

Photoinduced skeletal rearrangement of 1,1-diarylspiropentanes

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The photochemical reactivities of 1,1-diarylspiropentanes **1a–c** have been investigated under various photolysis conditions. Upon direct photolysis or acetone-sensitized photolysis, **1** underwent skeletal rearrangement to afford methylidenecyclobutanes **2**, **3** and **4**. A mechanism involving diradical intermediates has been proposed. Also studied were the photochemical and thermal reactions of the electron donor–acceptor (EDA) complexes of **1** with tetracyanoethylene (TCNE). Photoirradiation of the charge-transfer (CT) absorption bands of the EDA complexes resulted in the skeletal rearrangement of **1** to **2** and **3**, with concomitant formation of TCNE adducts **11b,c** and **12a–c**. The X-ray structure of **11c** is reported. A mechanism involving ion radical pairs [$1^{+\cdot}$, $TCNE^{\cdot-}$] is proposed for the photoreaction. In contrast, no skeletal rearrangement was observed in the thermal reaction of the EDA complexes although **11b** and **11c** were produced.

The photochemical and thermal reactions of strained hydrocarbons¹ have been the subject of considerable attention. For example, the thermolysis² and photolysis^{3,4} of cyclopropanes have been thoroughly investigated and have been shown to give stereomutation, skeletal rearrangements and fragmentation. The charge-transfer (CT) and electron-transfer (ET) chemistry⁵ of cyclopropanes has also attracted attention and cyclopropanes have been used as reactive electron donors for isomerizations,⁶ cycloadditions,⁷ nucleophile-assisted ring cleavage⁸ and oxygenations.⁹

Spiropentanes are also remarkable strained compounds. In conjunction with the thermal reactions of cyclopropanes, the thermal reactivity of spiropentanes has been investigated with particular interest in their skeletal rearrangement.¹⁰ However, little attention has been paid to the photochemical rearrangement of spiropentanes and although the parent spiropentane is known to undergo fragmentation reactions when photolyzed in the gas-phase,¹¹ its skeletal rearrangement has never been observed. It is not known whether spiropentane derivatives can undergo any photochemical rearrangements.

We report here the photochemical reactivity of 1,1-diarylspiropentanes **1a–c** upon direct photolysis and triplet photosensitization. These exploratory studies show that **1a–c** undergo photochemical skeletal rearrangements to 1-diaryl-methylidenecyclobutanes **2**, 2,2-diaryl-1-methylidenecyclobutanes **3** and 3,3-diaryl-1-methylidenecyclobutanes **4**. We have also studied the photochemical and thermal reactions of the electron donor–acceptor (EDA) complexes derived from **1** and TCNE in order to exploit their ET and CT chemistry.

Results and discussion

Direct photolysis of spiropentanes **1**

Direct photolyses of **1** were performed with 254 nm light. After photolysis of acetonitrile solutions containing 2.0×10^{-2} mol dm^{-3} of **1**, three types of methylidenecyclobutanes, **2**, **3** and **4** were produced together with 1,1-diaryllenes **5**. The results are summarized in Table 1.

A possible mechanism for the photoreaction can be deduced from the position of the diarylmethylene moiety of the photolysis products. As shown below, a mechanism employing hypothetical diradical intermediates **6–9** rationalizes the photorearrangement. Photolysis of **1** would cause C-1–C-2 bond fission [eqn. (1)] and C-1–C-3 bond fission [eqn. (2)] competitively to afford 1,3-diradicals **6** and **8**, respectively. The

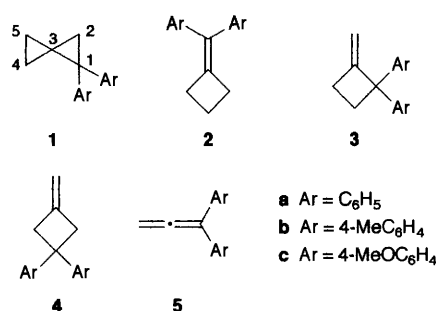
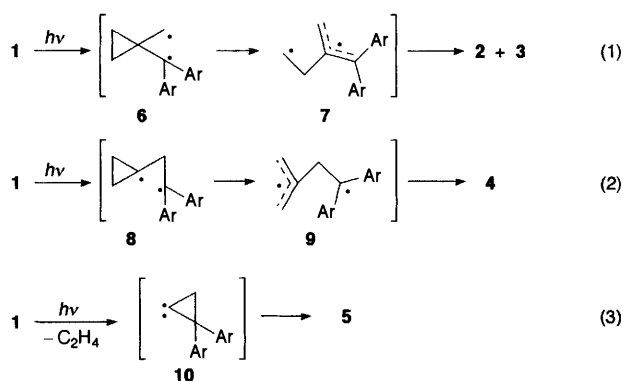


Table 1 Direct^a and acetone sensitized photolysis^b of **1**

Spiropentane	Direct/yield (%) ^c				Recov.	Sens./yield (%) ^c		
	2	3	4	5		2	3	Recov.
1a	10	9	10	38	30	21	27	38
1b	12	11	6	35	31	27	40	22
1c	12	20	2	12	37	21	45	9

^a Solutions of **1** (0.12 mmol) in acetonitrile (6 cm^3) were photolysed (254 nm) for 3 h. ^b Solutions of **1** (0.12 mmol) in acetone (6 cm^3) were photolysed (300 nm) for 5 h. ^c By 90 MHz ^1H NMR.

former species is converted into **7** by C-3–C-4 bond cleavage, and the latter into **9** through ring opening of the cyclopropyl radical moiety. Ring closure of the resulting 1,4-diradicals **7** and **9** leads to respective methylidenecyclobutanes, **2**, **3** and **4**.



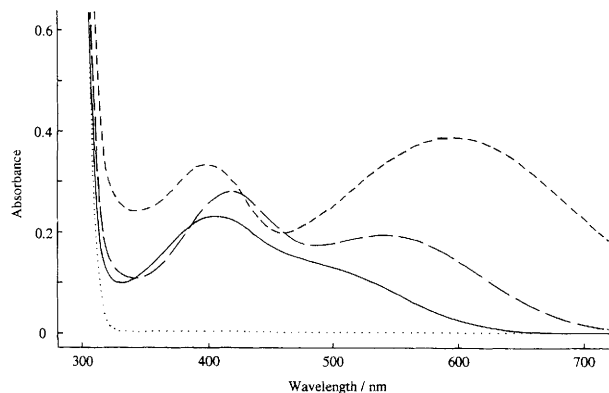


Fig. 1 The charge-transfer absorption spectra of the EDA complexes derived from **1** and TCNE (2.5×10^{-2} mol dm⁻³ each) in dichloromethane at 25 °C: **1a** (—), **1b** (---) and **1c** (-·-). The dotted line (· · ·) is absorption due to TCNE only

As for the formation of **5**, it seemed possible that the secondary photoreaction of **2**, **3** and/or **4** would afford **5** through loss of ethene. However, the possibility was ruled out by control experiments, showing that none of **2**, **3** and **4** gave **5** under the photolysis conditions. It was also confirmed that **2**, **3** and **4** did not interconvert with one another. Therefore, it is most likely that the fragmentation reaction [eqn. (3)] occurs in the direct photolysis of **1** to generate 2,2-diarylcyclopropylidene **10** as a third reaction pathway. Ring opening of **10** would afford **5**. Similar retro-1,2-addition to generate carbenes has been observed in the photolyses of cyclopropanes.^{12a} In addition, **10a** and the related systems have been reported to undergo facile ring opening to give allenes.^{12b,c} A characteristic feature of the direct photolysis of **1** is lack of positional selectivity for the initial bond fission. Presumably this is due to the excess vibrational energy of the photoexcited **1**.

