3200, 3100, 1677, 1641 cm^{-1}; ^{1}H NMR (D_2O, 400 MHz) δ 4.22 (1 H, m), 3.90 (1 H, d, J = 2.6 Hz), 3.39 (2 H, m), 1.83 (2 H, m); ^{13}C NMR (D_2O, 100 MHz) δ 172.87, 158.40, 71.29, 60.81, 39.58, 31.78; HRMS (FAB, monothioglycerol + HCl) 191.1170, calcd for $C_6H_{15}N_4O_3$ 191.1144.

X-ray Crystallography of $C_{20}N_2O_5H_{22}$ (8a). Examination of the crystal by Weissenberg photography established that it belongs to the orthorhombic system. The systematic absences ($h0l$, $l = 2n + 1$; $0kl$, $l = 2n + 1$) and the chirality of the molecule are uniquely accommodated by the space group $Pca2_1$. Intensity data were collected at Molecular Structure Corporation with Cu Kα radiation on a Rigaku AFC6 diffractometer equipped with a graphite crystal, incident beam monochromator, and 12-kW rotating anode generator. The intensities of three representative reflections, measured after every 150 reflections throughout data collection, were constant.

The structure was solved and refined with use of the TEXSAN crystallographic software package. With the exception of C14 and C17, the positions of the C, N, and O atoms were determined from the direct methods program MITHRIL. The atoms C14 and C17 were located from an ensuing electron density synthesis. Eleven of the H atoms were located on difference electron density syntheses following partial refinement. All H atoms were subsequently placed in calculated positions and assigned isotropic thermal parameters of value one greater than that of the atom to which it binds, with the exception of the H atom bound to the carboxyl group which was not located. An absorption correction was not applied. The final cycle of refinement with anisotropic thermal parameters for the non-hydrogen atoms affords a value of 0.050 for the conventional index R on F for those 1045 reflections having $F_0^2 \geq 3\sigma(F_0^2)$. The final difference electron density map contains no features greater than 1.9% of the height of an O atom. Analysis of F_0^2 vs. F_c^2 as a function of F_0^2, $\lambda^{-1}\sin\theta$, and Miller indices reveals no unusual trends.

Acknowledgment. This work was supported by Public Health Service Research Grant GM32110 to S.J.G. We are grateful to Rodger Kohnert for acquisition of NMR and mass spectra and to Karen Jones and Tom Newton for help in the preparation of synthetic intermediates. Donald Griffin is thanked for obtaining the high-resolution FAB mass spectra. The multinuclear Bruker AM 400 spectrometer was purchased in part through grants from the National Science Foundation (CHE-8216190) and from the M. J. Murdock Charitable Trust to Oregon State University. The Kratos MS 50 TC spectrometer was purchased with grants from the National Institutes of Health Division of Research Resources (DRR 1S10RR01409) and from the Anheuser-Busch Company. We thank Jan Troupe and Paul Swepston of Molecular Structure Corporation for making the TEXSAN package available to D.A.K.

Supplementary Material Available: Tables of relevant details of the X-ray crystallographic studies (Table I) and Tables of final atomic parameters, anisotropic thermal parameters, and selected bond distances and bond angles (Tables II, III, and V) (4 pages); table of structure amplitudes (8 pages). Ordering information is given on any current masthead page.

Reaction of 1,8-Bis(phenylethynyl)naphthalene with Phenylchlorocarbene: Formation of an Intramolecular Cyclization Product from the Carbene Monoadduct and of 1,8-Naphthylenebis(diphenylcyclopropenylium) Dication from the Bisadduct

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The reactions of 1,8-bis(phenylethynyl)naphthalene (4) with phenylchloro- and dichlorocarbenes and chemistry of the obtained products have been studied. The reaction of 4 with 1 equiv of phenylchlorocarbene exclusively affords spirocyclopropene 8, whose structure has been determined by X-ray crystallography. The formation of 8 is interpreted by intramolecular "ene"-type cyclization of the carbene monoadduct 5. Upon thermolysis, 8 cleanly rearranges into chloro-8*H*-cyclopent[*a*]acenaphthylene 7 by way of cyclopropene ring cleavage. From the results of kinetic studies, the activation energy for this rearrangement has been determined as 23.8 kcal/mol. The reaction of 4 with dichlorocarbene generated under the phase-transfer catalytic conditions affords cyclopropenone 12a, which undergoes thermal rearrangement to acecyclone (14) in addition to decarbonylation. Hydroxycyclopropenylium ion 19a has been generated from 12a and characterized with ^{13}C NMR. The reaction of 4 with 2 equiv or an excess of phenylchlorocarbene affords dicyclopropenylnaphthalene 6 or 21, which can be converted to the new face-to-face dication 3. The effects of electrostatic repulsion of the two cationic rings in 3 upon the properties of the monocation unit is discussed based on ^{13}C NMR data and values of pK_{R^+} and reduction potential. The zinc reduction of dication 3 smoothly affords fluoranthene 30, which has been produced supposedly by way of intramolecular coupling of cyclopropenyl radicals followed by bis(cyclopropenyl)–benzene rearrangement.

The compounds containing two or more π-electronic systems which are held in a face-to-face conformation can serve as fundamental models for study of intermolecular π-electronic interaction. Especially when the interacting π-systems can act as a pair of electron donor and acceptor, the whole system is regarded as an undissociable charge-transfer complex.[2,3] Among various compounds with such structural features, 1,8-disubstituted naphthalenes are characteristic in that the σ-bonds at the 1,8-positions stand

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(1) (a) Kyoto University. (b) Tottori University. (c) Present address: Institute for Protein Research, Osaka University, Suita, Osaka 565, Japan.

(2) For example, see: O'Connor, J. G.; Keehn, P. M. *J. Am. Chem. Soc.* 1976, *98*, 8446. Horita, H.; Otsubo, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* 1976, 3899. Nakazawa, T.; Murata, I. *J. Am. Chem. Soc.* 1977, *99*, 1996. Komatsu, K.; Takahashi, K.; Okamoto, K. *Tetrahedron Lett.* 1979, 4747. Yamamura, K.; Nakasuji, K.; Murata, I.; Inagaki, S. *J. Chem. Soc., Chem. Commun.* 1982, 396. Staab, H. A.; Hinz, R.; Knaus, G. H.; Krieger, C. *Chem. Ber.* 1983, *116*, 2835 and the earlier publications.

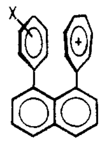
0022-3263/87/1952-2183$01.50/0

Table I. Melting Points and Spectral Data for 7 and 8

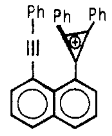
compd	mp, °C	IR (KBr), cm^{-1}	UV (CH_2Cl_2) λ_{max}, nm (log ϵ)	^1H NMR ($CDCl_3$) δ	^{13}C NMR[a] ($CDCl_3$) δ
7	217 dec	3060, 3030, 1600, 1495, 1442, 1357, 1030, 835, 780, 765, 720, 700	251 (4.59), 282 (4.45), 393 (4.14)	7.27–7.73 (m, 19 H),[a] 7.80 (d, 2 H, J = 7.0 Hz)[b]	88.6 (s), 119.8 (d), 126.1 (d), 126.6 (d), 127.8 (d), 128.1 (d), 128.2 (d, 2 peaks), 128.3 (d), 128.5 (d), 131.9 (s), 132.0 (s), 133.8 (s), 137.0 (s), 142.0 (s), 142.8 (s), 145.6 (s)
8	186.5–188	3055, 1835, 1590, 1495, 1442, 1070, 940, 830, 780, 760, 705, 685	236 (4.63), 246 sh (4.56), 317 (4.53), 333 (4.53), 351 sh (4.25)	6.73 (m, 4 H, =C(Cl)Ph),[c] 6.78 (d, 1 H, J = 7.0 Hz, H-7), 6.99 (tt, 1 H, =C(Cl)Ph), 7.27 (m, 10 H, Ph), 7.36 (dd, 1 H, J = 8.2, 7.0 Hz, H-6), 7.64 (d, 1 H, J = 8.2 Hz, H-5), 7.70 (dd, 1 H, J = 8.3, 7.3 Hz, H-2), 7.85 (d, 1 H, J = 8.3 Hz, H-3), 8.60 (d, 1 H, J = 7.3 Hz, H-1)	39.9 (s), 111.4 (s), 114.7 (d), 122.5 (d), 122.9 (d), 125.5 (s), 125.5 (d), 126.2 (s), 127.1 (d), 127.2 (d), 127.9 (d), 128.1 (d), 128.2 (d), 128.7 (d), 129.1 (d), 130.2 (d), 131.1 (s), 138.0 (s), 138.6 (s), 138.9 (s), 139.9 (s), 145.5 (s)

[a] Peak multiplicity in the off-resonance spectra is shown in the parentheses. [b] 60 MHz. [c] 400 MHz. Numbering system is shown on the structural formula.

