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Cycloaddition Reaction of Some Representative 1-Cyclopropyl-1,3-butadienes with Tetracyanoethylene and Reaction of the Resultant Vinylcyclobutanes. An Easy Vinylcyclobutane–Cyclohexene Rearrangement[1a,2]

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Abstract: In the reaction with TCNE, (*Z*)-1-cyclopropyl-1,3-butadiene (**1b**) as well as several 1,1-disubstituted 1,3-butadienes (**1c–f**) yielded vinylcyclobutane **2** as the major product particularly in a polar solvent, whereas the *E* isomer **1a** gave the cyclohexene **3** exclusively. The resultant vinylcyclobutanes, except for **2f,** isomerized easily to **3**. The most reactive of all was **2c** while **2b** was the least reactive. The isomerization of **2c** in acetonitrile in the presence of **1a** yielded virtually no cross product **3a,** supporting the intramolecular nature of the transformation. Since the intermediate was trapped by *p*-toluenethiol, the rearrangement will most probably be stepwise. The solvent effects and the substituent effects on the rate of the reaction indicate that the ionic mechanism is operating. In contrast, **2f** did not rearrange at all, but, especially at elevated temperatures, it split into the two fragments, i.e., methylenemalononitrile and **4f.** The lack of effect of solvent polarity on the rate suggests that the fragmentation would be a diradical stepwise process. In the reaction of other vinylcyclobutanes, also, the fragmentation became appreciable at elevated temperatures in solvents of low polarity. The extent of the fragmentation depends upon the substituent(s) at the terminal carbon of the vinyl group.

1,1-Disubstituted 1,3-butadienes are known to react with tetracyanoethylene (TCNE) preferentially in a [2 + 2] manner.[3] This is most probably due to the fact that the substituents sharply diminish the rate of the concerted [2 + 4] cycloaddition as the cisoid conformation of the diene[4] becomes difficult to attain. In contrast, however, we observed some time ago that 1,1-dicyclopropyl-1,3-butadiene (**1c**) produced a significant amount of the Diels–Alder adduct[5] in a polar solvent in a somewhat prolonged reaction time. Eventually, we unraveled the discrepancy by finding out that the primary product of the reaction was a vinylcyclobutane **2c,** but it easily isomerized to the cyclohexene **3c** under the reaction conditions.[2]

The vinylcyclobutane–cyclohexene rearrangement is known to occur at elevated temperatures and the diradical mechanism

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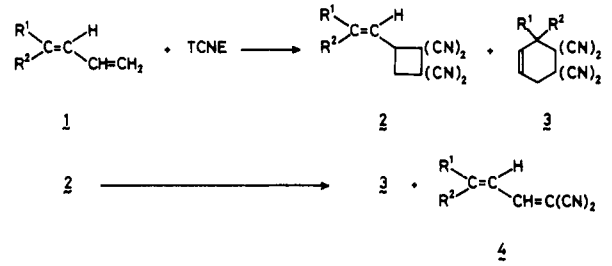
is proposed.[6] The aforementioned observations suggest, however, that an ionic pathway may also be feasible in such vinylcyclobutanes as those substituted by a cation stabilizing group at the terminal position of the vinyl group and two cyano groups at the ring carbon next to the one bearing the vinyl side chain. Eisch and Husk[3c] have indeed observed a slow transformation of 2,2,3,3-tetracyano-1-(2,2-diphenylvinyl)cyclobutane to the cyclohexene, but they have postulated a dissociation-recombination mechanism.[7] We carried out the reaction of some representative 1-cyclopropyl-1,3-butadienes (**1a–e**) with TCNE and demonstrated the intramolecular isomerization of the resultant vinylcyclobutanes (**2b–e**) to **3**.



1 **2** **3**

2 **3** **4**

a: R^1 = cyclo-C_3H_5, R^2 = H
b: R^1 = H, R^2 = cyclo-C_3H_5
c: $R^1 = R^2$ = cyclo-C_3H_5
d: R^1 = cyclo-C_3H_5, R^2 = CH_3
e: R^1 = CH_3, R^2 = cyclo-C_3H_5
f: $R^1 = R^2 = (CH_3)_2CH$
g: $R^1 = R^2 = CH_3$

As a result, the easy vinylcyclobutane-cyclohexene rearrangement was exemplified.

Results

Reactions of 1,3-Butadienes with TCNE. When **1a** was mixed with TCNE either in acetonitrile or in dichloromethane, the resultant color (red or blue) faded after 50–55 s at room temperature, and **3a** was produced exclusively.[8] The effect of the solvent polarity on the rate was small.[9] In contrast, the reaction of **1b** was completed after 90 min in acetonitrile or 270 min in dichloromethane at room temperature, and the major product was **2b. 3a** was also produced in a minor amount but the isomeric **2a** was not detected.

The diene substituted by the two cyclopropyl groups (**1c**) reacted rapidly. Thus, the developed purple color in dichloromethane faded within 1 s, and immediate workup gave **2c** free from **3c**. The same was also true in acetonitrile or tetrahydrofuran (THF). The reaction in benzene, however, yielded a mixture of **2c** and **3c** in 95:5 ratio. The control experiments indicated that the isomerization of **2c** to **3c** was very slow in benzene. In contrast to the reaction of **1b**, the reaction of **1e** as well as that of **1d** was not stereospecific; the vinylcyclobutane was contaminated by an appreciable amount of the geometrical isomer (Table I).[10] The sterically most hindered **1f**[11] produced only **2f** in all solvents examined. For the purpose of comparison, the reaction of **1g** was also studied. The time of decolorization allowed us to estimate the relative reactivity of the butadienes. All results are summarized in Table I. As to the solvent effect, the [2 + 2] cycloaddition proceeded more rapidly in acetonitrile than in either THF or dichloromethane with no exception.

