Photochemistry of Cyclopropene Derivatives. 34. Photocycloaddition Reactions of 2-Alkenyl-Substituted Cyclopropenes[1]

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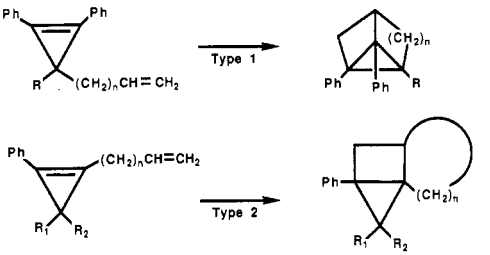
The sensitized irradiation of 2-(4-pentenyl)-substituted cyclopropenes produces tricyclo[3.3.0.0^{1,3}]octanes by means of a novel intramolecular [2 + 2] cycloaddition. In dramatic contrast to the photochemical results, thermolysis affords a product containing the bicyclo[4.1.0]heptane ring. The thermal reaction proceeds via ring opening of the cyclopropene to give a vinylcarbene, which subsequently adds across the neighboring π-bond. The sensitized photolysis of a 2-allyl-substituted cyclopropene was studied and found to give a 2-vinyl-substituted butadiene. The formation of the diene has been interpreted in terms of a di-π-methane rearrangement. During the course of these studies we found that sulfonyl-substituted cyclopropenes react with a variety of alkyllithium reagents to give disubstituted cyclopropenes in good yield. The reaction is unique in that it formally involves addition of the lithium reagent across the "wrong" end of the vinyl sulfone. Several mechanistic possibilities are proposed to account for the formation of the product.

Small ring hydrocarbons play an important role in many aspects of organic chemistry.[1-3] Recently, cyclopropenes have found growing utility in organic synthesis as precursors to cyclic and acyclic molecules.[4-6] In ground-state chemistry, it is observed that the cyclopropene ring system often undergoes unusual and sometimes unexpected chemical transformations to species of lower energy content.[7-18] Similarly, ring strain would be anticipated to have a pronounced effect upon the reactivity of cyclopropenes in the excited state. Our research group has been involved over the past few years in a program of synthesizing unusual polycyclic ring systems, which uses the intramolecular [2 + 2] cycloaddition of cyclopropene derivatives as the primary strategy.[19,20] Photocycloaddition across the double bond of cyclopropene proceeds quite readily since it reduces ring strain by 26 kcal/mol.[21] Two basic structural variants of the intramolecular [2 + 2] cycloaddition can be achieved by altering the point of attachment of the alkenyl side chain to the cyclopropene ring. We refer to these two modes as type 1 and type 2 internal cycloaddition routes. In our previous studies with type



1 molecules, we observed that the triplet-sensitized irradiation results in smooth cycloaddition to give novel polycyclic ring systems.[19] Since chemical reactivity in the intramolecular [2 + 2] cycloaddition process can be significantly modified by the appropriate choice of substituents and geometry,[22] we have undertaken an investigation of the photochemistry of type 2 cyclopropenes with the hope of gaining additional information concerning the nature of the intramolecular cycloaddition reaction. The results reported below summarize various aspects of this effort.

A. Synthesis and Photochemistry of Alkenyl-Substituted Cyclopropenes. In our previous hydrogen transfer studies with aryl-substituted cyclopropenes,[1] we have examined the sensitized behavior of cyclopropenyl-5-hexene **1** in order to determine whether a δ-allylic hydrogen could be transferred to the π–π^* triplet state. Interestingly, the sensitized irradiation of **1** gave rise to a single photoproduct whose structure was assigned as the intramolecular [2 + 2] cycloadduct **2**. No sign of the internal hydrogen-transfer product **3** was evident in the crude photolysate. With this system the triplet excited state prefers to undergo an intramolecular [2 + 2] cycloaddition rather than the hydrogen-transfer reaction.

In view of the stringent spatial requirements associated with the intramolecular [2 + 2] cycloaddition reaction of cyclopropenes, we thought it worthwhile to consider what effect a variation in the spatial proximity between the cyclopropene and the internal double bond would have on the course of the intramolecular cycloaddition. This led

(1) For Part 33, see: Padwa, A.; Chou, C. S.; Rosenthal, R.; Terry, L. W. *J. Org. Chem.* **1988**, *53*, 4193.
(2) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978. de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809.
(3) Closs, G. L. *Advances in Alicyclic Chemistry*; Hart, H., Karabatsos, G. J., Eds.; Academic Press: New York, 1966; Vol. 1, p 53.
(4) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1984**, *106*, 805; *Tetrahedron Lett.* **1984**, 5611; *J. Org. Chem.* **1985**, *50*, 3524; *Tetrahedron Lett.* **1986**, 2777; *J. Am. Chem. Soc.* **1986**, *108*, 6695; **1986**, *108*, 6713.
(5) Albert, R. M.; Butler, G. B. *J. Org. Chem.* **1977**, *42*, 674.
(6) Weber, W.; de Meijere, A. *Chem. Ber.* **1985**, *118*, 2450. Kostikov, R.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1528. Liese, T.; de Meijere, A. *Chem. Ber.* **1986**, *119*, 2995; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 65. Seyed-Mahdavi, F.; Teichmann, S.; de Meijere, A. *Tetrahedron Lett.* **1986**, 6185. Bengston, G.; Keyaniyan, S.; de Meijere, A. *Chem. Ber.* **1986**, *119*, 3607.
(7) Schleyer, P. V. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.
(8) Streeper, R. D.; Gardner, P. D. *Tetrahedron Lett.* **1973**, 767.
(9) York, E. J.; Dittmar, W.; Stevenson, R. J.; Bergman, R. *J. Am. Chem. Soc.* **1973**, *95*, 5680; **1972**, *94*, 2882.
(10) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461.
(11) Deem, M. L. *Synthesis* **1972**, 675.
(12) Arnold, D. R.; Pincock, J. A.; Morchat, R. *J. Am. Chem. Soc.* **1973**, *95*, 7536.
(13) Newmann, M. F.; Buchecker, C. *Tetrahedron Lett.* **1973**, 2875.
(14) Battiste, M. A.; Halton, B.; Grubbs, R. H. *Chem. Commun.* **1967**, 907.
(15) Durr, H. *Tetrahedron Lett.* **1967**, 1649.
(16) 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.
(17) Padwa, A.; Rieker, W. F.; Rosenthal, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1710.
(18) Padwa, A. *Acc. Chem. Res.* **1979**, *12*, 310; *Org. Photochem.* **1979**, *4*, 261.
(19) Padwa, A.; Kennedy, G. D.; Newkome, G. R.; Fronczek, F. R. *J. Am. Chem. Soc.* **1983**, *105*, 137. Padwa, A.; Rieker, W. F.; Rosenthal, R. J. *J. Org. Chem.* **1984**, *49*, 1353; *J. Am. Chem. Soc.* **1983**, *105*, 4446. Padwa, A.; Kennedy, G. D.; Wannamaker, M. W. *J. Org. Chem.* **1985**, *50*, 5334.
(20) For some related work, see: Zimmerman, H. E.; Fleming, S. A. *J. Org. Chem.* **1985**, *50*, 2539. Zimmerman, H. E.; Kreil, D. J. *J. Org. Chem.* **1982**, *47*, 2060. Zimmerman, H. E.; Bunce, R. A. *J. Org. Chem.* **1982**, *47*, 3377.
(21) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395.
(22) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.

