Reactions of Some Cyclopropanes Activated by a Spiro-Linked Fluorene. Importance of Electronic Matching of a Reacting Partner in Thermal Cycloaddition with TCNE and Ring-Opening Dehydrogenation with DDQ[1]

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Cyclopropanes **1a–c** substituted both by a fluorene group, linked in a spiro fashion, and by *gem*-dialkyl groups were found to be highly reactive in the reaction with a certain strongly electron-demanding unsaturated compound, such as TCNE and DDQ. Namely, **1** reacted with TCNE in the dark to give a $[\sigma^2 + \pi^2]$ type cycloadduct **5**, whereas **1** was dehydrogenated by DDQ to afford **4** when one of the alkyl substituents is a methyl. The resulting **4** reacted with another molecule of DDQ to afford **10** ultimately. In contrast to **1**, the corresponding diphenyl derivatives **2a–c** were reluctant to undergo these reactions. Moreover, chloranil was unable to dehydrogenate spiro-activated **1** under similar conditions. It is thus concluded that the dark reaction occurs when the reagent and reactant match electronically in a donor–acceptor sense. Under the illumination of visible light, however, the same type of reactions was found to take place even with a mismatched pair. Namely, the reactions of **2a** with TCNE, **2b** or **2c** with DDQ, and **1b**, **1c**, **2b**, or **2c** with chloranil were all brought about when the mixture was irradiated by a halogen lamp. In the chloranil dehydration, the expected diene remained intact in the product mixture. All these results suggest that the TCNE cycloaddition as well as the quinone dehydrogenation are initiated by a single-electron transfer (SET). The effect of alkyl substituents in **1** on the rate (reactivity sequence: **1a** > **1b** > **1c** > **8**) and the solvent polarity effect on the rate are indicative of the rate-controlling production of a radical ion pair, which would then react to give ultimate products. Possible routes for the observed products are proposed (Scheme I) and discussed.

In 1970, Martini and Kampmeier[2] reported that 1,1-diphenylcyclopropane reacts with ethenetetracarbonitrile (TCNE) at 125 °C in benzene to give, in addition to an acyclic adduct, 3,3-diphenylcyclopentane-1,1,2,2-tetracarbonitrile. The reaction is of particular interest since a strained cyclopropane σ-bond is incorporated in the cycloaddition, and a five-membered ring is constructed in a single operation. Since then, several workers have demonstrated the formation of a five-membered ring in the reaction of a certain cyclopropane with an ethylenic linkage.[3]

We[1a] have uncovered recently the fact that the same type of cycloaddition with TCNE takes place readily in some cyclopropanes **1**, activated by a fluorene group, linked in a spiro fashion to the cyclopropane, and by efficient cation-stabilizing groups in a geminal manner to the three-membered ring. The high reactivity of **1** is in fact partly due to the presence of spiro-linked aryl groups, since similarly substituted diphenyl derivatives **2** fail to exhibit a high reactivity in their reaction with TCNE. During the course of these investigations, we observed that **3b** was produced as the second product in the reaction of **1c** with TCNE. Since **3b** was found to be a Diels–Alder adduct of a diene **4b** with TCNE, it was inferred that TCNE brought about the ring-cleaving dehydrogenation of **1b**.

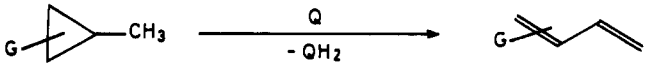
1 **2**

a: $R^1 = R^2 =$ cyclo-C_3H_5
b: $R^1 = CH_3$, $R^2 =$ cyclo-C_3H_5
c: $R^1 = R^2 = CH_3$

3 **4**

a: R = cyclo-C_3H_5
b: R = CH_3

Although it has been known that certain hydroaromatic compounds suffer dehydrogenation with TCNE to give benzene derivatives,[4] the present transformation is unique in that the methylcyclopropane is dehydrogenated with a cleavage of the cyclopropane ring to afford a 1,3-diene.



Accordingly, we have examined the reactions of **1** as well as those of **2** with some representative high potential quinones.[1b,5] In fact, DDQ readily dehydrogenates **1b** at room temperature. In the present paper, the results are summarized and a mechanism of the reaction is proposed and discussed.

Results

Reaction of 1 and 2 with TCNE. 1,1-Dicyclopropyldibenzo[*d*,*f*]spiro[2.4]heptane (**1a**) reacted with TCNE at

(1) Preliminary accounts: (a) Nishida, S.; Murakami, M.; Mizuno, T.; Tsuji, T.; Oda, H.; Shimizu, N. *J. Org. Chem.* **1984**, *49*, 3428. (b) Murakami, M.; Tsuji, T.; Oda, H.; Nishida, S. *Chem. Lett.* **1987**, 863.

(2) Martini, T.; Kampmeier, L. A. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 236.

(3) (a) Nishida, S.; Moritani, I.; Taraji, T. *J. Chem. Soc. D* **1971**, 36. (b) Noordstrand, A. A. P.; Steinberg, H.; de Boer, Th. J. *Tetrahedron Lett.* **1975**, 2611. (c) Berkowitz, W. F.; Grenetz, S. C. *J. Org. Chem.* **1976**, *41*, 10. (d) Kataoka, F.; Nishida, S. *Chem. Lett.* **1980**, 1115. (e) Wiering, P. G.; Steinberg, H. *J. Org. Chem.* **1981**, *46*, 1663. (f) Wiering, P. G.; Verhoeven, J. W.; Steinberg, H. *J. Am. Chem. Soc.* **1981**, *103*, 7675.

(4) (a) Longone, D. T.; Smith, G. L. *Tetrahedron Lett.* **1962**, 205. (b) Nishiguchi, T.; Ohki, A.; Sakakibara, H.; Fukuzumi, F. *J. Org. Chem.* **1978**, *43*, 2803. (c) Jacobson, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 886.

(5) (a) Jackman, L. M. *Adv. Org. Chem., Methods and Results* **1960**, *2*, 329. (b) Walker, D.; Hiebert, J. D. *Chem. Rev.* **1967**, *67*, 153. (c) Bruce, J. M. *Quart. Rev.* **1967**, *21*, 405. (d) Dannenberg, H. *Synthesis* **1970**, 74. (e) Becker, H.-D. In *The Chemistry of the Quinoid Compounds*; Patai, S., Ed.; Wiley: New York, 1974; Chapter 7. (f) Bruce, J. M. *Ibid.* Chapter 9.

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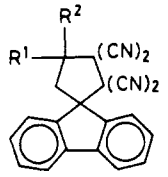
room temperature to give 3,3-dicyclopropyldibenzo[*f*,*h*]-spiro[4.4]nonane-1,1,2,2-tetracarbonitrile (**5a**).[6] The reaction was found to proceed rapidly in a polar solvent such as acetonitrile whereas it was relatively slow in benzene.[7] The same adduct **5a** was obtained in 67–92% yield in all the solvents examined.

The reaction of **1b** with TCNE proceeded analogously but more slowly, and **5b** was isolated in 55% yield (12 h at room temperature in dichloromethane). When 10 mol of methanol were added to the starting mixture, a 1:1:1 adduct, 9-(2-cyclopropyl-2-methoxypropyl)-9-(1,1,2,2-tetracyanoethyl)fluorene (**6**), was obtained in 74% yield. No indication of the formation of **5b** was noted, implying that the trapping of the intermediate by methanol is very efficient.



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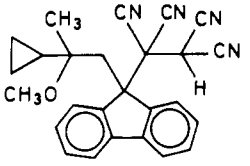


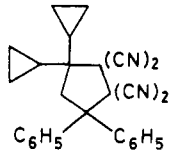
6

a : $R^1 = R^2 =$ cyclo-C_3H_5

b : $R^1 = CH_3$, $R^2 =$ cyclo-C_3H_5

c : $R^1 = R^2 = CH_3$

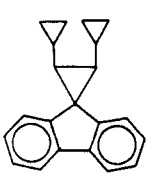
In marked contrast to **1a**, the corresponding diphenyl derivative **2a** exhibits a greatly reduced reactivity. Thus, after 120 h at room temperature in dichloromethane, we observed no indication for the occurrence of the reaction. Even in acetonitrile, the consumption of **2a** was no more than 6% after 20 h at room temperature.[8] However, when the yellow solution of **2a** and TCNE in acetonitrile was irradiated with a 500-W halogen lamp, **2a** was found to react with TCNE. After 4-h irradiation at 12 °C, the consumption of **2a** reached 42% and 3,3-dicyclopropyl-5,5-diphenylcyclopentane-1,1,2,2-tetracarbonitrile (**7**) was obtained in 51% yield.[9]



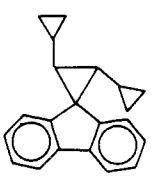
7

The reaction of **1c** was much slower and less clean than those of **1a** and **1b**. After 5 days of heating in 1,2-dichloroethane, **5c** was obtained merely in 6% yield. A second product formed in an amount larger than **5c** was characterized as 9-methyldibenzo[*a*,*c*]spiro[4.5]dec-9-ene-6,6,7,7-tetracarbonitrile (**3b**, 21% yield). The structure of **3b** was proved by comparing it with an authentic sample prepared from 9-(2-methylprop-2-enylidene) fluorene (**4b**) and TCNE. We observed the concurrent formation of **5c** and **3b** in various solvents, although the reaction rates were markedly influenced by the solvent polarity. Namely, yields (HPLC) of **5c** and **3b** were 24% and 30% in acetonitrile, 15% and 24% in 1,2-dichloroethane, and 3% and 10% in benzene.

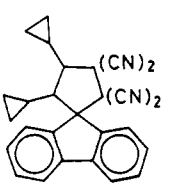
In contrast to *gem*-dicyclopropyl **1a**, *vic*-dicyclopropyl **8** exhibited a markedly reduced reactivity. At room temperature in 1,2-dichloroethane in the dark, no reaction took place even after 12 days.[10] It is thus evident that the high reactivity of **1a** is not only due to the spiro-activation[11] but also caused by the *gem*-dicyclopropyl groups. At a higher temperature, the same type of cycloaddition was found to occur at least in the reaction of *cis*-**8**. After 60 h at 100 °C in 1,2-dichloroethane, *cis*-**8** was consumed to an extent of 42% whereas the consumption of *trans*-**8** was merely ca. 3%. Under these conditions, no stereochemical interconversion of **8** was observed. In the reaction of a mixture of *cis*-**8** and *trans*-**8** (68:32), **5d**[12] was obtained in 50% yield after 7 days at 100 °C in 1,2-dichloroethane (the consumption of **8** being 44%; *cis*-**8**:*trans*-**8** in the recovered substrate being 41:59).



cis-8

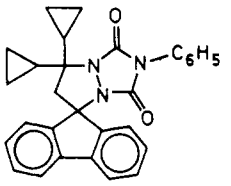


trans-8



5d

The most highly reactive **1a** reacted also with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in a manner similar to that with TCNE. A 1:1 cycloadduct **9** was obtained in 76% yield after 72 h in nitromethane at room temperature. On the other hand, **1a** failed to react with fumaronitrile even after being refluxed in nitromethane for 22 h.



