ABCP were decomposed in parallel at 50 °C, E was lost no more quickly than BHT at low conversions (Figure 3 and Table III). A plot of $-\Delta$[E] vs. $-\Delta$[BHT] had an initial slope of 1.07 ± 0.09, which gives $n = 1.86 \pm 0.1$ in good agreement with the result in acetonitrile. A least-squares regression of all data gave $n = 1.6 \pm 0.2$. Varying [ABCP] over the range 2.5×10^{-3} to 2.8×10^{-2} did not affect n when [E] ranged from 2×10^{-4} M to 4×10^{-4} M.

Conclusion

Oxidation of E by peroxy radicals follows the same pathway found for other hindered phenols, but the chemistry is more complicated than for 2,6-di-*tert*-butyl phenols because about half the interactions between E· and $RO_2\cdot$ lead to products other than peroxy ketal **2**, probably addition at *o*-methyl positions. Neither dimers nor tocopherylquinone were observed in our studies, and their reported occurrence probably reflects special conditions of one-electron oxidation by metal ions or, in the case of tocopherylquinone, subsequent hydrolysis of initially formed peroxy ketal. We should note that $RO_2\cdot$ oxidations of E sequestered in phosphatidylcholine bilayers suspended in pH 7 buffer solutions gave only tocopherylquinone in about 25% yield. One explanation is that water intrudes into the bilayer no promptly hydrolyze the peroxy ketal. Another possibility is that peroxy radicals (generated from lipophilic ABCP) and E· interact at or near the polar head groups of the lipid, and thus peroxy ketal is readily exposed to hydrolytic conditions.[31]

The close agreement between two kinds to measurements for n gives us confidence in the value of 2 as an accurate measure of the stoichiometry of the E + $RO_2\cdot$ interaction and reaffirms our conclusion that all of the oxidized E ultimately binds with RO_2. Our experiments do not provide a measure of k_1 directly but do demonstrate that E is much more reactive with $RO_2\cdot$ than ordinary phenols as was previously determined by Niki[14] and Burton and Ingold.[15] We estimate $k_1 > 2 \times 10^5$ M^{-1} s^{-1}.

Acknowledgment. This work was supported by NIH National Institutes of Aging Grant No. HD08841-02. We thank E. Niki and K. U. Ingold for useful comments and prepublication data and Maria Buyco for preparation of this manuscript.

Registry No. *d*-**1**, 59-02-9; *dl*-**1**, 10191-41-0; *d*-**3**, 7559-04-8; **4**, 1604-73-5; **5a**, 88056-74-0; **5b**, 88083-17-4; **7** ($R' = C(CN)(CH_3)_2$) (isomer 1), 88056-75-1; **7** ($R' = C(CN)(CH_3)_2$) (isomer 2), 88056-76-2; **7** ($R' = (CH_3)_2CCOOBu$) (isomer 1), 88056-77-3; **7** ($R' = (CH_3)_2CCOOBu$) (isomer 2), 88056-78-4; ABCP, 21302-38-5; AIBN, 78-67-1; 2,6-di-*tert*-butyl-4-methoxyphenol, 489-01-0; 2,6-di-*tert*-butyl-*p*-quinone, 719-22-2.

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(31) Barclay et al.[32] have shown that inhibition of methyl linoleate oxidation by E in micelles is significantly enhanced by ascorbic acid in the aqueous phase.

(32) Barclay, L. R. C., Locke, S. J.; MacNeil, J. M. *Can. J. Chem.* **1983**, *61*, 1288.

Chemical Behavior of Cyclopropylmethyl Radicals: Relative Unimportance of Cyclopropylmethyl to 3-Butenyl Rearrangement in the Cycloaddition Reactions Proceeding via Allylically Stabilized Diradicals[1a]

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The reaction of *cis*-1-cyclopropyl-1,3-butadiene (**1c**) with fluorenylidene (Fl:), which was thermally generated from 9-diazofluorene (**2**), produced **3c** in addition to fluorenone azine (**4**) and 9,9′-bifluorenylidene (**5**). The reaction of **1t** with **2** gave a mixture of two adducts, **3t** and **6**, in which **6** was proved to be the secondary product derived from **3t**. The addition of Fl: was thus regiospecific and gave **3**, and the stereochemistry of the C1–C2 double bond in **1** was retained throughout the addition. The reaction of 1,1-dicyclopropyl-1,2-propadiene (**7**) with Fl: took place exclusively at the C2–C3 double bond in **7** to give **8**, whereas dibromocarbene attacked **7** exclusively at the C1–C2 double bond to give **13**. On being heated at 140 °C, **13** underwent the anticipated skeletal isomerization to give **14**. At 180 °C, more extensive rearrangements took place to produce **15**, **16Z**, and **16E** in a 2.9:1.0:3.7 ratio. 1,1-Dibromo-2,2-dicyclopropylcyclopropane (**19**), on the other hand, produced a mixture of **20Z** and **20E** on being heated at 140 °C. In contrast to the results obtained in the Fl: addition reactions, the radical addition of bromotrichloromethane (**22**) to **1** yielded cyclopropane-cleaved **23** as the exclusive product. It may thus be concluded that the cyclopropylmethyl to 3-butenyl rearrangement in the diradicals, in which the cyclopropyl-substituted site is stabilized with allylic resonance, is unimportant relative to the intramolecular coupling of the two radical sites at least at 140 °C or below, whereas the intermolecular atom abstraction of the cyclopropyl-substituted allyl radical occurs relatively slowly and hence is accompanied by the cyclopropane cleavage.

Some time ago, we[2] demonstrated that cyclopropyl-substituted ethylene is a valuable substrate to investigate radical cycloadditions. It was observed that the addition, which proceeded in a stepwise fashion via a diradical intermediate, yielded a significant amount of cyclo-

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(2) (a) Shimizu, N.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1972**, 389. (b) Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1974**, *96*, 6451. (c) Shimizu, N.; Ishikawa, M.; Ishikura, K.; Nishida, S. *Ibid.* **1974**, *96*, 6456. (d) Shimizu, N.; Fujioka, T.; Ishizuka, S.; Tsuji, T.; Nishida, S. *Ibid.* **1977**, *99*, 5972.

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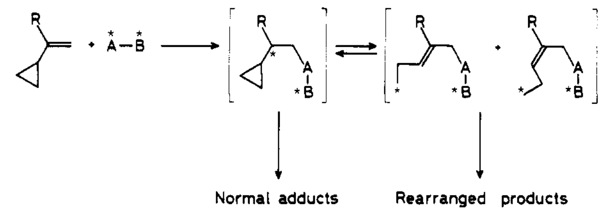
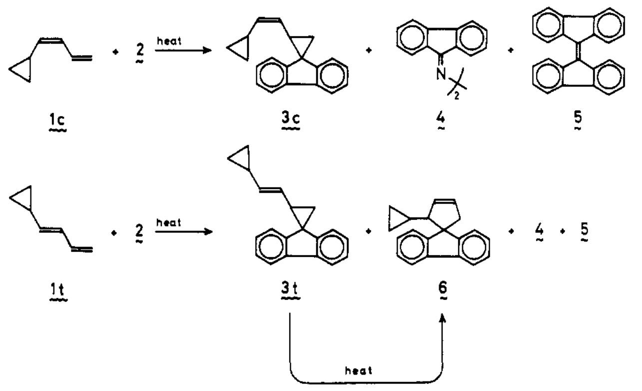
Scheme I



propane-cleaved products under appropriate reaction conditions, whereas no cyclopropane cleavage took place in predictably concerted reactions. The technique, therefore, will provide an effective means to discriminate between stepwise diradical cycloadditions and concerted reactions. The discrimination of these two types of cycloadditions may sometimes meet with difficulty, since the two cycloadditions will exhibit similar characteristics in the solvent polarity effect upon reaction rates,[3] and there may be a possibility that they cannot be firmly differentiated on the basis of the stereochemical behavior of the cycloaddition.[4] The cyclopropylmethyl to 3-butenyl rearrangement,[5,6] on the other hand, would take place in the discrete radical species, and hence the formation of the cyclopropane-cleaved products can be a strong indication supporting the fact that the cycloaddition in question is a stepwise process proceeding via a diradical intermediate.

