

Ketene Formation in Benzdiyne Chemistry: Ring Cleavage versus Wolff Rearrangement

Tadatake Sato,* Hiroyuki Niino, and Akira Yabe

Contribution from the Photoreaction Control Research Center, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Received April 28, 2003; E-mail: sato-tadatake@aist.go.jp

Abstract: In the chemistry toward generating benzdiyne from five benzenetetracarboxylic dianhydride derivatives, ketene formation was exclusively observed in the photolysis of difluorobenzenetetracarboxylic dianhydride in a nitrogen matrix at 13 K. Two ketenes were formed concomitantly with difluorobenzdiyne. These ketenes were identified on the basis of good agreement between the observed and calculated (B3LYP/6-31G* level) IR spectra. Neither ketene contained the five-membered-ring moiety as cyclopentadienylideneketene, which is formed by Wolff rearrangement in the benzyne chemistry. The first generated ketene was assigned to a ketene with a cyclopropene moiety, and the second, to a ketene with a butadiyne moiety. The first generated ketene was a major product in the photolysis and was formed by cleavage of the bond connecting the ketene group and the C–F carbon and not the bond connecting the ketene group and the carbene moiety. Thus the structures of these ketenes indicated that a unprecedented ring cleavage, rather than Wolff rearrangement, is the dominant process in the benzdiyne chemistry.

Introduction

Arynes¹ often react with carbon monoxide to form ketene species in low-temperature matrixes. For instance, *o*-benzyne and carbon monoxide react in low-temperature matrixes to form cyclopentadienylideneketene, which shows characteristic IR bands around 2090 cm⁻¹. This IR band caused vigorous debate on the assignment of the triple-bond stretching vibration in *o*-benzyne.² Benzdienes (tetrahydrobenzenes) are arynes having two triple bonds in a benzene ring. Because of their extraordinary lability owing to the high ring strain that arises from the two triple bonds, experimental study of benzdienes is challenging and, hence, limited,^{3–6} although their existence has been suggested by the final products obtained from various organic reactions^{7–9} and by early theoretical studies.^{10–12} We

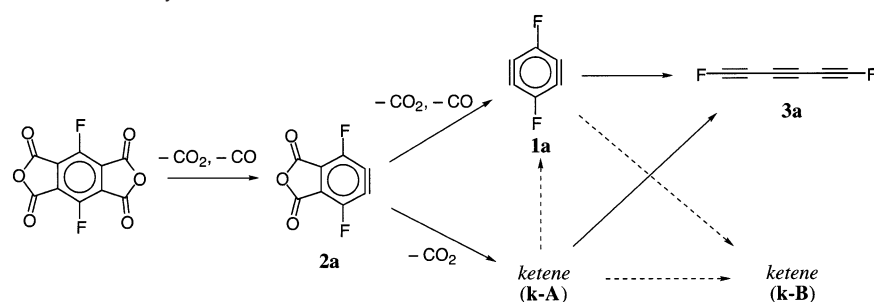
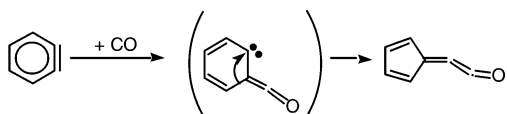
have recently directly observed two benzdiyne derivatives, 3,6-difluoro-1,4-benzdiyne (**1a**) and 3,6-bis(trifluoromethyl)-1,4-benzdiyne (**1b**), by means of the matrix isolation technique.¹³ Benzdiyne was generated by decarboxylation and decarbonylation of benzenetetracarboxylic dianhydride. Specifically, in the photolysis of difluorobenzenetetracarboxylic dianhydride, concomitant formation of ketenes was observed (Scheme 1). The characterization of these generated ketenes remains an issue in the chemistry of benzdienes.

In the case of *o*-benzyne, cyclopentadienylideneketene is generally thought to be formed by Wolff rearrangement of a singlet ketocarbene-like intermediate (Scheme 2).¹⁴

Ketene formation has also been observed in other systems^{15–17} and has often shown an intriguing structure dependence. For instance, ketene formation could be suppressed by benzoannulation at a specific location¹⁵ and the existence of the heteroatom adjacent to carbene moiety resulted in ring cleavage.¹⁸ Given this structure dependence, ketene formation in benzdiyne chemistry is a stimulating issue. Ketenes with unique structures could be formed because of the extraordinary large ring strain of benzdienes. In this article, we discuss the structures and mechanism of generation of the ketenes on the basis of geometries, energies, and calculated IR spectra

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Scheme 1. Generation of Difluorobenzdiyne and Ketenes**Scheme 2.** Generation of Cyclopentadienyldeneketene by Wolff Rearrangement of a Ketocarbene-Like Intermediate

estimated by means of density functional theory (DFT) calculations.