9

Ring-Cleaving Dehydrogenation of Methylcyclopropanes with High-Potential Quinones. When a mixture of 1 mol of **1c** and 2 mol of DDQ was refluxed in benzene for 12 h, there was obtained 7-(*o*,*o*′-biphenylene)-3,4-dichloro-1,6-dicyano-9-methylbicyclo-[4.4.0]deca-3,8-diene-2,5-dione (**10b**) in 78% yield. The product was proved to be a Diels–Alder adduct of **4b** with

(6) For additional informations with regard to the reactions of **1** and **2** with TCNE, as well as the structural studies of **5a**, see supplementary data given in ref 1a.

(7) The time required to obtain a colorless solution (bleaching time) was taken as an index for the relative reaction rate. Indeed, the rates of **1b** with TCNE followed both by the CT absorption change and by the HPLC analysis were found to be the same within experimental error. In the reaction of **1a**, the bleaching time (seconds) and yield (%) of **5a** in various solvents were as follows: acetonitrile <1, 91; nitromethane <1, 92; acetone 1–2, 69; dichloromethane ~30, 67; ethyl acetate ~150, 69; benzene ~5400, 73. Workup of the reaction mixture was usually carried out after more than 10 bleaching times.

(8) A very small peak corresponding to **7** was observed on the HPLC analysis of a crude reaction mixture.

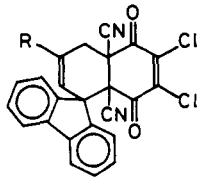
(9) In dichloromethane, the illumination resulted in the formation of a complex mixture. The yield given hereafter is based on a consumed amount of the substrate.

(10) Under room light, **8** was consumed slowly.

(11) A term "spiro-activation" has been used by Danishefsky for the nucleophilic ring opening of geminally activated cyclopropane derivatives (Danishefsky, S. *Acc. Chem. Res.* **1979**, *12*, 66). Although the present reaction is widely different from his reaction, the term appears to express the features observed here in the most appropriate way. Accordingly, we should like to use this term in the following sections.

(12) **5d** was obtained in a single isomer. However, we could not assign its stereochemistry conclusively at present, since we had so far been unsuccessful in obtaining the corresponding stereoisomer for the comparison.

DDQ[13] by an independent synthesis. The reactive site of DDQ was assumed on the analogy to reported examples.[13b] From the reaction mixture, 2,3-dichloro-5,6-dicyanohydroquinone ($DDQH_2$) was obtained quantitatively.

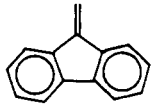


10

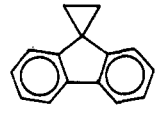
a: R = cyclo-C_3H_5

b: R = CH_3

The reaction of **1b** with DDQ took place even at room temperature. In benzene, **10a** was obtained in 56% yield after 20 h of the reaction. From the reaction mixture, a second product was isolated in 19% yield and it was found to be 9-methylenefluorene (**11**),[14] which was characterized further by the transformation to a spiro compound **12**.[15]



11

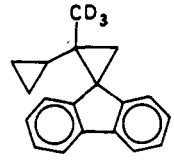


12

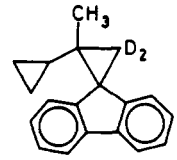
The same reaction proceeded more rapidly in acetonitrile (the bleaching time being less than a second), but the reaction was less clean than that in benzene. The yields of **10a** and **11** were 20% and 7%, respectively. In dichloromethane, the reaction proceeded somewhat slowly and **10a** and **11** were obtained in 46% and 11% yield, respectively. Thus, both **10a** and **11** are produced in the solvent of a wide variety of polarity.

In the hope to obtain further informations for the concurrent dehydrogenation and fragmentation observed in the reaction of **1b**, the reactions of deuterated substrates, **1b-*d*$_2$** and **1b-*d*$_3$**, were examined. Unfortunately, synthetic difficulties (see Experimental Section) allowed us to obtain merely 88% deuterated **1b-*d*$_2$**; **1b-*d*$_3$** was prepared as an 82% deuterated sample. In their reactions, we observed that **1b-*d*$_3$** produced **10a-*d*$_2$** (91% deuterated) and **11** in 51% and 8% yield, respectively, whereas **1b-*d*$_2$** gave **10a-*d*$_1$** (88% deuterated) and **11-*d*$_2$** (82-86% deuterated) in 46% and 15% yield, respectively. Although a slight preference for the loss of protium might be present (see Experimental Section for additional results), we conclude that both the dehydrogenation and fragmentation seem not to discriminate significantly between deuterium and protium.

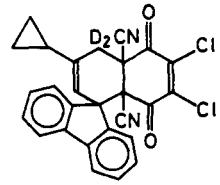
In an attempted reaction of **1a** with DDQ, the consumption of **1a** was observed at room temperature, but the reaction products were found to be a multicomponent mixture, from which 1,4-bis[[4-cyclopropyl-5-(9-fluorenylidene)pent-3-enyl]oxy]-2,3-dichloro-5,6-dicyanobenzene (**13**) was isolated in 24% yield. The dehydrogenation product had not been obtained.



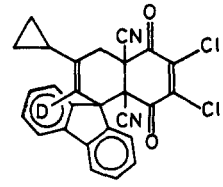
1b-*d*$_3$



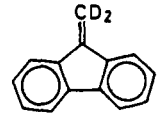
1b-*d*$_2$



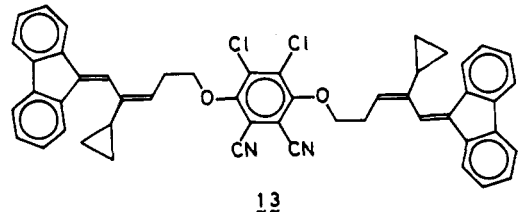
10a-*d*$_2$



10a-*d*$_1$



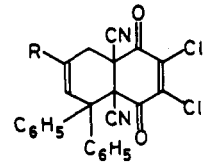
11-*d*$_2$



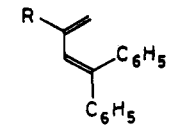
13

In contrast to DDQ, 2,3,5,6-tetrachloro-*p*-benzoquinone (chloranil) failed to dehydrogenate either **1c** in refluxing benzene or **1b** in benzene at room temperature. Furthermore, it was observed that even DDQ was unable to dehydrogenate the corresponding diphenyl derivatives, **2b** and **2c**, under conditions similar to those for **1b** and **1c**. It is thus apparent that matched pairing of the reagent and the reactant is essential for the present reactions.

Photochemical Dehydrogenation. We found that illumination of the reacting mixture with visible light effected the dehydrogenation of mismatched pairs. Thus, when a mixture of **2b** with DDQ in benzene was irradiated with a halogen lamp, the consumption of **2b** amounted to 90% after 6 h at 12 °C. From the reaction mixture, **14a** was obtained in 35% yield. In this case, 8% of **15a** was also obtained. Similarly, photodehydrogenation of **2c** with DDQ in benzene gave **14b** in 42% yield (the consumption of **2c** after 6 h illumination being 81%).



14



15

a: R = cyclo-C_3H_5

b: R = CH_3

In the photostimulated dehydrogenation of either **1b** or **1c** with chloranil, the corresponding diene, **4a** or **4b**, was obtained in 22–30% yield. Chloranil has been known to be less reactive than DDQ in Diels–Alder reactions.[16] The irradiation of a benzene solution of **2c** and chloranil with

(13) (a) Braude, E. A.; Jackman, L. M.; Linstead, R. P.; Lowe, G. *J. Chem. Soc.* **1960**, 3124. (b) Asato, A. E.; Kiefer, E. F. *J. Chem. Soc., Chem. Commun.* **1968**, 1684. (c) Pointer, D. J.; Wilford, J. B.; Hodder, O. J. R. *J. Chem. Soc. B* **1971**, 2009.

(14) Schluback, H. H.; Fallings, A. *Chem. Ber.* **1952**, *85*, 514.

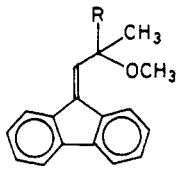
(15) Since **11** has been known to polymerize in a condensed phase, it was converted to **12** (Wieland, H.; Probst, O. *Justus Liebigs Ann. Chem.* **1937**, *530*, 274).

(16) Gaertner, R. *J. Am. Chem. Soc.* **1954**, *76*, 6150.

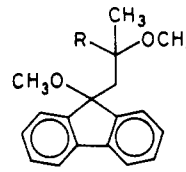
a halogen lamp likewise produced **15b** in 47% yield (the consumption of **2c** after 1.5 h being 73%). The reaction of **2b** with chloranil under the same conditions produced **15a** in 25% yield at 81% conversion.

In these photostimulated dehydrogenations, we noted that the rate of consumption of the starting compound seemed not to be affected significantly by the alkyl substituents. This observation contrasts to that found in the thermal reactions.

Trapping of the Intermediate with Methanol in Quinone Dehydrogenation. In benzene–methanol solvent system, the dehydrogenation was totally quenched and two methanol adducts were produced. Thus, the reaction of **1b** with DDQ in benzene–methanol at room temperature gave 9-(2-cyclopropyl-2-methoxypropylidene)fluorene (**16a**) and 9-(2-cyclopropyl-2-methoxypropyl)-9-methoxyfluorene (**17a**) in 24% and 62%



16



17

a: R = cyclo-C_3H_5

b: R = CH_3

yield, respectively; **11** was also obtained in 7% yield, but neither **4a** nor **10a** was detected in the product mixture. Similarly, the photostimulated reaction of **1b** with chloranil in benzene–methanol produced **16a** and **17a** in 20% and 60% yield, respectively. In the photoreaction with chloranil in the same solvent, **1c** gave **17b** in 68% yield.

Although we anticipated that methanol might trap a fragment other than **11** in the fragmentation of **1b**,[17] we have so far been unsuccessful in observing the formation of any products characterizable as those derived from the C_5 fragment.

Discussion

Role of the Fluorene Group in Thermal Reactions. In both cycloaddition and dehydrogenation, it appears that electronic matching is essential for ready thermal reactions. Namely, it has been demonstrated that the reactions are practically limited to occur between the *gem*-dialkyl substituted, spiro-activated cyclopropane, and a strongly electron-demanding acceptor olefin, such as TCNE and DDQ. Thus, it is highly likely that the substrate will be oxidized in contact with the acceptor and the resulting radical cation will be a key intermediate in the following transformations. The fact that methanol totally quenched both TCNE cycloaddition and DDQ dehydrogenation suggests that the polar nature in the intermediate(s) is common to the two reactions.

The spiro-activation[11] is most probably related with high oxidizability of the substrate, and it may be caused either by a planar biphenyl moiety and/or a fixed, bisected geometry in the spiro-linked phenylcyclopropane. According to Scott et al.,[18] an electron transfer is thermodynamically favored when the difference between the IP of a donor and electron affinity of an acceptor is less than 4–5 eV. The electronically matched pair which undergoes ready thermal reactions appears to meet with this requirement in view of the fact that the IP of **12** is 7.84 eV[19] and λ_{max}^{TCNE} for **1a–c** were observed at somewhat longer wave length than that for **12** (Table I).

