Preferential Incorporation of a Cyclopropyl σ Bond Over an Ethylenic π Bond in the TCNE Cycloaddition of 1,2-Dicyclopropylethylene. Occurrence of the Type-II Reaction in Some Disubstituted Substrates

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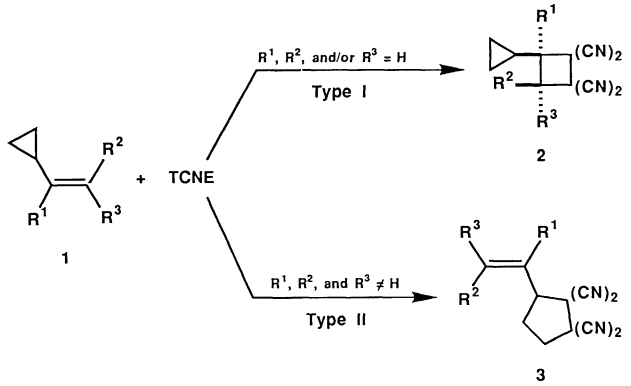
Among the two types of cycloadditions known to take place in the reactions of cyclopropyl-substituted ethylenes (**1**) with tetracyanoethylene (TCNE) (type-I gives a cyclobutane derivative (**2**) and type-II yields a vinylcyclopentane derivative (**3**)), the type-II reaction has been practically limited to occur in reactions of tetrasubstituted substrates. However, some disubstituted substrates, namely *cis*- and *trans*-1,2-dicyclopropylethylene (**4** and **5**), were found to produce a mixture of **2** (R^1=R^2 or R^3=H, R^2 or R^3=*cyclo*-Pr) and **3** (R^1=R^2 or R^3=H, R^2 or R^3=*cyclo*-Pr). In acetonitrile at 80 °C, **2** predominated in the reactions of both **4** and **5**, but **3** became the major adduct in 1,2-dichloroethane or benzene. The other 1,2-disubstituted ethylenes, such as 1-cyclopropylpropene, 1-cyclopropyl-3-methyl-1-butene and 1-cyclopropyl-3,3-dimethyl-1-butene, produced a small amount of **3** in solvents of low polarity; the type-II, however, has never become a major process. Parent vinylcyclopropane failed to give the type-II adduct in all of the solvents examined. Participation of the cyclopropyl σ bond in the reaction with TCNE is thus shown to have a scope wider than that presumed previously; hence, both the type-I and the type-II processes may be the two principal modes of the reaction of **1** with TCNE.

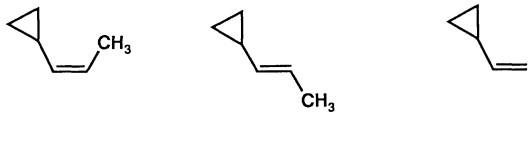
It may be natural to expect that an ethylenic π bond is more reactive than a cyclopropyl σ bond towards an electrophilic reagent.[1] Thus, it was not surprising when we observed that mono- and disubstituted cyclopropylethylenes **1** (R^1, R^2, and/or R^3=H) reacted with electrophilic tetracyanoethylene (TCNE) at their π bond to give a cyclobutane derivative **2** (type I reaction).[2] However, we found successively that TCNE preferentially reacted with the cyclopropyl σ bond of certain trisubstituted **1** (R^1, R^2, and R^3≠H) to give a vinylcyclopentane derivative **3** (type II reaction).[3] Although it has recently been demonstrated that the spiro-activation of a cyclopropane ring brought about a change of the reaction course from type-I to type-II in the reaction of 1,1,2-tricyclopropylethylene,[4] the type-II reaction has actually been limited to occur only in the reaction of tetrasubstituted olefins.[3]

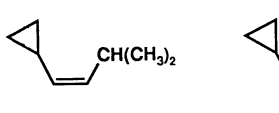


In a previous paper[2] we reported that *cis*- and *trans*-1,2-dicyclopropylethylenes (**4** and **5**) were not exceptions for the disubstituted substrates. Namely, they gave crystalline **2**, albeit in relatively low yields, in a reaction with TCNE at elevated temperature in a polar solvent.[5] Recently, however, we noticed a second oily product, which was assignable to **3**. This finding occurred to us when we examined the mutual isomerization of **4** and **5** in the presence of some acceptor molecules. The observation suggests that the type-II reaction could have a scope wider than what we had presumed.[3,4] Accordingly, we carried out minute investigations on the reactions of some rather simple cyclopropylethylenes. In the present paper we report that the type-II reaction, indeed, gains significance to a certain extent in the reaction of some 1,2-disubstituted substrates.

Results and Discussion

Substrates. The ethylenes examined in the present study include, in addition to **4** and **5**,[6,7] *cis*- and *trans*-1-cyclopropylpropene (**6** and **7**),[8] vinylcyclopropane (**8**),[9] *cis*-1-cyclopropyl-3-methyl-1-butene (**9**), and *cis*-1-cyclo-





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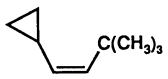

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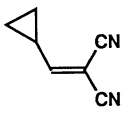

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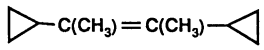

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propyl-3,3-dimethyl-1-butene (**10**). The relative reactivities of these substrates toward TCNE were **5**>**4**>**6**=**7**=**8**>**9**>**10**.