Experimental Section

Details of the matrix experiment and computational method are described in a previous report.¹³ In the photolysis, an EXL-300 ArF excimer laser ($\lambda = 193$ nm, repetition rate 5 Hz, laser fluence $3\text{--}4$ mJ cm^{-2} pulse⁻¹; Japan Storage Battery Co., Ltd.) was used in addition to a XeCl excimer laser and the fourth-harmonic-generated (FHG) pulses of a Nd:YAG laser. The fluence of the irradiation was kept constant in each series of the experiments. All DFT calculations were performed with the Gaussian 98 program package.¹⁹ The geometries of the compounds were optimized by using the B3LYP method^{20,21} in combination with the 6-31G* basis set. The computations on the benzdiynes were executed by using the spin-unrestricted DFT method because of their multireference nature.²² The nature of the stationary points was assessed by means of vibrational frequency analysis: all optimized structures have no imaginary frequencies. Theoretical IR spectra were obtained by vibrational frequency analyses. Vibrational frequencies predicted at the B3LYP/6-31G* level were scaled by 0.9614 on the basis of the literature.²³ All calculations were done on the TACC Quantum Chemistry Grid/Gaussian Portal system at the Tsukuba Advanced Computing Center (TACC).

Results and Discussion

In the course of the generation of the benzdiynes, benzynedicarboxylic anhydrides **2** were formed upon 308 nm irradiation (Scheme 3). These reactions are similar to the reaction generating benzyne.²⁴ However, the corresponding ketenes were not

observed at the photostationary state upon 308 nm irradiation; that is, the characteristic IR bands around 2090 cm^{-1} were not observed.

In the photolyses of 1,2-naphthalenedicarboxylic anhydride and 1,2,5,6-naphthalenetetracarboxylic dianhydride, ketene formation was observed, whereas the corresponding ketenes were not formed in the cases of their 2,3- and 2,3:6,7-isomers, respectively.^{15,16} These results suggested that ketene formation was suppressed by the condensation of a benzo group at 4,5-positions in the 1,2-dehydrobenzene moiety. In the case of **2**, the anhydride moiety condensed at 4,5-positions suppressed the formation of ketenes.

In contrast, ketene bands were observed in the 266 nm photolyses of **2a** and **2b**, for which the generation of benzdiynes was confirmed. In the case of **2b**, the IR band around 2090 cm^{-1} was weak (Figure 1a,b). As generally recognized, the ketene band has a large extinction coefficient.²⁵ Therefore, the generation of ketene species should be a minor process in the case of **2b**. This supposition was corroborated since the reaction could be analyzed by assuming a successive reaction sequence including benzyne, benzdiyne, and hexatriyne (Scheme 4).¹³

In the case of **2a** (Figure 1c,d), the IR bands of the ketenes were more intense than in the case of **2b**, implying a major contribution of the ketenes. We could not analyze the reaction dynamics of **2a** by assuming a successive reaction involving only three chemical species (benzyne, benzdiyne, and hexatriyne). This result revealed that other chemical species were involved in the photolysis.

Moreover, Figure 1d shows that two kinds of ketene species were generated during the 266 nm photolysis: the IR band at 2109 cm^{-1} observed in the beginning was replaced by an IR band at 2129 cm^{-1} . Both bands can be ascribed to ketene species. The dynamics of the two ketenes were analyzed by separating the complex IR band of the two ketenes and CO: the details of this analysis are described in the Supporting Information. The separated peaks of the two ketenes and their dynamic behaviors indicated that both benzdiyne **1a** and the first generated ketene (**k-A**) were the primary products in the photolysis of **2a**, whereas the other ketene (**k-B**) and hexatriyne (**3a**) were secondary products (Figure 2).