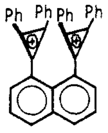
parallel to each other[4] to keep the substituents, especially when they are planar, in an essentially face-to-face conformation without causing too much steric strain. For such an example, we previously reported the syntheses and properties of a series of 1-aryl-8-tropilionaphthalenes **1**.[3] In contrast to 1,8-diphenylnaphthalene which exhibits no appreciable electronic interaction between the facing phenyl rings,[5] cations **1** showed definitive evidence for the intramolecular charge-transfer interaction based on the results of electronic spectroscopy and measurements of the stability of the tropylium ring.[3]



1



2

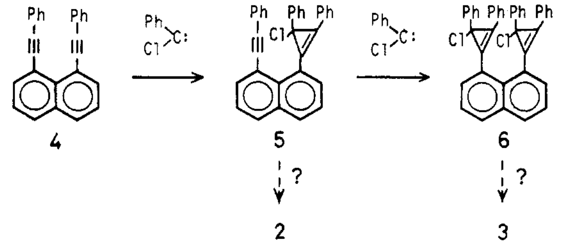


3

In this paper we describe the results of our study aimed at the syntheses of cyclopropenylium ions **2** and **3**, in which possible intramolecular reaction or electronic interaction between the 1,8-substituents seemed of particular interest. At the outset of this research, it was anticipated that, as is shown in Scheme I, stepwise addition of phenylchlorocarbene to 1,8-bis(phenylethynyl)naphthalene (**4**) would lead to the consecutive formation of monoadduct **5** and bisadduct **6**.

If the cyclopropenyl group in **5** could be readily ionized to give the stable cation **2**, some electronic interaction between the ethynyl group and the cyclopropenylium ring might be observed as the charge-transfer interaction.[6] Alternatively, the cyclopropenyl group in **5** might go into reaction with the closely standing triple bond before any chance of ionization. On the other hand, ionization of the two cyclopropenyl groups in **6** would give the dication **3**,

Scheme I



which would be the first example of the system having two cationic rings directly facing each other.[7] Then, it will be quite interesting to evaluate the effect of electronic repulsion between the cationic units located at such a close proximity upon the intrinsic stability of the monocationic unit itself.

Results and Discussion

Reaction of 1,8-Bis(phenylethynyl)naphthalene (4) with 1 equiv of Phenylchlorocarbene. Thermal as well as photochemical decomposition of phenylchlorodiazirine is known to generate phenylchlorocarbene, which can be efficiently trapped by substituted acetylenes to give cyclopropenyl compounds.[8] When a solution of diethynylnaphthalene **4** and an equimolar amount of phenylchlorodiazirine in benzene was heated to reflux for 2 h, a clean reaction took place with quantitative evolution of nitrogen. There was formed a new compound as a main product (94% yield) together with a minor product (2% yield), both of which gave the analytical data compatible with a molecular formula $C_{33}H_{21}Cl$, identical with that of **5**. The structure of the minor product was readily determined as **7** on the basis of the spectral data shown in Table I and by comparison with the authentic sample prepared via a straightforward synthetic route shown in the Experimental Section. In contrast, the structure of the major product seemed to be more complex as is discussed below on the basis of the spectral data shown in Table I.

First, its IR spectrum exhibited an absorption at 1835 cm^{-1}, indicating the presence of a cyclopropene ring, but

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(3) Komatsu, K.; Abe, N.; Takahashi, K.; Okamoto, K. *J. Org. Chem.* **1979**, *44*, 2712.

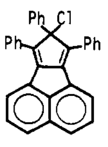
(4) For the review on chemistry and intramolecular effects in 1,8-disubstituted naphthalenes, see: Balasubramaniyan, V. *Chem. Rev.* **1966**, *66*, 567.

(5) House, H. O.; Magin, R. W.; Thompson, H. W. *J. Org. Chem.* **1963**, *28*, 2403.

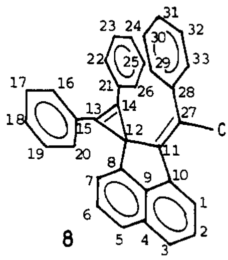
(6) For example, the intramolecular charge-transfer interaction between the 2-π-electronic system(s) (i.e., the ethylenic unit(s)) and a Hückeloid cation (i.e., tropylium ion) has been reported: Nakazawa, T.; Kubo, K.; Murata, I. *Angew. Chem.* **1981**, 93, 195; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 189. Yamochi, H.; Nakasuji, K.; Nakazawa, T.; Murata, I. *Chem. Lett.* **1982**, 459.

(7) Synthesis and properties of 1,8-naphthylenebis(diphenylcyclopropenylium) dication have been reported previously as a communication: Komatsu, K.; Arai, M.; Okamoto, K. *Tetrahedron Lett.* **1982**, *23*, 91.

(8) Padwa, A.; Eastman, D. *J. Org. Chem.* **1969**, *34*, 2728.



7



8

no absorption corresponding to a triple bond. Next, the ^{13}C NMR spectrum showed smaller number of signals (22 peaks) than expected for cyclopropene 5 (27 peaks). Especially, the absence of any signals for sp-hybridized carbons and the presence of only one signal at δ 111.4 for sp^2 carbons of a cyclopropene's double bond in the characteristic region of δ 110–120 definitively rule out the expected structure 5 for this compound. The ^{1}H NMR spectrum also exhibited an anomaly that a peak corresponding to one phenyl group is markedly shifted upfield (δ 6.73). Furthermore, this compound was found to rearrange very cleanly to 7 after melting point determination. The only structure which conforms to the above-mentioned observations appears to be spirocyclopropene 8, and this was finally verified by the X-ray crystallography as summarized in Figure 1 and Table II.

This structure of 8 successfully explains all the spectral characteristics described above. Especially the *Z* configuration of the ethylenic phenyl group with respect to the spiro-fused cyclopropene ring nicely explains the unusual upfield shift of the phenyl proton signals, since the cyclopropene's double bond is now found to be fixed at such a closely facing position as to exert the maximum shielding effect to the ethylenic benzene ring. The same effect also causes one of the naphthalene's β-protons (H-7) to resonate at unusually high field (δ 6.78), whereas the other (H-1) is forced to resonate at much lower field (δ 8.60) owing to the steric compression effect exerted by the ethylenic chlorine atom.

The possible reaction pathway for the formation of 8 is considered as follows. As will be shown later, the reaction of dichlorocarbene with diethynylnaphthalene 4 under the phase-transfer catalytic conditions afforded cyclopropenone **12a** formed by addition of dichlorocarbene to one of the triple bonds followed by alkaline hydrolysis (Scheme VII). Therefore, although we could not isolate the carbene adduct 5, it would be reasonable to assume that 8 was produced by facile rearrangement of the initially formed adduct 5.[9] By comparing the structures 5 and 8, it is supposed that this rearrangement involves the formation of a new C–C bond with migrations of a double bond and a chlorine atom, which are occuring in a highly concerted and stereospecific manner such as in the "ene" reaction[10] (Scheme II).

As for an example of such a concerted reaction involving a cyclopropenyl group, Padwa and co-workers recently reported that an intramolecular "ene" reaction occurs thermally between a cyclopropenyl group (as the "enophile") and an allyl group (as the "ene") placed at the ortho positions of a benzene ring.[11] In contrast, the cyclopropenyl group in 5 can not act as an "enophile" but only as an "ene" moiety, with the migration of a chlorine atom[12] instead of hydrogen.

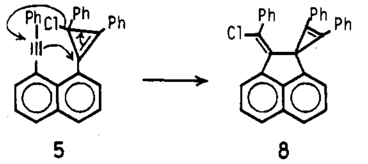
Table II. Selected Bond Lengths (Å) and Angles (deg) for Spirocyclopropene 8[a]

Bond Lengths			
C(8)–C(12)	1.502 (4)	C(10)–C(11)	1.479 (4)
C(12)–C(13)	1.510 (4)	C(12)–C(14)	1.514 (4)
C(13)–C(14)	1.303 (4)	C(11)–C(12)	1.525 (4)
C(13)–C(15)	1.438 (4)	C(14)–C(21)	1.446 (4)
C(11)–C(27)	1.335 (4)	C(27)–C(28)	1.477 (5)
C(27)–Cl	1.757 (4)		

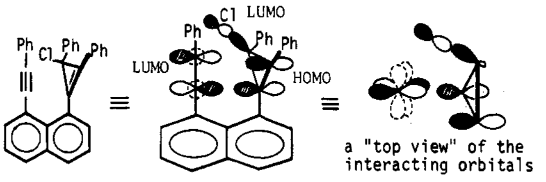
Bond Angles			
C(7)–C(8)–C(12)	132.3 (3)	C(9)–C(8)–C(12)	106.9 (3)
C(1)–C(10)–C(11)	134.5 (3)	C(9)–C(10)–C(11)	107.3 (3)
C(10)–C(11)–C(12)	106.5 (2)	C(10)–C(11)–C(27)	129.4 (3)
C(12)–C(11)–C(27)	124.1 (3)	C(8)–C(12)–C(11)	105.4 (2)
C(8)–C(12)–C(13)	122.4 (2)	C(8)–C(12)–C(14)	120.2 (2)
C(11)–C(12)–C(13)	125.8 (2)	C(11)–C(12)–C(14)	124.1 (2)
C(13)–C(12)–C(14)	51.1 (2)	C(12)–C(13)–C(14)	64.7 (2)
C(12)–C(13)–C(15)	142.8 (3)	C(14)–C(13)–C(15)	152.3 (3)
C(12)–C(14)–C(13)	64.3 (2)	C(12)–C(14)–C(21)	140.3 (3)
C(13)–C(14)–C(21)	155.0 (3)	C(11)–C(27)–C(28)	128.6 (3)
C(11)–C(27)–Cl	120.3 (3)	C(28)–C(27)–Cl	111.0 (2)

[a] Esd's given in parentheses.

