

Reinvestigation on Thermal Cycloaddition of 1-Aryl-2-(9-fluorenylidene)-1-haloethylenes¹⁾

Masahiro MINABE, Masaaki YOSHIDA, Seiji SAITO, Keisuke TOBITA, and Takashi TODA*
 Department of Industrial Chemistry, Faculty of Engineering, Utsunomiya University, Ishiicho, Utsunomiya 321
 (Received December 10, 1987)

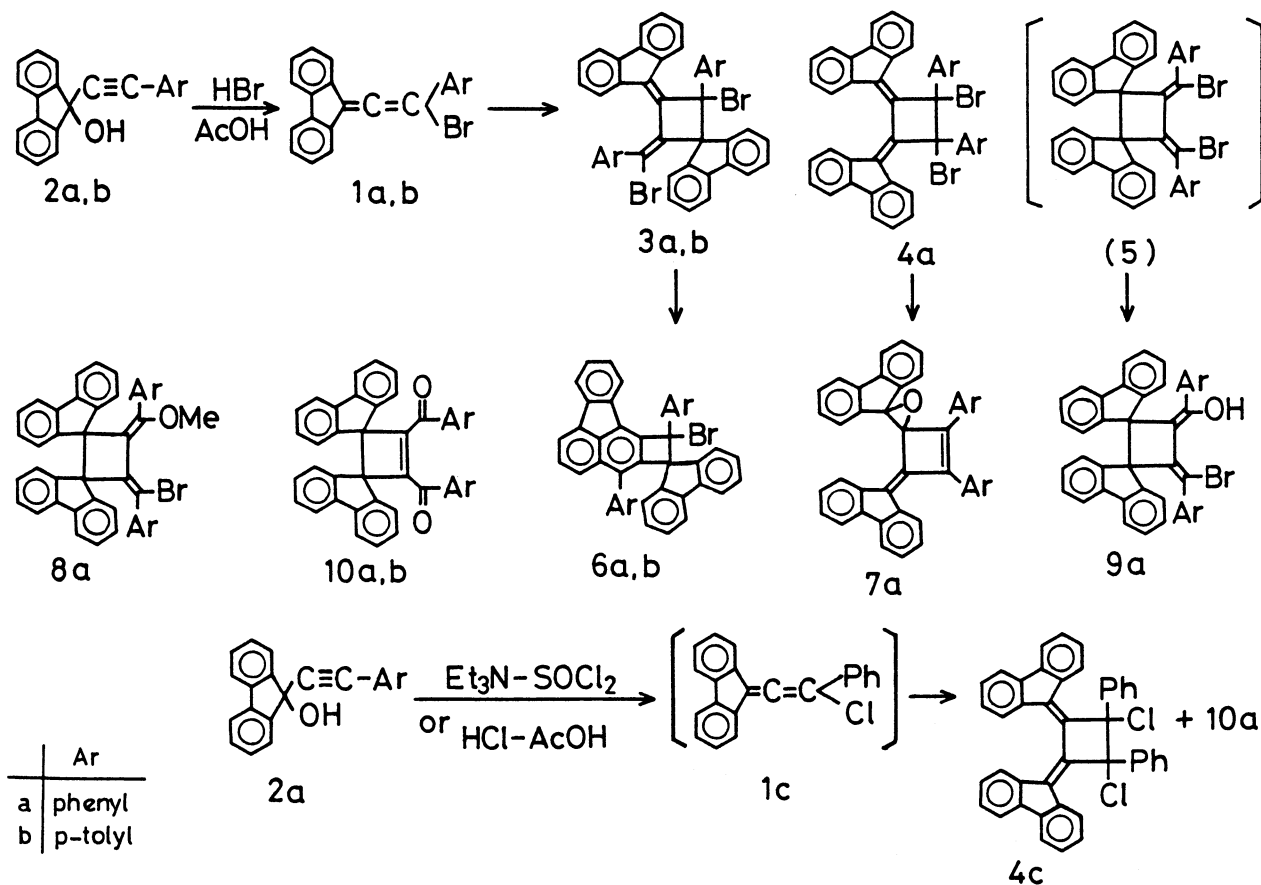
The thermal treatment of 1-bromo-2-(9-fluorenylidene)-1-phenylethylene afforded three different types of [2+2]cycloaddition products. The 1-tolyl homolog showed similar trends, but the chloro analog gave only two types. These results suggest that reactions of the rigid and bulky allenes take place through a 2,2'-biradical giving head-to-head, head-to-tail, and tail-to-tail adducts through the expected processes.