Thermal Reactions of Vinylcyclobutanes. In polar solvents, **2c** easily isomerized to **3c** (several hours at room temperature in acetonitrile). The rearrangement in acetonitrile proceeded severalfold faster than that in chloroform-*d*. Similarly, a mixture of **2d** and **2e**[12] gave **3d** but their rates were slower than that of **2c** by a factor of 26 in chloroform-*d* at 61 °C. The isomerization of **2b** was still slower than that of **2d** or **2e** and hence some heat was applied to effect the reaction.

Table I. Reaction of 1,3-Butadiene with TCNE[a]

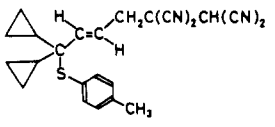
diene	solvent	product ratio 2	product ratio 3	rel rate for [2 + 2][b]
1a	CH_3CN		>99	
	CH_2Cl_2		>99	
1b	CH_3CN	97[c]	3	
	THF	95[c]	5	2
	CH_2Cl_2	94[c]	6	
	C_6H_6	77[c]	23	
1c	CH_3CN	>99		
	THF	>99		2000
	$(CH_2Cl)_2$	>99		
	C_6H_6	95	5	
1d	THF	95[d]	5	70
	C_6H_6	88[c]	12	
1e	THF	>99[e]		60
	C_6H_6	97[f]	3	
1f	any solvent[g]	>99		0.9
1g	THF	86	14	1.0
	C_6H_{12}	70	30	

[a] The isolated yield of the adducts was more than 80% in all cases. [b] In THF. [c] The geometrical isomer was practically absent. [d] A mixture of **2d** and **2e** in 97:3 ratio. [e] A mixture of **2d** and **2e** in 14:86 ratio. [f] A mixture of **2d** and **2e** in 5:95 ratio. [g] Benzene, cyclohexane, THF, 1,2-dichloroethane, or acetronitrile.

On the other hand, the rearrangement was totally absent in the thermal reaction of **2f.** At 100 °C *in acetronitrile,* it split into methylenemalononitrile and **4f.** The rate of the fragmentation was virtually independent of the solvent polarity effects: $k_1(CH_3CN):k_1(CDCl_3)$ = 1.05:1.0 at 115 °C. The fragmentation became appreciable in other vinylcyclobutanes as well when they were heated in the solvent of low polarity. For example, at 130 °C in chloroform, the ratio of **3**:**4** was 98:2 for **2c,** 78:22 for **2d,e,** and 39:61 for **2b.** The effect of the solvent polarity could be seen in the following ratio: **3**:**4** = 56:44 in THF, 39:61 in chloroform, and 28:72 in cyclohexane in the reaction of **2b** at 130 °C. The fragmentation of **2b** produced a ca. 1:1 mixture of **4a** and **4b.** Since the control experiments showed that the geometrical isomerization of **4b** to **4a** was slow, the isomerization occurred in the initial cyclobutane rather than in the product **4.** When the reaction was interrupted at ca. 20% conversion (7 h in $CDCl_3$ at 70 °C), the vinylcyclobutane was indeed found to be a mixture of **2a** and **2b** in ca. 1:1 ratio.

Rearrangement of 2c in the Presence of 1a. 2c was mixed with a large excess (five times molar excess) of **1a** and the reaction was allowed to proceed. In acetonitrile at 30 °C, the product isolated was virtually pure **3c.** On the other hand, **3c** was accompanied by **3a** in a considerable amount in chloroform (**3c**:**3a** = 70:30 at 30 °C and 27:73 at 130 °C). A reasonable amount of **1c** was also produced. Apparently, the cycloreversion took place in chloroform. Heating of the mixture of **3c** and **1a** in chloroform at 130 °C gave no **3a,** ruling out the possible retro-Diels–Alder reaction of **3c** to give **3a.**

Rearrangement of 2c in the Presence of *p*-Toluenethiol.[13] In chloroform, the reaction of **2c** was carried out in the presence of *p*-toluenethiol. The product isolated after 24 h was a 1:1 adduct, **5. 3c** was produced only in a small amount (3.6%).



5

The adduct **5** had the *E* configuration at the double bond (NMR coupling constant). In contrast, the reaction of **1c** with TCNE in the presence of the same thiol in THF at −30 °C resulted in the formation of **2c** (40%), 1,1,2,2-tetracyanoethane (39%), and *p*-toluene disulfide (50%). A similar result was obtained in the reaction in chloroform at room temperature. The cycloaddition of **1c** with TCNE proceeded as rapidly as the oxidation of thiol by TCNE.[14]

Discussion

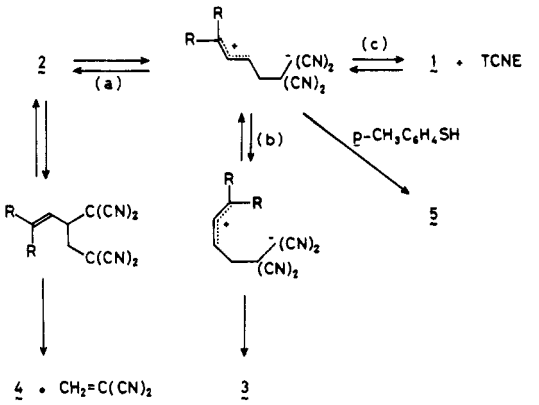
Cycloadditions. As expected, vinylcyclobutane formation is the major course of the reaction of all the dienes except for **1a.** In accordance with the arguments given by the previous workers.[3a,b] cyclohexene formation may be the concerted process whereas vinylcyclobutane formation will certainly be a stepwise ionic process. Since the control experiments proved that **3c** was not derived from **2c** in benzene, concomitant formation of **2c** and **3c** should be an outcome of the competing [2 + 2] and [2 + 4] cycloaddition. From the steric point of view, the cisoid conformation of the diene[4] will become difficult to attain in the following order: **1a** ≪ **1d** ≃ **1g** < **1b** ≃ **1c** ≃ **1e** < **1f.** The amount of **3** decreases as expected, but it should also be noted that the proportion of **3** in the adducts increases when the [2 + 2] cycloaddition becomes slow either because of the low solvent polarity or because of the less effective substitution at C-1 of the butadiene (Table I).

