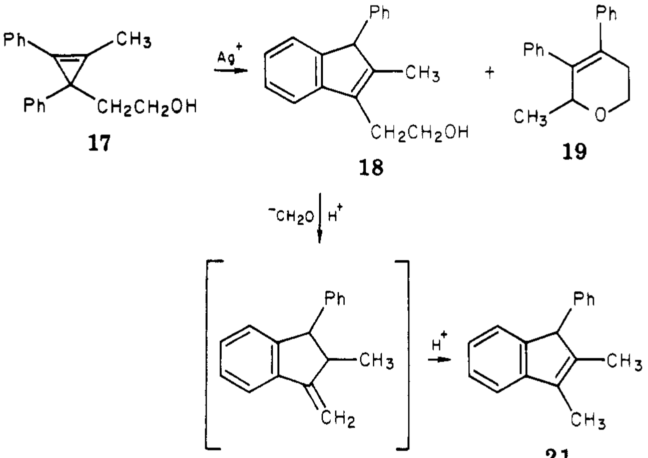
---

(18) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N.; Loza, R. *J. Org. Chem.* **1978**, *43*, 1481. Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2345.

(19) Zimmerman, H. E.; Aasen, S. M. *J. Org. Chem.* **1978**, *43*, 1493. Zimmerman, H. E.; Hovey, M. C. *Ibid.* **1979**, *44*, 2331.

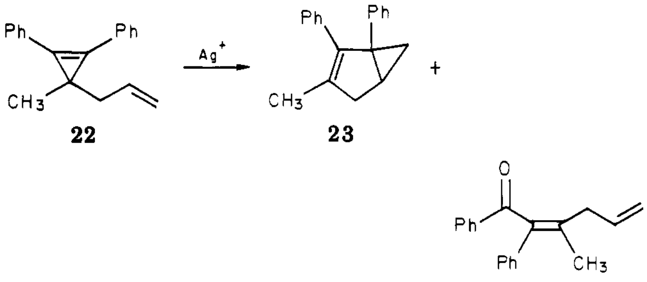
Hz, 1 H), 6.75–7.30 (*m*, 10 H).

Attention was next turned to the silver-induced behavior of the isomeric 2-methyl-1,3-diphenyl-2-cyclopropene-2-ethanol (**17**) system. The reaction of **17** with silver perchlorate in benzene gave a mixture of two compounds in a 2:1 ratio. The major product obtained was identified as 3-(2-hydroxyethyl)-2-methyl-1-phenylindene (**18**; 67%). Under slightly acidic conditions, indene **18** was quantitatively converted to 1-phenyl-2,3-dimethylindene (**21**). This reaction probably proceeds via loss of formaldehyde from **18** followed by isomerization of the transient 3-methyleneindan (**20**) under the reaction conditions. The minor compound present in the reaction mixture was identified as 5,6-dihydro-2-methyl-3,4-diphenyl-2*H*-pyran (**19**) on the basis of its characteristic spectral properties (see Experimental Section).



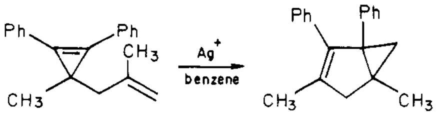
17 **18** **19** **20** **21**

Placement of an allyl group on the C_3 position of the cyclopropene ring causes a different mode of behavior to occur on exposure to silver ion. The reaction of 1,2-diphenyl-3-methyl-3-allylcyclopropene (**22**) with a catalytic quantity of silver perchlorate in benzene gave 1,2-diphenyl-3-methylbicyclo[3.1.0]hex-2-ene (**23**) in 85% yield. When the reaction was carried out in methanol as the solvent, a small amount (9%) of another compound was isolated whose structure was identified as 3-methyl-1,2-diphenyl-2,5-hexadien-1-one (**24**). The major product present in the reaction mixture was bicyclohexene **23**.

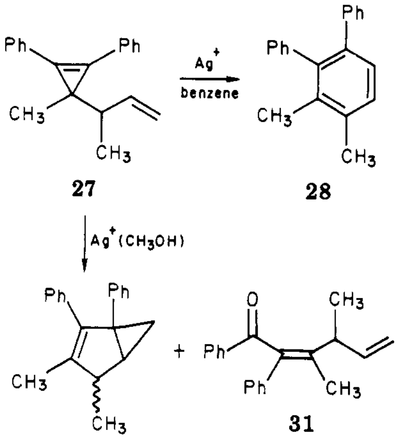


22 **23** **24**

Subjection of cyclopropene **25** to similar reaction conditions gave bicyclohexene **26** as the exclusive product in good yield. Treatment of the closely related cyclopropene **27**, on the other hand, afforded 1,2-dimethyl-3,4-diphenylbenzene (**28**) as the only identifiable product in low yield (25%). When **27** was treated with silver perchlorate in methanol, a different set of products was obtained. Chromatography of the crude reaction mixture gave *exo*- (**29**; 26%) and *endo*-3,4-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**30**; 13%), as well as 3,4-dimethyl-1,2-diphenyl-2,5-hexadien-1-one (**31**; 8%).



25 **26**

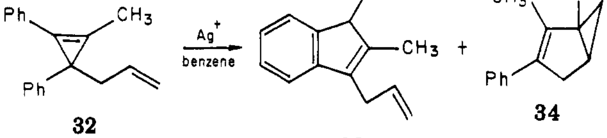


27 **28**

29, exo
30, endo

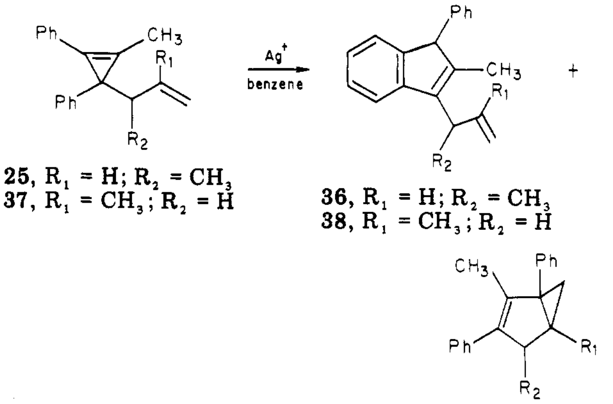
31

Attention was next turned to the silver ion induced reaction of the unsymmetrically substituted 1,3-diphenyl-2-methyl-3-allylcyclopropene system. Treatment of **32** with trace amounts of silver ion in benzene gave indene **33** (90%) and bicyclohexene **34** (10%).



32 **33** **34**

Subjection of cyclopropene **35** to similar reaction conditions gave indene **36** as the exclusive product. We also studied the behavior of cyclopropene **37** and found that it was converted to a mixture of indene **38** and bicyclohexene **39** when subject to silver ion. The products obtained from the silver-induced reaction of the 1,3-diphenyl-substituted cyclopropenes are all derived from preferential cleavage of the cyclopropene bond attached to the phenyl group. Aside from the case with cyclopropene **17**, there were no detectable quantities of products derived from cleavage of the alternate σ bond. This stands in marked contrast to the direct irradiation of these systems, which results in cleavage of the cyclopropene bond attached to the methyl group.