The chemistry of allenes has widely been investigated owing to the unique reactivities, important as synthetic intermediates, as well as the unique structures.²⁾ The thermal [2+2]cycloaddition of haloallenes has suggested that it proceeds nonconcertedly via 2,2'-biradical and gives head-to-head and tail-to-tail adducts as the major products.^{2,3)} The reaction of 1-chloro-2-(9-fluorenylidene)ethylene has been reported to yield a head-to-head dimer, 3,4-dichloro-1,2-bis(9-fluorenylidene)cyclobutane.^{4,5)} However, a detailed study of the reaction showed that the above cycloaddition product was confirmed as a head-to-tail compound, 2-chloro-4-chloromethylene-3-(9-fluorenylidene)spiro[cyclobutane-1,9'-[9H]fluorene], with

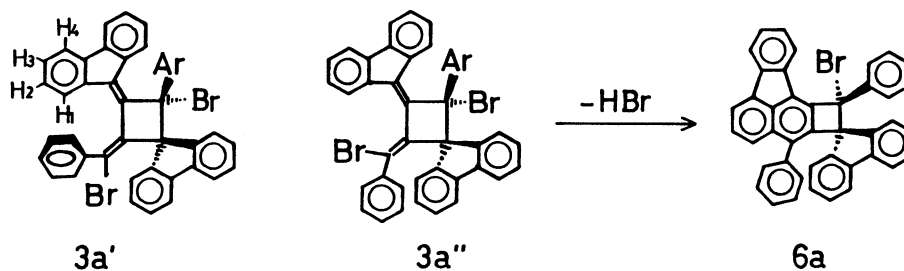
evidence of a similar product of bromo analog.^{6,7)} The thermal treatment of 1-bromo-2-(9-fluorenylidene)-1-phenylethylene (**1a**),⁵⁾ which was derived from 9-(phenylethynyl)-9-fluorenone (**2a**), also afforded a head-to-tail adduct **3a**^{6,8)} (Scheme 1).

The present paper deals with a reinvestigation of the thermal cycloaddition of 1-bromo- and 1-chloroallenes **1**. This suggests that the reaction takes place to give all three possible dimers: head-to-head, head-to-tail, and tail-to-tail adducts.

By refluxing in benzene, **1a** afforded **3a** as the major product, accompanied by the formation of several other products: **4a**, **6a**, **7a**, **8a**, **9a**, and **10a** (Scheme 1). The reaction of 9-fluorenone with (*p*-tolylethynyl)-



Scheme 1.

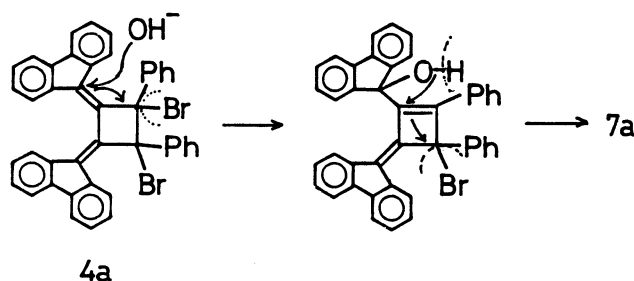


Scheme 2.

magnesium bromide, which was derived from *p*-tolylacetylene,⁹⁾ gave 9-(*p*-tolylethynyl)-9-fluorenol (**2b**); the alcohol was converted into another allene, **1b**. The reaction of **1b** gave **6b** as the major product and **3b** and **10b** as the minor products. Several attempts to obtain chloroallene **1c** failed as the result of reactions of **2a** with thionyl chloride in the presence of amine and with hydrochloric acid in acetic acid, though small amounts of **4c** and **10a** were isolated.