The lack of stereospecificity observed in the reactions of **1d** and **1e** supports the stepwise mechanism. The seemingly stereospecific cycloaddition observed in the reaction of **1b** may be due both to the relatively high energy barrier for the allylic isomerization and to the lifetime of the dipolar intermediate. The additional methyl group in the reaction of **1d** or **1e** will not only decrease the energy barrier[15] but it also will stabilize the intermediate so that it will last long enough to undergo the allylic isomerization to a considerable extent. As a support of the latter argument, it should be pointed out that the geometrical isomerization is more pronounced in THF than in benzene (Table I).[16]

Rearrangement. The transformation of **2** to **3** took place relatively easily, particularly in the polar solvent. The transformation will most probably be a stepwise rearrangement via dipolar intermediates.[17] The cycloreversion–recombination mechanism[3c] is unlikely since, in acetonitrile, no cross product was obtained in the rearrangement of **2c** in the presence of a large amount of **1a.** Under such conditions, **3a** should be produced if the cycloreversion of **2c** takes place. This is because the concentration of **1a** must be very high compared to that of **1c,** which will be produced only in the cycloreversion.[18] The preferred formation of **3a** can also be predicted on the basis of relative reactivities of **1a** and **1c** in the [2 + 4] cycloaddition. In chloroform, on the other hand, a substantial amount of **3a** is produced, indicating that the cycloreversion occurs in the solvent of low polarity. Huisgen and Steiner[3g] found that the TCNE cycloadditions to an enol ether and anethole were accompanied by a strong increase of the dipole moment. Since the same may be true for the reaction of **1c** with TCNE, the cycloaddition-reversion equilibrium must be shifted further to the adduct side in the more polar solvents. Therefore, the dissociation of the intermediate zwitterion to **1c** and TCNE gains in importance in going from acetronitrile to chloroform. The considerations of the relatively high reactivity of **1a** to **1c** in the [2 + 4] cycloaddition and the exceedingly high relative concentration of **1a** to **1c** suggest that **3c** produced in chloroform may not totally be the product of the cycloreversion–recombination as well. A possibility that TCNE is produced in the retro-Diels–Alder reaction of **3c** and the reaction of the resultant TCNE with **1a** gives **3a** is ruled out by the control experiments.

The first step of the rearrangement will be reversible,[19]

Scheme I



which is indicated by the partial isomerization of **2b** to **2a** during the reaction. The incipient zwitterion will have the *E* configuration, which is indeed trapped by *p*-toluenethiol. In order to form **3**, the geometrical isomerization at the allylic portion of this dipolar intermediate must be assumed. As to the ease of the isomerization in allyl cations, it has been demonstrated that alkyl substitution at the terminal carbons of the cation will greatly decrease the energy barrier for the isomerization.[15] In the present study, it was observed that a mixture of **2d** and **2e** was produced in the reaction of geometrically pure 1,3-diene with TCNE and isomerization of **2b** to **2a** took place during the rearrangement. Although these results are concerned with the relatively easy isomerization at the other end of the allyl cation, they allow us to assume that the isomerization required to accomplish the six-membered ring closure will also be feasible under the reaction conditions.[20]

The substituent effects at the terminal carbon of the vinyl group (**2c** > **2d,e** > **2b**) are also in accordance with the proposed mechanism. The substrate which produces the zwitterion with the lower rotational barrier and the longer lifetime will rearrange more rapidly. The relative importance of the three routes (a, b, and c) for the intermediate zwitterion will be a function of the effects of solvent polarity and the degree of substitution at the terminal carbon of the allylic cation.

Fragmentation. 2f does not rearrange at room temperature, but it splits into methylenemalononitrile and **4f** at 100 °C or higher even in acetonitrile. The heterolytic cleavage of the ring bond as discussed above may also occur, but the isomerization of the incipient intermediate to the cisoid allylic zwitterion and/or the cyclization to **3** will be sterically hindered.[11] Therefore, the recyclization back to **2** will take place and the energetically less feasible fragmentation sets in. The lack of solvent polarity effects on the rate suggests that the fragmentation is most likely a diradical process.

At elevated temperatures in a solvent of low polarity, fragmentation becomes an appreciable pathway even in other vinylcyclobutanes. For example, it was indeed the major course of the reaction for **2b** at 130 °C in cyclohexane (**3**:**4** = 28:72). Although the fragmentation of **2b** was nonstereospecific, the result is of little help in discussing the reaction mechanism because prior isomerization of **2b** to **2a** was observed. Since the homolytic fragmentation is in competition with the heterolytic rearrangement, the extent of the fragmentation in the overall reaction depends upon the degree of substitution by the cation stabilizing group at the side chain (**2b** > **2d,e** > **2c**) as well as the solvent polarity. Similar fragmentations are known to occur in related compounds.[21] The first step should be the homolytic cleavage of the ring bond connecting the two carbons bearing the cyano groups. This is supported by the observations that the resultant **4a–e** retain the cyclopropyl group(s).[22]

Experimental Section

General. IR spectra were recorded on a Hitachi Model 215 grating

spectrophotometer. UV spectra were taken on a Cary Model 17 spectrophotometer. NMR spectra were obtained with a JEOL PS-100 spectrometer; chemical shifts are given in parts per million from Me_4Si. Mass spectra were recorded on a Hitachi Model RMU-6E spectrometer (70–80 eV); ions of each spectrum were normalized to the most intense ion set equal to 100, and the relative intensities are given parentheses. GC work was done on a Hitachi Type 063 gas chromatograph. Microanalyses were carried out by the Microanalytical Laboratory, Faculty of Pharmaceutical Science, Hokkaido University. Melting points and boiling points are uncorrected.

