tensity) 265 (9.7) (M^+), 138 (9), 106 (70), 96 (100), 55 (55); IR (film) 2210, 2230 cm^{-1}.

Reactions of Halides 1 with Metal Hydrides. The following general procedure was used. To a solution of 0.1 mmol of metal hydride in 0.5 mL of solvent was added a solution of 0.1 mmol of substrate and 10 mg of dodecane (standard) in 0.5 mL of solvent via syringe. After the appropriate amount of time, the reaction mixture was treated with water and worked up by a conventional extractive method, and the product mixture was analyzed by GC.

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Single-Electron-Transfer Pathway in the Coupling of Cyclopropenyl Cations with Organometallic Reagents

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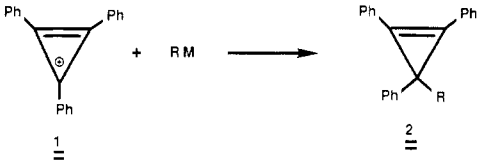
Treatment of diphenylmethylcyclopropenylium perchlorate with various Grignard reagents produced substituted cyclopropenes in excellent yield. Alkyl and vinylic Grignard reagents react at the methylated carbon atom. The substantial increase in formation of the 1,3-diphenyl-substituted isomer when allylic or benzylic Grignard reagents are used can be attributed to the involvement of a single-electron-transfer (SET) mechanism. The cyclopropenyl radical prefers to localize the odd electron on the phenylated carbon, thereby accounting for the preferential formation of the 1,3-diphenyl-substituted isomer. Reduction of the cyclopropenyl cation with activated magnesium metal leads to four products that have been identified as the unsymmetrical bicyclopropene dimer, a Dewar benzene derivative, and *o*- and *m*-dimethyltetraphenylbenzene The thermal and triplet-sensitized behaviors of the bicyclopropene and Dewar benzene systems were investigated and were found to give rearranged dimethyltetraphenylbenzenes. Mechanisms to explain these results involve rearrangement of a series of radical cation, prismane, and diradical intermediates.

Strained organic molecules have always fascinated organic chemists[1] as well as theoreticians.[2] Three-membered rings have attracted special attention because of severe enforced bond angle deformation and cyclopropene is of particular interest in this context.[3] Cyclopropene itself was first prepared some 60 years ago,[4] but, despite its unusual structure, the molecule received minimal attention until the late 1950s.[5] Two factors led to a resurgence of interest with this highly strained ring system. First, developments in carbene chemistry led to a new and convenient synthesis of cyclopropene derivatives.[6] Secondly, it was realized that the cyclopropenyl cation obeyed the Hückel $[4n + 2]$ π rule.[7] Since the initial preparation of a cyclopropenyl cation,[7] many aryl, alkyl and heteroatomic substituted derivatives of this simplest cyclic aromatic system have been synthesized.[8] Of particular interest are the intrinsic stability of the parent ion and the relative stabilities of its substituted derivatives. On the pK_{R+} scale,[9] it is clear that arylcyclopropenyl cations are generally less stable than alkyl-substituted varieties,[9-11] while the latter are less stable than dialkylaminocyclopropenyl cations.[8]

A variety of cyclopropenes can be readily prepared and their application as synthons in natural product synthesis has raised considerable interest in recent years.[12-16] For some time our group has been interested in the thermal and photochemical transformations of variously substituted cyclopropenes.[17] We have found that a variety of



1 2

substituted cyclopropenes can be readily prepared by treating variously substituted cyclopropenyl cations with Grignard reagents according to the general procedure of Breslow and co-workers.[9] In spite of the synthetic utility of this reaction, the mechanistic details of the process are still not well-understood. We report here the results of our studies, which provide evidence for an electron-transfer component in the coupling of cyclopropenyl cations with various organometallic reagents.

Results and Discussion

Electron-transfer mechanisms are increasingly being invoked to describe the reactions of alkylmetal compounds with organic substrates.[18] Recent work by Ashby[19] as well

(1) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.
(2) Newton, M. D. in *Modern Theoretical Chemistry*; Schaefer, H. F., E.; Plenum: New York, 1977; Vol. 4, Chapter 6.
(3) de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809.
(4) Demyanov, N. Y.; Ooyarenko, M. N. *Bull. Acad. Sci. Russ.* **1922**, *16*, 297.
(5) Closs, G.L. *Advances in Alicyclic Chemistry*; Hart, H., Karabatsos, G. J., Eds.; Academic Press: New York, 1966; Vol. 1, p 53.
(6) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971.
(7) Breslow, R. *J. Am. Chem. Soc.* **1957**, *79*, 5318.
(8) Yoshida, Z. I. *Top. Curr. Chem.* **1973**, *40*, 47.
(9) Breslow, R.; Hover, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168.
(10) Ciabattoni, J.; Nathan, E. C. *Tetrahedron Lett.* **1969**, 4997.
(11) Kerber, R. C.; Hsu, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 3239.
(12) Itoh, T.; Djerassi, C. *J. Am. Chem. Soc.* **1983**, *105*, 4407. Itoh, T.; Sica, D.; Djerassi, C. *J. Org. Chem.* **1983**, *48*, 890.
(13) Halton, B. *Chem. Rev.* **1973**, *73*, 113.
(14) Billups, W. E. *Acc. Chem. Res.* **1978**, *11*, 245.
(15) Thummel, R. P. *Isr. J. Chem.* **1982**, *22*, 11.
(16) Boger, D.; Brotherton, C. E. *J. Am. Chem. Soc.* **1984**, *106*, 805; **1986**, *108*, 6695; **1986**, *108*, 6713.
(17) For a review, see: Padwa, A. *Org. Photochem.* **1979**, *4*, 261.

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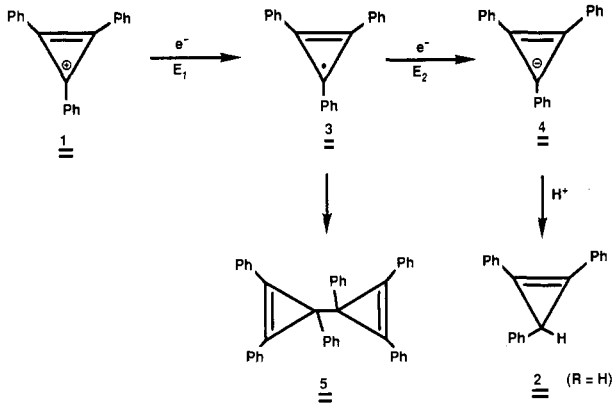
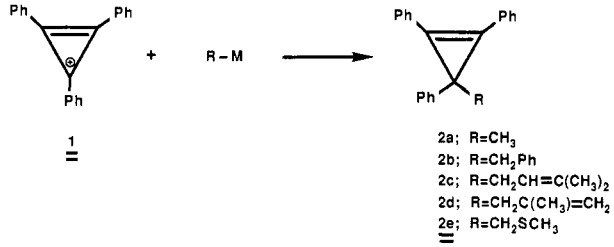
as others[20-22] has demonstrated the involvement of single electron transfer (SET) in the reaction of Grignard reagents with aromatic ketones. In 1974, Breslow and Drury[23]

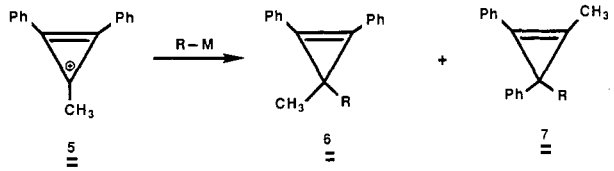


proposed that the very effective trapping of the triphenylcyclopropenyl anion **4** by cyclopropenyl cation **1** proceeds by an electron transfer, with large collisional cross-section, followed by coupling of the resulting radicals. This suggestion was based on the observation that capture of the cyclopropenyl carbanion **4** by the cation **1** was much more effective than capture by protonation with guanidinium cation, even though this species was in 100-fold excess over the cyclopropenyl cation **1**.

During the course of our studies, we have found that the reaction of triphenylcyclopropenyl cation **1** with various organometallic reagents in ether or THF at 0 °C, and even at −78 °C, was complete in 5 min and produced the 3-substituted cyclopropene **2** in excellent yield.

