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.

Acknowledgment. The present research was supported by a Grant-in-Aid for Scientific Research (No. 60470020) and the Special Grant-in-Aid for Promotion of Education and Science in Hokkaido University provided by the Ministry of Education, Science, and Culture of Japan to which we are very grateful.

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.

(46) Nelsen, S. F.; Kapp, D. L.; Akaba, R.; Evans, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 6863.

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

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Received January 11, 1988

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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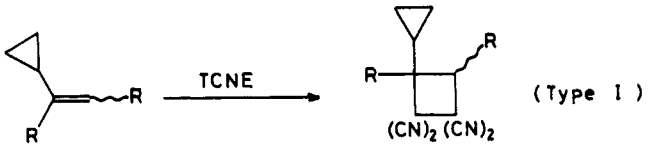
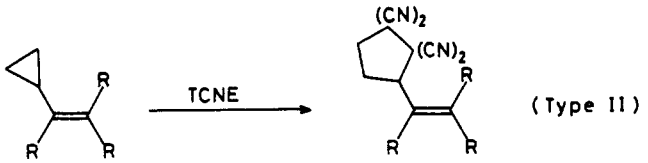
moiety.[2] Thus, mono-, di-, and trisubstituted vinylcyclopropanes 1 react with TCNE in a $[\pi^2 + \pi^2]$ manner to give cyclobutane derivatives 2 (type I reaction), whereas some tetrasubstituted olefins 3 react at their cyclopropane sigma bond in a $[\sigma^2 + \pi^2]$ fashion to afford vinylcyclopentane derivatives 4 (type II reaction).[3] After extensive



1 2

(R = H, alkyl, cyclo-C_3H_5, or C_6H_5)



3 4

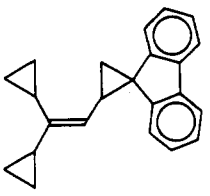
(R = alkyl, cyclo-C_3H_5, or C_6H_5)

investigations,[2] we have come to the conclusion that the type I reaction is a typical donor–acceptor type cycloaddition proceeding via a zwitterionic intermediate,[4] whereas the type II reaction may involve a single-electron transfer (SET) process at an early stage of the reaction, and the resultant radical ion pair reacts to afford 4.[2b,d,e]

As reported in the preceding paper,[5] we have observed that certain spiro-activated cyclopropanes are highly reactive in the reaction with TCNE or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), and we conclude that the reactions would involve a rate-controlling SET at an initiating stage for the observed products. Since the spiro-activation is believed to be related to the SET process,[5] the first step of such reactions of spiro-activated cyclopropanes will be closely similar to that proposed for the type II reaction. Accordingly, it is of considerable interest to examine the effect of introducing a spiro-linked fluorene to one of the cyclopropanes in a cyclopropylethylene, which undergoes the type I reaction. The results are in fact remarkable.[1] The introduction of the spirofluorene group not only increases a reactivity but also brings about a dramatic change of the reaction course from the type I to the type II. In the present paper, we summarize our results and give some discussions on the cycloaddition of cyclopropylethylenes with TCNE.

Results

Substrates. 1-(2,2-Dicyclopropylvinyl)dibenzo[*d,f*]-spiro[2.4]heptane (**5**), 1-(2,2-dicyclopropylvinyl)-2,2-diphenylcyclopropane (**6**), 1-(*trans*-2-cyclopropylvinyl)dibenzo[*d,f*]spiro[2.4]heptane (**7**),[6] and 1,1-dicyclopropyl-2-(2,2-dicyclopropylvinyl)dibenzo[*d,f*]spiro[2.4]heptane (**8**) were prepared by the addition of an appropriate carbene (fluorenylidene or diphenylcarbene) to the corresponding 1,3-diene. The addition was regiospecific in all cases to give **5**–**8** in reasonable yields.