Acetone-sensitized photolysis of spiropentane **1**

It is interesting to compare the results of direct photolysis with those of triplet sensitized photoreaction. We have examined several triplet sensitizers such as fluorenone ($E_T = 225$ kJ mol⁻¹)¹³ and benzophenone ($E_T = 289$ kJ mol⁻¹)¹⁴ but it turned out that these sensitizers were ineffective. In the case of xanthone ($E_T = 309$ kJ mol⁻¹),¹⁴ the sensitized photolysis of **1a** resulted in only ca. 3% of **3a**. However, acetone ($E_T = 334$ kJ mol⁻¹)¹⁴ was effective for the photorearrangement of **1** and the skeletal rearrangement of **1** was successfully induced by irradiation (300 nm) of acetone solutions containing 2.0×10^{-2} mol dm⁻³ of **1**. Intriguingly, acetone-sensitized photolysis of **1** selectively led to the formation of **2** and **3** in high yields as shown in Table 1. Control experiments showed that **2** and **3** did not interconvert with each other in the presence of acetone.

It should be noted that no formation of **4** or allene **5** was observed in the acetone-sensitized photoreaction of **1**. These results suggest that the rearrangement of **1** in a triplet manifold proceeds selectively through the sequential C-1–C-2 and C-3–C-4 bond cleavage as described in terms of eqn. (1). Again, diradical intermediates **6** and **7** play an important role in the formation of **2** and **3**. The other pathways [eqns. (2) and (3)], which are feasible in the direct photolysis, are not involved in the acetone-sensitized photoreaction.

Formation of EDA complexes of spiropentane **1** with TCNE

Spiropentanes **1a–c** are good electron donors with oxidation potentials (E_{ox}) +1.67, +1.42 and +1.17 V *vs.* SCE, respectively. When a colourless solution of TCNE was mixed with colourless **1a** in dichloromethane, the orange-red coloration of the EDA complex immediately developed. Compounds **1b** and **1c** with TCNE gave red-brown and purple colours, respectively. As shown in Fig. 1, the colour change is due to the appearance of distinctive charge transfer (CT)

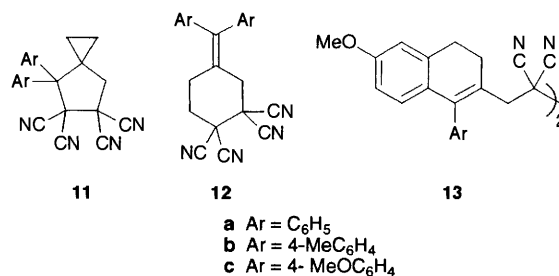
absorption bands of the resulting EDA complexes. The absorption spectrum of the **1a**–TCNE complex appears as a composite of two partially resolved bands at λ_{max} 406 and λ_{sh} 486 nm. For **1b** and **1c**, the longer wavelength bands were significantly red-shifted and their absorption spectra appeared with two well-resolved bands. Their absorption maxima were located at 419 and 540 nm for **1b** and at 398 and 598 nm for **1c**.

The observed red-shifting of the CT bands of the EDA complexes of **1b** and **1c** is as expected from the electron donating effects of the methyl and methoxy substituents on the aromatic rings. By way of comparison, CT absorption maxima of arene complexes such as benzene–TCNE (λ_{max} 390 nm), toluene–TCNE (λ_{max} 414 nm) and anisole–TCNE (λ_{max} 388, 512 nm) are progressively red-shifted. Electron transfer (ET) from donors to acceptors occurs upon photoirradiation of their EDA complexes.¹⁵ Accordingly, photoirradiation of the CT bands of the EDA complexes of **1a–c** is a straightforward method to investigate their ET photochemistry.

Photochemistry of the 1–TCNE EDA complexes

The 1–TCNE EDA complexes were found to be photoreactive. Irradiation ($\lambda > 390$ nm) of a solution of **1a** and TCNE in dichloromethane resulted in skeletal rearrangement to give **2a** and **3a** in 44 and 7% yield, respectively (Table 2). It should be noted that, unlike direct and acetone-sensitized photolyses,† **2a** was produced in preference to **3a**. Also noteworthy is that the ratio of **2a**:**3a** is dependent on the solvent polarity. Thus in a polar solvent, acetonitrile, exclusive formation of **2a** was observed whereas the yield of **3a** increased to 13% in nonpolar benzene.

Similar trends were observed in the photoreactions of **1b** and **1c**. In acetonitrile **2b** or **2c** was produced in (almost) complete preference to **3b** or **3c**. In dichloromethane or benzene, formation of **2b** or **2c** was still favoured but the yield of **3b** and **3c** increased with decreasing solvent polarity (Table 2). In these cases appreciable amounts of TCNE adducts **11b,c** and **12b,c** were obtained in addition to the rearranged products. With **1c**, a novel 2:1 adduct **13c** was also produced. Control experiments showed that **2** and **3** did not interconvert with each other and that **12** was not produced from **2** or **3**.



X-Ray crystallographic analysis of **11c** was carried out for the unequivocal determination of the structure since inspection of the spectroscopic data did not completely eliminate a possible alternative structure which could arise from the C-1–C-3 bond fission of **1**. The result is shown in Fig. 2. Adduct **11c** has indeed a composite structure in which TCNE is incorporated into the C-1–C-2 bond of **1c**, not the C-1–C-3 bond.

Related studies on the ET reactions of various strained hydrocarbons^{5–9} have revealed that the strained σ -bonds can

† Involvement of electron transfer in the acetone-sensitized photoreaction of **1** is highly unlikely. Acetone is a poor acceptor and the reduction peak by CV cannot be seen up to -2.5 V *vs.* SCE in MeCN. We presume that the E_{red} may be ca. -3 V. Based on this value and the triplet excitation energy of 3.47 eV (334 kJ mol⁻¹), the E_{red} of triplet excited acetone is estimated to be ca. $+0.5$ V *vs.* SCE, which is not positive enough to oxidize even the most electron-rich **1c**.