The cyclopropylmethyl to 3-butenyl radical rearrangement is in fact known as one of the basic "free radical clocks",[6c] and it has been used in the studies of a variety of transformations to prove that the transformation involves a discrete radical intermediate.[7] The lifetime of short-lived diradicals has also been investigated with this technique.[8] In principle, the technique is based on the fact that the rearrangement of cyclopropylmethyl radical to 3-butenyl radical is so rapid[5,6] that it can compete efficiently with the terminating processes of radical intermediates, even with the ring closure of diradicals.[2,9] The rate of the rearrangement of the parent cyclopropylmethyl radical is in fact known to be very high,[5,6] but we should remind ourselves that, when the technique is applied to the mechanistic studies of certain reactions, there may be several factors which are related to the effective production of the cyclopropane-cleaved products. First of all, the rate of the rearrangement will be a function of the electronic effects[10] and steric effects of the substituents. Conformational effects as well as spin correlation effects[11] will also have some effect on the ring cleavage rates. Second, the rearranged 3-butenyl radical should have proper terminating processes, either cyclization or atom abstraction; otherwise the 3-butenyl radical will rebind back to the cyclopropylmethyl radical,[12] and seemingly unrearranged products will be obtained. With regard to the electronic effects on the rate of the rearrangement, we previously observed that a substituent such as a phenyl at the cyclopropylmethyl site in the diradical resulted in a lowering of the extent of the rearrangement.[2] In the present study, we examined the reactions which proceeded via an intermediate whose cyclopropylmethyl site was stabilized with allylic resonance (Scheme I). It was observed that the cyclopropane cleavage process in such diradicals was no more important compared to the intramolecular coupling of the two radical sites at or lower than 140 °C. In contrast, the intermolecular atom abstraction process resulted in the total formation of the ring-cleaved products even at 80 °C.

Scheme II



Results

Reactions of 1-Cyclopropyl-1,3-butadienes (1) with Fluorenylidene. Since our previous studies[2] on the reaction of 1,1-dicyclopropylethylene with fluorenylidene (Fl:) indicated that the formation of cyclopropane-cleaved products was significant in the reactions carried out in decalin at 140 °C, the reactions of *cis*-1-cyclopropyl-1,3-butadiene (**1c**)[13] and its trans isomer (**1t**)[13] with 9-diazofluorene (**2**) were examined under similar conditions (Scheme II). For the purpose of comparison, the same reactions were also carried out in refluxing benzene. Under both reaction conditions, **1c** gave simply 1-(*cis*-2-cyclopropylvinyl)dibenzo[*d*,*f*]spiro[2.4]heptane (**3c**) aside from fluorenone azine (**4**) and 9,9′-bifluorenylidene (**5**).[14] The yield of **3c** was 78% in refluxing benzene and 42% in decalin at 140 °C. On the other hand, the reaction of **1t** with **2** gave a mixture of two adducts, namely, 1-(*trans*-2-cyclopropylvinyl)dibenzo[*d*,*f*]spiro[2.4]heptane (**3t**) and 1-cyclopropyldibenzo[*f*,*h*]spiro[4.4]non-2-ene (**6**). The stereochemical assignments of **3c** and **3t** were done on the

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(3) Bartlett, P. D. *Q. Rev., Chem. Soc.* **1970**, *24*, 473.

(4) Epiotis, N. D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 751.

(5) Montgomery, L. K.; Matt, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 6556. Cristol, S. J.; Barbour, R. V. *Ibid.* **1968**, *90*, 2832. Carlson, D. J.; Ingold, K. U. *Ibid.* **1968**, *90*, 7047. Sheldon, R. A.; Kochi, J. K. *Ibid.* **1970**, *92*, 4395, 5175.

(6) (a) Wilt, J. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 8. (b) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Essay 4. (c) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(7) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59 and references cited therein. House, H. O.; McDaniel, W. C.; Sieloff, R. F.; Vanderveer, D. *J. Org. Chem.* **1978**, *43*, 4316. Krusic, P. J.; Fagan, P. J.; Filippo, J. S., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 250. Filippo, J. S., Jr.; Silbermann, J.; Fagan, P. J. *Ibid.* **1978**, *100*, 4834. Mihailovic, M. Li.; Bosnjak, J.; Cekovic, Z. *Helv. Chim. Acta* **1976**, *59*, 475. MacInnes, I.; Nonhebel, D. C.; Orszulik, S. T.; Suckling, C. J. *J. Chem. Soc., Chem. Commun.* **1982**, 121. Nonhebel, D. C.; Orszulik, S. T.; Suckling, C. J. *Ibid.* **1982**, 1146. Chung, S.-K.; Park, S.-U. *J. Org. Chem.* **1982**, *47*, 3197. Barclay, L. R. C.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1982**, *104*, 4399. van Niel, J. C. G.; Pandit, U. K. *J. Chem. Soc., Chem. Commun.* **1983**, 149.

(8) (a) Wagner, P. J.; Liu, K.-C.; Noguchi, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3837. (b) Engel, P. S.; Keys, D. E. *Ibid.* **1982**, *104*, 6860.

(9) Bergman, R. G., in ref 6a, Vol. 1, Chapter 5.

(10) Doyle, M. P.; Raynolds, P. W.; Barents, R. A.; Bade, T. R.; Danen, W. C.; West, C. T. *J. Am. Chem. Soc.* **1973**, *95*, 5988. See also: Martin, J. C.; Schults, J. E.; Timberlake, J. W. *Tetrahedron Lett.* **1967**, 4629. Bolsman, B. M.; de Boer, T. J. *Tetrahedron* **1973**, *29*, 3579. House, H. O.; Weeks, P. D. *J. Am. Chem. Soc.* **1975**, *97*, 2778.

(11) Jones, G., II *J. Chem. Educ.* **1974**, *51*, 175.

(12) Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734.

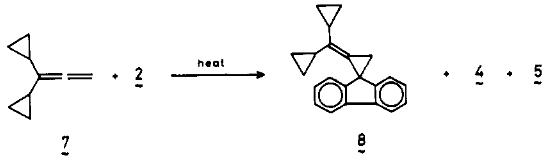
(13) Kataoka, F.; Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1980**, *102*, 711. Kataoka, F.; Nishida, S.; Tsuji, T.; Murakami, M. *Ibid.* **1981**, *103*, 6878.

(14) A small amount of Fl: insertion products with decalin might also be produced.[2b] However, no further attempt was made to isolate and characterize such minor byproducts.

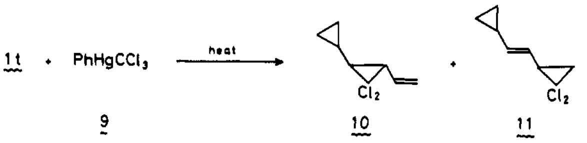
basis of relative magnitudes of the vicinal coupling constants between vinyl protons.[15] The yields of **3t** and **6** were 46% and 2% in refluxing benzene and 17% and 15% in decalin at 140 °C. Since **6** appeared to be produced from **3t** in the vinylcyclopropane to cyclopentene rearrangement,[16] control experiments were carried out to prove the possibility. In fact, it was observed that **3t** readily rearranged to **6** at 140–150 °C.

The HPLC analyses of the crude reaction mixtures showed that crossover of the products was practically absent in the reactions carried out with isomeric **1c** and **1t**, and none of the products involving the cleavage of the originally substituted cyclopropyl group in **1** were detected in an appreciable amount.

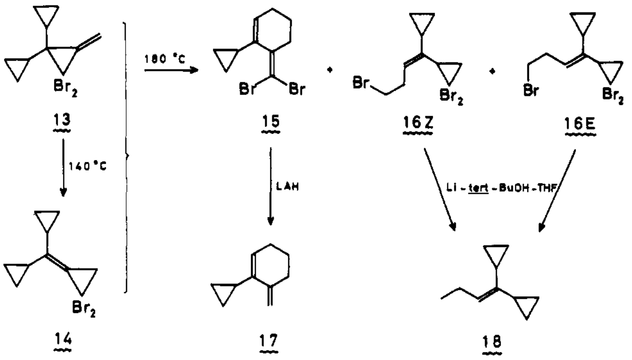
Reaction of 1,1-Dicyclopropyl-1,2-propadiene (7) with Fl:. The reaction of 1,1-dicyclopropyl-1,2-propadiene (**7**)[17] with **2** was carried out under conditions similar to those above, and 2-(dicyclopropylmethylene)dibenzo[*d*,*f*]spiro[2.4]heptane (**8**) was obtained as a single adduct. The yield of **8** was 19% in refluxing benzene and 13% in decalin at 140 °C. Higher yields of **8** were realized in the reactions carried out without solvents; namely, 36% at 140 °C and 31% at 80 °C. Although the yields were considerably lower than those observed in the reactions of **1** with **2**, no product other than **8**, **4**, and **5** was isolated from the reaction mixture. Since **7** is prone to polymerize at higher temperature,[17] the polymer formation might be responsible for the relatively low yields of the adduct. The HPLC analyses of the crude hydrocarbon fractions obtained in the column chromatographic separation of the reaction mixture supported the conclusion that no adduct other than **8** was produced in an appreciable amount. When **2** was decomposed photochemically at 15 °C, **8** was obtained only in 17% yield together with **4** (20%) and **5** (5%).



