Preparation, X-ray Crystal Structures, and Reactivity of Alkynylcyclopropenylium Salts

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Several 1,2-diphenyl-3-alkynylcyclopropenes were prepared by the reaction of acetylenic nucleophiles with diphenylcyclopropenylium perchlorate. The cyclopropenes were converted into alkynylcyclopropenylium salts via hydride abstraction with triphenylmethyl cation. Attempts to prepare a dication from either ethyne-bridged or butadiyne-bridged biscyclopropenes produced only the corresponding monocations. A dication was prepared when an ethylene spacer was inserted between the acetylene groups of the butadiyne-bridged biscyclopropene. Single-crystal X-ray structures of three of the cyclopropenylium ions were obtained. pK_{R+} titrations were carried out on two of the salts, which showed that acetylene substituents provide about the same degree of stability to the cyclopropenylium core as a phenyl group. Nucleophilic addition to the alkynylcyclopropenylium ions under kinetic conditions gave a statistical mixture of products; however, under thermodynamic reaction conditions, nucleophilic addition followed by ring opening produced only one of three possible products. Calculations at the ab initio level were carried out to determine the charge distribution of the cations.

Introduction

Although numerous derivatives of the cyclopropenylium ion have been prepared during the past 40 or more years,[1] there are very few cyclopropenylium ions that are conjugated with substituents other than phenyl groups or heteroatoms. While theoretical treatments of cyclopropenylium ions with acetylene substituents have been published,[2] we were unaware of the preparation or characterization of this type of system. Diederich et al. have reported a tris(trimethylsilylethynyl)cyclopropenylium ion as a highly reactive intermediate; however, this molecule proved to be unstable at temperatures above −40 °C and could not be isolated.[3] A recent report by Komatsu described the preparation of related alkynyl-substituted tropylium ions[4] including an ethyne-bridged ditropylium ion. For an affiliated project using functionalized *cis*-3-(2-halovinyl)cyclopropenes as ligands for metallabenzene formation,[5] we required a number of 3-alkynylcyclopropenes. Since the conversion of cyclopropenes to cyclopropenylium ions is generally trivial, a unique opportunity to observe the interaction of acetylenic moieties with the three-membered cyclopropenylium ring presented itself. We report herein the preparation of several 3-alkynylcyclopropenes and their subsequent conversion into alkynylcyclopropenylium salts.

Results and Discussion

Hydride abstraction from cyclopropenes is one of several methods used to prepare cyclopropenylium ions.[1] This technique was particularly attractive in our study because of the ease of preparing the cyclopropene precursors. Although reports of the requisite 3-alkynylcyclopropenes are limited,[6] there are many preparations of cyclopropenes involving cyclopropenylium ions and various nucleophiles.[7] Cyclopropenylium ions are highly electrophilic and their reactions with nucleophiles ordinarily proceed in high yields. While reactions of trisubstituted cyclopropenylium cations often show little or no regioselectivity, regardless of the ring substituents, disubstituted cyclopropenylium cations are attacked preferentially at the unsubstituted position.[1]

Cyclopropene and Cyclopropenylium Syntheses. Treatment of 1,2-diphenylcyclopropenylium perchlorate (**1**)[8] with the appropriate acetylenic nucleophile in THF at −78 °C afforded cyclopropenes **2a**−**d** in good to excellent yields (Scheme 1). The trimethylsilyl group of **2a** was readily removed by K_2CO_3 in methanol and ether to give the terminal acetylene **3** in quantitative yield. Cyclopropene **3** was then converted into a 1,4-bis(cyclopropenyl)-1,3-butadiyne system (**4**) using a modified Eglinton−Glaser reaction.[9] The blue to green color change of the reaction was accompanied by precipitation of the dimeric cyclopropene, making isolation of **4** elementary. The reaction was somewhat temperature sensitive; in one case a temperature range of 55−60 °C resulted in a brown solution and a significant reduction in yield. The corresponding ethynyl-linked biscyclopropene **5** was pre-

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(1) For a comprehensive review of the cyclopropenylium ion, see: Komatsu, K.; Yoshida, Z. In *Methods of Organic Chemistry (Houben-Weyl)*; de Meijere, A., Ed.; Thieme: Stuttgart, 1996; Vol. E17d, pp 3079−3192.

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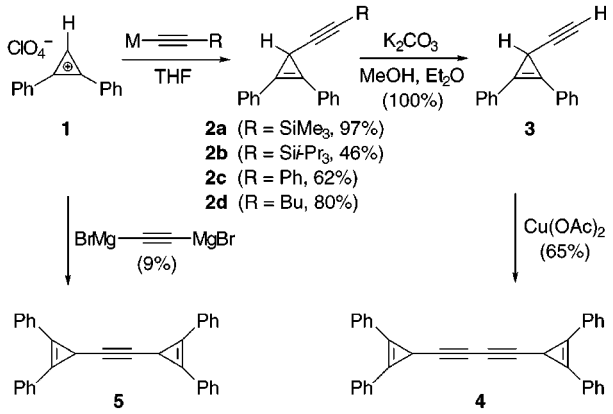
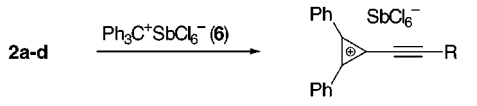
Scheme 1



Scheme 2



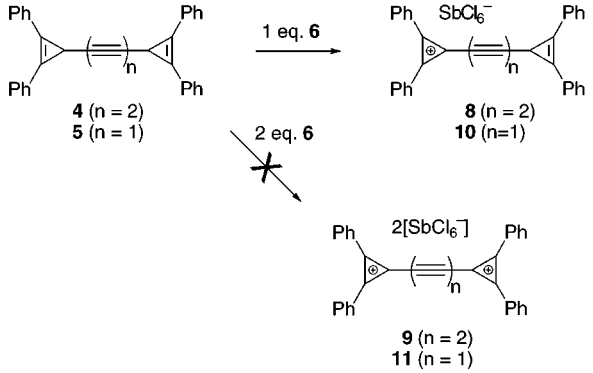
7a (R = $SiMe_3$, 74%)
7b (R = Si-Pr_3, 70%)
7c (R = Ph, 66%)
7d (R = Bu, 71%)

pared in low yield by treating **1** with 0.5 equiv of ethynyldimagnesium dibromide.

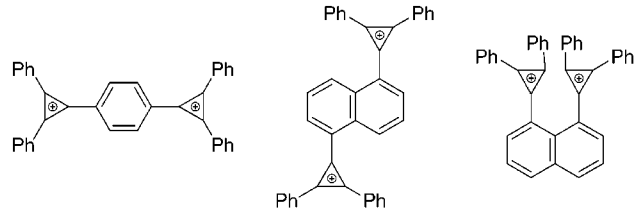
Cyclopropenylium salt **7a** was generated in CH_2Cl_2 by hydride abstraction from **2a** with triphenylmethyl hexachloroantimonate (**6**, Scheme 2). The initial orange color of the solution gradually developed a greenish tint, whereupon addition of ether to the mixture precipitated **7a** as a yellow powder in 74% yield. An analogous procedure was used to prepare salts **7b**−**d** with similar yields. The salts were all readily recrystallized from acetonitrile. Attempts to prepare a terminal alkynylcyclopropenylium ion from **3** using the same methodology led to an unidentified dark brown powder (presumably a polymer or decomposition product) which showed several broad resonances in the ^{1}H NMR spectrum. Cyclopropenylium salts **7a**−**d** were relatively stable in the solid state. Their ^{1}H NMR spectra remained unchanged after several months of storage at ambient temperature. Solutions of **7a**−**d** in CD_3CN could be stored at −35 °C for several weeks with no evident discoloration or decomposition. Room temperature solutions darkened after 24 h yet remained spectroscopically homogeneous.

Cyclopropene **4** was also subjected to hydride abstraction using triphenylmethyl ion (Scheme 3). When 1 equivalent of **6** was employed, monocation **8** was observed by ^{1}H NMR spectroscopy. The cyclopropenylium salt was precipitated from CH_2Cl_2 on addition of ether to give a bright yellow powder that was quite sensitive to atmospheric moisture. Attempts to isolate the powder by vacuum filtration caused the material to decompose to a brown, oily solid within seconds of exposure to the air. By conducting the filtration in a stream of N_2, the cyclopropenylium ion could be isolated without extensive decomposition. Efforts to purify **8** by recrystallization were hampered by its low stability; thus, the molecule was not isolated in analytically pure form. Use of 2 equiv of **6** in the reaction with **4** surprisingly failed to produce **9**; only monocation **8** was observed in the ^{1}H NMR spectrum. Hydride abstraction from **5** with 1 equiv of **6** similarly gave monocation **10** in moderate yield after

Scheme 3



precipitation with ether. Cation **10** was significantly more stable than **8** toward moisture, as there were no problems with decomposition of **10** during isolation. Use of 2 equiv of **6** in the reaction with cyclopropene **5** again furnished only the corresponding monocation **10** and no dication **11**.