Scheme II

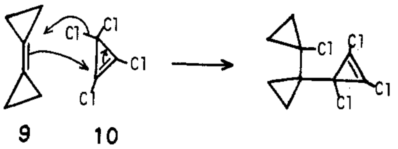


Scheme III



(Non-interacting 2p orbitals of the triple bond are shown by dashed lines.)

Scheme IV



According to frontier orbital theory, the thermal "ene" reaction can be described in terms of a three-orbital interaction among the HOMO of the π-bond in the "ene" moiety, the LUMO of the π-bond of the "enophile", and the LUMO of the σ-bond to be cleaved in the "ene" molecule.[13] When applied to the present system, this three-orbital interaction is represented as in Scheme III. Since the chlorine atom employs a 2p orbital for bonding, it can migrate selectively to the "outer-side" orbital of the acetylenic carbon in order to avoid the occurence of much

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[9] Even when the reaction was followed by taking the ^{13}C NMR spectra of the whole mixture from early stage of the reaction (e.g., after 20 min of refluxing in benzene, with about 30% conversion), there were observed only the signals for starting materials and spirocyclopropene 8. Chloride 7 is supposed to be produced from 8 by much slower thermal reaction (vide infra).

[10] Hoffmann, H. M. R. *Angew. Chem.* **1969**, *81*, 597; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. Oppolzer, W.; Snieckus, V. *Angew. Chem.* **1978**, *90*, 506; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476. Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426.

[11] Padwa, A.; Rieker, W. F. *J. Am. Chem. Soc.* **1981**, *103*, 1859. Padwa, A.; Rieker, W. F.; Rosenthal, R. J. *Ibid.* **1985**, *107*, 1710.

[12] As for the examples of such nonionic chlorine migrations, 1,5- and 1,3-sigmatropic shifts of a chlorine atom have been reported: Looker, J. J. *J. Org. Chem.* **1972**, *37*, 1059. Roedig, A.; Renk, H.-A.; Schaal, V.; Scheutzow, D. *Chem. Ber.* **1974**, *107*, 1136. Strohmeier, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1974**, *29*, 282.

[13] Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4693.

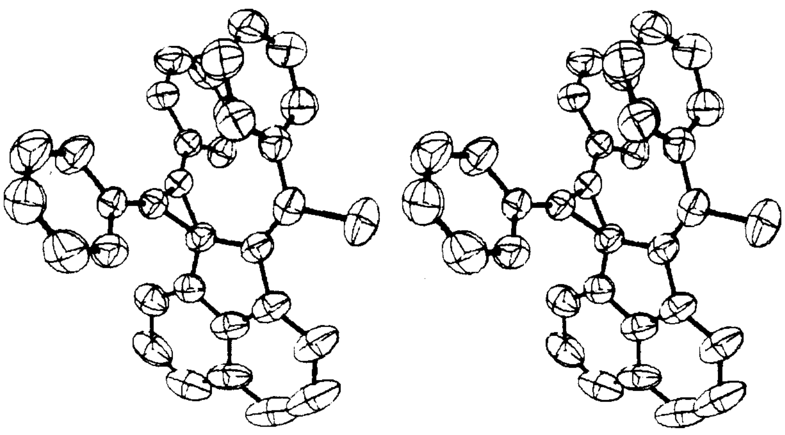
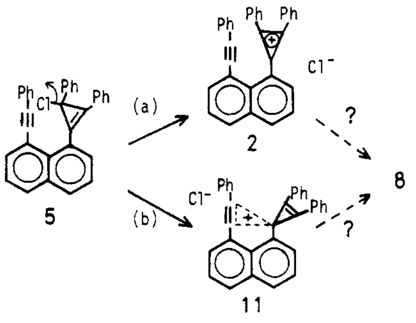


Figure 1. Stereoscopic view of spirocyclopropene 8.

Scheme V

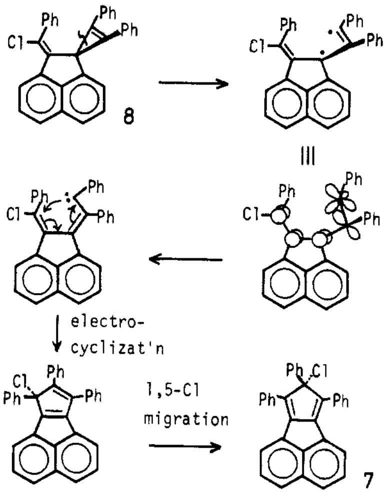


steric congestion at the space between the ethynyl and cyclopropenyl groups. This migration is assumed to take place with the concomitant C–C bond formation and double bond shift to accomplish the stereospecific formation of spirocyclopropene 8.

Heretofore, 1,2-[14] and 1,3-diphenylcyclopropenes[15] have been shown to add to electron-deficient π-bonds, according to the "ene" reaction pathway, but not to the unactivated π-bond such as the one in diphenylacetylene.[15] Thus, the readiness of the present reaction seems to be ascribed to the presence of the two reacting groups at such a close proximity as in naphthalene's 1,8-positions. A seemingly analogous type of *inter*molecular reaction has been reported; that is, the addition of the unsaturated carbon of tetrachlorocyclopropene (**10**) to the double bond of bicyclopropylidene (**9**) accomplished by heating at 80 °C for 50 h (Scheme IV).[16] However, this reaction has been described as "nucleophilic addition to the cyclopropene in an S_N2' fashion", on the basis of the electron-rich nature of the double bond in **9**.

Compared with the nonionic process described above, the ionic pathway appears less likely, since the ionization of the C–Cl bond would lead to the formation of the supposedly stable cyclopropenylium ion **2** [Scheme V (a)]: in fact, the hydroxycyclopropenylium ion with the related structure **19a** (Scheme X, vide infra) was found to be stable at 35 °C for prolonged period as will be mentioned later. The only possibility, if any, for the ionic pathway leading to **8** would be the one via a less stable intermediate cation **11**, to which the chloride ion could approach only from the "outer side" of the triple bond [Scheme V (b)]. This process can be looked upon as the ionic counterpart for the "ene"-type reaction described above and is considered less plausible when the nonpolar reaction conditions (i.e., refluxing in benzene) is taken into account.

Scheme VI



Thermal Rearrangement of Spirocyclopropene 8. As has already been mentioned, spirocyclopropene **8** rearranges quantitatively into **7** at the temperature of its melting point (188 °C). This reaction is apparently the ring enlargement of a 3-vinylcyclopropene to a cyclopentadiene, which involves the cyclopropene ring opening as a key step. On the basis of the results of both experimental[17,18] and theoretical studies,[18,19] the cleavage of a cyclopropene ring has been shown to proceed via homolytic dissociation of a C–C single bond to a diradical state, which subsequently decays to a vinylcarbene. In the case of 3-vinylcyclopropene, this process gives butadienylcarbene, which can be finally transformed to cyclopentadiene by electrocyclic ring closure.[18,20] According to this mechanism, the rearrangement of **8** to **7** in the present study can be formulated as in Scheme VI.

So far, the available kinetic data for the thermal ring enlargement of 3-vinyl- or 3-arylcyclopropene have been

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(14) Yoshida, Z.; Miyahara, H. *Chem. Lett.* **1972**, 335.

(15) Komatsu, K.; Niwa, T.; Akari, H.; Okamoto, K. *J. Chem. Res. Synop.* **1985**, 252; *J. Chem. Res. Miniprint* **1985**, 2882.

(16) Weber, W.; Behrens, U.; de Meijere, A. *Chem. Ber.* **1981**, *114*, 1196.

(17) York, E. J.; Dittmar, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 5680.

(18) For review, see: Padwa, A. *Acc. Chem. Res.* **1979**, *12*, 310.

(19) (a) Davis, J. H.; Goddard, W. A., III; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2427. (b) Pincock, J. A.; Boyd, R. J. *Can. J. Chem.* **1977**, *55*, 2482.

(20) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N.; Loza, R. *J. Org. Chem.* **1978**, *43*, 1481. Zimmerman, H. E.; Aasen, S. M. *Ibid.* **1978**, *43*, 1493. Zimmerman, H. E.; Hovey, M. C. *Ibid.* **1979**, *44*, 2331. Chiacchio, U.; Compagnini, A.; Grimaldi, R.; Purrello, G.; Padwa, A. *J. Chem. Soc., Perkin Trans. 1* **1983**, 915.