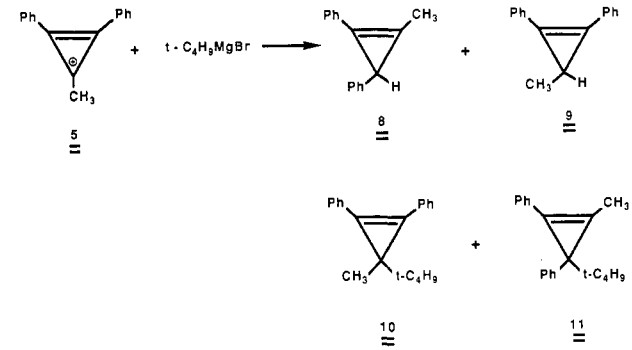


In order to explore the mechanism of the coupling reaction, we examined the reaction of diphenylmethylcyclopropenyl cation **5** with a variety of organometallic reagents. We found that with alkyl-substituted Grignard reagents, nucleophilic attack is predominant at the methylated carbon of **5**, giving rise to the symmetrical

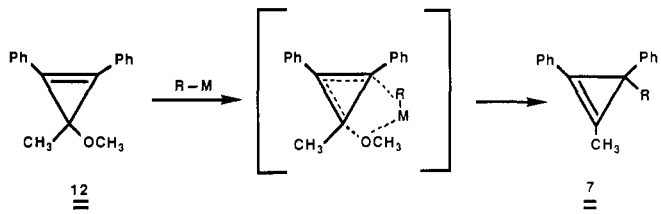


1,2-diphenyl-substituted isomer as the major product (75–95%). When allylic or benzylic Grignard reagents were used, however, substantial quantities of the unsymmetrical isomer were formed (20–45%). In fact, with secondary or tertiary benzylic Grignard reagents, the major product (>85%) corresponded to the unsymmetrically substituted cyclopropene. The SET nature of the Grignard addition reaction with ketones has been related to the stability of the intermediate radical produced.[22,24] The substantial increase in the formation of the 1,3-diphenyl-substituted isomer when substituted benzylic Grignard reagents are used can likewise be attributed to the involvement of the SET mechanism. The stability of the radical center derived from the Grignard reagent seemingly determines the amount of SET character observed in the reaction.

When the *tert*-butyl-Grignard reagent was allowed to react with cyclopropenyl cation **5**, the predominant products corresponded to the reduced cyclopropenes **8** (50%) and **9** (40%). In addition, small quantities of the alkylated products **10** (2%) and **11** (7%) were also formed. It appears that the *tert*-butyl-Grignard, which is sterically much larger than the other alkyl-Grignard reagents employed, prefers to transfer a hydrogen atom to the radical center. Since a radical pair is involved here, it is not surprising that the steric bulk of the *tert*-butyl group plays a major role in the reaction. The increase in steric size slows down the collapse of the diradical pair so that hydrogen transfer becomes the dominant path. In simple cases, the activation energies for recombination and disproportionation of radicals have been found to be equal.[25] The fact that reduction is the major path with the *tert*-butyl group is a reflection of the greater steric hindrance to recombination of a tertiary site compared with a primary or secondary site.[26]



We also treated 1,2-diphenyl-3-methyl-3-methoxycyclopropene (**12**) with various organometallic reagents. The result of these experiments shows that the major product (70–90%) corresponds to the unsymmetrically substituted isomer. This observation indicates that either

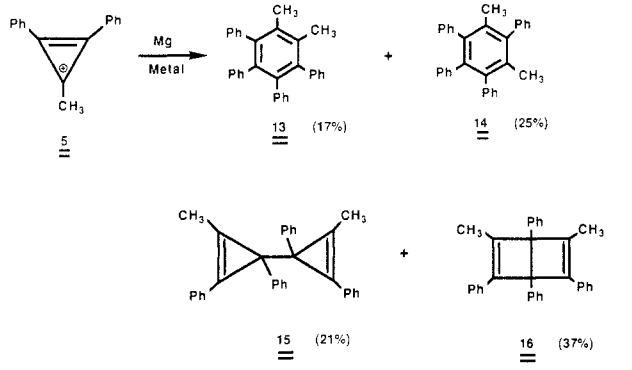


the reaction proceeds by a route involving predominant electron transfer or via a SN'_2-like path. This latter process would involve coordination of the metal to the methoxy group at the same time that the carbanionic center is attacking the π-bond.[27] In any case, the important point

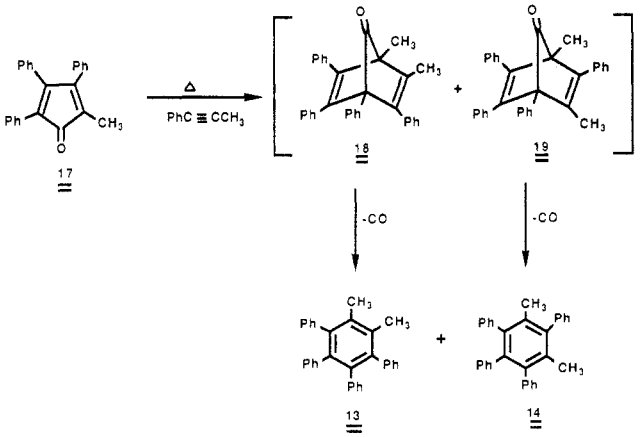
(18) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978.
(19) Ashby, E. C.; Wiesmann, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 189.
(20) Blomberg, C.; Salinger, R.; Mosher, H. *J. Org. Chem.* **1969**, *34*, 2385.
(21) Maruyama, K. *Bul. Chem. Soc. Jpn.* **1964**, *37*, 897.
(22) Holm, T.; Crossland, I. *Acta Chem. Scand.* **1971**, *25*, 59; **1973**, *27*, 1552.
(23) Breslow, R.; Drury, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 4702.
(24) Schaart, B. J.; Blomberg, C.; Akkerman, O. S.; Bickelhaupt, F. *Can. J. Chem.* **1980**, *58*, 932.
(25) Kraus, J.; Calvert, J. *J. Am. Chem. Soc.* **1957**, *79*, 5921.
(26) Engle, P. S.; Bishop, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 2148.
(27) Addition of TMEDA to the reaction mixture resulted in significant quantities (i.e. 30–50%) of the symmetrical 1,2-isomer, thereby providing support for the SN'_2-like pathway.

is that by employing the 3-methoxy-substituted cyclopropene, it becomes possible to prepare the unsymmetrically 1,3-diphenyl-substituted isomer in much higher yield.

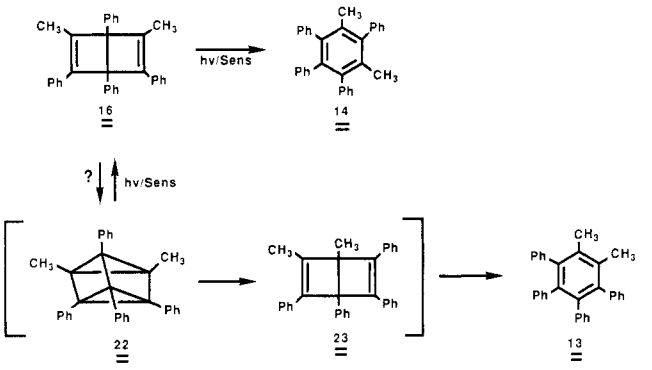
During the course of these studies, we found that some additional byproducts were formed in the reaction of several of the Grignard reagents with cyclopropenyl cation **5**. The quantity of byproducts seemed to depend upon the ratio of the Grignard reagent to the cyclopropenyl perchlorate, the "purity" of the magnesium used to prepared the Grignard reagent, and the manner in which the Grignard was prepared. Treatment of cyclopropenyl perchlorate **5** with a slurry of activated magnesium metal produced a mixture of four compounds that corresponded to the minor products previously isolated from the Grignard reactions. The four products produced were identified as 1,2-dimethyl-3,4,5,6-tetraphenyl- (**13**) and 1,3-dimethyl-2,4,5,6-tetraphenylbenzene (**14**), bi-1,1′-(2-methyl-1,3-diphenyl-2-cyclopropene) (**15**), and 1,3-dimethyl-2,4,5,6-tetraphenylbicyclo[2.2.0]hexa-1,3-diene (**16**).