Table 2 Photoreaction of the EDA complexes derived from **1** and TCNE^a

Donor	Solvent (irrad. time)	Yield (%) ^b					Recov.
		2	3	11	12	13	
1a	CH ₃ CN (20 h)	38	0	0	0	0	60
1a	CH ₂ Cl ₂ (20 h)	44	7	0	0	0	35
1a	C ₆ H ₆ (20 h)	71	13	0	t ^c	0	5
1b	CH ₃ CN (20 h)	51	t ^c	2	0	0	43
1b	CH ₂ Cl ₂ (20 h)	38	5	5	0	0	12
1b	C ₆ H ₆ (20 h)	40	15	6	0	0	7
1c	CH ₃ CN (6 h)	19	0	4	t ^c	11	48
1c	CH ₂ Cl ₂ (6 h)	4	2	17	8	34	25
1c	C ₆ H ₆ (6 h)	13	5	19	6	29	11

^a Solutions (4 cm³) of **1** and TCNE (0.20 mmol each) were irradiated using a 2 kW xenon lamp ($\lambda > 390$ nm). ^b Analysed by 90 MHz ¹H NMR. ^c Less than 2%.

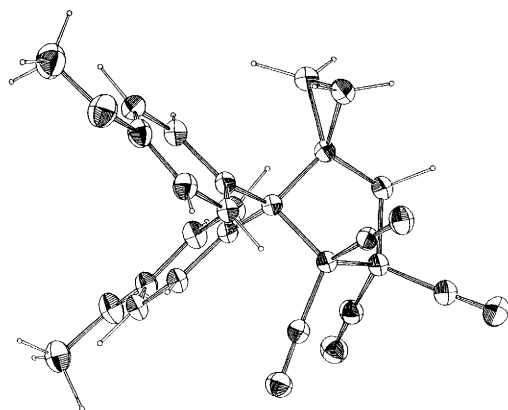
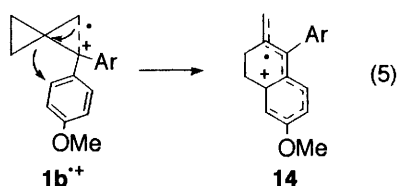
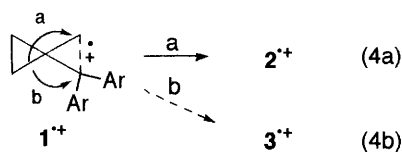
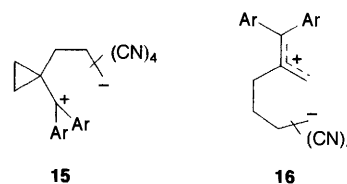


Fig. 2 Molecular structure of **11c**



be weakened or cleaved by ET. The observed rearrangement of **1** to **2** is explained as a result of C-1–C-2 bond fission of **1**⁺ in a photogenerated ion pair [**1**⁺, TCNE^{•-}] followed by migration of the C-4 (or C-5) onto C-2 to give **2**⁺ [eqn. (4a)]. Reverse electron transfer from TCNE^{•-} then leads to **2**. A similar skeletal rearrangement possibly involving initial C-1–C-2 bond fission followed by C-4 (C-5) migration was observed for the parent spiro-pentane cation radical.¹⁶ The photosensitized ET reaction of **1** also resulted in the skeletal rearrangement.¹⁷ In the present case the formation of **13** suggests that the cation radical **1c**⁺ undergoes an additional type of rearrangement employing C-4 migration onto the 4-methoxyphenyl ring to give **14** as shown in eqn. (5). Deprotonation followed by the reaction with TCNE is a possible pathway for the formation of **13c**.



It is interesting that a notable amount of **3** was produced in less polar solvents since formation of **3**⁺ from **1**⁺ is thermodynamically much less favourable than **2**⁺. Calculations based on the redox potentials of **2**, **3** and TCNE[‡] suggest that ion pairs [**2a**⁺, TCNE^{•-}], [**2b**⁺, TCNE^{•-}] and [**2c**⁺, TCNE^{•-}] are more stable than ion pairs [**3a**⁺, TCNE^{•-}], [**3b**⁺, TCNE^{•-}] and [**3c**⁺, TCNE^{•-}] by 0.55, 0.40 and 0.30 eV, respectively. In this respect it is unlikely that formation of **3** is due to cation radical transformation as shown in eqn. (4b). Solvent polarity plays an important role in many ET photoreactions and photogenerated ion pairs sometimes show diverse reactivities depending on the solvent polarity.¹⁸ In a polar solvent, acetonitrile, solvation of the photogenerated ion pair [**1**⁺, TCNE^{•-}] would result in elongation of the interionic distance. Under the circumstances migration of C-4 (or C-5) of **1**⁺ onto C-2 to give **2**⁺ [eqn. (4a)] is expected to proceed with diminished electronic and steric effects due to pairing TCNE^{•-}.

In dichloromethane or benzene shorter interionic distances between **1**⁺ and TCNE^{•-} would bring about an appreciable electronic effect upon fission of the C-1–C-2 bond of **1**⁺. It is conceivable that a 1,3-diradical similar to **6** is generated to some extent through the C-1–C-2 bond cleavage of **1**⁺ followed by reverse ET from the paired TCNE^{•-}. The results of the direct photolysis of **1** suggest that the hypothetical diradical **6** leads to the formation of **2** and **3** through **7**. Formation of cycloadducts **11b,c** and **12c** in dichloromethane or benzene can be interpreted as a result of the reaction of **6b,c** and **7c** with TCNE.

It should be mentioned that **1b** and **1c** afforded cycloadducts **11b,c** and **12c** whereas **1a** gave no **11a** but a trace amount of **12a**. A simple explanation for this is that the reactivity of **6** and **7** would be enhanced by electron donating substituents such as methyl or methoxy groups. Diradicals **6b,c** and **7c** may be more reactive than **6a** and **7a**, respectively, and trapping with TCNE would give **11b,c** and **12c**. It is also conceivable that polar intermediates like **15** and **16** are precursors for adducts **11** and **12**. Stabilizing effects of the methyl and methoxy substituents on such species would be advantageous for the formation of the cycloadducts.

Thermal activation of the 1–TCNE EDA complexes

The EDA complexes of **1** and TCNE are stable at room temperature in solutions and they persist for hours without detectable chemical change. However, we noticed that **1c** afforded 2% of **11c** when a solution of **1c** and TCNE in dichloromethane was kept in the dark at room temperature for 2 days. Therefore the thermal reaction of the EDA complexes of **1** and TCNE was investigated.