The orange needles, **3a**, were concluded to be the head-to-tail compound previously described in the literature^{6,8)} through a comparison with their UV data. The UV spectrum of **3b** is similar to that of **3a**. Characteristic peaks of the NMR spectra of **3a** and **3b** are high-field one-proton doublets, at δ 5.13 for **3a** and δ 5.18 for **3b**. The *J*-coupling and COSY data show that the doublets connect vicinally triplet at δ 6.29, successively triplet at δ 6.97, and doublet at δ 7.48 for **3a**, and triplet at δ 6.29, triplet at δ 6.97, and doublet at δ 7.53 for **3b**. These four-proton sets were reasonably assigned to H_1 , H_2 , H_3 , and H_4 , respectively, of the 9-fluorenylidene moiety, which is located in the same plane as the cyclobutane ring, as shown as **3a'** (Scheme 2). The high-field shift of H_1 is due to the ring current of the adjacent phenyl moiety of the arylbromomethylene group.

Compound **3a'** was stable under refluxing in cyclohexane. The geometrical isomer of **3a'** (**3a''**) should form by cycloaddition, but convert easily into a fluorenylidene derivative **6a** by dehydrobromination during a reaction and/or separation. The UV spectra of **6a** and **6b** are very similar to that of fluorenylidene, showing a red shift (about 40 nm). The molecular model of **6a** indicates that the aryl group attached to the fluorenylidene moiety can rotate freely, but that the aryl group situated on the cyclobutane ring is restricted from free rotation. The two phenyl groups of **6a** are distinguishable by COSY spectra: the two-proton doublet at δ 5.95 is correlated to the two-proton triplet (δ 6.65), successively a one-proton triplet (δ 6.79); these were assigned to be attached to the free-rotating phenyl group connected to the fluorenylidene. The other phenyl protons appear separately at δ 6.38 (d), 6.89 (t), 7.15 (t), 7.59 (t), and 7.36 (d); this suggests that the ring is fixed sterically. The NMR spectra of **6b** show similar trends; the methyl-proton singlet (δ 1.96) and a



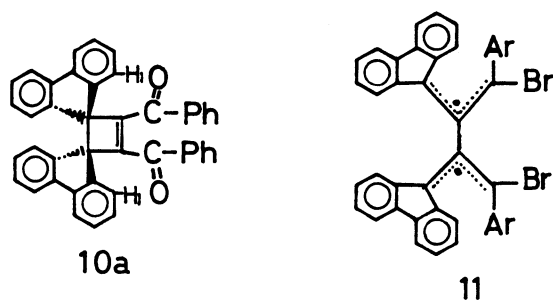
Scheme 3.

couple of two-proton doublets at δ 5.81 and 6.47 are due to the tolyl protons attached to the fluorenylidene moiety. Also, the methyl protons (δ 2.02), the one-proton singlet (δ 6.16), and the one-proton doublet (δ 6.94) belong to the restricted-rotating tolyl group of the cyclobutane moiety.¹⁰⁾

The absorption maxima (480–490 nm) of reddish **4a** and **4c** are similar to those of the head-to-head cycloadducts⁷⁾ obtained from 2,3-dibromo-1,4-bis(9-fluorenylidene)-1,3-butadiene. A molecular model of **4** shows that a part of the two 9-fluorenylidene plane accumulates each other. The NMR spectrum of **4c** is relatively simple and shows slightly broad signals, because of the symmetrical molecule and of the mutual interaction of the two fluorenylidene moieties.

The UV spectrum of **7a** is similar to that of **3a** and supports the conjugating system being 9-(4-phenyl-1,3-butadienyl)fluorene. However, **3a** may not be easy to give a compound having a molecular formula of $C_{42}H_{26}O$: **7a** is postulated to form by the hydrolysis of **4a** during the reaction and/or its separation, since **7a** does not show any carbonyl or hydroxyl absorption band in its IR spectrum (Scheme 3). The NMR signals of **7a** indicate an intramolecular mutual interaction that is similar to **4c**.