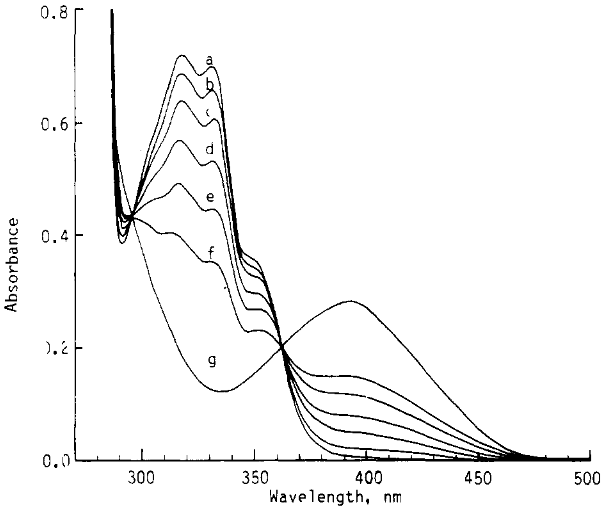


Figure 2. The spectral change observed for the thermal rearrangement of 8 to 7 in diphenyl ether at 136.0 °C: initial concentration, 2.01×10^{-2} M; reaction time, (a) 0 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min, (f) 1 h, (g) 10 h. All the spectra were obtained after 10^{-3} dilution with CH_2Cl_2.

Table III. First-Order Rate Constants and Arrhenius Parameters for the Thermal Rearrangement of 8 to 7[a]

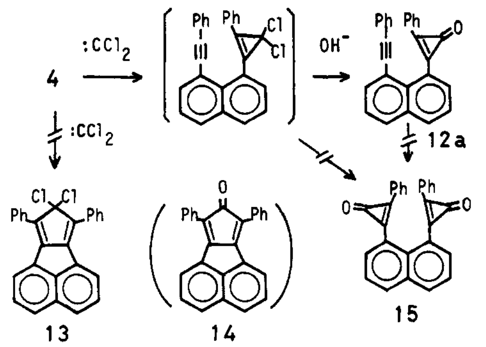
temp, °C	$k \times 10^4$,[b] s^{-1}	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta G^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg
126.0	1.04				
136.0	2.10	23.8	23.2	28.9	−19.2
146.0	4.35				

[a] Arrhenius parameters were calculated for the temperature of 25.0 °C. [b] Error limits are ±2.5%.

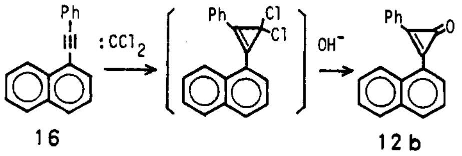
quite limited.[21] It seemed intriguing to examine the value of activation energy for the thermal rearrangement of 8, which involves the cleavage of the cyclopropene ring rigidly held in a bisected conformation with respect to the olefinic bond. Thus, the rate of rearrangement was determined spectrophotometrically at 126, 136, and 146 °C in diphenyl ether in sealed tubes under vacuum. The typical spectral change is shown in Figure 2, which demonstrates the presence of only one set of isosbestic points indicative of the quantitative change of 8 directly into 7. The reaction obeyed good first-order kinetics, giving the values of rate constants and activation parameters shown in Table III.

As was expected, the activation energy required for the cyclopropene ring cleavage of 8 (23.8 kcal/mol) was found to be remarkably lower than the values reported for the similar reactions, for example, 40 kcal/mol for the cleavage of tetraphenylcyclopropene[21a] and 33.3 kcal/mol for that of 3-benzyl-2-methyl-1,3-diphenylcyclopropene.[21b] According to theoretical calculations (MINDO/3),[19b] which agree well with experimental results,[21b] a vinyl substituent on C-3 lowers (by 6.2 kcal/mol) the activation energy for the cyclopropene ring opening due to conjugation with the developing radical center, whereas the same substituent on C-1 (C-2–C-3 bond cleaving) raises (by 8.2 kcal/mol) the activation energy. As has been shown in Scheme VI, the conjugative stabilization of the diradical formed in the present system is greatly enhanced, since not only the vinyl group but also the naphthalene ring is rigidly fixed at the best arrangement for the maximum conjugation with the radical center. This explains the substantial decrease in activation energy observed for the ring cleavage in 8.

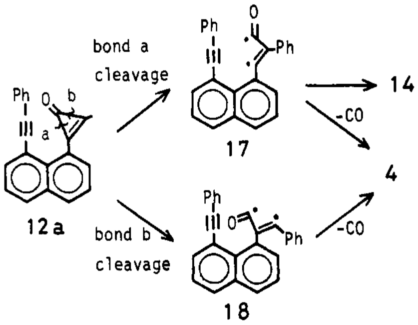
Scheme VII



Scheme VIII



Scheme IX



Reaction of Diethynylnaphthalene 4 with Dichlorocarbene. In order to clarify the generality of carbene addition toward diethynylnaphthalene 4, addition of dichlorocarbene was examined under the phase-transfer catalytic conditions.[22] When the reaction was carried out at 0 °C for 10 min, cyclopropenone **12a** was isolated as air-stable white crystals in a good yield (71% based on consumed 4) at 25% conversion (Scheme VII); at higher conversion, the formation of intractable decomposition products became competing with the formation of **12a**. However, the careful examination of the product mixture indicated no evidence for the formation of even a trace amount of either the compound 13 (or 14), which could be produced by the pseudo-1,4-addition[23] of dichlorocarbene to 4 (and subsequent hydrolysis), or bis(cyclopropenone) 15, which could be formed by double carbene addition. Under similar conditions at room temperature, ethynylnaphthalene 16 reacted much slower and afforded cyclopropenone **12b** in a 15% yield after the reaction time of 1.5 h (Scheme VIII).

Cyclopropenones are generally known to decarbonylate to give acetylenes upon thermolysis,[24] presumably by way of diradical intermediates.[25] When cyclopropenone **12a**

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[21] (a) Battiste, M. A.; Halton, B.; Grubbs, R. H. *Chem. Commun.* **1967**, 907. (b) Padwa, A.; Blacklock, T. J.; Loza, R. *J. Org. Chem.* **1982**, *47*, 3712. (c) It has been mentioned that 1,2,3-triphenyl-3-vinylcyclopropene readily rearranges to 1,2,3-triphenylcyclopentadiene at 180 °C, but no kinetic data has been reported: Breslow, R. In *Molecular Rearrangements*; De Mayo, P., Ed.; Interscience: New York, 1963.

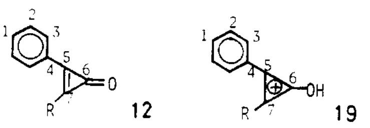
[22] This method has been reported for the synthesis of diphenylcyclopropenone: Dehmlow, E. V.; Schonefeld, J. *Justus Liebigs Ann. Chem.* **1971**, *744*, 42.

[23] For examples of 1,4- or pseudo-1,4-addition of carbenes to conjugated or homoconjugated dienes, see: Hart, H.; Raggon, J.W. *Tetrahedron Lett.* **1983**, *24*, 4891 and the references cited therein.

[24] Potts, K. T.; Baum, J. S. *Chem. Rev.* **1974**, *74*, 189.

[25] Farnum, D. G.; Chickos, J.; Thurston, P. E. *J. Am. Chem. Soc.* **1966**, *88*, 3075.

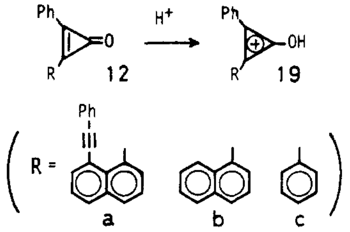
Table IV. ^{13}C NMR (in $CDCl_3$) Data for Cyclopropenones 12 and Hydroxycyclopropenylium Ions 19



	δ								
compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	acetylenic[a] carbons	other carbons
12a	132.3	128.9	131.3	123.8	148.5	155.7	152.0	88.5, 95.6	120.3, 122.7, 123.9, 125.3, 126.2, 128.0, 128.2, 128.4, 129.3, 130.3, 131.3, 131.4, 134.0, 134.5
12b	132.5	129.2	131.4	123.8	147.0	155.5	132.9		121.9, 125.1, 126.2, 127.0, 128.1, 128.2, 128.3, 129.7, 130.1, 133.5
12c	132.4	129.1	131.2	123.7	148.1	155.5			
19a	134.9	129.3	132.5	122.1	145.9	158.7	148.4	88.2, 96.2	119.8, 121.4, 121.9, 125.5, 126.8, 127.8, 128.3, 128.8, 129.6, 130.5, 131.1, 131.5, 134.1, 134.2
19b	134.3	129.7	132.5	122.1	145.3	158.2	144.2		120.0, 125.1, 125.2, 127.5, 128.7, 129.1, 132.1, 132.4, 133.5, 135.4
19c	134.5	129.7	132.5	121.9	145.5	158.3			

[a] For comparison, the acetylenic carbons in **16** show the signals at δ 87.3 and 94.3 with the phenyl carbon signals at δ 123.3, 128.3, 130.2, and 131.5 and the naphthalene carbon signals at δ 120.6, 125.1, 126.1, 126.3, 126.7, 128.2, 128.3, 128.6, and 133.1.