Assignment of three of the products was made by comparison with independently synthesized samples. Structures **13** and **14** were prepared in high yield from the Diels–Alder reaction of 2-methyl-3,4,5-triphenylcyclopentadienone (**17**) with 1-phenylpropyne followed by cheletropic extrusion of carbon monoxide from the regioisomeric cycloadducts **18** and **19**. The previously unknown para isomer **20** was also synthesized via a Diels-Alder decarboxylation sequence using 2,5-dimethyl-3,4-diphenylcyclopentadienone (**21**)[28] as the diene and diphenylacetylene as the dienophile at 485 °C. No signs of



the para isomer could be detected, however, in the crude reaction mixture derived from the treatment of cyclopropenyl cation **5** with activated magnesium metal. The structure of bi-cyclopropene **15** was also confirmed by comparison with an authentic sample.[29] The assignment of **16** as a Dewar benzene derivative is based on its spectral and chemical properties. The decoupled ^{13}C NMR spectrum showed lines at δ 9.45, 39.51, 112.4, 115.8, 124.6, 127.4, 127.6, 127.9, 128.5, 129.2, and 147.1. The UV spectrum exhibited a maximum at 265 nm (ϵ 26 000), which is consistent with the presence of the 1-phenylpropene chromophore. Most importantly, heating a sample of **16** at 160 °C resulted in the quantitative formation of 1,3-dimethyltetraphenylbenzene **14**. The triplet-sensitized behavior of Dewar benzene **16** was also studied. The major isomer obtained corresponded to the meta-substituted benzene **14**. A small but significant quantity of the ortho-substituted benzene **13** (15%) was also formed. The formation of this material can be attributed to an intramolecular [2 + 2]-cycloaddition to give prismane **22** as a transient species. This material may open to give two

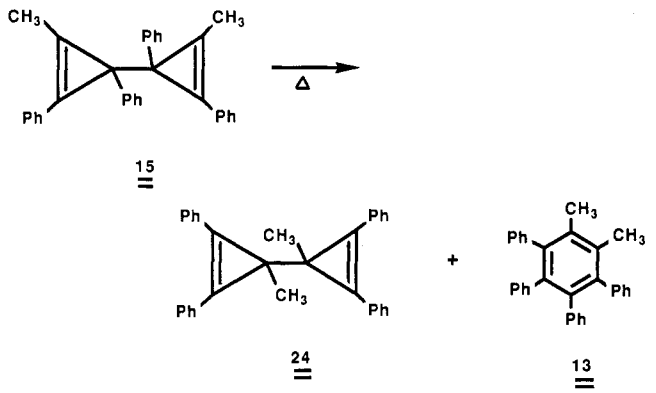


different Dewar benzenes (i.e. **16** or **23**) leading, respectively, to **14** and **13**. We carried out the sensitized photolysis to low conversion but were unable to detect the suspected intermediates. This is probably related to their high reactivity under the conditions used.

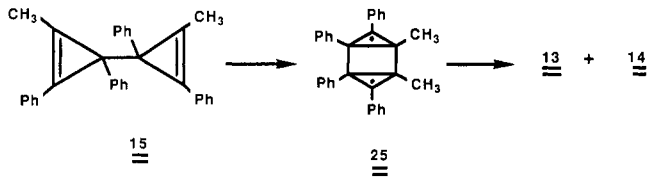
The rearrangement of 3,3′-bicyclopropenyls to benzene derivatives represents one of the more fascinating unimolecular isomerizations known in the cyclopropene field.[30-38] Its mechanism has been a source of controversy over the years. At various times the rearrangement has been postulated to proceed through Dewar benzene,[32] benzvalene,[38] prismane,[30] or diradical[35] and ionic pathways.[32] The most recent data are consistent with a path involving initial homolytic cleavage of one of the cyclopropene rings followed by expansion of the other ring, closure to a Dewar benzene, and finally opening of the Dewar intermediate to form aromatic products (see Scheme I).[36,37] Keeping this controversy in mind, we thermolyzed a sample of bicyclopropene **15** and found that it smoothly rearranged to the isomeric bicyclopropene **24** (52%) as well as to the ortho-substituted benzene **13** (48%). No signs of either the meta (**14**) or para (**20**)

(28) Japper, F. R.; Medlrum, AN. *J. Chem. Soc.* **1901**, *79*, 1024. Gray, F. W. *J. Chem. Soc.* **1909**, *95*, 2131.

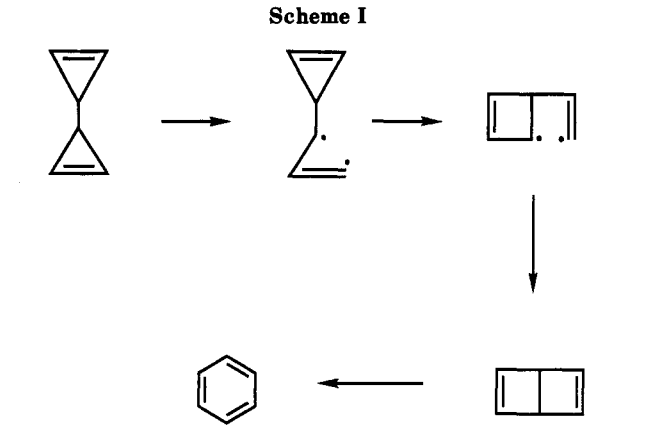
(29) Weiss, R.; Kolbl, H. *J. Am. Chem. Soc.* **1975**, *97*, 3224.
(30) Breslow, R.; Gal, P.; Chang, H. W.; Altman, L. J. *J. Am. Chem. Soc.* **1965**, *87*, 5139.
(31) Weiss, R.; Kempeke, H. P. *Tetrahedron Lett.* **1974**, 155.
(32) Weiss, R.; Andrae, S. *Angew. Chem.* **1973**, *85*, 145, 147; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 150, 152.
(33) DeWolf, W. H.; Stol, W.; Landheer, I. J.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 405.
(34) DeWolf, W. H.; Landheer, I. J.; Bickelhaupt, F. *Tetrahedron Lett.* **1975**, 179.
(35) Weiss, R.; Kobl, H. *J. Am. Chem. Soc.* **1975**, *97*, 3222, 3224.
(36) Davis, J. H.; Shea, K. J.; Bergman, R. G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 232; *J. Am. Chem. Soc.* **1977**, *99*, 1499.
(37) Turro, N. J.; Schuster, G. B.; Bergman, R. G.; Shea, K. J.; Davis, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 4758.
(38) Landheer, I. J.; DeWolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1975**, 349; **1974**, 2813.