Reactions of 4 and 5 with TCNE. In the previous study we examined the reactions of **4** and **5** as a part of an investigation aimed to show the generality of the type-I reaction.[2] Thus, the reaction of **4** was previously observed to occur at 100 °C in nitromethane[5] and crystalline *cis*-3,4-dicyclopropylcyclobutane-1,1,2,2-tetracarbonitrile (**2**: R^1=R^3=H, R^2=cyclo-Pr) was obtained in 25% isolated yield; **5** yielded *trans*-**2** (R^1=R^2=H, R^3=*cyclo*-Pr) in 11% yield. Since **2** was usually obtained in crystalline forms and was known to undergo fragmentation readily upon heating,[10] no effort, such as GC analysis, was made for the remaining oily portion of the reaction mixture.

In the present study we reexamined the same reaction in various solvents and found that 3-(2-cyclopropylvinyl)-cyclopentane-1,1,2,2-tetracarbonitrile (**3**: R^2 or R^3=*cyclo*-Pr) is produced as an oily product in addition to crystalline **2** (R^2 or R^3=*cyclo*-Pr). We realized that **3** is stable under GC conditions; it was therefore purified by preparative GC. As expected, **2** (R^2 or R^3=*cyclo*-Pr) underwent fragmentation under GC conditions to give two molecules of cyclopropylmethylenemalononitrile (**11**). Although the GC peak of **2** (R^2 or R^3=*cyclo*-Pr) was not symmetric (a steep maximum with a relatively long tailing), the shape was reproducibly recorded during each analysis. It was therefore possible to analyze the reactions of **4** and **5** with GC.[11]

As summarized in Table 1, heating **4** and TCNE in acetonitrile for 30 h resulted in a 76% consumption of **4**; **2** and **3** were produced in 74 and 18% GC yields, respectively.[12] The recovered olefin was found to be a mixture of **4** and **5** in a 53:47 ratio. In a separate experiment, **2** was isolated in 62% yield as an 84:16 mixture of geometrical isomers,[13,14] whereas **3** was collected by preparative GC in 11% yield; it was found to be a 52:48 mix-

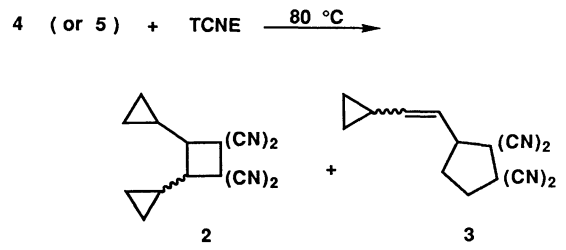
Table 1. Reactions of Cyclopropylethylenes with TCNE at 80 °C

Substrate	Solvent (Time[a])/h)	Conversion %	Recov. olefin *c* : *t*	Yield of product[b])/% **2** (*c* : *t*)[c]	**3** (*c* : *t*)[c]
4[d]	A (30)	76	53 : 47	74 (4 : 1)[e,f]	18 (2 : 1)[g,f]
	D (48)	74	99 : 1	16 (9 : 1)[e]	82 (24 : 1)[g]
	B(168)	55	99 : 1	4 (s)[e]	62 (s)[g]
	C(960)	73	98 : 2	4 (s)[e]	43 (16 : 1)[g]
5[d]	A (48)	81	12 : 88	45 (1 : 9)[e,f]	44 (1 : 32)[g,f]
	D (48)	82	5 : 95	—[h]	99 (s)[g]
	B(168)	71	2 : 98	—[h]	66 (s)[g]
	C(960)	76	2 : 98	3 (s)[e]	45 (s)[g]
6[d]	A (27)	77	27 : 73	65 (6 : 4)[i]	—[h]
	D(144)	78	—[j]	63 (4 : 1)[i]	2 (s)[g]
	B(912)	48	—[j]	31 (s)[i]	5 (s)[g]
7[d]	A (48)	86	20 : 80	67 (3 : 7)[i]	<1 (s)[g]
	D(132)	82	—[j]	47 (s)[i]	3 (s)[g]
	B(864)	62	—[j]	25 (s)[i]	10 (s)[g]
8	A (8)	83		65	—[h]
	D (90)	81		69	—[h]
	B(912)	57		—[k]	—[h]
9[d]	A(648)	55	99 : 1	—[l]	4 (s)[g]
	D(600)	66	—[j]	—[l]	10 (s)[g]
10[d]	D(648)	58	—[j]	—[l]	7 (s)[g]
12[m]	A (2)	87		76[n]	6
	D (2)	81		17	65
	B (18)	85		—[h]	68

a) A=acetonitrile, D=1,2-dichloroethane, B=benzene, and C=carbon tetrachloride. Reaction time is given in h. b) In the reactions of **4** and **5**, yields of **2** and **3** were determined by GC analysis, whereas yields in the reactions of **6**—**10** were based on the amount of the adduct isolated. c) An abbreviation "s" refers to stereochemically practically single (>99 : <1) on either HPLC or GC analysis. d) More than 99% isomerically pure. e) Based on the HPLC analysis. f) In the text, the ratio of isomers (500 MHz ^{1}H NMR) observed in isolation experiments is given.[13] g) Analyzed by GC. h) Undetectable either by HPLC or by GC. i) By 100 MHz ^{1}H NMR. j) On the GC analysis with an $AgNO_3$-glycerol column, the peak of the olefin overlapped badly with the solvent peak so that no reliable figure could be obtained. k) See the text. l) No characterizable material corresponding to **2** was isolated although the yield of **3** was relatively low. m) A mixture of stereoisomers in a 6 : 4 ratio. n) See the experimental section.

ture of isomeric **3** possessing a *cis*- and a *trans*-2-cyclopropylvinyl side chain.