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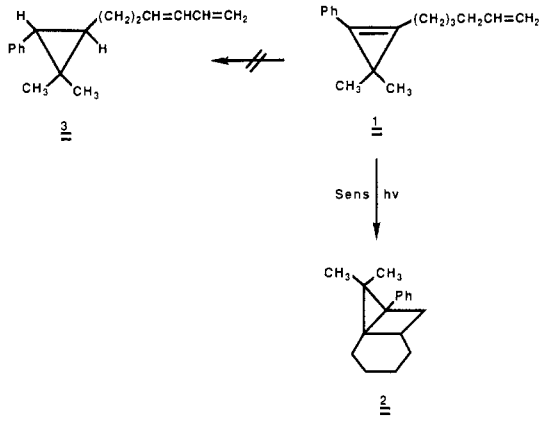
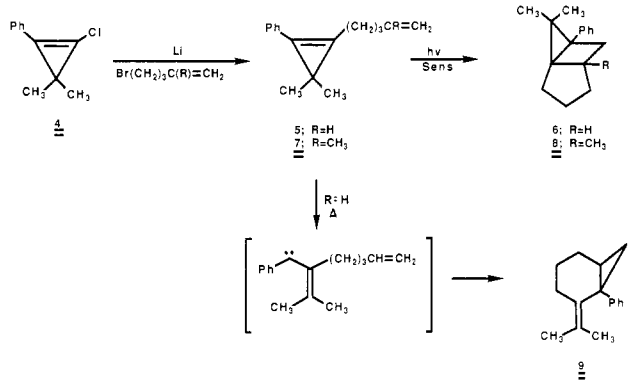
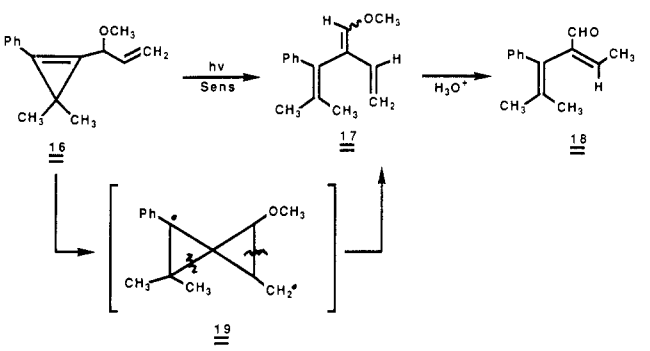


us to examine the photochemical behavior of several 4-pentenyl-substituted cyclopropenes so as to compare their behavior with the homologous 5-hexenyl system (i.e. 1). The several new compounds employed in this study were synthesized by treating 1-phenyl-2-chloro-3,3-dimethylcyclopropene[23] (4) with lithium metal followed by reaction with the appropriate alkenyl bromide. The sensitized photolysis of cyclopropene **5** in benzene (thioxanthone) produced 2,2-dimethyl-3-phenyltricyclo[3.3.0.0^{1,3}]octane (**6**) in 59% isolated yield. The structure of the tricyclic ring system was assigned on the basis of its spectral properties (see Experimental Section). Subjection of the closely related 4-methyl-4-pentenylcyclopropene **7** to similar photolysis conditions gave cycloadduct 8 in 92% yield.

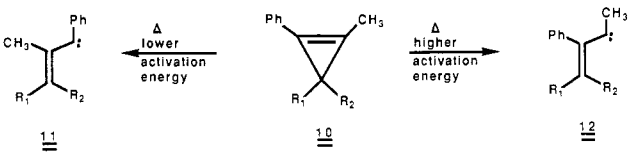


In contrast to the sensitized irradiation results, direct irradiation or thermolysis of a sample of **5** at 135 °C afforded a single product in 65% isolated yield, whose structure was assigned as 2-isopropylidene-1-phenylbicyclo[4.1.0]heptane (**9**) on the basis of its spectral properties. The most reasonable explanation to account for the formation of **9** involves a sequence consisting of opening of the cyclopropene ring to give a vinylcarbene intermediate. Attack of the carbene carbon on the neighboring double bond generates the bicyclo[4.1.0]heptane skeleton. Molecular orbital calculations by Goddard suggest that the thermal ring opening first proceeds to a diradical planar intermediate, which then decays to the vinylcarbene.[25] The preferential cleavage of the cyclopropene ring to give the phenyl-substituted vinylcarbene is consistent with earlier observations[10] and can be rationalized by some MO calculations reported by Pincock

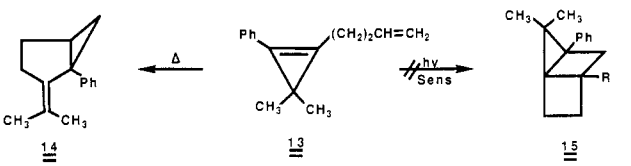
Scheme I



and Boyd.[26] These workers have found that the presence of a phenyl group on the cyclopropene double bond opposite the σ-bond that is breaking results in a substantial increase (ca. 8 kcal/mol) in the activation barrier for bond cleavage. Their results suggest that cross-conjugated carbenes such as **12** are less stable than linearly conjugated systems like **11**.



As an extension of our studies in this area we have also examined the sensitized behavior of the next lower homologue so as to determine what effect a variation in the spatial proximity between the cyclopropene and the internal double bond would have on the course of the reaction. In contrast to the pentenyl system, no signs of an intramolecular cycloadduct could be detected in the crude reaction mixture derived from the sensitized irradiation of cyclopropene **13**. Clearly, the spatial relationship of the two π-bonds plays an important role in controlling the facility of the internal [2 + 2] cycloaddition reaction of these alkenyl-substituted cyclopropenes. Inspection of molecular models indicates that the geometry associated with the parallel plane approach of π-bonds is not easily obtained with the butenyl system. We have also studied the thermal behavior of cyclopropene **13** and found that heating this material at 135 °C for 16 h gave bicyclohexane **14** in 62% isolated yield. The formation of **14** corresponds to ring opening of the cyclopropene followed by addition of the resulting vinylcarbene intermediate across the adjacent π-bond.



Cyclopropene photochemistry has been unusual in the rich variety of different types of photochemical transformations encountered.[18] One of the most general of photochemical reactions is the di-π-methane (Zimmerman) rearrangement.[27] In our previous studies we reported on the photochemical rearrangement of 3-vinylcyclopropenes to cyclopentadienes.[28] Similar observations have also been recorded by the Zimmerman group.[16,20] This transfor-

(23) Padwa, A.; Chiacchio, U.; Hatanaka, N. *J. Am. Chem. Soc.* **1978**, *100*, 3928. Padwa, A.; Blacklock, T. J.; Chou, C. S.; Hatanaka, N. *J. Am. Chem. Soc.* **1979**, *101*, 5743. Padwa, A.; Chou, C. S.; Rosenthal, R. J.; Rubin, B. *J. Am. Chem. Soc.* **1981**, *103*, 3057; Padwa, A.; Terry, L. W. *J. Org. Chem.* **1986**, *51*, 3738.

(24) Henseling, K.; Weyerstahl, P. *Chem. Ber.* **1975**, *108*, 2803.

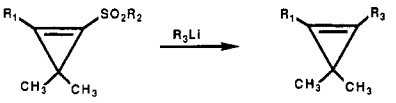
(25) Davis, J. H.; Goddard, W. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 4017; **1977**, *99*, 2427.

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

(27) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531.

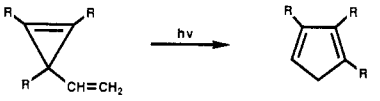
(28) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N. *J. Am. Chem. Soc.* **1977**, *99*, 2344; *J. Org. Chem.* **1978**, *43*, 1481.

Table I. Reaction of Sulfonyl-Substituted Cyclopropenes with Alkyllithium Reagents



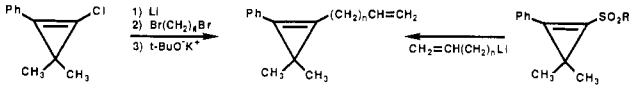
R_1	R_2	R_3	% yield of product
Ph	CH_3	CH_3	48
Ph	CH_3	n-C_4H_9	81
Ph	CH_3	Ph	32
Ph	CH_3	n-C_4H_7	68
Ph	Ph	CH_3	50
Ph	Ph	n-C_4H_9	85
Ph	Ph	t-C_4H_9	40
Ph	Ph	vinyl	35
Ph	Ph	allyl	35
Me_3Si	p-$CH_3C_6H_4$	CH_3	85
Me_3Si	p-$CH_3C_6H_4$	n-C_4H_9	90
Me_3Si	p-$CH_3C_6H_4$	t-C_4H_9	98
Me_3Si	p-$CH_3C_6H_4$	Ph	85
Me_3Si	p-$CH_3C_6H_4$	CH=CHPh	85

mation represents a mechanistically intriguing example of the di-π-methane reaction. In order to establish whether

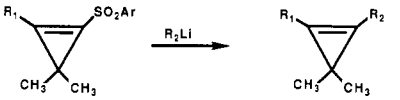


2-allyl-substituted cyclopropenes of type 2 would also undergo the di-π-methane rearrangement, we studied the photochemical behavior of cyclopropene **16**. The sensitized irradiation of **16** afforded a 2:3 mixture of Z and E trienes **17** in high yield. The two isomeric trienes could be separated and were observed to be readily interconverted on sensitized irradiation. Acid hydrolysis of either isomer produced the dienyl aldehyde **18**, thereby providing additional support for the structure assignment. We consider that the most economical explanation for the formation of triene **17** is that illustrated in Scheme I. Vinyl–vinyl bridging of the π–π^* triplet state leads to spiro diradical **19**, which is ultimately converted to **17** by scission of both cyclopropyl rings. Thus, the sensitized irradiation of a 2-allyl-substituted cyclopropene provides still another example of the ubiquitous di-π-methane rearrangement.