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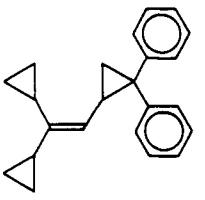

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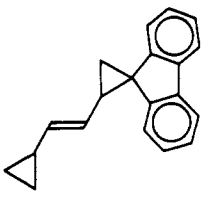

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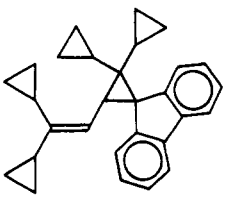

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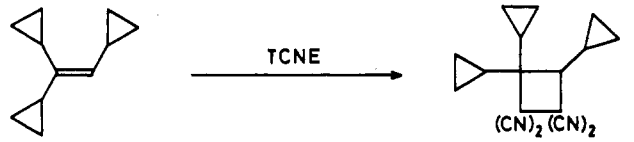
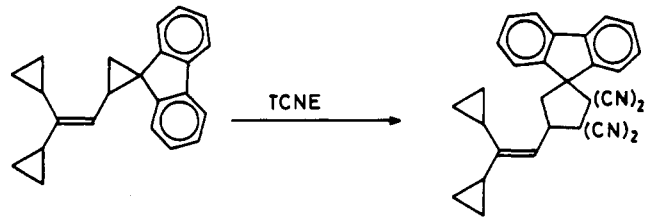
Reaction with TCNE. Previously, 1,1,2-tricyclopropylethylene (**9**) has been shown to react with TCNE to give **10**.[2a,c,e] In dichloromethane, a blue solution (λ_{max} 635 nm) became colorless after ca. 20 min at room temperature. The addition of **5** into a dichloromethane solution of TCNE, however, resulted in only instantaneous development of faint blue color.[7] The product isolated in 83–94% yield was characterized as 3-(2,2-dicyclopropylvinyl)dibenzo[*f,h*]spiro[4.4]nonane-1,1,2,2-tetracarbonitrile (**11**). No four-membered cycloadduct was detected in the product mixture. Thus, **5** exhibited higher reactivity than **9**,[7b] and it produces exclusively the type II adduct.



9 10



5 11

With **6**, however, the reaction was found to proceed slowly (the bleaching time being ca. 30 min at room tem-

(1) Preliminary account of the present results: Nishida, S.; Murakami, M.; Mizuno, T.; Oda, H.; Shimizu, N. *J. Org. Chem.* **1984**, *49*, 3428.

(2) (a) Nishida, S.; Moritani, I.; Teraji, T. *J. Chem. Soc., Chem. Commun.* **1970**, 501. (b) Nishida, S.; Moritani, I.; Teraji, T. *Ibid.* **1971**, 36. (c) Nishida, S.; Moritani, I.; Teraji, T. *J. Org. Chem.* **1973**, *38*, 1878. (d) Kataoka, F.; Nishida, S. *Chem. Lett.* **1980**, 1115. (e) Tsuji, T.; Nishida, S. *Acc. Chem. Res.* **1984**, *17*, 56.

(3) In the reactions of 1,1-dicyclopropyl-2-methylpropene (alkyl groups being two methyls) and 1,1-dicyclopropyl-2-ethyl-1-butene (alkyl groups being two ethyls), the type I reaction and the type II reaction have competed.[2d,e]

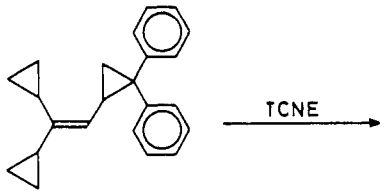
(4) (a) Bartlett, P. D. *Q. Rev., Chem. Soc.* **1970**, *24*, 473. (b) Ciganek, E.; Linn, W. J.; Webster, O. W. In *The Chemistry of the Cyano Group*; Rappoport, Z., Ed.; Interscience: London, 1970; Chapter 9. (c) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117. (d) Fatiadi, A. J. *Synthesis* **1987**, 749.