Materials. Tetracyanoethylene was purified by recrystallization followed by sublimation before use.[23] 1-Cyclopropyl-1,3-butadiene[8,24] rich in **1a** (9:1) was obtained in the dehydrobromination of 4-bromo-1-cyclopropyl-1-butene[8] with potassium *tert*-butoxide. A diene mixture rich in **1b** (8:2) was prepared from (cyclopropylmethyl)triphenylphosphonium bromide[25] and 2-propenal at −70 °C in THF with sodium bis(trimethylsilyl)amide as the base.[26] Since **1a** reacted with TCNE in 1 min whereas **1b** took 4.5 h, most of **1a** was removed by treatment with an appropriate amount of TCNE in dichloromethane followed by column chromatography (silica gel). **1c**[10,27] (boiling point, IR, and NMR were the same as those given in the literature[27]) and a mixture of **1d** and **1e**[20,28] were prepared by the Wittig reactions (allyltriphenylphosphorane with cyclopropyl ketones, 49 and 28% yield, respectively). Separation of the geometrical isomers and purification of the sample were carried out by means of preparative GC (1,2,3-tris(2-cyanoethoxy)propane on Celite 545, 20%, 4 m, 60 °C for **1a** and **1b** and 80 °C for **1d** and **1e**).[24] The geometrically pure dienes gave the following data.

1a:[8,24,29] bp 107–109 °C (lit.[8] bp 111–113 °C): IR (thin film) 3100, 3020, 1650, 1610, 1025 cm^{-1}; UV max (hexane) 236 nm (ϵ 32 000); NMR (CCl_4) δ 0.1–0.5 (m, 2 H), 0.5–0.9 (m, 2 H), 1.2–1.6 (m, 1 H), 4.84 (d of d, J = 9 and 2 Hz, 1 H), 4.98 (d of d, J = 16 and 2 Hz, 1 H), 5.14 (d of d, J = 14.5 and 8.5 Hz, 1 H), 6.04 (d of d, J = 14.5 and 10 Hz, 1 H), 6.20 (d of d of d, J = 16, 10, and 9 Hz, 1 H).

1b:[29,30] bp 106–110 °C; IR (thin film) 3090, 3010, 1640, 1610, 1020 cm^{-1}; UV max (hexane) 237 nm (ϵ 22 500); NMR (CCl_4) δ 0.1–0.5 (m, 2 H), 0.5–0.9 (m, 2 H), 1.4–1.9 (m, 1 H), 4.92 (d of t, J = 1 and 10.5 Hz, 1 H), 5.22 (d of d, J = 10.5 and 2 Hz, 1 H), 5.30 (d of d, J = 17 and 2 Hz, 1 H), 5.85 (t, J = 10.5 Hz, 1 H), 6.64 (d of d of t, J = 17, 1, and 10.5 Hz, 1 H). Anal. (C_7H_{10}) C, H.

1d: bp 59–61 °C (50 mm) as the mixture (lit.[10] bp 60–62 °C (50 mm); IR (thin film) 3100, 3020, 1645, 1605, 1020 cm^{-1}; UV max (hexane) 243 nm (ϵ 20 400); NMR (CCl_4) δ 0.45–0.8 (m, 4 H), 1.2–1.6 (m, 1 H), 1.62 (s, 3 H), 4.86 (d of d, J = 10.5 and 2 Hz, 1 H), 4.98 (d of d, J = 16.5 and 2 Hz, 1 H), 5.80 (d, J = 10.5 Hz, 1 H), 6.46 (d of t, J = 16.5 and 10.5 Hz, 1 H). Anal. (C_8H_{12}), C, H.

1e: IR (thin film) 3100, 3020, 1640, 1600, 1025 cm^{-1}; UV max (hexane) 241 nm (ϵ 22 800); NMR (CCl_4) δ 0.4–0.8 (m, 4 H), 1.48 (s, 3 H), 1.6–2.0 (m, 1 H), 4.92 (d of d, J = 10.5 and 2 Hz, 1 H), 5.01 (d of d, J = 16.5 and 2 Hz, 1 H), 5.82 (d, J = 10.5 Hz, 1 H), 6.68 (d of t, J = 16.5 and 10.5 Hz, 1 H). Anal. (C_8H_{12}), C, H.

5-Methyl-4-(1-methylethyl)-1,3-hexadiene (**1f**) was prepared from 2-methyl-3-(1-methylethyl)-5-hexen-3-ol (bp 53–54 °C (4 mm), obtained from allylmagnesium bromide with diisopropyl ketone, 87%) in 38% yield (shaking with concentrated HCl followed by treatment with potassium *tert*-butoxide in dimethyl sulfoxide). **1f:** bp 87–88 °C (89 mm); IR (thin film) 1640 cm^{-1}; NMR (CCl_4) δ 1.04 (d, J = 7 Hz, 12 H), 2.34 (septet, J = 7 Hz, 1 H), 2.94 (septet, J = 7 Hz, 1 H), 4.91 (d of d, J = 11 and 2 Hz, 1 H), 4.96 (d of d, J = 17 and 2 Hz, 1 H), 5.76 (d, J = 11 Hz, 1 H), 6.62 (d of t, J = 11 and 17 Hz, 1 H). Anal. ($C_{10}H_{18}$) C, H. **1a** was prepared by the procedures given in the literature.[3b]

Reaction of 1 with TCNE. General. A 0.1 M solution (10 mL) of TCNE was introduced into a flask, which was placed in a constant-temperature bath at 25 °C, and 1.0 mmol of **1** was aded to it. After the solution became colorless, the solvent was removed and the residue was examined by NMR for the **2:3** ratio. For isolation of the product, column chromatographic separation (Florisol, chloroform as the eluent) was frequently employed. Recrystallization from benzene–hexane (1:1 to 1:7) gave the pure sample. The results are summarized in Table I. In preparative experiments, higher concentrations of the two reactants were sometimes applied.