Table I. Electrochemical and Related Data for the Interaction of 1 and 2 with TCNE and DDQ

substrate	λ_{max}^{TCNE},[a] nm	E_p,[b] V	ΔG_{ET} (TCNE),[c] kcal/mol	ΔG_{ET} (DDQ),[c,d] kcal/mol
1a	~595[e]	1.3	26[f]	19[g]
1b	587	1.4	27[h]	20
1c	585	1.5	29[i]	22[j]
8[k]	575	1.5	29	22[l]
12	567[m]	1.65	33	26
2a	417	1.7	35[n]	28[n]
2b	410	1.8	36[n]	29[n]
2c	403	2.0	40[n]	33[n]

[a] In dichloromethane. [b] In acetonitrile with tetraethylammonioum perchlorate as a supporting electrolyte, vs SCE. All measurements were performed at 25 °C on ca. 10^{-3} M solution of the substrate with a Ag/0.1 N $AgNO_3$ reference electrode. The values given are corrected to the SCE scale by adding +0.34 V. The oxidation was irreversible in all cases, and the E_p value varied with the sweep rate, see the text. Accordingly, merely round numbers are tabulated. [c] Approximate ΔG_{ET} values were calculated from the relationship: $\Delta G_{ET} = 23[E^{ox} - E^{red}]$. The E^{red} values for TCNE, DDQ, and chloranil were +0.22, +0.52, and +0.01 V vs SCE, respectively. Reported values are as follows: TCNE = +0.24 in acetonitrile (Peover, *Trans. Faraday Soc.* **1962**, *58*, 2370; *Nature* **1961**, *191*, 702. Cf. also: Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370. Kaplan, M. L.; Haddon, R. C.; Bramwell, F. B.; Wudl, F.; Marshall, J. H.; Cowan, D. O.; Gronowitz, S. *J. Phys. Chem.* **1980**, *84*, 427. Rieger, P. H.; Bernal, I.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1961**, *83*, 3918), DDQ = +0.51, and chloranil = +0.02 V vs SCE (Peover, loc. cit. *J. Chem. Soc.* **1962**, 4540). [d] ΔG_{ET} value for **1a** with chloranil is calculated to be 30 kcal/mol, and that for **2c** is 45 kcal/mol. The values for other substrates are between these two values. [e] Because rapid reaction took place, the λ_{max}^{TCNE} value is somewhat approximate. [f] Rapid reaction took place. [g] **1a** was consumed at room temperature but a complex mixture was produced. [h] The reaction took place at a moderate rate. [i] The reaction occurred when the mixture was heated. [j] The reaction took place relatively slowly at room temperature. [k] Both cis and trans isomers showed practically the same λ_{max}^{TCNE} and E_p. [l] Not examined. [m] IP^v = 7.84 eV.[19] [n] Practically no reaction took place in the dark where the corresponding spiro-activated substrates underwent the reaction.

In order to discuss the feasibility of the SET in solution, however, it is more adequate to do so on the bases of electrochemical data. Thus, electrochemical studies of **1** and **2** were carried out by cyclic voltammetry. All cyclopropanes gave a wave with E_p at 1.3–2.0 V with reference to a Ag/0.1 N $AgNO_3$ standard potential. Unfortunately, however, the oxidation was irreversible and the E_p^{ox} value varied with sweep rates. Apparently, some follow-up reactions disturbed the oxidation wave and hence the electrochemical data obtained here were not good for quantitative treatment of the SET process. However, the E_p^{ox} values given in Table I were reproducible within ±0.06 V under a standard set of conditions with the sweep rate of 400 mV/s. Therefore, the values may be valid for qualitative comparisons.

Although it would be very crude, an approximate free energy change for the SET process of various pairs was calculated from the aforementioned electrochemical data.[20]

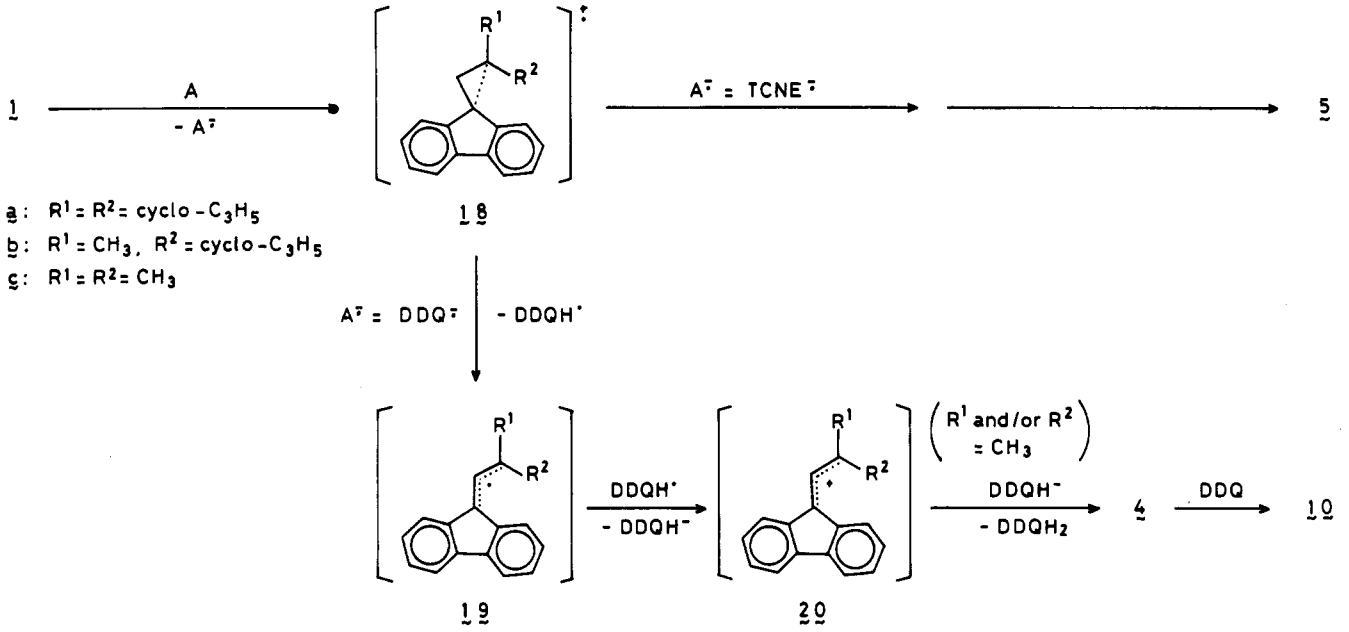
(17) It might be a carbene radical cation. Recently, the reactions of diphenylcarbene radical cation have been reported (Parker, V. D.; Bethell, D. *J. Am. Chem. Soc.* **1987**, *109*, 5066).

(18) Scott, L. T.; Erden, I.; Brunsvold, W. R.; Schultz, Y. H.; Houk, K. N.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1982**, *104*, 3659. See also: Houk, K. N. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II, Chapter 4.

(19) Jason, M. E.; Gleiter, R., unpublished results. We are very grateful to them for sending us the IP^v values of **12** and related compounds prior to their publication. IP^v of fluorene has been reported to be 7.93 eV (Dewar, M. J. S.; Haselbach, E.; Worley, S. D. *Proc. Roy. Soc. London A* **1970**, *315*, 431).

(20) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834; *Isr. J. Chem.* **1970**, *8*, 259.

Scheme I



The results thus obtained (Table I) appear to suggest that the SET process in all pairs will be endothermic. Actually, however, the ready thermal reaction takes place at room temperature when the estimated ΔG_{ET} is in a range of 20–26 kcal/mol (**1a** + TCNE and **1b** + DDQ). With this regard, it should be noted that Peacock and Schuster[21] have demonstrated that the thermal isomerization of hexamethyl(Dewar)benzene to hexamethylbenzene catalyzed by an electron acceptor occurs at room temperature when the ΔG_{ET} is +24 kcal/mol. It may be concluded, therefore, that the SET initiation of the present reactions will not be unacceptable.

If the present reactions are truly initiated by the SET, it should be expected that the photostimulation is effective to enforce the reaction of a mismatched pair.[22] In fact, the reactions of **2a** with TCNE, **2b** or **2c** with DDQ, and **1b**, **1c**, **2b**, or **2c** with chloranil were all brought about when the mixture was irradiated with visible light. The thermal SET may be unfavorable when the ΔG_{ET} is significantly larger than 26 kcal/mol, but the photochemically excited CT complex can readily collapse into a pair of radical cation and a radical anion. When the CT complex was not formed to a substantial extent,[23] the photon would merely be absorbed by the acceptor but the excited acceptor would have a high reduction potential, and hence the SET process will become exothermic.[20,22]

In several studies,[24] a linearity between the IP and E^{ox} has been documented. In the present series of compounds, however, the λ_{max}^{TCNE} were not correlated with the E_p^{ox} by a single line (Figure 1). The spirocyclopropanes **1a–c**, **8**, and **12** constitute a group, in which the linearity may be seen, but the correlation line for **2a–c** deviated widely from the line of the spiro compounds. The results appear

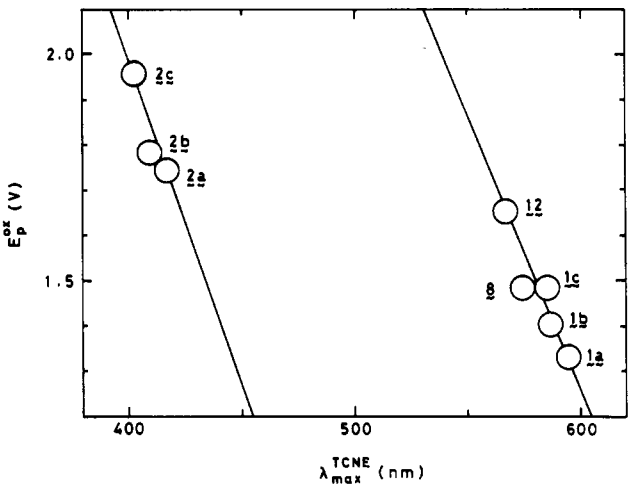


Figure 1. A plot of E_p^{ox} vs λ_{max}^{TCNE}.

to imply that the λ_{max}^{TCNE} (IP) will in principle be related to an energy change required in vertical ionization[25] whereas the E^{ox} will more likely refer to an energy change associated with the formation of a geometrically relaxed, nonvertical radical cation.[26] When the nonvertical radical cation has a geometry significantly different from that of the vertical species as in the present cases, a lack of simple correlation between λ_{max}^{CT} and E^{ox} may be engendered.