In 1,2-dichloroethane (48 h at 80 °C), **3** was found to be the major product (82%) accompanied by **2** (16%). Both **2** and **3** obtained in this solvent were more rich in the cis isomer (9:1 and 24:1, respectively) than those obtained in acetonitrile. In benzene, the reaction was found to proceed slowly to give 4% of **2** and 62% of **3**,[15] which were practically free from contamination of the corresponding trans isomer. The recovered **4** was also not contaminated by **5**. Since TCNE was hardly soluble in carbon tetrachloride, even at 80 °C, the reaction in this solvent was heterogeneous throughout; stereochemically, though, nearly single **2** and **3** were produced in 4 and 43% yields, respectively, after 40 d at 80 °C (73% conversion).[15]



The trans isomer **5** behaved similarly to **4**, except for the fact that the production of **3** was more prominent than that observed in the reaction of **4**. Thus, after 48 h at 80 °C in acetonitrile (81% conversion), **2** and **3** were produced in 45 and 44% yields, respectively. In a separate experiment, a 38% yield of **2** (*cis*:*trans*=20:80)[13,16] and 30% of **3** (*cis*:*trans*=4:96) was isolated; the recovered olefin was found to be a mixture of **4** and **5** (see Table 1). GC analysis of the product mixture obtained in the reaction of **5** in 1,2-dichloroethane indicated that **2** was practically absent, and quantitatively produced **3** was free from the corresponding geometrical isomer. Similarly, *trans*-**3** (66%) was the sole detectable adduct produced in benzene. In a reaction in carbon tetrachloride, although a small amount of **2** (ca. 3% yield) was detected, the major product was pure *trans*-**3** (45% yield).[15]

Reactions of Other Cyclopropylethylenes. Since the type-II process is observed to occur even in reactions of disubstituted **4** and **5**, we were interested in examining the reactions of **6**, **7**, **9**, and **10**, as well as **8**. In acetonitrile, although both **6** and **7** produced practically no **3**, a small amount (2—10%) of **3** (R^2 or R^3=Me) was found in the product mixtures obtained in 1,2-dichloroethane or in benzene. In contrast to the reactions of **4** and **5**, however, **2** (R^2 or R^3=Me) remained the major product (25—31%), even in benzene.[15] The stereochemical results (Table 1) were similar to those observed in the reactions of **4** and **5**.

The reaction of parent **8** proceeded nicely in acetonitrile to give **2** (R^1=R^2=R^3=H) in 65% yield after 8 h at 80 °C (83% conversion). In 1,2-dichloroethane, the reaction proceeded much more slowly to give **2** (69% yield), which was not contaminated by **3** (GC). In a reaction in benzene (38 d at 80 °C; 57% conversion), no **2** could be isolated, although its production was suggested by observing the signals of fragments on the ^{1}H NMR analysis of the product mixture.[15] It should be noted, however, that no peak corresponding to **3** was observed in the GC analysis. Apparently, the type-II process is totally unimportant in the reaction of **8**.

The reactivities of **9** and **10** were much lower than those of **4**—**8** and, hence, a prolonged reaction time was required. We failed to isolate **2** in these reactions, probably because of the thermal instability of **2**; however, a small amount of **3** (R^2 or R^3=*i*-Pr or *t*-Bu; 4—10% yield) was unambiguously produced, as indicated by a GC analysis.[15]

Reaction of 2,3-Dicyclopropyl-2-butene. Since it appears that **4** and **5** are somewhat exceptional among the substrates examined for undergoing a preferential type-II reaction, it is of interest to investigate the reaction of a tetrasubstituted ethylene which maintains a substitution pattern similar to that of **4** or **5**. Accordingly, we studied the reaction of 2,3-dicylopropyl-2-butene (**12**). Although this olefin was readily prepared by a McMurry coupling[17] of cyclopropyl methyl ketone, the separation of stereoisomers was unsuccessful in all attempts. Thus, a 6:4 mixture of the stereoisomers was unavoidably used in the present study. The olefin **12** reacted smoothly with TCNE in acetonitrile to give a 76% yield of **2** and 6% yield of **3** after 2 h at 80 °C (87% conversion). In 1,2-dichloroethane, **12** gave **2** in 17% yield and **3** in 65% yield. We anticipated that tetrasubstituted **12** would give **3** in an amount larger than that produced in the reaction of **4** or **5**; actually, though, **12** produced a somewhat smaller amount of **3**. The calculated yields of **2** and **3** to be produced in the reaction of a 4:6 mixture of **4** and **5** are 57 and 32% in acetonitrile and 6 and 91% in 1,2-dichloroethane, respectively.