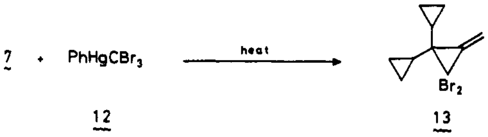
Reaction of 1t with Dichlorocarbene. When a 1:1 mixture of **1t** and (trichloromethyl)phenylmercury (**9**)[18] in benzene was heated at reflux for 72 h, two 1:1 adducts were obtained in 60% yield, besides two additional minor products. The relative peak area of the four components in GC analysis was 13:82:4:1. The two 1:1 adducts were assigned as *trans*-1,1-dichloro-2-cyclopropyl-3-vinylcyclopropane (**10**) and 1,1-dicyclopropyl-2-(*trans*-2-cyclopropylvinyl)cyclopropane (**11**), respectively. Since the remaining two products were produced in such small quantities and they showed considerably long retention times (probably bis adducts) on the GC analysis, no further attempt was made to isolate and characterize them.



Scheme III



Reaction of 7 with Dibromocarbene. The reaction of **7** with (tribromomethyl)phenylmercury (**12**)[18] in refluxing benzene resulted in the formation of 2,2-dibromo-3,3-dicyclopropylmethylenecyclopropane (**13**) in 67% yield. In contrast to the reaction of **7** with Fl:, the addition of dibromocarbene took place exclusively at the C1–C2 double bond in **7**.[19] The better yield (80%) of **13** was achieved with the utilization of the phase-transfer-catalyzed procedure.



Thermal Isomerization of 13. On being heated at 140 °C in decane for 15 h, **13** isomerized cleanly to 2,2-dibromo-1-(dicyclopropylmethylene)cyclopropane (**14**), which was isolated in 80% yield (Scheme III). The structure of **14** was unambiguously established by means of spectroscopic studies, in particular ^{1}H NMR spectra. After 15 h at 180 °C, either **13** or **14** produced a mixture of three products in a 2.7:1.0:3.7 ratio in 50–70% yield. The first product was characterized as 3-(dibromomethylene)-2-cyclopropylcyclohexene (**15**), which was transformed into 2-cyclopropyl-3-methylenecyclohexene (**17**) in the reductive debromination with lithium aluminum hydride. The other two products were found to contain three bromine atoms in a molecule, and they were assigned as (*Z*)-4-bromo-1-(2,2-dibromocyclopropyl)-1-cyclopropyl-1-butene (**16Z**) and its *E* isomer (**16E**). Upon reduction with lithium/*tert*-butyl alcohol/THF, both **16Z** and **16E** gave known 1,1-dicyclopropyl-1-butene (**18**).[20] The stereochemical assignments of **16Z** and **16E** were done on the basis of ^{1}H NMR spectral analyses in the following manner. Since both **16Z** and **16E** gave **18** on the reductive debromination, they must be geometrically isomeric to each other. The product obtained in a larger amount exhibited signals due to the hydrogens at the C4 and C3 methylene groups in the 4-bromo-1-butene unit as a triplet at δ 3.33 (J = 8 Hz) and a doublet of triplets at δ 2.77 (J = 8, 8 Hz), whereas the minor one showed them as two multiplets at δ 3.38 and 2.90. On irradiation of the hydrogens at C3, the multiplet signal at δ 3.38 of the minor product changed its shape to an AB quartet pattern. Intrinsically, the two hydrogens in the methylene groups in these products are diastereotopic because of the presence

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[15] Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution NMR Spectroscopy"; Pergamon Press: New York, 1966; Vol. 2, p 711.

[16] Sarel, S.; Yovell, J.; Sarel-Imber, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 577. Frey, H. M.; Walsh, R. *Chem. Rev.* **1969**, *69*, 122. Doering, W. v. E.; Sachdev, K. *J. Am. Chem. Soc.* **1975**, *97*, 5512. Andrews, G. D.; Baldwin, J. E. *Ibid.* **1976**, *98*, 6705 and references cited therein.

[17] Komiya, Z.; Nishida, S. *J. Org. Chem.* **1983**, *48*, 1500.

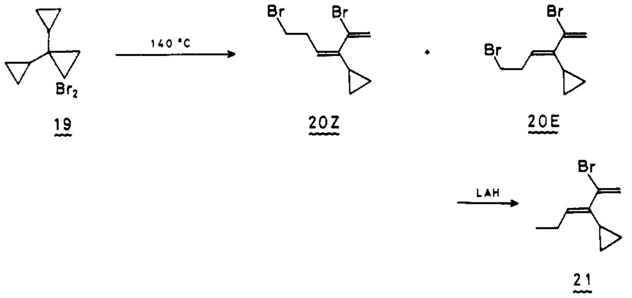
[18] Seyferth, D. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1973; Vol. I, p 101. Seyferth, D. *Acc. Chem. Res.* **1972**, *5*, 65.

[19] Russian workers have reported that the addition of dichlorocarbene to **7** produces a mixture of chloro analogues of **13** and **14** (Nefedov, O. M.; Dolgii, I. E.; Bulusheva, E. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, *6*, 1454). We, however, observed that the addition of dibromocarbene to **7** was cleanly regiospecific even in refluxing benzene. The rearrangement of **13** to **14** required a much higher temperature (see the text).

[20] Kataoka, F.; Nishida, S. *Chem. Lett.* **1980**, 1115.

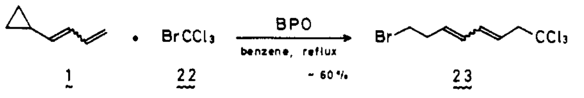
of a chiral center at C1 of the 2,2-dibromocyclopropyl group, but the magnitude of its effect will be a function of the distances between the methylene hydrogens and the chiral center. Accordingly, it might be reasonable to conclude that the major product was the *E* isomer, whose methylene hydrogens exhibited the first-order coupling patterns, whereas the minor product was the *Z* isomer, which showed complex ^{1}H NMR patterns because of the effects of the proximate chiral center.

Thermal Isomerization of 1,1-Dibromo-2,2-dicyclopropylcyclopropane (19). At 140 °C, 1,1-dibromo-2,2-dicyclopropylcyclopropane (19)[2] produced two rearranged products in a 2:1 ratio. They were characterized as 2,6-dibromo-3-cyclopropyl-1,3-hexadienes (**20Z**, **20E**) on the basis of spectral data. The reduction of the major product with lithium aluminum hydride gave (*E*)-2-bromo-3-cyclopropyl-1,3-hexadiene (**21**). The stereochemical assignments of the two products were done on the basis of relative magnitudes in the allylic coupling in the ^{1}H NMR spectra.[21] The coupling constant observed between the C4 hydrogen and the C1′ hydrogen of the cyclopropyl group was 1.6 Hz in the major product, whereas that in the minor one was 2.0 Hz. Accordingly, the major isomer was assigned as the *E* isomer, and the minor product was assigned as the *Z* isomer.



19 20Z 20E 21

Reaction of 1 with Bromotrichloromethane Catalyzed by Benzoyl Peroxide. The diene 1 (a mixture of **1c** and **1t** in a 2:8 ratio) and a small amount of benzoyl peroxide were dissolved in bromotrichloromethane (**22**) and heated at 80 °C. There was obtained a mixture of 1-bromo-8,8,8-trichloro-3,5-octadienes (**23**) in 60% yield. The product was a mixture of the geometrical isomers, but their separation was unsuccessful because of their thermal instability and poor separation in GC analysis. On the basis of ^{1}H NMR spectral studies, it was concluded that neither the cyclopropane-retained adduct nor the adduct at the C1–C2 double bond was produced.