Reaction Scheme. We may be able to depict that the present reactions are initiated by rate-controlling SET and the resulting radical cation yields the ultimate products.[27,28]

(21) Peacock, N. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 3632.
(22) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425.
(23) When the substrate was mixed with TCNE or DDQ, a broad CT band was developed. In the case of chloranil, however, we observed no peak but a slight change at the end absorption region of the quinone.
(24) (a) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124. (b) Neikam, W. C.; Desmond, M. M. *Ibid.* **1964**, *86*, 4811. (c) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916. (d) Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308; *Tetrahedron* **1982**, *38*, 1113. (e) Gassman, P. G.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5793. (f) Howell, J. O.; Concalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *Ibid.* **1984**, *106*, 3968.
(25) Hanstein, W.; Berwin, H. J.; Traylor, T. G. *J. Am. Chem. Soc.* **1970**, *92*, 829; Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *Ibid.* **1971**, *93*, 5715.
(26) Recently, a term "nonvertical radical cation" has been proposed (Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343).
(27) For the reactions of some prototype cyclopropanes under the SET conditions, see, for example: (a) Arnold, D. R.; Humphreys, R. W. R. *J. Am. Chem. Soc.* **1979**, *101*, 2743. (b) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 871. (c) Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 6458. (d) Mizuno, K.; Ogawa, J.; Otsuji, Y. *Chem. Lett.* **1981**, 741. Mizuno, K.; Yoshioka, K.; Otsuji, Y. *Ibid.* **1983**, 941.
(28) In the chloranil dehydrogenation, there has been a proposal that electron transfer within charge-transfer complexes could be the rate-controlling step in the reaction of 1,4-dihydronaphthalene (Hashish, Z. M.; Hoodless, I. M. *Can. J. Chem.* **1976**, *54*, 2261). The proposal was based on the lack of isotope effect in the dehydrogenation, but it has been questioned. (Müller, P.; Joly, D. *Tetrahedron Lett.* **1980**, *21*, 3033).

The thermal reactions of 1 are taken as the representative and are shown in Scheme I. In the first-formed intermediate 18, we suppose that a one electron bond is significantly stretched[29] and the positive charge will be localized largely on the tertiary alkyl carbon and the odd electron density on the fluorene system. This is primarily because the fluorene unit will prefer to avoid an antiaromatic nature.[30,31]

The observed reactivity sequence (**1a** > **1b** > **1c** > **8**) appears to be compatible with the aforementioned supposition. Although the cyclopropyl group is known to stabilize a radical intermediate, it does so more effectively a cationic species.[32] The ability of alkyl substituents in 1 to stabilize an adjacent carbocation will be in the following order: *gem*-dicyclopropyl > *gem*-cyclopropylmethyl > *gem*-dimethyl ≃ monocyclopropyl. The sequence coincides with the observed relative reactivity except for the last two. Since cation stabilizing ability of a cyclopropyl group has been known to be unusually high,[32] cyclopropyl-substituted secondary alkyl cation will be similar to or greater than tertiary alkyl cation in its stability.[33] Accordingly, we expected that **8** might exhibit a reactivity at least similar to that of **1c**, which is also suggested from the electrochemical data (Table I). Actually, however, the reactivity of **8** was significantly lower than that of **1c**. Thus, we suppose that release of steric congestion on going from **1c** to **18c** might raise the reactivity of **1c** relative to that of **8**.[34,35] The steric acceleration will also play a part in the reactivity sequence mentioned above. Namely, the substituent effect in the present reactions may be both electronic and steric in origin.[36]

An equally compatible result with the rate-controlling SET is that the effect of alkyl groups is practically absent in the photostimulated dehydrogenation. In the photodehydrogenation, the energy barrier for the formation of radical ions should be very small and hence the substituent effect on the rate will be minimal. The practical absence of the discrimination between deuterium and protium in the dehydrogenation of **1b**[28] may also be consistent with the conclusion.

In the reaction with TCNE, **18** reacted in a stepwise manner with a nearby $TCNE^{\bullet-}$ to afford **5**. In the DDQ dehydrogenation, the most plausible pathway includes the deprotonation of **18** by $DDQ^{\bullet-}$ to give allyl radical **19**, which in turn is oxidized to allylic cation **20**. On the analogy to usual quinone dehydrogenation,[5,37] the final step of the reaction is depicted as the deprotonation of **20** (R = CH_3) by $DDQH^-$.

The deprotonation of **18** by $DDQ^{\bullet-}$ will raise no question since radical cations are known to have a substantially high acidity.[38] The oxidation of **19** to **20**, however, may be a subject of some discussions because the antiaromatic nature will be anticipated in **20**.[30] An alternative route from **19** to **4** will be disproportionation of **19** with $DDQH^{\bullet}$ to give **4** and $DDQH_2$. This process has an advantage to avoid the formation of **20**, but the fact that **17** was produced as the major product in the methanol trapping experiments, and control experiments indicated that **17** was not produced from **16**, suggests that the antiaromaticity in the fluorene system might not be large enough to suppress the formation of 9-fluorenyl cation under the present reaction conditions.

One should also consider a pathway to **4** proceeding via **21**. This is because mass spectral investigations[39] as well as theoretical studies[40] have indicated that ring-open radical cation of cyclopropane is prone to rearrange to the corresponding propene radical cation with little or no activation barrier. If **18** takes such a route, **21** might be produced,[41] which will be dehydrogenated to **4**. In order

(29) Closely similar radical cations derived from spiro[cyclopropane-1,9′-fluorene] derivatives have been studied by the CIDNP technique (Roth, H. D.; Schilling, M. L. M.; Schilling, F. C. *J. Am. Chem. Soc.* **1985**, *107*, 4152).

(30) 9-Bromofluorene exhibits a solvolytic reactivity which is 10^{-3} to that of diphenylmethyl bromide (Vovins, R. E.; Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1962**, *84*, 3959).

(31) The one-electron bond in radical cation is calculated to be fairly strong (Wayner, D. D. M.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1983**, *61*, 2310), and the geometrical isomerization of 1,2-diphenylcyclopropane radical cation is slow at room temperature (Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1981**, *103*, 7210). However, when the cyclopropane is substituted by *p*-anisyl group(s), the cis–trans isomerization takes place readily (Mizuno, K.; Kamiyama, N.; Ichinose, N.; Otsuji, Y. *Tetrahedron* **1985**, *41*, 2207; Dinnocenzo, J. P.; Schmittel, M. *J. Am. Chem. Soc.* **1987**, *109*, 1561). Thus, it may be reasonable to assume that the substituent can shift the structure of the intermediate from a relatively closed radical cation to a more open form. As an extreme, **18** could be a totally open radical cation such as 0,0-trimethylene radical cation or a perpendicular 0,90 species. The refinement of the structure of radical cations involved in the present study will be a subject of further investigations. A debate with regard to the presence of a ring-closed radical cation and a ring-open radical cation exists (Qin, X.-Z.; Williams, F. *Chem. Phys. Lett.* **1984**, *112*, 89. Quin, X.-Z.; Snow, L. D.; Williams, F. *J. Am. Chem. Soc.* **1984**, *106*, 7640; *Chem. Phys. Lett.* **1985**, *117*, 383. Quin, X.-Z.; Williams, F. *Tetrahedron* **1986**, *42*, 6301. Symons, M. C. R. *Chem. Phys. Lett.* **1985**, *117*, 381. Wayner, D. D. M.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 3283. Hrovat, D. A.; Du, P.; Borden, W. T. *Chem. Phys. Lett.* **1986**, *123*, 337. Du, P.; Hrovat, A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 3405).

(32) (a) Charton, M. In *The Chemistry of Alkenes*; Zabicky, J., Ed.; Wiley: New York, 1970; Vol. 2, Chapter 10. (b) Tidwell, T. T. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1988; Part 1, Chapter 10. (c) Friedrich, E. C. *Ibid.*; Part 1, Chapter 11.

(33) The estimation is based on the following results. (i) Although cyclopropylmethyl β-naphthalenesulfonate is a primary alkyl sulfonate, it solvolyzes ca. 10^3–10^5 times faster than typical secondary alkyl sulfonates, such as isopropyl, cyclohexyl, and cyclopentyl β-naphthalenesulfonate (Brown, H. C.; Nishida, S., unpublished results). (ii) The σ^+ value for the cyclopropyl group is reported to be −0.462, which is ca. 1.7 times larger than that for isopropyl, −0.280 (Brown, H. C.; Cleveland, J. D. *J. Org. Chem.* **1976**, *41*, 1792. Brown, H. C.; Gnedin, B. G.; Takeuchi, K.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, *97*, 610). (iii) An equilibration of 1-cyclopropylethyl cation with 1-methylcyclobutyl cation in SbF_5–S-O_2ClF is in favor of the former secondary alkyl cation (Saunders, M.; Rosenfeld, J. *J. Am. Chem. Soc.* **1970**, *92*, 2548). (iv) Merely, parent primary cyclopropylmethyl derivatives produce a nearly 1:1 mixture of cyclopropylmethyl and cyclobutyl derivatives. Nitrous acid deamination of 1-cyclopropylethylamine gives 1-cyclopropylethanol exclusively, implying that cyclopropyl-substituted secondary alkyl cation is far more stable than cyclobutyl cation (Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 2509. Silver, M. S.; Caserio, M.; Rice, H. E.; Roberts, J. D. *Ibid.* **1961**, *83*, 3671).

(34) There will also be the possibility that the charge and spin density separation is not so extensive as surmized, since CIDNP studies[29] indicate that significant spin density locates on the tertiary alkyl carbon.

(35) A referee suggested an alternative explanation for the lower reactivity of **8**: steric hindrance. The spiro juncture in **8** will require that the pendant cyclopropyl groups protrude both above and below the fluorene plane, whereas the methyl groups will all be on one side of that plane in **1c**. We cannot rigorously rule out this possibility, but the steric hindrance will not explain the reactivity sequence observed here. In addition, it should be noted that more heavily substituted spirocyclopropane reacted with TCNE rather smoothly as described in the following paper.

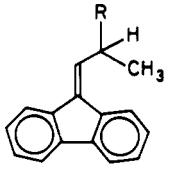
(36) The higher reactivity of *cis*-**8** relative to *trans*-**8** might also be caused by the steric factor. In **18**, the one electron bond is supposed to be stretch significantly, and hence the substituents in **18** will not be held as tightly as in the starting cyclopropane. Accordingly, geometrical deformation of the three-membered ring carbons will be able to occur to reduce the steric congestions between the substituents.

(37) (a) Braude, E. A.; Jackman, L. M.; Linstead, R. P. *J. Chem. Soc.* **1954**, 3548, 3564. Braude, E. A.; Brook, A. G.; Linstead, R. P. *Ibid.* **1954**, 3569. Braude, E. A.; Jackman, L. M.; Linstead, R. P.; Lowe, G. *Ibid.* **1960**, 3123, 3133. (b) Trost, B. M. *J. Am. Chem. Soc.* **1967**, *89*, 1847. (c) Müller, P.; Roček, J. *Ibid.* **1972**, *94*, 2719. (d) Müller, P. *Helv. Chim. Acta* **1973**, *56*, 1243. Müller, P.; Joly, D. *Ibid.* **1984**, *67*, 105. (e) Thummel, R. P.; Cravey, W. E.; Cantu, D. B. *J. Org. Chem.* **1980**, *45*, 1633.

(38) Nicholas, A. M. D.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

(39) (a) McLafferty, F. W.; Barbalas, M. P.; Turecek, F. *J. Am. Chem. Soc.* **1983**, *105*, 1. (b) Sack, T. M.; Miller, D. L.; Gross, M. L. *Ibid.* **1985**, *107*, 6975.

(40) (a) Haselbach, E. *Chem. Phys. Lett.* **1970**, *7*, 428. (b) Collins, J. R.; Gallup, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 1530. (c) Bouma, W. J.; Poppinger, D.; Radom, L. *Isr. J. Chem.* **1983**, *23*, 21.