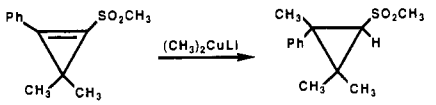
B. Sulfonyl-Substituted Cyclopropenes. Reaction with Organolithiates. During the course of our research with these alkenyl-substituted cyclopropenes, we found that these compounds could also be prepared in good yield by treating 1-phenyl-2-sulfonyl-3,3-dimethylcyclopropenes (i.e. **20** or **21**) with alkenyllithiates as well as by the more traditional route employing 1-chloro-2-phenylcyclopropene **4**.[29] We were quite surprised to discover that the reaction



of these sulfonyl-substituted cyclopropenes with an alkenyllithium gave **22** in good yield since lithium reagents generally add across the π-bond of vinyl sulfones. The stabilization of carbanionic centers by adjacent sulfur groups is the basis of many valuable transformations in organic synthesis.[30–34] Vinyl sulfones undergo conjugate addition with various reagents, and the resulting α-sulfonyl anions may be protonated or trapped by an assortment of electrophiles.[35,36] We have found that this nucleophilic substitution reaction also occurs with 1-(trimethylsilyl)-2-(p-tolylsulfonyl)cyclopropenes **24**. Table I presents the



results of the reaction with a variety of alkyllithium reagents. As the table indicates, the reactions derived from the trimethylsilyl-substituted cyclopropene **24**[37] proceed in better yield than those derived from the phenyl-substituted compound (i.e. **23**). In experiments where TMEDA or HMPA were present, the yield of product was significantly lower. Addition of m-dinitrobenzene also caused a significant diminution in product formation. In contrast to the sulfonyl displacement reaction that occurred when **20** was treated with methyllithium, reaction of **20** with lithium dimethyl cuprate afforded the trimethyl-substituted cyclopropane **27** in 85% isolated yield.

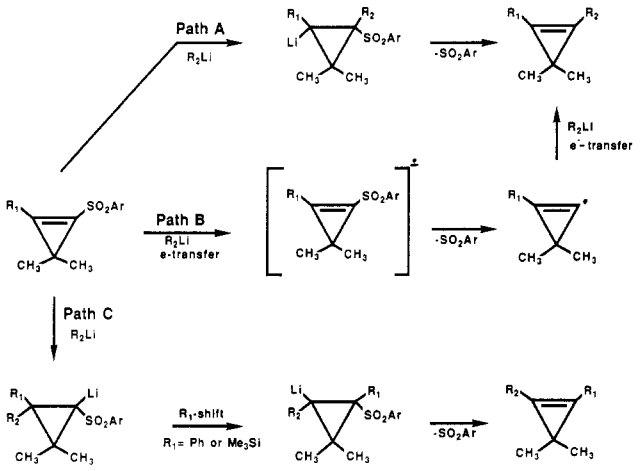


Interestingly, the silylsulfonyl-substituted cyclopropene **24** did not undergo conjugate addition with the above cuprate reagent. The equilibrium position for the reversible transfer of an electron can be estimated from a knowledge of the oxidation (E_{ox}) and reduction (E_{red}) potentials of the reactants.[38] Electrode potentials are measured by standard polarographic or cyclic voltammetry techniques in an aprotic solvent with respect to a saturated calomel electrode.[39] Since these techniques determine the reduction process, the most powerful reducing agents have the most negative E_{ox} values, and those compounds that are the moxt difficult to reduce possess the most negative E_{red} values. These considerations led us to determine the reduction potentials of cyclopropenes **20**, **23**, and **24**. The values obtained (**20** = −1.66 eV; **23** = −1.51 eV, and **24** = −1.88 eV) were determined in DMF solution by using a platinum electrode with a sweep time of 50 mV/s with respect to a saturated calomel electrode.[40] A 0.1 M of tetrabutylammonium perchlorate was used as the supporting electrolyte. The value of −1.88 eV for the reduction potential of **24** represents a strikingly high negative value. Moreover, the difference in reduction potentials between

(29) The reaction of cyclopropene **4** with lithium metal followed by treatment of the corresponding cyclopropenyl anion with 4-bromo-1-butene led to a complex mixture of products. As a consequence, cyclopropene **13** was prepared from **4** by this two-step sequence employing 1,3-dibromopropane.

(30) Posner, G. H.; Brunelle, D. J. *J. Org. Chem.* **1973**, *38*, 2747.
(31) Conrad, P. C.; Fuchs, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 346. Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* **1985**, *107*, 6137; *Tetrahedron Lett.* **1986**, 1429.
(32) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1980**, *45*, 4534.
(33) Taber, D. F.; Saleh, S. A. *J. Org. Chem.* **1981**, *46*, 4817.
(34) Ford-More, A. H.; Peters, R. A.; Wakelin, R. W. *J. Chem. Soc.* **1949**, 1754.
(35) Block, E. *Reaction of Organosulfur Compounds*; Academic Press: New York, 1978.
(36) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.
(37) Padwa, A.; Wannamaker, M. W. *Tetrahedron Lett.* **1986**, 5817. Padwa, A.; Wannamaker, M. W.; Dyszlewski, A. D. *J. Org. Chem.* **1987**, *52*, 4760.
(38) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59.
(39) Horner, L.; Lund, H. *Organic Electrochemistry*; Baizer, M. M., Ed.; M. Dekker: New York, 1983.
(40) We wish to thank Professor Paul Gassman, University of Minnesota, for these measurements.

Scheme II

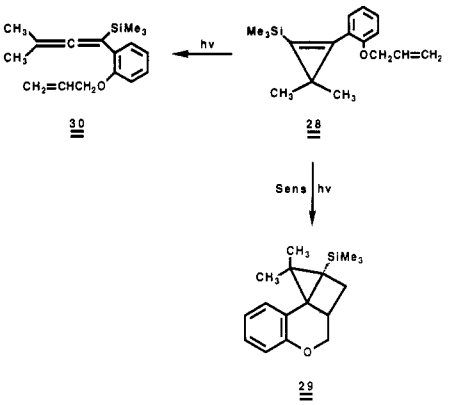


20 and 24 (0.22 eV) corresponds to ca. 5 kcal/mol and could account for the difference in reactivity of the two cyclopropenes toward the cuprate reagent. Thus, the silyl-substituted cyclopropene **24** is reduced with much greater difficulty than **20**, which undergoes ready conjugate addition with dimethylcopper lithium.

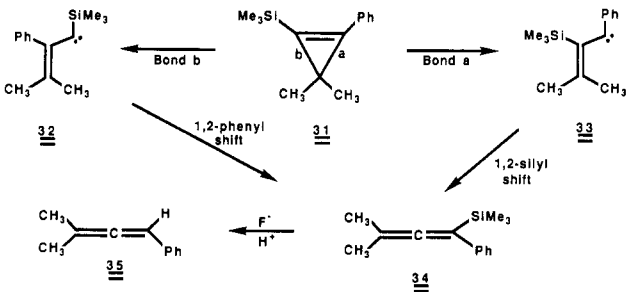
The mechanism by which these sulfonyl-substituted cyclopropenes undergo the displacement reaction with alkyllithium reagents is of considerable interest. Three fundamentally different paths seem possible and these are presented in Scheme II. Path A is somewhat unique in that it involves addition of the lithium reagent to the "wrong" end of the π-bond. It should be pointed out, however, that various nucleophilic reagents are known to add to unactivated cyclopropenes presumably as a consequence of relief of strain.[41] In this case, the bulky trimethylsilyl substituent may actually block attack of the reagent at the β-position as well as stabilize the resulting carbanion. Chelation of the incoming alkylithium with the oxygen atoms of the sulfonyl group may also be a factor in promoting path A. Recently, Russell has shown that phenyl vinyl sulfones react with alkylmercury reagents by an addition–elimination sequence.[42] The mechanism suggested for that process may also be applicable to the cyclopropenyl system.