When a solution of **1a** with TCNE in xylene was heated at reflux (140 °C) for 3 days, no reaction was observed and **1a** was recovered in 97% yield. On the other hand, reaction of **1b** and TCNE afforded adduct **11b** as the sole product in 51% yield with recovery of **1b** (44%) under comparable conditions. In the case of **1c**, similar reaction with TCNE in xylene or propionitrile for 2 days gave **11c** in 43% or 24% yield with recovery of **1c** (45% or 74%). No reaction was observed when **1b** and **1c** were heated without TCNE under comparable conditions. It is noteworthy that, unlike the photochemistry,

[‡] E_{ox} Values of **2a**, **2b**, **2c**, **3a**, **3b** and **3c** are +1.46, +1.38, +1.19, +2.01, +1.78 and +1.49 V (vs. SCE in MeCN), respectively. E_{red} Of TCNE is +0.22 V (vs. SCE in MeCN).

the thermal reactions gave no rearranged products even when the reaction was carried out in polar propionitrile with **1c**, the most electron-rich substrate.

We have examined another acceptor, 2,3,6,7-tetracyano-pyrazino[2,3-*b*]pyrazine (TCPP),¹⁹ whose reduction potential (E_{red}) is +0.30 V *vs.* SCE. The E_{red} value indicates that TCPP is a better acceptor than TCNE and therefore stronger CT interactions may result between **1c** and TCPP than between **1c** and TCNE. However, no trace of rearrangement product **2c** or **3c** could be detected and **1c** was recovered almost quantitatively (>97%) when **1c** was heated with TCPP in refluxing propionitrile. Similar reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (E_{red} , +0.51 V *vs.* SCE) also failed to give **2c** or **3c**.

It is interesting that the TCNE adducts **11b** and **11c** can be obtained also by the thermal reaction of **1b** and **1c**. The thermally activated EDA complexes of **1b** and **1c** would be akin to the corresponding photogenerated ion radical pairs. Obviously, formation of ion radicals is not involved in the thermal reaction since no formation of the rearranged products was observed. In fact ET processes from **1** to TCNE are thermodynamically unfavourable with the calculated free energy changes being highly endothermic, +1.45, +1.20 and +0.95 eV for **1a**, **1b** and **1c**, respectively. Nevertheless strong bonding EDA interactions can be involved in the transition states for the thermal reactions of **1b** and **1c**. During bonding interactions between **1b** (or **1c**) and TCNE, enhanced CT interactions would simultaneously reduce the electron density of the peripheral bond (C-1–C-2) of **1b** or **1c**. As a result, the thermally activated EDA complex selectively leads to the formation of the cycloadduct **11b** and **11c** without giving rearranged products. In the case of the **1a**–TCNE complex, the amount of CT during the thermal reaction may not be great enough since **1a** is the weakest donor.

In this context the thermal EDA reaction should be referred to as an inner sphere type ET reaction^{20a–c} or a polar process,^{20c–g} which involves bond reorganization synchronously with ET. A dipolar species **15** postulated in the photoreaction may also play a role as an intermediate. Analogous cycloadditions of some cyclopropane derivatives with TCNE have been observed and intermediates similar to **15** have been postulated.^{7a,b,e}

Conclusion

The results of the investigation of the photoreactions of **1** provided unprecedented examples of photochemical rearrangement of spiropentanes to methylidenecyclobutanes. Electronically excited **1** and cation radicals **1⁺** play an important role in the photoinduced reactions of **1**. Although the mechanism varies according to the mode of excitation, change in the electronic configuration of **1** generally leads to the skeletal rearrangement. The photoinduced ET reaction of **1** presents an intriguing example, in which degree of interionic interaction in the photogenerated ion pairs may be controlled by solvent polarity and hence the subsequent chemical reactions can be diversified.

Experimental

Melting points were measured on a Yamato MP-21 melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian EM-390 or XL-200 NMR spectrometer; J values are given in Hz. A Shimadzu IR-435 spectrometer was used for IR measurements. UV–VIS absorption spectra were measured on a Hitachi 340 spectrometer. Cyclic voltammetric measurements were made in acetonitrile with 0.1 mol dm⁻³ tetraethylammonium perchlorate as supporting electrolyte and SCE as the reference electrode by using a Yanagimoto P-1000 voltammetric analyser equipped with a function generator. Spiropentanes **1** were synthesized by dibromomethylation²¹

of 1-diarylmethylidenecyclopropanes followed by tin hydride reduction. 1-Diarylmethylidenecyclopropanes were synthesized according to literature methods.^{22,23} 2,2-Diaryl-1-methylidenecyclobutanes **3** were obtained and characterized previously.¹⁷ Direct photolyses were carried out on a Rayonet photoreactor with four RUL-2540 lamps. For triplet sensitized photolyses four RUL-3000 lamps were used. Photolyses of the EDA complexes of **1** were performed by using a 2 kW xenon lamp with a Toshiba L-42 glass filter ($\lambda > 390$ nm). Diethyl ether is referred to as “ether”.

Direct photolysis of spiropentanes 1

A solution of **1** (0.12 mmol) in acetonitrile (6 cm³) in a quartz tube was irradiated for 3 h (λ 254 nm). After irradiation, the mixture was evaporated and the resulting photolysate was analysed by NMR with 1,1,2,2-tetrachloroethane as an internal standard. The results are summarized in Table 1. The photoproducts **2** and **3** were identified by ¹H NMR spectral comparison with the authentic samples prepared according to the literature method.^{17,24} Methylidenecyclobutanes **4** were independently synthesized as described below and characterized.²⁵ Allenes **5** were identified by their ¹H NMR (200 MHz, CDCl₃) and IR (neat). Their olefinic singlets at δ_{H} 5.22–5.26 and the IR absorptions²⁶ at 1935–1936 cm⁻¹ are characteristic: compound **5a**, δ_{H} 5.26 and ν_{max} 1935 cm⁻¹; **5b**, δ_{H} 5.22 and 1935 cm⁻¹; **5c**, δ_{H} 5.21 and 1936 cm⁻¹. Control experiments with **2**, **3** and **4** showed that they did not interconvert with one another and were recovered in yields of 92–97% under the photolysis conditions.

Independent synthesis of 4

3,3-Diaryl-1-methylidenecyclobutanes **4** were synthesized from 3,3-diarylcyclobutan-1-ones^{27,28} and diiodomethane according to a literature method for the synthesis of methylidenecyclobutane.^{29,30} The synthesis of **4a** is described below as a typical procedure. In a 200 cm³ flask mercury (200 g, 1 mol) was placed under a dry nitrogen atmosphere and magnesium ribbon (600 mg, 24.7 mmol) was added. The mixture was stirred and heated gently with a heat gun to dissolve the magnesium, after which dry ether (15 cm³) was added. While the mixture was vigorously stirred, a solution of 3,3-diphenylcyclobutan-1-one (2.22 g, 10.0 mmol) and diiodomethane (0.90 cm³, 11 mmol) in ether (20 cm³) was added dropwise over a period of 20 min. The mixture was stirred for a further 1 h, after which the ether layer was poured into aq. ammonium chloride and extracted with ether. The ether extracts were combined, washed with water three times, dried (Na₂SO₄) and evaporated to give a pale yellow oil (1.46 g), which was then chromatographed on a silica gel column. Elution with hexane gave 1.30 g (5.90 mmol, 59%) of practically pure **4a**.