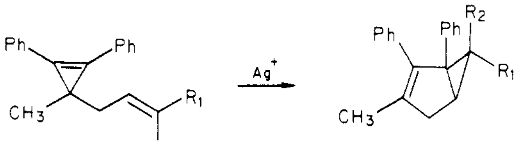


25, R_1 = H; R_2 = CH_3
37, R_1 = CH_3; R_2 = H

36, R_1 = H; R_2 = CH_3
38, R_1 = CH_3; R_2 = H

39, R_1 = CH_3; R_2 = H

At this stage of our studies we decided to investigate the stereochemical course of the silver-induced intramolecular cycloaddition reaction. Treatment of (*E*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**40**) with 2 mol % of silver perchlorate in benzene gave a 96% yield of *exo*-3,6-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**41**). Similarly, the reaction of the corresponding *Z*-isomer **42** with silver ion gave *endo*-bicyclohexene **43** as the sole product in 97% yield. The structures of the *endo*-methyl- and *exo*-methyl-substituted bicyclo[3.1.0]hex-2-enes were easily assigned on the basis of their characteristic NMR spectra. Spin-decoupling experiments indicate that the cyclopropyl protons in the exo-substituted isomer **41** are coupled by 3.7 Hz, whereas the coupling with the endo isomer **43** is 8.5 Hz. These results indicate that complete retention of stereochemistry about the π system has occurred in the silver-catalyzed cycloaddition reaction.

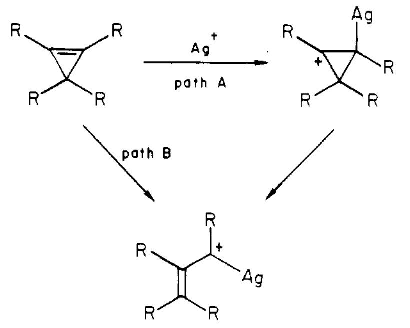


40, $R_1 = CH_3$; $R_2 = H$
42, $R_1 = H$; $R_2 = CH_3$

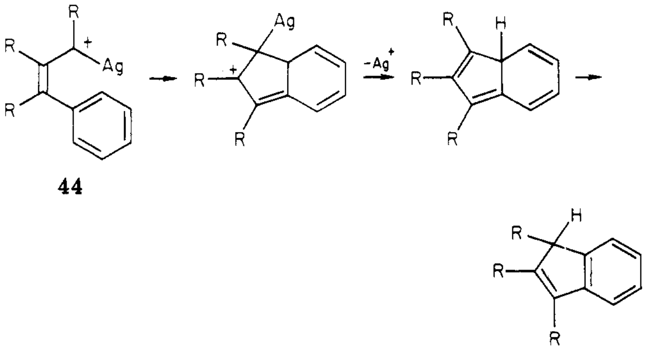
41, $R_1 = CH_3$; $R_2 = H$
43, $R_1 = H$; $R_2 = CH_3$

Discussion

The reaction of electrophilic reagents such as silver ion with strained σ bonds has been extensively studied in recent years.[12,14] Since electrophilic reagents are also known to react with π systems of olefins, the interesting question is raised of σ vs. π reactivity.[20] Cyclopropenes represent an unusual class of molecules where a strained σ bond is incorporated into a substrate that already possesses a reactive π system. Fragmentation of the σ bond of cyclopropenes thermodynamically releases ca. 55 kcal/mol of strain.[4] In cyclopropene and related systems, there are numerous literature postulates concerning reactions that occur preferentially with strained σ bonds.[14,21-29] In line with earlier evidence for the intermediacy of a metal-bonded carbonium ion–metal complexed carbene hybrid intermediate in the transition metal promoted rearrangement of strained ring systems,[30,31] it is tempting to suggest the involvement of a related species in the silver-induced rearrangements of the above systems. Thus, we propose that silver ion behaves as a very specific Lewis acid that attacks the cyclopropene ring to yield argentiocarbonium ion **44**. This can take place by two different mechanisms. Formation of the argentiocarbonium ion (**44**) may occur via attack on the cyclopropene π bond, followed by a rapid ring opening of the transient cyclopropyl cation (path A). Alternatively, silver ion attack could occur on the σ bond to give the argentiocarbonium ion directly. When a phenyl group is present on the 3-position of the cyclopropene ring, the argentiocarbonium ion readily undergoes an electrocyclization, followed by loss of silver ion, to give the observed indene skeleton. This process is catalytic in silver ion.

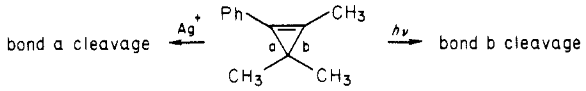


44



44

Analysis of the results obtained from the silver-induced reaction of the unsymmetrically substituted cyclopropenes provides a basis for distinguishing between the two mechanistic possibilities. In all the cases studied, the major products obtained were always derived from cleavage of the cyclopropene bond attached to the phenyl group (bond a). These silver-induced reactions differ dramatically from the well-established photochemical rearrangements[18,19] in that different carbon–carbon bonds are cleaved in the two processes. The major product obtained from the irradiation of a 1,3-diphenyl-2-methyl-substituted cyclopropene was always found to correspond to preferential cleavage of the cyclopropene bond, which is methyl rather than phenyl substituted.[18,19] This unusual photochemical effect has been attributed to a funneling of the excited state of the cyclopropene to the energy state of the higher lying vinylcarbene state.[18] The factors that control the regioselectivity associated with the silver-induced reactions of the above systems require some comment.



Electrophilic addition of silver ion to the π bond can give cyclopropyl cations **46** or **47**. In the latter ion there are canonical forms in which the positive charge can be delocalized over the aromatic ring. The initially produced cyclopropyl cation can undergo a subsequent ring opening to give an allylic argentiocarbonium ion (i.e., **48** or **49**). If addition of silver ion to the π bond is the product-determining step, then the products obtained should be preferentially derived from argentiocarbonium ion **49** (i.e., bond b cleavage). Electrophilic addition mediated by π addition to the cyclopropene ring gives results opposite to

---

(20) Lambert, J. B.; Black, R. D. H.; Shaw, J. H.; Papay, J. J. *J. Org. Chem.* **1970**, *35*, 3214.

(21) Hogeveen, H.; Kwant, P. *Tetrahedron Lett.* **1972**, 5361.

(22) Mikhailov, B. M.; Bubnov, Y. N.; Nesneyanova, O. A.; Kiselev, V. G.; Rudashevskeya, J.; Kazansky, B. A. *Tetrahedron Lett.* **1972**, 4627. *Ibid.* **1971**, 2153.

(23) Moerck, R. E.; Battiste, M. A. *Tetrahedron Lett.* **1973**, 4421.

(24) Shirafugi, T.; Yamamoto, Y.; Nazaki, H. *Tetrahedron Lett.* **1971**, 4713.

(25) Closs, G. L.; Closs, L. E.; Boll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796.

(26) Friedrich, L. E.; Fiato, R. A. *J. Org. Chem.* **1974**, *39*, 2267.

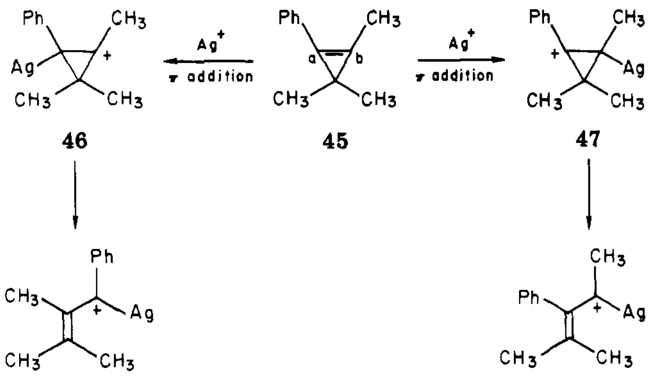
(27) Shea, K. J.; Davis, J. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1499.