1 22 23

Discussion

Carbene Additions. In their reactions with Fl:, **1c** produced a single adduct, **3c**, whereas **1t** gave a mixture of **3t** and **6**. The adduct **6** is perfunctorily a 1,4-adduct of Fl: with **1t**;[22] however, **6** was in fact the secondary product derived from **3t** as demonstrated in the control experiments. The transformation is a well-known vinylcyclopropane to cyclopentene rearrangement,[16] and the fact that **3c** was relatively inert toward the same rearrangement is reasonable, since **3c** may hardly take the prerequisite *s*-cis conformation to carry out the rearrangement.[16] On the basis of these results, it can be concluded that the reaction of 1 with Fl: is essentially cleanly regiospecific and gives **3**, and the stereochemistry of the C1–C2 double bond in **1** is retained in the products. Although this fact appears to suggest that the addition of Fl: to 1 takes place in a concerted manner, it has been well established that Fl: generated from **2** under conditions similar to the present ones will be at least largely in its triplet spin state.[2a,b,23,24] Accordingly, the addition of Fl: should be considered to proceed in a stepwise fashion via diradical intermediates. It might be expected in such reactions that the stereochemical integrity of the starting olefin will be lost, but, in the present case, it can be argued that the geometrical isomerization in **24** is slow compared to the ring closure because of the allylic stabilization present in the intermediates. The fact that the geometrical isomerization of allyl radicals is slower than the termination process of radical species is well precedented.[25] With regard to the above discussion, it should also be pointed out that 1,3-dienes are known as effective trappers for the triplet carbenes.[26]

Now, with regard to the regioselectivity in the carbene additions, it was observed that the Fl: addition occurred regiospecifically at the C3–C4 double bond in **1** whereas the :CCl_2 attacked both C1–C2 and C3–C4 double bonds in **1t**. These results appear to support the above conclusion that Fl: adds to **1** in the stepwise fashion via diradical intermediates. Namely, singlet :CCl_2 generated from the Seyferth's reagent[18] will add to a double bond in a concerted manner, which may not discriminate between the two double bonds in **1** to an extreme degree.[27] On the other hand, if we accept the conclusion that Fl: adds to **1** in a stepwise manner, the regiospecificity observed here may be understood in terms of both steric effects and electronic effects operating in the intermediates.[28] Among the anticipated diradicals **24**–**26**, **24** would be most favorably produced,[28] and **24** would inevitably result in the formation of **3**. The regiospecificity observed in the reaction of **1** with **22** might be explained on the same basis.[29]

The absence of the cyclopropane-cleaved products in the reaction of **1** with Fl: might be explained either with the

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[21] Reference 15, p 731.

[22] Cf.: Woodworth, R. C.; Skell, P. S. *J. Am. Chem. Soc.* **1957**, *79*, 2542. Orchin, M.; Herrick, E. C. *J. Org. Chem.* **1959**, *24*, 139.

[23] (a) Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4013, 4015. (b) Kirmse, W. "Carbene Chemistry", 2nd Ed.; Academic Press: New York, 1971. (c) Other chapters in ref 18.

[24] The present study has little concern with recent arguments on the chemical behavior and spin correlation effect of Fl: (Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 5958; **1981**, *103*, 944. Zupancic, J. J.; Grasse, P. B.; Schuster, G. B. *Ibid.* **1981**, *103*, 2423. Wong, P. C.; Griller, D.; Scaiano, J. C. *Ibid.* **1981**, *103*, 5934; **1982**, *104*, 6631. Griller, D.; Montgomery, C. R.; Scaiano, J. C. *Ibid.* **1982**, *104*, 6813. Brauer, B.-E.; Grasse, P. B.; Kaufmann, K. J.; Schuster, G. B. *Ibid.* **1982**, *104*, 6814).

[25] (a) Walling, C.; Thaler, W. *J. Am. Chem. Soc.* **1961**, *83*, 3877. (b) Thaler, W. A.; Oswald, A. A.; Hudson, B. E., Jr. *Ibid.* **1965**, *87*, 311. (c) Golden, D. M. *Int. J. Chem. Kinet.* **1969**, *1*, 127. (d) Golden, D. M.; Gac, N. A.; Benson, S. W. *J. Am. Chem. Soc.* **1969**, *91*, 2137. (e) Gorton, P. J.; Walsh, R. *J. Chem. Soc., Chem. Commun.* **1972**, 783. See, however: (f) Denney, D. B.; Hoyte, R. M.; MacGregor, P. T. *Ibid.* **1967**, 1241.

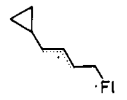
[26] Closs, G. L. *Top. Stereochem.* **1968**, *3*, 193. Bethell, D.; Stevens, G.; Tickl, P. *J. Chem. Soc. D* **1970**, 792. Turro, N. J. *Tetrahedron* **1982**, *38*, 809. Reference 23b.

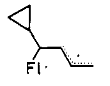
[27] Skattebøl, L. *J. Org. Chem.* **1964**, *29*, 2951. Kostikov, R. R.; Molchanov, A. P.; Bespalov, A. Ya. *J. Org. Chem. USSR (Engl. Transl.)* **1974**, *10*, 8. Kostikov, R. R.; Aksenov, V. S.; D'yakonov, I. A. *Ibid.* **1974**, *10*, 2115.

[28] Although the preferred attack of a radical on the unsubstituted end of the double bond can be attributed to the degree of steric compression associated with the formation of the new bond, electron delocalization involving C–C π orbitals can play an important part in determining the regiospecificity of radical additions to conjugated dienes (Tedder, J. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 401. See also: Rüchardt, C. *Ibid.* **1970**, *9*, 830. Rüchardt, C.; Beckhaus, H.-D. *Ibid.* **1980**, *19*, 429).

[29] In the reaction of 1 with ethenetetracarbonitrile (TCNE), the addition took place regiospecifically at the C3–C4 double bond.[13] The reaction is believed to proceed in the stepwise fashion via a zwitterionic intermediate. Electron delocalization plays the dominant role in this case.


24c


24t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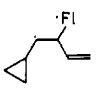
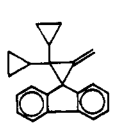
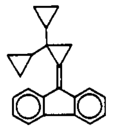

26

$$\begin{tikzcd}
\mathbf{1c} \arrow[r] & \mathbf{24c} \arrow[r] \arrow[d, shift left] & \mathbf{3c} \\
\mathbf{1t} \arrow[r] & \mathbf{24t} \arrow[r] \arrow[u, shift left] & \mathbf{3t}
\end{tikzcd}$$

possibility that the rearranged diradical has no proper terminating pathway or with the assumption that the allylic stabilization in the intermediate may result in the lowering of the rate of the rearrangement. On the basis of additional results discussed below, we propose that the latter is in fact the possibility.

Now, in the reactions with **7**, the two representative carbenes, Fl: and :CBr$_2$, exhibited a sharp contrast in regioselectivity in the addition. Namely, Fl: cycloadded exclusively to the C2–C3 double bond whereas :CBr$_2$ reacted only with the C1–C2 double bond. In his studies on the reactions of some aryl carbenes with 1,1-dimethylallene, Creary[30] argued that singlet carbenes attack the C1–C2 double bond while triplet carbenes react with the C2–C3 double bond. The present results appear to be in accord with his arguments, granting the assumption that all the Fl: that reacted with **7** was in its triplet manifold. However, there is a possibility that the adduct at the C1–C2 double bond, **27**, was indeed produced but that it rearranged to **8** under the reaction conditions. In order to examine this possibility, we attempted to obtain **27** by carrying out the reaction without solvent, since the singlet Fl: might play a part in the addition reaction under such conditions.[2a,b,23] However, we were unsuccessful in detecting **27** in every attempt, including the thermolysis at 80 °C and photolysis at 15 °C. Accordingly, we were unable to rule out the aforementioned possibility. Irradiation of a benzene solution of **8** resulted in the formation of **28**, but not **27**.[31]

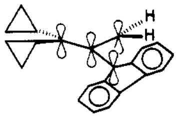

27

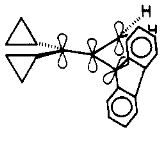

28

In any event, it is clear that none of the cyclopropane-cleaved products was detected in the reaction mixture for the second time. If we accept the assumption that the Fl: reacts mostly in its triplet spin state under the present reaction conditions, we can consider the reaction course for the formation of **8** in the following manner. The initial attack of Fl: occurs at the C2 in **7** with the rotation of the allenic framework to produce **29** or **30**.[30,32] Since the ground state of triplet trimethylenemethane is known to take planar structure,[33] it appears probable that the intermediate will be the planar **29**. Now, the fact that the reaction of Fl: with **7** produced only **8**, but not **28**,[34] suggests that the rotation of the fluorenylidene group in **29** occurs far more readily than that of the dicyclopropylmethylene. The resultant **30** will preferentially give **8**, but not **27**, on the basis of the relative thermodynamic stability of the two adducts.[30] The preferential rotation of the fluorenylidene group will be reasonable since the 9-fluorenyl radical should be more stable than the dicyclopropylmethyl radical. Since the steric point of view may suggests that **29** is significantly destabilized, an attractive alternative possibility exists in that **30** was the first intermediate

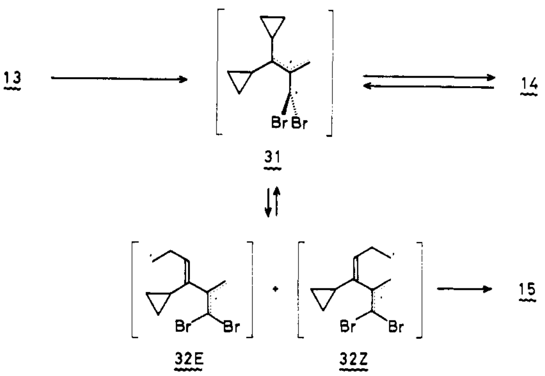
$$\mathbf{7} \xrightarrow{\text{Fl:}} \mathbf{30} \rightarrow \mathbf{8}$$

and that it cyclized directly to **8** without passing through **29**. In any event, **30** is a product-determining intermediate in the present cycloaddition. On the basis of the reaction scheme discussed above, the lack of the cyclopropane-cleaved products will be rationalized in terms of the consideration that the cyclopropyl-substituted site in either **29** or **30** is stabilized with allylic resonance. The cyclopropylmethyl to 3-butenyl radical rearrangement in such an intermediate will be slow compared to the ring closure, as discussed in the previous case.