The major contribution of ketenes in the photolysis of **2a** was also indicated by the analysis of the peak dynamics of CO and CO₂ and the decomposition ratio of **2a**. As discussed previously,¹³ if simultaneous decarboxylation and decarbonylation of **2a** were induced by photoirradiation, the dynamics of the CO peak and the CO₂ peak must correspond with each other. However, the dynamic behaviors of the peaks are different

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Scheme 3. Generation of Benzyne-dicarboxylic Anhydride

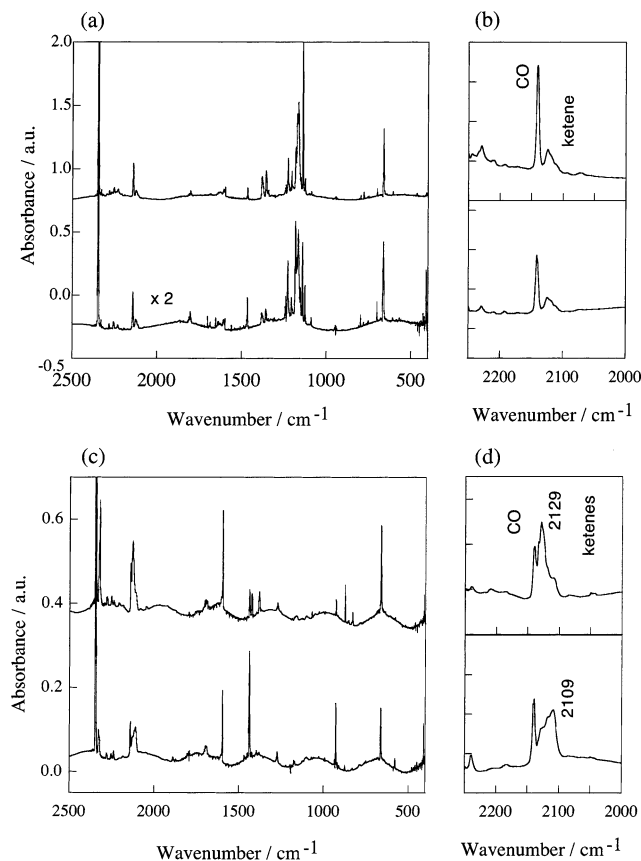
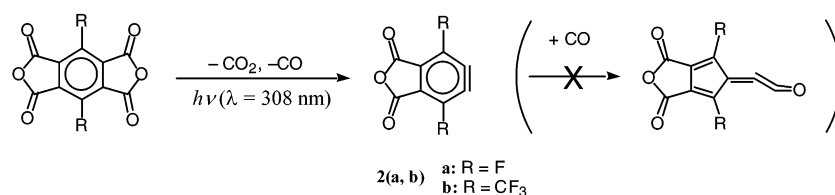
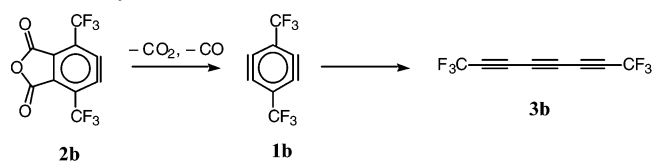


Figure 1. (a) IR spectra observed upon 266 nm photolysis of **2b** in a nitrogen matrix at 13 K: (top) 396 000 pulses, (bottom) 108 000 pulses, where 85% of **2b** and 51% of **2b** were photolyzed. (b) IR bands of CO and ketene. (c) IR spectra observed upon 266 nm photolysis of **2a** in a nitrogen matrix at 13 K: (top) 27 000 pulses, (bottom) 4800 pulses, where 98% of **2a** and 69% of **2a** were photolyzed. (d) IR bands of CO and ketene.

Scheme 4. Successive Reaction Assumed for the Analysis of Reaction Dynamics



(Supporting Information, Figure S4). The difference between the peaks was large at the beginning of the photolysis and decreased upon irradiation. Interestingly, the dynamics of the difference between the two peaks showed a good correspondence with that of the **k-A** peak (see Supporting Information). These results indicated that **k-A** was a major product in the photolysis of **2a** and that **k-B** was a minor product.