12 **13** **14**

It is noteworthy that only monocations were produced in both cases in Scheme 3, considering that a number of cyclopropenylium dications have been reported.[10] Most of the reported dications contained heteroatom substituents,[10a−h] which significantly increase the stability of the ions, or were linked through an alkyl chain which precluded conjugation of the ions.[10i] There are a few examples of two cyclopropenylium ions linked by a phenyl (**12**) or naphthyl group (**13** and **14**), which allows conjugation of the cations through the linker.[10j−l] Additionally, a ditropylium cation was recently prepared in which the two cationic cores were connected by an acetylene moiety.[4] The tropylium cation, however, is inherently more stable than the cyclopropenylium cation since the positive charge is delocalized over seven sp^2 carbon atoms versus the three sp^2 carbon atoms in the cyclopropenylium ions.

Although one cannot make direct comparisons regarding stability between tropylium and cyclopropenylium cations, comparisons of the stability changes in the respective ions relative to substituent changes should be valid. For example, the first pK_{R+} of the ethyne-bridged ditropylium cation was lowered by 5−6 units compared

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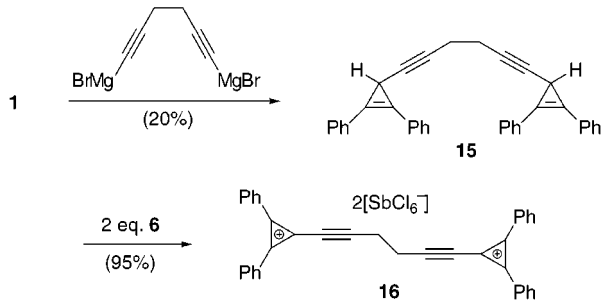
Scheme 4



with similar monotropylium ions. In addition, the second neutralization revealed that the pK_{R+} of the half-neutralized ion changed little from similar tropylium ions. The exceptional destabilization of the dication was attributed to electrostatic repulsion of the two cationic centers.[4] It is likely that a similar destabilization would occur in an alkynyl-bridged dicyclopropenylium dication like **9** or **11**. The pK_{R+} of a cyclopropenylium ion is already well below the pK_{R+} of the corresponding tropylium ion. Accordingly, a similar drop in the pK_{R+} of **9** or **11** may lower the pK_{R+} enough to make these dications inaccessible through hydride abstraction. To remove a hydride from a cyclopropene, the product cyclopropenylium ion must have a pK_{R+} that is larger than the triphenylmethyl cation. Therefore, an upper limit of −6.63 (the value of the triphenylmethyl ion)[11] can be placed on the pK_{R+} values of **9** and **11**.

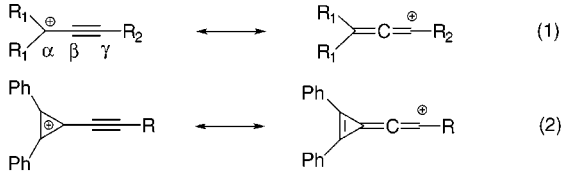
To determine if the alkyne linkages of **4** and **5** were inhibiting formation of the dications, cyclopropene **15** was prepared from the di-Grignard reagent derived from 1,5-hexadiyne and 2 equiv of **1** (Scheme 4). The ethylene spacer of **15** served to eliminate any conjugation between the acetylene groups, so the ionic centers produced in **16** should not influence each other greatly. When **15** was treated with 2 equiv of **6** in CH_2Cl_2, a yellow solid immediately precipitated from the solution whose spectral data were consistent with the dicationic structure shown in Scheme 4. The ^{1}H NMR spectrum, however, showed significant contamination from unknown impurities. The dication was sparingly soluble in acetonitrile at ambient temperature, and attempts to purify **16** by recrystallization from boiling acetonitrile resulted in decomposition of the material. An alternate preparation, in which the dication was generated in acetonitrile and crystallized by cooling the reaction solution to −35 °C, provided brown crystals of **16** in 95% yield. Although **16** was stable indefinitely in the absence of solvent, it decomposed (possibly through a Ritter-type reaction) in the presence of CD_3CN over a 24 h period when stored at 5 °C. In contrast, no significant decomposition was observed after several days when stored in acetonitrile at −35 °C. Unfortunately, the poor solubility of dication **16** in CD_3CN prevented the acquisition of its ^{13}C NMR spectrum; dissolution in deuterated DMSO led to immediate decomposition.

Spectral Data. All of the cyclopropenylium salts show a strong absorption near 1400 cm^{-1} in their IR spectra, which is characteristic of cyclopropenylium ring stretching.[1] The cationic cores significantly deshield the phenyl protons, which is evident from downfield shifts of the corresponding signals in the ^{1}H NMR spectra of cyclopropenylium ions **7a**−**d** when compared to cyclopropenes **2a**−**d**.[12] Signals from the ortho and para protons of **7a**−**d** are shifted downfield by 0.65−0.70 ppm, while the meta protons are shifted by 0.35−0.40 ppm, both of which are consistent with resonance delocalization of the positive charge around the phenyl rings.

As expected, the ^{13}C NMR spectra also show significant shifts after the cyclopropenes are ionized. The resonances for the cyclopropenylium rings of **7a**−**d** appear at 155−157 ppm for the phenyl-substituted carbons and at 140−147 ppm for the alkyne-substituted carbons. The para carbons of the phenyl groups are shifted downfield by 11−12 ppm relative to benzene, whereas the ipso carbons are shifted upfield by 7−8 ppm. No definitive assignments of the ortho and meta carbons were made. For the purpose of unequivocal assignment of the ^{13}C NMR acetylene resonances, cyclopropene **2c** and cyclopropenylium ion **7c** were prepared with a ^{13}C label at the acetylene carbon adjacent to the phenyl ring. The ^{13}C-labeled carbon appeared at 74.66 ppm in **2c** and is shifted downfield to 126.90 ppm in **7c**. As expected, the alkyne stretches of ^{13}C-labeled **2c** and **7c** move to lower wavenumbers in the IR spectrum. The ^{1}H and ^{13}C NMR spectra of cations **7a**,**b** show only subtle differences with respect to the chemical shifts of the acetylene substituents opposite the three-membered ring when compared to the NMR spectra of cyclopropenes **2a**,**b**. The changes in chemical shifts of the corresponding acetylene substituents upon ionization of **2c**,**d** are somewhat larger for **7c**,**d**.

The electronic absorption spectra of cations **7a**,**b**,**d** look essentially identical to the spectrum of the triphenylcyclopropenylium ion (**17**), which is dominated by the phenyl $\pi-\pi^*$ transitions. For example, λ_{max} of **7a** is 304 nm, which corresponds well to the analogous absorption in **17** (307 nm).[13] The spectrum of **7c**, however, is more interesting because of extended conjugation of the pendant phenylacetylene moiety. In this instance, the bands of **7c** are shifted to longer wavelengths (λ_{max} = 317 nm), with the end absorption (380 nm) increased by ca. 30−40 nm relative to **7a** and **17**.

Distribution of Charge. For comparative purposes, we looked at the structurally related propargylic cations, which have been generated by ionization of propargyl alcohols in superacid solutions.[14] The significant downfield shifts in the ^{13}C NMR resonances of the γ carbons were explained by delocalization of the positive charge to the γ carbon in the allenic resonance structure shown in eq 1. The ^{13}C NMR data for alkynylcyclopropenylium



ions **7a**−**d** also suggested a contribution from an allene-

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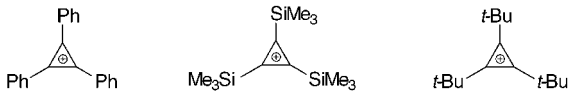
type resonance structure, albeit to a much smaller degree (eq 2). In **7a**−**d** the γ carbon was shifted 25−60 ppm downfield, whereas in a typical propargylic cation the corresponding carbon was shifted downfield by as much as 150 ppm.[14] A smaller contribution from an allene-type resonance structure is expected for alkynylcyclopropenylium ions compared to propargyl cations since the cyclopropenylium ions are aromatic. Thus, the degree of aromaticity would be lowered by delocalization of the charge to the acetylene moiety. Also, the charge at each ring carbon should be significantly smaller than the charge on a typical propargyl cation because of charge delocalization throughout the cyclopropenylium ring.