The alternate path (B) involves a $S_{RN}1$ type radical anion chain mechanism.[43-45] The ability of alkyllithiums to serve as a one-electron donor toward other organic substrates has been established by Ashby.[46] The propagation cycle for the reaction is sketched in Scheme II. According to this mechanism, the alkyllithium reagent initiates the process by transferring an electron to the cyclopropenyl sulfone. The resulting radical anion undergoes loss of the sulfinate group to give a cyclopropenyl radical. Further reaction of this species with more alkyllithium produces the radical anion of the product, which, in turn, transfers an electron to the starting material. Still an additional possibility (path C) involves conjugate addition of the alkyllithium to the cyclopropenyl sulfone. The resulting cyclopropyllithiate could then undergo a 1,2-phenyl (or 1,2-silyl) shift to produce a rearranged carbanion, which subsequently ejects the sulfinate group. At the current time, the available data do not distinguish among these possibilities.

C. Photochemistry of Silyl-Substituted Cyclopropenes. We have taken advantage of this novel substitution process to synthesize cyclopropene **28** by treating **24** with [*o*-(allyloxy)phenyl]lithium. The triplet-sensitized irradiation of **28** cleanly afforded the novel intramolecular cycloadduct **29** in 85% yield. In contrast to the sensitized reaction, direct irradiation of **28** in benzene produced allene **30** in 90% yield. Similar results were obtained upon direct



irradiation of the simpler phenyl-substituted cyclopropene **31**, which gave allene **34** in 95% yield. This material could readily by desilylated to produce 3-methyl-1-phenyl-1,2-butadiene (**35**). The formation of allenes **30** and **34** as singlet derived products is quite unusual since, in general, allenes are minor cyclopropene photoproducts.[18]



The photochemistry of cyclopropene derivatives has been shown to be remarkably dependent on the multiplicity of the excited state involved.[16-20] The formation of a vinylcarbene in the direct irradiation experiments can be viewed as the result of homolytic cleavage and simultaneous rotation of the disubstituted methylene carbon.[25,47] Once formed, the reactive intermediate undergoes a subsequent 1,2-phenyl (or silyl shift) to give the observed allene **34**. Ring opening of an unsymmetrically substituted cyclopropene such as **31** can occur in either of two directions to generate vinylcarbenes **32** or **33**. There is some difficulty in interpreting the regioselectivity of ring opening for this reaction since the formation of allene **34** can be explained by either a 1,2-phenyl shift from **32** or a 1,2-silyl shift from **33**. Cyclopropene to vinylcarbene conversions are known to be reversible both thermally[9] and photochemically.[48] This means that the product distribution may reflect different rates of return to cyclopropene for the two possible carbenes rather than selectivity of ring opening. In the earlier cases studied,[16-20] the product distribution obtained in the direct irradiation experiments favored cleavage of an alkyl- rather than a phenyl-substituted σ-bond. With cyclopropene **31**, however, direct

(41) Hauck, G.; Durr, H. *J. Chem. Res.* **1981**, 180.
(42) Russell, G. A.; Ngoviwatchai, P. *Tetrahedron Lett.* **1986**, 3479.
(43) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.
(44) Russell, G. A.; Mudryk, B.; Jawdosink, M. *J. Am. Chem. Soc.* **1981**, *103*, 4610.
(45) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.
(46) Ashby, E. C.; Pham, T. N.; Park, B. *Tetrahedron Lett.* **1985**, 4691.
(47) Morchat, R. M.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* **1978**, 743.
(48) Pincock, J. A.; Mathur, N. C. *J. Org. Chem.* **1982**, *47*, 3699.

photolysis may actually give vinylcarbene **33** since this electrophilic species would be considerably stabilized by the β-situated silyl group.[49,50] We believe that the unusual photochemistry encountered with cyclopropenes **28** and **34** is related to a facile trimethylsilyl shift from a vinylcarbene intermediate.

In conclusion, the results obtained from this investigation indicate that the triplet states of type 2 alkenyl-substituted cyclopropenes undergo novel photochemistry. The subtle variation of behavior as a function of the nature of the substituent groups and geometry of the side chain attached to the cyclopropene ring continues to provide mechanistic challenge. Further studies on the photochemical behavior of other unsaturated cyclopropenes are in progress and will be reported in due course.

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 a Varian EM-390 and a Nicolet NMC-360 MHz spectrometer. ^{13}C NMR spectra were recorded on an IBM NB 200 SY FT spectrometer. Microanalyses were performed at Atlantic Microlabs, Atlanta, GA. Mass spectra were determined with a VG MM-7070S mass spectrometer at an ionizing voltage of 70 eV.

Preparation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-4-pentene (5). To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenylcyclopropene[24] (**4**) in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C, and 3 mL of freshly distilled HMPA was added. The resulting mixture was stirred for 30 min at this temperature and was quenched by the addition of 1.30 g of 5-bromo-1-pentene in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at room temperature, and this was followed by quenching with a saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column with hexane as the eluent to give 1.30 g (70%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-4-pentene (**5**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.28 (s, 3 H), 1.78 (p, 2 H, J = 7.2 Hz), 2.16 (q, 2 H, J = 7.2 Hz), 2.62 (t, 2 H, J = 7.2 Hz), 4.96 (dd, 1 H, J = 10.0 and 2.0 Hz), 5.02 (dd, 1 H, J = 17.0 and 2.0 Hz), 5.78 (ddt, 1 H, J = 17.0, 10.2, and 7.2 Hz), and 7.10–7.35 (m, 5 H); IR (neat) 3090–2860, 1835, 1645, 1600, 1490, 1445, 1365, 990, 915, 785, 760, and 690 cm^{-1}; UV (95% ethanol) 268 (ε 15 300), 222 (ε 11 000), and 217 nm (ε 10 560); m/e 212 (M^+), 143 (base), 115, 91, and 77. Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.44; H, 9.51.

Triplet-Sensitized Irradiation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-4-pentene (5). A solution containing 213 mg of **5** and 21 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium glass filter sleeve for 2 h. The solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography with hexane as the eluent. The major fraction contained 124 mg (59%) of a clear oil whose structure was assigned as 2,2-dimethyl-3-phenyltricyclo[3.3.0.$0^{1,3}$]octane (**6**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 0.88 (s, 3 H), 1.29 (s, 3 H), 1.62 (dd, 1 H, J = 11.7 and 2.5 Hz), 1.64–1.90 (m, 6 H), 2.01–2.09 (m, 1 H), 2.13 (dd, 1 H, J = 11.7 and 4.9 Hz), and 7.00–7.20 (m, 5 H); IR (neat) 3060–2860, 1695, 1600, 1490, 1445, 1390, 1315, 925, 810, 760, and 700 cm^{-1}; UV (95% ethanol) 217 mm (ε 6730); m/e 212 (M^+), 197, 183, 168, 155, 141, 105, 91, and 77. Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.42; H, 9.44.

Thermolysis of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-4-pentene (5). A solution containing 200 mg of **5** in 40 mL of benzene was thermolyzed in a sealed tube at 180 °C for 64 h. The solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography with hexane as the eluent. The major fraction contained 110 mg (56%) of a clear oil whose structure was assigned as 2-isopropylidene-1-phenylbicyclo[4.1.0]heptane (**9**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 0.40 (dd, 1 H, J = 8.1 and 4.6 Hz), 0.55 (t, 1 H, J = 4.6 Hz), 1.18 (m, 1 H), 1.53 (s, 3 H), 1.55–1.85 (m, 5 H), 1.89 (s, 3 H), 1.96 (dd, 1 H, J = 12.3 and 8.1 Hz), and 7.05–7.32 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.56, 20.95, 21.10, 22.42, 25.98, 27.71, 32.57, 33.08, 125.48, 127.68, 128.05, 128.86, 137.09, and 144.25; IR (neat) 3060–2860, 1600, 1495, 1440, 1380, 1100, 1075, 1025, 790, 750, and 705 cm^{-1}; UV (95% ethanol) 236 nm (ε 3770); m/e 212 (M^+, base), 197, 169, 155, 141, 12, 115, and 91; HRMS calcd for $C_{16}H_{20}$ 212.1565, found 212.1561.