Reaction of 1a with TCNE. The reaction of **1a** (94 mg, 1 mmol) with TCNE (128 mg, 1 mmol) in dry acetonitrile (10 mL) gave **3a** (191 mg, 86%): mp 117–118 °C; IR (KBr) 3090, 3060, 3020, 2250, 1650, 1025 cm^{-1}; NMR ($CDCl_3$) δ 0.3–0.7 (m, 1 H), 0.7–1.3 (m, 4 H), 2.31 (br d, J = 10 Hz, 1 H), 3.13 (br d, J = 2 Hz, 2 H), 5.86 (br s, 2 H); mass spectrum m/e 222 (M^+, 6). Anal. ($C_{13}H_{10}N_4$) C, H, N. In dichloromethane, the yield of **3a** was 98%. The times of decoloration were 50 s in acetonitrile and 55 s in dichloromethane at room temperature.

Reaction of 1b with TCNE. A mixture of **2b** and **3a** in 94:6 ratio was produced in dichloromethane (4.5 h). **2b** was isolated from the mixture in 71% yield. **2b:** mp 88–89 °C; IR (KBr) 3100, 3020, 2260, 1655, 1025 cm^{-1}; NMR ($CDCl_3$) δ 0.3–0.7 (m, 2 H), 0.7–1.2 (m, 2 H), 1.3–1.7 (m, 1 H), 3.00 (d of d, J = 12.5 and 11 Hz, 1 H), 3.25 (d of d, J = 12.5 and 8.5 Hz, 1 H), 4.40 (d of t, J = 11 and 8.5 Hz, 1 H), 5.27 (d of d, J = 10.5 and 9 Hz, 1 H), 5.43 (d of d, J = 10.5 and 8.5 Hz, 1 H). Anal. ($C_{13}H_{10}N_4$) C, H, N. The reaction in other solvents resulted in **2b:3a** = 77:23 in benzene (70 h), 95:5 in THF (4 h), and 97:3 in acetonitrile (1.5 H).

Reaction of 1c with TCNE. In acetonitrile, THF, or 1,2-dichloroethane, immediate workup gave **2c** free from **3c** in more than 90% yield. **2c:** mp 99–100 °C; IR (Nujol) 3100, 3025, 2250, 1640, 1020 cm^{-1}; NMR (CCl_4) δ 0.4–1.1 (m, 9 H), 1.60 (m, 1 H), 2.90 (d of d, J = 12 and 10 Hz, 1 H), 3.16 (d of d, J = 12 and 8 Hz, 1 H), 4.46 (d of t, J = 10 and 8 Hz, 1 H), 5.12 (d, J = 8 Hz, 1 H); mass spectrum m/e 262 (M^+, 0.5), 91 (100). Anal. ($C_{16}H_{14}N_4$) C, H, N. In benzene at room temperature, a mixture of **2c** and **3c** in 95:5 ratio was obtained. Both **2c** and **3c** gradually darkened on standing in air.

Reaction of 1c with TCNE in the Presence of *p*-Toluenethiol. Into a cold (−40 °C) stirred solution of TCNE (384 mg, 3 mmol) in dry THF (20 mL) was added a solution of **1c** (402 mg, 3 mmol) and *p*-toluenethiol (372 mg, 3 mmol) in dry THF (10 mL) over a period of 30 s. The purple color faded after 3 min. Solvent evaporation gave a residue which was washed with 10 mL of benzene–hexane (1:1). The residue was recrystallized from acetone to give 1,1,2,2-tetracyanoethane (152 mg, 39%), mp 187–188 °C (lit.[31] mp 187 °C). The mother liquor of the recrystallization was concentrated and the residue was washed with hexane. The remaining white solid was recrystallized from benzene–hexane (1:1) to give **2c** (311 mg, 40%). On cooling of the hexane washings, a white solid was separated, which was found to be *p,p'*-ditolyl disulfide (345 mg, 90%), mp 46–47 °C (lit.[32] mp 45.5 °C). From the filtrates, **1c** was recovered by distillation (220 mg, 55%). The oxidation of *p*-toluenethiol by TCNE occurred slightly faster than the reaction of **1c** with TCNE (by a factor of 1.15). The reaction in chloroform at room temperature resulted in similar results as above.

Reactions of 1d and 1e with TCNE. From the product mixture obtained in the reaction of **1d** and **1e** (5:1) with TCNE in THF, **2d** was isolated in 75% yield. **2d:** mp 74–75 °C; IR (Nujol) 3100, 2250, 1645, 1020 cm^{-1}; NMR ($CDCl_3$) δ 0.52–0.90 (m, 4 H), 1.54 (m, 1 H), 1.63 (d, J = 1 Hz, 3 H), 2.89 (d of d, J = 12 and 10 Hz, 1 H), 3.15 (d of d, J = 12 and 8 Hz, 1 H), 4.28 (d of t, J = 10 and 8 Hz, 1 H), 5.28 (d, J = 9 Hz, 1 H). Anal. ($C_{14}H_{12}N_4$) C, H, N. The reaction of 98% pure **1e** with TCNE in benzene (25 °C, 17 min) gave a mixture of **2d, 2e,** and **3d** in 5:92:3 ratio, from which **2e** was isolated in 85% yield. **2e:** mp 87–88.5 °C; IR (KBr) 3100, 3020, 2250, 1645, 1025 cm^{-1}; NMR ($CDCl_3$) δ 0.5–1.0 (m, 4 H), 1.55 (d, J = 1.5 Hz, 3 H), 1.4–1.7 (m, 1 H), 2.95 (d of d, J = 12.5 and 11 Hz, 1 H), 3.22 (d of d, J = 12.5 and 8.5 Hz, 1 H), 4.46 (d of t, J = 11 and 8.5 Hz, 1 H), 5.35 (br d, J = 8.5 Hz, 1 H). Anal. ($C_{14}H_{12}N_4$) C, H, N. The results obtained in the reactions of geometrically pure **1d** and **1e** in THF (6 min for **1d** and 8 min for **1e**) or in benzene (14 min for **1e**) are given in Table I. The total yield of the adducts in these experiments was more than 83%.