21

a: R = cyclo-C_3H_5

b: R = CH_3

to check this possibility, we prepared 9-(2-alkylpropylidene)fluorene (21)[42] and examined its reaction with DDQ. In fact, both **21a** and **21b** were smoothly dehydrogenated by DDQ in refluxing benzene, but the reaction of **21a** at room temperature was found to be too slow to account for the dehydrogenation of **1b** via **21a**.[43] Namely, the DDQ dehydrogenation of **21a** proceeded to an extent of only ca. 14% after 24 h at room temperature, whereas the reaction of **1b** practically completed under similar conditions. Moreover, **16** and **17** would not be produced from **21**. Accordingly, we conclude that the pathway shown in Scheme I will be appropriate at present to account for the production of **4**.

In the DDQ dehydrogenation, the resulting **4** reacts with another molecule of DDQ to form **10**, whereas **4** and **15** remained intact in the chloranil dehydrogenation. Chloranil will thus be a reagent of choice when the dehydrogenation yields a reactive product such as a conjugated diene. The fact that the dehydrogenation of **1a** gave rather poor results may be due to the formation of a strained methylenecyclopropane subunit at the diene-forming stage. The formation of a diether with DDQ like **13** has been precedented.[5]

Although the fragmentation of **1b** to give **11** will be of considerable interest,[17] we cannot discuss it in detail in the present paper, since we have so far been unsuccessful at uncovering the fate of the other half of the fragments. The fact that methanol did not quench the production of **11** will suggest that **18** is not the precursor of **11**. The details of the fragmentation will be reported in due course when additional information becomes available.

Conclusion

The spiro-activation is shown to be very effective in the thermal reaction of certain cyclopropanes with a strongly electron-demanding olefinic reagent. The results are interpreted in terms of the rate-controlling SET initiation. The photostimulation was effective to enforce the reaction of a mismatched pair of the reacting partner. It appears to suggest that the illumination with visible light will be effective in general for the dehydrogenation of certain substrates with DDQ or chloranil.

Experimental Section

General Methods. IR spectra were recorded on a Hitachi 215 grating spectrophotometer. UV–visible spectra were taken on a Cary Model 17 spectrophotometer. NMR spectra were recorded on either JEOL PS-100, JEOL FX-100, or JEOL FX-500 spectrometers and are reported in parts per million downfield of internal tetramethylsilane. Mass spectra were taken on a JEOL LMS-D300 mass spectrometer. GLC analyses were carried out with Hitachi 063 and 163 gas chromatographs. HPLC analyses were done with Hitachi 635 and 655 liquid chromatographs. Elemental analyses were performed by the Center for Instrumental Analysis of Hokkaido University. Melting points and boiling points are uncorrected.

Substrates. Cyclopropanes were prepared by decomposing either 9-diazofluorene or diphenyldiazomethane in an appropriate olefin at 80–140 °C. **1a**: mp 91–92 °C.[44] **1b**: mp 100.5–101.5 °C.[1a] **1c**: mp 89.0–89.5 °C, 30% yield; IR (KBr disk) 3060, 3000, 2960, 2930, 2880, 1480, 1450, 1439, 1118, 1100, 810, 780, 730 cm^{-1}; UV max (hexane) 209^{sh} nm (log ϵ 4.72), 213 (4.76), 222 (4.55), 230^{sh} (4.47), 272 (4.26), 283^{sh} (4.10), 293 (3.69), 305 (4.00); ^1H NMR (100 MHz, $CDCl_3$) δ 1.44 (s, 6 H), 1.81 (s, 2 H), 7.18–7.45 (m, 6 H), 7.77–7.94 (m, 2 H); mass spectrum (70 eV) m/z (relative intensity) 220 (M^+, 69), 205 (100), 190 (14), 178 (24), 165 (65). Anal. ($C_{17}H_{16}$) C, H. **2a**: mp 64–65 °C.[44] **2b**: bp ca. 110–120 °C (0.003 Torr); n^{20}_D 1.5702; 40% yield; IR (liquid film) 3090, 3070, 3030, 3000, 2950, 2875, 1600, 1495, 1450, 1380, 1110, 1090, 1015, 770, 750, 705, 695 cm^{-1}; UV max (hexane) 226 nm (log ϵ 4.05), 256 (2.55), 262 (2.64), 268 (2.53); ^1H NMR (100 MHz, $CDCl_3$) δ −0.16 to 0.94 (m, 5 H), 1.05 (s, 3 H), 1.09 (d, 1 H, J = 5.0 Hz), 1.20 (d, 1 H, J = 5.0 Hz), 7.10–7.45 (m, 6 H), 7.45–7.66 (m, 4 H); mass spectrum (70 eV) m/z (rel intensity) 248 (M^+, 23), 219 (100), 203 (28), 204 (30), 167 (36), 165 (40), 129 (31). Anal. ($C_{19}H_{20}$) C, H. **2c**: mp 40–41 °C; 44% yield; IR (KBr disk) 3000, 2950, 1605, 1500, 1450, 705 cm^{-1}; UV max (hexane) 225 nm (log ϵ 4.13), 256 (2.58), 262 (2.66), 268 (2.49); ^1H NMR (100 MHz, $CDCl_3$) δ 1.02 (s, 6 H), 1.19 (s, 2 H), 7.09–7.46 (m, 10 H); mass spectrum (70 eV) m/z (rel intensity) 222 (M^+, 57), 207 (100), 129 (91). Anal. ($C_{17}H_{18}$) C, H. *cis*-**8**: mp 147.0–147.5 °C; 12% yield in the reaction of 9-diazofluorene with a 1:1 mixture of *cis*- and *trans*-1,2-dicyclopropylethylene; IR (KBr disk) 3080, 3064, 3004, 1482, 1448, 1012, 896, 756, 740, 728 cm^{-1}; UV max (hexane) 213 nm (log ϵ 4.69), 221^{sh} (4.49), 229 (4.43), 236^{sh} (4.24), 261^{sh} (4.15), 266^{sh} (4.19), 271 (4.43), 283^{sh} (3.98), 293 (3.96), 304 (4.08); ^1H NMR (100 MHz, $CDCl_3$) δ 0.00–0.32 (m, 2 H), 0.44–1.03 (m, 6 H), 1.23–1.57 (m, 2 H), 1.57–1.80 (m, 2 H), 6.87–7.05 (m, 1 H), 7.25–7.73 (m, 5 H), 7.84–8.08 (m, 2 H); mass spectrum (70 eV) m/z (rel intensity) 272 (M^+, 32), 243 (27), 231 (19), 229 (26), 217 (43), 216 (34), 215 (51), 203 (29), 202 (33), 178 (100). Anal. ($C_{21}H_{20}$) C, H. *trans*-**8**: mp 109.5–110.0 °C; 11% yield in the same reaction as above; IR (KBr disk) 3076, 2996, 1480, 1450, 1020, 736, 726 cm^{-1}; UV max (hexane) 213 (log ϵ 4.63), 220^{sh} (4.50), 229 (4.44), 262^{sh} (4.13), 266^{sh} (4.18), 271 (4.21), 283^{sh} (4.00), 293 (3.93), 304 (4.03); ^1H NMR (100 MHz, $CDCl_3$) δ 0.05–0.38 (m, 2 H), 0.38–0.85 (m, 6 H), 0.85–1.23 (m, 2 H), 1.62 (br s, 2 H), 1.85–2.04 (m, a part of AA'XX', 2 H), 7.25–7.52 (m, 6 H), 7.85–8.02 (m, 2 H); mass spectrum (70 eV) m/z (rel intensity) 272 (M^+, 38), 243 (29), 231 (22), 229 (30), 217 (49), 216 (39), 215 (60), 203 (35), 202 (39), 178 (100). Anal. ($C_{21}H_{20}$) C, H.

Deuterated cyclopropanes were prepared by the reaction of the corresponding deuterated olefin with 9-diazofluorene. In the preparation of 2-cyclopropylpropene-*1,1-*d_2 by Wittig reaction, the protium–deuterium exchange took place unavoidably,[45] and hence the deuterium content in the olefin was considerably low. 2-Cyclopropylpropene-*3,3,3-*d_3 (83% deuterated) was prepared from the corresponding ketone, which was obtained in the repeated treatments of cyclopropyl methyl ketone with D_2O in the presence of potassium hydroxide. Thus, ca. 88% deuterated **1b**-d_2 and 82% deuterated **1b**-d_3 were prepared. On the dehydration of 2-cyclopropyl-2-propanol-*3,3,3-*d_3 with sulfuric acid, a mixture of 2-cyclopropylpropene-*1,1-*d_2 and -*3,3,3-*d_3 (24:76) was obtained, from which a mixture of **1b**-d_2 and **1b**-d_3 in a 24:76 ratio was prepared. **1b**-d_2; ^1H NMR (100 MHz, $CDCl_3$) δ 0.22–0.49 (m, 1 H), 0.54–1.12 (m, 4 H), 1.44 (s, 2.99 H), 1.65 (br s, 0.11 H), 1.78 (br s, 0.12 H), 7.13–7.57 (m, 6 H), 7.88–7.89 (m, 2 H); mass spectrum (70 eV) m/z (rel intensity) 248 (M^+, 19), 246 (1.3), 233 (10), 218 (48), 207 (35), 192 (15), 180 (60), 179 (39), 178 (100), 165 (60). **1b**-d_3: ^1H NMR (100 MHz, $CDCl_3$) δ 0.20–0.53 (m, 1 H), 0.55–1.15 (m, 4 H), 1.40 (m, 0.55 H), 1.66 (d, 0.99 H, J = 5.3 Hz), 1.79 (d, 0.94 H, J = 5.3 Hz), 7.09–7.62 (m, 6 H), 7.70–7.95 (m, 2 H); mass spectrum (70 eV) m/z (rel intensity) 249 (M^+, 11), 246

(41) Alternatively, 9-(2-alkyl-1-propenyl)fluorene might also be considered, but its production appears to be less likely because of lesser extended conjugation than in **21**.

(42) Prepared by the reaction of fluorene with an appropriate aldehyde in the presence of Triton B (Ghera, E.; Sprinzak, Y. *J. Am. Chem. Soc.* **1960**, *82*, 4945). Details of the preparation will be reported elsewhere.

(43) We noted that the dehydrogenation of **21** was more facile than that of the corresponding diphenyl derivative, 1,1-diphenyl-3-methyl-1-butene. The results will be reported elsewhere.

(44) Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1974**, *96*, 6451.

(45) Atkinson, J.; Fischer, M.; Holey, D.; Morse, A. *Can. J. Chem.* **1965**, *43*, 1614.

(0.3), 220 (24), 208 (24), 203 (15), 191 (14), 178 (100), 165 (43).