Scheme X



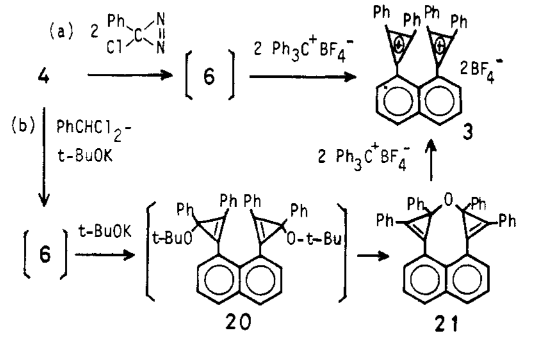
was heated to reflux in toluene for 4 h, it underwent rearrangement to acecyclone (**14**) (15%) in addition to decarbonylation regenerating **4** (63%). The formation of **14** can be interpreted as the result of trapping of diradical **17** by the triple bond located closely in front of the diradical in such a favorable geometry as shown in Scheme IX.

In acidic solutions, cyclopropenones are readily protonated to give hydroxycyclopropenylium ions (Scheme X).[24,26] For the purpose of comparison with the thermal reactivity described above, the stability of cyclopropenones **12** under protonated conditions was examined next. When 10 molar excess of either trichloro- or trifluoroacetic acid was added to solutions of cyclopropenones **12a–c** in $CDCl_3$, they all exhibited the ^{13}C NMR spectra assigned to hydroxycyclopropenylium ions **19a–c** as shown in Table IV. All the spectra did not show any appreciable change over 2 days at 35 °C, and the starting cyclopropenones were quantitatively recovered by neutralization. The inertness of hydroxycyclopropenylium ion **19a** toward intramolecular cyclization suggests that the ionic cyclization such as shown in Scheme V is not plausible for the rearrangement of **5** to **8**. Furthermore, the ^{13}C NMR chemical shifts for the carbons of cationic three-membered ring and of the phenyl ring bonded to it in **19a** are quite similar to those for the corresponding carbons in **19b,c**. Thus, there seems to be no appreciable positive charge delocalization from the hydroxycyclopropenylium ring to the facing triple bond.

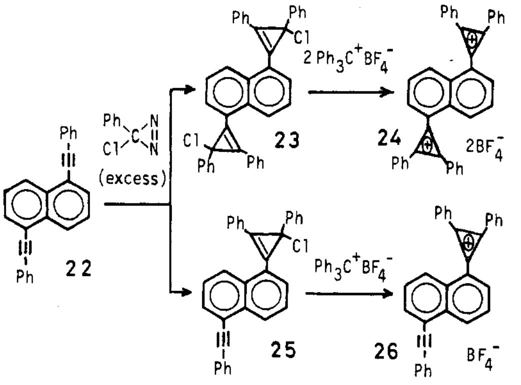
Reaction of Diethynylnaphthalene 4 with 2 equiv of Phenylchlorocarbene. When a solution of diethynylnaphthalene **4** and 2 molar equiv of phenylchlorodiazirine in benzene was heated to reflux for 1 h and the product mixture separated by using preparative TLC followed by HPLC, there was isolated the carbene bisadduct **6**, albeit in a very low yield (1.5%) [Scheme XI (a)]. On the other hand, an alternative method, i.e., the reaction of **4** with a large excess of benzal chloride and potassium *tert*-butoxide,[27] afforded the intramolecular dicyclopropenyl ether **21** in a better yield (33%), supposedly via **6** and **20** [Scheme XI (b)]. Upon treatment with 2 equiv of trityl tetrafluoroborate, both **6** and **21** were transformed quantitatively into dication salt **3**·$2BF_4^-$, which was isolated as air-stable pale yellow crystals.

For the purpose of comparison, the structurally related dication **24** and monocations **26** and **28** were also prepared

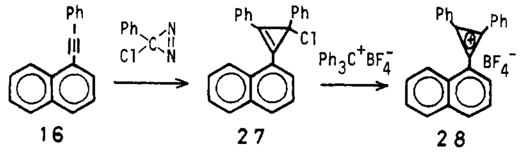
Scheme XI



Scheme XII



Scheme XIII



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(26) Quirk, R. P.; Gambill, C. R.; Thyvelikakath, G. X. *J. Org. Chem.* **1981**, *46*, 3181. Stang, P. J.; Maas, G.; Smith, D. L.; McCloskey, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4837.

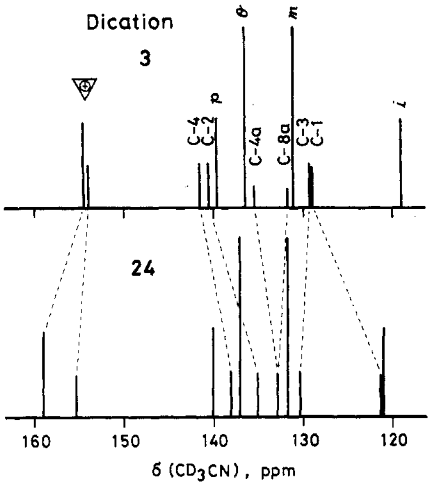


Figure 3. ^{13}C NMR spectra of dications **3** and **24**.

by the method utilizing phenylchlorodiazirine as shown in Schemes XII and XIII. In all of these reactions, the first formed carbene adducts, **23**, **25**, and **27**, were isolated as fairly stable covalent chlorides in 67%, 16%, and 34% yields, respectively. Cations **24**, **26**, and **28** were all obtained as air-stable white to yellow crystals in excellent yields (94–100%) from the corresponding chlorides.

Upon comparison of the spectral data of the cations, noteworthy is the remarkable upfield shift of the ^1H NMR signals of phenyl protons in dication **3**. For instance, the difference in chemical shift ($\Delta\delta$) between **3** and the reference dication **24** is 0.55, 0.32, and 0.32 ppm for the ortho, meta, and para protons, respectively; thus, the difference in weighted average of all the phenyl protons is 0.41 ppm. This upfield shift is ascribed to the mutual shielding effects of benzene rings at the facing positions and can be taken as strong evidence for the essentially face-to-face conformation of the diphenylcyclopropenylium systems in dication **3**. It is to be noted that comparable amounts of upfield shifts have been reported for 1,8-diphenylnaphthalene ($\Delta\delta$ 0.53 with reference to 1-phenylnaphthalene)[5] and for **4** ($\Delta\delta$ 0.30 with reference to **16**).[28]

The upfield shift is also observed for the ^{13}C NMR signals of the cyclopropenylium ring carbons in **3**, whereas the downfield shift is noted for most of the naphthalene ring carbons, as is shown schematically in Figure 3 with reference to dication **24**. This is assumed to reflect the change in charge densities due to flowing out of the positive charge from the cyclopropenylium rings through the 1,8-σ-bonds into the naphthalene π-system in order to reduce the electrostatic repulsion between the two cationic rings placed at such a close distance.

It is anticipated, then, that such electrostatic repulsion would result in destabilization of the dicationic system as a whole. In order to examine such structural effects upon cation's stability, the values of pK_{R^+} and reduction potential were determined to give the results shown in Table V. In the case of dications, the neutralization was found to occur in two steps in pK_{R^+} determinations, and the values corresponding to the second neutralization, i.e., those for the half-neutralized monocyclopropenylium ions, are shown in the parentheses. Upon complete neutralization of dication **3**, the intramolecular ether **21** was isolated in a quantitative yield.

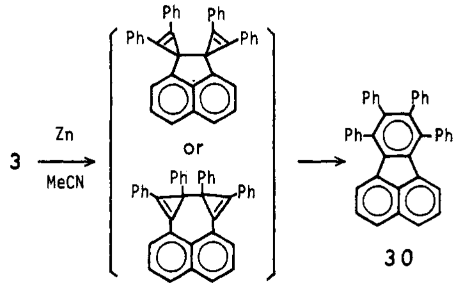
The pK_{R^+} difference between **3** and **24**, which amounts to 1.66 pK units, should have arisen from the purely geometrical reason, and is ascribed to the destabilization of **3** due to the electrostatic repulsion of the cationic rings placed at the closely facing positions. On the other hand, dication **24** having two cyclopropenylium rings at remote positions is less destabilized than dication **29**[27] having the cationic rings spaced by the p-phenylene π-system, thus demonstrating the presence of less π-conjugative interaction between the two positive rings across the 1,5-naphthylene π-system. The slight destabilization of cation **26** as compared with **28** is supposedly due to the electron-withdrawing effect of the ethynyl group at the 5-position.

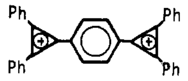
Table V. pK_{R^+} Values and Reduction Potentials for Dications 3, 24, and 29 and for Monocations 26 and 28

cation	pK_{R^+} (50% MeCN)	E_{redn} (MeCN),[a] V vs. Ag/Ag$^+$
3	-2.08^b $(1.11)^c$	-0.54
24	-0.42^b $(1.78)^c$	-0.75
29^d	-1.1^b $(3.5)^{c,d}$	$-0.32^{d,e}$
26	1.16	-1.04
28	1.62	-1.07

[a] Peak potentials obtained by cyclic voltammetry at the scan rate of 0.1 V/s with $Bu_4N^+ClO_4^-$ as the supporting electrolyte. [b] Measured in 50% EtOH–dilute H_2SO_4 by the use of the C_0 acidity function. [c] Values for the second neutralization. [d] Reference 27. [e] Determined in DMF.