29


30

Scheme IV



Thermal Isomerization of 13. At 140 °C, **13** isomerized cleanly to **14** (Scheme IV). Such an isomerization occurs most probably via a trimethylenemethane diradical.[33] Since the diradical is derived from a covalently bonded precursor, **13**, it is expected to be in the singlet spin state,[9,11] and hence the more stable dibromomethyl radical site will take a perpendicular configuration. For the third time, the absence of the cleavage of original cyclopropyl groups was noted at 140 °C. At 180 °C, however, **15** was produced as one of the products. The formation of **15** will be explained by the process in that one of the original cyclopropyl groups is cleaved, and the resultant diradical **32Z** terminates with the intramolecular coupling of two radical sites. The preferential incorporation of the unsubstituted site in the coupling is reasonable at least from a steric point of view. The geometrically isomeric **32E** might also be produced but it would simply rebind back to **31**. The formation of **15** is in fact very important be-

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(30) Creary, X. *J. Am. Chem. Soc.* **1980**, *102*, 1611.

(31) An unpublished observation to be published elsewhere.

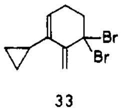
(32) Pasto, D. J.; Warren, S. E.; Morrison, M. A. *J. Org. Chem.* **1981**, *46*, 2837. Pasto, D. J.; Warren, S. E. *Ibid.* **1981**, *46*, 2842; *J. Am. Chem. Soc.* **1982**, *104*, 3670. Pasto, D. J.; Heid, P. E.; Warren, S. E. *Ibid.* **1982**, *104*, 3676.

(33) Doering, W. v. E.; Roth, H. D. *Tetrahedron* **1970**, *26*, 2825. Weiss, F. *Q. Rev. Chem. Soc.* **1970**, *24*, 278. Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. Doering, W. v. E.; Birladeanu, L. *Tetrahedron* **1973**, *29*, 499. Crawford, R. J.; Tokunaga, T. *Can. J. Chem.* **1974**, *52*, 4033. Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446. Berson, J. A., in ref 6b, Vol. 1, Essay 5. Dowd, P.; Chow, M. *Tetrahedron* **1982**, *38*, 799. Gajewski, J. J.; Benner, C. W.; Stahly, B. N.; Hall, R. F.; Sato, R. I. *Ibid.* **1982**, *38*, 853.

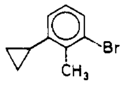
(34) **28** was found to be thermally stable under the reaction conditions and did not rearrange to **8**.[31]

cause it indicates the presence of a proper terminating process for the rearranged diradical **32Z**. It might be reasonable to conclude, therefore, that the absence of the original cyclopropane-cleaved products either in the Fl: addition to **7** or in the thermal isomerization of **13** at 140 °C are due to the relative unimportance of the cyclopropylmethyl to 3-butenyl rearrangement when the cyclopropylmethyl site is stabilized to a significant extent.

The remaining two products, **16Z** and **16E**, produced in the thermal isomerization of **13** or **14** at 180 °C appear to be formed in the reaction of **14** with hydrogen bromide. We were, however, unable to unravel the source of hydrogen bromide in these reactions. A possible source will be **33**, isomeric to **15**, which will readily eliminate hydrogen bromide since an aromatic compound, 2-bromo-6-cyclopropyltoluene (**34**), may ultimately be produced. All attempts to detect such byproducts in the reaction mixture were, however, unsuccessful. The thermal isomerization of either **13** or **14** in basic solvents such as triethylamine and pyridine, as well as in polar solvents like *N*,*N*-dimethylformamide, did not produce any characterizable products. We also failed to prepare authentic **16** in the attempted reaction of **14** with hydrogen bromide. Thus, the uncovering of the process for the production of **16** requires further investigation.



33



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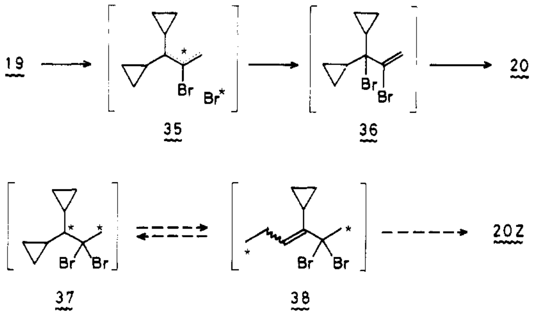
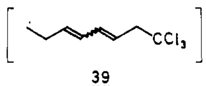
Thermal Isomerization of 1,1-Dibromo-2,2-dicyclopropylcyclopropane (19). If the exomethylene group in **13** was removed, a totally different rearrangement took place, which occurred at only 140 °C and involved the cleavage of the original cyclopropyl group. Thus, on being heated at 140 °C, **19** produced a mixture of **20Z** and **20E**.



The transformation might proceed via **36**, which is the product expected in the *gem*-dihalocyclopropane rearrangement of **19**.[35] Since **36** is a tertiary dicyclopropylmethyl bromide, if it were produced, it would not survive under the present reaction conditions, and **20** would be produced. An intermediate, **37**, the alternative one to account for the formation of **20**, would not play a part in the present isomerization, since the bond in **19** to be ruptured most readily will be the C1–C2 bond and not the C2–C3 bond. If the reaction were taking a route via **37**, we should observe the preferential formation of **20Z**, provided the geometrical isomerization of **20Z** to **20E** is slow.

Radical Chain Additions of 22 to 1. Bromotrichloromethane (**22**) added efficiently to **1** to produce **23** in 60% yield. Apparently, rapid abstraction of bromine from **22** by **39** suppressed the extensive polymerization of **1**. Notable observations obtained in this reaction were that (i) the addition took place exclusively at the C4 in **1** and that (ii) totally cyclopropane-cleaved products resulted. The regiospecificity observed here can be explained in the same manner as that discussed in the previous section. The exclusive formation of **23** indicates that the allylically stabilized cyclopropylmethyl radical is also prone to undergo the rearrangement when the terminating process is considerably slow, as is in the intermolecular atom abstraction.



39

Conclusion

If we accept the presumption that Fl: generated in a dilute solution is primarily rich in its triplet spin states,[2a,b,23] the incipient diradical will be in the same spin state and hence will last relatively long. Thus, the cyclopropylmethyl to 3-butenyl radical rearrangement can compete effectively with the rapid intramolecular coupling of two radical sites, as was demonstrated in the reaction of 1,1-dicyclopropylethylene with Fl:.[2] In the reactions of Fl: with **1** or **7**, on the other hand, the cyclopropyl-substituted site in the intermediates was stabilized with allylic resonance, and hence the cyclopropylmethyl to 3-butenyl rearrangement became less important compared to the intramolecular coupling. The conclusion is supported by the results obtained in the thermal isomerization of **13** and its related compounds. The cyclopropane cleavage might be an important pathway only when the reactions were carried out at temperatures significantly higher than 140 °C. In contrast to Fl: cycloadditions, the addition of **22** to **1** in the radical chain transfer manner resulted in the exclusive formation of the cyclopropane-cleaved adducts even at 80 °C. Apparently, the termination of the reaction with intermolecular atom abstraction is slow enough to allow the intermediates to undergo the cyclopropane cleavage. It seemed probable that the rates of terminating processes would be an important factor in determining the possibility that the cyclopropylmethyl to 3-butenyl rearrangement takes place in the reaction in question. The intramolecular coupling of two radical sites is undoubtedly a very rapid process,[9] and hence the rearrangement is unimportant in the cycloadditions which proceed via diradicals with the allylically stabilized cyclopropylmethyl site.