(5) Nishida, S.; Murakami, M.; Oda, H.; Tsuji, T.; Mizuno, T.; Matsubara, M.; Kikai, N. *J. Org. Chem.*, preceding paper in this issue.

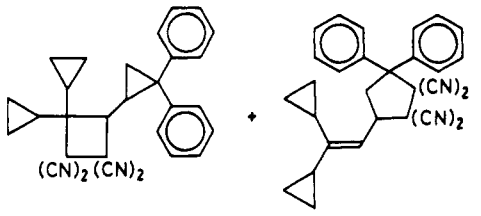
(6) Nishida, S.; Komiya, Z.; Mizuno, T.; Mikuni, A.; Fukui, T.; Tsuji, T.; Murakami, M.; Shimizu, N. *J. Org. Chem.* **1984**, *49*, 495.

(7) (a) The consumption of TCNE was so rapid, even at −60 °C, that reliable λ_{max} could not be obtained. (b) The bleaching time was taken as an index for the reactivity. See footnote 7 in ref 5.

perature in dichloromethane, λ_{max} 597 nm), and the major product isolated in 72% yield was found to be 3,3-dicyclopropyl-4-(2,2-diphenylcyclopropyl)cyclobutane-1,1,2,2-tetracarbonitrile (**12**), the type I adduct. A small amount (9% yield) of the type II product **13** was also obtained.



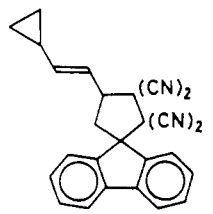
6



12 **13**

Since it has been known[4c,8] that the cycloaddition of an activated olefin with TCNE is reversible, we examined the thermal stability of **12** under the reaction conditions. At room temperature, the retrocycloaddition was practically absent in all solvents examined. At 80 °C, the reverse reaction in fact took place in acetonitrile or 1,2-dichloroethane, but not in benzene.[9] We thus conclude that **13** is indeed a primary reaction product. The ratio of **12**/**13** produced in various solvents at room temperature was 96/4 in acetonitrile, 86/14 in 1,2-dichloroethane, and 52/48 in benzene (80 °C).[10] The production of the type II adduct being more pronounced in a less polar solvent is in accordance with the previous observations.[2d]

A decrease in the number of the substituents in the vinyl side chain results in a reduction of reactivity. Thus, the reaction of **7** with TCNE in dichloromethane (λ_{max} 574 nm) required 12 h at room temperature. The product isolated in 37% yield was characterized as **14**. When no cyclopropyl substituent is present in the vinyl side chain as in **15**, totally different reaction takes place as reported previously.[11]



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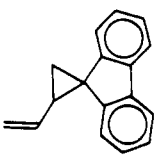
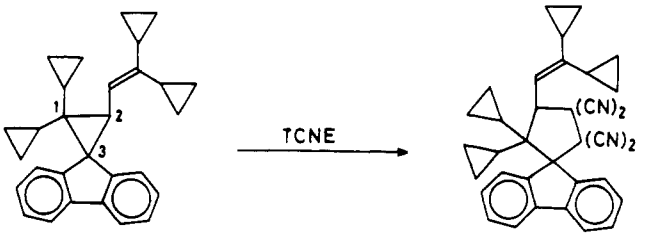


15

When additional pendant cyclopropyl groups were introduced to **5**, the reactivity with TCNE was found to drop again. Thus, the bleaching time in the reaction of **8** (λ_{max} 592 nm) was more than 6 h at room temperature in dichloromethane. The product isolated in 68% yield was characterized as 4,4-dicyclopropyl-3-(2,2-dicyclopropylvinyl)dibenzo[*f*,*h*]spiro[4.4]nonane-1,1,2,2-tetracarbonitrile (**16**), the type II product. The position of the substituents were assigned on the basis of the ^{1}H NMR spectrum as well as on mechanistic consideration (vide infra). In **16**, one of the cyclopropyl protons was found to resonate at δ −0.85 to −1.02 ppm. This extraordinarily high field resonance may be characteristic of highly congested 1,1-dicyclopropyl-substituted spirofluorene derivatives.[12] Steric congestion in the spiro compounds will swing the pendant cyclopropyl group into the strongly shielding cone region of the fluorene group. The structure of **16** thus deduced indicates that the C(2)–C(3) bond in **8**, rather than the C(1)–C(3) bond, participates in the cycloaddition.