Authentic **4b** was prepared in 80% yield by the acid catalyzed dehydration of 9-(2-methyl-2-propenyl)-9-fluorenol (mp 112–113 °C), which was synthesized by the Grignard reaction of 2-methyl-2-propenylmagnesium chloride with fluorenone. The diene could not be successfully distilled and hence purified by silica gel column chromatography. **4b**: IR (liquid film) 3070, 1630, 1445, 900, 770, 720 cm^{-1}; UV max (hexane) 227 nm (log ϵ 4.52), 250 (4.81), 258 (4.51) 284 (4.01), 297 (4.04), 312 (4.06); ^1H NMR (100 MHz, $CDCl_3$) δ 2.08 (s, 3 H), 5.35 (m, 2 H), 7.04 (s, 1 H), 7.10–7.44 (m, 4 H), 7.57–7.76 (m, 3 H), 8.26 (dd, 1 H, J = 6.6 and 1.5 Hz); mass spectrum (70 eV) m/z (rel intensity) 218 (M^+, 43), 203 (100), 101 (18). Anal. ($C_{17}H_{14}$) C, H.

Reaction of 1 with TCNE. In dichloromethane, **1a** and **1b** reacted with TCNE to give **5a** and **5b**, respectively, at room temperature.[1a] The results of the reaction of **1a** in a solvent other than dichloromethane are given in the ref 7.

In the case of **1c**, standing of a mixture of **1c** (220 mg, 1 mmol) and TCNE (129 mg, 1 mmol) in dichloromethane (25 mL) at room temperature for 11 days resulted in no bleaching of the CT color. Accordingly, the solvent was replaced by 1,2-dichloroethane and the mixture was heated at reflux under argon atmosphere for 5 days. The resultant dark brown solution was then subjected to silica gel column chromatography. From fractions eluted by benzene, a mixture of **5c** and **3b** was obtained. Fractional recrystallization from heptane–ethyl acetate (2:1) gave a pure sample of **5c** (20 mg, 6% yield) and **3b** (74 mg, 21% yield). **5c**: mp 220–221 °C; IR (KBr disk) 3090, 3010, 2990, 2950, 1485, 1475, 1450, 1400, 1380, 770, 745, 730 cm^{-1}; UV max (acetonitrile) 212 nm (log ϵ 4.51), 222 (4.40), 275 (4.16), 284 (4.14); ^1H NMR (100 MHz, $CDCl_3$) δ 1.89 (s, 6 H), 2.83 (s, 2 H), 7.27–7.94 (m, 8 H); mass spectrum (70 eV) m/z (rel intensity) 348 (M^+, 42), 220 (100), 205 (79), 178 (31), 165 (53). Anal. ($C_{23}H_{16}N_4$) C, H, N. **3b**: mp 196–197 °C; IR (KBr disk) 3075, 2985, 2950, 2925, 1450, 1440, 765, 750, 735 cm^{-1}; UV max (acetonitrile) 234 nm (log ϵ 4.42), 243 (4.39), 251 (4.10), 277 (4.15), 284 (4.13); ^1H NMR (100 MHz, $CDCl_3$) δ 2.06 (m, 3 H), 3.35 (m, 2 H), 5.43–5.48 (m, 1 H), 7.26–7.81 (m, 8 H); mass spectrum (70 eV) m/z (rel intensity) 346 (M^+, 20), 218 (42), 203 (100), 202 (29), 108 (11), 101 (15). Anal. ($C_{23}H_{14}N_4$) C, H, N.

The reaction of authentic **4b** (168 mg, 0.77 mmol) with TCNE (99 mg, 0.77 mmol) in 1,2-dichloroethane (20 mL) proceeded smoothly at room temperature (the bleaching time was ca. 15 min). After 5 h, the solvent was removed and the residue was recrystallized from heptane–ethyl acetate (2:1) to give **3b**, which was identical in all respects with the product obtained above. The reaction of **1c** with TCNE in another solvent produced also a mixture of **5c** and **3b**. The results are given in the text.

Reaction of 1b with TCNE in the Presence of Methanol. In the reaction of **1b** (63 mg, 0.25 mmol) with TCNE (32 mg, 0.25 mmol) in dichloromethane (6 mL) in the presence of methanol (82 mg, 2.56 mmol), the bleaching time was ca. 30 min at room temperature. After an overnight standing, the solvent was removed and the residue was recrystallized from cyclohexane to give **6** (76 mg, 74%): mp 120–130 °C dec; IR (KBr disk) 3075, 3020, 2950, 2900, 1450, 1075, 1025, 740 cm^{-1}; UV max (acetonitrile) 229 nm (log ϵ 4.46), 236^{sh} (4.38), 237 (4.39), 247 (4.14), 256 (4.37), 271^{sh} (4.15), 276 (4.17), 306 (3.67); ^1H NMR (100 MHz, $CDCl_3$) δ –0.36 to 0.26 (m, 5 H), 0.49 (s, 3 H), 2.86 (s, 3 H), 3.08 (split into 2 s at low temperature, 2 H), 3.26 (s, 1 H), 7.35–7.96 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 1.2 (t), 2.5 (t), 18.9 (d or q), 19.6 (d or q), 26.8 (d), 44.3 (t), 49.0 (s), 49.0 (q), 56.5 (s), 76.0 (s), 106.6 (s), 110.8 (s), 120.9 (d), 126.9 (d), 128.3 (d), 131.0 (d), 139.0 (s), 141.1 (s); mass spectrum (70 eV) m/z (rel intensity) 406 (M^+, 0.7), 178 (30), 99 (100), 76 (13), 67 (16). Anal. ($C_{26}H_{22}N_4O$) C, H, N.

Reactions of 8 with TCNE. In analytical scale experiments, a mixture of *cis*-**8** (5.1 mg, 0.019 mmol) and TCNE (6.0 mg, 0.046 mmol) in 1,2-dichloroethane (1.5 mL) and a mixture of *trans*-**8** (3.1 mg, 0.011 mmol) and TCNE (3.5 mg, 0.027 mmol) in the same solvent (0.9 mL) were sealed in glass ampoules separately and kept in the complete dark. After 12 days, there was observed no reaction as well as no isomerization (HPLC, μ-Bondapack C18, methanol–water, 6:1) in the both mixtures. At 100 °C, 29% of *cis*-**8** was consumed after 60 h, whereas the consumption of *trans*-**8** was only ca. 3%. In the reaction of *cis*-**8**, a peak corresponding to *trans*-**8** was detected but it remained only ca. 2% of the total area of **8**. In a preparative scale experiment, a mixture of *cis*-**8** and *trans*-**8** (68:32, 27 mg, 0.10 mmol) and TCNE (24 mg, 0.19 mmol) in 1,2-dichloroethane (5 mL) was sealed in a glass tube and heated at 100 °C in the dark for 7 days. After the solvent was evaporated, the residue was subjected to silica gel column chromatography. From a hexane–benzene (4:1) fraction, 15 mg of **8** (cis:trans = 41:59) was obtained (56% recovery). Benzene fractions gave **5d** (9 mg, 50%) as colorless crystals. **5d**: mp 253.5–254.5 °C; IR (KBr disk) 3080, 3010, 2900, 2250, 1452, 1038, 1024, 746 cm^{-1}; UV max (acetonitrile) 212 nm (log ϵ 4.53), 228^{sh} (4.34), 237^{sh} (4.16), 272 (4.12), 283 (4.04); ^1H NMR (100 MHz, $CDCl_3$) δ –1.00 to –0.70 (m, 1 H), –0.55 to –0.18 (m, 1 H), 0.03–0.75 (m, 4 H), 0.75–1.30 (m, 4 H), 2.08 (dd, 1 H, J = 8.0 and 12.5 Hz), 2.31 (dd, 1 H, J = 8.0 and 12.5 Hz), 7.30–7.88 (m, 8 H); mass spectrum (70 eV) m/z (rel intensity) 400 (M^+, 100), 228 (86), 178 (86). Anal. ($C_{27}H_{20}N_4$) C, H, N.

Reaction of 1a with PTAD. A mixture of **1a** (132 mg, 0.49 mmol) and PTAD (82 mg, 0.47 mmol) in nitromethane (5 mL) was stirred at room temperature. After 72 h, a red color due to PTAD practically faded. Purification of the product by florisil column chromatography allowed **9** (160 mg, 76% yield) to be isolated: mp 210.0–211.5 °C; IR (KBr disk) 3090, 3020, 2960, 2930, 1760, 1705, 1600, 1500, 1455, 1405, 1395, 1260, 1120, 1015, 755, 725 cm^{-1}; UV max (acetonitrile) 223 nm (log ϵ 4.53), 231 (4.39), 260 (4.09), 285^{sh} (3.90), 298^{sh} (3.49), 310 (3.24); ^1H NMR (100 MHz, $CDCl_3$) δ 0.66–0.82 (m, 8 H), 1.52–1.65 (m, 2 H), 2.94 (s, 2 H), 7.25–7.47 (m, 9 H), 7.55–7.71 (m, 4 H); mass spectrum (70 eV) m/z (rel intensity) 447 (M^+, 63), 220 (100), 164 (79), 150 (82). Anal. ($C_{29}H_{25}N_3O_2$) C, H, N.

Reaction of 1a with DDQ. When **1a** (272 mg, 1 mmol) and DDQ (454 mg, 2 mmol) were dissolved in benzene (30 mL), a dark green solution resulted. Although the color persisted, **1a** was consumed, and $DDQH_2$ (145 mg, 65%, after 15 h) was separated from the solution as gray precipitate. The TLC analysis of the crude reaction mixture indicated that there were at least four compounds in it. From benzene fractions of silica gel column chromatography, a component was isolated as a resinous material, which was characterized as **13** (94 mg, 24% yield): orange resin; IR (KBr disk) 3010, 2240, 1450, 1430, 1360, 1010, 775, 730 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 0.45–0.78 (m, 8 H), 1.61–1.88 (m, 2 H), 2.53 (br q, 4 H, J = ca. 6.8 Hz), 4.05 (t, 4 H, J = 7.4 Hz), 5.75 (br t, 2 H, J = ca. 7 Hz), 6.85 (br s, 2 H), 7.11–7.45 (m, 8 H), 7.57–7.70 (m, 6 H), 7.85–8.00 (m, 2 H); ^{13}C NMR δ 4.9 (q), 17.2 (d), 30.0 (t), 75.4 (t), 108.4 (s), 111.9 (s), 119.5 (d), 120.1 (d), 120.8 (d), 122.5 (d), 124.8 (d), 126.9 (d), 128.2 (d), 128.4 (d), 134.9 (s), 136.7 (s), 137.7 (s), 138.3 (s), 138.9 (s), 140.7 (s), 140.8 (s), 154.7 (s); mass spectrum (70 eV) m/z (rel intensity) 768 (M^+, 0.8), 498 (11), 243 (100). Anal. ($C_{50}H_{38}N_2Cl_2O_2$) C, H, N, Cl.