Preparation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-4-methyl-4-pentene (7). To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenylcyclopropene (**4**) in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C, and 3 mL of freshly distilled HMPA was added. The resulting mixture was stirred for 30 min and was quenched by the addition of 1.41 g of 5-bromo-2-methyl-1-pentene in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at room temperature, and this was followed by quenching with a saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column with hexane as the eluent to give 1.40 g (71%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenyl-cyclopropen-1-yl)-4-methyl-4-pentene (**7**) on the basis of its spectral properties: NMR ($CDCl_3$, 90 MHz) δ 1.30 (s, 3 H), 1.70 (s, 3 H), 1.80–2.30 (m, 4 H), 2.60 (t, 2 H, J = 7.2 Hz), and 7.05–7.40 (m, 5 H); IR (neat) 3070–2800, 1830, 1640, 1590, 1480, 1440, 1360, 1165, 1060, 880, 750, and 680 cm^{-1}; UV (95% ethanol) 272 (ε 14 250) and 222 nm (ε 11 600); m/e 226 (M^+), 211, 183, 143 (base), 115, 91, and 77. Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 90.12; H, 9.82.

Triplet-Sensitized Irradiation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-4-methyl-4-pentene (7). A solution containing 200 mg of **7** and 20 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex glass filter sleeve for 15 min. The solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography with hexane as the eluent. The major fraction contained 185 mg (92%) of a clear oil whose structure was assigned as 2,2,5-trimethyl-3-phenyltricyclo[3.3.0.$0^{1,3}$]octane (**8**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 0.95 (s, 3 H), 1.05 (s, 3 H), 1.50 (s, 3 H), 1.76–1.86 (m, 2 H), 1.89 (d, 1 H, J = 11.7 Hz), 1.94–2.04 (m, 4 H), 2.08 (d, 1 H, J = 11.7 Hz), and 7.20–7.40 (m, 5 H); IR (neat) 3060–2830, 1600, 1500, 1440, 1370, 1070, 1030, 760, and 700 cm^{-1}; UV (95% ethanol) 272 (ε 4200) and 228 nm (ε 4900); m/e 226 (M^+), 211, 197 (base), 155, 141, 129, 115 and 91; HRMS calcd for $C_{17}H_{22}$ 226.1721, found 226.1725.

Preparation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-3-butene (13). To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenylcyclopropene (**4**) in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C, and 3 mL of freshly distilled HMPA was added. The resulting mixture was stirred for 30 min and was quenched by the addition of 1.23 g of 1,4-dibromobutane in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at room temperature, and this was followed by quenching with a saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column with hexane as the eluent to give 1.05 g (43%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-4-bromobutane on the basis of its spectral

(49) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.
(50) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

properties: NMR ($CDCl_3$, 90 MHz) δ 1.26 (s, 6 H), 1.73–2.00 (m, 4 H), 2.60 (t, 2 H, J = 6.0 Hz), 3.37 (t, 2 H, J = 6.0 Hz), and 7.10–7.35 (m, 5 H); IR (neat) 3090–2840, 1830, 1600, 1490, 1440, 1360, 755, and 690 cm^{-1}; UV (95% ethanol) 270 (ϵ 12400) and 229 nm (ϵ 20700).

A solution containing 1.05 g of the above bromide, 0.46 g of potassium *tert*-butoxide, and 0.10 g of 18-crown-6 in 10 mL of petroleum ether was heated at 60 °C at 3 h. The mixture was poured into water, and the aqueous layer was extracted with petroleum ether. The combined organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column with hexane as the eluent to give 0.50 g (66%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-3-butene (**13**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.28 (s, 6 H), 2.38–2.46 (m, 2 H), 2.72 (t, 2 H, J = 7.4 Hz), 4.99–5.03 (m, 1 H), 5.07–5.14 (m, 1 H), 5.85–5.98 (m, 1 H), and 7.25–7.45 (m, 5 H); IR (neat) 3060–2840, 1830, 1630, 1590, 1430, 900, 750, and 680 cm^{-1}; UV (95% ethanol) 272 (ϵ 11900) and 220 nm (ϵ 10300); m/e 198 (M^+), 183 (base), 143, 115, 91, and 77; HRMS calcd for $C_{15}H_{18}$ 198.1408, found 198.1406.

Thermolysis of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-3-butene (13). A solution containing 96 mg of **13** in 40 mL of benzene was thermolyzed in a sealed tube at 135 °C for 16 h. The solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography with a 10% silver nitrate impregnated column with 10% ether–hexane as the eluent. The major fraction contained 60 mg (62%) of a clear oil whose structure was assigned as 2-isopropylidene-1-phenylbicyclo-[3.1.0]hexane (**14**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 0.76, (t, 1 H, J = 4.8 Hz), 1.28 (s, 3 H), 1.44 (dt, 1 H, J = 8.5 and 4.8 Hz), 1.55 (s, 3 H), 1.67–1.78 (m, 2 H), 2.08–2.26 (m, 2 H), 2.65–2.78 (m, 1 H), and 7.10–7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 19.43, 21.55, 22.32, 26.62, 31.58, 33.32, 37.02, 122.66, 124.94, 127.80, 127.95, 139.01, and 144.97; IR (CCl_4) 3060–2860, 1605, 1500, 1440, 915, and 700 cm^{-1}; UV (95% ethanol) 232 nm (sh, ϵ 6500); m/e 198 (M^+), 183 (base), 155, 141, 129, 115 and 91; HRMS calcd for $C_{15}H_{18}$ 198.1408, found 198.1414.

Preparation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-1-methoxy-2-propene (16). To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenylcyclopropene (**4**) in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C, and 3 mL of freshly distilled HMPA was added. The resulting solution was stirred for 30 min and was quenched by the addition of 0.48 g of acrolein in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at room temperature, and this was followed by the addition of 2.47 g of iodomethane. After being stirred for an additional 10 h, the mixture was quenched with a saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column with a 5% ether–hexane mixture as the eluent to give 1.10 g (59%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-1-methoxy-2-propene (**16**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.12 (s, 3 H), 1.13 (s, 3 H), 3.21 (s, 3 H), 4.64 (d, 1 H, J = 6.9 Hz), 5.03–5.07 (m, 2 H), 5.68–5.79 (m, 1 H), and 7.05–7.30 (m, 5 H); IR (neat) 3080–2810, 1830, 1730, 1675, 1490, 1440, 1080, 770, and 690 cm^{-1}; UV (95% ethanol) 270 (ϵ 12200) and 217 nm (sh, ϵ 11500); m/e 214 (M^+), 199, 167, 143 (base), 128, 115, 105, and 71. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.02; H, 8.32.

Triplet-Sensitized Irradiation of 1-(3,3-Dimethyl-2-phenylcyclopropen-1-yl)-1-methoxy-2-propene (16). A solution containing 100 mg of **16** and 10 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Pyrex glass filter sleeve for 15 min. The solvent was removed under reduced pressure, and the residue was subjected to medium-pressure silica gel chromatography with use of a 10% silver nitrate impregnated silica gel column with 10% ether–hexane as the eluent. The first fraction collected contained 32 mg (32%) of a clear oil whose structure was assigned as (*Z*)-1-methoxy-4-methyl-3-phenyl-2-vinyl-1,3-pentadiene (**17**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.84 (s, 3 H), 1.85 (s, 3 H), 3.73 (s, 3 H), 4.97 (dd, 1 H, J = 10.6 and 2.0 Hz), 5.07 (dd, 1 H, J = 17.5 and 2.0 Hz), 6.03 (s, 1 H), 6.78 (dd, 1 H, J = 17.5 and 10.6 Hz), and 7.20–7.30 (m, 5 H); IR (CCl_4) 3100–2850, 1600, 1500, 1440, 1210, 1140, 1090, and 990 cm^{-1}; UV (95% ethanol) 231 nm (ϵ 7700); m/e 214 (M^+), 199, 187, 170, 155, 128, 115, and 91; HRMS calcd for $C_{15}H_{18}O$ 214.1357, found 214.1349.