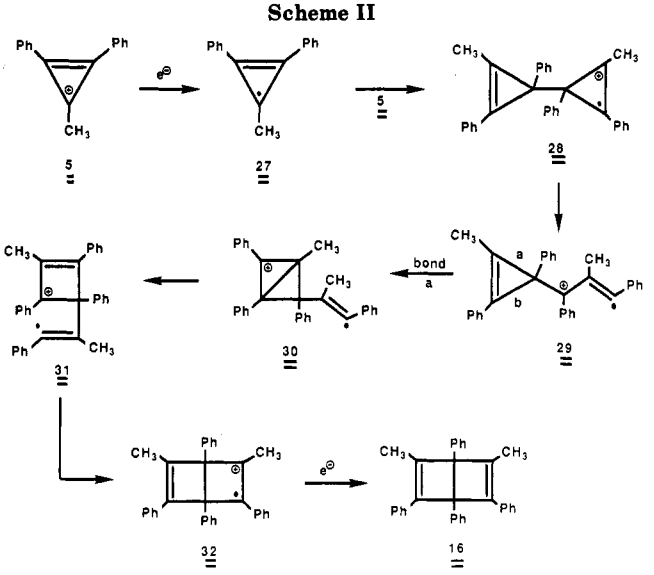
benzene isomers could be detected in the crude reaction mixture.[39] This result is incompatible with the mechanism previously suggested by Bergman[36,37] and co-workers to explain the results encountered with the simple alkyl-substituted bicyclopropenes.[40] Instead, the reaction is best interpreted in terms of diradical intermediate **25**. Subsequent fragmentation of this species affords the Cope rearrangement product **24**. An alternate path available to **25** involves cyclopropyl ring cleavage to ultimately give the ortho-substituted isomer **13**. The exclusive formation of



the ortho isomer is undoubtedly related to the fact that π–π bridging will give the most stable diradical intermediate.[43] The triplet (thioxanthone) sensitized photolysis of **15**, on the other hand, produced a 4:1 mixture of the ortho (**13**) and meta (**14**) isomers. It would appear as

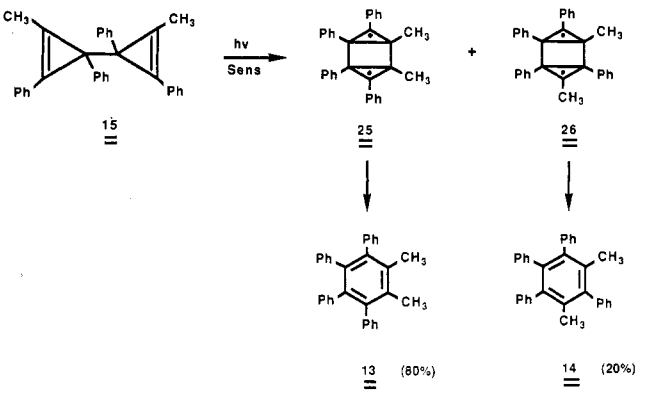


Scheme I



Scheme II

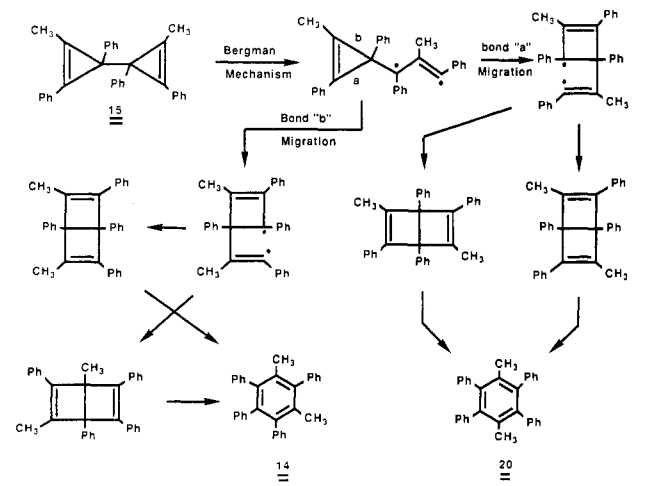
though the higher energy triplet excited state of **15** is not as selective in the π–π^* bridging process and affords a mixture of 1,4-tricyclohexane intermediates.



Previous studies have shown that the dimerization of cyclopropenyl cations can be induced by metals such as lithium and zinc as well as via electrochemical methods.[30,44] Thus, it seems reasonable to assume that the reaction of cyclopropenyl cation **5** with activated magnesium metal proceeds in a similar fashion and involves an initial electron transfer to give the three π-electron cyclopropenyl radical. Coupling of the radical produces the unsymmetrical dimer **15**.[45] Formation of the dimethyltetraphenyl

(39) For some related thermal transformations, see ref 35.

(40) The thermolysis of a 1-alkyl-2-aryl-substituted cyclopropene is known to result in the preferential cleavage of the aryl-substituted cyclopropene bond so as to produce the most stable diradical (vinylcarbene) intermediate.[41,42] Consequently, the Bergman mechanism should have produced significant quantities of both the meta (**14**) and para (**20**) substituted isomers.



(41) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N. *J. Am. Chem. Soc.* **1977**, *99*, 2344; *J. Org. Chem.* **1978**, *43*, 1481.

(42) Zimmerman, H. E.; Aasen, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 2342; *J. Org. Chem.* **1978**, *43*, 1493. Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331. Zimmerman, H. E.; Kreil, D. *J. Org. Chem.* **1982**, *47*, 2060.

(43) For a closely related process with allyl-substituted cyclopropenes, see: Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2797.

(44) Breslow, R.; Gal, P. *J. Am. Chem. Soc.* **1959**, *81*, 4747.

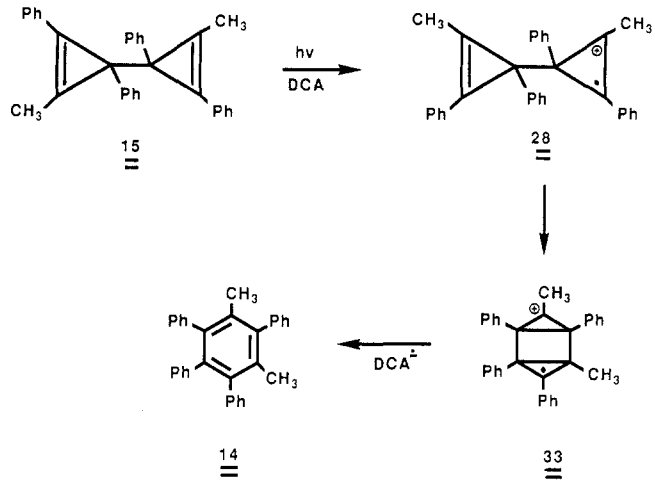
(45) Johnson, R. W.; Widlanski, T.; Breslow, R. *Tetrahedron Lett.* **1975**, 4685.

aromatics as well as Dewar benzene **16** requires some alternate pathway. We suggest that the initially formed radical reacts further with the cyclopropenyl cation to give a coupled radical cation intermediate (**28**). Cleavage of this species leads to a ring-opened cyclopropenyl carbinyl radical cation (**29**). A subsequent ring expansion produces rearranged cyclobutenyl cation radical **31**.[46] The preferential migration of bond "a" is probably related to the fact that the ring expansion proceeds via the most stable bicyclo[1.1.0]butyl cation intermediate (i.e. **30**). Cyclization followed by electron transfer ultimately produces Dewar benzene **16** (see Scheme II). In support of the above mechanism, we find that the electrolytic reduction of **5** produced a 1:1 mixture of bicyclopropene **15** and Dewar benzene **16**. To our knowledge this represents the first example of the isolation of a Dewar benzene derivative from the electrolysis of a cyclopropenyl cation.

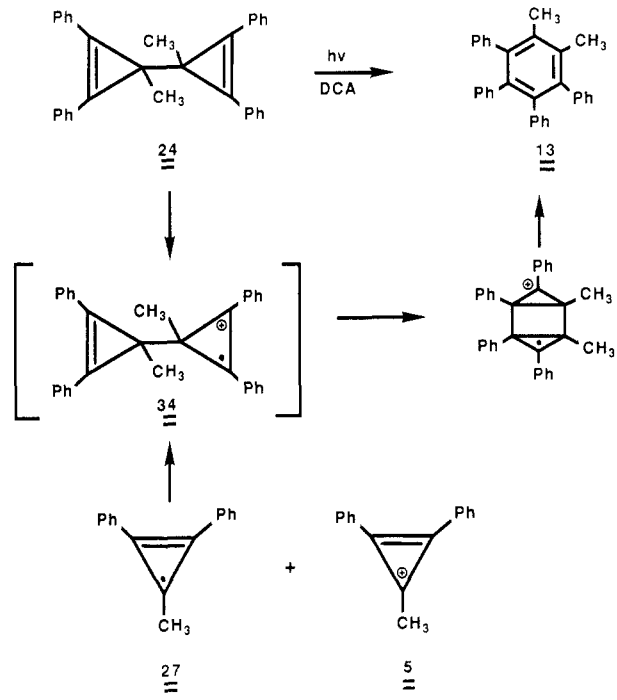
Formation of the two aromatic compounds (**13** and **14**) from the magnesium-induced coupling of **5** is also of some interest and merits discussion. Neither of these compounds are formed in the electrolysis experiment. This result would tend to suggest that radical cation **32** is not the precursor of the meta isomer. One reasonable explanation to account for the formation of compounds **13** and **14** involves the further chemistry of the initially coupled radical cation **28**. Cyclization of **28** might be expected to give both **13** and **14** as was encountered on thioxanthone-sensitized photolysis of **15**. In order to probe this possibility, we decided to investigate the DCA-sensitized reaction of **15**.