Experimental Section

General Methods. IR spectra were recorded on a Hitachi 215 grating spectrophotometer. UV spectra were taken on a Cary Model 17 spectrophotometer. NMR spectra were recorded on either JEOL PS-100, JEOL FX-100, or JEOL FX-400 spectrometer. Mass spectra were taken on a JEOL LMS-D300 mass spectrometer. GC analyses were carried out with Hitachi 063 and 163 gas chromatographs. HPLC analyses were done with Hitachi 635 and 655 liquid chromatographs with μ-Bondapak C-18 (methanol/water in a ratio of 3:1) unless otherwise stated. Elemental analyses were performed by the Center for Instrumental Analysis of Hokkaido University.[36] Melting points and boiling points are uncorrected.

Reaction of 1c with 2. In Benzene. A mixture of **1c**[13] (310 mg, 3.3 mmol), **2** (192 mg, 1.0 mmol), and hydroquinone (3 mg) in benzene (2.5 mL) was heated at reflux with stirring. After 10 h, the evolution of nitrogen gas ceased; 92% of the theoretical amount of nitrogen gas was evolved. After removal of the solvents

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(35) Parham, W. E.; Soeder, R. W.; Throckmorton, J. R.; Kunch, K.; Dodson, R. M. *J. Am. Chem. Soc.* **1965**, *87*, 321.

(36) Satisfactory analytical data (±0.4% for C, H, N, Cl, and Br) were reported for all new compounds unless otherwise stated.

and excess **1c** under reduced pressure (41 mm), a small amount of hexane was added to the resultant residue. The reddish precipitate formed in this treatment was characterized as **4** (11 mg) by the comparison with an authentic sample; mp 265–266 °C (lit.[37] mp 266 °C). The hexane solution was then placed on the top of an alumina column (50 g). The elution of the column with hexane gave a hydrocarbon fraction (200 mg), which was practically pure **3c** (HPLC). Vacuum distillation of the fraction gave a distillate [bp 125 °C (bath temperature, 0.0003 mm)] which crystallized when allowed to stand. Recrystallization from pentane gave colorless, crystalline **3c**: mp 53.0–54.5 °C; IR (KBr) 3080, 3020, 2050, 1450, 940, 760, 730 cm^{-1}; UV (hexane) λ_{max} 207 nm (log ϵ 5.11), 230 sh (4.35), 239 sh (4.21), 256 sh (4.24), 260 (4.25), 270 (4.25), 293 (3.96), 304 (3.98); ^1H NMR (100 MHz, CCl_4) δ 0.06–0.81 (m, 4 H), 1.12–1.54 (m, 1 H), 1.73 (dd, 1 H, J = 4.5, 7.5 Hz), 2.08 (dd, 1 H, J = 4.5, 9.0 Hz), 2.71 (dddd, 1 H, J = 1, 7.0, 7.5, 9.0 Hz), 4.88 (dt, 1 H, J = 1, 10.5 Hz), 5.46 (dd, 1 H, J = 7.0, 10.5 Hz), 6.92–7.52 (m, 6 H), 7.66–7.96 (m, 2 H); mass spectrum, *m/e* (relative intensity) 258 (M^+, 34), 178 (100). Anal. ($C_{20}H_{18}$) C, H.

The elution of the column with hexane–benzene (4:1) gave **5** (69 mg), which was characterized by the comparison of its IR spectrum with that of an authentic sample; mp 186–188 °C (lit.[38] mp 185–187 °C). The further elution of the column with benzene followed by methanol gave a small amount (total of 16 mg) of unidentified materials. The yields of **3c**, **4**, and **5** were thus 78%, 6%, and 15%, respectively.

In Decalin. A mixture of **1c** (141 mg, 1.5 mmol), **2** (288 mg, 1.5 mmol), and decalin (414 mg, 3.0 mmol) was heated at 140 °C for 1 h under an argon atmosphere with stirring. A workup of the resultant reaction mixture similar to that above gave **3c** (161 mg, 42%), **4** (60 mg, 23%), and **5** (69 mg, 28%). HPLC analysis of the hydrocarbon fraction indicated that no adduct other than **3c** was produced in an appreciable amount.

Reaction of 1t with 2. In Benzene. Under an argon atmosphere, a mixture of **1t**[13] (169 mg, 1.8 mmol) and **2** (346 mg, 1.8 mmol) in benzene (13.6 mL) was stirred and heated at reflux for 19 h. A workup of the resultant reaction mixture similar to that described in the reaction of **1c** with **2** gave two hydrocarbon fractions (10 mg and 214 mg) in addition to the recovered **2** (50 mg), **4** (92 mg), and **5** (7 mg). The hydrocarbon obtained in a minor amount crystallized when allowed to stand, and it was characterized as **6**: mp 90–91.5 °C (hexane); IR (KBr) 3060, 3000, 2930, 2840, 1615, 1480, 1445, 1440, 1425, 1110, 1015, 935, 900, 855, 820, 750, 740, 730, 685 cm^{-1}; UV (hexane) λ_{max} 225 nm (log ϵ 4.37), 232.5 (4.18), 260 sh (4.27), 267 (4.31), 270 (4.30), 278 sh (4.20), 295 (3.86), 306 (4.02); ^1H NMR (100 MHz, $CDCl_3$) δ −0.74 to −0.51 (m, 1 H), −0.36–0.62 (m, 4 H), 2.40–2.63 (m, 1 H), 2.67–3.10 (m, 2 H), 5.87–6.10 (m, 2 H), 7.10–7.62 (m, 8 H); mass spectrum, *m/e* (relative intensity) 258 (M^+, 59), 178 (100). Anal. ($C_{20}H_{18}$) C, H. Attempted purification of the hydrocarbon obtained in a major amount by vacuum distillation resulted in an unavoidable, partial isomerization of the product to **6**. Thus, a distillate collected at bp 125 °C (bath temperature) under 2 × 10^{-4} mm was found to be a mixture of **3t** and **6** in a 3:1 ratio. The analytically pure sample of **3t** was obtained by the exhaustive removal of the solvents from a pure fraction given in the column chromatography. **3t** (oil): IR (liquid film) 3080, 3020, 1450, 950, 750, 730 cm^{-1}; UV (hexane) λ_{max} 212 nm (log ϵ 4.81), 231 sh (4.33), 260 (4.26), 265 sh (4.25), 270 (4.25), 293 (3.94), 305 (3.97); ^1H NMR (100 MHz, CCl_4) δ 0.14–1.02 (m, 4 H), 1.12–1.56 (m, 1 H), 1.76 (dd, 1 H, J = 4.5, 9.0 Hz), 1.98 (dd, 1 H, J = 4.5, 9.0 Hz), 2.48 (ddd, 1 H, J = 7.0, 7.0, 9.0 Hz), 5.18 (dd, 1 H, J = 9.0, 15.5 Hz), 5.62 (dd, 1 H, J = 7.0, 15.5 Hz), 6.86–7.56 (m, 6 H), 7.56–7.96 (m, 2 H). Anal. ($C_{20}H_{18}$) C, H. Yields of **3t**, **6**, **4**, and **5** based on the consumed amount of **2** were 54%, 3%, 33%, and 3%, respectively.

In control experiments, solutions of **3t** in decalin were heated at 140–150 °C, and the isomerization of **3t** was followed by means of HPLC analysis. After 1 h, the ratio of **3t**/**6** was 2:8, and no more **3t** was detected in the mixture heated for 2 h.

In Decalin. The reaction of **1t** (141 mg, 1.5 mmol) and **2** (288 mg, 1.5 mmol) in decalin (414 mg, 3.0 mmol) at 140 °C for 1 h resulted in the formation of **3t** (67 mg, 17%), **6** (73 mg, 19%), **4** (51 mg, 19%), and **5** (29 mg, 12%). The HPLC analyses of the hydrocarbon fractions indicated the absence of products other than **3t** and **6**.

Reaction of 7 with 2. A mixture of **7**[17] (1.0 g, 8.3 mmol) and **2** (227 mg, 1.18 mmol) was heated at 140 °C under a nitrogen atmosphere. After the evolution of nitrogen gas ceased (1 h), excess **7** (603 mg) was recovered by vacuum distillation. On the addition of a small amount of a benzene–hexane (4:1) mixture to the resultant residue, a red solid (26 mg), which was characterized as **4**, was formed and was separated. Concentration of the mother liquor gave an oily residue (439 mg), which was placed on the top of a silica gel column (30 g). Elution of the column with hexane gave a hydrocarbon fraction (101 mg), which was found to be a mixture of **7** and its dimers.[17] From the following fractions, **8** was obtained in a crystalline form: 119 mg; mp 91.5–92 °C (hexane); IR (KBr) 3100, 3080, 3010, 1450, 1445, 1350, 1085, 1020, 735 cm^{-1}; UV (95% ethanol) λ_{max} 231 nm (log ϵ 4.87), 247 (4.56), 257 (4.73), 315 (4.37); ^1H NMR (100 MHz, CCl_4) δ 0.18–0.62 (m, 8 H), 1.2–1.6 (m, 2 H), 1.30 (s, 2 H), 7.05–7.40 (m, 4 H), 7.50–7.80 (m, 4 H). Anal. ($C_{22}H_{20}$) C, H. Further elution of the column with hexane–benzene (4:1) gave **5** (58 mg). Yields of **8**, **4**, and **5** were 36%, 12%, and 30%, respectively.