(28) Johnson, G. C.; Bergman, R. G.; *Tetrahedron Lett.* **1979**, 2093.

(29) Bee, L. K.; Garratt, P. J.; Mansuri, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 7076.

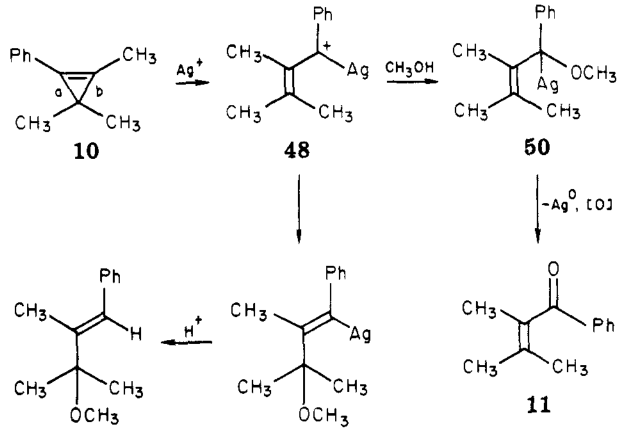
(30) Gassman, P. G.; Williams, F. J. *J. Am. Chem. Soc.* **1972**, *94*, 7733. Gassman, P. G.; Meyer, G. R.; Williams, F. J. *Ibid.* **1972**, *94*, 7741. Gassman, P. G.; Atkins, T. J. *Ibid.* **1972**, *94*, 7748. Gassman, P. G.; Nakai, T. *Ibid.* **1971**, *93*, 5897. *Ibid.* **1972**, *94*, 2877, 5497.

(31) Paquette, L. A. *Acc. Chem. Res.* **1971**, *4*, 280.



46 45 47

48 49

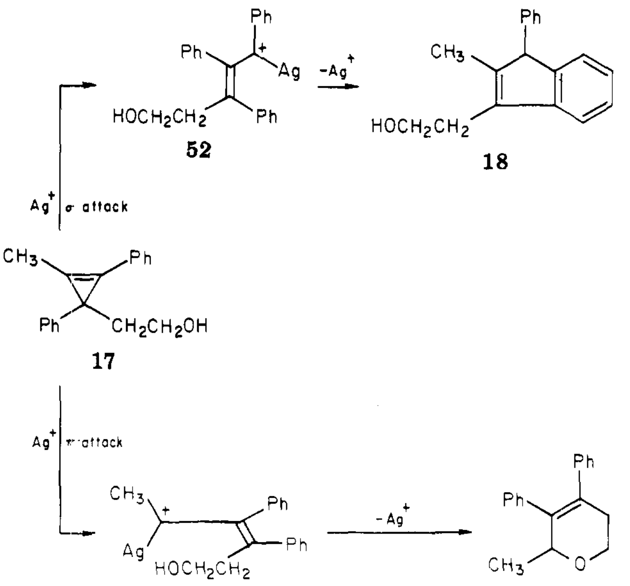


10 48 50

12 51 11

this prediction, however. For example, the products obtained from the treatment of **10** in methanol with silver perchlorate are **11** and **12**. In this case, a full equivalent of silver ion was used. The clean conversion of **10** in the presence of silver ion into **11** and **12** in methanol can be explained in terms of an oxidation–reduction reaction. It should be pointed out that the production of metallic silver in the conversion of **10** to **11** also leads to the formation of perchloric acid. Control experiments established, however, that the cyclopropene ring system is stable to perchloric acid in methanol under the experimental conditions used. Furthermore, the reaction of **10** in methanol with Ag(I) ion readily occurs in the presence of an excess of triethylamine. These observations indicate that the conversion of **10** to **11** does not proceed via an acid-induced pathway. The reduction of Ag(I) to the metallic state is somewhat reminiscent of results reported by Koser and Faircloth.[32] These workers found that quadricyclane was oxidized and silver ion was reduced to silver metal in the reaction between silver trifluoroacetate and quadricyclane in methanol.

The silver-induced reactions of 3-hydroxyethyl-substituted cyclopropenes proceed in an analogous fashion. With these systems, the initially produced allylic argentiocarbonium ion reacts intramolecularly with the neighboring hydroxy group to give the dihydro-2*H*-pyran system. With the 2-methyl-1,3-diphenyl-2-cyclopropene-2-ethanol (**17**) system, σ attack (which clearly governs most of the cases studied) and π attack are not that dramatically different in kinetic preference. Consequently, a mixture of products derived from both possible allylic argentiocarbonium ions (i.e., **52** and **53**) are formed. The major pathway, however, does correspond to σ attack of silver ion in the plane of the cyclopropene (i.e., preferential formation of **52**). Thus,



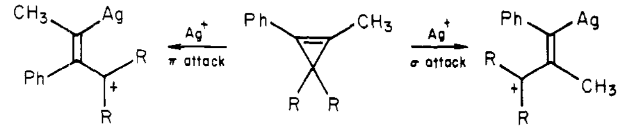
52 18

17

53 19

σ attack leads to cation **52**, which is the precursor to indene **18**. On the other hand, π attack gives cation **53**, which then closes to dihydropyran **19**. The ratio between **18** and **19** (i.e., 2:1) reflects the relative importance of the two pathways.

The above results suggest that the crucial step which dictates the regioselectivity of the silver-induced reaction is strongly dependent upon substituent effects. The stabilities of the ring-opened species (i.e., **54** and **55**) should



54 55

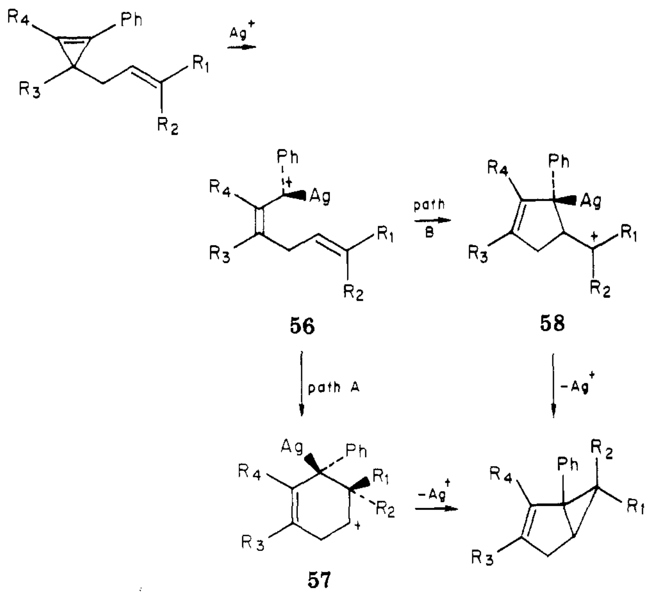
parallel allylic carbonium stability, **55** being more stable than **54**. Preferential σ attack of silver ion in the plane of the cyclopropene fits this pattern perfectly and nicely accounts for the regiochemistry of the reaction.