The aforementioned results indicate that **4** and **5** are two particular substrates prone to undergo a type-II reaction. In the reactions of 1-cyclopropyl-1-alkenes only a limited amount of **3** is produced, even in a solvent of low polarity. From steric grounds, **4** and **5** should be intermediate between **6**—**7** and **9**—**10**. Therefore, it can be concluded that the steric hindrance around the π bond is not the major factor for the relative importance of the type-II process. The present results might perhaps be rationalized in a way similar to that proposed in previous cases,[2-4,18] since **4** and **5** (IP^V=8.4 eV, E_p^{ox} vs. SCE=1.5 V[19]) can be oxidized more readily than **6**, **7** (IP^V=8.9 eV, E_p^{ox} vs. SCE=1.7 V) or **8** (IP^V=9.3 eV,[20] E_p^{ox} vs. SCE=2.1 V). However, the thermal SET, even in the case of **4** or **5**, is expected to be highly endothermic.[21] If we grant that the previous scheme for the formation of **3** can be applied in the present cases, we must therefore assume that the cation radical, which is produced only in

a very minute amount, is extremely prone to be attacked by a nearly TCNE anion radical. Since it is known that the cyclopropane to be cleaved in a nucleophilic attack should be substituted by appropriate activating groups, preferably by two electron-withdrawing groups in a geminal manner,[22] the cyclopropyl group in the present type-II reaction should be activated by some means. Although activation of the cyclopropyl group in the transformation of **1** to $\mathbf{1}^{\ddagger}$ and the anticipated nucleophilicity of the TCNE anion radical may make the ring cleavage probable, the highly endothermic nature of the SET process requires further consideration. A mechanistic justification must, therefore, await additional investigations.

It was unfortunate that considerable isomerization of the starting olefin took place, particularly in acetonitrile. However, the isomerization was less significant in 1,2-dichloroethane and practically absent in benzene; the **2** and **3** produced in benzene were nearly, or totally, free from contamination of the stereoisomer. From these results it may be concluded that both the type-I and type-II cycloadditions are stereospecific, at least in a solvent of low polarity. The extensive isomerization of the starting olefin observed in acetonitrile may be due to the reversibility of the type-I cycloaddition.[23]

In conclusion, it is demonstrated that both the type-I and type-II reactions may be the two principal modes of the reaction of **1** with TCNE. In the reaction of 1,1-disubstituted substrates, the type-I process is so facile[2,3] that the type-II process can hardly compete with it. However, when the type-I reactivity of the substrate is relatively low, as in **4**—**7** and **9** and **10**, the type-II process gains significance to a certain extent. The fact that the type-II process is somewhat less prominent in the reaction of **12** than those of **4**/**5** might be rationalized on the basis that the intermediate for the type-I process produced in the reaction of **12** holds the tertiary carbocationic center, whereas that yielded in the reaction of **4**/**5** merely has a secondary carbocationic portion. The type-I process is therefore somewhat more facilitated in the reaction of **12**.

Experimental

General Methods. IR spectra were recorded on a Hitachi 270-30 spectrophotometer. ^{1}H NMR spectra were recorded on either a JEOL FX-100, JEOL GX-270, JEOL FX-500, or Hitachi R-600 NMR spectrometer and are reported in parts per million downfield of internal tetramethylsilane. Mass spectra were taken on a JEOL LMS-D300 mass spectrometer. GC analyses were carried out with Hitachi 063 and 163 gas chromatographs with a column packed by APL 15% on Celite 545, 2m, and with temperature programing from 80 to 220 °C, unless otherwise specified. In analyses of stereoisomeric olefins, an $AgNO_3$–glycerol column was used. HPLC analyses were performed with Hitachi 635 and 655 liquid chromatographs with a μ-Polasil column. A mixture of hexane–ether (2:1) was used as an eluant and a UV detector was set at 215 nm. E^{ox} were obtained in the same manner as reported previously.[4b] IP^V were obtained from the UPS spectra, which were recorded on a VG ADES400 photoelectron spectrometer with a He(I) resonance lamp. The resolution was 34 meV for the Ar(^{3}P) signal. Elemental analyses were performed at the Center for Instrumental Analysis of Hokkaido University. The melting and boiling points are uncorrected.

Substrates. Olefins rich in the cis isomer were prepared by the Wittig reaction.[6] The cis/trans ratios observed in the preparation of **4**,[6] **6**,[7] **9**, and **10** were 86/14, 73/27, 90/10, and >99/<1, respectively. Stereochemically pure substrates (> 99%) were obtained with preparative GC. Trans olefins **5**[6] and **7**[7] were alternatively prepared by the addition of dibromocarbene to 1-cyclopropyl-1,3-butadiene[10b,24] or 1,3-pentadiene, both rich in the trans isomer, followed by reduction with sodium in ethanol.[9] As in the reactions with the Seyferth's reagent, however, an addition of dibromocarbene to the 1-substituted-1,3-butadiene under the phase-transfer reaction conditions was not as regioselective as that observed in the addition of fluorenylidene to 1-cyclopropyl-1,3-butadiene.[7] Accordingly, the overall yields of **5** and **7** were relatively low. Vinylcyclopropane (**8**) was prepared by following procedures reported previously.[9]