Thermodynamic Stability. The thermodynamic stability of a cyclopropenylium ion can be determined by measuring the pK_{R+} value of the ion.[1] Most pK_{R+} values are acquired using either spectrophotometric titration or potentiometric titration. In our case, the pK_{R+} values of **7a** and **7c** were measured using the standard potentiometric method in 50% aqueous acetonitrile. The titrations gave classical pH curves, and the pK_{R+} values were taken as the pH of the solutions at the equivalence points. An average of at least three runs for each cation gave values of 2.93 and 3.00 for **7a** and **7c**, respectively. The pK_{R+} of **17** was measured at 3.15 using the same technique.[13] On the basis of these values, the acetylene substituents appear to have roughly the same capacity to stabilize the ions as a phenyl group. Additionally, the acetylene substituents opposite the ion did not appear to have a significant effect on the stability of the ions in these two cases. The data however is restricted to observations of only two systems and cannot be called comprehensive by any means. Electron-donating substituents have been shown to dramatically increase the pK_{R+} values of cyclopropenylium ions[15] as well as other cations.[11] Therefore, replacement of the acetylene substituents of **4a** and **4c** with electron-donating groups such as dialkylamino or alkoxy groups should increase the pK_{R+} of the resulting cyclopropenylium ions.



17 **18** **19**

Crystal Structure Analysis. Single crystals of **7a**−**c** were grown from acetonitrile by cooling solutions of the salts to −30 °C. Data sets for all three structures were collected at 295 K. The ORTEP views of **7a**−**c** are shown in Figures 1−3 respectively, and pertinent bond lengths and bond angles are given in Table 1. Many of the features are typical of cyclopropenylium ions, although some interesting distortions, most likely due to packing effects, are evident. The acetylenic carbon attached to the cyclopropenylium ring (C4) in **7a** is bent slightly out of the plane of the three-membered ring by a distance of 0.088 Å. The adjacent acetylene carbon (C5) and the terminal silicon atom are further bent out of the plane of the three-membered ring with increasing magnitudes of 0.304 and 0.804 Å, respectively. Furthermore, the acetylene bond angles of **7a** are distorted from linearity

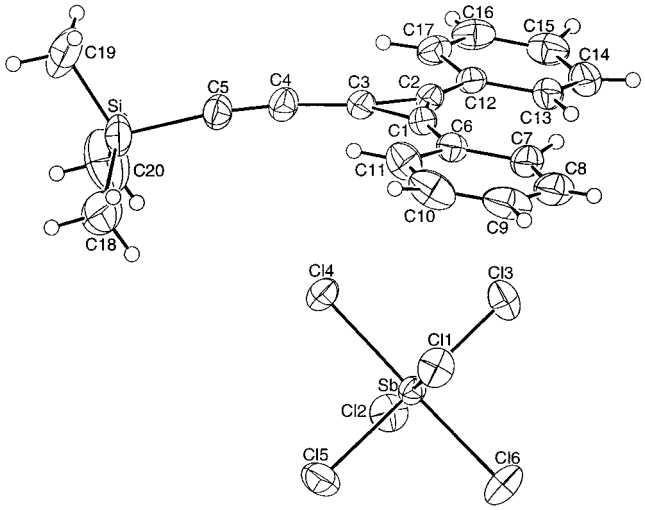


Figure 1. Molecular structure of **7a**. Ellipsoids are drawn at the 30% probability level.

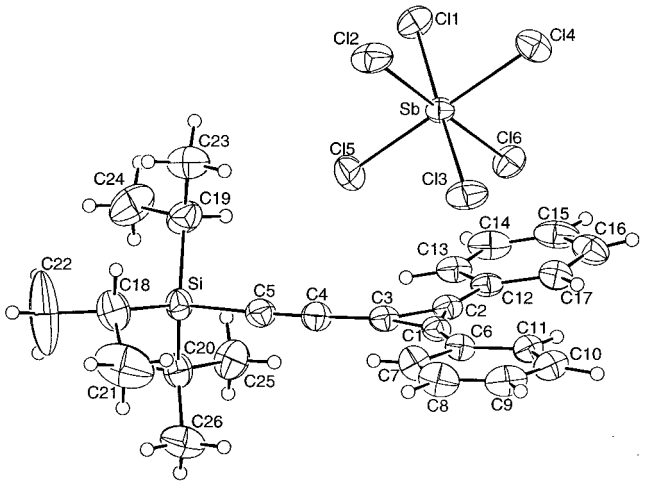


Figure 2. Molecular structure of **7b**. Ellipsoids are drawn at the 30% probability level.

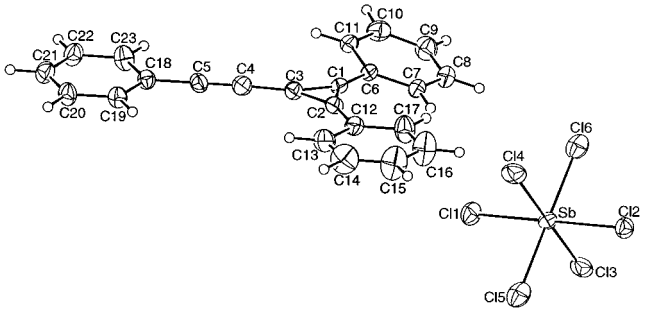


Figure 3. Molecular structure of **7c**. Ellipsoids are drawn at the 30% probability level.

ca. 7° in the plane of the cyclopropenylium ring (Table 1). Similar effects have been observed in both the tris(trimethylsilyl)cyclopropenylium[16] (**18**) and the tri-*tert*-butylcyclopropenylium[17] (**19**) cations and have been attributed to close contacts between the ring carbons and

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Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Phenyl Twist Angles (deg) for Cyclopropenyliums 7a−c and 17

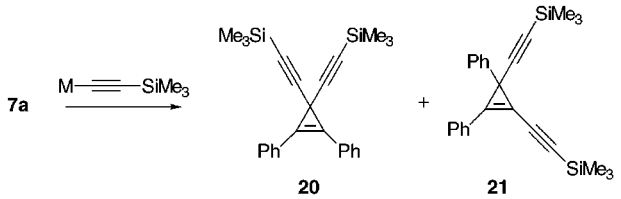
	17[a]	7a	7b	7c
C(1)−C(2)	1.373	1.379(4)	1.375(4)	1.364(7)
C(1)−C(3)		1.365(4)	1.358(4)	1.363(7)
C(2)−C(3)		1.368(4)	1.367(5)	1.362(7)
C(3)−C(4)	1.436	1.401(4)	1.397(5)	1.402(7)
C(4)−C(5)		1.189(4)	1.201(5)	1.183(7)
C(3)−C(4)−C(5)		173.1(4)	172.6(4)	178.0(6)
C(4)−C(5)−R		173.5(4)	172.8(3)	178.4(6)
C(2)−C(3)−C(4)		150.9(4)	145.5(3)	150.3(6)
twist angle[b]	13.6[c]	5.7, 7.6	2.7, 5.9	2.8, 14.6

[a] Reference 18. [b] The twist angle refers to the dihedral angles between the planes of the phenyl groups in the 1 and 2 positions and the cyclopropenylium ring. [c] Average of all three phenyl groups.

the chlorine atoms of the counterion. The magnitude of the out-of-plane bend of C(4) in **7a** is nearly identical to that observed for **19** (0.090 Å), yet the distortion is twice as large as that reported for **18** (0.044 Å). For **18**, the closest contact distance between a ring carbon and counterion is 3.460 Å. The smallest corresponding intermolecular distance in **7a** is 3.394 Å between Cl(5) and C(3), significantly smaller than in **18**. Therefore, the out-of-plane bending in **7a** can confidently be ascribed to this intermolecular contact. Similar out of plane bending distortions are evident in **7b**, although not as large as those observed in **7a** (Table 1). In **7c**, the out-of-plane bending distortions are considerably smaller than in **7a** or **7b**, with the acetylene bond angles being nearly linear at 178.4° and 178.0°. The hexachloroantimonate ion in **7c** is oriented to the side of the plane containing the cyclopropenylium ring rather than above the ring as in **7a** and **7b**. Consequently, the only intermolecular contacts between the cyclopropenylium ring and the $SbCl_6^-$ ion under 3.6 Å are Cl(1)−C(20) and Cl(6)−C(4) at 3.594 and 3.512 Å, respectively. Because there are no evident intermolecular interactions between the ring and the counterion in **7c**, the bond lengths of the cyclopropenylium ring are nearly identical (1.364, 1.363, and 1.362 Å). The structure of **7a**, however, does show a disparity in the bond lengths in the cyclopropenylium ring. The C(1)−C(2) (1.379 Å) bond is slightly longer than either the C(2)−C(3) (1.368 Å) or the C(1)−C(3) (1.365 Å) bonds. Similar to **7a**, the structure of **7b** exhibits noticeable differences in cyclopropenylium ring bond lengths (Table 1).