Identification of the First Ketene (k-A). In addition to the intense ketene bands, some photoproduct IR bands could be assigned to neither **1a** nor **3a**. These bands should be ascribed to the skeletal vibrations of the ketenes. Generally, ketenes show

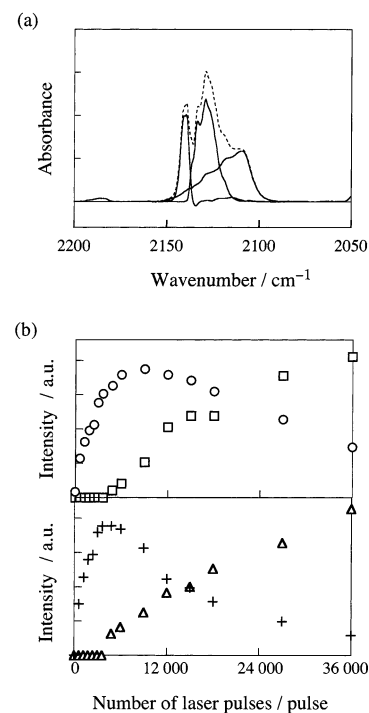


Figure 2. (a) Separation of the complex ketene + CO band observed upon irradiation with 18 000 FHG pulses of a Nd:YAG laser into two ketene peaks and one CO peak. (b) Dynamic behaviors of IR intensities of the two ketenes (top: O, **k-A**; square, **k-B**); the corresponding dynamic behaviors of **1a** (+) and **3a** (triangle) are shown for comparison (bottom).

absorption bands in the UV–vis region.^{15,17} Absorption bands ascribable to **k-A** were observed at 326 and 308 nm (see Supporting Information for UV–vis absorption spectra). Upon 308 nm irradiation, **k-A** could be selectively photolyzed. Therefore, repeated cycles of irradiation with 266 nm irradiation followed by 308 nm irradiation resulted in the cyclical generation–decomposition of **k-A**. From the dynamics of the peaks observed during the 266 and 308 nm irradiations, six IR bands ascribable to **k-A** could be identified (Figure 3). Among these bands, the band at 1697 cm⁻¹ overlapped with other IR bands, which was confirmed from the temporal increase and decrease of the line width of this IR band during the irradiation cycle. The main product of the 308 nm photolysis of **k-A** was **3a**.

The reactions presumed for generating various ketenes are depicted in Scheme 5. Considering the case of benzyne, the most probable ketene should be that with a five-membered ring (**5**).^{14,24} Ketene **5** was presumed to be formed by Wolff rearrangement of ketocarbene-like intermediate **4**. Interestingly, **4** could be optimized as a local minimum in the difluoro species,²⁶ although the corresponding species for the parent system (unsubstituted) could not be optimized as a local minimum. In contrast, when the heteroatom was adjacent to the carbene moiety, ring cleavage occurred at the carbonyl–

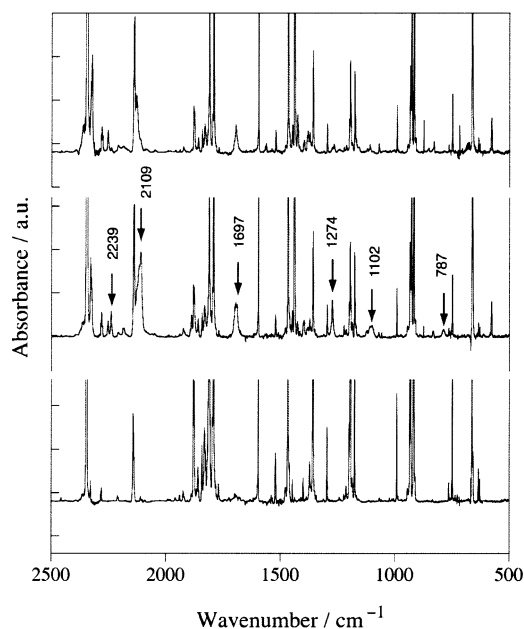
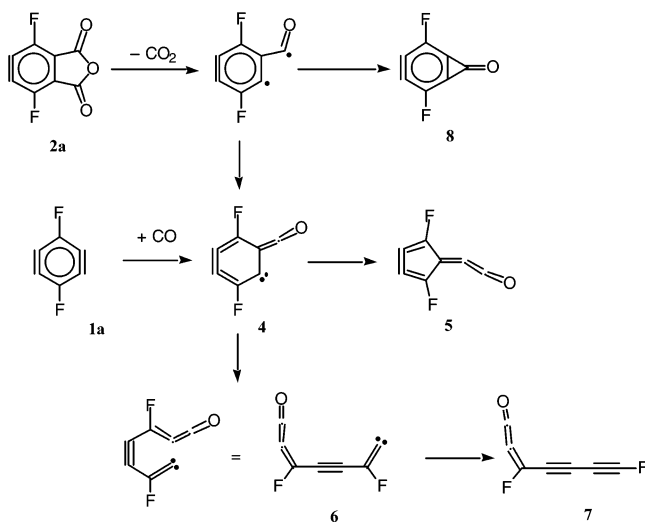