The second fraction collected contained 50 mg (50%) of a clear oil whose structure was assigned as (*E*)-1-methoxy-4-methyl-3-phenyl-2-vinyl-1,3-pentadiene (**17**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.74 (s, 3 H), 1.82 (s, 3 H), 3.67 (s, 3 H), 4.81 (dd, 1 H, J = 10.4 and 1.9 Hz), 4.98 (dd, 1 H, J = 17.1 and 1.9 Hz), 6.17 (dd, 1 H, J = 17.1 and 10.4 Hz), 6.20 (s, 1 H), and 7.15–7.30 (m, 5 H); IR (neat) 3090–2840, 1690, 1630, 1440, 1240, 1140, 790, and 700 cm^{-1}; UV (95% ethanol) 236 nm (ϵ 10860); m/e 214 (M^+), 199, 182 (base), 167, 141, 128, 91, and 77; HRMS calcd for $C_{15}H_{18}O$ 214.1357, found 214.1353.

Acid-Catalyzed Hydrolysis of 1-Methoxy-4-methyl-3-phenyl-2-vinyl-1,3-pentadiene (17). To a solution of 50 mg of (*E*)- or (*Z*)-1-methoxy-4-methyl-3-phenyl-2-vinyl-1,3-pentadiene (**17**) in 5 mL of tetrahydrofuran was added 0.5 mL of a 10% solution of hydrochloric acid. The solution was stirred for 3 h and was neutralized by the dropwise addition of a saturated sodium bicarbonate solution. The mixture was extracted with ether, and the ether extracts were dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure afforded 30 mg (65%) of a yellow oil whose structure was assigned as 4-methyl-3-phenyl-2-propylidenepent-4-enal (**18**) on the basis of its spectroscopic properties: NMR ($CDCl_3$, 90 MHz) δ 1.60 (s, 3 H), 1.76 (s, 3 H), 3.67 (s, 3 H), 1.91 (d, 1 H, J = 7.2 Hz), 6.60 (q, 1 H, J = 7.2 Hz), 7.10–7.30 (m, 5 H), and 9.35 (s, 1 H); IR (neat) 2980–2850, 2710, 1685, 1440, 1380, 1260, 1090, 770, and 700 cm^{-1}; UV (95% ethanol) 236 nm (ϵ 8960); HRMS calcd for $C_{14}H_{16}O$ 200.1201, found 200.1203.

Preparation of 3,3-Dimethyl-1-(methylsulfonyl)-2-phenylcyclopropene (20). To a solution of 2-diazopropane in ether at −78 °C was added 11.3 g of methyl phenylethynyl sulfone[51] in 60 mL of tetrahydrofuran. The red solution was stirred for 30 min at −78 °C under nitrogen and was then warmed to 25 °C and stirred for 12 h. The organic layer was washed twice with dilute aqueous hydrochloric acid and once with brine, dried over magnesium sulfate, and concentrated to dryness to give a yellow solid, which was recrystallized from benzene–hexane to give 14.1 g (94%) of 3,3-dimethyl-5-(methylsulfonyl)-4-phenyl-3*H*-pyrazole as a yellow solid: mp 89–90 °C; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.79 (s, 6 H), 2.86 (s, 3 H), 7.56–7.58 (m, 3 H), and 8.17–8.20 (m, 2 H), IR (KBr) 3020, 2940, 1620, 1600, 1320, 1150, 990, 770, 705, and 560 cm^{-1}; UV (95% ethanol) 228 (ϵ 9600) and 288 nm (ϵ 7600); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 20.29, 43.03, 99.73, 126.89, 128.48, 129.87, 130.85, 147.85, and 153.02. Anal. Calcd for $C_{12}H_{14}O_2N_2S$: C, 57.58; H, 5.64; N, 11.19; S, 12.81. Found: C, 57.42; H, 5.65; N, 11.01; S, 12.70.

A solution containing 5.0 g of the above compound in 1.5 L of benzene was irradiated for 90 min with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve under an argon atmosphere. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column with a 20% ethyl acetate–hexane mixture as the eluent. The main fraction contained 4.22 g (95% yield) of a yellow oil whose structure was assigned as 3,3-dimethyl-1-(methylsulfonyl)-2-phenylcyclopropene (**20**) on the basis of the following spectral properties: ^1H NMR ($CDCl_3$, 360 MHz) δ 1.57 (s, 6 H), 3.15 (s, 3 H), 7.46–7.50 (m, 3 H), and 7.68–7.72 (m, 2 H); IR (neat) 3080, 3040, 2930, 1790, 1610, 1585, 1500, 1455, 1315, 1140, 970, 780, and 700 cm^{-1}; UV (95% ethanol) 282 nm (ϵ 7900); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 24.44, 32.96, 43.85, 123.29, 125.14, 128.68, 131.31 and 140.41. Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35; S, 14.42. Found: C, 64.84; H, 6.33; S, 14.43.

Preparation of 3,3-Dimethyl-2-phenyl-1-(phenylsulfonyl)cyclopropene (21). To a solution of 2-diazopropane in ether at −78 °C was added 19.0 g of phenyl phenylethynyl

(51) Brandsma, L.; Wijers, H. E.; Jonker, C. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 208.

sulfone. The red solution was stirred for 30 min at −78 °C under nitrogen and was then warmed to 25 °C and stirred for 12 h. The organic layer was washed twice with dilute aqueous hydrochloric acid and once with brine, then dried over magnesium sulfate, and concentrated to dryness to leave behind 23.71 g (95%) of 3,3-dimethyl-4-phenyl-5-(phenylsulfonyl)-3*H*-pyrazole as a yellow solid: mp 76–77 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.79 (s, 6 H), 7.25–7.59 (m, 8 H), and 7.69–7.85 (m, 2 H); IR (KBr) 3080, 3000, 2960, 1630, 1600, 1330, 1165, and 740 cm^{-1}; UV (95% ethanol) 286 nm (ε 7800); ^{13}C NMR ($CDCl_3$) δ 20.73, 99.29, 125.20, 126.84, 127.78, 128.39, 129.92, 130.31, 133.55, 139.71, 149.55, and 154.62. Anal. Calcd for $C_{17}H_{16}O_2N_2S$: C, 65.36; H, 5.16; N, 8.97; S, 10.26. Found: C, 65.29; H, 5.17; N, 8.96; S, 10.18.

A solution containing 5.0 g of the above pyrazole in 1.5 L of benzene was irradiated for 90 min with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve under an argon atmosphere. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column with a 20% ethyl acetate–hexane mixture as the eluent. The major fraction contained 4.32 g (95% yield) of a light yellow oil whose structure was assigned as 3,3-dimethyl-2-phenyl-1-(phenylsulfonyl)cyclopropene (**21**) on the basis of the following spectral properties: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.35 (s, 6 H), 7.31–7.62 (m, 8 H), and 7.91–8.06 (m, 2 H); IR (neat) 3060, 2980, 1780, 1600, 1590, 1450, 1370, 930, and 800 cm^{-1}; UV (95% ethanol) 222 (ε 14 500) and 294 nm (ε 14 000); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 24.16, 33.13, 124.29, 125.45, 127.05, 128.75, 129.07, 131.06, 131.28, 133.37, 139.53, and 141.41. Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67; S, 11.28. Found: C, 71.79; H, 5.68; S, 11.26.

Substitution Reaction of 3,3-Dimethyl-1-sulfonyl-2-phenylcyclopropene with Various Alkyllithiums. The following general procedure was used in the reaction of cyclopropenes **20–24** with various lithium reagents. To a stirred solution containing 2.0 mmol of the appropriate cyclopropene in 50 mL of anhydrous tetrahydrofuran under a nitrogen atmosphere at −78 °C, was added 4.0 mmol (2 equiv) of the alkyllithium reagent. After the addition was complete, stirring was continued at −78 °C for an additional hour at which time the deeply colored solution was allowed to warm to 0 °C and was stirred for an additional 30 min at this temperature. The reaction was quenched with a saturated solution of ammonium chloride, and the solvent was removed under reduced pressure. The crude residue was diluted with ether, washed twice with water, and dried over magnesium sulfate, the solvent was removed, and the resulting oil was chromatographed on a silica gel column with hexane as the eluent. The yields obtained are listed in Table I. All products were compared to previously synthesized compounds.