8 **16**

Discussion

The present results clearly demonstrated that the spiro-activation indeed plays an important role in determining the reactivity and modes of the reaction of vinylcyclopropane with TCNE. Previously, the type II reaction had been observed only in the reaction of tetrasubstituted cyclopropylethylenes.[2,3] Accordingly, one might expect that **5** and **7** react with TCNE in the type I manner, but they actually react with TCNE in the type II fashion.

The reasons for the observed change in the reaction modes from the type I to the type II cannot be ascribed to steric hindrance for TCNE attack at the ethylenic linkage because **5** exhibits a reactivity significantly higher than that of **9**. Moreover, **6** is nearly as reactive as **9**, and **6** reacts with TCNE mainly at its π bond to afford the type I product. It is apparent, therefore, that the spiro-activation,[5] which may primarily be electronic in origin, plays an important role in these reactions, also. The reaction will thus be initiated by SET as in the cases reported in the preceding paper.[5]

The SET process in the present reaction would also be rate-controlling,[5] because **5** exhibits significantly higher reactivity than **7**, and the reaction of **15** is much slower than those of **5** and **7**. In fact, **15** requires several days at 55–60 °C in its reaction with TCNE and produces totally different products.[11] It has been concluded that TCNE attacks the terminal carbon atom of the vinyl side chain and extensive rearrangements follow. Accordingly, we may classify the reaction as a modified type I.

The electrochemical studies did not help to understand the difference observed between **5** and **6**. Both substrates gave nearly the same E_p^{ox} (1.1 V vs SCE). Although the

(8) In fact, it has been frequently observed that the recrystallization of the [π^2 + π^2] cycloadduct gives a colored solution, indicating the occurrence of the reverse reaction. Care should be taken, therefore, in the recrystallization of the product.

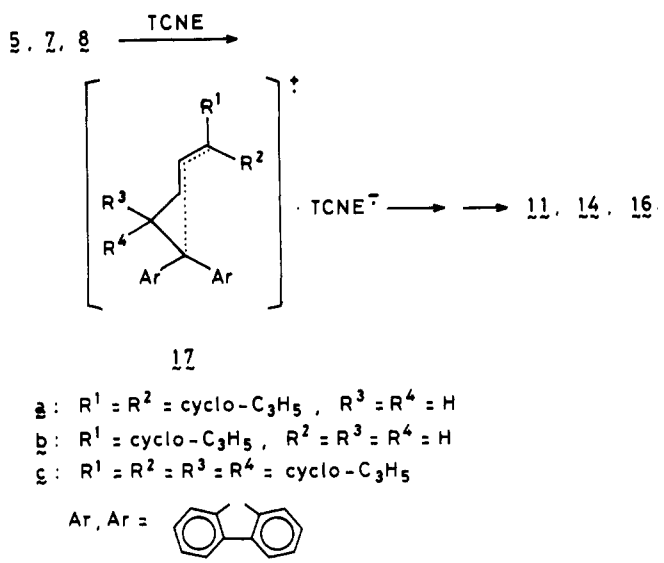
(9) **13** was found to be stable even in acetonitrile at 80 °C.

(10) In benzene, the reaction was very slow at room temperature.

(11) Shimizu, N.; Ishizuka, S.; Tsuji, T.; Nishida, S. *Chem. Lett.* **1975**, 751. Shimizu, N.; Fujioka, T.; Ishizuka, S.; Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1977**, *99*, 5972.