9,10-Dicyanoanthracene (DCA) is a typical sensitizer for photogeneration of radical ions.[47] Electron-transfer quenching of the fluorescence of DCA by a variety of substrates has been postulated from correlations of quenching rate constants and free energies of electron transfer,[48] from solvent-dependent exciplex emissions,[49] and on the basis of distinctive photochemistry.[50,51] Phenyl-substituted cyclopropenes have also been found to react with the singlet state of 9,10-dicyanoanthracene (DCA*[1]) at a diffusion-controlled rate to produce the radical ions of cyclopropene and anthracene.[52-54]

In dramatic contrast to the 4:1 mixture of ortho and meta isomers obtained on sensitization of **15** with thioxanthone, the DCA-sensitized photolysis gave only the meta isomer. The irradiation was carried out in acetonitrile under conditions where only the sensitizer absorbed light. In the time required to complete the conversion of **15**, little if any of the sensitizer was consumed. Our rationale to account for the exclusive formation of **14** is that radical cation **28** derived from **15** undergoes regioselective radical cyclization to give the more stable radical cation **33**. Back electron transfer from the DCA radical anion followed by diradical fragmentation nicely accounts for the formation of the meta isomer. A similar sequence of reactions would account for the formation of **14** in the magnesium metal induced coupling reaction of cyclopropenyl cation **5**.



A clue to the formation of the ortho isomer **13** from the magnesium-induced coupling reaction of **5** comes from the DCA-sensitized reaction of the isomeric bicyclopropene **24**.



With this system, the only material isolated corresponded to 1,2-dimethyl-3,4,5,6-tetraphenylbenzene (**13**). Thus, if the cyclopropenyl radical **27** were to couple with cation **5** to give radical cation **34**, then one should expect to find some of the ortho isomer. The substituted benzenes **13** and **14** are the end products of a sequence initiated by an electron transfer from the metal surface to the cyclopropenyl cation.

We are continuing to investigate the electron-transfer-mediated reactions of other arylcyclopropene radical cations and will report additional findings at a later date.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 283 infrared spectrometer. Proton NMR spectra were obtained on Varian EM-390 and JEOL 100-MHz spectrometer. ^{13}C NMR spectra were recorded on an IBM 200-MHz spectrometer. Microanalyses were performed at Atlantic Microlabs, Atlanta, GA. Mass spectra were determined

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with a Finnegan 4000 mass spectrometer at an ionizing voltage of 70 eV.

General Procedure for the Preparation of 1,2-Diphenyl-3,3-dialkyl and 1,3-Diphenyl-2-methyl-3-alkyl Disubstituted Cyclopropenes. A general method that was used to prepare a variety of substituted cyclopropenes consisted of treating an appropriate cyclopropenyl perchlorate with a given organometallic reagent at either 0 °C or −78 °C. A solution of the organometallic reagent in the appropriate solvent was added to a stirred suspension of the substituted cyclopropenyl perchlorate in anhydrous ether or tetrahydrofuran. The mixture was stirred for 2–6 h and was allowed to warm to room temperature. A saturated ammonium chloride was then added and the mixture was stirred until both phases became clear. The organic layer was taken up in ether, washed twice with equal volumes of water and a saturated salt solution, and dried over magnesium sulfate. The solvent was removed under reduced pressure and the resulting clear yellow oil was chromatographed on a medium pressure silica gel column using hexane as the eluent. The first component isolated from the column always contained the 1,2-diphenyl-substituted isomer. Some of the cyclopropenes have already been synthesized[55] while others have not been reported. Using the above procedure, the following unknown cyclopropenes were prepared.

3-Benzyl-1,2,3-triphenylcyclopropene (2b): 89%; mp 105-106 °C; IR (KBr) 3030, 1828, 1605, 1490, 1445, 1075, 935, 780, 755, 740, 695, and 685 cm^{-1}; UV (95% ethanol) 336, 318, and 227 nm (ϵ 21 500, 25 700, and 29 200); NMR ($CDCl_3$, 100 MHz) δ 3.71 (s, 2 H), 6.98 (s, 5 H), and 6.6–7.2 (m, 15 H); MS, m/e 358 (M^+), 267 (base), 252, 232, and 91. Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 94.08; H, 6.34.

3-(2-Methylallyl)-1,2,3-triphenylcyclopropene (2): 76%; mp 79–80 °C; IR (KBr) 3040, 1830, 1600, 1495, 1450, 895, 775, 755, 740, and 685 cm^{-1}; UV (95% ethanol) 333, 317, and 228 nm (ϵ 18 300, 22 300, and 23 300); NMR ($CDCl_3$, 100 MHz) δ 1.59 (s, 3 H), 3.01 (s, 2 H), 4.62 (br s, 2 H), and 7.0–7.7 (m, 15 H);MS, m/e 322 (M^+), 267 (base), and 186. Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.28; H, 6.81.

3-[(Methylthio)methyl]-1,2,3-triphenylcyclopropene (2e): 96%; mp 66–67 °C; IR (KBr) 3050, 1810, 1600, 1480, 1430, 1225, 1050, 1010, 900, 740, and 675 cm^{-1}; UV (95% ethanol) 330, 314, and 228 nm (ϵ 26 100, 24 700, and 21 500); NMR ($CDCl_3$, 100 MHz) δ 2.02 (s, 3 H), 3.50 (s, 2 H), 7.0–7.8 (m, 15 H); MS, m/e 328 (M^+), 313, 267, 205, 178, and 77. Anal. Calcd for $C_{23}H_{20}S$: C, 84.10; H, 6.14. Found: C, 84.05; H, 6.14.

2-(1,2,3-Triphenylcyclopropenyl)dithiane (2f): 82%; mp 209–210 °C; IR (KBr) 3075, 1810, 1605, 1500, 1370, 1300, 1260, 1230, 1160, 1100, 1060, 1010, 885, 825, 790, 750, and 675 cm^{-1}; UV (95% ethanol) 330, 314, and 228 nm (ϵ 25 300, 24 800, and 20 700); NMR ($CDCl_3$, 60 MHz) δ 1.77–2.18 (m, 2 H), 2.76–3.06 (m, 4 H), 5.30 (s, 1 H), and 7.0–7.9 (m, 15 H). Anal. Calcd for $C_{25}H_{22}S_2$: C, 77.68; H, 5.74; S, 16.58. Found: C, 77.63; H, 5.78; S, 16.59.

1,2-Diphenyl-3-methyl-3-propylcyclopropene (6a): 76%; IR (neat) 2950, 1820, 1600, 1495, 1445, 1070, 915, 760, and 690 cm^{-1}; UV (95% ethanol) 338, 321, and 229 nm (ϵ 21 700, 28 900, 16 300); NMR ($CDCl_3$, 100 MHz) δ 0.84 (t, 3 H, J = 8.0 Hz), 1.08–1.37 (m, 2 H), 1.42 (s, 3 H), 1.72–1.93 (m, 2 H), and 7.2–7.8 (m, 10 H); MS m/E 248 (M^+), 233, 219, 205 (base), 105, 91, and 77. Anal. Calcd for $C_{19}H_{20}$: C, 91.88, H, 8.12. Found: C, 91.58; H, 8.16.

1,3-Diphenyl-2-methyl-3-propylcyclopropene (7a): 24%; IR (neat) 2940, 1860, 1605, 1450, 1075, 760, 700, and 690 cm^{-1}; UV (95% ethanol) 264 nm (ϵ 16 300); NMR ($CDCl_3$, 100 MHz) δ 0.89 (t, 3 H, J = 7.0 Hz), 1.09–1.47 (m, 2 H), 2.01–2.22 (m, 2 H), 2.26 (s, 3 H), and 7.0–7.6 (m, 10 H); MS, m/e 248 (M^+ and base), 219, 205, 105, 91, and 77. Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.79; H, 8.24.