The UV spectra of the other cycloadducts, **8a**, **9a**, **10a**, and **10b**, significantly differ from those of head-to-tail and head-to-head addition products, and have absorption maxima between 300 and 310 nm. These compounds should be derived from tail-to-tail adduct **5**, which could not be isolated. The methoxy compound **8a** (OCH_3 , 1H NMR, δ = 2.67) may be a tail-to-tail adduct formed from **1a**, **2a**, or **5a**. A small amount of methoxyallene could be formed from **2a** with contam-



Scheme 4.

inating methanol which was used for the recrystallization of **2a**; the methanol should be contained in **2a** since it is difficult to remove the methanol from **2a** due to the inclusion complex of **2a** with methanol, as in the case of 9-(1-propynyl)-9-fluorenone.¹¹⁾

The molecular formula ($C_{42}H_{27}OBr$) and the IR spectrum (3500 cm^{-1}) of **9a** indicate that one bromine of the primary product **5a** was hydrolyzed during the reaction and/or separation process.

Analytical data and strong absorptions (ca. $1650\text{--}1655\text{ cm}^{-1}$) in the IR spectra of **10a** and **10b** suggest that **10a, b** possess two carbonyl groups which were formed by removing two halogen atoms of **5** by hydrolyses and a following oxidation. Phenyl protons of **10a** appear at δ 7.11 as a four-proton triplet, at δ 7.30 as a two-proton triplet, and at δ 7.74 as a four-proton doublet. The two-proton doublet at δ 8.36 is assigned to H_1 (Scheme 4, **10a**), which is sterically deshielded by the carbonyl group. Similarly, the tolyl groups of **10b** are a singlet at δ 2.22 and doublets at δ 6.90 and 7.62; the doublet at δ 8.35 is H_1 .

The small amounts of these minor products did not allow for any further investigation. The [2+2]cycloaddition of **1** afforded mainly head-to-tail product **3** accompanied by the formation of head-to-head **4** and tail-to-tail **5**, in spite of the fact that the material balance of the reaction products was not good. These results could reasonably explained why the thermal [2+2]cycloaddition proceeds via 2,2'-biradical **11** from the 1-haloallene **1**, and **11** cyclizes by three possible ways, giving cyclobutanes.

Experimental

All melting points are uncorrected. The ^1H NMR spectra were measured on a Varian VXR 300 or (a part) a Jeol C-60 HL spectrometer in CDCl_3 (0.62 ml for 2–10 mg samples in 5 mm tube). The UV data were recorded using a Shimadzu UV-180 or a Hitachi U-3400 apparatus in CH_2Cl_2 .

1-Bromo-2-(9-fluorenylidene)-1-phenylethylene (1a). According to the method described in literature,⁶⁾ to a cooled solution of **2a** (0.50 g, 1.77 mmol) in AcOH (15 ml) was added dropwise a solution of hydrobromic acid (47%, 1.5 g, 8.71 mmol) in H_2O (5 ml). Upon stirring for 1 h with cooling, the precipitate was filtered, washed with water in order to be neutralized, dried, and recrystallized from hexane giving yellow needles, **1a**: 0.546 g (89%); mp $117\text{--}119^\circ\text{C}$

(decomp); IR (KBr), 1936 cm^{-1} ($\text{C}=\text{C}=\text{C}$) (lit,⁶⁾ 1940 cm^{-1} ; UV, λ_{max} 319 (log ϵ 4.28), 284 (4.27), 260 (4.74), and 253 nm (4.63); MS (70 eV), m/z 346, 344 (M^+), 265, and 187; ^1H NMR, $\delta=7.27\text{--}7.42$ (7H, m), 7.61–7.67 (4H, m), and 7.72 (2H, dt, $J=7.5, 0.9\text{ Hz}$).

The allene **1a** (100 mg, 0.29 mmol) was percolated through silica-gel column (1 cm i.d. 10 cm) with benzene and 72 mg (72%) of **1a** was recovered. When alumina was used instead of silica, only 15 mg (18%) of 2-(9-fluorenylidene)-1-phenylethanone was isolated; mp $137\text{--}139^\circ\text{C}$ (lit,¹²⁾ 137°C ; IR (KBr), 1650 cm^{-1} ($\text{C}=\text{O}$) and 1591 cm^{-1} ($\text{C}=\text{C}$).