(12) During the course of related studies, we frequently observed that one of the pendant cyclopropyl protons resonates at significantly high field when the substrate is heavily substituted.

(13) In order to discuss the reactivity difference between **5** and **6**, additional investigations with related substrates appear to be necessary. A possibility may exist in which the SET takes place *via* a CT complex whereas the type I reaction does not.



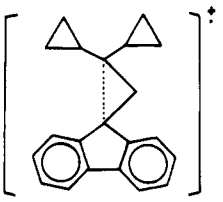
17

a: $R^1 = R^2 =$ cyclo-C_3H_5, $R^3 = R^4 = H$
b: $R^1 =$ cyclo-C_3H_5, $R^2 = R^3 = R^4 = H$
c: $R^1 = R^2 = R^3 = R^4 =$ cyclo-C_3H_5

Ar, Ar =

data were crude as in the previous cases,[5] it appears to suggest that both **5** and **6** are capable of forming the corresponding radical cations in the contact with TCNE. Actually, however, the SET initiated process is important only in the reaction of **5**. The type I reaction and the type II reaction appear to be different in the reaction channels.

With regard to the reaction of **8** to give **16**, it should be noted that Roth et al.[14] have demonstrated by CIDNP studies that radical cations derived from spiro[cyclopropane-1,9′-fluorene] derivatives are in a $^2A_1$ type structure, and the participation of an allylic cyclopropane carbon favors over that of a tetrasubstituted bond in the case of a 1,1-dimethyl-2-(2-methyl-1-propenyl) derivative. On the bases of their conclusion, the radical cation derived from **8** will be **17c**, which may account for the formation of **16**. The relatively low reactivity of **8** might be caused by a Thorpe–Ingold effect operated in the transformation of **8** into **17c**. The *gem*-dicyclopropyl groups in **8** would bring about resistance to open its ring to produce **17c**. The retarding effect of the *gem*-dicyclopropyl groups is opposite to that surmised in the reactions reported in the previous paper,[5] in which the steric congestion is considered to result in the reactivity increase. This contrasting result is in line with the present conclusion, because, unlike **17c** in which the C(2)–C(3) bond participates, the radical cation involved in the previous reaction should be **18** with the participation of the tetrasubstituted C(1)–C(3) bond.



18

After all, the present results substantiate our previous conclusions that the spiro-activation is concerned with the rate-controlling SET[5] and the type II reaction is initiated by such a process.[2b,d,e] The very first substrate that underwent the type II reaction was 1,1,2,2-tetracyclopropylethylene,[2b] which lacks not only the spiro-activation but also aryl groups. The π bond system, a tricyclopropylvinyl group, in this compound might function both as an electron pool and a cation-stabilizing group.

Experimental Section

General methods are the same as those described in the preceding paper.[5] Spectral data for **5**, **6**, **11**, **12**, and **13** are given in supplementary material in ref 1.