The reaction of **7** (998 mg, 8.32 mmol) and **2** (232 mg, 1.21 mmol) at 80 °C for 18 h resulted in the formation of **8** (106 mg, 31%), **4** (27 mg, 13%), and **5** (41 mg, 21%). In the photochemical reaction, a mixture of **7** (1.26 g, 10.5 mmol) and **2** (230 mg, 1.20 mmol) was irradiated with a 500-W high-pressure mercury arc lamp through a Pyrex filter at 15 °C for 17 h. A similar workup of the reaction mixture as described above gave **8** (58 mg, 17%), **4** (42 mg, 20%), and **5** (10 mg, 5%).

In Benzene. A solution of **7** (839 mg, 7.0 mmol) and **2** (229 mg, 1.19 mmol) in benzene (3.1 mL) was refluxed for 2 h. A workup of the resultant reaction mixture in a manner similar to that above gave **8** (64 mg, 19%), **4** (16 mg, 7%), and **5** (13 mg, 7%).

In Decalin. The reaction of **7** (498 mg, 4.15 mmol) with **2** (159 mg, 0.83 mmol) in decalin (1.7 g, 12.3 mmol) at 140 °C for 1 h produced **8** (30 mg, 13%), **4** (5 mg, 3%), and **5** (55 mg, 41%).

In all of these reactions of **7** with **2**, none of the cyclopropane-cleaved products or **27** was detected in the HPLC analysis of the hydrocarbon fractions obtained in the column chromatography.

Reaction of 1t with 9. A mixture of **1t** (523 mg, 5.6 mmol) and **9** (2.20 g, 5.6 mmol) in benzene (11 mL) was heated at reflux for 79 h under a nitrogen atmosphere. After collection of phenylmercuric chloride, the mother liquor was concentrated. Vacuum distillation of the resultant residue gave a fraction [bp 100–110 °C (13 mm); 594 mg] which was found to be a mixture of **10**, **11**, and two unidentified components in a 13:82:4:1 ratio (GC, SE-30). The first two components were isolated by means of preparative GC and characterized as **10** and **11** on the basis of the following spectral and analytical data. **10** (oil): IR (liquid film) 3090, 3010, 1635, 1460, 1430, 1260, 1190, 1070, 1050, 1040, 1020, 980, 910, 810, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.28–0.39 (m, 2 H), 0.55–0.62 (m, 1 H), 0.66–0.73 (m, 1 H), 0.85–0.94 (m, 1 H), 1.28 (dd, 1 H, J = 6.35, 7.92 Hz), 1.92 (dd, 1 H, J = 7.92, 8.18 Hz), 5.22 (dd, 1 H, J = 1.22, 10.13 Hz), 5.27 (dd, 1 H, J = 1.22, 17.09 Hz), 5.54 (ddd, 1 H, J = 8.18, 10.13, 17.09 Hz); ^{13}C NMR ($CDCl_3$) δ 3.9 (t), 4.4 (t), 10.0 (d), 38.2 (d), 40.6 (d), 65.5 (s), 118.3 (t), 134.1 (d); mass spectrum, *m/e* (relative intensity) 178 (M + 2^+, 0.38), 176 (M^+, 0.63), 77 (100). Anal. ($C_8H_{10}Cl_2$) H. C: calcd, 54.26; found, 54.70. Cl: calcd, 40.05; found, 39.18. Because of the limited amount of **10**, the repeated purification could not be carried out, and hence the analytical result was somewhat unsatisfactory, but the spectral data described above were in complete agreement with the proposed structure. **11** (oil): IR (liquid film) 3090, 3010, 1655, 1425, 1220, 1110, 1040, 1015, 960, 855, 805, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.36–0.45 (m, 2 H), 0.69–0.78 (m, 2 H), 1.34 (dd, 1 H, J = 6.84, 7.82 Hz), 1.39–1.45 (m, 1 H), 1.74 (dd, 1 H, J = 6.84, 10.26 Hz), 2.20–2.24 (m, 1 H), 5.22–5.31 (m, 2 H); mass spectrum, *m/e* (relative intensity) 178 (M + 2^+, 0.46), 176 (M^+, 0.67), 77 (100). Anal. ($C_8H_{10}Cl_2$) C, H, Cl.

Reaction of 7 with 12. A solution of **7** (1.2 g, 10.0 mmol) and **12** (2.6 g, 4.9 mmol) in benzene (10 mL) was heated at reflux for

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[37] Wieland, H.; Rosean, A. R. *Justus Liebigs Ann. Chem.* **1911**, *381*, 229.

[38] Sawpey, J. R.; Reid, E. E. *J. Am. Chem. Soc.* **1947**, *69*, 234.

1 h. After removal of the precipitated phenylmercuric bromide, the mother liquor was concentrated. Vacuum distillation of the resultant residue gave a fraction [bp 90–100 °C (13 mm); 0.98 g (67%)] which was practically pure **13**: IR (liquid film) 3090, 3010, 1745, 1015, 910, 890 cm^{-1}; ^{1}H NMR (100 MHz, CCl_4) δ 0.1–0.8 (m, 8 H), 1.05–1.40 (m, 2 H), 5.23 (br s, 1 H), 5.85 (br s, 1 H). Anal. ($C_{10}H_{12}Br_2$) C, H, Br.

In the preparation of **13** by a phase-transfer technique, a mixture of **7** (8.9 g, 74 mmol), bromoform (22.5 g, 89 mmol), cetyltrimethylammonium bromide (0.5 g), methylene dichloride (160 mL), and 50% aqueous sodium hydroxide solution (200 mL) was stirred vigorously and heated at 50 °C for 5 h. After separation of the organic layer, the aqueous layer was extracted with methylene dichloride, and the combined organic layer was washed with water and dried over anhydrous magnesium sulfate. The solvents were then removed, and the resultant residue was dissolved in chloroform. The chloroform solution was passed through a silica gel column and concentrated. The vacuum distillation of the residual oil (22.5 g) gave a fraction [bp 75–89 °C (0.4 mm); 18.8 g, (87%)] which was found to be practically pure **13** by means of GC analysis.

Thermal Rearrangement of 13. At 140 °C. In a glass ampule was placed a solution of **13** (1.5 g, 5.1 mmol) in decane (20 mL). After the solution was purged with a stream of nitrogen for several minutes, the ampule was sealed and heated at 140 °C for 15 h. The resultant reaction mixture was distilled under reduced pressure, and a fraction [bp 84–89 °C (0.3 mm); 1.2 g (80%)] was collected, which was characterized as **14**: IR (liquid film) 3080, 3005, 1740, 1080, 1060, 1020 cm^{-1}; UV (hexane) λ_{max} 202 nm (log ϵ 4.06); ^{1}H NMR (100 MHz, CCl_4) δ 0.0–0.6 (m, 8 H), 1.08–1.40 (m, 2 H), 1.11 (s, 2 H). Anal. ($C_{10}H_{12}Br_2$) C, H, Br.

At 180 °C. In a manner similar to that above, **13** and **14** were heated in separate ampules at 180 °C for 20 h. A fraction [bp 80–120 °C (0.01 mm)] obtained in the vacuum distillation of the reaction mixtures was found to be a mixture of three components in a 2.9:1.0:3.7 ratio. The first component was isolated by means of preparative GC and characterized as **15**: IR (liquid film) 3080, 3000, 2930, 1710, 1250, 1015, 790 cm^{-1}; UV (hexane) λ_{max} 251 nm (log ϵ 4.04); ^{1}H NMR (100 MHz, CCl_4) δ 0.3–0.6 (m, 2 H), 0.6–1.0 (m, 2 H), 1.58–2.25 (m, 5 H), 2.40–2.60 (m, 2 H), 5.68 (m, 1 H). Anal. ($C_{10}H_{12}Br_2$) C, H, Br. The second and third components were obtained in a pure form by means of preparative HPLC and characterized as **16Z** and **16E**. **16Z** (oil): IR (liquid film) 3080, 3005, 1640, 1425, 1265, 1015, 850 cm^{-1}; UV (hexane) λ_{max} 205 nm (log ϵ 4.04); ^{1}H NMR (100 MHz, CCl_4) δ 0.25–0.8 (m, 4 H), 0.95–1.30 (m, 1 H), 1.90 (d, 2 H, J = 10 Hz), 2.38 (t, 1 H, J = 10 Hz), 2.90 (m, 2 H), 3.38 (m, 2 H), 5.45 (t, 1 H, J = 7 Hz). Anal. ($C_{10}H_{13}Br_3$) C, H, Br. **16E** (oil): IR (liquid film) 3090, 3010, 1650, 1430, 1270, 1050 cm^{-1}; UV (hexane) λ_{max} 207 nm (log ϵ 4.08); ^{1}H NMR (100 MHz, CCl_4) δ 0.6–1.0 (m, 4 H), 1.6–2.0 (m, 4 H), 2.77 (dt, 2 H, J = 8, 8 Hz), 3.33 (t, 2 H, J = 8 Hz), 5.17 (t, 1 H, J = 8 Hz). Anal. ($C_{10}H_{13}Br_3$) C, H, Br.