The intramolecular trapping of the ring-opened species by the neighboring allyl π bond provides additional evidence for the carbenoid character of the intermediate. Two stepwise pathways are possible. One path involves a stepwise attack of the terminal double bond on the argentiocarbonium ion so as to generate a six-membered ring (**57**). The alternate possibility involves cyclization through a five-membered transition state to produce intermediate **58**, which undergoes a subsequent ring closure. Molecular models show that there are no steric constraints for either pathway. Baldwin's rules[33] suggest that both the 6-endo-trig (path A) and 5-exo-trig (path B) are allowed processes. The isolation of 1,2-dimethyl-3,4-diphenylbenzene (**28**) from the reaction of **27** with silver ion is best explained, however, in terms of the six-membered ring intermediate (i.e., **57**). The formation of the α,β-unsaturated ketones **24** and **31** when the reaction is carried out in methanol is presumably due to a competitive oxidation–reduction sequence as discussed earlier. Finally, the results with the *E* (**40**) and *Z* (**42**) substituted cyclopropenes indicate that complete retention of stereochemistry about the π bond has occurred in the cycloaddition reaction. As long as the loss of silver ion occurs simultaneously with bond making, the cycloaddition will proceed with retention of configuration.

---

[32] Koser, G. F.; Faircloth, J. N. *J. Org. Chem.* **1976**, *41*, 583.

[33] Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.



In summary, we feel that the data we have presented offers a reasonable rationale for the reactions of cyclopropene derivatives with silver ion. We are continuing to investigate the more intriguing synthetic and mechanistic aspects of these interesting silver ion promoted reactions.

Experimental Section[34]

Preparation of 1,2,3-Triphenyl-3-benzylcyclopropene (3). To a stirred slurry containing 10.0 g of triphenylcyclopropenyl perchlorate[35] in 250 mL of tetrahydrofuran at −78 °C was added 50 mL of a 1.0 M solution of benzylmagnesium chloride in ether. The mixture was stirred at 0 °C for 12 h and was then hydrolyzed with a saturated ammonium chloride solution. The solution was concentrated under reduced pressure and diluted with ether. The ether layer was washed with water and dried over magnesium sulfate. Removal of the solvent left a yellow residue, which was passed through a silica gel column with hexane as the eluent. The major fraction contained 8.7 g (89%) of 3-benzyl-1,2,3-triphenylcyclopropene (3) as a crystalline solid: mp 105–106 °C; NMR (CDCl$_3$, 100 MHz) δ 3.71 (s, 2 H), 6.98 (s, 5 H), 7.12–7.60 (m, 15 H); IR (KBr) 3.30, 5.47, 6.24, 6.71, 6.93, 9.31, 10.93, 12.85, 13.25, 13.47, 14.42, 14.52 μm; UV (95% ethanol) max 336, 318, 227 nm (ϵ 21 500, 25 700, 29 200); mass spectrum, *m/e* 358 (M$^+$), 267 (base), 265, 252, 232 and 91. Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 94.08; H, 6.34.

Thermolysis of 1,2,3-Triphenyl-3-benzylcyclopropene (3). A solution containing 0.5 g of 3 in 5 mL of xylene was heated in a sealed tube at 190 °C for 24 h. Removal of the solvent left a brown oil, which was subjected to preparative thick-layer chromatography. The first component isolated from the plate contained 210 mg (42%) of a white solid, mp 117–118 °C, whose structure was identified as 1,2-diphenyl-3-benzylindene (4): NMR (CDCl$_3$, 100 MHz) δ 4.43 (s, 2 H), 5.04 (s, 1 H), 7.07–7.40 (m, 19 H); UV (95% ethanol) max 294 nm (ϵ 16 700); mass spectrum, *m/e* 358 (M$^+$), 357 (base), 279, 268, 252, 178, 91. Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.75; H, 6.07.

The structure of this material was unambiguously verified by comparison with an authentic sample. A 0.8-g sample of 2,3-diphenylindanone[36] was treated with 3.4 mL of a 1.0 M solution of benzylmagnesium chloride in ether. Standard workup procedures gave indene 4, which was identical in every detail with the sample obtained from the thermolysis of 3.

The second component isolated from the thick-layer preparative plate contained 220 mg (44%) of 1-benzyl-2,3-diphenylindene (5): mp 118–119 °C; NMR (CDCl$_3$, 100 MHz) δ 2.55 (dd, 1 H, *J* = 14.0 and 4.0 Hz), 3.28 (dd, 1 H, *J* = 14.0 and 8.0 Hz), 4.27 (dd, 1 H, *J* = 8.0 and 4.0 Hz), 6.8–7.3 (m, 14 H); IR (KBr) 3.32, 6.24, 6.72, 6.91, 7.17, 12.67, 13.06, 14.42 μm; UV (95% ethanol) max 303 and 237 nm (ϵ 16 700 and 22 200); mass spectrum, *m/e* 358 (M$^+$), 267 (base), 252, 91. Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.54; H, 6.24.

The structure of this material was verified by comparison with an authentic sample. To a solution containing 1.15 g of diisopropylamine in 50 mL of tetrahydrofuran was added 4.7 mL of a 2.3 M solution of *n*-butyllithium in hexane at −78 °C. The mixture was stirred for 45 min and then 1.0 g of 2-methylindanone[37] in 25 mL of tetrahydrofuran was added. The mixture was allowed to stir at 25 °C for 3 h and was then cooled to −10 °C. To this solution was added 0.99 g of benzyl bromide in 15 mL of tetrahydrofuran. After stirring for 15 min, the solution was quenched with a 10% hydrochloric acid solution. The solvent was dried and removed under reduced pressure. The resulting residue was chromatographed on silica gel to give 1.08 g (75%) of 3-benzyl-2-phenylindanone: NMR (CDCl$_3$, 100 MHz) δ 3.0–3.98 (m, 4 H), 6.8–8.0 (m, 14 H); IR (neat) 3.32, 5.83, 6.24, 6.71, 6.90, 7.79, 12.65, 13.12, 14.35 μm.

To a solution of 1.08 g of the above ketone in 50 mL of ether was added 1.5 mL of a 2.9 M solution of phenylmagnesium bromide in ether. The mixture was heated at reflux for 5 h and was then hydrolyzed with a saturated ammonium chloride solution. Removal of the solvent left a yellow oil, which was taken up in 25 mL of glacial acetic acid. To this mixture was added 5 mL of concentrated sulfuric acid and 0.5 mL of water. After stirring at 25 °C for 30 min, the mixture was poured into ice–water and extracted with ether. Standard workup procedures gave 1-benzyl-2,3-diphenylindene (5) as the exclusive product produced. This material was identical in every detail with the sample of 5 produced from the thermolysis of 3.

Treatment of cyclopropene 3 with silver perchlorate in benzene gave indene 4 in 92% yield.

Rate Studies. Stock solutions containing 0.75 g of the appropriate cyclopropene and 5.0 mL of toluene were prepared. From each stock solution, 0.4-mL aliquots were withdrawn and sealed in glass ampules under an argon atmosphere. The ampules were immersed in a thermostated (±0.1 °C) oil bath at the designated temperatures and were periodically withdrawn for analysis. The solvent was removed under reduced pressure, and the residue was taken up in deuterated chloroform. The concentration of product was determined by NMR spectroscopy and was further verified by high-pressure column chromatography on an Altex 3.2 × 250 mm, LiChroSorb, 5-μm, C-18, reverse-phase silica gel column.