9-(*p*-Tolyethynyl)-9-fluorenone (2b). To a ethylmagnesium bromide (obtained from ethyl bromide (13.10 g, 120 mmol) and magnesium (2.92 g, 120 mmol) in ether (100 ml) under an argon atmosphere) was added dropwise *p*-tolylacetylene (12.76 g, 110 mmol) with ice-cooling; the resulting mixture was refluxed for an additional 16 h. A solution of 9-fluorenone (18.0 g, 100 mmol) in benzene (150 ml) was added dropwise to the Grignard solution and the mixture was refluxed for an additional 26 h. Upon the usual treatment, 26.5 g (90%) of **1b** was isolated by means of column chromatography on silica gel: mp $44.5\text{--}46.5^\circ\text{C}$; IR, 3530 cm^{-1} (OH); MS (70 eV), m/z 296 (M^+), 281, and 181; ^1H NMR (CCl_4), $\delta=2.24$ (3H, s), 3.07 (1H, bs), and 6.88–7.77 (12H, m).

9-Methoxy-9-(*p*-tolylethynyl)fluorene was obtained as colorless oil by percolation of **2b** on silica gel with methanol: MS (70 eV), m/z 310 (M^+) and 279; ^1H NMR (CCl_4), $\delta=2.28$ (3H, s), 3.01 (3H, s), and 6.78–7.68 (12H, m).

1-Bromo-2-(9-fluorenylidene)-1-(*p*-tolylethylene) (1b). The foregoing alcohol **2b** was treated in a manner similar to the case of **2a** to give **1b**: yield 84%; mp $125\text{--}127^\circ\text{C}$ (decomp); IR (KBr), 1920 cm^{-1} ($\text{C}=\text{C}=\text{C}$); UV, λ_{max} 321 (log ϵ 4.38), 285 (4.34), 261 (4.80), and 253 nm (4.68); MS (70 eV), m/z 360, 358 (M^+), and 279; ^1H NMR, $\delta=2.35$ (3H, s), 7.14 (2H, d, $J=8.1\text{ Hz}$), 7.28 (2H, t, $J=7.5\text{ Hz}$), 7.38 (2H, t, $J=7.5\text{ Hz}$), 7.52 (2H, d, $J=8.1\text{ Hz}$), 7.61 (2H, d, $J=7.5\text{ Hz}$), and 7.71 (2H, d, $J=7.5\text{ Hz}$). Found: C, 74.09; H, 4.33%. Calcd for $\text{C}_{22}\text{H}_{15}\text{Br}$: C, 73.55; H, 4.21%.

Thermal Treatment of 1a. A solution of **1a** (1.99 g, 5.8 mmol) in benzene (40 ml) was refluxed in the dark under an atmosphere of argon for 4 h. Upon evaporation of the solvent, the residue was fractionally recrystallized from ethyl acetate to give **3a** (590 mg, 30%), **6a** (158 mg, 9%), and **4a** (75 mg, 3.8%). The separation of the mother liquor by silica-gel column chromatography with dichloromethane-cyclohexane (1:3) successively afforded **7a** (25 mg, 1.6%) and **8a** (65 mg, 3.5%). The eluent was exchanged into ethyl acetate and afforded **10a** (33 mg, 2%) and **9a** (54 mg, 3%). These compounds were recrystallized from dichloromethane-hexane. **3a**: mp $206\text{--}208^\circ\text{C}$ (decomp) (lit,⁶⁾ $203\text{--}204^\circ\text{C}$), orange needles; UV, λ_{max} 412 (log ϵ 4.35), 276 (4.59), and 237 nm (4.75); MS (19 eV), m/z 692, 690, 688 (M^+), 611, 609, 529, 452, 365, and 265; ^1H NMR, $\delta=5.13$ (1H, d, $J=7.6\text{ Hz}$), 6.29 (1H, dt, $J=7.6, 1.0\text{ Hz}$), 6.68 (2H, t, $J=7.1\text{ Hz}$), 6.78–6.88 (3H, m), 6.97 (1H, dt, $J=7.6, 1.0\text{ Hz}$), 7.03–7.10 (2H, m), 7.13–7.20 (1H, m), 7.22–7.47 (7H, m), 7.48 (1H, d, $J=7.6\text{ Hz}$), 7.57 (1H, d, $J=7.8\text{ Hz}$), and 7.63–7.83 (6H, m). Found: C, 72.53; H, 4.03%. Calcd for $\text{C}_{42}\text{H}_{26}\text{Br}_2$: C, 73.06; H, 3.80%.