1,1,4,4-Tetracyclopropyl-1,3-butadiene. 1-Chloro-2,2-dicyclopropylethylene (14.3 g, 0.1 mol)[15] was added dropwise to a suspension of activated magnesium (prepared from 38 g, 0.40 mol, of anhydrous magnesium chloride and 33 g, 0.77 mol, of anhydrous potassium iodide)[16] in THF (300 mL). The mixture was stirred at room temperature for 2 h and then cooled at −80 °C. The cold solution of (2,2-dicyclopropylvinyl)magnesium chloride thus prepared was transferred into a cold (−80 °C) suspension of freshly purified cuprous chloride (60 g, 0.60 mol) in THF (150 mL) by keeping the temperature of the suspension below −60 °C. After the mixture was stirred for additional 30 min at −80 °C, the cooling bath was removed. At ca. −30 °C, a vigorous reaction took place to raise the temperature of the mixture to ca. 50 °C. The resultant mixture was left to stand at room temperature for 12 h, and 4 mL of ethanol followed by 40 mL of water was added to it. Finally, the whole mixture was poured into ice-cooled water (400 mL), and the black precipitate that separated was removed by passing the mixture through a short column of cerite 545. The organic material was then collected by the extraction of the product mixture with three portions of pentane. The combined pentane solutions were washed with water, dried with anhydrous magnesium sulfate, and concentrated. The distillation of the resultant oily residue under reduced pressure gave 1,1-dicyclopropylethylene (bp ca. 100 °C at 20 Torr, 2.5 g) and 1,1,4,4-tetracyclopropyl-1,3-butadiene (bp 115–120 °C at 1 Torr, 6.3 g, 59% yield). The latter crystallized on standing: mp 41–43 °C; IR (KBr) 3090, 3010, 1590, 1020, 925 cm^{-1}; UV max (hexane) 264 nm (log ϵ 4.41), 269 (4.43), 282^{sh} (4.23); ^1H NMR (100 MHz, $CDCl_3$) δ 0.29–0.87 (m, 16 H), 0.87–1.26 (m, 2 H), 1.68–1.97 (m, 2 H), 6.21 (s, 2 H); mass spectrum (70 eV) m/z (rel intensity) 214 (M^+, 38), 91 (100). Anal. ($C_{16}H_{22}$) C, H; exact mass calcd m/z 214.1718, found 214.1705.

Cyclopropanes. Compounds **5**, **6**, **7**, and **8** were prepared by the reaction of an appropriate diene[17] with either 9-diazofluorene or diphenyldiazomethane at 100–140 °C. **5**: bp ca. 150 °C at 0.005 Torr, 75%. **6**: bp ca. 150 °C at 0.02 Torr, 85%. **7**: an oil; an attempted purification of the cyclopropane by distillation resulted in the rearrangement to a cyclopentane derivative.[6] **8**: mp 110.5–111.5 °C, 11%; IR (KBr) 3090, 3010, 1635, 1485, 1445, 1030, 1015, 935, 915, 905, 825, 815, 730 cm^{-1}; UV max (hexane) 216 nm (log ϵ 4.66), 233^{sh} (4.32), 263 (4.13), 273 (4.13), 285^{sh} (3.99), 293 (3.85), 304 (3.78); ^1H NMR (100 MHz, $CDCl_3$) δ −0.27 to 0.03 (m, 1 H), 0.10–1.07 (m, 17 H), 1.11–1.47 (m, 2 H), 2.85 (dd, 1 H, J = 5.1 and ca. 1 Hz), 5.53 (d, 1 H, J = 5.1 Hz), 7.08–7.42 (m, 5 H), 7.53–7.71 (m, 1 H), 7.75–7.87 (m, 2 H); mass spectrum (70 eV) m/z (rel intensity) 378 (M^+, 26), 95 (100). Anal. ($C_{29}H_{30}$) C, H.

Reaction of 5 with TCNE. Under an argon atmosphere, a solution of **5** (150 mg, 0.50 mmol) in dichloromethane (3 mL) was added dropwise to a solution of TCNE (64 mg, 0.50 mmol) in dichloromethane (17 mL). When a drop of the solution of **5** hit the TCNE solution, a blue color was observed but it faded immediately with the diffusion of the drop. After 30 min, the solvent was removed and the residue was placed on the top of a silica gel column (25 g). Elution of the column with benzene gave a slightly yellowish solid, which was recrystallized from benzene to give **11**: mp 170.5–171.5 °C; 192 mg, 90%.