Thermal and Silver-Induced Rearrangement of 3-Benzyl-2-methyl-1,3-diphenylcyclopropene (6) in Benzene. A solution containing 104 mg of 3-benzyl-2-methyl-1,3-diphenylcyclopropene[18] (6) and 210 mg of silver perchlorate in 20 mL of benzene was heated at 45 °C under a nitrogen atmosphere for 36 h in the dark. The reaction mixture was diluted with ether, and the organic layer was washed several times with a saturated salt solution and dried over magnesium sulfate. Removal of the solvent left behind a yellow oil, which solidified on treatment with ethanol. Recrystallization from ethanol afforded 80 mg (77%) of a white crystalline solid, mp 103–104 °C, which was identified as 3-benzyl-2-methyl-1-phenylindene (7): NMR (CDCl$_3$, 100 MHz) δ 1.88 (s, 3 H), 3.88 (s, 2 H), 4.30 (s, 1 H), 6.8–7.3 (m, 14 H); UV (95% ethanol) max 265 nm (ϵ 9400). The structure of this material was further verified by comparison with an authentic sample.[18] This same material was formed in high yield when a sample of 6 was heated in toluene at 200 °C for 48 h.

Silver-Induced Rearrangement of 2,3,3-Trimethyl-1-phenylcyclopropene (10) in Methanol. A solution containing 170 mg of 2,3,3-trimethyl-1-phenylcyclopropene[18] (10) and 320 mg of silver perchlorate in 25 mL of methanol containing 1 mL

---

(34) All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer, with 1-cm matched cells. The proton magnetic resonance spectra were determined at 90 MHz with a Varian EM-3 90-MHz spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV.

(35) Breslow, R.; Hover, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168.

(36) Hiscock, H.; Porter, G. B. *J. Chem. Soc. B.* **1971**, 1631.

(37) Fuson, R. C.; Ross, W. E.; McKeever, C. H. *J. Am. Chem. Soc.* **1938**, *60*, 2935.

of water was stirred at room temperature for 1.5 h in the dark. The reaction mixture was extracted with ether, and the ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil, which was chromatographed on a 1.5 × 100 cm silica gel column with a 3% ether–hexane mixture as the eluent. The first component isolated from the column contained 38 mg (18%) of a clear oil, which was identified as 3-methoxy-2,3-dimethyl-1-phenyl-1-butene (**12**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.38 (s, 6 H), 1.83 (d, *J* = 1 Hz, 3 H), 3.09 (s, 3 H), 6.44 (br s, 1 H), 7.12–7.33 (m, 5 H); IR (neat) 3.38, 6.24, 6.69, 6.95, 7.28, 8.00, 8.54, 8.69, 9.00, 9.27, 9.95, 10.90, 11.90, 12.19, 13.13, 13.96, 14.46 μm; UV (95% ethanol) max 224 nm (ϵ 13 200); mass spectrum, *m/e* 190 (M^+), 175, 158, 143 (base), 128, 115, 91, 77. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.91; H, 9.57.

The second component isolated contained 43 mg (23%) of a clear oil, which was identified as 2,3-dimethyl-1-phenyl-2-buten-1-one (**11**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.56–1.69 (m, 3 H), 1.86–1.92 (m, 6 H), 7.36–7.56 (m, 3 H), 7.77–7.93 (m, 2 H); IR (neat) 3.24, 6.00, 6.24, 6.90, 7.59, 7.78, 8.10, 8.74, 9.93, 10.52, 12.43, 13.87 μm; mass spectrum, *m/e* 174 (M^+ and base), 159, 131, 105, 91, 77. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.68; H, 8.03.

The structure of this material was further verified by comparison with an authentic sample.[38]

Silver-Induced Rearrangement of 1-Methyl-2,3-diphenyl-2-cyclopropene-2-ethanol (15). A solution containing 194 mg of 1-methyl-2,3-diphenyl-2-cyclopropene-2-ethanol[39] (**15**) and 120 mg of silver perchlorate in 25 mL of benzene was stirred under a nitrogen atmosphere for 24 h at 50 °C. The mixture was diluted with ether, and the organic layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil, which was chromatographed on a preparative thick-layer plate with a 5% ether–hexane mixture as the eluent. The major component isolated contained 140 mg (72%) of a light yellow oil, which was identified as 5,6-dihydro-4-methyl-2,3-diphenyl-2*H*-pyran (**16**) on the basis of its spectral properties: NMR ($CDCl_3$, 60 MHz) δ 1.67 (d, *J* = 1 Hz, 1 H), 2.13–2.14 (m, 2 H), 3.52–4.18 (m, 2 H), 5.30 (q, *J* = 1 Hz, 1 H), 6.75–7.30 (m, 10 H); IR (neat) 3.26, 3.29, 3.48, 6.24, 6.71, 6.86, 7.03, 7.91, 8.90, 9.28, 10.94, 13.2, 13.6, 14.2 μm; UV (95% ethanol) max 235 nm (ϵ 6630); mass spectrum, *m/e* 250 (M^+), 235 (base), 205, 173, 129, 115, 105, 77. Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.36; H, 7.29.

Silver-Induced Rearrangement of 2-Methyl-1,3-diphenyl-2-cyclopropene-2-ethanol (17). A solution containing 260 mg of 2-methyl-1,3-diphenyl-2-cyclopropene-2-ethanol[39] (**17**) and 300 mg of silver perchlorate in 25 mL of benzene was stirred at room temperature for 22 h. The benzene solution was diluted with ether, and the organic layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a brown oil, which was chromatographed on a preparative thick-layer plate with a 10% acetone–hexane mixture as the eluent. The first component isolated contained 75 mg (29%) of a light yellow oil, which was identified as 5,6-dihydro-2-methyl-3,4-diphenyl-2*H*-pyran (**19**) on the basis of its spectral properties: NMR ($CDCl_3$, 100 MHz) δ 1.16 (*d*, *J* = 7 Hz, 3 H), 2.29 (dddd, *J* = 18, 5, 4, and 2 Hz, 1 H), 2.78 (dddd, *J* = 18, 5, 4, and 2 Hz, 1 H), 3.78–4.29 (m, 2 H), 4.62–4.90 (m, 1 H), 6.86–7.31 (*m*, 10 H); IR (neat) 3.28, 3.31, 3.36, 3.42, 3.50, 6.24, 6.72, 6.94, 8.70, 8.97, 12.8, 13.2, 14.3 μm; UV (95% ethanol) max 246, 220 nm (ϵ 8430 and 11 600); mass spectrum, *m/e* 250 (M^+), 236, 235 (base), 206, 205, 179, 178, 173, 129, 105, 91. Anal. Calcd for $C_{18}H_{18}O$: P^+, 250.1358. Found: P^+, 250.1346.

The second component isolated contained 170 mg (65%) of a yellow oil identified as 3-(2-hydroxyethyl)-2-methyl-1-phenylindene (**18**) on the basis of its characteristic spectral properties: NMR ($CDCl_3$, 60 MHz) δ 1.83 (s, 3 H), 2.12 (br s, 1 H), 2.78 (t, *J* = 7 Hz, 2 H), 3.77 (t, *J* = 7 Hz, 2 H), 4.23 (s, 1 H), 6.73–7.31 (m, 9 H); IR (neat) 3.00, 3.28, 3.31, 3.42, 3.48, 6.24, 6.72, 6.85, 6.93, 9.61, 12.7, 13.2, 14.4 μm; UV (95% ethanol) max 264 nm (ϵ 7420); mass spectrum, *m/e* 251, 250 (M^+), 232, 219, 218, 217, 207, 206 (base), 205, 204, 203, 202, 191, 178, 129, 115, 100, 91. Anal. Calcd for $C_{18}H_{18}O$: P^+, 250.1358. Found: P^+, 250.1333.