The structure of the triphenylcyclopropenylium ion[18] (**17**) revealed a propeller like twist in all three of the phenyl groups about the cyclopropenylium ring with an average value of 13.6°. Twisting of this sort, caused by interaction of the ortho hydrogen atoms of the phenyl groups, has been observed in other diphenylcyclopropenylium ions as well.[19] In the structures of **7a**−**c**, the phenyl groups are also twisted about the cyclopropenylium core; however, the addition of the linear acetylene moiety effectively eliminates any steric interactions between the phenyl groups in the 1 and 2 positions of the three membered ring and the acetylene group. As a result, the twisting of the phenyl groups in **7a**−**c** is of smaller magnitude than that in **17** (Table 1). For example, the twist angles of the phenyl groups in **7b** are

Scheme 5



2.7° and 5.9°, compared to 13.6° as previously determined in **17**. In **7a** the phenyl groups are rotated 5.7° and 8.6° with respect to the cyclopropenylium plane; however, both rotations are in the same direction relative to the cyclopropenylium core. Accordingly, the planes of the phenyl groups in **7a** have a dihedral angle of 3.0° which still provides some relief of the strain caused by interaction of the ortho hydrogen atoms.

Reactivity with Nucleophiles. One would expect a mixture of products from the reactions of **7a**−**d** with nucleophiles because of the lack of regioselectivity in the reaction of nucleophiles with trisubstituted cyclopropenylium ions. There is also a possibility of a conjugate addition of the nucleophile to the acetylene moiety, which has been observed in a similar system.[3] When the reaction of **7a** with a nucleophile was carried out under kinetic control, indeed, a mixture of products was observed. Treatment of **7a** with excess (trimethylsilyl)-ethynylmagnesium bromide at −78 °C gave a 1:2 mixture of products **20** and **21** (measured by ^{1}H NMR spectroscopy), respectively (Scheme 5). No products resulting from conjugate addition to the acetylene were detected in the crude mixture. Although the two molecules were virtually identical by TLC, purification of the oily **20**/**21** mixture by chromatography followed by crystallization from absolute ethanol afforded pure **20** as a white solid.

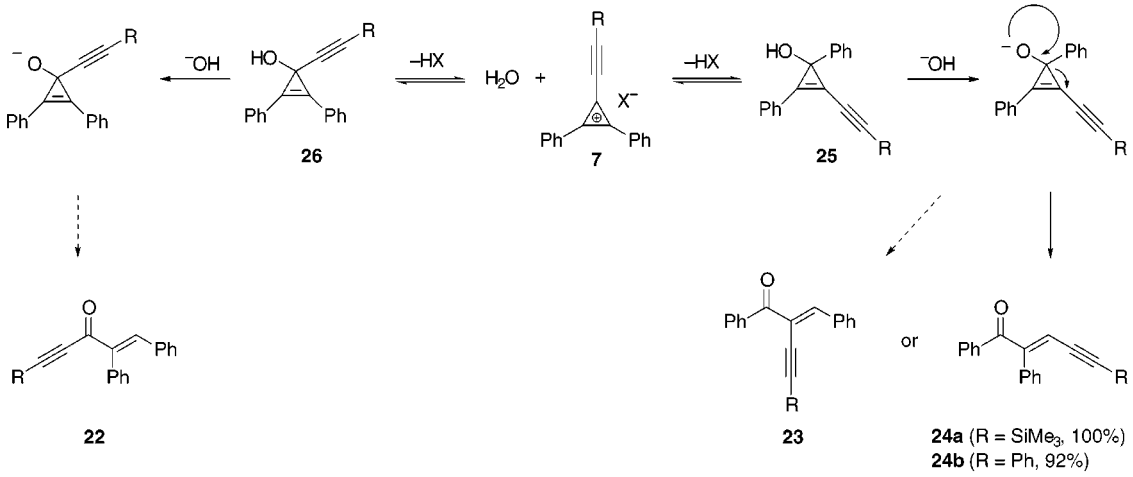
The results of nucleophile addition under thermodynamic conditions were markedly different. Cyclopropenylium ions **7a** and **7c** were titrated in aqueous acetonitrile (1:1 v/v) with 0.1 M NaOH in a manner consistent with that described for determination of pK_{R+} values. While standing in basic solution the resultant cyclopropenols underwent ring opening as depicted in Scheme 6.[20] Of the three possible structural motifs (**22**−**24**) that could result from hydrolysis of the cyclopropenylium ring, only ketones **24a** and **24b** were observed. The stereochemistry of the double bonds in **24a** and **24b** was assigned in accord with that observed in the basic ring opening of **1**.[20] Once again, no evidence of conjugate addition to the acetylenic carbon was encountered. ^{1}H NMR spectra for **24a** and **24b** showed a resonance attributed to the vinyl protons at 6.31 and 6.57 ppm, respectively. Chemical shifts of α-styrene protons generally appear at 7 ppm or higher; therefore, **22** and **23** were discounted as possible structures. To ascertain that the structures of **24a** and **24b** were correctly assigned, an independent synthesis of **24b** was carried out using an aldol condensation of deoxybenzoin and phenylpropargyl aldehyde. Spectroscopic data from the aldol product were identical to those of **24b**. Additionally, when **24a** was allowed to stand in basic solution for a period of ∼2 d, the $SiMe_3$ group was hydrolyzed. IR spectroscopic data of the resulting material was consistent with a terminal acetylene. The ^{1}H NMR spectrum of this compound

(18) Sundaralingam, M.; Jensen, L. H. *J. Am. Chem. Soc.* **1966**, *88*, 198−204.

(19) Sime, R. L.; Sime, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 892−896.

(20) For an example of ring opening of other cyclopropenols in basic solution, see: Farnum, D. G.; Burr M. *J. Am. Chem. Soc.* **1960**, *82*, 2651.

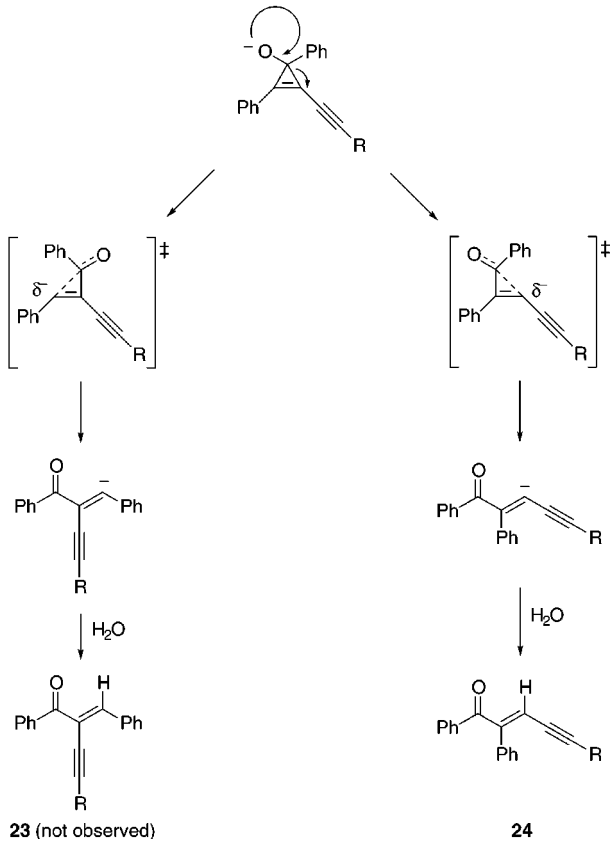
Scheme 6



showed J^4 coupling between the terminal acetylenic proton and the vinyl proton (J = 2.4 Hz), typical for an ene−yne system such as **24**.[21]