Figure 3. IR spectra observed upon photolysis of **2a** in a nitrogen matrix at 13 K: (bottom) before 266 nm irradiation; (center) after 266 nm irradiation with 300 pulses; (top) after successive 308 nm irradiation with 21 000 pulses. IR bands ascribable to **k-A** are marked (center).

Scheme 5. Reactions Presumed for Ketene Generation from **2a**



carbene bond.^{14,18} The corresponding ring cleavage would result in the formation of the vinylidene intermediate (**6**). Given that difluorovinylidene could be observed in the matrix,²⁷ intermediate **6** might be isolated in a cryogenic matrix. Intermediate **6** would be converted to a ketene with a butadiyne moiety (**7**) upon irradiation.

The calculated IR spectra of species **4**, **5**, **6**, and **7** were compared with the observed IR peaks of the ketene (Figure 4). None of the calculated IR spectra showed a good correspondence with the IR bands of **k-A**. It is worth noting that the IR band at 2239 cm^{-1} is located at larger wavenumber than the ketene band. This IR band could be ascribed to the $\text{C}\equiv\text{C}$ stretching vibration

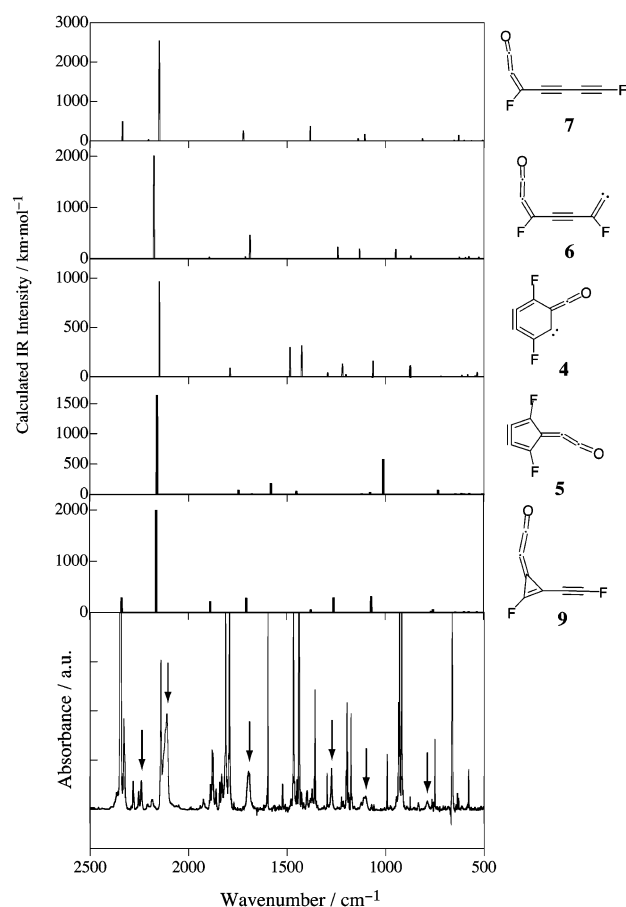


Figure 4. Calculated IR spectra for possible ketenes (B3LYP/6-31G* level) and experimental IR bands ascribed to **k-A**.

admixed with the $\text{C}-\text{F}$ stretching vibration in the $-\text{C}\equiv\text{C}-\text{F}$ moiety, indicating that **k-A** is the ketene with the $-\text{C}\equiv\text{C}-\text{F}$ moiety formed by ring cleavage. As previously reported, the benzdienes underwent a ring-opening reaction to form hexatriyne: this reaction proceeded easily under photoirradiation, probably owing to the large ring strain in the benzdiyne ring. Ketocarbene-like **4** or ketene **5** should have a similar extraordinary large ring strain, resulting in ring-opening rather than rearrangement. Among the possible ketenes containing the $-\text{C}\equiv\text{C}-\text{F}$ moiety, the ketene with the cyclopropene ring (**9**) showed good agreement with the observed IR bands of **k-A** (Figure 4). Thus **k-A** was ascribed to ketene **9**.