4a: mp $169\text{--}171^\circ\text{C}$ (decomp), red needles; UV, λ_{max} 490 (log ϵ 5.30), 330 (4.97), 275 (5.58), and 244 nm (5.73); MS (70 eV), m/z 692, 690, 688 (M^+), 611, 609, 530, and 453.

6a: mp $317\text{--}319^\circ\text{C}$ (decomp), yellow crystals; UV, λ_{max} 398

(log ϵ 4.28), 378 (4.55), 359 (4.48), 343 (4.27), 307 (4.15), 295 (4.12), and 264 nm (4.96); MS (19 eV), m/z 610, 608 (M^+), 529, 452, 375, and 224; $^1\text{H NMR}$, δ =5.95 (2H, d, J =7.5 Hz), 6.38 (1H, dd, J =7.5, 1.2 Hz), 6.65 (2H, t, J =7.5 Hz), 6.79 (1H, t, J =7.5 Hz), 6.89 (1H, dd, J =7.5, 1.2 Hz), 7.15 (1H, dt, J =7.5, 1.2 Hz), 7.22–7.26 (3H, m), 7.36 (1H, dd, J =7.5, 1.2 Hz), 7.40–7.45 (6H, m), 7.55 (2H, d, J =8.6 Hz), 7.59 (1H, dd, J =7.8, 1.3 Hz), 7.88 (2H, d, J =7.5 Hz), and 7.94 (2H, d, J =7.5 Hz). (Found: C, 81.68; H, 3.77%. Calcd for $\text{C}_{42}\text{H}_{25}\text{Br}$: C, 82.76; H, 4.13%.)

7a: mp 291–292 °C (decomp), orange-red needles; no halogen; IR (KBr), 1085 cm^{-1} ; UV, λ_{max} 378 (log ϵ 4.55), 266 (4.61), and 246 nm (4.80); MS (20 eV), m/z 546 (M^+), 529, 453, 365, and 265; $^1\text{H NMR}$, δ =6.76–6.90 (6H, m), 7.13 (2H, dt, J =7.4, 1.0 Hz), 7.23–7.39 (12H, m), 7.56 (2H, d, J =7.9 Hz), 7.69 (2H, d, J =7.0 Hz), and 7.75 (2H, d, J =7.3 Hz). Found: C, 92.07; H, 5.13%. Calcd for $\text{C}_{42}\text{H}_{26}\text{O}$: C, 92.28; H, 4.79%.

8a: mp 242–244 °C (decomp), colorless crystals; IR (KBr), 1085 cm^{-1} (C–O–C); UV, λ_{max} 309 (log ϵ 4.31) and 267 nm (4.50); MS (19 eV), m/z 642, 640 (M^+), 611, 609, 561, 529, 365, and 195; $^1\text{H NMR}$, δ =2.67 (3H, s), 6.30 (2H, bs), 6.68 (2H, bs), 6.88–7.44 (16H, m), 7.58 (2H, d, J =6.6 Hz), 7.68 (2H, d, J =6.6 Hz), and 7.80 (2H, d, J =6.8 Hz). Found: C, 80.27; H, 4.55%. Calcd for $\text{C}_{43}\text{H}_{29}\text{OBr}$: C, 80.50; H, 4.56%.

9a: mp 214–216 °C (decomp), colorless crystals; IR (KBr), 3500 cm^{-1} (OH); UV, λ_{max} 311 (log ϵ 4.30) and 266 nm (4.52); MS (19 eV), m/z 628, 626 (M^+), 547, 546, 447, 445, and 181; $^1\text{H NMR}$, δ =4.52 (1H, bs), 6.0–7.8 (24H, m), and 7.94 (2H, d, J =8.1 Hz). Found: C, 80.43; H, 4.44%. Calcd for $\text{C}_{42}\text{H}_{27}\text{OBr}$: C, 80.38; H, 4.34%.