Previously published work dealing with the thermodynamic stability of 1,2-diphenylcyclopropenylium ions assumed that the hydroxyl nucleophile attacked the nonphenyl substituted carbon because of the resonance stabilization derived from stilbene-like conjugation in the cyclopropenol.[15b] If this were the case for the system shown in Scheme 6, one would still expect a single product from the reaction. However, the resultant molecule would be **22** and not **24**, which is the observed product. The most likely explanation of the nucleophile selectivity involves the distribution of the charge in the cyclopropenylium ion. In a nonsymmetrically substituted cyclopropenylium ion it is likely that the charge is not equally distributed to the three ring carbons. If one of the carbon atoms (for example, one of the phenyl-substituted carbons in **24**) was slightly more electrophilic than the other ring carbons, the incoming nucleophile would preferentially attack that carbon. This argument, of course, neglects any steric directing effects of the ring substituents of **7a** and **7b**. However, any steric interactions between the incoming nucleophile and cyclopropenylium substituents should be relatively small because of the planarity of the cyclopropenylium ring and of the phenyl groups (Figures 1 and 3). Since the addition of water to cyclopropenylium ions is reversible at low pH,[1] the equilibrium in Scheme 6 would be driven toward cyclopropenol **25** when the pH of a solution containing **7** is slowly increased. Indeed, theoretical calculations on **7a** predict that the positive charge is not symmetrically distributed. NBO analysis of the HF/6-31G* wave function indicated that the phenyl-substituted ring carbons (+0.19) were slightly more electropositive than the alkyne-substituted carbon (+0.13).[22] Although this result explains the preference of **25** over **26** (and thus **24** over **22**), ring opening of **25** could still lead to either **23** or **24**. The explanation of selectivity in the ring opening stems from stabilization of the developing negative charge in the transition state provided by the acetylene moiety as

Scheme 7



depicted in Scheme 7. Apparently the acetylene is more effective at stabilizing the developing negative charge in the transition state than the phenyl group. Considerable stabilization of vinylic anions by acetylenes has been documented both theoretically and experimentally in several vinylacetylenes.[23]

In conclusion, we have synthesized several alkynylcyclopropenylium cations from the corresponding 3-alkynylcyclopropenes by hydride abstraction with triphenylmethyl ion. While the monocations were prepared easily in very good yields, we were unable to generate alkyne-bridged dications using this method. A dication, however, was prepared when an ethylene spacer was inserted between the two acetylenes in a butadiyne-bridged biscyclopropene. As detailed within this report, the chemical and physical properties of these novel cations have been

(21) Silverstein, R. B.; Webster, F. R. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1998.

(22) Calculations were performed on a SGI workstation using Spartan molecular modeling software (Version 5.0).

(23) Brandsma, L.; Hommes, H.; Verkruijsse, H. D.; Kos, A. J.; Neugebauer, W.; Baumgärtner, W.; Schleyer, P. v. R. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 286−295.

studied thoroughly in the solution and in the solid state. Further experiments exploring the reactivity of 3-alkynylcyclopropenes are currently in progress. The results of these studies will be published shortly.

Experimental Section

General. Triphenylmethyl hexachloroantimonate (**6**) was purchased from Lancaster Synthesis and used as received. Phenylethyne, bromoethane, deoxybenzoin, (triisopropylsilyl)-ethyne, ^{13}C-labeled acetophenone, and magnesium turnings were purchased from Aldrich Chemical Co. and used as received. (Trimethylsilyl)ethyne and 1,5-hexadiyne were purchased from Farchan Chemicals and were used as received. Diphenylcyclopropenylium perchlorate (**1**) was prepared according to the literature.[8] Reagent grade pyridine and dioxane were used without further purification. THF and diethyl ether were distilled from sodium/benzophenone ketyl immediately prior to use. Acetonitrile was distilled from CaH_2 and stored over 4 Å molecular sieves. Dichloromethane was distilled from CaH_2 immediately prior to use. ^{1}H and ^{13}C NMR spectra were acquired at 299.95 and 75.43 MHz, respectively. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane using the residual solvent signal as an internal standard. Coupling constants are reported in hertz. Elemental analyses were performed by Robertson Microlit Laboratories.

1,2-Diphenyl-3-(trimethylsilylethynyl)cyclopropene (2a). Ethylmagnesium bromide was prepared from magnesium (0.30 g, 12 mmol) and dropwise addition of bromoethane (1.30 g, 12 mmol) in THF (20 mL). Once the addition of bromoethane was complete, the reaction was heated at reflux for 20 min. The suspension was then cooled to 0 °C under an atmosphere of N_2 and (trimethylsilyl)ethyne (1.4 g, 14 mmol) was added quickly via syringe. The resulting gray suspension was stirred at 0 °C for 15 min with the evolution of ethane gas. The mixture was then warmed to ambient temperature and stirred for an additional 15 min. THF (10 mL) was added to dissolve the solids.

In a separate flask THF (175 mL) was cooled to −78 °C under N_2, and diphenylcyclopropenyl perchlorate (**1**) (0.73 g, 2.5 mmol) was added to the cold THF. The solution of (trimethylsilyl)ethynylmagnesium bromide was added to the cold suspension of **1** using a double-ended needle under N_2 pressure over a 5 min period. The flask was rinsed with THF (10 mL) and the rinse was added to the suspension of **1**. After stirring at −78 °C for 1 h, the cooling bath was removed and the mixture was stirred at ambient temperature for 3 h. Excess Grignard reagent was quenched with saturated aqueous NH_4-Cl. Ether and water were added. The phases were separated, and the aqueous phase was extracted with ether. The combined organics were washed with water, saturated $NaHCO_3$ solution, and brine. The organic layer was dried ($MgSO_4$) and filtered through Celite. Removal of solvents by rotary evaporation gave a crude yellow oil which was purified by preparative radial thin-layer chromatography (2 mm rotor, hexanes) to give 0.70 g (97%) of a white solid. **2a**: mp 97−98 °C; ^{1}H NMR ($CDCl_3$) δ 7.76 (d, J = 7 Hz, 4H), 7.50 (t, J = 7 Hz, 4H), 7.40 (t, J = 7 Hz, 2H), 2.62 (s, 1H), 0.13 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 129.69, 128.99, 128.81, 127.92, 111.16, 109.96, 78.14, 8.38, 0.26; IR (KBr) 2158, 1836 cm^{-1}; UV (CH_3CN) 295, 308, 326 nm. Anal. Calcd for $C_{20}H_{20}Si$: C, 83.28; H, 6.99. Found: C, 83.15; H, 7.05.

1,2-Diphenyl-3-(triisopropylsilylethynyl)cyclopropene (2b). (Triisopropylsilyl)ethyne (0.40 g, 2.2 mmol) was dissolved in ether (10 mL) and cooled to 0 °C under N_2. Butyllithium (0.7 mL of 2.5 M solution in hexanes, 1.8 mmol) was added via syringe and the reaction was stirred at 0 °C for 20 min. The solution was warmed to room temperature and stirred for 30 min. The lithium acetylide solution was added to a cold (−78 °C) suspension of diphenylcyclopropenyl perchlorate in THF (75 mL) using a double-ended needle under N_2 pressure. The suspension stirred for 1 h at −78 °C and 12 h at −20 °C. The resulting solution was concentrated to ∼20 mL by rotary evaporation. Ether was added and the solution was washed with saturated NH_4Cl solution and brine. The organic phase was dried ($MgSO_4$) and concentrated to give a yellow oil. The oil was purified by preparative radial thin-layer chromatography (2 mm rotor, petroleum ether) to yield 0.122 g (46%) of a colorless oil. **2b**: ^{1}H NMR ($CDCl_3$) δ 7.77 (d, J = 8 Hz, 4H), 7.50 (t, J = 8 Hz, 4H), 7.40 (t, J = 8 Hz, 2H), 2.64 (s, 1H), 1.04 (s, 21H); ^{13}C NMR ($CDCl_3$) δ 129.60, 128.88, 128.77, 128.09, 111.95, 111.45, 73.97, 18.65, 11.33, 8.47; IR (neat) 2157, 1834 cm^{-1}.