Scheme XIV





29

The values of reduction potentials shown in Table V also exhibit the general trend similar to that for the pK_{R^+} values, indicating the highest susceptibility of dication **3** toward one-electron reduction. Actually, the chemical reduction of **3** with zinc powder smoothly afforded fluoranthene **30**[29] as a single product in a good yield (80%), which was most probably formed by way of the intramolecular coupling of the cyclopropenyl radicals followed by bis(cyclopropenyl)–benzene rearrangement[30] as shown in Scheme XIV.

Experimental Section

General. Melting points were determined on a Yamato MP-21 apparatus and are uncorrected. Elemental analysis were performed by Microanalytical Center, Kyoto University, Kyoto. IR and UV–vis spectra were recorded on Hitachi 215 and Hitachi 200-10 spectrophotometers, respectively. ^1H NMR spectra were taken on a JEOL GX-400 (400 MHz), a Varian HR-220 (220 MHz), or a Hitachi R-24 (60 MHz) spectrometer using Me_4Si as an internal standard. ^{13}C NMR spectra were obtained on a JEOL FX-100 spectrometer (25 MHz). High-performance liquid chromatography (HPLC) was carried out with a Waters apparatus equipped with a U6K injector, a 6000A pump, a 440 UV detector, and an R401 refractive index detector, using a Microporasil

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(27) Eicher, T.; Berneth, H. *Tetrahedron Lett.* **1973**, 2039.

(28) Bossenbroek, B.; Sanders, D. C.; Curry, H. M.; Shechter, H. *J. Am. Chem. Soc.* **1969**, *91*, 371.

(29) Rasheed, K. *Tetrahedron* **1966**, *22*, 2957.

(30) For leading references, see: Padwa, A.; Pulwer, M. J.; Rosenthal, R. J. *J. Org. Chem.* **1984**, *49*, 856.

column. Medium-pressure liquid chromatography (MPLC) was performed with Merck silica gel 60 (230–400 mesh). Preparative thin-layer chromatography (TLC) was performed with Merck silica gel 60 PF_{254} containing $CaSO_4$.

1,8-Bis(phenylethynyl)naphthalene (4) and 1,5-bis(phenylethynyl)naphthalene (22) were prepared according to the literature method.[28] 4: mp 103.7–104.2 °C (lit.[28] mp 105–106 °C); ^{13}C NMR ($CDCl_3$) δ 89.9 (s), 96.8 (s), 121.0 (s), 123.9 (s), 125.7 (d), 128.0 (d, two peaks), 129.7 (d), 131.7 (d + s, two peaks), 134.2 (s), 135.0 (d). 22: mp 198.5–199.4 °C (lit.[28] mp 198–199 °C); ^{13}C NMR ($CDCl_3$) δ 87.3 (s), 94.6 (s), 121.3 (s), 123.2 (s), 126.1 (d), 126.9 (d), 128.4 (d, two peaks), 130.8 (d), 131.6 (d), 133.0 (s). Phenylchlorodiazirine was prepared following the method of Padwa.[8] Benzene and ether were dried over Na. Dichloromethane was dried and distilled over P_2O_5.

8-Chloro-7,8,9-triphenyl-8*H*-cyclopent[*a*]acenaphthylene (7). To a stirred solution of phenyllithium (18 mmol) in ether (20 mL) was slowly added acecyclone (14)[31] (3.49 g, 9.79 mmol) in small portions. After being stirred for 2 h at room temperature, the mixture was quenched with 10% HCl and extracted with ether and with dichloromethane. The combined organic layers were washed with 10% NaCl and dried over $MgSO_4$. Removal of the solvent followed by recrystallization from benzene afforded 7,8,9-triphenyl-8*H*-cyclopent[*a*]acenaphthylen-8-ol (3.94 g, 92.6%) as greenish yellow crystals: mp 235.5–237.0 °C; IR (KBr) 3550, 3060, 1600, 1495, 1440, 1355, 990, 830, 780, 770, 720, 700 cm^{-1}; UV–vis (MeCN) λ_{max} (log ϵ) 252 (4.52), 283 sh (4.35), 398 nm (4.14); ^1H NMR ($CDCl_3$, 60 MHz) δ 2.60 (s, 1 H, OH), 7.07–7.64 (m, 19 H), 7.86 (d, 2 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 97.1 (s), 119.4 (d), 125.2 (d), 125.6 (d), 126.8 (d), 127.6 (d), 127.7 (d), 127.8 (d), 128.1 (d), 128.2 (d), 131.8 (s), 132.1 (s), 133.9 (s), 140.1 (s), 142.2 (s), 142.4 (s), 145.2 (s). Anal. Calcd for $C_{33}H_{22}O$: C, 91.22; H, 5.10. Found: C, 91.35; H, 5.00.

To a stirred suspension of the cyclopent[*a*]acenaphthylen-8-ol (0.674 g, 1.55 mmol) in benzene (4 mL) was slowly added thionyl chloride (1.02 g, 8.54 mmol), dropwise, with heating to reflux. After heating for 30 min, the solution was cooled at 0 °C. An orange solid which separated was filtered and recrystallized from benzene to give 7 (0.590 g, 84.0%) as yellowish orange crystals: melting point and spectral data are shown in Table I. Anal. Calcd for $C_{33}H_{21}Cl$: C, 87.50; H, 4.67; Cl, 7.83. Found: C, 87.72; H, 4.63; Cl, 7.79.

Reaction of 1,8-Bis(phenylethynyl)naphthalene (4) with 1 equiv of Phenylchlorodiazirine. A solution of 4 (0.331 g, 1.01 mmol) and phenylchlorodiazirine (0.168 g, 1.10 mmol) in benzene (10 mL) was heated to reflux for 2 h with stirring, which resulted in evolution of 25 mL of nitrogen. Removal of the solvent afforded a light-brown solid, which was subjected to MPLC. Elution with hexane–chloroform (9:1) gave spirocyclopropene 8 (0.430 g, 94.0%) as a yellowish orange solid. Recrystallization from ligroin afforded pale yellow crystals: melting point and spectral data are shown in Table I. Anal. Calcd for $C_{33}H_{21}Cl$: C, 87.50; H, 4.67; Cl, 7.83. Found: C, 87.76; H, 4.50; Cl, 8.03.

The following fractions in MPLC afforded 7 (0.0081 g, 1.8%) as an orange solid.

X-ray Crystallography. Crystal data are as follows: $C_{33}H_{21}Cl$, M = 453.0, monoclinic, space group $P2_1/a$, a = 15.409 (3) Å, b = 12.409 (3) Å, c = 12.276 (3) Å, β = 94.29 (3)°, V = 2375 Å^3, Z = 4, D_c = 1.267 g/cm^3.

Diffraction data were collected with Ni-filtered Cu Kα radiation on a microcomputer-controlled four-circle diffractometer.[32] The crystal was coated with collodion. The unit cell dimensions were determined by a least-squares fit to the observed value of 2θ for 37 reflections. intensities of 3429 independent reflections were measured up to $2\theta = 120°$ with θ–2θ scan technique. Two periodically monitored reflections showed no significant change in intensity during data collection. The intensities were corrected for the Lorentz and polarization factors but not for absorption.

The structure was solved by the direct method.[33] The positional and anisotropic thermal parameters for non-hydrogen atoms were refined by the block-diagonal least-squares method.[34] Initial positional parameters of hydrogen atoms were calculated from known geometry. The positional and isotropic thermal parameters for hydrogen atoms were included in the refinement. The weighting scheme used in the final cycle of the refinement was $w = 1.0$ for $F_o \leq 20$ and $w = [1.0 + 0.1(F_o - 20)]^{-1}$ for $F_o > 20$. The final R value was 0.065 for 3179 reflections. The atomic scattering factors were taken from the literature.[35]

Thermal Rearrangement of Spirocyclopropene 8. About 5 mg of 8 was sealed in a capillary tube under vacuum and was heated to melt at 187–188 °C for 1 min. When cooled at room temperature, the sample resolidified and exhibited an IR spectrum completely identical with that of 7.

Kinetic Studies. From a solution of 8 (2.04×10^{-2} M) in freshly distilled diphenyl ether, 1-mL aliquots were withdrawn and sealed in Pyrex glass ampules under vacuum (<10^{-3} mmHg). The ampules were immersed in a thermostated (±0.1 °C) oil bath at the designated temperatures and were periodically withdrawn for analysis with UV–vis spectroscopy. The concentration of the product 7 was determined from the characteristic absorption of 7 at 393 nm on the sample solution prepared by 10^{-3} dilution with dichloromethane. Addition of quinoline (10 vol %) to the solvent did not affect the observed rate.