Identification of the Second Ketene (k-B). Upon prolonged irradiation at 266 nm, the initial photoproducts, **1a** and **k-A**, were photolyzed, while **3a** and **k-B** increased in the matrix (Figure 2). Among these species, ketene **k-B** could be selectively photolyzed upon 193 nm irradiation. The difference IR spectrum between those observed before and after irradiation at 193 nm (Figure 5) shows that while the characteristic ketene band disappeared upon irradiation, the IR bands ascribable to **3a** increased: the major photoproduct of this photolysis was **3a**. Accordingly, the IR bands at 830, 875, 1426, and 2322 cm^{-1} were assigned to **3a**, and those at 854, 1163, 1381, and 2129 cm^{-1} were assigned to **k-B**. Since **k-B** was the secondary photoproduct, it would be formed by rearrangement of **k-A** or by recombination between benzdiyne and CO. The IR bands ascribable to **k-B** did not correspond to the predicted IR bands of **5**. Additionally, ketene **k-B** produced **3a** upon 193 nm

(26) DFT computational results showed that ketocarbene-like **4** had a singlet ground state. The lowest triplet state lay 33 kcal mol^{-1} higher than the singlet state.

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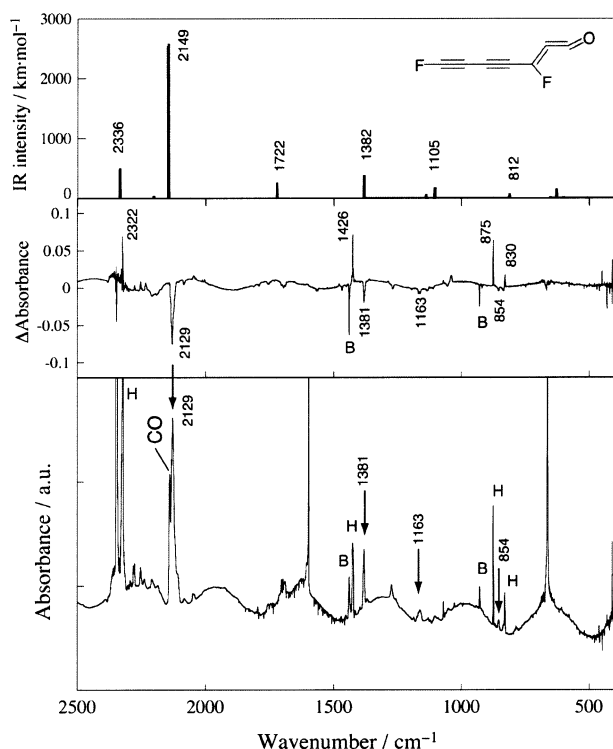
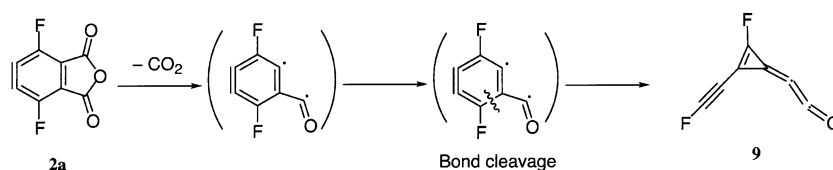
Scheme 6. Possible Mechanism for Generation of Ketene **9**

Figure 5. (Top) Calculated IR spectrum of ketene **7** (B3LYP/6-31G* level). (Center) Difference IR spectrum for 193 nm irradiation; peaks pointing up correspond to photoproducts (**3a**), whereas peaks pointing down correspond to the photolyzed species (**1a** and **k-B**). (Bottom) IR spectrum observed upon prolonged 266 nm irradiation (before 193 nm photolysis). Peaks marked **B** are ascribed to benzdiyne, and peaks marked **H** are ascribed to hexatriyne.

photolysis. Considering these results, ketene **k-B** should be the ring-opened ketene **7**. Indeed, the calculated IR bands of ketene **7** (Figure 5) were in fair agreement with the observed IR bands of **k-B**. Thus, the second ketene **k-B** was assigned to ketene **7**.