Reaction of 1f with TCNE. In THF (7 h at room temperature), **2f** was isolated in 98% yield. **2f:** mp 140–141 °C; IR (Nujol) 2255, 1650 cm^{-1}; NMR ($CDCl_3$) δ 1.02 (d, J = 7 Hz, 6 H), 1.08 (d, J = 7 Hz, 6 H), 2.45 (septet, J = 7 Hz, 1 H), 2.75 (septet, J = 7 Hz, 1 H), 2.95 (d of d, J = 12 and 11 Hz, 1 H), 3.24 (d of d, J = 12 and 10 Hz, 1 H), 4.20 (d of t, J = 12 and 10 Hz, 1 H), 5.07 (d, J = 10 Hz, 1 H). Anal. ($C_{16}H_{18}N_4$), C, H, N. The reaction in acetonitrile, benzene, or cyclohexane (80 °C) gave **2f** in nearly quantitative yield. **3f** could not be detected in all cases.

Thermal Rearrangement of 2c to 3c. A solution of **2c** (265 mg, 1 mmol) in 1,2-dichloroethane (10 mL) was heated under argon atmosphere in a glass ampule at 100 °C for 1 h. Removal of the solvent under reduced pressure left a solid which was recrystallized from benzene–hexane (1:1) to give **3c** (254 mg, 96%). **3c:** mp 103–104 °C; IR (Nujol) 2250, 1655, 1030 cm^{-1}; NMR ($CDCl_3$) δ 0.67 (m, 4 H), 0.78 (m, 4 H), 1.25 (m, 2 H), 3.13 (d of d, J = 4 and 2 Hz, 2 H), 5.25 (d of t, J = 11 and 2 Hz, 1 H), 5.88 (d of t, J = 11 and 4 Hz, 1 H).

Anal. ($C_{16}H_{14}N_4$) C, H, N. The rearrangement was completed after several hours at room temperature in acetonitrile. The rate of the rearrangement was determined by monitoring the NMR peaks. In chloroform-*d*, 10^5k_1 (s^{-1}) values were 5.60 at 35 °C, 9.20 at 41 °C, 33.4 at 56 °C, 61.5 at 61 °C, and 106 at 69 °C.[33] In acetonitrile at 35 °C, k_1 was 3.6×10^{-4} s^{-1}.[34]

Thermal Rearrangement of 2c in the Presence of 1a. A solution of **2c** (79 mg, 0.30 mmol) and **1a** (141 mg, 1.5 mmol) in acetonitrile (3 mL) was kept in a constant-temperature bath at 30 °C. After 24 h, the solution was analyzed by GC (Apiezon L, 2 m, at 130 °C with temperature programming up to 230 °C with the rate of 5 °C/min, octadecane as the internal standard). **3a** was not detected in the analysis. Workup similar to those described above gave **3c** in 80% yield. In chloroform at 30 °C after 7 days (95% conversion by NMR), a mixture of **1c** (22%), **3c**, and **3a** (73% as a total, in 70:30 ratio) was obtained. At 130 °C, **1c** amounted to 25% and the ratio of **3c:3a** to 27:73 (81% yield). In a separate experiment, **3c** (79 mg, 0.30 mmol) was mixed with **1a** (141 mg, 1.5 mmol) in chloroform (3 mL), and the mixture was heated at 130 °C for 20 h. GC analysis indicated that no **3a** was formed; the recovered yield of **3c** was 95%.

Thermal Rearrangement of 2c in the Presence of *p*-Toluenethiol. A mixture of **2c** (500 mg, 1.91 mmol) and *p*-toluenethiol (240 mg, 1.94 mmol) in chloroform (20 mL) was left standing at 30 °C for 24 h. Solvent evaporation gave a residue which was recrystallized from 1,2-dichloroethane to give **5** (671 mg, 91%). **5**: mp 94–95 °C; IR (Nujol) 2250, 1650, 1020 cm^{-1}; NMR ($CDCl_3$) δ 0.4–0.6 (m, 8 H), 0.88 (m, 2 H), 2.36 (s, 3 H), 2.92 (d, J = 6 Hz, 2 H), 3.52 (s, 1 H), 5.54 (d of t, J = 16 and 6 Hz, 1 H), 5.76 (d, J = 16 Hz, 1 H), 7.10 (d, J = 8 Hz, 2 H), 7.38 (d, J = 8 Hz, 2 H). Anal. ($C_{23}H_{22}N_4S$), C, H, N, S. Evaporation of the filtrates gave a solid residue, from which **3c** (18 mg, 3.6%) was isolated.

Thermal Rearrangement of 2d. The rearrangement was carried out at 100 °C in 1,2-dichloroethane for 3 h. **3d** was isolated in 70% yield from the product mixture. **3d:** oil; IR (thin film) 3100, 3025, 2250, 1640, 1030 cm^{-1}; NMR (CCl_4) δ 0.54–0.84 (m, 4 H), 1.50 (s, 3 H), 1.2–1.8 (m, 1 H), 3.12 (d of d, J = 4 and 2 Hz, 2 H), 5.80 (d of t, J = 11 and 4 Hz, 1 H), 5.48 (d of t, J = 11 and 2 Hz, 1 H). Anal. ($C_{14}H_{12}N_4$) C, H, N. The kinetic study gave $k_1 = 2.4 \times 10^{-5}$ s^{-1} in chloroform-*d* at 61 °C.