Reaction of 4 with Dichlorocarbene. To a vigorously stirred mixture of 4 (2.97 g, 9.04 mmol) and benzyltriethylammonium chloride (0.216 g, 0.949 mmol) in chloroform (28 mL), which had been cooled with an ice bath, was added 36 g of 50% NaOH. After being stirred for 10 min with ice-bath cooling, the mixture was separated, and the aqueous layer extracted with chloroform. The combined organic layers were washed with 10% NaCl, dried over $MgSO_4$, and evaporated to give 3.29 g of a brown solid, which was then subjected to MPLC. From the fractions eluted with benzene–ether (9:1) was recovered unchanged 4 (2.23 g, 75.1%). From the fractions eluted with benzene–ether (1:1) was obtained 1-phenyl-2-[8-(phenylethynyl)-1-naphthyl]cyclopropenone (**12a**) (0.569 g, 17.7%; 71.1% based on consumed 4) as white crystals, which were recrystallized from hexane–benzene (1:1): mp 138.0–138.5 °C; IR (KBr) 3060, 2215, 1850, 1615, 1490, 1447, 1375, 1340, 1318, 1218, 935, 830, 765, 700, 690 cm^{-1}; UV (MeCN) λ_{max} (log ϵ) 239 (4.79), 263 sh (4.46), 310 (4.33), 327 (4.33), 334 (4.32), 345 nm (4.29); ^1H NMR ($CDCl_3$, 60 MHz) δ 7.15–7.53 (m, 10 H), 7.61–8.04 (m, 6 H); ^{13}C NMR data are shown in Table IV. Anal. Calcd for $C_{27}H_{16}O$: C, 90.99; H, 4.52. Found: C, 90.81; H, 4.52.

When the reaction was carried out for 30 min, the yield of **12a** was 30.8% and 41.7% of 4 was recovered.

Reaction of 1-(Phenylethynyl)naphthalene (16) with Dichlorocarbene. Similarly, a mixture of 16[36] (0.379 g, 1.66 mmol), benzyltriethylammonium chloride (0.0446 g, 0.196 mmol), chloroform (7 mL), and 6 g of 50% NaOH was vigorously stirred for 1.5 h at room temperature. After the workup as described for **12a**, the crude product was purified by MPLC using benzene–ether (4:1) as an eluent to give 1-(1-naphthyl)-2-phenylcyclopropenone (**11b**) (0.0635 g, 14.9%) as white crystals, which were recrystallized from hexane–benzene (1:2): mp 166.0–168.0 °C; IR (KBr) 3060, 1855, 1617, 1595, 1510, 1445, 1350, 1265, 810, 777, 690 cm^{-1}; UV (CH_2Cl_2) λ_{max} (log ϵ) 235 (4.41), 256 (4.17) 267 (4.19), 276 (4.05), 321 (4.26), 337 (4.29), 360 nm (3.96); ^1H NMR ($CDCl_3$, 60 MHz) δ 7.40–8.11 (m); ^{13}C NMR data are shown in Table IV. Anal. Calcd for $C_{19}H_{12}O$: C, 89.04; H, 4.72. Found: C, 88.77; H, 5.02.

Thermolysis of Cyclopropenone 12a. A solution of **12a** (0.216 g, 0.606 mmol) in toluene (3 mL) was heated to reflux for 4 h under a nitrogen atmosphere. After removal of the solvent, the product mixture was separated by the use of MPLC. From the fractions eluted with hexane–ether (95:5) was obtained 4 (0.125 g, 62.9%). The fractions eluted with hexane–ether (8:1) afforded 14 (0.0320 g, 14.8%).

Hydroxycyclopropenylium Ions 19a–c. Each of cyclopropenones **11a** (0.036 g, 0.10 mmol), **11b** (0.026 g, 0.10 mmol), and **11c** (0.021 g, 0.10 mmol) was dissolved in a solution of tri-

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chloroacetic acid (0.16 g, 1.0 mmol) in $CDCl_3$ (0.5 mL) and was subjected to ^{13}C NMR measurements. Essentially the same spectra were obtained with trifluoroacetic acid, but the measurements using trichloroacetic acid were preferred because of the less interference with solvent signals. Neither sample showed an change in spectrum after being kept at 35 °C for 2 days. After the measurements, each sample was neutralized by addition of triethylamine (0.15 g, 1.5 mmol). The ^{13}C NMR spectra indicated that the starting cyclopropenones **12a–c** were completely regenerated. This was further confirmed by quantitative recovery of **12a–c** by aqueous workup and extraction with dichloromethane.

Reaction of 4 with 2 equiv or an Excessive Amount of Phenylchlorocarbene. Method A. A stirred solution of **4** (1.00 g, 3.05 mmol) and phenylchlorodiazirine (0.920 g, 6.02 mmol) in benzene (20 mL) was heated to reflux for 2 h with stirring. Removal of the solvent afforded a product mixture, which was separated by the use of preparative TLC developed with hexane–benzene (3:1). From the fraction with R_f 0.6 was isolated **8** (1.20 g, 86.9%). The fraction with R_f 0–0.1 afforded a brown viscous oil, which was again subjected to preparative TLC developed with benzene. From the fraction with R_f 0.7 was separated a yellow, viscous oil. This oil was purified by HPLC using hexane–chloroform (92.5:7.5) to give 1,8-bis(3-chloro-2,3-diphenyl-1-cyclopropen-1-yl)naphthalene (**6**) (0.0272 g, 1.5%) as a yellow solid, which does not show a clear melting point and slowly decomposes under air: IR (CCl_4) 3060, 1810, 1595, 1498, 1445, 1340, 1110, 1033, 980, 840, 690 cm^{-1}. No further analysis was made because of the instability of **6**.

Method B. To a solution of **4** (1.00 g, 3.04 mmol) in benzene (70 mL) stirred with an efficient and sturdy mechanical stirrer, was added potassium *tert*-butoxide (7.8 g, 70 mmol) under a nitrogen atmosphere. To this suspension was added freshly distilled benzal chloride (9.82 g, 61.0 mmol), dropwise over a period of 10 min, with vigorous stirring and occasional cooling with a water bath to keep the reaction temperature below 60 °C. After the resulting jelly-like mixture was stirred for 1 h at room temperature, the mixture was filtered through a Buchner funnel and washed well with benzene. The filtrate was evaporated and the residue distilled with a Kugelrohr apparatus at 40 °C (0.01 mmHg) to remove most of the unchanged benzal chloride. The residual viscous oil was subjected to preparative TLC developed with hexane–benzene (1:2). A light brown, viscous oil obtained from the fraction with R_f 0.4–0.6 was crystallized from hexane–chloroform (30:1) to give the intramolecular ether **21** (0.520 g, 32.7%) as a yellowish white powder, which was recrystallized from THF to give white crystals: mp 173.5–174.3 °C dec; IR (KBr) 3060, 1800, 1600, 1495, 1445, 1125, 1100, 1070, 1040, 1015, 828, 770, 700, 690 cm^{-1}; UV (MeCN) λ_{max} (log ϵ) 230 (4.64), 239 sh (4.62), 246 sh (4.61), 314 (4.38), 328 (4.38), 350 nm (4.26); ^1H NMR ($CDCl_3$, 220 MHz) δ 6.97 (m, 6 H, meta and para H), 7.17 (d, 4 H, ortho H), 7.46 (m, 6 H, meta′ and para′ H), 7.60 (dd, 2 H, H-3, J = 8.0, 7.0 Hz), 7.87 (d, 4 H, ortho′ H), 7.91 (d, 2 H, H-2), 8.26 (d, 2 H, H-4, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 65.8 (s), 117.9 (s), 119.2 (s), 124.2 (s), 125.5 (d), 125.8 (d), 125.9 (d), 126.9 (s), 127.6 (d), 127.7 (s), 128.9 (d), 129.5 (d), 130.2 (d), 130.4 (d), 131.1 (d), 134.5 (s), 144.1 (s) Anal. Calcd for $C_{40}H_{26}O$: C, 91.92; H, 5.01. Found: C, 91.52; H, 5.07.

Reaction of 1,5-Bis(phenylethynyl)naphthalene (22) with Phenylchlorocarbene. A solution of **22** (0.328 g, 0.997 mmol) and phenylchlorodiazirine (0.760 g, 4.98 mmol) in benzene (18 mL) was heated to reflux for 30 min with stirring. After removal of the solvent, dichloromethane (3 mL) and acetonitrile (3 mL) were added to the residual viscous oil. The crystals which separated upon cooling at 0 °C were filtered, washed with acetonitrile, and dried under vacuum to give 1,5-bis(3-chloro-2,3-diphenyl-1-cyclopropen-1-yl)naphthalene (**23**) (0.385 g, 67.0%) as an unstable pale yellow powder, which was recrystallized from dichloromethane: mp 250.3–251.0 °C dec; IR (KBr) 3060, 1792, 1600, 1500, 1460, 1450, 1192, 1140, 1080, 1033, 940, 820, 788, 770, 710, 690 cm^{-1}. No further analysis was made because of the instability of **23**.