3,3-Diphenyl-1-methylidenecyclobutane 4a. Mp 25–25.5 °C (from ethanol) (Found: C, 92.4; H, 7.3. C₁₇H₁₆ requires C, 92.68; H, 7.32%); ν_{max} (KBr)/cm⁻¹ 3050, 3000, 2950, 2900, 1679, 1598, 1495, 1445, 1410, 1020, 875, 758 and 698; δ_{H} (90 MHz, CCl₄) 3.35 (4 H, t, J 2.0), 4.87 (2 H, q, J 2.0) and 7.09 (10 H, m); m/z (80 °C, 25 eV) 220 (M⁺, 50%) and 205 (100).

3,3-Bis(4-methylphenyl)-1-methylidenecyclobutane 4b. Mp 44.5–45.5 °C (from ethanol) (Found: C, 91.8; H, 8.2. C₁₉H₂₀ requires C, 91.88; H, 8.12%); ν_{max} (KBr)/cm⁻¹ 2950, 2900, 1675, 1510, 1400, 1295, 1195, 1018, 890, 815, 725 and 550; δ_{H} (90 MHz, CCl₄) 2.27 (6 H, s), 3.32 (4 H, t, J 2.5), 4.78 (2 H, q, J 2.5) and 6.89–7.10 (8 H, m); m/z (80 °C, 13.5 eV) 248 (M⁺, 43%), 233 (31) and 156 (100).

3,3-Bis(4-methoxyphenyl)-1-methylidenecyclobutane 4c. Mp 52.5–53.5 °C (from ethanol) (Found: C, 82.3; H, 7.4. C₁₉H₂₀O₂ requires C, 81.39; H, 7.19%); ν_{max} (KBr)/cm⁻¹ 2950, 2900, 1680, 1610, 1510, 1245, 1030, 820, 600 and 560; δ_{H} (90 MHz, CCl₄) 3.28 (4 H, t, J 2.0), 3.71 (6 H, s), 4.80 (2 H, q, J 2.0), 6.68 (4 H, m) and 7.05 (4 H, m); m/z (80 °C, 13.5 eV) 280 (M⁺, 13%), 249 (37) and 172 (100).

Attempted triplet sensitized photolysis of **1a**

Typically, a solution of **1a** (26.5 mg, 0.12 mmol) in acetonitrile (6 cm³) and a sensitizer (1 × 10⁻² mol dm⁻³) in a quartz tube was irradiated for 5 h (λ 300 nm). After irradiation, the mixture was evaporated and the resulting photolysate was analysed by NMR with 1,1,2,2-tetrachloroethane as an internal standard. Fluorenone and benzophenone were ineffective sensitizers, giving no observable rearrangement and **1a** was recovered in 90–97% yield. Using xanthone as a sensitizer, ca. 2% of **3a** was formed (as detected by ¹H NMR).

Acetone sensitized photolysis of **1**

A solution of **1** (0.12 mmol) in acetone (6 cm³) in a quartz tube was irradiated for 5 h with light (λ 300 nm). After irradiation, the mixture was evaporated and the resulting photolysate was analysed by NMR with 1,1,2,2-tetrachloroethane as an internal standard. The results are summarized in Table 1. Control experiments with **2** and **3** showed that they did not interconvert with each other and were recovered in yields of 92–98%.

Photoreaction of the 1–TCNE complexes

Acetonitrile, dichloromethane and benzene were used as solvents. Typically, a solution (4 cm³) of **1** and TCNE (0.20 mmol each) was irradiated (λ > 390 nm) for 20 h (6 h for **1c**), after which the mixture was evaporated and the residue was analysed by 90 MHz NMR with nitromethane as an internal standard. Identification of **2** and **3** was based on spectral comparison with the authentic samples obtained independently.^{17,24} Irradiation of **2** or **3** with TCNE in dichloromethane gave no reaction and recovery of **2** or **3**.

Isolation of **12a**

Irradiation of **1a** and TCNE (0.20 mmol each) in benzene as described above gave **2a** and **3a** together with a trace amount of **12a**. Photolysates obtained by triplicate photolyses were combined and subjected to preparative TLC. Development with hexane–dichloromethane (2:3 v/v) afforded 4-(diphenylmethylidene)cyclohexane-1,1,2,2-tetracarbonitrile **12a** (ca. 2 mg) (*R*_f 0.35), mp 46–49 °C; ν_{max}(KBr)/cm⁻¹ 3060, 2930, 2850, 2212 (CN), 1620, 1590, 1445, 1392, 1240, 1130, 1110, 1075, 1030, 1010, 765, 685 and 630; δ_H(200 MHz, CDCl₃) 2.54 (2 H, A₂B₂, *J* 4.0 and 7.5), 2.66 (2 H, A₂B₂, *J* 4.0 and 7.5), 3.19 (2 H, s) and 7.10–7.45 (10 H, m); *m/z* (90 °C, 25 eV) 349 (M⁺ + 1, 17), 348 (M⁺, 70), 347 (100), 320 (9), 281 (16), 255 (37), 254 (17), 252 (15), 240 (13), 219 (5) and 205 (30).

Isolation of **11b**

A solution (4 cm³) of **1b** (50 mg, 0.20 mmol) and TCNE (26 mg, 0.20 mmol) was photolysed as described above for 20 h, after which the mixture was evaporated and subjected to silica gel TLC with hexane–dichloromethane (2:3 v/v). A mixture of **2c**, **3c** and **1c** was obtained from the upper band (*R*_f 0.91) and quantified by 90 MHz NMR with nitromethane as an internal standard. The lower band (*R*_f 0.35) was collected and crystallized from benzene–hexane to give 4,4-bis(4-methylphenyl)spiro[2.4]heptane-5,5,6,6-tetracarbonitrile **11b**, mp 236.5–237.5 °C (decomp.) (Found: C, 80.2; H, 5.3; N, 14.8. C₂₅H₂₀N₄ requires C, 79.76; H, 5.36; N, 14.88%); ν_{max}(KBr)/cm⁻¹ 2920, 2250 (CN), 2220 (CN), 1510, 1460, 1420, 1195, 1035, 815, 780, 540 and 500; δ_H(90 MHz, CDCl₃) 0.96 (4 H, br s), 2.32 (6 H, s), 3.10 (2 H, br s) and 7.1–7.4 (8 H, m); *m/z* (90 °C, 25 eV) 376 (M⁺, 25), 248 (13), 234 (20), 233 (100), 220 (15), 218 (10) and 205 (6).