When this material was heated in benzene with a trace of *p*-toluenesulfonic acid for 12 h, 2,3-dimethyl-1-phenylindene (**21**) was obtained: mp 67–68 °C; NMR ($CDCl_3$, 100 MHz) δ 1.85 (br s, 3 H), 2.10 (br s, 3 H), 4.28 (br s, 1 H), 6.95–7.47 (m, 9 H); UV (95% ethanol) max 263 nm (ϵ 10 000). The physical properties of this material are identical with those reported by Smith and Hanson.[40]

Silver-Induced Rearrangement of 1,2-Diphenyl-3-allyl-3-methylcyclopropene (22). A solution containing 100 mg of **22**[41] in 10 mL of a 0.1 N solution of silver perchlorate in benzene was heated at 80 °C for 48 h. At the end of this time a saturated sodium chloride solution was added, and the mixture was stirred for 1 h. The benzene layer was then washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 80 mg (80%) of a crystalline solid, mp 44–45 °C, whose structure was assigned as 3-methyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**23**) by comparison with an authentic sample:[41] NMR ($CDCl_3$, 100 MHz) δ 0.76 (t, 1 H, *J* = 4.0 Hz), 1.39–1.68 (m, 1 H), 1.72 (dd, 1 H, *J* = 8.0 and 4.0 Hz), 1.80 (s, 3 H), 2.36 (d, 1 H, *J* = 17.0 Hz), 3.02 (dd, 1 H, *J* = 17.0 and 7.0 Hz), 7.0–7.2 (m, 10 H).

When the reaction of **22** was carried out in methanol, the major product was bicyclohexene **23** (62%). In addition, a 9% yield of 3-methyl-1,2-diphenyl-2,5-hexadien-1-one (**24**) was also obtained as a colorless oil: NMR ($CDCl_3$, 100 MHz) δ 1.73 (s, 3 H), 2.91 (d, 2 H, *J* = 5.0 Hz), 4.93–5.27 (m, 2 H), 5.71–6.15 (*m*, 1 H), 7.00–7.34 (m, 8 H), 7.89–8.05 (m, 2 H); IR (CCl_4) 3.28, 3.44, 5.99, 6.24, 6.70, 6.92, 8.15, 8.53, 10.89, 14.30 μm; UV (95% ethanol) max 246 nm (ϵ 14 900); mass spectrum, *m/e* 262 (M^+), 247, 246, 205, 129, 105 (base), 77. Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 86.75; H, 7.02.

Silver-Induced Rearrangement of 1,3-Diphenyl-2-methyl-3-allylcyclopropene (32) in Benzene. A solution containing 100 mg of **32**[41] and 120 mg of silver perchlorate in 25 mL of benzene was heated at 52 °C for 24 h. The mixture was diluted with ether, and the ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil, which was chromatographed on a silica gel column with hexane as the eluent. The first component isolated from the column (90%) was identified as 3-allyl-2-methyl-1-phenylindene (**33**) by comparison with an authentic sample:[41] NMR ($CDCl_3$, 100 MHz) δ 1.84 (s, 3 H), 3.32 (d, 2 H, *J* = 5.5 Hz), 4.28 (s, 1 H), 4.76–5.20 (m, 2 H), 5.72–6.18 (m, 1 H), 6.90–7.38 (m, 9 H). The second component isolated from the column (10%) was assigned the structure of 2-methyl-1,3-diphenylbicyclo[3.1.0]hex-2-ene (**34**): mp 43–44 °C; IR (KBr) 3.26, 3.32, 3.43, 3.50, 6.19, 6.67, 6.89, 7.19, 9.13, 9.66, 13.24, 14.27 μm; NMR ($CDCl_3$, 100 MHz) δ 0.77 (t, 1 H, *J* = 4.0 Hz), 1.48 (dd, 1 H, *J* = 8.0 and 4.0 Hz), 1.60–1.84 (*m*, 1 H), 1.70 (t, 3 H), *J* = 2.0 Hz), 2.76 (br d, 1 H, *J* = 17.5 Hz), 3.24 (ddd, 1 H, *J* = 17.5, 8.0, and 2.0 Hz), 7.2–7.4 (m, 10 H); UV (95% ethanol) max 261 nm (ϵ 14 400); mass spectrum, *m/e* 246 (M^+, base), 231. Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.46; H, 7.08.

Silver-Induced Rearrangement of 2-Methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-propene (25) in Benzene. A solution containing 300 mg of 2-methyl-3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-propene[42] and 300 mg of silver perchlorate in 20 mL of dry benzene was heated for 90 h at 60 °C under a nitrogen atmosphere in the dark. The benzene solution was diluted with ether and washed with a saturated salt solution, and then the organic layer was dried over magnesium sulfate. The solvent was removed under reduced pressure, leaving behind a brown oil, which was chromatographed on a 1.5 × 65 cm silica gel column with hexane as the eluent. The major component isolated contained 170 mg (65%) of a colorless oil, which was identified as 3,5-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**26**)

---

[38] Cologne, J.; Chambion, J. *Bull. Soc. Chim. Fr.* **1947**, *14*, 999.

[39] Padwa, A.; Blacklock, T. J.; Loza, R.; Polniaszek, R. *J. Org. Chem.* **1980**, *45*, 2181.

[40] Smith, L. I.; Hanson, J. R. *J. Am. Chem. Soc.* **1935**, *57*, 1326.

[41] Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2797.

[42] Padwa, A.; Blacklock, T. J.; Chou, C. S.; Hatanaka, N. *J. Am. Chem. Soc.* **1979**, *101*, 5743.

by comparison with an authentic sample:[41] NMR (CDCl$_3$, 100 MHz) δ 0.83 (d, 1 H, J = 4.0 Hz), 0.94 (s, 3 H), 1.49 (*d*, 1 H, J = 4.0 Hz), 1.80 (s, 3 H), 2.49 (d, 1 H, J = 17.0 Hz), 2.78 (d, 1 H, J = 17.0 Hz), 6.95–7.28 (m, 10 H).

Silver-Induced Rearrangement of 2-Methyl-3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-propene (37) in Benzene. A solution containing 230 mg of 2-methyl-3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-propene (**37**)[42] and 270 mg of silver perchlorate in 25 mL of benzene was heated for 48 h at 60 °C in the dark. The mixture was diluted with ether, and the ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent left behind a yellow oil, which was chromatographed on a 1.5 × 100 cm silica gel column with hexane as the eluent. The first component isolated contained 35 mg (15%) of a colorless oil, identified as 2,5-dimethyl-1,3-diphenylbicyclo[3.1.0]hex-2-ene (**39**) on the basis of its spectral properties: NMR (CDCl$_3$, 100 MHz) δ 0.67 (d, J = 4 Hz, 1 H), 1.01 (s, 3 H), 1.26 (d, J = 4 Hz, 1 H), 1.67 (t, J = 2 Hz, 3 H), 2.87 (q, J = 2 Hz, 2 H), 7.08–7.32 (m, 10 H); IR (neat) 3.30, 3.48, 6.24, 6.70, 6.92, 7.27, 8.30, 9.50, 9.71, 13.08, 13.65, 14.22 μm; UV (95% ethanol) max 262 nm (ϵ 14 700); mass spectrum, *m/e* 260 (M$^+$, base), 245, 230, 205, 169, 167, 165, 115, 105, 91, 77. Anal. Calcd for C$_{20}$H$_{20}$: C, 92.26; H, 7.74. Found: C, 92.13; H, 7.86.