1,2-Diphenyl-3-(phenylethynyl)cyclopropene (2c). Phenylethynylmagnesium bromide, prepared from Mg (0.070 g, 2.9 mmol), bromoethane (0.29 g, 2.7 mmol), and phenylethyne (0.30 g, 2.9 mmol) in THF (5 mL) as described in the preparation of **2a**, was cooled to 0 °C. In a separate flask THF was cooled to −78 °C under a N_2 atmosphere and **1** (0.200 g, 0.688 mmol) was suspended in the cold THF. The solution of phenylethynylmagnesium bromide was added to the suspension of **1** using a double-ended needle and N_2 pressure. The suspension was stirred at −78 °C for 30 min and then at ambient temperature for 1 h. Workup of the reaction in a manner consistent with that described for **2a** gave an orange solid as the crude product. The solid was purified by preparative radial thin-layer chromatography (2 mm rotor, hexanes) to give 0.154 g (62%) of a light yellow solid. The solid was recrystallized from petroleum ether to yield colorless prisms. **2c**: mp 123−125 °C; ^{1}H NMR (CD_2Cl_2) δ 7.83 (dd, J = 7, 2 Hz, 4H), 7.54 (tt, J = 7, 2 Hz, 4H), 7.43 (tt, J = 7, 2 Hz, 2H), 7.40−7.30 (m, 2H), 7.28−7.20 (m, 3H), 2.80 (s, 1H); ^{13}C NMR (CD_2Cl_2) δ 132.09, 130.24, 129.71, 129.47, 128.69, 128.41, 127.90, 124.53, 111.94, 93.82, 74.67, 8.55; IR (KBr) 2226, 2198, 1830 cm^{-1}. Anal. Calcd for $C_{23}H_{16}$: C, 94.48; H, 5.52. Found: C, 94.46; H, 5.55.

^{13}C-Labeled Cyclopropene 2c. Ethylmagnesium bromide was prepared from Mg (0.058 g, 2.4 mmol) and bromoethane (0.23 g, 2.1 mmol) as described previously. ^{13}C-Labeled phenylethyne was prepared from ^{13}C-carbonyl-labeled acetophenone (0.250 g, 2.06 mmol) according to a standard procedure.[24] The labeled phenylethyne was added to the ethylmagnesium bromide solution, and the reaction was stirred at 0 °C for 45 min with the evolution of ethane. The resulting labeled Grignard reagent was added to a suspension of **1** (0.580 g, 2 mmol) in THF at −78 °C. Stirring was continued at −78 °C for 1 h and at ambient temperature for 14 h. Workup of the reaction was consistent with that for **2a**. The crude solid obtained was chromatographed on silica gel to give 0.257 g (54% based on **1**) of a white solid. **2c-^{13}C**: mp 124−125 °C; ^{1}H NMR (CD_2Cl_2) δ 7.83 (d, J = 7 Hz, 4H), 7.53 (t, J = 7 Hz, 4H), 7.43 (tt, J = 7, 2 Hz, 2H), 7.39−7.21 (m, 5H), 2.81 (d, J_{C-H} = 4 Hz, 1H); ^{13}C NMR (CD_2Cl_2) δ 132.11 (d, J = 2 Hz), 130.25, 129.73, 129.47, 128.73, 128.66, 128.42, 127.91, 111.95 (d, J = 2 Hz), 93.79, 74.66 (^{13}C label), 8.54 (d, J = 14 Hz); IR (KBr) 2166, 1830 cm^{-1}. Anal. Calcd for $C_{23}H_{16}$: C, 94.48; H, 5.52. Found: C, 94.36; H, 5.50.

1,2-Diphenyl-3-(1-hexynyl)cyclopropene (2d). 1-Hexynylmagnesium bromide was prepared from Mg turnings (0.077 g, 3.2 mmol), bromoethane (0.34 g, 3.2 mmol), and 1-hexyne (0.32 g, 3.9 mmol) in THF (10 mL) as described in the preparation of **2a**. In this case, however, the reaction was stirred at ambient temperature for 2 h to ensure complete deprotonation of the 1-hexyne. The resulting Grignard solution was added to a suspension of **1** (0.359 g, 1.23 mmol) at −78 °C in THF (25 mL). The reaction was stirred at −78 °C for 1 h then ambient temperature for 12 h. Workup in a manner consistent with the preparation of **2a** gave an orange oil that was purified by preparative radial thin-layer chromatography (2 mm rotor, hexanes) to yield 0.268 g (80%) of a pale yellow oil. **2d**: ^{1}H NMR (CD_2Cl_2) δ 7.75 (d, J = 7 Hz, 4H), 7.51 (t, J = 7 Hz, 4H), 7.41 (t, J = 7 Hz, 2H), 2.56 (s, 1H), 2.11 (td, J = 7, 1 Hz, 2H), 1.46−1.35 (m, 4H), 0.87 (t, J = 7 Hz, 3H); ^{13}C

(24) Negishi, E.-I.; King, A. O.; Tour, J. M. In *Organic Syntheses Collective Volume VII*, Freeman, J. P., Ed.; Wiley: New York, 1990; pp 63−66.

NMR (CD_2Cl_2) δ 130.14, 129.53, 129.42, 128.70, 112.76, 83.24, 74.67, 31.86, 22.51, 18.92, 13.95, 7.97; IR (neat) 1830 cm^{-1}.

1,2-Diphenyl-3-ethynylcyclopropene (3). Cyclopropene **2a** (0.46 g, 1.6 mmol) was dissolved in ether (10 mL) and methanol (30 mL). Anhydrous K_2CO_3 (0.24 g, 1.7 mmol) was added and the resulting suspension was stirred at ambient temperature for 18 h. Ether and water were added, the layers were separated, and the aqueous phase was extracted with ether. The combined organics were washed with brine and dried ($MgSO_4$). The suspension was filtered through Celite and concentrated to give 0.346 g (100%) of a light yellow solid. **3**: mp 93−95 °C; ^{1}H NMR (CD_2Cl_2) δ 7.77 (d, J = 7 Hz, 4H), 7.52 (t, J = 7 Hz, 4H), 7.43 (t, J = 7 Hz, 2H), 2.57 (d, J = 1 Hz, 1H), 1.76 (d, J = 1 Hz, 1H); ^{13}C NMR δ (CD_2Cl_2) 130.18, 129.79, 129.47, 128.11, 111.22, 87.81, 62.29, 7.46; IR (KBr) 3281, 2102, 1837 cm^{-1}; UV (CH_3CN) 294, 307, 325 nm.

1,4-Bis(2,3-diphenylcycloprop-2-enyl)-1,3-butadiyne (4). Cyclopropene **3** (0.10 g, 0.46 mmol) and cupric acetate (0.25 g, 1.2 mmol) were suspended in pyridine (1 mL), water (0.7 mL), and dioxane (0.5 mL). The suspension was warmed with stirring to 45 °C, and all solids were dissolved to give a blue solution. A precipitate started to form after 20 min at 45−50 °C. After a total of 2 h of stirring at 45−50 °C, during which the blue color gradually changed to green, the flask was cooled to 0 °C and the precipitate was collected by filtration. The tan precipitate was washed with 10% HCl solution and water and then dried in vacuo. The precipitate was recrystallized from benzene (∼2 mL) to give 0.065 g (65%) of white needles. **4**: mp 183 °C (discoloration), 211−213 °C (decomposed to a black tar); ^{1}H NMR ($CDCl_3$) δ 7.74 (d, J = 7 Hz, 8H), 7.69 (t, J = 7 Hz, 8H), 7.37 (t, J = 7 Hz, 4H), 2.59 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 129.73, 129.15, 128.84, 127.45, 110.41, 79.64, 59.79, 7.83; IR (KBr) 2127, 1828 cm^{-1}. Anal. Calcd for $C_{34}H_{22}$: C, 94.85; H, 5.15. Found: C, 95.15; H, 4.95.

Bis(2,3-diphenylcycloprop-2-enyl)ethyne (5). A 0.5 M solution of ethynyldimagnesium dibromide in THF was prepared according to the literature procedure.[25] A portion of the solution (1.4 mL, 0.70 mmol) was diluted with THF (50 mL) and cooled to −78 °C under N_2. Diphenylcyclopropenyl perchlorate (0.209 g, 0.718 mmol) was added to the cold Grignard solution and the reaction was stirred for 2 h. The reaction was warmed to ambient temperature and stirred for an additional 12 h. Ether and saturated NH_4Cl solution were added. The phases were separated, and the organic phase was washed with saturated $NaHCO_3$ solution, water, and brine. The organic phase was dried ($MgSO_4$), filtered through Celite, and concentrated. The residual material was chromatographed (preparative radial thin-layer chromatography, 2 mm rotor, 10% ethyl acetate/petroleum ether) to yield 0.084 g of a yellow solid that contained at least three different compounds judging from analytical TLC analysis. Recrystallization of this material in boiling hexane (∼5 mL) yielded 0.024 g (9%) of white needles. **5**: mp 167 °C (dec); ^{1}H NMR (CD_2Cl_2) δ 7.73 (d, J = 7 Hz, 8H), 7.48 (t, J = 7 Hz, 8H), 7.39 (t, J = 7 Hz, 4H), 2.55 (s, 2H); ^{13}C NMR (CD_2Cl_2) δ 130.12, 129.46, 129.35, 128.68, 112.66, 77.05, 8.13; IR (KBr) 1833 cm^{-1}.