Reaction of 1b with DDQ. Mixing of **1b** (246 mg, 1 mmol) and DDQ (454 mg, 2 mmol) in benzene resulted in a dark green solution. The solution turned to dark brown at room temperature. After an overnight standing, separated $DDQH_2$ (212 mg, 93%) was removed by filtration and the mother liquor was concentrated. The residue was subjected to silica gel column chromatography. From the very first fraction eluted by benzene, **11**, mp 51–53 °C (lit.[14] mp 51 °C; 33 mg,. 19% yield), was isolated. It crystallized in needles on concentration of the benzene solution, but it polymerized on standing and further purification was difficult. Accordingly, **11** was transformed into **12** by the reaction with diazomethane in benzene.[15] Compound **12**, mp 71–71.5 °C (lit.[15] mp 73–73.5 °C), was obtained in 80% yield. The following fractions of the column chromatography gave **10a** as reddish crystals (263 mg, 56% yield). **10a**: mp 200.5–201.5 °C dec; IR (KBr disk) 3075, 3020, 2240, 1735, 1715, 1560, 1450, 1425, 1200, 1125, 910, 790, 765, 735 cm^{-1}; UV max (acetonitrile) 215^{sh} nm (log ϵ 4.62), 240 (4.26), 277.5 (4.36); ^1H NMR (100 MHz, $CDCl_3$) δ 0.59–0.97 (m, 4 H), 1.48–1.75 (m, 1 H), 3.12 (ddd, 1 H, J = 18.3, 2.5, and 1 Hz), 3.71 (dd, 1 H, J = 18.3 and 1 Hz), 5.28 (m, 1 H), 6.62 (d of m, 1 H, J = 7.6 Hz), 7.04–7.84 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 5.4 (t), 5.9 (t), 16.9 (d), 29.0 (t), 50.9 (s), 57.4 (s), 61.3 (s), 114.1 (s), 115.3 (s), 118.3 (d), 120.2 (d), 121.5 (d), 126.8 (d), 127.7 (d), 127.9 (d), 130.4 (d), 130.5 (d), 138.6 (s), 140.3 (s), 140.6 (s), 142.6 (s), 143.8 (s), 175.2 (s), 176.9 (s); mass spectrum (70 eV) m/z (rel intensity) 474 (M^+ + 4, 2), 472 (M^+ + 2, 9), 470 (M^+, 14), 244 (100), 229 (44), 215 (66), 203 (42), 202 (40). Anal. ($C_{27}H_{16}N_2Cl_2O_2$) C, H, N.

In acetonitrile, the same reaction gave **10a** and **11** in 20% and 7% yield, respectively. When **1b** (246 mg, 1 mmol) was allowed to react with a lesser amount of DDQ (113 mg, 0.5 mmol) in acetonitrile, there were two products in hydrocarbon fractions, in addition to recovered **1b** (113 mg, 46%). One of them was found to be **11** (36 mg, 37% based on the consumed amount of **1b**). The second hydrocarbon (46 mg, 37% based on the same basis as above) was characterized as **4a**, although its purification was unsuccessful. **4a**: oil; IR (liquid film) 3080, 3020, 1615, 1450, 1445, 775, 730 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 0.52–0.98, 1.62–1.88 (m, total of 5 H), 5.23–5.30 (m, 2 H), 6.96 (s, 1 H), 7.11–7.41 (m, 4 H), 7.63–7.74 (m, 3 H), 8.20–8.28 (m, 1 H); mass spectrum (70 eV) m/z (rel intensity) 244 (M^+, 83), 229 (61), 215 (100), 202 (86), 108 (21). Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 92.91; H, 6.49.

Reaction of 1c with DDQ. Under an argon atmosphere, a mixture of **1c** (220 mg, 1 mmol) and DDQ (454 mg, 2 mmol) in benzene (30 mL) was heated at reflux. The color of the solution turned from dark green to yellowish brown after 1 h. After 12 h of heating, $DDQH_2$ (219 mg, 96%) was collected by filtration and the mother liquor was concentrated. Silica gel chromatography of the residue gave **10b** (346 mg, 78%) in benzene fractions. **10b**: orange crystals, mp 219–220 °C dec; IR (KBr disk) 3075, 2980, 2925, 2240, 1720, 1710, 1560, 1450, 1420, 1210, 785, 760, 735 cm^{-1}; UV max (acetonitrile) 218 nm (log ϵ 4.63), 233 (4.43), 241 (4.38), 277 (4.41); ^1H NMR (100 MHz, $CDCl_3$) δ 2.05 (s, 3 H), 3.12 (d of m, 1 H, J = 18.6 Hz), 3.76 (br d, 1 H, J = 18.6 Hz), 5.35 (br s, 1 H), 6.67 (d, 1 H, J = 7.6 Hz), 7.05–7.68 (m, 6 H), 7.74–7.87 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.3 (q), 30.9 (t), 50.9 (s), 57.6 (s), 63.7 (s), 114.2 (s), 115.3 (s), 120.2 (d), 120.5 (d), 121.5 (d), 126.8 (d), 127.7 (d), 127.8 (d), 130.3 (d), 130.5 (d), 133.4 (s), 140.3 (s), 140.6 (s), 142.5 (s), 143.7 (s), 175.2 (s), 176.9 (s); mass spectrum (70 eV) m/z (rel intensity) 448 (M^+ + 4, 1), 446 (M^+ + 2, 7), 444 (M^+, 10), 218 (76), 203 (100). Anal. ($C_{25}H_{14}N_2Cl_2O_2$) C, H, N, Cl. The reaction of authentic **4b** (107 mg, 0.47 mmol), freshly prepared and purified by silica gel column chromatography, with DDQ (125 mg, 0.55 mmol) proceeded smoothly in benzene at room temperature to give **10b** (173 mg, 79% yield), which was identical with the product obtained in the above experiment.

Reactions of Deuterated 1b with DDQ. The deuterium contents in all compounds were based on the ^1H NMR analyses. The amount of deuterium in **11** was deduced from those involved in **12** and 3-(*o,o'*-biphenylene)-1-pyrazoline, which were obtained in the treatment of the crude reaction mixture with diazomethane.[15] In the reaction of **1b-d_2** (88% deuterated) with DDQ in benzene at room temperature, **10a-d_1** (88% deuterated) and **11-d_2** (82–86% deuterated) were obtained in 46% and 15% yield, respectively. The reaction of **1b-d_3** (82% deuterated at the methyl group and ca. 3% at the ring methylene group) with DDQ under the same reaction conditions produced **10a-d_2** (91% deuterated) and **11** (ca. 1% deuterated) in 51% and 8% yield, respectively. When a mixture of **1b-d_2** and **1b-d_3** in a 24:76 ratio was allowed to react with DDQ, there were obtained **10a** (81–83% deuterated at the vinylic C(8) proton and 21–22% deuterated at the ring-methylene C(10) protons) and **11** (27–28% deuterated) in 21–24% and ca. 9% yield, respectively. The recovered **1b** held 79–80% deuterium at the methyl group and 21–26% at the ring methylene position.

Reaction of 1b with DDQ in Benzene–Methanol. The bleaching time for the reaction of **1b** (123 mg, 0.5 mmol) with DDQ (227 mg, 1 mmol) in a mixture of benzene (20 mL) and methanol (5 mL, 120 mmol) was ca. 2 min. After 1 h, the solvent was evaporated and the resultant residue was repeatedly extracted by hexane followed by benzene. The extracts were concentrated and subjected to silica gel column chromatography. From fractions eluted by benzene, **16a** (34 mg, 24%, after purification by repeated chromatography) was obtained as a colorless oil. Further elutions of the column with benzene–ethyl acetate (4:1) gave **17a** (95 mg, 62% yield). **16a**: oil, bp ca. 130 °C at 0.002 Torr; IR (liquid film) 3070, 3010, 2980, 2940, 1610, 1585, 1455, 1380, 1370, 1140, 1110, 1085, 1060, 1020, 775, 730 cm^{-1}; UV max (hexane) 228 nm (log ϵ 4.64), 240 (4.37), 250 (4.60), 259 (4.77), 274 (4.18), 284 (4.20), 300 (4.18), 313 (4.18); ^1H NMR (100 MHz, $CDCl_3$) δ 0.25–0.70 (m, 4 H), 1.25–1.63 (m, 1 H), 1.48 (s, 3 H), 3.27 (s, 3 H), 6.32 (br s, 1 H), 7.18–7.48 (m, 4 H), 7.55–7.82 (m, 3 H), 8.59–8.78 (m, 1 H); mass spectrum (70 eV) m/z (rel intensity) 276 (M^+, 36), 261 (16), 245 (14), 235 (33), 229 (30), 215 (27), 203 (30), 195 (100). Anal. ($C_{20}H_{20}O$) C, H. In NOE experiments, it was observed that the irradiation of the methoxy group (δ 3.27) resulted in the increase in signal intensities of methyl (δ 1.48), vinyl (δ 6.32), and aromatic (δ 8.59–8.78) protons. The result is consistent with the proposed structure for **16a**. **17a**: oil; bp ca. 130 °C at 0.002 Torr; IR (liquid film) 3070, 3000, 2970, 2930, 2820, 1610, 1590, 1450, 1380, 1080, 770, 735 cm^{-1}; UV max (hexane) 209 nm (log ϵ 4.62), 222 (4.42), 231 (4.45), 239 (4.33), 259^{sh} (3.96), 271 (4.15), 276 (4.18), 287^{sh} (4.05), 298 (3.70), 310 (3.53); ^1H NMR (100 MHz, $CDCl_3$) δ −0.27 to 0.45 (m, 5 H), 0.49 (s, 3 H), 2.71 (s, 3 H), 3.01 (s, 3 H), 7.26–7.73 (m, 8 H); mass spectrum (70 eV) m/z (rel intensity) 308 (M^+, 4), 195 (61), 180 (15), 99 (100). Anal. ($C_{21}H_{24}O_2$) C, H.

Reaction of 21 with DDQ. In the reactions of both **21a** and **21b**[42] with DDQ in benzene, the dehydrogenation proceeded at room temperature to give **10a** and **10b**, respectively. However, the amount of the substrate consumed after 24 h was 14% in both cases (HPLC, μ-Bondapack C18, methanol–water 6:1). The reaction of **21a** with DDQ at 50 °C produced **10a** in 66% yield.

Reaction of 2a with TCNE under Illumination. Under the irradiation with a halogen lamp, **2a** reacted with TCNE to give **7**.[1a]

Photostimulated Dehydrogenation of 2b with DDQ. A solution of **2b** (248 mg, 1 mmol) and DDQ (454 mg, 1 mmol) in benzene (25 mL) was irradiated with a 500-W halogen lamp under an argon atmosphere. HPLC analysis (μ-Bondapack C18) indicated that the consumption of **2b** reached 90% after 6 h at 12 °C. $DDQH_2$ (233 mg, 110% based on consumed **2b**) was separated from the solution as gray precipitates. The mother liquor was concentrated, and the residue was subjected to silica gel column chromatography. From hexane–benzene fractions, a mixture of **2b** and **15a** was obtained. Elution of the column with benzene gave **14a** (152 mg, 35% yield based on consumed **2b**), which was purified by recrystallization from heptane–ethyl acetate. The separation of **2b** (9 mg, 9% recovery) and **15a** (17 mg, 8% based on consumed **2b**) was performed by means of preparative GLC. **14a**: yellow crystals, mp 149.0–150.5 °C dec; IR (KBr disk) 3080, 3020, 2940, 2245, 1720, 1705, 1550, 1495, 1490, 1445, 1420, 1275, 1230, 1205, 1195, 1125, 780, 770, 750, 745, 700, 695, 680 cm^{-1}; UV max (acetonitrile) 280 nm (log ϵ 3.92); ^1H NMR (100 MHz, $CDCl_3$) δ 0.65–1.05 (m, 4 H), 0.55–0.85 (m, 1 H), 2.92 (dd, 1 H, J = 18.1 and 1.7 Hz), 3.42 (dd, 1 H, J = 18.1 and 1.1 Hz), 6.10 (br s, 1 H), 6.58–6.82 (m, 2 H), 7.05–7.50 (m, 4 H), 7.65–7.85 (m, 2 H); mass spectrum (70 eV) m/z (rel intensity) 472 (M^+, 0.4), 246 (100). Anal. ($C_{27}H_{18}N_2Cl_2O_2$) C, H, N, Cl. **15a**: oil, bp ca. 90 °C at 0.03 Torr; IR (liquid film) 3080, 3060, 3020, 1660, 1600, 1490, 1445, 1070, 1020, 890, 880, 760, 690 cm^{-1}; UV max (hexane) 238 nm (log ϵ 4.14), 283 (4.11); ^1H NMR (100 MHz, $CDCl_3$) δ 0.41 (m, 2 H), 0.48 (m, 2 H), 0.95–1.40 (m, 1 H), 4.75 (m, 1 H), 4.82 (m, 1 H), 6.50 (br s, 1 H), 7.25 (m, 10 H); mass spectrum (70 eV) m/z (rel intensity) 246 (M^+, 100), 231 (26), 217 (76), 205 (66). Anal. ($C_{19}H_{18}$) C, H.