The second component isolated contained 170 mg (74%) of a colorless oil, identified as 2-methyl-1-phenyl-3-(2-methyl-2-propen-1-yl)indene (**38**) on the basis of its spectral data: NMR (CDCl$_3$, 100 MHz) δ 1.75 (s, 3 H), 1.80 (s, 3 H), 3.25 (s, 2 H), 4.25 (s, 1 H), 4.80 (s, 2 H), 6.88–7.33 (m, 9 H); IR (neat) 3.28, 3.46, 6.05, 6.24, 6.70, 6.82, 6.91, 7.30, 9.66, 11.22, 13.22, 13.64, 14.30 μm; UV (95% ethanol) max 263 nm (ϵ 9540); mass spectrum, *m/e* 260 (M$^+$), 206, 205 (base). Anal. Calcd for C$_{20}$H$_{20}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.78.

Silver-Induced Rearrangement of 3-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (27) in Benzene. A solution containing 300 mg of 3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**27**)[41] and 320 mg of silver perchlorate in 25 mL of dry benzene was refluxed for 67 h in the dark. The dark-green mixture was diluted with ether and extracted with a saturated salt solution. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure, leaving behind a dark brown oil. This dark oil was initially percolated through silica gel, followed by chromatography on a 1.5 × 65 cm silica gel column with hexane as the eluent. The major fraction contained 75 mg (25%) of a colorless oil, which solidified when triturated with cold methanol. Recrystallization from methanol afforded a white crystalline solid, whose structure was assigned as 1,2-dimethyl-3,4-diphenylbenzene (**28**) on the basis of its physical and spectral properties: mp 95–96 °C; NMR (CDCl$_3$, 100 MHz) δ 2.01 (s, 3 H), 2.31 (s, 3 H), 6.84–7.32 (m, 12 H); IR (KBr) 3.48, 6.24, 6.86, 6.99, 9.35, 10.13, 10.90, 12.03, 12.78, 13.14, 13.39, 14.31 μm; UV (95% ethanol) sh 234 nm (ϵ 20 900); mass spectrum, *m/e* 258 (M$^+$, base) 257, 244, 243, 242, 241, 228. Anal. Calcd for C$_{20}$H$_{18}$: C, 92.98; H, 7.02. Found: C, 92.71; H, 7.28.

Silver-Induced Rearrangement of 3-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (27) in Methanol. A solution containing 300 mg of 3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**27**)[41] and 350 mg of silver perchlorate in 25 mL of methanol was refluxed for 280 h in the dark. The mixture was extracted with ether. The organic layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of solvent left behind a dark yellow oil, which was chromatographed on a 1.5 × 65 cm silica gel column with 5% ether in hexane as the eluent. The first fraction isolated contained 78 mg (26%) of a colorless oil, which was shown by NMR analysis to contain a 1.5:1 mixture of two components. Chromatography of this mixture on a 1.5 × 100 cm silica gel column with hexane as the eluent resulted in the separation of these two products. The first fraction isolated contained 23 mg (8%) of a white solid, mp 65–66 °C, which was identified as *exo*-3,4-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**29**) by comparison with authentic material:[41] NMR (CDCl$_3$, 100 MHz) δ 0.71 (t, 1 H, J = 4.0 Hz), 1.20–1.33 (m, 5 H), 1.76 (s, 3 H), 2.51 (q, 1 H, J = 7.0 Hz), 6.88–7.25 (m, 10 H). The second fraction consisted of an inseparable mixture of *exo*- (**29**) and *endo*-3,4-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**30**), which could not be separated upon extensive chromatography. The endo isomer **30** showed the following NMR spectrum (CDCl$_3$, 100 MHz): δ 0.72 (t, 1 H, J = 4.0 Hz), 1.10 (d, 3 H, J = 7.0 Hz), 1.19–1.32 (*m*, 1 H), 1.56 (dd, 1 H, J = 9.0 and 4.0 Hz), 1.64 (s, 3 H), 3.27 (p, 1 H, J = 7.0 Hz), 6.85–7.22 (m, 10 H).

The second fraction isolated from the original chromatography contained 6 mg (2%) of a yellow oil, which was identified as 3,4-dimethyl-1,2-diphenyl-2,5-hexadien-1-one (**31**) on the basis of its characteristic NMR spectrum: (CDCl$_3$, 100 MHz) δ 1.17 (d, J = 7 Hz, 3 H), 1.63 (s, 3 H), 3.32–3.54 (m, 1 H), 4.88–5.18 (*m*, 2 H), 5.86 (ddd, J = 18, 10, and 8 Hz, 1 H), 7.16–7.49 (m, 8 H), 7.87–8.00 (m, 2 H).

Silver-Induced Rearrangement of 3-(2-Methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (35) in Methanol. A solution containing 350 mg of a 1:1 diastereomeric mixture of 3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**35**)[41] and 350 mg of silver perchlorate in 30 mL of methanol was refluxed for 48 h in the dark. The mixture was extracted with ether, and the ether layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent left behind a yellow oil, which was chromatographed on a 1.5 × 100 cm silica gel column with hexane as the eluent. The major fraction isolated contained 317 mg (91%) of a colorless oil, which was identified as a 1:1 diastereomeric mixture of 2-methyl-1-phenyl-3-(1-methyl-2-propen-1-yl)indene (**36**) on the basis of its spectral properties: NMR (CDCl$_3$, 100 MHz) δ 1.40 and 1.42 (*d*, J = 7 Hz, 3 H), 1.80 (s, 3 H), 3.49–3.80 (m, 1 H), 4.17 (s, 1 H), 4.94–5.22 (*m*, 2 H), 5.92–6.29 (m, 1 H), 6.80–7.37 (m, 9 H); IR (neat) 3.27, 3.35, 3.40, 6.19, 6.69, 6.83, 9.30, 9.69, 10.95, 12.93, 13.26, 13.50, 14.31 μm; UV (95% ethanol) max 264 nm (ϵ 9480); mass spectrum, *m/e* 260 (M$^+$), 206, 205 (base). Anal. Calcd for C$_{20}$H$_{20}$: C, 92.26; H, 7.74. Found: C, 92.15; H, 7.84.

Silver-Induced Rearrangement of (*E*)-1-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (40) in Methanol. A solution containing 100 mg of (*E*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**40**)[39] and 100 mg of silver perchlorate in 20 mL of methanol was refluxed for 95 h in the dark. The solvent was removed under reduced pressure, and the residue was taken up in ether. The ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent left behind a dark yellow oil, which was chromatographed on a 1.5 × 100 cm silica gel column with hexane as the eluent. The first component isolated contained 36.4 mg (36%) of unreacted starting material. The second component contained 60.6 mg (61%) of a solid, mp 52–53 °C, which was identified as *exo*-3,6-dimethyl-1,2-diphenylbicyclo[3.1.0]hex-2-ene (**41**) by comparison with authentic material:[39] NMR (CDCl$_3$, 270 MHz) δ 0.97–1.00 (m, 4 H), 1.42 (dd, 1 H, J = 6.6 and 3.7 Hz), 1.63 (s, 3 H), 2.47 (d, 1 H, J = 18.0 Hz), 2.98 (dd, 1 H, J = 18.0 and 6.6 Hz), 6.97–7.19 (m, 10 H).