Reaction of 6 with TCNE. A mixing of **6** (150 mg, 0.50 mmol) and TCNE (64 mg, 0.50 mmol) in dichloromethane (20 mL) gave a greenish blue solution, which became a pale yellow after 30 min and colorless after 80 min. After the solution stood for 48 h, the solvent was removed and the residue was placed on the top of a silica gel column (25 g). Elution of the column with benzene gave a solid (190 mg). Recrystallization of this solid with a benzene–heptane mixture followed by that of an ethyl acetate–

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heptane (2:3) mixture gave **12**: mp 195–196.5 °C dec; 95 mg, 44%. The mother liquor of the recrystallization was concentrated, and additional **12** (13 mg) was collected. The remaining solution was evaporated, and the residue was recrystallized from a mixture of dichloromethane–cyclohexane to give **13**: mp 175–178 °C dec; 22 mg, 10%. In a repeated run, **12** and **13** were isolated in 72% and 9% yield, respectively.

Thermal Stability of 12 and 13. Purified **12** (22 mg) and diphenyl ether (an internal standard) were dissolved in either acetonitrile, 1,2-dichloroethane, or benzene, and the isomerization of **12** was examined by HPLC analysis (μ-Bondapack C18, methanol–water, 3:1, UV detector at 240 nm; ε at 240 nm being **12**, 1070; **13**, 6270; **6**, 13000). In acetonitrile at 80 °C, the amounts of **12:13:6** were 47:18:11 after 4.2 h and 31:29:9 after 8.3 h. When 1,1-dicyclopropylethylene (8 mg) was added to the starting mixture to trap the regenerated TCNE, the amounts of **12:13:6** were 25:1:58 after 4.2 h and 20:2:61 after 8.3 h. Apparently, the reverse process to regenerate **6** and TCNE took place in a reasonable rate. Even in 1,2-dichloroethane, the amounts of **12:13:6** after 8 h at 80 °C were 87:8:5. In benzene, however, the isomerization was practically not observed. At room temperature, the isomerization was found to be very slow in all three solvents examined; less than 2% after 15 h in acetonitrile. In contrast to **12**, **13** was stable in either acetonitrile or 1,2-dichloroethane at 80 °C.

The HPLC-determined ratio of **12:13** in the reaction of **6** with TCNE at room temperature in these three solvents was as follows: in acetonitrile 96:4, in 1,2-dichloroethane 86:14, and in benzene 60:40 (52:48 at 80 °C)[10] after 14–16 h.

Reaction of 7 with TCNE. A blue-violet solution obtained by mixing **7** (142 mg, 0.55 mmol) and TCNE (67 mg, 0.52 mmol) in 1,2-dichloroethane (13 mL) turned brown after 12 h at room temperature. Since HPLC analysis indicated that the consumption of **7** was 93%, the solution was concentrated. From the concentrated solution, **14** (73 mg, 37% yield) was separated as crystals and recrystallized from benzene. **14**: mp 241.5–242.5 °C dec; IR (KBr) 3090, 3070, 3020, 2940, 2860, 2250, 1660, 1450, 970, 950, 770, 740, 730 cm^{-1}; UV max (acetonitrile) 274 nm (log ε 4.05), 284 (3.99); ^1H NMR (100 MHz, acetone-d_6) δ 0.44–0.72 (m, 2 H), 0.72–1.00 (m, 2 H), 1.52–1.82 (m, 1 H), 2.73–3.27 (m, 2 H), 4.30–4.68 (m, 1 H), 5.62–6.16 (m, 2 H), 7.30–7.80 (m, 4 H), 7.80–8.22 (m, 4 H); mass spectrum (70 eV) *m/z* (rel intensity) 386 (M^+, 16), 258 (20), 191 (12), 178 (100), 93 (22). Anal. ($C_{26}H_{18}N_4$) C, H, N.