10a: mp 290–292 °C (decomp), yellow crystals; IR (KBr), 1653 (C=O), 1593, and 1578 cm^{-1} ; UV, λ_{max} 302 (log ϵ 4.24) and 264 nm (4.90); MS (20 eV), m/z 562 (M^+), 456, and 351; $^1\text{H NMR}$, δ =6.96 (2H, dt, J =7.5, 1.2 Hz), 7.05 (2H, dt, J =7.5, 1.2 Hz), 7.11 (4H, t, J =7.6 Hz), 7.25–7.31 (8H, m), 7.63 (4H, dt, J =8.5, 1.0 Hz), 7.74 (4H, dd, J =7.6, 1.2 Hz), and 8.36 (2H, dd, J =7.8, 0.9 Hz). Found: C, 89.60; H, 4.57%. Calcd for $\text{C}_{42}\text{H}_{26}\text{O}_2$: C, 89.66; H, 4.66%.

Thermal Reaction of 1b. A solution of **1b** (1.436 g, 4 mmol) in benzene (50 ml) was refluxed for 5 h. Upon evaporation of the solvent, the residue was recrystallized from ether, yielding yellow needles, **6b** (244 mg, 19.2%). The mother solution was chromatographed on silica gel with hexane and **10b** (37 mg, 1.6%) was isolated as yellow crystals (from dichloromethane–hexane).

Another experiment using **1b** (718 mg, 2 mmol) in cyclohexane (7.5 ml) was carried out by refluxing for 4 h and concentrating into a small volume; yellow needles, **3b** was obtained in yield of 143 mg (19.9%). **3b**: mp 195.5–197.0 °C (decomp); UV, λ_{max} 413 (log ϵ 4.30), 277 (4.62), and 271 nm (s, 4.60); MS (70 eV), m/z 720, 718, 716 (M^+), 639, 637, and 558; $^1\text{H NMR}$, δ =2.02 (3H, s), 2.34 (3H, s), 5.18 (1H, d, J =7.5 Hz), 6.29 (1H, dt, J =7.5, 1.2 Hz), 6.46 (2H, d, J =7.8 Hz), 6.66 (2H, d, J =8.4 Hz), 6.93 (1H, dt, J =8.1, 1.9 Hz), 6.97 (1H, dt, J =7.5, 1.2 Hz), 7.04–7.14 (2H, m), 7.19–7.50 (7H, m), 7.53 (1H, dd, J =7.5, 1.4 Hz), 7.55–7.64 (2H, m), and 7.69–7.82 (4H, m). Found: C, 73.47; H, 4.13%. Calcd for $\text{C}_{44}\text{H}_{30}\text{Br}_2$: C, 73.55; H, 4.21%.

6b: mp 314–316 °C (decomp); UV, λ_{max} 404 (log ϵ 4.37), 383 (4.57), 364 (4.50), 350 (s, 4.31), 306 (4.23), 295 (4.23), and 265 nm (4.70); MS (70 eV), m/z 638, 636 (M^+), 557, 449, and 277; $^1\text{H NMR}$, δ =1.96 (3H, s), 2.02 (3H, s), 5.81 (2H, d, J =8.3

Hz), 6.16 (1H, s), 6.47 (2H, d, J =8.3 Hz), 6.94 (1H, d, J =8.0 Hz), 7.23–7.49 (11H, m), 7.54 (2H, d, J =8.0 Hz), 7.86 (2H, d, J =7.5 Hz), and 7.93 (2H, d, J =6.9 Hz). Found: C, 82.34; H, 4.73%. Calcd for $\text{C}_{44}\text{H}_{29}\text{Br}$: C, 82.88; H, 4.58%.