Fragmentation of 2f. A solution of **2f** (215 mg, 0.81 mmol) in acetonitrile (10 mL) was heated at 120 °C for 24 h in a glass ampule under argon atmosphere. Column chromatographic purification (alumina, 50 g, chloroform as the eluent) gave **4f** (140 mg, 86%). **4f:** oil; IR (thin film) 2230, 1610 cm^{-1}; UV max (95% ethanol) 313 nm (ϵ 27 000); NMR (CCl_4) δ 1.16 (d, J = 7 Hz, 6 H), 1.18 (d, J = 7 Hz, 6 H), 2.66 (septet, J = 7 Hz, 1 H), 3.18 (septet, J = 7 Hz, 1 H), 6.44 (d, J = 12 Hz, 1 H), 7.90 (d, J = 12 Hz, 1 H); mass spectrum *m/e* 188 (M^+, 1), 43 (100). Anal. ($C_{12}H_{16}N_2$) C, H, N. In benzene at 120 °C, **4f** was obtained in 94% yield after 24 h. When the thermolysis was carried out in an NMR tube, a transient signal ascribable to methylenemalononitrile (δ 6.8 (s)) was observed. The signal gradually broadened and finally disappeared. Methylenemalononitrile is known to polymerize easily in contact with organic solvents.[35]

The rate of the fragmentation was followed by NMR: k_1 ($CDCl_3$) = 3.04×10^{-5} s^{-1} and k_1 (CH_3CN) = 3.20×10^{-5} s^{-1} at 115 °C.

Thermal Reactions of 2 at 130 °C. A. Rearrangement and Fragmentation of 2b. A solution of **2b** (111 mg, 0.50 mmol) in cyclohexane (5 mL) was heated in a sealed tube at 130 °C for 20 h. After the insoluble material (presumably methylenemalononitrile polymer) was filtered off, the solvent was removed and the residue was placed on the top of a silica gel column (30 g). The column was eluted by benzene and 12 fractions (30 mL) were collected. From fractions no. 5 and 6, **3a** (29 mg, 26%) was obtained. Fractions no. 7–10 gave a mixture of **4a** and **4b** (68 mg, 67%). Pure **4b** was isolated from fraction no. 7 by recrystallization. **4b:** mp 88–89.5 °C(cyclohexane); IR (KBr) 3055, 3045, 2230, 1660, 1610, 1035 cm^{-1}; UV max (95% ethanol) 320 nm (ϵ 24 900); mass spectrum *m/e* 144 (M^+, 46), 143 (100); NMR ($CDCl_3$) δ 0.6–1.0 (m, 2 H), 1.0–1.4 (m, 2 H), 1.7–2.2 (m, 1 H), 5.73 (t, J = 10.5 Hz, 1 H), 6.50 (d of d, J = 12 and 10.5 Hz, 1 H), 7.92 (d, J = 12 Hz, 1 H). Anal. ($C_9H_8N_2$) C, H, N. Pure **4a** was obtained by preparative GC (Apiezon L, 15%, 2 m, 200 °C). **4a:** oil; IR (thin film) 3100, 3045, 3020, 2230, 1620, 1030 cm^{-1}; UV max (95% ethanol) 316 nm (ϵ 29 600); mass spectrum *m/e* 144 (M^+, 55), 143 (100); NMR ($CDCl_3$) δ 0.6–1.0 (m, 2 H), 1.0–1.4 (m, 2 H), 1.5–2.0 (m, 1 H), 6.10 (d of d, J = 14.5 and 10 Hz, 1 H), 6.72 (d of d, J = 14.5 and 11 Hz, 1 H), 7.34 (d, J = 11 Hz, 1 H). The ratio of **4a:4b** was 3:4 (GC). The results in the solvents other than cyclohexane were given in the text. The mixture of **4a:4b** = 3:2 was obtained in chloroform (20 h) and 1:1 in THF (20 h). In a control experiment, **4b** (15 mg, 0.1 mmol) was dissolved in $CDCl_3$ (130 μL) and the solution was heated in an NMR tube at 130 °C for 30 h. NMR analysis indicated that the isomerization of **4b** to **4a** took place only to an extent of ca. 10%. **4a** did not isomerize to **4b** under the same conditions.

In a separate experiment, a solution of **2b** (0.2 M) in $CDCl_3$ was sealed in an NMR tube and heated at 70 °C for 35 h. The NMR spectrum of the resultant solution indicated that there were **2a, 2b,** and **3a** in 44:40:16 ratio. Recrystallization of the product mixture, which was obtained by the evaporation of the solvent, from benzene–hexane (1:1) gave a 1:1 mixture of **2a** and **2b** free from **3a.** Since the separation of **2a** from **2b** was unsuccessful, the analysis was carried out with the mixture. The substraction of the peaks due to **2b** from the spectrum gave an NMR spectrum, which was consistent with **2a:** NMR ($CDCl_3$) δ 0.4–0.7 (m, 2 H), 0.7–1.1 (m, 2 H), 1.3–1.7 (m, 1 H), 2.98 (d of d, J = 12 and 11 Hz, 1 H), 3.15 (d of d, J = 12 and 7 Hz, 1 H), 3.86 (d of t, J = 11 and 7 Hz, 1 H), 5.38 (d of d, J = 15 and 8 Hz, 1 H), 5.64 (d of d, J = 15 and 7 Hz, 1 H). Anal. as the mixture ($C_{13}H_{10}N_4$) C, H, N.

B. Reactions of 2d, 2e, and 2c. Heating of a solution of **2d,e** (1:4) in chloroform at 130 °C for 20 h produced **3d, 4d,** and **4e** in 78:13:8 ratio. The separation of each component was carried out as above. **4d:** mp 133–134 °C (hexane); IR (KBr) 3100, 3050, 2240, 2225, 1600, 1020 cm^{-1}; UV max (95% ethanol) 331 nm (ϵ 32 000); NMR ($CDCl_3$) δ 0.7–1.2 (m, 4 H), 1.6–1.9 (m, 1 H), 1.81 (d, J = 1.1 Hz, 3 H), 6.52 (br d, J = 12 Hz, 1 H), 7.70 (d, J = 12 Hz, 1 H). Anal. ($C_{10}H_{10}N_2$) C, H, N. **4e:** mp 109.5–110.5 °C (hexane); IR (KBr) 3050, 2230, 1590, 1030 cm^{-1}; UV max (95% ethanol) 331 nm (ϵ 39 000); NMR ($CDCl_3$) δ 0.8–1.2 (m, 4 H), 1.74 (d, J = 1 Hz, 3 H), 1.8–2.2 (m, 1 H), 6.52 (br d, J = 12 Hz, 1 H), 7.95 (d, J = 12 Hz, 1 H). Anal. ($C_{10}H_{10}N_2$), C, H, N.