Isolation of **11c**, **12c** and **13c**

A solution (4 cm³) of **1c** (56 mg, 0.20 mmol) and TCNE (26 mg, 0.20 mmol) was photolysed as described above. After irradiation for 6 h, the mixture was evaporated and subjected to silica gel TLC with hexane–dichloromethane (1:2 v/v). A mixture of **2c**, **3c** and **1c** was obtained from the top band (*R*_f 0.7)

and quantified by 90 MHz NMR with nitromethane as an internal standard. Other bands gave the following compounds:

4,4-Bis(4-methoxyphenyl)spiro[2.4]heptane-5,5,6,6-tetracarbonitrile 11c. (*R*_f 0.32) Mp 230–231 °C (from benzene) (Found: C, 73.4; H, 4.7; N, 13.6. C₂₅H₂₀N₄O₂ requires C, 73.51; H, 4.94; N, 13.72%); ν_{max}(KBr)/cm⁻¹ 2930, 2830, 2230 (CN), 1607, 1510, 1260, 1180, 1030, 830 and 580; δ_H(90 MHz, CDCl₃) 0.97 (4 H, br s), 3.11 (2 H, br s), 3.83 (6 H, s), 6.90 (4 H, m) and 7.33 (4 H, m); δ_C(50 MHz, CDCl₃) 27.06 (t), 27.21 (s), 28.56 (t), 42.19 (s), 45.50 (t), 53.61 (s), 55.36 (q), 65.38 (s), 111.24 (s), 111.48 (s), 114.39 (d), 129.20 (s), 129.68 (s) and 160.12 (s); *m/z* (100 °C, 25 eV) 409 (M⁺ + 1, 12), 408 (M⁺, 87), 280 (69), 279 (100), 265 (13), 252 (23), 249 (99), 159 (9) and 121 (22).

4-Bis(4-methylphenyl)methylidene-cyclohexane-1,1,2,2-tetracarbonitrile 12c. (*R*_f 0.50) Mp 153.5–154 °C (from dichloromethane–hexane) (Found: C, 73.8; H, 5.1; N, 13.6. C₂₅H₂₀N₄O₂ requires C, 73.51; H, 4.94; N, 13.72%); λ_{max}(MeCN) 244 and 272 (sh) nm (ε 21 400 and 14 400 dm³ mol⁻¹ cm⁻¹); ν_{max}(KBr)/cm⁻¹ 2930, 2820, 2280 (CN), 2240 (CN), 1605, 1510, 1440, 1240, 1170, 1027, 830 and 575; δ_H(200 MHz, CDCl₃) 2.53 (2 H, A₂B₂, *J* 3.5 and 7.0), 2.66 (2 H, A₂B₂, *J* 3.5 and 7.0), 3.22 (2 H, s), 3.80 (3 H, s), 3.82 (3 H, s), 6.88 (4 H, m) and 7.05 (4 H, m); δ_C(50 MHz, CDCl₃) 25.78 (t), 33.01 (t), 36.84 (t), 40.81 (s), 41.39 (s), 55.27 (q), 110.47 (s), 110.58 (s), 113.97 (d), 114.29 (d), 120.30 (s), 129.98 (d), 130.10 (d), 131.93 (s), 132.44 (s), 146.76 (s), 159.30 (s) and 159.38 (s); *m/z* (100 °C, 25 eV) 408 (M⁺, 12), 282 (11), 281 (100), 279 (83), 266 (52), 253 (13), 252 (11) and 250 (27).

1,4-Bis[6-methoxy-1-(4-methoxyphenyl)-3,4-dihydro-2-naphthyl]butane-2,2,3,3-tetracarbonitrile 13c. (*R*_f 0.43). Recrystallized from dichloromethane–hexane, mp 176–177 °C (decomp.); ν_{max}(KBr)/cm⁻¹ 2930, 2830, 2250 (CN), 2220 (CN), 1640, 1610, 1570, 1510, 1460, 1305, 1280, 1250, 1175, 1110, 1035, 830 and 580; δ_H(200 MHz, CDCl₃) 2.59 (4 H, dd, *J* 5.5 and 8.5), 2.92 (4 H, dd, *J* 5.5 and 8.5), 3.06 (4 H, s), 3.78 (6 H, s), 3.83 (6 H, s), 6.59 (4 H, br s), 6.73 (2 H, s) and 6.93–7.10 (8 H, m); δ_C(50 MHz, CDCl₃) 27.00 (t), 28.51 (t), 39.57 (t), 44.67 (s), 55.27 (q), 55.36 (q), 110.78 (d), 111.22 (s), 113.28 (d), 114.46 (d), 122.88 (s), 128.54 (s), 128.74 (s), 128.97 (d), 131.27 (d), 137.25 (s), 142.38 (s), 159.21 (s) and 159.34 (s); *m/z* (FAB, NBA matrix) 688 (M⁺ + 2, 3), 687 (M⁺ + 1, 7), 686 (M⁺, 7), 343 (5), 280 (27), 279 (100), 154 (18), 136 (12) and 128 (1).

X-ray crystallography of **11c**

A crystal of **11c**, obtained as a colourless rod, approximate dimensions 0.25 × 0.15 × 0.1 mm was used for data collection on a Rigaku automated four-circle diffractometer (AFC-5R) with rotating anode (200 mA, 40 kV). A total of 2388 reflections was collected by using graphite monochromated Cu-Kα radiation (λ = 1.5418 Å) within 2θ = 105°. Crystal data: *a* = 20.867(2), *b* = 11.875(1), *c* = 16.883(3) Å, β = 95.29(3)°, *V* = 4165.7(9) Å³, monoclinic, *C*2/*c*, *Z* = 8 and *D*_{calc} = 1.303 g cm⁻³. The ORTEP³¹ drawing is shown in Fig. 2. The structure was solved by the direct method using RANTAN 81 program³² with some modification, and refined by the block-diagonal least-squares method with anisotropic temperature factors.³³ All the hydrogen atoms were located in the difference Fourier map which were included in the refinement to give the final *R* value of 5.42 for 360 variable parameters and 1805 independent reflections with |*F*_o| > 3σ|*F*_o|. No absorption correction was applied. The atomic scattering factors from the International Tables for X-ray Crystallography (Vol. III) were used. All the computation were carried out by using an ACOS 2020 computer at Tohoku University and the applied library program of UNICS III system.³³

Reaction of **1** with TCNE in the absence of light

A solution of **1** and TCNE (0.20 mmol each) in dichloromethane (4 cm³) was stirred for 2 d at room temp. (23 °C) in the dark, after which the mixture was evaporated

and analysed by ^1H NMR with nitromethane as an internal standard. No reaction was observed for **1a** and **1b** and the starting material was recovered quantitatively. In the case of **1c**, formation of **11c** (2%) was observed with recovery of **1c** (94%).