2,3-Diphenyl-1-(trimethylsilylethynyl)cyclopropenylium Hexachloroantimonate (7a). Cyclopropene **2a** (0.053 g, 0.18 mmol) was dissolved in CH_2Cl_2 (10 mL) at ambient temperature. Triphenylmethyl hexachloroantimonate (**6**) (0.105 g, 0.18 mmol) was added as a solid to the CH_2Cl_2 solution. The triphenylmethyl salt dissolved to give an orange solution which gradually (after 5 min) developed a greenish tint. After 10 min the volume of the solution was concentrated to ∼2 mL and ether was added to precipitate the cyclopropenylium salt as light yellow powder. The precipitate was collected by filtration and washed with ether. Recrystallization of the solid from acetonitrile yielded 0.083 g (74%) of light yellow needles. **7a**: mp 165 °C (dec); ^{1}H NMR (CD_3CN) δ 8.44 (d, J = 7 Hz, 4H), 8.09 (t, J = 7 Hz, 2H), 7.89 (t, J = 7 Hz, 4H), 0.46 (s, 9H); ^{13}C NMR (CD_3CN) δ 156.90, 144.10, 140.71, 139.80, 137.41, 131.57, 120.44, 85.76, −1.16; IR (KBr) 2158, 1837, 1395 cm^{-1}; UV (CH_3CN) 295 sh, 304, 321 nm. Anal. Calcd for $C_{20}H_{19}SiSbCl_6$: C, 38.63; H, 3.08. Found: C, 38.35; H, 3.12.

2,3-Diphenyl-1-(triisopropylsilylethynyl)cyclopropenylium hexachloroantimonate (7b) was prepared in a manner analogous to **7a** from cyclopropene **2b** (0.042 g, 0.11 mmol) and **6** (0.067 g, 0.12 mmol) to yield a light yellow precipitate. Recrystallization from acetonitrile gave 0.054 g (70%) of colorless needles. **7b**: mp 161 °C (dec); ^{1}H NMR (CD_3CN) δ 8.42 (d, J = 7 Hz, 4H), 8.09 (t, J = 7 Hz, 2H), 7.89 (t, J = 7 Hz, 4H), 1.40 (m, 3H), 1.24 (d, J = 7 Hz, 18H); ^{13}C NMR (CD_3CN) δ 156.76, 144.30, 140.72, 137.88, 137.40, 131.63, 120.56, 88.35, 18.91, 11.93; IR (KBr) 2158, 1838, 1391 cm^{-1}. Anal. Calcd for $C_{26}H_{31}SbCl_6$: C, 44.23; H, 4.43. Found: C, 44.38; H, 4.41.

2,3-Diphenyl-1-(phenylethynyl)cyclopropenylium hexachloroantimonate (7c) was prepared in a manner analogous to **7a** from cyclopropene **2c** (0.097 g, 0.33 mmol) and **6** (0.195 g, 0.34 mmol) to give a yellow powder. Recrystallization from acetonitrile gave 0.137 g (66%) of yellow needles. **7c**: mp 167 °C (dec); ^{1}H NMR (CD_3CN) δ 8.53 (dd, J = 7, 2 Hz, 4H), 8.14−8.00 (m, 4H), 7.91 (t, J = 7 Hz, 4H), 7.80 (tt, J = 7, 2 Hz, 1H), 7.67 (t, J = 7 Hz, 2H); ^{13}C NMR (CD_3CN) δ 155.78, 143.71, 140.43, 137.29, 135.91, 135.55, 131.56, 130.65, 126.90, 120.66, 119.31, 74.63; IR (KBr) 2197, 1835, 1401 cm^{-1}; UV (CH_3CN) 275, 300 sh, 317, 340, 364 sh nm. Anal. Calcd for $C_{23}H_{15}SbCl_6$: C, 44.14; H, 2.42. Found: C, 43.92; H, 2.41.

^{13}C-Labeled Cyclopropenylium 7c was prepared in a manner analogous to **7a** from ^{13}C-labeled **2c** (0.112 g, 0.38 mmol) and **6** (0.215 g, 0.372 mmol) to give a yellow powder. Recrystallization from acetonitrile gave 0.185 g (79%) of yellow needles. **7c-^{13}C**: mp 168 °C (dec); ^{1}H NMR (CD_3CN) δ 8.53 (m, 4H), 8.12−8.01 (m, 4H), 7.90 (t, J = 7 Hz, 4H), 7.80 (t, J = 7 Hz, 1H), 7.67 (t, J = 7 Hz, 2H); ^{13}C (CD_3CN) δ 126.9 (^{13}C-labeled carbon); IR (KBr) 2158, 1832, 1402 cm^{-1}.

2,3-Diphenyl-1-(1-hexynyl)cyclopropenylium hexachloroantimonate (7d) was prepared in a manner analogous to **7a** from **2d** (0.091 g, 0.33 mmol) and **6** (0.193 g, 0.33 mmol) to give a yellow powder. Recrystallization from acetonitrile gave 0.144 g (71%) of yellow crystals. **7d**: mp 151 °C (dec); ^{1}H NMR (CD_3CN) δ 8.43 (d, J = 7 Hz, 4H), 8.06 (t, J = 7 Hz, 2H), 7.88 (t, J = 7 Hz, 4H), 2.99 (t, J = 7 Hz, 2H), 1.82, (pentet, J = 7 Hz, 2H), 1.59 (sextet, J = 7 Hz, 2H), 1.02 (t, J = 7 Hz, 3H); ^{13}C NMR (CD_3CN) δ 156.71, 146.05, 140.68, 137.47, 134.77, 137.90, 120.88, 66.47, 30.44, 23.22, 22.35, 14.27; IR (KBr) 1409 cm^{-1}; UV (CH_3CN) 294 sh, 303, 321 nm. Anal. Calcd for $C_{21}H_{19}SbCl_6$: C, 41.63; H, 3.16. Found: C, 41.59; H, 3.15.

1-[(2,3-Diphenylcycloprop-2-enyl)ethynyl]-2,3-diphenylcyclopropenylium Hexachloroantimonate (10). Cyclopropene **5** (0.010 g, 0.024 mmol) was dissolved in CH_2Cl_2 (5 mL) at ambient temperature and **6** (0.016 g, 0.028 mmol) was added to the solution. The reaction was allowed to stir for 15 min. The volume of the solution was concentrated to ∼1 mL by rotary evaporation and ether was added to precipitate **10**. The orange precipitate was collected by filtration and washed with ether. Recrystallization from acetonitrile gave 0.014 g (77%) of pale orange crystals. **10**: ^{1}H NMR (CD_3CN) δ 8.36 (dd, J = 7, 1 Hz, 4H), 8.01 (tt, J = 7, 1 Hz, 2H), 7.90 (d, J = 7 Hz, 4H), 7.82 (t, J = 7 Hz, 4H), 7.62, (t, J = 7 Hz, 4H), 7.55 (t, J = 7 Hz, 2H), 3.29 (s, 1H); ^{13}C NMR (CD_3CN) δ 154.70, 145.13, 140.61, 139.96, 136.83, 131.51, 131.45, 131.07, 130.44, 126.91, 120.65, 109.45, 62.19, 11.83; IR (KBr) 2177, 1859, 1834, 1394 cm^{-1}.

Attempted Synthesis of Dication 11. Cyclopropene **5** (0.014 0 g, 0.0344 mmol) was dissolved in CH_2Cl_2 (5 mL) at ambient temperature and **6** (0.0407 g, 0.0704 mmol) was added. The solution was stirred for 20 min at ambient temperature. The volume was concentrated to ∼1 mL by rotary evaporation and ether was added. The resulting precipitate was collected by filtration, washed with ether (5 mL), and then dried in vacuo. A ^{1}H NMR (CD_3CN) spectrum of the material appeared to be identical to the corresponding spectrum of **10**. The spectrum also showed signals arising from **6**.