Discussion: Ketene Formation in Benzdiyne Chemistry.

As described earlier, ketene **9** was not formed by cleavage of the bond between the ketene group and carbene moiety in **4** as seen in hetaryne chemistry.¹⁸ Given that ketene **9** was the primary product of the photolysis of **2a**, this ketene would be generated via a diradical state directly formed by decarboxylation of **2a**. A possible mechanism for the generation of ketene **9** is shown in Scheme 6. The ring cleavage would occur at the bond connecting the ketene group and the C–F carbon and not at the bond connecting the ketene group and the carbene moiety.

On the other hand, ketene **7** was the secondary product and would therefore be formed from **1a** or **9**: carbonylation of **1a** or a 1,2-F-shift concerted with bond cleavage of ketene **9** would produce ketene **7** (Scheme 7). When it is considered that the ketene formation in the photolysis of **2b** was a minor process, the ketene formed from **2b** may correspond to ketene **7**.

Figure 6 shows the energy diagram for the possible chemical

species participating in the photolysis of **2a**. The corresponding energy diagram for benzyne chemistry is shown for comparison (Figure 7). Ketenes **9** and **7** were 30 and 49 kcal mol⁻¹ more stable than **1a** + CO, respectively. On the other hand, ketene **5** was estimated to be only 2 kcal mol⁻¹ more stable than **1a** + CO, whereas cyclopentadienyliideneketene was 23 kcal mol⁻¹ more stable than benzyne + CO. These results revealed that ketene **5** was not a relatively stable species in contrast to the benzyne case. Thus, the ketene with the five-membered ring was greatly destabilized by introducing the unsaturated bond. Hence ring-opened ketenes **9** and **7** represent alternative low-energy structures. As described earlier, one interesting point is that ketocarbene-like intermediate **4** with the singlet ground state²⁶ could be optimized as a local minimum. A similar ketocarbene-like species could also be obtained as a local minimum in the bis(trifluoromethyl)-substituted derivatives. Electron-withdrawing groups would stabilize such ketocarbene-like species. Owing to the stabilization, the energy relationship between the ketocarbene(like) state and the ketene was reversed from that of other ketocarbene-ketene systems.^{28,29} This reversed energy relationship makes the Wolff rearrangement to ketene **5** difficult. From these thermodynamic data, ketocarbene-like **4** and cyclopropanone **8** should be observed as primary products. Given that the decarbonylation of the cyclopropanone intermediate proceeded efficiently upon photoirradiation,¹⁵ the latter intermediate must be converted to **1a**. Additionally, we could not confirm the generation of ketocarbene-like **4**, indicating it would be efficiently converted to ketene **9**.