10b: mp 298.5–299.5 °C (decomp); IR (KBr), 1654 (C=O) and 1602 cm^{-1} (C=C); UV, λ_{max} 301 (log ϵ 4.38), 264 (4.86), and 258 nm (4.58); MS (70 eV), m/z 590 (M^+), 471, 352, and 119; $^1\text{H NMR}$, δ =2.22 (6H, s), 6.90 (4H, d, J =7.8 Hz), 6.96 (2H, dt, J =7.8, 1.2 Hz), 7.03 (2H, dt, J =7.5, 1.5 Hz), 7.22–7.31 (6H, m), 7.60 (4H, d, J =7.5 Hz), 7.62 (4H, d, J =7.8 Hz), and 8.35 (2H, d, J =7.8 Hz). Found: C, 89.78; H, 4.95%. Calcd for $\text{C}_{44}\text{H}_{30}\text{O}_2$: C, 89.46; H, 5.12%.

Reaction of 2a with Thionyl Chloride. A cooled (0 °C) mixture of **2a** (282 mg, 1.0 mmol) and triethylamine (0.3 g, 3 mmol) in dry ether (5 ml) was added dropwise to thionyl chloride (0.3 g, 2.5 mmol). Upon stirring for 1 h, the reaction mixture was filtered; the filtrate was evaporated and chromatographed on silica gel with dichloromethane–cyclohexane (1 : 3) to yield **4c** (8 mg, 4%) and **10a** (2 mg, 1%, mp 290–292 °C, decomp). **4c**: mp 247.5–249.5 °C (decomp), red crystals; UV (EtOH), λ_{max} 481 (log ϵ 4.41), 330 (3.75), 272 (4.64), and 247 nm (4.75); MS (70 eV), m/z 604, 602, 600 (M^+), 567, 565, 530, 453, 365, and 265; $^1\text{H NMR}$, δ =6.93 (2H, dt, J =7.7, 1.1 Hz), 6.98 (2H, dt, J =7.6, 1.1 Hz), 7.18 (2H, t, J =7.7 Hz), 7.23–7.30 (4H, m), 7.34–7.39 (4H, m), 7.45–7.49 (4H, m), 7.57–7.65 (6H, m), and 8.40 (2H, d). Found: C, 83.72; H, 4.51%. Calcd for $\text{C}_{42}\text{H}_{26}\text{Cl}_2$: C, 83.86; H, 4.36%.

The present work was partially supported by a Grant-in-Aid for Scientific Research (No. 61470022) from the Ministry of Education, Science and Culture.

References

- 1) Presented at 53rd Annual Meeting of the Chemical Society of Japan, Nagoya, Oct. 1986, Abstr., No. 1D25.
- 2) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967); W. Swadja, *ibid.*, **83**, 263 (1983); "The Chemistry of the Allenes," ed by S. R. Landor Vol. I–III, Academic Press, London (1982).
- 3) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 5624 (1973); D. J. Pasto, *ibid.*, **101**, 37 (1979).
- 4) G. F. Hennion and B. R. Fleck, *J. Am. Chem. Soc.*, **77**, 3253 (1955); T. Nagase, *Bull. Chem. Soc. Jpn.*, **34**, 139 (1961); H. Kollmar and H. Fischer, *Tetrahedron Lett.*, **1968**, 4291.
- 5) R. Kuhn and D. Rewicki, *Chem. Ber.*, **98**, 2611 (1965).
- 6) Y. Takehira, M. Ohoi, and F. Toda, The 30th Spring Meeting of Chemical Society of Japan, preprint, p. 1800 (1974).
- 7) F. Toda, H. Motomura, and H. Oshima, *Bull. Chem. Soc. Jpn.*, **47**, 467 (1974).
- 8) K. Ueda and F. Toda, *Chem. Lett.*, **1975**, 257.
- 9) L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1175 (1941).
- 10) Unexpected singlet at δ 6.16 is correlated to the peaks at δ 2.02 and 6.94 by normal and long-range COSY technique and is concluded to be the tolyl protons on the cyclobutane. However, the other two protons of the tolyl group are failed to confirm on the spectra due to overlap of peaks.
- 11) F. Toda, K. Tanaka, G. U. Daumas, and M. C. Sanchez, *Chem. Lett.*, **1983**, 1521.
- 12) C. Dufraisse and A. P. de Carvalho, *Bull. Soc. Chim. Fr.* [5], **3**, 882 (1936); *Chem. Abstr.*, **30**, 358 (1936).