Thermal reaction of **1** with TCNE

Typically a solution of **1** (0.20 mmol) and TCNE (0.30 mmol) in xylene (4 cm³) was heated to reflux (140 °C) for 2–3 d, after which the mixture was evaporated under reduced pressure and analysed by ^1H NMR with nitromethane as an internal standard. No reaction was observed for **1a** and it was recovered in 97% yield. A similar reaction with **1b** for 3 d afforded **11b** as the sole product in 51% yield with recovery of **1b** (44%). The reaction of **1c** with TCNE in refluxing xylene or propionitrile (bp 97 °C) for 2 d gave **11c** (43 or 24%) with recovery of **1c** (45 or 74%). Adducts **11b** and **11c** were isolated by silica gel TLC and their spectral data were identical with those obtained photochemically.

Attempted thermal reaction of **1c** with 2,3,6,7-tetracyano-pyrazino[2,3-*b*]pyrazine (TCPP)

A solution of **1c** and TCPP (0.20 mmol each) in dry propionitrile (4 cm³) was heated at reflux for 3 d. After evaporation of the mixture, analysis of the residue by ^1H NMR with nitromethane as an internal standard showed that **1c** remained intact (97% recovery). A similar reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone gave **1c** with 71% recovery. No formation of **2c** or **3c** was observed.