Reaction of 8 with TCNE. A blue solution obtained by mixing **8** (76 mg, 0.20 mmol) and TCNE (26 mg, 0.20 mmol) in dichloromethane (10 mL) turned slightly blue after 6 h. Since this color persisted for additional hours, 5 mg of TCNE was added to the solution, and the resultant mixture was kept standing for 50 h. The solvent was removed, and the residue was placed on the top of a florisil column (2 g). Elution of the column with dichloromethane gave a solid (97 mg), which was recrystallized from benzene and then from a 1:1 mixture of ethyl acetate and heptane to give **16** (69 mg, 68% yield): mp 322–323 °C dec; IR (KBr) 3100, 3080, 3020, 2250, 1635, 1480, 1450, 1430, 1030, 1020, 930, 745, 730 cm^{-1}; UV max (acetonitrile) 201 nm (log ε 4.51), 208 (4.51), 228^{sh} (4.33), 262 (4.24), 272 (4.24), 281^{sh} (4.14); ^1H NMR (100 MHz, $CDCl_3$) δ −1.02 to −0.85 (m, 1 H), −0.40 to 0.69 (m, 11 H), 0.79–1.25 (m, 7 H), 1.80–2.01 (m, 1 H), 4.03 (d, 1 H, *J* = 10.3 Hz), 5.06 (d, 1 H, *J* = 10.3 Hz), 7.28–7.57 (m, 4 H), 7.65–7.76 (m, 3 H), 8.04–8.17 (m, 1 H); mass spectrum (70 eV) *m/z* (rel intensity) 506 (M^+, 0.7), 278 (35), 134 (100). Anal. ($C_{35}H_{30}N_4$) C, H, N.

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Radical Addition to the Carbonyl Carbon Promoted by Aqueous Titanium Trichloride: Stereoselective Synthesis of α,β-Dihydroxy Ketones

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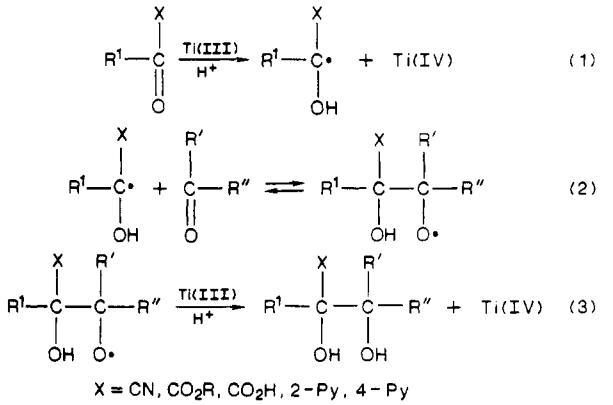
Ketyl radicals, formed by chemoselective Ti(III) reduction of α,β-dicarbonyl compounds, add to the carbonyl carbon of aldehydes under mild conditions to afford α,β-dihydroxy ketones in good to excellent yields. Simple diastereoselectivity strongly depends on the bulk of groups bonded to both the ketyl radical and the aldehydic function. The relative configuration of two of the keto diols was established by single-crystal X-ray diffractometry.

During our investigation of new synthetic reactions promoted by aqueous Ti(III) ion, we reported that carbon-centered radicals RĊ(X)OH, generated by reduction of the corresponding carbonyl compounds (eq 1), add to the carbonyl carbon of aldehydes and ketones (eq 2) to afford α,β-dihydroxy nitriles (X = CN),[1,2] α,β-dihydroxy esters or acids (X = CO_2R or CO_2H),[2,3] pyridyl diols (X = 2-Py or 4-Py),[4] and allylpinacols (eq 3).[5]

Radical addition to carbonyl carbon (eq 2) is not considered a useful reaction in σ carbon–carbon bond formation because the intermediate alkoxy radical undergoes fast β-bond cleavage.[6,7] Nevertheless, under our reaction conditions,[1-5] aldehydes and ketones can be used as intermolecular radical traps because rapid reduction of the intermediate alkoxy radicals by Ti(III) ion (eq 3) makes the addition step (eq 2) practically irreversible, leading to the formation of a new carbon–carbon bond in synthetically useful yields. Besides, the presence of metal ions, which restrict the number of possible transition states by



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