***cis*-1-Cyclopropyl-3,3-dimethyl-1-butene (10).** In a 500 ml three-necked flask fitted with a mechanical stirrer and a reflux condenser, 20.2 g (110 mmol) of sodium bis(trimethylsilyl)amide in 200 ml of THF was placed. Under a nitrogen atmosphere, 43.7 g (110 mmol) of (cyclopropylmethyl)triphenylphosphonium bromide[6] was added; the mixture was refluxed for 1 h. A resulting orange suspension was cooled to −78 °C, and then 9.5 g (110 mmol) of 2,2-dimethylpropanal was slowly added with a syringe. The mixture was stirred at −78 °C for 1 h, and then at room temperature for 12 h. To the resultant mixture, 200 ml of water was added and organic material was extracted with 5 portions of pentane (100 ml). The combined pentane solution was washed with dilute hydrochloric acid, aqueous sodium hydrogencarbonate, and water, and dried over anhydrous sodium sulfate. An oily residue obtained by evaporation of the solvent was distilled to give a fraction boiled at 55—85 °C at 150 Torr (15.1 g; 1 Torr=101, 325/760 Pa), which was found to contain 10.0 g (74%) of *cis*-**10** (GC); *trans*-**10** was not detected. Rectification of the fraction gave pure *cis*-**10** (7.1 g, 53% yield); Bp 130—134 °C; IR (liquid film) 3088, 3008, 2960, 1660 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ=5.27 (d, 1H, J=12 Hz), 4.53 (dd, 1H, J=12, 10 Hz), 1.90—1.57 (m, 1H), 1.17 (s, 9H), 0.83—0.54 (m, 2H), 0.50—0.03 (m, 2H); MS (70 eV) m/z (rel intensity) 124 (M^+, 33), 67 (100). Anal. (C_9H_{16}) C, H.

***cis*-1-Cyclopropyl-3-methyl-1-butene (9).** In a similar manner, **9**, which was contaminated by 10% of the trans isomer, was obtained in 62% yield. Pure **9** was obtained by preparative GC followed by distillation: Bp 116—117 °C; IR (liquid film) 3088, 3008, 2960, 2872, 1655 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ= 5.14 (dd, 1H, J=9, 11 Hz), 4.61 (dd, 1H, J=9, 11 Hz), 2.93—2.57 (m, 1H), 1.72—1.37 (m, 1H), 1.00 (d, 6H, J=6.5 Hz), 0.80—0.21 (m, 4H); MS (70 eV) m/z (rel intensity) 110 (M^+, 33), 43 (100). Anal. (C_8H_{14}) C, H.

2,3-Dicyclopropyl-2-butene (12). A McMurry coupling of cyclopropyl methyl ketone with a low valent titanium reagent prepared from titanium trichloride and metallic magnesium[25] gave **12** in 17% yield. Separation of geometrical isomers by means of GC was unsuccessful in all attempts. Accordingly, the mixture was used in the following investigations: Bp 75—

80 °C at 17 Torr; IR (liquid film) 3084, 3004, 2920, 1650, 1600 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ=2.2—1.5 (m, 2H), 1.52 (s, 3.6H), 1.39 (s, 2.4H), 0.9—0.3 (m, 8H). Anal. ($C_{10}H_{16}$) C, H.

GC Analyses of the Reactions. The relative reactivities of **4**—**10** with TCNE under given conditions were determined by following the consumption of the starting olefin at appropriate time intervals. The time required for the half-consumption of the olefin in 1,2-dichloroethane at 80 °C was: **4**: 18 h, **5**: 10 h, **6**: 32 h, **7**: 32 h, **8**: 32 h, **9**: 168 h, and **10**: 312 h. The reactions of **4** and **5**, but not those of others, with TCNE were analyzed directly by GC (see Table 1).[11]

Reaction of 4 with TCNE in Acetonitrile. A reddish violet solution obtained on mixing of **4** (108 mg, 1.0 mmol) with TCNE (135 mg, 1.06 mmol) in acetonitrile (10 ml, containing 56 mg of octane as an internal standard) was degassed and sealed in a tube. After being heated at 80 °C for 48 h, the tube was opened (the consumption of **4** being 83% and recovered olefin being a mixture of **4** and **5** in a 41 : 59 ratio). The solution was then concentrated and a residue (230 mg) was subjected to column chromatography with silica gel (40 g). Elution of the column with chloroform gave a white solid (159 mg), which was recrystallized from cyclohexane to give colorless needles (121 mg, 62%) as a mixture of *cis*-**2** and *trans*-**2** in a ratio of 84 : 16. Repeated recrystallizations from cyclohexane gave an analytically pure *cis*-**2** (R^2=*cyclo*-Pr, R^1=R^3=H), mp 156—158 °C (lit,[2] mp 165—167 °C). Since the mp of the adduct differed significantly from that reported previously, the product was subjected to a precise analysis. IR (KBr disc) 3092, 3016, 2250 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ=2.66—2.42 (AA′XX′, 2H, J_{AA}=9, J_{AX}=11, J_{AX}=0.3 Hz), 1.49—1.20 (m, 2H), 1.10—0.70 (m, 4H), 0.56—0.28 (m, 4H); MS (70 eV) *m*/*z* (rel intensity) 236 (M^+, 0.2), 91 (100). Anal. ($C_{14}H_{12}N_4$) C, H, N.