Removal of the solvent from the filtrate afforded a yellow-brown oil, which was subjected to preparative TLC developed with benzene. From the fraction with R_f 0.4–0.5 was isolated 1-(3-chloro-2,3-diphenyl-1-cyclopropen-1-yl)-5-(phenylethynyl)naphthalene (**25**) (0.0722 g, 16.0%) as an unstable yellow viscous oil, which was further purified by HPLC using hexane–chloroform (95:5): IR ($CHCl_3$) 2220, 1810, 1600, 1492, 1445, 1145, 1110, 1070, 995, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 7.10–7.81 (m, 18 H), 8.00 (d, 1 H, J = 7.0 Hz), 8.32 (d, 1 H, J = 8.0 Hz), 8.46 (d, 1 H, J = 8.0 Hz). No further analysis was made because of the instability of **25**.

Reaction of 16 with Phenylchlorocarbene. A solution of **16** (0.342 g, 1.50 mmol) and phenylchlorodiazirine (0.230 g, 1.51 mmol) in benzene (15 mL) was heated to reflux for 30 min with stirring. Removal of the solvent afforded a light brown oil, which was subjected to preparative TLC developed with benzene. From the fraction with R_f 0.3 was obtained 1-(3-chloro-2,3-diphenyl-1-cyclopropen-1-yl)naphthalene (**27**) (0.180 g, 34.0%) as an unstable yellow viscous oil, which was purified by HPLC using hexane–chloroform (95:5): IR (CCl_4) 3060, 1805, 1600, 1492, 1442, 1390, 1165, 1140, 1120, 995, 860, 690 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 7.07–7.99 (m, 16 H), 8.28 (m, 1 H). No further analysis was made because of the instability of **27**.

1,8-Naphthylenebis(2,3-diphenylcyclopropenylium) Tetrafluoroborate ($3{\cdot}2BF_4^-$). To a stirred solution of **21** (0.172 g, 0.329 mmol) in dichloromethane (18 mL) was added trityl tetrafluoroborate (0.239 g, 0.726 mmol) in one portion. After the mixture was stirred at room temperature for 20 min, ether (20 mL) was added to the mixture, which was then cooled at 0 °C. The separating precipitates were filtered and dried under vacuum to give $\mathbf{3}{\cdot}2BF_4^-$ (0.219 g, 97.8%) as a pale yellow powder: melting point and spectral data are given in the supplementary material. Anal. Calcd for $C_{40}H_{26}B_2F_8$: C, 70.62; H, 3.85. Found: C, 70.34; H, 4.01.

Similarly, the reaction of **6** with 2 equiv of trityl tetrafluoroborate afforded $\mathbf{3}{\cdot}2BF_4^-$ in a 98.0% yield.

1,5-Naphthylenebis(2,3-diphenylcyclopropenylium) Tetrafluoroborate ($24{\cdot}2BF_4^-$). By the same method, the reaction of **23** (0.221 g, 0.383 mmol) with trityl tetrafluoroborate (0.286 g, 0.865 mmol) gave $\mathbf{24}{\cdot}2BF_4^-$ (0.246 g, 94.4%) as a pale yellow powder: melting point and spectral data are given in the supplementary material. Anal. Calcd for $C_{40}H_{26}B_2F_8$: C, 70.62; H, 3.85. Found: C, 70.20; H, 3.72.

1,2-Diphenyl-3-[5-(phenylethynyl)-1-naphthyl]cyclopropenylium Tetrafluoroborate ($26{\cdot}BF_4^-$). Similarly, the reaction of **25** (0.0280 g, 0.0618 mmol) with trityl tetrafluoroborate (0.0318 g, 0.0964 mmol) yielded $\mathbf{26}{\cdot}BF_4^-$ (0.0318 g, 95.5%) as a yellow powder: melting point and spectral data are given in the supplementary material. Anal. Calcd for $C_{33}H_{21}BF_4$: C, 78.59; H, 4.20. Found: C, 78.64; H, 4.27.

1-(1-Naphthyl)-2,3-diphenylcyclopropenylium Tetrafluoroborate ($28{\cdot}BF_4^-$). Similarly, the reaction of **27** (0.0320 g, 0.0908 mmol) with trityl tetrafluoroborate (0.0350 g, 0.106 mmol) afforded $\mathbf{28}{\cdot}BF_4^-$ (0.0348 g, 94.9%) as a white powder: melting point and spectral data are given in the supplementary material. Anal. Calcd for $C_{25}H_{17}BF_4$: C, 74.28; H, 4.24. Found: C, 74.30; H, 4.27.

Zinc Reduction of $3{\cdot}2BF_4^-$. To a stirred solution of $\mathbf{3}{\cdot}2BF_4^-$ (0.134 g, 0.197 mmol) in acetonitrile (10 mL) was added zinc powder (0.264 g, 4.04 mmol). After the mixture was stirred at room temperature for 1 h, the solvent was evaporated and the residue extracted with ether. Removal of ether afforded 7,8,9,10-tetraphenylfluoranthene (**30**) (0.0796 g, 79.8%) as white crystals, which were recrystallized from benzene: mp 312.0–313.5 °C (lit.[29] mp 312–314 °C); IR (KBr) 3060, 1600, 1498, 1442, 1428, 1413, 1070, 1030, 830, 780, 768, 700 cm^{-1}; UV ($CHCl_3$) λ_{max} (log ϵ) 237 (4.73), 294 (4.50), 328 (3.92), 362 (3.99), 372 nm (4.01); ^1H NMR ($CDCl_3$, 60 MHz) δ 6.58 (d, 2 H, H-1,6, J = 7 Hz), 6.86 (s, 8 H), 7.26 (s + m, 14 H), 7.70 (d, 2 H, H-3,4, J = 8 Hz).

pK_{R^+} Measurements. The pK_{R^+} values corresponding to the first neutralization of dications **3** and **24** were determined by means of the UV spectrophotometric method at 25 °C in 50% ethanol acidified with sulfuric acid, using the acidity function C_0[37] and the correlation in eq 1, where c refers to the concentration.

$$C_0 = pK_{R^+} - \log\,(c_{R^+}/c_{ROH}) \qquad (1)$$

The C_0 values for the respective acidic solvents were calibrated

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by determining spectrometrically the extent of ionization for *p*-anisyldiphenylmethanol and correlated it with the known $\mathrm{p}K_{\mathrm{R}^+}$ value (-1.24)[37] of *p*-anisyldiphenylmethyl cation.

The $\mathrm{p}K_{\mathrm{R}^+}$ values for the monocations and also the values corresponding to the second neutralization of the dications were determined at 25 °C in 50% acetonitrile by means of the UV spectrophotometric method described in a previous paper.[38]

Cyclic Voltammetry. The measurements were done with the method and apparatus described in the previous paper.[38] Sample solutions were 1 mM in cation and 0.1 M in tetrabutylammonium perchlorate as a supporting electrolyte. Scan rate was 0.1 V/s. All the cations exhibited the irreversible cathodic peak at the potential given in Table V. Immediately after each measurement, ferrocene (0.2 mM) was added as an internal standard,[39] and the peak potential was corrected with reference to this standard.

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Supplementary Material Available: Tables of all the bond lengths and angles, of atomic coordinates and thermal parameters, and of anisotropic thermal parameters and a table of melting points and spectral data for the tetrafluoroborates of cations **3**, **24**, **26**, and **28** (7 pages). Ordering information is given on any current masthead page.

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Perpendicular Effects on Transition States. 2. Energy Profiles and Reaction Surfaces

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It is shown how the free energy profiles along and perpendicular to the reaction coordinate determine a two-dimensional energy surface for describing substituent effects in organic reactivity. This affords a generalization of the hyperbolic–paraboloid surfaces, extendible to large energy variations. It also shows that the reaction surface and curve-crossing approaches lead to a similar mathematical description of the problem. The various models are compared with experimental results for free energy of activation of proton-transfer reactions between benzoic acids and methanol and of Cope and Claisen rearrangements.

Use of two-dimensional plots to discuss effects along and perpendicular to the reaction coordinate has become increasingly popular.[1-16] In this picture, substituents can affect the free energy of activation (that is, the energy of the saddle point in the two-dimensional free energy surface) in two ways: The free energies of reactants and products (G_1, G_2) along the reaction coordinate may vary, resulting in the customary Hammond effect,[17,18] or the free energies of the perpendicular structures (G_3, G_4) may be perturbed, leading to an anti-Hammond effect,[3] where the transition state moves *toward* the state of lowered energy.

Most authors who model such surfaces quantitatively[6,12,14,16] use a hyperbolic–paraboloid function, namely a quadratic polynomial in two variables, with parameters determined so that the surface has a maximum along one direction and a minimum along the perpendicular direction. Such a potential necessarily reduces[14] to Marcus'[19] quadratic energy profile along the reaction coordinate. This is rather restrictive, especially since the Marcus relation is not expected to give a good description of experiment over a large energy range.[20]

Since much more is known on the general form of the profile along the reaction coordinate[20] than on the shape of the surface, it seems natural to begin its construction from such profiles. This has been my approach in a recent publication.[15] That model (model I) is based on a free

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