Silver-Induced Rearrangement of (*Z*)-1-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (42) in Methanol. A solution containing 150 mg of (*Z*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**42**)[39] and 150 mg of silver perchlorate in 30 mL of methanol was refluxed for 95 h in the dark. The solvent was removed under reduced pressure, and the residue was taken up in ether. The ethereal layer was washed with water and a saturated salt solution and dried over magnesium sulfate. Removal of the solvent left behind a dark yellow oil, which was chromatographed on a 1.5 × 100 cm silica gel column with hexane as the eluent. The first component isolated contained 77 mg (51%) of unreacted starting material. The second component isolated contained 56 mg (37%) of a colorless oil identified as *endo*-3,6-dimethyl 1,2-diphenylbicyclo[3.1.0]hex-2-ene (**43**) by comparison with authentic material:[39] NMR (CDCl$_3$, 270 MHz) δ 1.05 (d, 3 H, J = 5.9 Hz), 1.52 (dd, 1 H, J = 8.8 and 8.5 Hz), 1.89–1.94 (m, 1 H), 2.15 (d, 1 H, J = 18.0 Hz), 2.93 (dd, 1 H, J = 18.0 and 8.8 Hz) and 7.00–7.22 (m, 10 H).

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation.

Registry No. **3**, 67961-33-5; **4**, 67961-34-6; **5**, 55255-20-4; **6**, 65086-13-7; **10**, 50902-98-2; **11**, 52776-41-7; **12**, 77734-67-9; **15**, 73377-57-8; **16**, 73377-58-9; **17**, 73377-59-0; **18**, 82482-64-2; **19**, 82482-65-3; **21**, 74272-43-8; **22**, 62907-50-0; **23**, 62907-52-2; **24**, 82482-66-4; **25**, 70412-26-9; **26**, 70412-27-0; **27**, 66221-05-4; **28**, 82482-67-5; **29**, 74964-29-7; **30**, 82482-68-6; **31**, 82494-80-2; **32**, 62907-51-1; **33**, 62907-54-4; **34**, 71956-72-4; **35**, 70412-29-2; **36**, 82482-69-7; **37**, 70412-28-1; **38**, 82482-70-0; **39**, 82482-71-1; **40**, 66221-12-3; **41**, 73377-61-4; **42**, 66221-10-1; **43**, 73464-49-0; triphenylcyclopropenyl perchlorate, 51778-20-2; benzylmagnesium chloride, 6921-34-2; 2,3-diphenylindanone, 7474-64-8; 2-methylindanone, 17496-14-9; 3-benzyl-2-phenylindanone, 10273-47-9; phenylmagnesium bromide, 100-58-3; silver perchlorate, 7783-93-9.

Effect of Remote Substituents upon the Long-Range Aryl Migration and Electrocyclic Ring Opening of *exo*-3,3-Diaryltricyclo[3.2.1.$0^{2,4}$]octan-*anti*-8-yl Tosylates in Solvolysis[1,2]

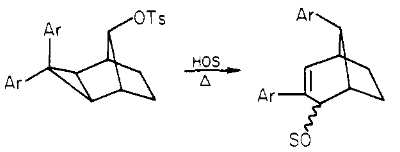
James W. Wilt,* Veronica A. Curtis, and Counde O-Yang[3]

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

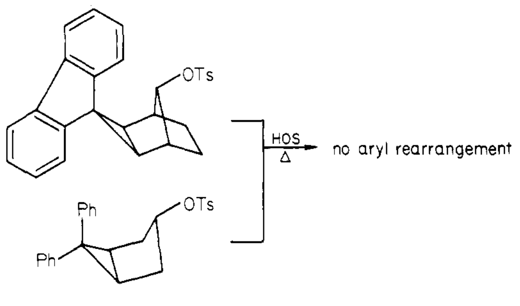
Received February 23, 1982

The processes of long-range aryl migration (LRAM) and electrocyclic ring opening (ERO) that occur in the solvolysis of the title substrates have been investigated with respect to their relative timing. By substituting an electron-withdrawing group (CN) or an electron-donating group (Et) in these substrates at the site of potential cationic charge development as ERO occurs, it has been determined that large rate differences in such substituted substrates are observed (>10^3). Moreover, the rate ratios of *p*-tolyl substrates to phenyl substrates in migration (LRAM) are not constant but rather increase as ERO becomes more facile. The mechanistic conclusion drawn from these results is that LRAM and ERO do occur in concert (LRAMERO) but not in synchrony in all cases. Instead, a continuum of LRAMERO transition states is proposed, with an approach to synchrony as ERO becomes more and more facile. Additionally, the synthesis and characterization of the title compounds and the intermediates involved in their (at times lengthy) synthesis are described.

Introduction

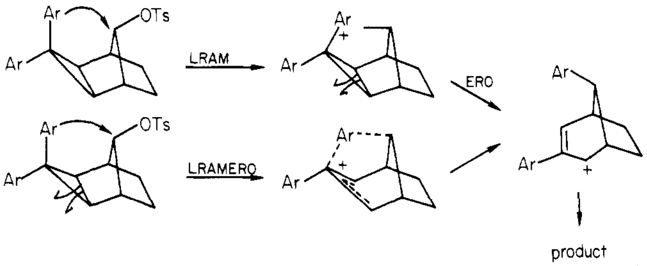


(1)

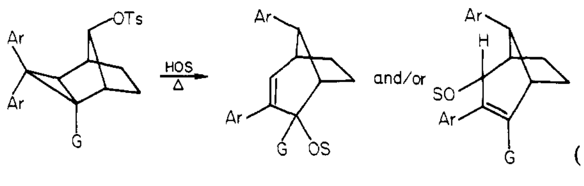


(2)

The solvolytic rearrangement shown in eq 1 presents some fascinating problems in mechanistic investigation. Earlier work from this laboratory has delineated reasonably clearly the overall course of the reaction: anchimeric participation of the Ar_1-5 type is involved; the reaction is clean, with essentially total conversion to the rearranged epimers shown;[4] a change to the fluorenylidene group or to a less rigid alicyclic framework (eq 2) eliminates the rearrangement.[5] But a vexing question remained. Is the long-range aryl migration (LRAM) antecedent to or concomitant with the disrotatory electrocylic ring opening (ERO) of the cyclopropane moiety (eq 3)? The suggestion was previously advanced that the two processes are in concert (LRAMERO), based upon the rather low ρ^+ values for the process (−1.68 for hydrolysis at 112 °C, −1.30 for acetolysis at 110.5 °C) and the slight retardation in solvolysis rate exhibited by the analogous tosylate possessing a Δ^6 double bond.[4] In the present study, this question has been pursued in another way. Placement of electron-donating or electron-withdrawing groups at putative cationic centers has long been a favorite probe for mechanistic study.[6] It was therefore hoped that LRAMERO could be distinguished from LRAM/ERO (the stepwise alternative) by noting the effect of such groups G upon the rate of solvolysis of compounds shown in eq 4. In principle, an



(3)



(4)

---

[1] Electrocyclic Effects in Solvolysis. 5. Part 4: Wilt, J. W.; Niinemae, R. *J. Org. Chem.* **1980**, *45*, 5402.

[2] Taken in part from the Dissertation of C.O-Y., Loyola University of Chicago, Dec 1979.

[3] Petroleum Research Fund Fellow, 1976–1978.

[4] Wilt, J. W.; Malloy, T. P.; Mookerjee, P. K.; Sullivan, D. R. *J. Org. Chem.* **1974**, *39*, 1327.

[5] Wilt, J. W.; Kurek, J.; Roberts, W. N. *J. Org. Chem.* **1980**, *45*, 4243.

[6] Such a probe forms the basis for the structure–reactivity concept developed for essentially all carbocationic reactions.

0022-3263/82/1947-3721$01.25/0