Preparation of 3,3-Dimethyl-1-phenyl-2-vinylcyclopropene. A vinyllithium solution was prepared by lithium–halogen exchange of vinyl bromide with *tert*-butyllithium, and the solution was transferred at 0 °C by cannula under a positive pressure of nitrogen to a stirred solution containing 2.0 mmol of 3,3-dimethyl-2-phenyl-1-(phenylsulfonyl)cyclopropene (**20**) at −78 °C. After standard workup, 3,3-dimethyl-1-phenyl-2-vinylcyclopropene was obtained in 35% yield as a colorless oil: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.55 (s, 6 H), 5.35 (dd, J = 10.11 and 2.10 Hz, 1 H), 5.55 (dd, J = 17.08 and 2.10 Hz, 1 H), 6.20 (dd, J = 17.08 and 10.11 Hz, 1 H), and 7.20–7.40 (m, 5 H); IR (neat) 3040, 2920, 1805, 1605, 1495, 1450, 980, 790, 770, and 695 cm^{-1}; UV (95% ethanol) 230 (ε 6500), 238 (ε 8200), 304 (ε 17 800), and 319 nm (ε 14 000); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 20.40, 24.36, 120.87, 123.23, 124.28, 127.79, 128.51, and 128.90; HRMS calcd for $C_{13}H_{14}$ 170.1095, found 170.1093.

Preparation of 2-Allyl-3,3-dimethyl-1-phenylcyclopropene. A solution of allyllithium was prepared by the method of Seyferth[52] and was transferred at 0 °C by cannula under a positive pressure of nitrogen to a stirred solution containing 2.0 mmol of 3,3-dimethyl-2-phenyl-1-(phenylsulfonyl)cyclopropene (**21**) at −78 °C. After standard workup, a 120 mg (35% yield) sample of 2-allyl-3,3-dimethyl-1-phenylcyclopropene was obtained: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.29 (s, 6 H), 3.35 (dt, J = 6.56 and 1.35 Hz, 2 H), 5.14 (dq, J = 10.05 and 1.53 Hz, 1 H), 5.20 (dq, J = 17.06 and 1.60 Hz, 1 H), 6.15 (m, 1 H), and 7.20–7.45 (m, 5 H); IR (neat) 3080, 2920, 1840, 1680, 1600, 1450, and 915 cm^{-1}; HRMS calcd for $C_{14}H_{16}$ 184.1251, found 184.1249.

Reaction of 3,3-Dimethyl-1-(methylsulfonyl)-2-phenylcyclopropene (20) with Lithium Dimethyl Cuprate. To a stirred solution containing 350 mg of copper bromide–dimethyl sulfide complex in 15 mL of ether and 15 mL of dimethyl sulfide at −10 °C under an atmosphere of nitrogen was added 2.8 mL of a 1.2 M solution of methyllithium solution. After the addition was complete, the resulting yellow suspension was stirred for an additional 15 min at which time 377 mg of cyclopropene **20** in 2 mL of tetrahydrofuran was added. The resulting mixture was stirred for 2 h at −10 °C, warmed to room temperature, quenched with a saturated ammonium chloride solution, and diluted with ether. The organic layer was washed with a 3:1 saturated ammonium chloride and ammonium hydroxide mixture, dried over magnesium sulfate, and concentrated to give 450 mg of a clear oil. Chromatography of this material on a silica gel plate with a 10% acetone–hexane mixture as the eluent gave 344 mg (85% yield) of 2,3,3-trimethyl-2-phenyl-1-(methylsulfonyl)cyclopropane (**27**) as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.35 (s, 3 H), 1.42 (s, 3 H), 1.49 (s, 3 H), 2.21 (s, 1 H), 2.85 (s, 3 H), and 7.10–7.49 (m, 5 H); IR (neat) 3020, 2930, 2260, 1740, 1605, 1500, 1450, 1300, 1150, and 800 cm^{-1}; HRMS calcd for $C_{13}H_{18}SO_2$ 238.1027, found 238.1019.

Preparation of 2-[*o*-(Allyloxy)phenyl]-3,3-dimethyl-1-(trimethylsilyl)cyclopropene (28). A solution of [*o*-(allyloxy)phenyl]lithium was prepared by the lithium–halogen exchange of allyl 2-bromophenyl ether with *tert*-butyllithium. The solution was transferred at 0 °C by cannula under a positive pressure of nitrogen to a stirred solution containing 2.0 mmol of 3,3-dimethyl-1-(*p*-tolylsulfonyl)-2-(trimethylsilyl)cyclopropene (**24**)[35] at −78 °C. After standard workup, a 428 mg (79% yield) sample of 2-[*o*-(allyloxy)phenyl]-3,3-dimethyl-1-(trimethylsilyl)cyclopropene (**28**) was obtained: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 0.24 (s, 9 H), 1.26 (s, 6 H), 4.66 (dt, J = 5.44 and 1.43 Hz, 2 H), 5.27 (dq, J = 10.50 and 1.40 Hz, 1 H), 5.36 (dq, J = 17.30 and 1.50 Hz, 1 H), 6.09 (m, 1 H), 6.85–7.00 (m, 2 H), 7.20–7.30 (m, 1 H), and 7.40–7.50 (m, 1 H); IR (neat) 3080, 2960, 1750, 1600, 1580, 1485, 1450, 1250, 840, and 750 cm^{-1}; UV (95% ethanol) 216 (ε 16 200), 274 (ε 11 600), and 314 nm (ε 9500). Anal. Calcd for $C_{17}H_{24}OSi$: C, 74.94; H, 8.88. Found: C, 74.83; H, 8.83.

Photosensitized Irradiation of 2-[*o*-(Allyloxy)phenyl]-3,3-dimethyl-1-(trimethylsilyl)cyclopropene (28). A 130-mg sample of cyclopropene **28** and 13 mg of thioxanthone were dissolved in 250 mL of anhydrous benzene, and the mixture was irradiated for 30 min with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Uranium filter sleeve under an argon atmosphere. The solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column with hexane as the eluent. The major fraction contained 110 mg (85% yield) of a clear oil whose structure was assigned as the [2 + 2] intramolecular cycloadduct **29** on the basis of the following spectral data: ^{1}H NMR ($CDCl_3$, 360 MHz) δ −0.10 (s, 9 H), 1.41 (s, 3 H), 1.60 (s, 3 H), 1.63 (dd, J = 11.9 and 5.7 Hz, 1 H), 1.72 (dd, J = 11.9 and 3.6 Hz, 1 H), 2.55 (m, 1 H), 4.07 (dd, J = 10.8 and 5.3 Hz, 1 H), 4.13 (dd, J = 10.8 and 5.5 Hz, 1 H), 6.79–6.88 (m, 2 H), 7.03–7.07 (m, 1 H), and 7.28 (dd, 1 H, J = 7.1 and 1.5 Hz); IR (neat) 3070, 3030, 2960, 1610, 1580, 1490, 1470, 1450, 1250, 1240, 850, and 760 cm^{-1}; UV (95% ethanol) 214 (ε 21 000), 246 (ε 7600), and 286 nm (ε 3100). Anal. Calcd for $C_{17}H_{24}OSi$: C, 74.94; H, 8.88. Found: C, 74.88; H, 8.90.

Direct Irradiation of 2-[*o*-(Allyloxy)phenyl]-3,3-dimethyl-1-(trimethylsilyl)cyclopropene (28). A solution containing 200 mg of **28** in 200 mL of anhydrous benzene was irradiated for 20 min with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve under an argon atmosphere. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column with hexane as the eluent. The major fraction contained 180 mg (90% yield) of a clear oil whose structure was assigned as [3-methyl-1-[*o*-(allyloxy)phenyl]-1,2-butadienyl]trimethylsilane (**30**) on the basis of the following spectral properties: ^{1}H NMR ($CDCl_3$, 360 MHz) δ −0.09 (s, 9 H), 1.63 (s, 6 H), 4.43 (dt, J = 5.4 and 1.4 Hz, 2 H), 5.16 (dq, J = 10.5 and 1.4 Hz, 1 H), 5.28 (dq, J = 17.3 and 1.5 Hz, 1 H), 5.92–6.03 (m, 1 H), 6.70–6.80 (m, 2 H), 6.95–7.05

(52) Seyferth, D.; Weiner, M. A. *J. Org. Chem.* **1959**, *24*, 1395.