A yellow oil obtained in the concentration of mother liquors of the recrystallizations (42 mg) was analyzed by GC and found to be a mixture of two components. These were collected by preparative GC to give 21 mg (11%) of a 52 : 48 mixture of *cis*-**3** and *trans*-**3**. Each isomer was purified by repeated GC collections. *cis*-**3** (R^2=*cyclo*-Pr, R^1=R^3=H): Oil; IR (liquid film) 3012, 2250, 1656 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=5.36—5.26 (AA′XX′, 2H, $J_{AA'}$=11, J_{AX}=9, J_{AX}=0.7), 4.06 (ddd, 1H, *J*=9, 7, 4 Hz), 2.92 (ddd, 1H, *J*=14.5, 9, 6 Hz), 2.83 (ddd, *J*=14.5, 10.5, 6 Hz), 2.54 (dddd, 1H, *J*=17, 9, 6, 7 Hz), 2.12 (dddd, 1H, *J*=17, 10.5, 6, 9 Hz), 1.65—1.53 (m, 1H), 1.02—0.86 (m, 2H), 0.63—0.46 (m, 2H); MS (70 eV) *m*/*z* (rel intensity) 236 (M^+, 39), 93 (100). Anal. ($C_{14}H_{12}N_4$) C, H, N. *trans*-**3** (R^3=*cyclo*-Pr, R^1=R^2=H): Oil; IR (liquid film) 3012, 2250, 1664, 968 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ=5.57—5.42 (AA′XX′, 2H, J_{AA}=16, J_{AX}=7, J_{AX}=0.7), 3.45 (ddd, 1H, *J*=9, 7, 4.5 Hz), 2.89 (ddd, 1H, *J*=14.5, 9, 6 Hz), 2.78 (ddd, 1H, *J*=14.5, 10.5, 6 Hz), 2.44 (dddd, 1H, *J*=18, 9, 6, 4.5 Hz), 2.15 (dddd, 1H, *J*=18, 10.5, 6, 9 Hz), 1.56—1.44 (m, 1H), 0.92—0.80 (m, 2H), 0.55—0.44 (m, 2H); MS (70 eV) *m*/*z* (rel intensity) 236 (M^+, 29), 93 (100). Anal. ($C_{14}H_{12}N_4$) C, H, N.

Reaction of 5 with TCNE in Acetonitrile. A reddish purple solution of **5** (109 mg, 1.01 mmol), TCNE (132 mg, 1.03 mmol), and octane (54 mg, as an internal standard) in acetonitrile (10 mL) was degassed in a tube and heated at 80 °C for 48 h. The consumption of **5** was 86%; recovered olefin was a mixture of **4** and **5** in a 12 : 88 ratio. After concentrating the resultant brown solution, a residue (254 mg) was subjected to column chromatography with silica gel (40 g). Elution of the column with chloroform gave adduct fractions comprising a white solid and a liquid (178 mg). Recrystallization of the solid from cyclohexane gave colorless needles (77 mg, 38% yield), mp 143—153 °C, which were a mixture of *cis*-**2** and *trans*-**2** in a 20 : 80 ratio. Repeated recrystallizations of the needles from cyclohexane gave analytically pure *trans*-**2** (R^3=*cyclo*-Pr, R^1=R^2=H): Mp 153—155 °C (lit,[2] mp 159—160.5 °C); IR (KBr disc) 3100, 3012, 2250 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ=2.53—2.27 (AA′XX′, 2H, J_{AA}=11, J_{AX}=9, J_{AX}=0.4 Hz), 1.25—0.74 (m, 6H), 0.66—0.43 (m, 4H); MS (70 eV) *m*/*z* (rel intensity) 236 (M^+, 0.1), 91 (100). Anal. ($C_{14}H_{12}N_4$) C, H, N. From the oily portion of the product, 61 mg (30%) of **3** (cis : trans=4 : 96) was obtained.

Reaction of 5 in 1,2-Dichloroethane. The reaction produced *trans*-**3** quantitatively (Table 1). When the reaction (108 mg, 1.00 mmol, of **5**, 132 mg, 1.03 mmol of TCNE, and 57 mg of octane in 10 ml of the solvent) was carried out in the presence of methanol (325 mg, 10 equivalent), **3** (cis : trans=4 : 96) was produced in 64% GC yield (46% by isolation). In no fraction on the silica-gel column chromatography was the MeO signal observed by ^{1}H NMR spectroscopy.

Reaction of 6. In acetonitrile (15 ml, containing 102 mg of heptane as an internal standard), the reaction of **6** (123 mg, 1.50 mmol) with TCNE (198 mg, 1.55 mmol) at 80 °C for 27 h (77% conversion; recovered olefin being a mixture of **6** and **7** in a 27 : 73 ratio) gave a geometrical mixture of **2** (cis : trans=6 : 4, 158 mg, 65%). In 1,2-dichloroethane at 80 °C for 144 h (78% conversion), the same reaction produced **2** (cis : trans=4 : 1, 155 mg, 63%) and **3** (5 mg, 2%). From this product mixture, *cis*-**2** (R^2=Me, R^1=R^3=H) was isolated by repeated recrystallization: Mp 156—157 °C; IR (KBr disc) 3008, 2250 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ=3.40 (dq, 1H, *J*=9.1, 7.2 Hz), 2.54 (dd, 1H, *J*=10.6, 9.1 Hz), 1.63 (d, 3H, *J*=7.2 Hz), 1.87—1.10 (m, 1H), 0.97—0.33 (m, 4H); MS (70 eV) *m*/*z* (rel intensity) 210 (M^+, 0.15), 67 (100). Anal. ($C_{12}H_{10}N_4$) C, H, N.