Photostimulated Dehydrogenation of 2c with DDQ. A solution of **2c** (222 mg, 1 mmol) and DDQ (454 mg, 2 mmol) in benzene (25 mL) was irradiated with a 500-W halogen lamp under an argon atmosphere for 6 h at 12 °C. $DDQH_2$ (207 mg, 110% based on consumed **2c**) precipitated was collected by filtration, and the mother liquor was concentrated. Silica gel column chromatography of the resultant residue gave **2c** (42 mg, 19% recovery) from hexane–benzene (4:1) fractions and **14b** (152 mg, 42% based on consumed **2c**) from benzene fractions. **14b**: yellow crystals, mp 154.4–155.5 °C dec; IR (KBr disk) 3070, 2990, 2945, 2910, 2245, 1720, 1705, 1550, 1495, 1450, 1440, 1230, 1135, 885, 855, 805 cm^{-1}; UV max (acetonitrile) 280 nm (log ϵ 3.86); ^1H NMR (100 MHz, $CDCl_3$) δ 2.10 (m, 3 H), 2.95 (d of m, 1 H, J = 18.5 Hz), 3.50 (d, 1 H, J = 18.5 Hz), 6.12 (br s, 1 H), 6.60–6.85 (m, 2 H), 7.05–7.52 (m, 4 H), 7.65–7.85 (m, 2 H); mass spectrum (70 eV) m/z (rel intensity) 446 (M^+, 2), 220 (69), 205 (100). Anal. ($C_{25}H_{16}N_2Cl_2O_2$) C, H, N, Cl.

Photodehydrogenation of 1b with Chloranil. A reddish orange solution of **1b** (123 mg, 0.5 mmol) and chloranil (246 mg, 1 mmol) in benzene (25 mL) was irradiated with a 500-W halogen lamp under an argon atmosphere. After 1 h of irradiation, the color of the solution merely turned to orange, but HPLC analysis (μ-Bondapack C18) indicated that **1b** was consumed completely. Accordingly, the solvent was removed and hexane was added to the resultant residue. Purification of the hexane soluble material

with silica gel column chromatography gave **4a** (26 mg, 22% yield) in hexane–benzene fractions; **4a** thus obtained exhibited olefinic protons at δ 5.20 and 6.87 ppm in a ^{1}H NMR spectrum. Characterization of **4a** was performed by transforming it to **10a** (51 mg, 22% yield).

Photodehydrogenation of 1c with Chloranil. In a similar manner as above, photoreaction of **1c** (110 mg, 0.5 mmol) and chloranil (246 mg, 1 mmol) in benzene (25 mL) was carried out. After 1.5 h, the consumption of **1c** was found to be ca. 80%. Similar workup and purification as above gave a mixture of **1c** and **4b** (57 mg, ca 3:7 ratio). ^{1}H NMR spectrum of the mixture showed an olefinic signal at δ 5.25 ppm. The mixture was allowed to react with DDQ in refluxing benzene, and **10b** (59 mg, 30% based on consumed **1c**) was isolated and characterized.

Photodehydrogenation of 2b with Chloranil. An orange solution of **2b** (124 mg, 0.5 mmol) and chloranil (246 mg, 1 mmol) in benzene (25 mL) was irradiated with a 500-W halogen lamp under an argon atmosphere. After 1.5 h, at 12 °C, the solution turned to yellow. The solvent was replaced by hexane to remove chloranil and 2,3,5,6-tetrachlorohydroquinone as insoluble materials. The hexane solution was subjected to silica gel column chromatography, and a mixture of **2b** and **15a** (68 mg, in a 48:52 ratio) was obtained in hexane–benzene (10:1) fractions. The result indicated that the reaction proceeded to 81% conversion of **2b**, and **15a** was obtained in 25% yield. Chloranil (120 mg, 0.49 mmol) and 2,3,5,6-tetrachlorohydroquinone (130 mg, 0.52 mmol) were separated by the difference of their solubilities in ether.

Photodehydrogenation of 2c with Chloranil. In a similar photoreaction of **2c** (111 mg, 0.5 mmol) and chloranil (246 mg, 1 mmol) in benzene (25 mL), chloranil (124 mg, 0.5 mmol), hydroquinone (88 mg, 0.35 mmol), and a mixture of **2c** and **15b** (68 mg, in a 44:56 ratio) were obtained; **15b** was purified by preparative GLC. **15b**: colorless oil; IR (liquid film) 3090, 3070, 3030, 2975, 2930, 1605, 1500, 1460, 1450, 1380, 1075, 1030, 900, 780, 765, 735, 700 cm^{-1}; UV max (hexane) 232 nm (log ε 4.18), 282 (4.26); ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.48 (s, 3 H), 4.99 (d, 2 H, J = ca. 1 Hz), 6.66 (s, 1 H), 7.10–7.45 (m, 10 H); mass spectrum (70 eV) m/z (rel intensity) 220 (M^+, 62), 205 (100); exact mass calcd for $C_{17}H_{16}$ (M^+) m/z 220.1253, found 220.1260. The result showed that the consumption of **2c** was 73% and the yield of **15b** was 47%.

Electrochemical Measurements.[27b,46] Cyclic voltammetric studies were carried out with a HA-501 potentiostat/galvanostat in combination with a HB-104 function generator (Hokuto Denko Corporation). The measurements were performed in a three-electrode cell (20-mL volume) fitted with a cooling jacket, a thermometer, and a gas inlet tube. A working electrode was a platinum disk (1-mm diameter) embedded in a glass tube and contacted with a copper wire. A counter electrode was a platinum plate (2 × 2 cm) to which a platinum wire was connected to be placed in the cell. A silver–silver ion electrode (Ag/0.1 N $AgNO_3$, CH_3CN) was used as reference. The working electrode was polished with a diamond compound just prior to use, wiped with a soft paper, rinsed with clean acetonitrile, and dried with a hot stream of air. The electrochemical cell was cleaned with detergents, rinsed with distilled water, rinsed with clean acetone, and dried at 60 °C.

The construction of the apparatus and procedures for the measurements were similar to those reported.[27b,46] An argon atmosphere was maintained throughout the measurement, and the solution was stirred with a Teflon-coated magnetic stirring bar. The concentration of the substrate was typically 10 mg in 10 mL of 0.1 N tetraethylammonium perchlorate solution of acetonitrile. The measurements were carried out at sweep rates of 50–400 mV/s. In the cases of **1a–c**, **8**, and **12**, in particular, the polishing of the working electrode for every scan was essential to obtain the reproducible cathodic wave. The results are summarized in Table I.

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Registry No. **1a**, 37568-24-4; **1b**, 91266-61-4; **1b**-d_2, 121125-29-9; **1b**-d_3, 121125-28-8; **1c**, 67525-00-2; **2a**, 54159-42-1; **2b**, 113519-95-2; **2c**, 32134-41-1; **3b**, 113519-93-0; **4a**, 112146-00-6; **4b**, 112146-01-7; **5a**, 91266-62-5; **5b**, 91266-63-6; **5c**, 113519-94-1; **5d**, 121125-26-6; **6**, 121125-18-6; **7**, 91549-28-9; (*E*)-**8**, 121125-27-7; (*Z*)-**8**, 121125-19-7; **9**, 121125-20-0; **10a**, 112145-98-9; **10a**-d_1, 121125-30-2; **10a**-d_2, 121141-63-7; **10b**, 112145-99-0; **11**, 4425-82-5; **11**-d_2, 121125-31-3; **12**, 167-02-2; **13**, 121125-21-1; **14a**, 121125-22-2; **14b**, 121125-32-4; **15a**, 121125-23-3; **15b**, 77915-31-2; **16a**, 121141-62-6; **17a**, 121125-24-4; **21a**, 121125-25-5; **21b**, 56150-47-1; DDQ, 84-58-2; PTAD, 15988-11-1; $Me_2C{=}CH_2$, 115-11-7; $(NCCH{=})_2$, 670-54-2; $ClMgCH_2C(Me){=}CH_2$, 5674-01-1; $N_2{=}CPh_2$, 883-40-9; fluorenone, 486-25-9; cyclopropyl methyl ketone, 765-43-5; 2-cyclopropylpropene, 4663-22-3; 9-diazofluorene, 832-80-4; (*E*)-1,2-dicyclopropylethylene, 10359-44-1; (*Z*)-1,2-dicyclopropylethylene, 23510-65-8; 2-cyclopropylpropylene-*1,1*-d_2, 121125-33-5; 2-cyclopropylpropylene-*3,3,3*-d_3, 121125-34-6; cyclopropylethanone-*2,2,2*-d_3, 14671-01-3; 9-(2-methyl-2-propenyl)-9-fluorenol, 121141-65-9; 2-cyclopropyl-2-propanol-*3,3,3*-d_3, 121141-64-8.

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Reactions of Some Cyclopropylethylenes with TCNE. A Remarkable Effect of Spiro-Activation in the Cycloaddition[1]

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Previously, mono-, di-, and trisubstituted vinylcyclopropanes **1** have been shown to react with TCNE to give a cyclobutane derivative **2** (type I reaction). However, it was observed that the introduction of a spiro-linked fluorene group to the three-membered ring, as in **5**, **7**, and **8**, resulted in a total change of the reaction pathway to produce a vinylcyclopentane derivative (type II reaction), which was formerly observed to occur only in the reaction of tetrasubstituted ethylene **3**. The results may be rationalized in terms of the SET initiation of the reaction, which is supposed to be ascribed to the spiro-activation. The chemical behavior of various substrates (**5–9** and **15**) as well as their relative reactivities are disucssed.

Some time ago, we have demonstrated that various vinylcyclopropanes react with ethenetetracarbonitrile (TCNE) in two distinct reaction pathways depending primarily upon a pattern of substitution at the ethylenic

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