Lithium Aluminum Hydride Reduction of 15. Into a cold (0 °C) suspension of lithium aluminum hydride (500 mg, 13.2 mmol) in THF was added dropwise a solution of **15** (450 mg, 1.54 mmol) in THF (20 mL). After reflux of the mixture for 5 h, the products were isolated in a usual manner.[39] The oily residue (239 mg) obtained by the evaporation of THF was found to be a mixture of two components in a 64:36 ratio. The major component was isolated by means of preparative GC and characterized as **17**: 102 mg (49%); IR (liquid film) 3090, 3000, 2930, 1635, 1600, 1040, 1015, 885 cm^{-1}; UV (hexane) λ_{max} 234 nm (log ϵ 4.20); ^{1}H NMR (100 MHz, CCl_4) δ 0.2–0.8 (m, 4 H), 1.2–1.45 (m, 1 H), 1.45–1.80 (m, 2 H), 1.9–2.45 (m, 4 H), 4.66 (br s, 1 H), 5.18 (br s, 1 H), 5.53 (br s, 1 H). Anal. ($C_{10}H_{14}$) C, H. The minor component was not examined further.

Reduction of 16. Into a solution of **16E** (405 mg, 1.09 mmol) in THF (20 mL) was added small pieces of metallic lithium (400 mg, 57.6 mmol) followed by *tert*-butyl alcohol (13 g). After the mixture was stirred for 2 h at room temperature, water was added, and the organic material was extracted with ether. The ether solution was dried over anhydrous magnesium sulfate. Evaporation of the solvents gave an oily residue, which was purified further by means of preparative GC. The product (118 mg, 80%) thus obtained was identical with authentic **18**.[20] The reduction of a 1:1 mixture of **16Z** and **16E** also resulted in the formation of **18** as the exclusive product.

Thermal Rearrangement of 19. A solution of **19**[2] (4.0 g, 14.3 mmol) in decane (20 mL) was heated at 140 °C in an ampule under a nitrogen atmosphere for 38 h. After removal of the solvents, the residue was distilled under reduced pressure to give a fraction [bp 80–95 °C (3 mm); 3.2 g (80%)] which was a mixture of two products in a 2:1 ratio. Each product was isolated by means of preparative GC, and the major product was characterized as **20E**: IR (liquid film) 3100, 3020, 2980, 2950, 1610, 1280, 1030 cm^{-1}; UV (hexane) λ_{max} 227 nm (log ϵ 4.00); ^{1}H NMR (100 MHz, CCl_4) δ 0.40–1.02 (m, 4 H), 1.40–1.45 (m, 1 H), 2.91 (dt, 1 H, J = 9.2, 10.0 Hz), 3.40 (t, 2 H, J = 10.0 Hz), 5.54 (d, 1 H, J = 1.6 Hz), 5.92 (d, 1 H, J = 1.6 Hz), 5.95 (dt, 1 H, J = 2.5, 9.2 Hz). Anal. ($C_9H_{12}Br_2$) C, H, Br. The minor product was characterized as the Z isomer, **20Z**: IR (liquid film) 3100, 3000, 2970, 2950, 1620, 1270, 1020, 890 cm^{-1}; UV (hexane) λ_{max} 220 nm (log ϵ 3.85); ^{1}H NMR (100 MHz, CCl_4) δ 0.43–0.88 (m, 4 H), 1.54 (m, 1 H), 2.70 (dt, 2 H, J = 9.0, 9.9 Hz), 3.34 (t, 2 H, J = 9.9 Hz), 5.36 (dt, 1 H, J = 1.6, 9.0 Hz), 5.51 (d, 1 H, J = 1.3 Hz), 5.65 (d, 1 H, J = 1.3 Hz). Anal. ($C_9H_{12}Br_2$) C, H, Br.

Lithium Aluminum Hydride Reduction of 20E. A solution of **20E** (2.45 g, 8.8 mmol) in dry THF (10 mL) was added to a suspension of lithium aluminum hydride (0.22 g, 5.84 mmol) in dry THF, and the resultant mixture was heated at 60 °C for 9 h. After treatment of the resultant reaction mixture in the usual manner,[39] the product was taken up in ether. The oily residue obtained by the evaporation of the solvents was distilled to give a fraction [bp 27–30 °C (bath temperature, 13 mm); 1.2 g (68%)] which was characterized as **21**: IR (liquid film) 3080, 3010, 2960, 1620, 1465, 1100, 890 cm^{-1}; UV (hexane) λ_{max} 224 nm (log ϵ 3.70); ^{1}H NMR (100 MHz, CCl_4) δ 0.42–0.77 (m, 4 H), 0.96 (t, 3 H, J = 10.4 Hz), 1.40–1.47 (m, 1 H), 2.10 (dq, 2 H, J = 9.6, 10.4 Hz), 5.25 (dt, 1 H, J = 1.6, 9.6 Hz), 5.40 (d, 1 H, J = 2.0 Hz), 5.56 (d, 1 H, J = 2.0 Hz). Anal. ($C_9H_{13}Br$) C, H, Br.

Reaction of 1 with 22 Catalyzed with BPO. A solution of **1** (1.9 g, 20 mmol; a mixture of **1t** and **1c** in a 8:2 ratio), **22** (4.06 g, 20 mmol), and benzoyl peroxide (0.2 g, 1 mmol) in benzene (20 mL) was heated at reflux under a nitrogen atmosphere for 10 h. After removal of the solvents, an oily residue was distilled under reduced pressure to give a fraction [bp 104–116 °C (1.5 mm); 3.55 g (61%)] which was a mixture mostly composed of **23**. The pure sample of **23** was obtained by redistillation: bp 132–137 °C (2.5 mm); IR (liquid film) 3030, 2960, 1650, 1420, 1270, 1210, 1020, 980, 940, 790, 760, 700 cm^{-1}; UV (95% ethanol) λ_{max} 236 nm (log ϵ 4.44); ^{1}H NMR (100 MHz, CCl_4) δ 2.65 (br q, 2 H, J = ca. 7 Hz), 3.34 (br t, 2 H, J = ca. 7 Hz), 3.37 (br, d, 2 H, J = ca. 7 Hz), 5.48–5.95 (m, 2 H), 5.98–6.48 (m, 2 H); mass spectrum, m/e (relative intensity) 296 ($M + 6^+$, 6), 294 ($M + 4^+$, 21), 292 ($M + 2^+$, 33), 290 (M^+, 17), 175 (100), 173 (93). Anal. ($C_8H_{10}BrCl_3$) C, H, Br, Cl. The separation of stereoisomers in **23** was unsuccessful because of their poor separation on GC analysis and their thermal instability.

Registry No. **1c**, 69508-41-4; **1t**, 23202-13-3; **2**, 832-80-4; **3c**, 88084-00-8; **3t**, 88084-02-0; **4**, 2071-44-5; **5**, 746-47-4; **6**, 88084-01-9; **7**, 60166-70-3; **8**, 88084-03-1; **9**, 3294-57-3; **10**, 88084-04-2; **11**, 88084-05-3; **12**, 3294-60-8; **13**, 87959-52-2; **14**, 88084-06-4; **15**, 88084-07-5; **16Z**, 88084-08-6; **16E**, 88084-09-7; **19**, 37568-28-8; **20E**, 67224-01-5; **20Z**, 67224-00-4; **21**, 88084-10-0; **22**, 75-62-7; **23**, 88084-11-1; BPO, 94-36-0; Fl, 2762-16-5.

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(39) Mićović, V. M.; Mihailović, M. L. J. *J. Org. Chem.* **1953**, *18*, 1190.