In the reaction in benzene at 80 °C for 912 h (48% conversion), 47 mg (31%) of *cis*-**2**, mp 155.0—156.5 °C, and 7 mg (5%) of **3** were isolated. The type-I adduct was not contaminated by *trans*-**2** (100 MHz ^{1}H NMR) in this case. From the combined oily products, *cis*-**3** (R^2=Me, R^1=R^3=H) was isolated by preparative GC: Oil; IR (liquid film) 3028, 2952, 2250, 1662 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ=6.09 (dq, 1H, *J*=10.7, 7.1 Hz), 5.57 (ddq, 1H, *J*=9.3, 10.7, 1.8 Hz), 3.94 (q, 1H, *J*=9.3 Hz), 2.97—2.78 (m, 2H), 2.70—1.95 (m, 2H), 1.85 (dd, 3H, *J*=7.1, 1.8 Hz); MS (70 eV) *m*/*z* (rel intensity) 210 (M^+, 5.4), 67 (100). Anal. ($C_{12}H_{10}N_4$) C, H, N.

Reaction of 7. In a similar manner (see Table 1 for the reaction conditions), the reaction of **7** (124 mg, 1.51 mmol) with TCNE (200 mg, 1.56 mmol) in acetonitrile (15 ml) gave colorless needles (181 mg, 67%), which were a 3 : 7 mixture of *cis*-**2** and *trans*-**2**, and oily **3** (3 mg, 1%). In 1,2-dichloroethane, practically pure *trans*-**2** (120 mg, 47%) was obtained in addition to oily **3** (8 mg, 3%). *trans*-**2** (R^3=Me, R^1=R^2=H): Mp 113—115 °C; IR (KBr disc) 3012, 2980, 2250 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ=3.24 (dq, 1H, *J*=11, 6.4 Hz), 2.17 (dd, 1H, *J*=11, 9.3 Hz), 1.51 (d, 3H, *J*=6.4 Hz), 1.38—1.15 (m, 1H), 1.11—0.38 (m, 4H); MS (70 eV) *m*/*z* (rel intensity) 210 (M^+, 0.14), 67 (100). Anal. ($C_{12}H_{10}N_4$) C, H, N.

The reaction in benzene gave 49 mg (25%) of *trans*-**2** and 20 mg (10%) of **3**, from the latter, pure *trans*-**3** (R^3=Me, R^1=R^2=H) was obtained: Oil; IR (liquid film) 2968, 2250, 1672, 968 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ=6.05 (dq, 1H, *J*=15,

6.4 Hz), 5.50 (dd, 1H, J=15, 7.9 Hz), 3.47 (dt, 1H, J=10, 8.6 Hz), 3.01—2.76 (m, 2H), 2.67—2.00 (m, 2H), 1.85 (d, 3H, J=6.4 Hz); MS (70 eV) m/z (rel intensity) 210 (M^+, 4.3), 67 (100). Anal. ($C_{12}H_{10}N_4$) C, H, N.

Reaction of 8. In degassed acetonitrile (20 ml), a mixture of **8** (136 mg, 2.00 mmol), TCNE (264 mg, 2.06 mmol), and octane (130 mg) was heated at 80 °C for 8 h (83% conversion) in an ampoule. From the reaction mixture, **2** (R^1=R^2=R^3=H; 211 mg, 65%), mp 123.5—124.5 °C (lit,[2] mp 124—125 °C), was obtained as colorless plates. Similarly, **2** was obtained in 69% yield in 1,2-dichloroethane (80 °C for 90 h; 81% conversion). In a reaction in benzene (912 h at 80 °C; 57% conversion), **2** did not crystallize out after a work-up as mentioned above. ^{1}H NMR analyses of fractions obtained on silica-gel column chromatography indicated the occurrence of fragmentation. In no case was the formation of **3** indicated by GC analyses.

Reaction of 9. A mixture of **9** (110 mg, 1.00 mmol), TCNE (134 mg, 1.05 mmol), and octane (103 mg) in degassed acetonitrile (10 ml) was heated in an ampoule for 648 h (45% conversion). Work-up of the reaction mixture (as mentioned above) gave an oily product (30 mg), from which oily **3** (4 mg, 4%) was obtained by preparative GC. The same reaction in 1,2-dichloroethane (66% conversion) gave 16 mg (10%) of *cis*-**3** (R^2=*i*-Pr, R^1=R^3=H): Oil; IR (liquid film) 3012, 2964, 2872, 2252, 1660 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=5.79 (t, 1H, J=11 Hz), 5.29 (t, 1H, J=11 Hz), 3.86 (q, 1H, J=10 Hz), 2.90 (ddd, 1H, J=15, 9, 5 Hz), 2.82 (ddd, 1H, J=15, 11, 6 Hz), 2.63 (dq, 1H, J=17, 6 Hz), 2.45 (ddt, 1H, J=14, 6, 9 Hz), 2.14—2.06 (m, 1H), 1.11 (d, 3H, J=7 Hz), 1.02 (d, 3H, J=7 Hz); MS (70 eV) m/z (rel intensity) 238 (M^+, 4.9), 69 (100). Anal. ($C_{14}H_{14}N_4$) C, H, N. Most of the material in the reaction mixture did not elute out of the silica-gel column.