1,6-Bis(2,3-diphenylcycloprop-2-enyl)-1,5-hexadiyne (15). Ethylmagnesium bromide was prepared from Mg (0.050

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g, 2.1 mmol) and bromoethane (0.22 g, 2.0 mmol) in THF (5 mL) as described in the preparation of **2a** and was cooled to 0 °C. 1,5-Hexadiyne (0.075 g, 1.0 mmol) was added via syringe and the reaction was warmed to ambient temperature. The reaction stirred at ambient temperature for 3 h during which a gray precipitate appeared. The suspension was diluted with 50 mL of THF and cooled to −78 °C. Diphenylcyclopropenyl perchlorate (**1**) (0.800 g, 2.75 mmol) was added to the cold suspension and the reaction was stirred at −78 °C for 1 h. The suspension was warmed to ambient temperature and stirred for an additional 16 h. Ether was added to the suspension along with 10% HCl solution. The layers were separated, and the aqueous phase was extracted ether. The combined organics were washed with saturated $NaHCO_3$ solution and brine. The organic phase was dried ($MgSO_4$), filtered through Celite, and concentrated to give 0.134 g of an orange solid. This material was first purified by preparative radial thin-layer chromatography (2 mm rotor, hexanes) to yield a light orange solid that contained a small amount of an impurity as judged by ^{1}H NMR spectroscopy. The solid was recrystallized from 10% benzene in hexane to give 0.091 g (20%) of light yellow needles. **15**: mp 168.5−171 °C (dec); ^{1}H NMR (CD_2Cl_2) δ 7.74 (d, J = 7 Hz, 8H), 7.49 (t, J = 7 Hz, 8H), 7.39 (t, J = 7 Hz, 4H), 2.54 (s, 2H), 2.27 (s, 4H); ^{13}C NMR (CD_2Cl_2) δ 130.14, 129.54, 129.41, 128.58, 112.45, 84.17, 73.22, 20.02, 7.93; IR (KBr) 1834 cm^{-1}.

1,6-Bis(2,3-diphenylcyclopropenylium)-1,5-hexadiyne Bis(hexachloroantimonate) (16). Cyclopropene **15** (0.015 g, 0.033 mmol) was dissolved in acetonitrile (10 mL) at ambient temperature. A solution of **6** (0.040 g, 0.069 mmol) in acetonitrile (2 mL) was added to the cyclopropene. The solution was allowed to stir for 15 min at ambient temperature, then the volume was concentrated to ∼2 mL. The solution was then cooled to −35 °C for 24 h during which crystals formed. The solid was collected by filtration and was rinsed with cold acetonitrile then dried in vacuo to yield 0.0349 g (95%) of dark brown crystals. **16**: mp 135 °C (dec); ^{1}H NMR (CD_3CN) δ 8.43 (d, J = 7 Hz, 8H), 8.03 (t, J = 7 Hz, 4H), 7.81 (t, J = 7 Hz, 8H), 3.50 (s, 4H); IR (KBr) 2224, 1404 cm^{-1}. Anal. Calcd for $C_{36}H_{24}Sb_2Cl_{12}$: C, 38.42; H, 2.15. Found: C, 38.61; H, 2.45.

3,3-Bis(trimethylsilylethynyl)-1,2-diphenylcyclopropene (20). Cyclopropenylium ion **7a** (0.175 g, 0.28 mmol) was suspended in THF (20 mL) at −78 °C. To this suspension was added a solution of (trimethylsilyl)ethynylmagnesium bromide (1.0 mL, 0.5 M, 0.5 mmol), prepared as described in the procedure for **2a**. The reaction was allowed to stir at −78 °C for 1 h and then at 25 °C for 18 h. Ether and saturated NH_4Cl solution were added to the reaction. The phases were separated, and the organic phase was washed with $NaHCO_3$ solution and brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated to give an orange oil. The oil was fractionated by preparative radial thin-layer chromatography (2 mm rotor, hexanes/EtOAc). The first fraction to elute contained a mixture of **20** and **21** in a 1:2 ratio (measured by ^{1}H NMR spectroscopy). This fraction was concentrated and then dissolved in a minimal amount of hot absolute ethanol. Upon cooling, 0.025 g (23%) of light orange needles were deposited. **20**: mp 157−159 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.79 (d, J = 7 Hz, 4H), 7.53 (t, J = 7 Hz, 4H), 7.44 (t, J = 7 Hz, 2H), 0.12 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 129.73, 129.55, 128.96, 125.789, 112.20, 106.63, 80.25, 10.93, 0.12; IR (KBr) 2145, 1842 cm^{-1}. Anal. Calcd for $C_{25}H_{28}Si_2$: C, 78.06; H, 7.34. Found: C, 77.85; H, 7.20.

1,2-Diphenyl-5-(trimethylsilyl)pent-2-en-4-yn-1-one (24a). Cyclopropenylium ion **7a** (0.049 g, 0.079 mmol) was dissolved in acetonitrile (20 mL). Water (20 mL) was added and the solution was titrated to pH 10 with 0.1 M NaOH following the procedure described for pK_{R+} determination. The solution was allowed to stand overnight (14 h), then water was added to precipitate **24a**. The precipitate was collected by filtration then taken up in ether. The ether solution was washed with water and brine. The organic layer was dried ($MgSO_4$), filtered through Celite, and concentrated to yield 0.024 g (100%) of a light brown solid. **24a**: mp 85−87 °C; ^{1}H NMR ($CDCl_3$) δ 8.01 (d, J = 8 Hz, 2H), 7.58 (t, J = 8 Hz, 1H), 7.49−7.32 (m, 7H), 6.31 (s, 1H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 197.21, 152.11, 136.42, 135.53, 133.58, 129.73, 129.20, 128.91, 128.60, 125.99, 108.46, 104.42, 101.54, −0.64; IR (KBr) 2141, 1668 cm^{-1}.

1,2,5-Triphenylpent-2-en-4-yn-1-one (24b). Exposure of cyclopropenylium ion **7c** (0.072 g, 0.12 mmol) to conditions identical to those described in the preparation of **24a** gave 0.034 g (92%) of a light yellow solid. **24b**: mp 105−108 °C; ^{1}H NMR ($CDCl_3$) δ 8.07 (d, J = 7 Hz, 2H), 7.62 (tt, J = 7, 2 Hz, 1H), 7.53−7.18 (m, 10H), 7.06−7.02 (m, 2H), 6.57 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 197.64, 151.48, 137.03, 136.26, 134.33, 131.84, 130.22, 129.73, 129.51, 129.34, 129.19, 128.79, 126.56, 123.04, 109.07, 98.36, 87.14; IR (KBr) 2189, 1672 cm^{-1}. Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.30; H, 5.22.

Alternate Synthesis of 24b. Deoxybenzoin (0.150 g, 0.764 mmol) and phenylpropargyl aldehyde (0.100 g, 0.768 mmol) were added to a solution of NaOH (0.50 g, 12 mmol) in absolute methanol (15 mL). The reaction was stirred at ambient temperature for 48 h, then water and ether were added. The layers were separated and the ether phase was dried ($MgSO_4$), filtered through Celite, and concentrated to give a brown, oily solid. The solid was dissolved in boiling pentane and cooled to −30 °C to produce light yellow needles. **24b**: mp 107−109 °C; spectroscopic data were identical to those of the reaction described above. Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.45; H, 5.22.

pK_{R+} Determination. The pK_{R+} values of **7a** and **7b** were determined by potentiometric titration 50% aqueous acetonitrile. A 0.1 M NaCl solution was boiled under a constant flow of N_2 for 20 min then allowed to cool under N_2 prior to use. The pH of the resulting solution was always 7.0 ± 0.1. The cyclopropenylium salt was dissolved in acetonitrile (10 mL) and diluted to a volume of 20 mL with the 0.1 M NaCl solution. The solution was then titrated with 0.10 N NaOH in 0.020 mL aliquots and was stirred vigorously throughout the titration. The pH of the solution was measured 30 s after each addition of NaOH with a Hanna Instruments 9023 pH meter. The pH meter was calibrated prior to each titration using standard phosphate buffers. The pH of the solution was plotted as a function of the volume of NaOH solution added, giving a classic titration curve. The midpoints of the resulting titration curves were taken as the pK_{R+} of the cyclopropenylium salts. All of the reported pK_{R+} values are averages of at least three titrations. The solutions remained clear in all cases through the endpoint. When the pH was increased past 11, the solutions exhibited turbidity in some cases. Triphenylcyclopropenylium bromide (reported 3.15)[13] and tri-*tert*-butylcyclopropenylium tetrafluoroborate (reported 6.5)[24] gave pK_{R+} values of 2.93 and 6.54, respectively, under these conditions.

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Supporting Information Available: X-ray crystal structures of **7a**−**c**, tables of atomic coordinates, thermal parameters, bond lengths and bond angles.

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