Since the fragmentation of **2c** occurred to a minor extent (**3c:4c** = 98:2 in chloroform at 130 °C), the thermolysis of **2c** was carried out in cyclohexane at 150 °C. After 2 h, a mixture of **3c** (63%) and **4c** (22%) was obtained. **4c:** mp 105–106 °C (hexane); IR (KBr) 3100, 3020, 2225, 1580, 1030 cm^{-1}; UV max (95% ethanol) 345 nm (ϵ 30 000); NMR ($CDCl_3$) δ 0.6–1.4 (m, 8 H), 1.4–1.7 (m, 1 H), 1.9–2.2 (m, 1 H), 6.13 (d, J = 12 Hz, 1 H), 7.96 (d, J = 12 Hz, 1 H). Anal. ($C_{12}H_{12}N_2$) C, H, N. The reaction at 130 °C gave **3c** and **4c** in 92:8 ratio.

References and Notes

(1) (a) Supported by a Grant-in-Aid for Scientific Research (384027) from the Ministry of Education of Japan; (b) Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812, Japan.

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(13) The zwitterion produced from alkoxy-substituted polycyanocyclobutanes has been trapped by alcohol.[3h-j] In the present reaction, however, the trapping by alcohol was unsuccessful. Fruitless trapping experiments are also reported (ref 3n, p 454. Hoffmann, R. W.; Bressel, U.; Gehlhaus, J.; Häusler, H. *Chem. Ber.* **1971,** *104,* 873).
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(16) A similar dependence of the stereoselectivity on the solvent polarity has been known in the reaction of vinyl ethers with TCNE.[3e,i]
(17) In the reaction of chlorosulfonyl isocyanate with isoprene, the rearrangement of a vinyl four-membered ring to a six-membered ring via a zwitterion has been postulated (Goebel, P.; Clauss, K. *Justus Liebigs Ann. Chem.* **1969,** *722,* 122).
(18) There is a possibility that the cycloreversion takes place also in acetonitrile but the produced TCNE reacts preferentially with nearby **1c.** In such cases, however, **1c** should regenerate **2c.** In a separate experiment, we observed that the reaction of **2d,e** at 130 °C in chloroform produced only a trace amount of **3d** if a large amount of **1a** was present. This result was contrasted with that of **2c,** which yielded 27% of **3c** under similar conditions. Since **1d** should produce a larger amount of **3** than **1c,** the results are not compatible with the cycloreversion–recombination as well. The ease of the rearrangement of **2c** relative to **2d,e** will be the reason for the difference.
(19) The reversibility of zwitterion formation has been demonstrated in the reaction of 1-butenyl ethyl ether with TCNE.[3f]
(20) In the vinylcyclopropane–cyclopentene rearrangement, it is argued that only the trans isomer is capable of undergoing the rearrangement (a review article: Sarel, S.; Yovell, J.; Sarel-Imber, M. *Angew. Chem., Int. Ed. Engl.* **1968,** *7,* 577). However, this was not the present case. Indeed, the most reactive **1c** unavoidably possesses the bulky cyclopropyl group at the *Z* position.
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The Ultraviolet Transitions of Benzoic Acid. 3. Effects of Hydrogen Bonding on the Emission Properties

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Abstract: Contrary to previously published results, the energies and quantum yields of the fluorescence and phosphorescence of benzoic acid in isopentane-methylcyclohexane at 77 K are found to be independent of the excitation wavelength in the 280-nm region. Further, the excitation spectra monitoring the fluorescence and phosphorescence are identical. These data are consistent with the fact that benzoic acid exists only as dimers in pure hydrocarbon glasses. Irradiation of methylcyclohexane gives photoproducts which hydrogen bond to benzoic acid. The absorption, emission, and excitation spectra of this latter solution of benzoic acid do agree with those previously reported. The earlier hypothesis that there is a $^3n\pi^*$ state close in energy to the ^1L_b state of benzoic acid remains valid, however. The role (acceptor or donor) of benzoic acid in hydrogen bonding and the effect of hydrogen bonding on the energies of both $\pi\pi^*$ and $n\pi^*$ states are considered in examining the emission properties of the molecule.

I. Introduction

There have been many studies describing the phosphorescence of benzoic acid but until recently no fluorescence was observed. Baba and Kitamura[1] were the first to report both types of emission from benzoic acid. They found that in an isopentane-methylcyclohexane (IP-MCH) glass (6:1 by volume) the fluorescence/phosphorescence intensity ratio of benzoic acid was much greater for 285-nm excitation than for excitation at 281 nm. The excitation spectra obtained by monitoring the fluorescence (310 nm) and phosphorescence (410 nm) were also quite different. The authors explained their results in terms of the molecular association of benzoic acid. They concluded that, while the dimer species can both fluoresce and phosphoresce, the monomer only phosphoresces.

It is well known that the emission properties of heteroatomic molecules are dependent upon the relative energies of the $\pi\pi^*$ and $n\pi^*$ singlet and triplet states.[2] Baba and Kitamura[1] offered the following mechanism to rationalize the emission behavior of benzoic acid in the hydrocarbon glass. They assumed that a $^3n\pi^*$ state lies slightly below the lowest $^1\pi\pi^*$ state and above the lowest $^3\pi\pi^*$ state in the monomer species. This leads to efficient intersystem crossing and only phosphorescence would be expected. The authors hypothesized that hydrogen bonding in the dimer raises the $^3n\pi^*$ state above the $^1\pi\pi^*$ state, decreasing the amount of intersystem crossing.

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0002-7863/80/1502-0716$01.00/0