(m, 1 H), and 7.15–7.20 (m, 1 H); IR (neat) 3080, 3020, 2960, 2915, 1950, 1605, 1590, 1490, 1450, 1250, 850, and 760 cm^{-1}; UV (95% ethanol) 278 nm (ε 2100). Anal. Calcd for $C_{17}H_{24}OSi$: C, 74.94; H, 8.88. Found: C, 74.83; H, 8.83.

Direct Irradiation of 3,3-Dimethyl-2-phenyl-1-(trimethylsilyl)cyclopropene (31). A solution containing 200 mg of **31** in 200 mL of a 9:1 methanol–pyridine mixture was irradiated for 50 min with a 450-W Hanovia medium-pressure mercury arc lamp equipped with a Pyrex filter sleeve under an argon atmosphere. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column with hexane as the eluent. The major fraction contained 190 mg (95% yield) of a clear oil whose structure was assigned as (3-methyl-1-phenyl-1,2-butadienyl)trimethylsilane (**34**) on the basis of the following spectral properties: ^1H NMR ($CDCl_3$, 360 MHz) δ 0.21 (s, 9 H), 1.77 (s, 6 H), and 7.30 (br s, 5 H); IR (neat) 3060, 2940, 1940, 1605, 1495, 1450, 1360, 1250, 930, and 840 cm^{-1}; UV (95% ethanol) 248 nm (ε 10 500). Anal. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32. Found: C, 77.84; H, 9.38.

A 200-mg sample of the above silane was dissolved in 10 mL of anhydrous tetrahydrofuran. To this mixture was added a 287-mg sample of tetrabutylammonium fluoride, and the mixture was allowed to stir for 15 min at 25 °C. The mixture was extracted with ether and washed with a saturated ammonium chloride solution. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to give 120 mg (89%) of a clear oil whose structure was assigned as 3-methyl-1-phenyl-1,2-butadiene (**35**) on the basis of the following spectroscopic properties: IR (neat) 3115, 3100, 3080, 3000, 2955, 1970, 1900, 1825, 1755, 1620, 1515, 1465, 1235, 760, and 720 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.35 (d, 6 H, J = 2.7 Hz), 6.02 (sept, 1 H, J = 2.7 Hz), and 7.25 (br s, 5 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 20.31, 92.60, 99.14, 126.67, 128.51, 136.02, 141.27, and 203.17; UV (95% ethanol) 252 nm (ε 11 650).

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Registry No. **4**, 56895-72-8; **5**, 119145-18-5; **6**, 119145-19-6; **7**, 119145-20-9; **8**, 119145-21-0; **9**, 119145-22-1; **13**, 119145-24-3; **14**, 119145-25-4; **16**, 119145-27-6; (*E*)-**17**, 119145-23-2; (*Z*)-**17**, 119145-28-7; **18**, 119145-29-8; **20**, 119145-30-1; **21**, 109900-77-8; **22** (n = 0), 109900-84-7; **22** (n = 1), 109900-85-8; **24** (R_2 = $CH_3C_6H_4$), 107696-98-0; **25** (R_2 = $(CH_2)_4Br$), 119145-26-5; **25** (R_2 = CH_3), 50902-98-2; **25** (R_2 = n-C_4H_9), 109900-82-5; **25** (R_2 = Ph), 50555-61-8; **25** (R_2 = t-C_4H_9), 109900-83-6; **26** (R_2 = n-C_4H_9), 109900-78-9; **26** (R_2 = t-C_4H_9), 109900-79-0; **26** (R_2 = PhCH=CH), 109900-81-4; **26** (R_2 = CH_3), 54599-15-4; **27**, 119145-31-2; **28**, 109900-86-9; **29**, 109900-87-0; **30**, 119145-32-3; **31**, 109900-80-3; **34**, 55967-10-7; **35**, 21020-31-5; $Br(CH_2)_3Ch{=}CH_2$, 1119-51-3; $Br(CH_2)_3C(CH_2){=}CH_2$, 41182-50-7; $Br(CH_2)_4Br$, 110-52-1; $CH_2{=}CHCHO$, 107-02-8; $(CH_3)_2C{=}N_2$, 2684-60-8; PhC≡CSO_2CH_3, 24378-05-0; PhC≡CSO_2Ph, 5324-64-1; $CH_2{=}CHBr$, 593-60-2; $CH_2{=}CHCH_2Li$, 3052-45-7; $CH_2{=}CHCH_2OC_6H_4$-*o*-Br, 60333-75-7; PhLi, 591-51-5; $CH_2{=}CH(CH_2)_2Li$, 14660-39-0; LiCH=CHPh, 4843-72-5; 3,3-dimethyl-5-(methylsulfonyl)-4-phenyl-3*H*-pyrazole, 119145-33-4; 3,3-dimethyl-4-phenyl-5-(phenylsulfonyl)-3*H*-pyrazole, 119145-34-5.

Biosynthetic Studies of Marine Lipids. 20.[1] Sequence of Double-Bond Introduction in the Sponge Sterol 24β-Methylcholesta-5,7,22,25-tetraen-3β-ol

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The biosynthesis of $\Delta^{5,7}$-sterols in *Ciocalypta* sp. was studied with radiolabeled Δ^5-sterol precursors. Of particular interest was the role of the tetraene, 24β-methylcholesta-5,7,22,25-tetraen-3β-ol, in the biosynthetic sequence. By examining C-24 epimeric pairs, stereospecific conversion of codisterol (but not epicodisterol) into the tetraene and ergosterol was demonstrated, which served also to establish the stereochemistry at C-24 of the natural sponge sterol. These biosynthetic steps are attributed to the sponge because of the absence of symbionts such as fungi and algae as shown by electron microscopy.

Introduction

A variety of unconventional sterols with unusual side chains and nuclei has been isolated from sponges.[2-4] Among these are the $\Delta^{5,7}$-sterols (**D**), encountered as major sterol components in some of these animals.[5] This particular nucleus, commonly found in sterols from yeast (fungi) and other terrestrial organisms, performs a role as pro-vitamin D.[6] In sponges these sterols possess 24-alkyl substituents typical of plant (algal) sterols and almost certainly function as components of the cell membranes.[7]

Three different $\Delta^{5,7}$-sterols comprise the total sterol mixture in the Australian sponge *Pseudaxinyssa* sp. Ergosterol (**4D**), which is the major component of the sterol mixture, was shown[5] to be formed from labeled codisterol (**7N**) through the intermediate tetraene (**1D**) (Chart I). This intermediate was not isolated or detected in *Pseudaxinyssa* sp., probably due to its rapid conversion to

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(1) For the preceding paper in this series, see: Malik, S.; Kerr, R. G.; Djerassi, C. *J. Am. Chem. Soc.* **1988**, *110*, 6895.
(2) Goad, L. J. In *Marine Products*; Scheuer, P. J. *Ed.*; Academic Press: New York, 1978; Vol. II, Chapter 2.
(3) Djerassi, C. *Pure Appl. Chem.* **1981**, *53*, 873.
(4) Ikekawa, N. In *Sterols and Bile Acids*; Danielson, N., Sjovall, J., Eds.; Elsevier: Amsterdam, 1985; pp 199–230.
(5) Stoilov, I. L.; Moreau, M. B.; Thompson, J. E.; Djerassi, C. *Tetrahedron* **1987**, *43*, 2213 and references therein.
(6) (a) For general references, see: Fieser, L. F.; Fieser, M. *Steroids*; Reinhold Publishing: New York, 1959; p 90. Shoppee, C. W. *Chemistry of the Steroids*; Butterworth: London, 1968; p 62. Heftman, E. *Steroids Biochemistry*; Academic Press: New York, 1970; p 31. (b) Wilbur, K. In *Chemical Zoology*; Florkin, M., Scheer, B. T., Eds.; Academic Press: New York, 1972; Vol. 7, p 103.
(7) Lawson, M. P.; Stoilov, I. L.; Thompson, J. E.; Djerassi, C. *Lipids* **1988**, *23*, 750.

0022-3263/89/1954-1642$01.50/0