References

- 1 J. A. Berson, in *Rearrangements in Ground and Excited States*, ed. P. de Mayo, Academic Press, New York, 1980, vol. 1, p. 311; A. Greenberg and J. F. Liebman, *Strained Organic Molecules*, Academic Press, New York, 1978.
- 2 J. J. Gajewski, *Hydrocarbon Thermal Isomerizations*, Academic Press, New York, 1981.
- 3 R. D. Doepker, *J. Phys. Chem.*, 1969, **73**, 8219; A. K. Dhingra and R. D. Koob, *J. Phys. Chem.*, 1970, **74**, 4490; K. L. Hill and R. D. Doepker, *J. Phys. Chem.*, 1972, **76**, 3153; K. Dees and R. D. Koob, *J. Phys. Chem.*, 1973, **77**, 759; E. Lopez and R. D. Doepker, *J. Phys. Chem.*, 1978, **82**, 752; E. Lopez and R. D. Doepker, *J. Phys. Chem.*, 1979, **83**, 573; T. S. Pendleton, M. Kaplan and R. D. Doepker, *J. Phys. Chem.*, 1980, **84**, 472; G. J. Collin, H. Gagnan-Deslauriers, M. Suguet, K. Bokka and J. L. Simard, *J. Photochem.*, 1978, **9**, 449; J. B. Binkewicz, M. Kaplan and R. D. Doepker, *Can. J. Chem.*, 1981, **59**, 537; G. J. Collin, *J. Chem. Phys.*, 1978, **100**, 3177.
- 4 D. L. Garin and D. J. Cooke, *J. Chem. Soc., Chem. Commun.*, 1972, 33; S. S. Hixson, *J. Am. Chem. Soc.*, 1973, **95**, 6144; S. S. Hixson and J. Borovski, *J. Am. Chem. Soc.*, 1975, **97**, 2930; P. H. Mazzocchi and R. S. Lustig, *J. Am. Chem. Soc.*, 1975, **97**, 3707, 3714; S. S. Hixson and J. Borovski, *J. Am. Chem. Soc.*, 1976, **98**, 2840; A. L. Lyons, Jr., and N. J. Turro, *J. Am. Chem. Soc.*, 1978, **100**, 3177.
- 5 P. G. Gassman, in *Photoinduced Electron Transfer, Part C*, eds. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988, p. 70; S. L. Mattes and S. Farid, in *Organic Photochemistry*, ed. A. Padwa, Marcel Dekker, New York, 1983, vol. 6, p. 233; M. A. Fox, in *Advances in Photochemistry*, ed. D. H. Volman, K. Gollnick and G. S. Hammond, Wiley, New York, 1986, vol. 13, p. 237; G. K. Kavarnos and N. J. Turro, *Chem. Rev.*, 1986, **86**, 401; X.-Z. Qin and F. Williams, *Tetrahedron Lett.*, 1986, **42**, 6301; H. D. Roth, *Acc. Chem. Res.*, 1987, **20**, 343; H. D. Roth and M. L. M. Schilling, *J. Am. Chem. Soc.*, 1980, **102**, 7956; H. D. Roth and M. L. M. Schilling, *J. Am. Chem. Soc.*, 1983, **105**, 6805; H. D. Roth, M. L. M. Schilling and F. C. Schilling, *J. Am. Chem. Soc.*, 1985, **107**, 4124.
- 6 D. R. Arnold and R. W. R. Humphreys, *J. Am. Chem. Soc.*, 1979, **101**, 2743; D. D. M. Wayner and D. R. Arnold, *Can. J. Chem.*, 1985, **63**, 871; Y. Takahashi, T. Miyashi and T. Mukai, *J. Am. Chem. Soc.*, 1983, **105**, 6511; T. Miyashi, Y. Takahashi, T. Mukai, H. D. Roth and M. L. M. Schilling, *J. Am. Chem. Soc.*, 1985, **107**, 1079.
- 7 (a) T. Martini and J. A. Kampmeier, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 236; (b) S. Nishida, I. Moritani and T. Teraji, *J. Chem. Soc., Chem. Commun.*, 1971, 36; (c) R. Noyori, N. Hayashi and M. Kato, *J. Am. Chem. Soc.*, 1971, **93**, 4948; (d) T. Tsuji and S. Nishida, *Acc. Chem. Res.*, 1984, **17**, 56; (e) P. G. Wiering and H. Steinberg, *J. Org. Chem.*, 1981, **46**, 1663; (f) S. Nishida, M. Murakami, H. Oda, T. Tsuji, T. Mizuno, M. Matsubara and N. Kikai, *J. Org. Chem.*, 1989, **54**, 3859; (g) S. Nishida, M. Murakami, T. Mizuno and T. Tsuji, *J. Org. Chem.*, 1989, **54**, 3868; (h) K. Maruyama, H. Imahori and Y. Ozawa, *Chem. Lett.*, 1989, 2117; (i) Y. Yakahashi, F. Endoh, H. Ohaku, K. Wakamatsu and T. Miyashi, *J. Chem. Soc., Chem. Commun.*, 1994, 1127.
- 8 V. R. Rao and S. S. Hixson, *J. Am. Chem. Soc.*, 1979, **101**, 6458; K. Mizuno, J. Ogawa, H. Kagano and Y. Otsuji, *Chem. Lett.*, 1981, 437; K. Mizuno, J. Ogawa, H. Kagano and Y. Otsuji, *Chem. Lett.*, 1981, 741; P. G. Gassman, K. D. Olson, L. Walter and R. Yamaguchi, *J. Am. Chem. Soc.*, 1981, **103**, 4977; P. G. Gassman and K. D. Olson, *J. Am. Chem. Soc.*, 1982, **104**, 3740; P. H. Mazzocchi, C. Somich, M. Edwards, T. Morgan and H. L. Ammon, *J. Am. Chem. Soc.*, 1986, **108**, 6828; P. H. Mazzocchi and C. Somich, *Tetrahedron Lett.*, 1988, **29**, 513; C. Somich, P. H. Mazzocchi, M. Edwards, T. Morgan and H. L. Ammon, *J. Org. Chem.*, 1990, **55**, 2624; J. P. Dinnocenzo, W. P. Todd, T. R. Simpson and I. R. Gould, *J. Am. Chem. Soc.*, 1990, **112**, 2462; S. S. Shaik and J. P. Dinnocenzo, *J. Org. Chem.*, 1990, **55**, 3434; S. S. Hixson and Y. Xing, *Tetrahedron Lett.*, 1991, **32**, 173; J. P. Dinnocenzo, D. R. Lieberman and T. R. Simpson, *J. Am. Chem. Soc.*, 1993, **115**, 366.
- 9 K. Mizuno, N. Kamiyama and Y. Otsuji, *Chem. Lett.*, 1983, 477; K. Mizuno, N. Kamiyama, N. Ichinose and Y. Otsuji, *Tetrahedron*, 1985, **41**, 2207; N. Ichinose, K. Mizuno, T. Tamai and Y. Otsuji, *J. Org. Chem.*, 1990, **55**, 4079; K. Gollnick, X.-L. Xiao and U. Paulmann, *J. Org. Chem.*, 1990, **55**, 5945; K. Gollnick and U. Paulmann, *J. Org. Chem.*, 1990, **55**, 5954; A. P. Schaap, L. Lopez, S. D. Anderson and S. D. Gagnon, *Tetrahedron Lett.*, 1982, 5493; T. Miyashi, M. Kamata and T. Mukai, *J. Am. Chem. Soc.*, 1986, **108**, 2755; T. Miyashi, M. Kamata and T. Mukai, *J. Am. Chem. Soc.*, 1987, **109**, 2780.
- 10 M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 1961, 5550; W. von E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, 1966, **7**, 397; J. C. Gilbert, *Tetrahedron*, 1969, **25**, 1459; M. C. Flowers and A. R. Gibbons, *J. Chem. Soc., Perkin Trans. 2*, 1972, 548, 555; J. J. Gajewski, *J. Am. Chem. Soc.*, 1970, **92**, 3688; J. J. Gajewski and L. T. Burka, *J. Am. Chem. Soc.*, 1971, **93**, 4952; J. J. Gajewski and L. T. Burka, *J. Am. Chem. Soc.*, 1972, **94**, 8857, 8860, 8865; P. N. Skancke, N. Koga and K. Morokuma, *J. Am. Chem. Soc.*, 1989, **111**, 1559; Y.-N. Tang and Y. Y. Su, *J. Chem. Phys.*, 1972, **57**, 4048; Y. Y. Su and Y.-N. Tang, *J. Phys. Chem.*, 1972, **76**, 2187.
- 11 G. R. DeMare, *J. Photochem.*, 1978, **9**, 4; Y.-N. Tang and C.-T. Yeh, *J. Chin. Chem. Soc.*, 1978, **25**, 21; M. Paller and R. D. Doepker, *Can. J. Chem.*, 1985, **63**, 3593.
- 12 (a) G. W. Griffin and N. R. Bertoniere, in *Carbenes*, ed. M. Jones, Jr., and R. A. Moss, Wiley, New York, 1973; vol. 1, p. 305; (b) W. M. Jones, M. H. Grasley and W. S. Brey, Jr., *J. Am. Chem. Soc.*, 1963, **85**, 2754; (c) L. Skattebøl, *Acta Chem. Scand.*, 1963, **17**, 1683.
- 13 K. Yoshihara and D. R. Kearns, *J. Chem. Phys.*, 1966, **45**, 1994.
- 14 S. L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973, pp. 3, 6.
- 15 R. Foster, *Organic Charge-Transfer Complexes*, Academic Press, New York, 1969; G. Jones, II, in *Photoinduced Electron Transfer, Part A*, eds. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988, p. 245.
- 16 K. Ushida, T. Shida and J. C. Walton, *J. Am. Chem. Soc.*, 1986, **108**, 2805.
- 17 T. Miyashi, Y. Takahashi, H. Ohaku and K. Yokogawa, *Tetrahedron Lett.*, 1990, **31**, 2411.
- 18 J. Matthey, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 825; J. Santamaria, in *Photoinduced Electron Transfer, Part B*, eds. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988, p. 483.
- 19 K. Mitsuhashi, T. Yanagida, A. Murakami, K. Oda and S. Shiraishi, *Chem. Abstr.*, 1979, **90**, 168545p.
- 20 (a) H. Taube, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 329; (b) A. Heim, *Acc. Chem. Res.*, 1975, **8**, 264; (c) L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag, Berlin, 1987; (d) S. S. Shaik and A. Pross, *J. Am. Chem. Soc.*, 1982, **104**, 2708; (e) A. Pross, *Adv. Phys. Org. Chem.*, 1985, **21**, 99; (f) S. S. Shaik, *Prog. Phys. Org. Chem.*, 1985, **15**, 197; (g) A. Pross, *Acc. Chem. Res.*, 1985, **18**, 212.
- 21 E. Dunkelblum and B. Singer, *Synthesis*, 1975, 323.
- 22 K. Sisido and K. Utimoto, *Tetrahedron Lett.*, 1966, 3267; K. Utimoto, M. Tamura and K. Sisido, *Tetrahedron*, 1973, **29**, 1169.
- 23 J. E. Baldwin and R. E. Peavy, *J. Org. Chem.*, 1971, **36**, 1441.
- 24 K. V. Scherer, Jr., and R. S. Lunt, III, *J. Org. Chem.*, 1965, **30**, 3215.
- 25 T. Miyashi, Y. Takahashi, K. Yokogawa and T. Mukai, *J. Chem. Soc., Chem. Commun.*, 1987, 175.
- 26 W. M. Jones, M. H. Grasley and W. S. Brey, Jr., *J. Am. Chem. Soc.*, 1963, **85**, 2754.
- 27 L. R. Krepski and A. Hassner, *J. Org. Chem.*, 1978, **43**, 2879.

- 28 R. C. de Selms, *Org. Prep. Proced. Int.*, 1973, **5**, 303.
29 F. Bertini, P. Grasselli and G. Zubiani, *Tetrahedron*, 1970, **26**,
1281.
30 D. Hasselmann, *Chem. Ber.*, 1974, **107**, 3486.
31 C. K. Johnson, ORTEP. Report ORNL-3794, Oak Ridge National
Laboratory, Tennessee, 1965.
32 Y. Jia-xing, *Acta Crystallogr.*, 1981, **A37**, 642; 1983, **A39**, 35.

- 33 T. Sakurai and K. Kobayashi, *Rikagaku Kenkusyo Hokoku*, 1979,
55, 69.

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