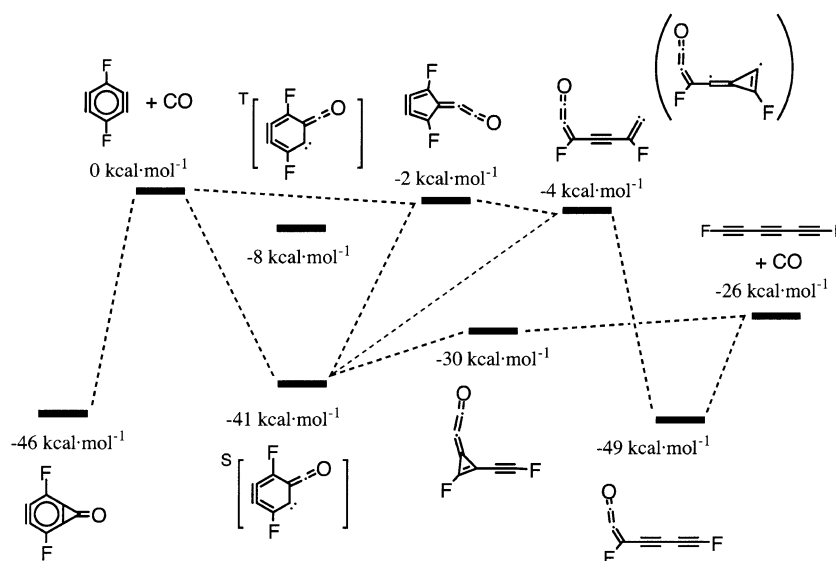
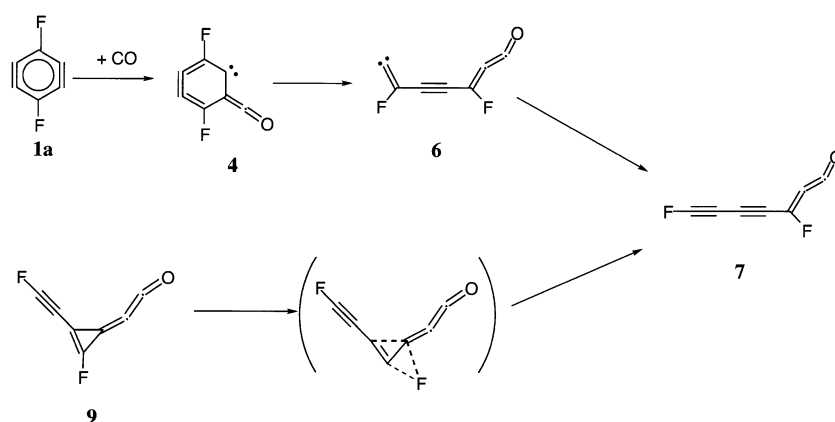
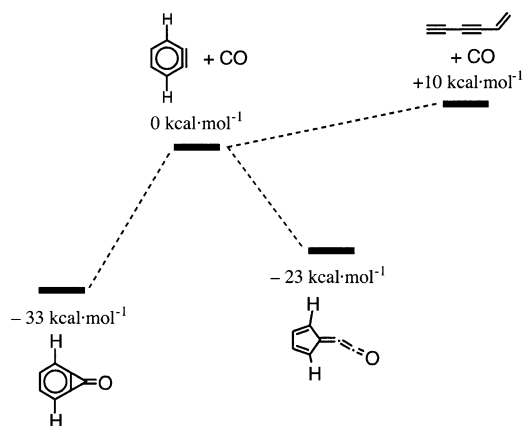
The fact that ketene **9** was exclusively observed in the difluoro system can be attributed to the different photochemistry induced by the resonance effect of the F atoms. The resonance effect of the F atoms resulted in the intense UV–vis absorption band of **1a**. Similarly, the resonance effect might produce a specific excited state, where the cleavage of the bond connecting the ketene group and the C–F carbon can be induced, with high population.

Conclusion

Ketene formation was observed in the photolysis of difluorobenzenetetracarboxylic dianhydride. The ketenes formed were identified on the basis of good agreement between the observed and calculated IR spectra. The ketenes were not those corresponding to the cyclopentadienyliideneketene formed in the benzyne chemistry. The first generated ketene was assigned to a ketene with a cyclopropene moiety, **9**, which probably was formed by the ring cleavage of ketocarbene-like intermediate **4**. The second ketene was assigned to a ketene with a butadiyne moiety, **7**. Ketenes **9** and **7** were 30 and 49 kcal mol⁻¹ more stable than **1a** + CO, respectively, whereas the ketene with the

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Scheme 7. Possible Mechanism for Generation of Ketene 7**Figure 6.** Energy diagram of possible $C_6F_2 + CO$ species estimated at the B3LYP/6-31G* level. Zero-point energies at the same computational level were used for correction after being scaled by 0.9806.²³**Figure 7.** Energy diagram of possible $C_6H_4 + CO$ species estimated at the B3LYP/6-31G* level. Zero-point energies were used for correction.

five-membered ring **5** was only 2 kcal mol⁻¹ more stable than **1a** + CO. Ketene **9** was one of major products in the photolysis and was formed by cleavage of the bond connecting the ketene

group and the C–F carbon and not the bond connecting the ketene group and the carbene moiety. The structures of this ketene indicated that this unprecedented ring cleavage, rather than Wolff rearrangement, was the dominant process in the chemistry of the strained ring system. The unique ketene formation in the difluoro system was attributed to the resonance effect of F atoms affecting the population of a specific photoexcited state resulting in the bond cleavage.

Acknowledgment. We thank Dr. T. Matsuura and S. Sasaki of NTT Advanced Technology Inc. for supplying the dianhydride precursors.

Supporting Information Available: Details of peak separation of the complex ketene + CO band, UV–vis. Absorption spectra observed during the photolysis of **2a**. Optimized geometries and frequencies of calculated species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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