1,2-Diphenyl-3-butyl-3-methylcyclopropene (6b): 54%; IR (neat) 2880, 1810, 1595, 1490, 1445, 1370, 1070, 1030, 910, 750, and 685 cm^{-1}; UV (95% ethanol) 338, 321, and 229 nm (ϵ 21 700, 28 900, 17 200); MS, m/e 262 (M^+), 233 219, 205 (base), 115, 91, and 77. NMR ($CDCl_3$, 100 MHz) δ 0.82 (t, 3 H, J = 6.5 Hz), 1.14–1.38 (m, 4 H), 1.46 (s, 3H), 1.84 (t, 2 H, J = 7.6 Hz), and 7.1–7.7 (m, 10 H). Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.54; H, 8.49.

1,3-Diphenyl-2-methyl-3-butylcyclopropene (7b): 46%; IR (neat) 2905, 1850, 1600, 1490, 1445, 1075, 910, 760, and 690 cm^{-1}; UV (95% ethanol) 263 nm (ϵ 17 500); NMR ($CDCl_3$, 100 MHz) δ 0.89 (t, 3 H, J = 6.5 Hz), 1.18–1.43 (m, 4 H), 2.15 (t, 2 H, J = 7.6 hZ), 2.29 (s, 3 H), and7.1–7.6 (m, 10 H); MS, m/e 262 (M^+), 219, 205 (base), 120, 105, 91, and 77. Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.69; H, 8.66.

1,2-Diphenyl-3-methyl-3-(3-phenylpropyl)cyclopropene (6c): 52%; IR (neat) 3300, 1815, 1605, 1495, 1445, 1370, 1075, 1030, 915, 760, and 690 cm^{-1}; UV (95% ethanol) 337, 320, and 312 nm (ϵ 21 000, 28 200, 23 700); NMR ($CDCl_3$, 100 MHz) δ 1.44 (s, 3 H), 1.40–1.95 (m, 4 H), 2.52 (t, 2 H, J = 8.0 Hz), 7.0–7.7 (m, 15 H); MS, m/e 324 (M^+), 262, 244, 220 (base), 205, 186, 91, and 77. Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.52; H, 7.43.

1,3-Diphenyl-2-methyl-3-(3-phenylpropyl)cyclopropene (7c): 48%; IR (neat) 3020, 1850, 1600, 1490, 1440, 1265, 1075, 1035, 915, 765, and 700 cm^{-1}; UV (95% ethanol) 262 nm (ϵ 16 300); NMR ($CDCl_3$, 100 MHz) δ 1.41–1.86 (m, 2 H), 2.28 (s, 3 H), 2.14–2.30 (m, 2 H), 2.64 (t, 2 H, J = 8.0 Hz), and 7.1–7.5 (m, 15 H); MS, m/e 324 (M^+), 220 (base), 205, 105, 91, and 77. Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46. Found: C, 92.59; H, 7.41.

1,2-Diphenyl-3-methyl-3-(4-pentenyl)cyclopropene (6d): 55%; IR (neat) 3020, 2875, 1795, 1630, 1585, 1480, 1430, 1065, 910, 755, and 685 cm^{-1}; UV (95% ethanol) 337, 319, and 223 nm (ϵ 21 100, 28 200, 17 000); NMR ($CDCl_3$, 100 MHz) δ 1.11–1.62 (m, 2 H), 1.51 (s, 3 H), 1.82–2.11 (m, 4 H), 5.01 (br d, 1 H, J = 11.0 Hz), 5.03 (br d, 1 H, J = 16.0 Hz), 5.68–6.15 (m, 1 H), 7.3–7.9(m, 10 H); MS, m/e 274 (M^+) 220, 205 (base), 178, 91, and 77. Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.89; H, 8.10.

1,3-Diphenyl-2-methyl-3-(4-pentenyl)cyclopropene (7d): 45%; IR (neat) 3333, 2900, 1850, 1640, 1600, 1490, 1440, 1070, 910, 760, and 700 cm^{-1}; UV (95% ethanol) 263 nm (ϵ 15 500); NMR ($CDCl_3$, 100 MHz) δ 1.21–1.58 (m, 2 H), 1.92–2.37 (m, 4 H), 2.30 (s, 3 H), 4.97 (br d, 1 H, J = 10.0 Hz), 4.99 (br d, 1 H, J = 18.0 Hz) 5.65–6.10 (m, 1 H), and 7.1–7.7 (m, 10 H); MS, m/e 274 (M^+), 259, 220, 205 (base), 141, 91, and 77. Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: c, 91.87; H, 8.08.

4-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (6e): 64%; IR (neat) 3030, 1810, 1640, 1600, 1490, 1440, 1365, 1070, 1030, 1000, 915, 910, 760, 755, and 690 cm^{-1}; UV (95% ethanol) 338, 320, 238, and 230 nm (ϵ 22 400, 29μtc300, 13 200, and 16 600); NMR ($CDCl_3$, 90 MHz) δ 1.46 (s, 3 H), 1.88–2.03 (m, 4 H), 4.78–5.10 (m, 2 H), 5.58–6.05 m, 1 H), 7.17–7.83 (m, 10 H); MS, m/e 260 (M^+, base), 245, 232, 219, 205, 141, 129, 115, 105, 91, and 77. Anal. Calcd for $C_{20}H_{20}$: C, 92.25; H, 7.74. Found: C, 92.24; H, 7.76.

4-(2-Methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (7e): 36%; IR (neat) 3050, 1850, 1645, 1600, 1490, 1445, 1430, 1075, 995, 915, 760, 700, and 690 cm^{-1}; UV (95% ethanol) 264 nm (ϵ 15 900); NMR ($CDCl_3$, 90 MHz) δ 1.83–2.38 (m, 4 H), 2.28 (s, 3 H), 4.81–5.12 (m, 2 H), 5.84 (ddt, 1 H, J = 17.0, 10.0, and 6.0 Hz), 7.0–7.5 (m, 10 H); MS, m/e 260 (M^+), 219 (base), 205, 129, 91, and 77. Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.78.

1,2-Diphenyl-3-methyl-3-(*o*-methylbenzyl)cyclopropene (6f): 41%; mp 81–82 °C; IR (KBr) 2900, 1810, 1600, 1490, 1440, 1380, 1120, 1070, 1030, 920, 770, 755, and 690 cm^{-1}; UV (95% ethanol) 344, 322, and 229 (ϵ 16 100, 22 800, 18 800); NMR ($CDCl_3$, 100 MHz) δ 1.49 (s, 3 H), 2.10 (s, 3 H), 3.10 (s, 2 H), and 7.0–7.5 (m, 14 H); MS, m/e 310 (M^+), 295, 219, 205 (base),203, and 77. Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.75; H, 7.21.

1,3-Diphenyl-2-methyl-3-(*o*-methylbenzyl)cyclopropene (7f): 59%; mp 64–65 °C; IR (KBr) 3030, 2930, 1845, 1605, 1495, 1450, 1385, 1175, 1160, 1070, 1040, 945, 920, 775, 765, 725, and 695 cm^{-1}; UV (95% ethanol) 266 nm (ϵ 21 100); NMR ($CDCl_3$, 100

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MHz) δ 2.07 (s, 3 H), 2.15 (s, 3 H), 3.44 (AB quartet, 2 H, J = 14.0 Hz), 7.0–7.5 (m, 14 H); MS, m/e 310 (M^+, base), 295, 215, 205, 105, 91, and 77. Anal. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.54; H, 7.23.

1,2-Diphenyl-3-methyl-3-(*m*-methoxybenzyl)cyclopropene (6g): 36%; mp 64–65 °C, IR (KBr) 2900, 1810, 1600, 1490, 1260, 1165, 1040, 860, 760, and 690 cm^{-1}; UV (95% ethanol) 317 and 227 nm (ε 23 000 and 28 700); NMR ($CDCl_3$, 100 MHz) δ 1.49 (s, 3 H), 3.07 (s, 2 H), 3.49 (s, 3 H), 7.0–7.9 (m, 14 H); MS, m/e 326 (M^+), 311, 242, 205 (base), and 78. Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 9.79. Found: C, 88.26; H, 6.58.