Reaction of 10. In acetonitrile, the reaction of **10** with TCNE did not proceed to a reasonable extent, even after 14 days at 80 °C. In 1,2-dichloroethane, 58% consumption of **10** was noted after 648 h at 80 °C. From the reaction mixture (124 mg, 1.00 mmol, of **10** and 132 mg, 1.03 mmol, of TCNE in 10 ml of the solvent), 35 mg of an oil was isolated after the work-up mentioned above. The oil comprised 4 products (GC), from which *cis*-**3** (R^2=*t*-Bu, R^1=R^3=H; 10 mg, 7% yield) was isolated: Oil; IR (liquid film) 2964, 2872, 2252, 1660 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ=5.91, (d, 1H, J=12 Hz,)5.23 (dd, 1H, J=12, 10 Hz), 4.22 (dt, 1H, J=9, 10 Hz), 2.94—2.76 (m, 2H), 2.67—1.98 (m, 2H), 1.20 (s, 9H); MS (70 eV) m/z (rel intensity) 252 (M^+, 1.7), 41 (100). HRMS Calcd for $C_{15}H_{16}N_4$: M, 252.1375. Found: m/z 252.1356.

Reaction of 12. A mixture of **12** (136 mg, 1.00 mmol), TCNE (132 mg, 1.03 mmol), and dodecane (60 mg) in acetonitrile (10 ml) was heated at 80 °C under a nitrogen atmosphere. After 2 h, 87% consumption of **12** was noted by GC analysis. Concentration of the reaction mixture gave a brown oil (270 mg), which was subjected to silica-gel colume chromatography (20 g). Elution of the column with benzene gave a white solid and a pale yellow oil (total of 188 mg). The solid was recrystallized from 99% ethanol to give colorless needles (158 mg, 69%), mp 130—135 °C, which was assigned to be **2** (R^1 and R^2 or R^3=Me, R^2 or R^3=*cyclo*-Pr): IR (KBr disc) 3012, 2250 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ=1.9—1.35 (m, 2H), 1.26 (s, 3.4H), 1.09 (s, 2.6H), 0.9—0.3 (m, 8H); MS (70 eV) m/z (rel intensity) 264 (M^+, 0.4), 105 (100). Anal. ($C_{16}H_{16}N_4$) C, H, N. The oily portion obtained in the column chromatography comprised mostly **2** (60 MHz ^{1}H NMR; **2**:**3**=93:7), and hence the total yield of **2** was calculated to be 76%. Concentrated mother liquors of the recrystallization gave an oil, from which **3** (R^1 and R^2 or R^3=Me, R^2 or R^3=*cyclo*-Pr; 13 mg, 6% yield) was isolated.

The reaction in 1,2-dichloroethane (2 h at 80 °C, 81% conversion) gave **2** in 17% and **3** in 65% yield, respectively. In the reaction in benzene (18 h at 80 °C; 85% conversion), 60 MHz ^{1}H NMR spectral analysis of the adduct fraction revealed no formation of **2**. An oily product obtained in silica-gel column chromatography was found to be **3** (68% yield). Repeated preparative GC of the products allowed isomeric **3** to be separated, although stereochemical assignments were not accomplished:

3-I: Oil; IR (liquid film) 3088, 3008, 2260, 1630 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ=4.77 (t, 1H, J=9 Hz), 2.95—2.78 (m, 2H), 2.48—2.23 (m, 2H), 2.0—1.4 (m, 1H), 1.85 (s, 3H), 1.60 (s, 3H), 0.90—0.50 (m, 4H); MS (70 eV) m/z (rel intensity) 264 (M^+, 39), 121 (100). Anal. ($C_{16}H_{16}N_4$) C, H, N.

3-II: Oil; IR (liquid film) 3088, 3004, 2260, 1632 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ=4.28 (t, 1H, J=9 Hz), 2.94—2.78 (m, 2H), 2.49—2.17 (m, 2H), 2.1—1.5 (m, 1H), 2.00 (s, 3H), 1.58 (s, 3H), 0.90—0.50 (m, 4H); MS (70 eV) m/z (rel intensity) 264 (M^+, 49), 121 (100). Anal. ($C_{16}H_{16}N_4$) C, H, N.

Fragmentation of 2. Since **2** is known to decompose during a GC analysis,[10] the decomposed material of **2** (R^1=R^3=H, R^2=*cyclo*-Pr and R^1=R^2=H, R^3=*cyclo*-Pr) was collected. From 25.0 mg (0.11 mmol) of *cis*-**2**, 20.4 mg (82%) of colorless liquid was obtained, which was found to be **11**: Oil; IR (liquid film) 3032, 2232, 1600 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ=6.63 (d, 1H, J=11 Hz), 2.35—1.99 (m, 1H), 1.57—0.96 (m, 4H); MS (70 eV) m/z (rel intensity) 118 (M^+, 27), 91 (100). Anal. ($C_7H_6N_2$) C, H, N. Similarly, *trans*-**2** gave **11** in 71% yield.

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12) The yield given hereafter is based on the consumed amount of the starting olefin.

13) Based on the ^{1}H NMR analysis of a fraction containing **2** obtained in the column chromatography. The figure determined by HPLC was somewhat low in accuracy, because **2** lacked a chromophore suitable for the HPLC analysis. In some cases, the ratio of the stereoisomers in **3** was also determined by ^{1}H NMR.

14) Previously, *cis*-**2** was obtained in 25% yield after repeated recrystallizations.[2)]

15) Whereas **3** was thermally stable, **2** decomposed gradually on prolonged heating.

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