1,3-Diphenyl-2-methyl-3-(*m*-methoxybenzyl)cyclopropene (7g): 64%; mp 43–44 °C; IR (KBr) 2900, 1850, 1600, 1490, 1265, 760, and 690 cm^{-1}; UV (95% ethanol) 257 nm (ε 21 800); NMR ($CDCl_3$, 100 MHz) δ 2.12 (s, 3 H), 3.32 (d, 1 H, J = 14.0 Hz), 3.24 (s, 3 H), 6.48 (d, 1 H, J = 14.0 Hz), 7.0–7.5 (m, 14 H); MS, m/e 326 (M^+), 205 (base), 144, and 121. Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.09; H, 6.86.

Reaction of Diphenylmethylcyclopropenylium Perchlorate (5) with *tert*-Butylmagnesium Chloride. To a stirred solution containing 1.1 g of diphenylmethylcyclopropenyl perchlorate (5)[55] in 50 mL of tetrahydrofuran at −78 °C was added 15 mL of a 0.4 M solution of *tert*-butylmagnesium chloride in tetrahydrofuran. The reaction mixture was stirred at −78 °C for 1 h and was then allowed to warm to 25 °C where it was stirred for an additional 2 h. The reaction was quenched with a saturated ammonium chloride solution and the mixture was worked up in the standard fashion. The resulting residue was shown to contain a 5:4 mixture of 1,2-diphenyl-3-methylcyclopropene (9) and 1,3-diphenyl-2-methyl-cyclopropene (8). The identity of these compounds was determined by comparison with authentic samples.[55]

1,3-Diphenyl-2-methyl-3-*tert*-butylcyclopropene (11): 7%; IR (neat) 2940, 1840, 1600, 1490, 1445, 1310, 760, 700, and 690 cm^{-1}; UV (95% ethanol) 274, 268, and 263 nm (ε 12 100, 12 μtc100, and 11 800); NMR ($CDCl_3$, 100 MHz) δ 1.00 (s, 9 H), 2.44 (s, 3 H), and 7.1–7.7 (m, 10 H); MS, m/e 262 (M^+), 205 (base), 193, 115, 105, 91, and 77. Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.53; H, 8.44.

Preparation of 1,2-Diphenyl-3-methoxy-3-methylcyclopropene (12). A mixture containing 500 mg of diphenylmethylcyclopropenyl perchlorate (5) and 100 mg of sodium bicarbonate in 20 mL of anhydrous methanol was stirred at room temperature for 30 min. The pH of the solution was maintained at 7.5 by the addition of solid sodium bicarbonate. At the end of 30 min the solution was diluted with ether, washed with water and a saturated sodium chloride solution, and dried over magnesium sulfate. Removal of the ether under reduced pressure left a colorless oil (92%) whose structure was assigned as 1,2-diphenyl-3-methoxy-3-methylcyclopropene (12) on the basis of its NMR spectrum which showed signals at δ 1.90 (s, 3 H) and 3.25 (s, 3 H).

Magnesium-Induced Dimerization of Diphenylmethylcyclopropenylium Perchlorate (5). To a stirred suspension containing 3.20 g of 5 in 150 mL of anhydrous ether at −78 °C under a nitrogen atmosphere was added a suspension of activated magnesium prepared according to the method of Rieke.[56] The reaction mixture was allowed to warm to room temperature overnight. After quenching with a saturated ammonium chloride solution, the organic layer was washed three times with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a pale yellow solid which was chromatographed on a 10 × 2.5 cm neutral alumina column using a 10% methylene chloride–hexane mixture as the eluent. The resulting residue contained a 4:3:2:2 mixture of 1,3-dimethyl-2,4,5,6-tetraphenylbicyclo[2.2.0]hexa-2,5-diene (16) (37%), 1,3-dimethyl-2,4,5,6-tetraphenylbenzene (14) (25%), 1,3-diphenyl-2-methyl-3-(1,2-diphenyl-3-methyl-2-cyclopropen-1-yl)cyclopropene (15) (21%), and 1,2-dimethyl-3,4,5,6-tetraphenylbenzene (13) (17%). The mixture was resubjected to chromatography on a 60 × 2.5 cm activated silica gel column using a 5% methylene chloride–hexane mixture as the eluent. The first fraction isolated contained 1,3-diphenyl-2-methyl-3-(1,2-diphenyl-3-methyl-2-cyclopropen-1-yl)cyclopropene (15). The structure of this material was assigned on the basis of its spectral properties and by comparison with an independently synthesized sample: mp 171–172 °C (lit.[35] 172–173 °C); IR (KBr) 3040, 3030, 2970, 2860, 1820, 1760, 1660, 1600, 1500, 1450, 1280, 1160, 1070, 1030, 920, 760, and 700 cm^{-1}; NMR ($CDCl_3$ 90 MHz) δ 2.38 (s, 6 H) and 7.1–7.5 (m, 20 H); UV (95% ethanol) 270 nm (ε 24 000); MS, m/e 410 (M^+), 294, 205 (base), and 116.

The second fraction isolated from the column was assigned the structure of 2,6-dimethyl-1,3,4,5-tetraphenylbicyclo[2.2.0]hexa-2,5-diene (16) on the basis of its spectral and chemical properties: mp 163–164 °C; IR (KBr) 3060, 3020, 3000, 1600, 1480, 1450, 1130, 1070, 920, 690, and 670 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.18 (s, 6 H) and 7.0–7.5 (m, 20 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 9.45, 39.51, 112.39, 115.81, 124.60, 127.36, 127.56, 127.90, 128.46, 129.21, and 147.04; UV (95% ethanol) 265 nm (ε 26 000); MS, m/e 410, 294, 178, 116, 91, and 77. Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.48; H, 6.43.

Heating a sample of 16 at 165 °C for 5 min gave rise to 1,3-dimethyl-2,4,5,6-tetraphenylbenzene (14) in quantitative yield: mp 264–265 °C; IR (KBr) 3050, 2950, 2860, 1600, 1550, 1450, 1350, 1050, 1000, 850, and 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.78 (s, 6 H) and 7.0–7.6 (m, 20 H); UV (95% ethanol) 233 nm (ε 34 000). Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.51; H, 6.39.

The third fraction isolated from the column was identified as 1,3-dimethyl-2,4,5,6-tetraphenylbenzene (14). The last fraction isolated was assigned the structure of 1,2-dimethyl-3,4,5,6-tetraphenylbenzene (13) on the basis of its spectral properties and by comparison with an independently synthesized sample: mp 229–230 °C (lit.[57] mp 230–231 °C); IR (KBr) 3050, 2950, 2900, 1500, 1475, 1450, 1375, 1150, 1050, 1000, and 800 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.12 (s, 6 H) and 7.0–7.8 (m, 20 H); UV (95% ethanol) 235 nm (ε 35 000). Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.65; H, 6.48.

Independently synthesized samples of 1,2- and 1,3-dimethyltetraphneylbenzene (13 and 14) were prepared by heating a solution containing 500 mg of 2-methyl-3,4,5-triphenylcyclopentadienone (17)[57] and 1-phenylpropyne in 15 mL of benzene in a sealed tube at 180 °C for 48 h. Removal of the solvent under reduced pressure followed by fractional crystallization from benzene–hexane gave rise to a 2:3 mixture of 13 and 14.

Synthesis of 1,4-Dimethyl-2,3,5,6-tetraphenylbenzene (20). In order to demonstrate that the para isomer was not formed in the magnesium-induced coupling reaction of 5, we independently synthesized this prevously unknown compound. A mixture containing 500 mg of the dimer of 2,5-dimethyl-3,5-diphenylcyclopentadienone (21)[28] and 1.00 g of diphenylacetylene was heated to approximately 500 °C at which point a white solid formed. Heating was continued in order to sublime off the excess diphenylacetylene from the reaction mixture. The reaction mixture was allowed to cool and the solid that remained was suspended in ethanol and filtered. The white crystalline material that was obtained (660 mg, 84%) was identified as 1,4-dimethyl-2,3,5,6-tetraphenylbenzene (20) on the basis of its characteristics spectral data: mp 348–349 °C; IR (KBr) 2950, 1500, 1475, 1375, 1025, 1000, and 870 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.75 (s, 6 H) and 7.10–7.40 (m, 20 H); UV (95% ethanol) 230 nm (ε 33 000). Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.53; H, 6.41.

Thermolysis and Sensitized Photolysis of 1,3-Diphenyl-2-methyl-3-(1,2-diphenyl-3-methyl-2-cyclopropen-1-yl)-cyclopropene (15). A solution containing 98 mg of 15 in 0.5 mL of a pyridine–benzene (1:4) mixture was heated in a sealed tube at 150 °C for 10 h. The solvent was removed under reduced pressure to leave behind a yellow residue which was subjected to silica gel chromatography using a hexane–benzene mixture as the eluent. The first fraction (53 mg) isolated from the column was a yellow solid, mp 168–169 °C (lit.[35] mp 169–170 °C), whose structure was assigned as 1,2-diphenyl-3-methyl-3-(2,3-diphenyl-1-methyl-2-cyclopropen-1-yl)cyclopropene (24) on the basis of its spectral properties and by comparison with an authentic sample: IR (KBr) 3080, 3060, 3020, 2880, 1840, 1670, 1600, 1500, 1450, 1270, 1070, 1020, 920, 690, and 600 cm^{-1}; NMR ($CDCl_3$, 90

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MHz) δ 1.56 (s, 6 H) and 7.2–7.7 (m, 20 H). The second fraction isolated from the column was identified as 1,2-dimethyl-3,4,5,6-tetraphenylbenzene (13) by comparison with an authentic sample.

A solution containing 128 mg of 15 and 50 mg of thioxanthone in 250 mL of benzene was irradiated for 1.25 h under an argon atmosphere with a 450-W Hanovia mercury arc lamp equipped with a Uranium filter sleeve. The solvent was removed under reduced pressure and the resulting residue was subjected to silica gel chromatography using a hexane–benzene mixture as the eluent. The two components isolated from the column corresponded to the ortho (80%) and meta (20%) isomers.

Independent Synthesis of 1,2-Diphenyl-3-methyl-3-(2,3-diphenyl-1-methyl-2-cyclopropen-1-yl)cyclopropene (24). To a solution containing 25 g of 1,4-diphenyl-1,3-butadiene in 1 L of anhydrous benzene was added 41.8 g of phenyl chlorodiazirine.[58] The mixture was heated at reflux for 4.5 h and cooled to room temperature, and the solvent was removed under reduced pressure. The pale yellow solid (31 g (56%)) that remained was identified as 3,3′-bi(1,2-diphenyl-1-chlorocyclopropane) on the basis of its characteristic spectral properties: mp 208–209 °C; NMR ($CDCl_3$, 90 MHz) δ 2.35–2.78 (m, 2 H), 2.89–3.20 (m, 2 H), and 6.8–7.7 (m, 20 H).

To a solution containing 15.0 g of the above material in 500 mL of anhydrous tetrahydrofuran under a nitrogen atmosphere was added 22.4 g of potassium *tert*-butoxide in one portion. The resulting reaction mixture was heated at reflux for 72 h. At the end of this time the reaction mixture was cooled to 25 °C and 100 mL of water was added. The resulting mixture was extracted with three 100-mL portions of ether. The combined ether extracts were washed with water and a saturated brine solution and were then dried over magnesium sulfate. Removal of the solvent under reduced pressure gave 10.5 g (83%) of a tan solid which was identified as bi(1,2-diphenyl-1-cyclopropene) on the basis of its spectral properties: mp 164–165 °C; IR (KBr) 3080, 3020, 1820, 1680, 1600, 1500, 1450, 1270, 1070, 1020, 920, 690, 670 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.46 (s, 2 H), 7.1–7.6 (m, 20 H).

To a slurry containing 10.0 g of the above solid in 175 mL of anhydrous acetonitrile was added 20.5 g of trityl perchlorate. The resulting reaction mixture was stirred at 0 °C for 30 min and then 500 mL of anhydrous ether was added. The resulting slurry was filtered and the white amorphous solid that was obtained was washed with anhydrous ether. This solid was not allowed to dry completely. The material was stirred in 250 mL of anhydrous ether at −78 °C under a nitrogen atmosphere. To this mixture was added 34 mL of a 2.8 M solution of methylmagnesium bromide over a 30-min period. The resulting mixture was allowed to warm to 5 °C overnight. After quenching with a saturated ammonium chloride, the ether layer was washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave 6.65 g (62%) of a yellow solid, which was identified as 1,2-diphenyl-3-methyl-3-(2,3-diphenyl-1-methyl-2-cyclopropen-1-yl)cyclopropene (24) on the basis of its characteristic spectral properties: mp 168–169 °C (lit.[35] mp 169–170 °C); IR (KBr) 3080, 3060, 3020, 2880, 1840, 1670, 1600, 1500, 1450, 1270, 1070, 1020, 920, 690, and 600 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.56 (s, 6 H) and 7.2–7.7 (m, 20 H).

Constant Potential Electrolysis of Diphenylmethylcyclopropenylium Perchlorate (5) in Acetonitrile. A solution containing 2.73 g of lithium perchlorate and 2.0 g of 5 in 200 mL of anhydrous acetonitrile was electrolyzed (1.35 V vs. the SCE and 500 A) to completion as indicated by a return to the background level of the current. The experimental setup consisted of a three-electrode system containing a mercury pool (instrumental grade) as the working cathode electrode, a standard saturated calomel reference electrode, and a silver auxiliary anode electrode which was separated from the solution by a fritted glass disk. The resulting solution was poured into a separatory funnel containing 100 mL of water and the mercury was removed. The reaction mixture was extracted with ether. The ethereal extracts were combined and washed repeatedly with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 1.32 g (98%) of a yellow solid, which was chromatographed on a 15 × 2.5 cm Florisil column using a 5% benzene–hexane mixture as the eluent. The first fraction isolated from the column contained 400 mg of 1,3-diphenyl-2-methyl-3-(1,2-diphenyl-3-methyl-2-cyclopropen-1-yl)cyclopropene (15). The second fraction contained 720 mg of 2,6-dimethyl-1,3,4,5-tetraphenylbicyclo[2.2.0]hexa-1,3-diene (16).

Dicyanoanthracene-Sensitized Irradiation of Bicyclopropenes 15 and 24. A solution containing 100 mg of 15 (or 24) and 73 mg of 9,10-dicyanoanthracene in 450 mL of acetonitrile was irradiated for 8 h under an argon atmosphere with a 450-W Hanovia lamp equipped with a Uranium glass filter. Removal of the solvent left a yellow residue, which was subjected to thick-layer chromatography using a hexane–benzene mixture as the eluent. In the case of bicyclopropene 15 the only product isolated in 92% yield corresponded to 1,3-dimethyl-2,4,5,6-tetraphenylbenzene (14). The DCA-sensitized irradiation of 24 produced 1,2-dimethyl-3,4,5,6-tetraphenylbenzene (13) in 94% isolated yield.

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1,3,5,7-Tetrathia-*s*-indacene-2,6-dione Chemistry. Synthesis of New Multisulfur Donor Molecules and Nickel–Dithiolene Electron-Transfer Complexes

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The synthesis of 1,3,5,7-tetrathia-*s*-indacene-2,6-dione is reported. This versatile synthon is used to prepare a variety of new multisulfur tetrathiafulvalene-analogous donors and nickel–dithiolene complexes. Donor or acceptor properties are investigated, and new materials, in the form of charge-transfer solids or ion–radical salts, derived from the new compounds are either electrically insulating or semiconducting.

We report the synthesis of new donor molecules analogous to BEDT-TTF[1] (bis(ethylenedithio)tetrathiafulvalene) (1) (Figure 1). The latter has been used extensively in the preparation of new superconducting molecular

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