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Revisit of the Dessy−White Intramolecular Acetylene−Acetylene [2 + 2] Cycloadditions

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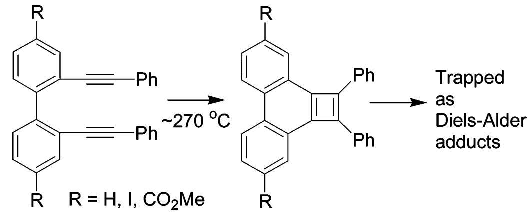
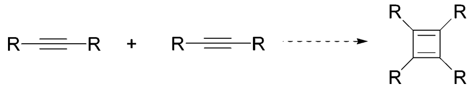


In this experiment, a series of thermal reactions of 4,4′-disubstituted 2,2′-bis(phenylethynyl)biphenyls with 2,3,4,5-tetraphenylcyclopenta-2,4-dienone were carried out under neat conditions and in diphenyl ether at temperatures between 260 and 270 °C to give rise to 9,10,11,12,13,14-hexaphenylcycloocta[l]-phenanthrenes as the adducts in 12−23% yields. We traced these results to the intramolecular [2 + 2] thermal cyclization of 2,2′-bis(phenylethynyl)biphenyls to form 1,2-diphenylcyclobuta[l]phenanthrenes, which were further trapped as bridged-ketone Diels−Alder adducts, followed by thermal decarbonylative ring opening, which gave rise to the products.

Introduction

Intra- and intermolecular cyclization of conjugated enynes have been of considerable value from synthetic as well as mechanistic points of view.[1] Among the large variety of the thermal cyclization reactions, transformation of two acetylene moieties to cyclobutadiene through a [2 + 2] cycloaddition reaction, as shown in Scheme 1, is an attractive experiment to attempt.[2] However, not many successful examples have been reported, proving it to be a challenging problem to tackle.

SCHEME 1



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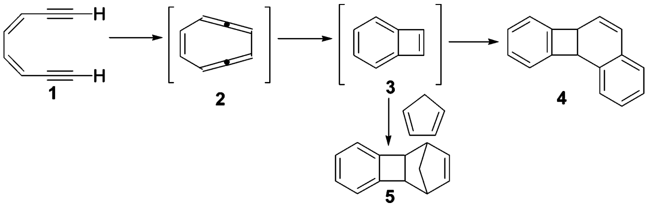

One related example reported in the literature is the Sondheimer cyclization of 3,5-octadiene-1,7-diyne (**1**) that involved formation of the diallenic cyclic hydrocarbon **2** and benzocyclobutene (**3**) to give the dimeric product **4** (Scheme 2).[3] The presence of the intermediate **3** was further evidenced by a trapping experiment with cyclopentadiene to give rise to the Diels−Alder adduct. The presence of **2** was also concluded on the basis of a hydrogenation experiment, in which 0.5% of cyclooctane was identified. The dimerization behavior of various benzocyclobutadiene derivatives under the Sondheimer cyclization conditions has recently been investigated.[4]

Thermal cyclization of the biphenyl homologue **6**, however, occurred in a different manner to afford polynuclear aromatic

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(1) For recent reviews and examples, see: (a) Schreiner, P. R.; Navarro-Vázquez, A.; Prall, M. *Acc. Chem. Res.* **2005**, *38*, 29. (b) Basak, A.; Mandal, S.; Bag, S. S. *Chem. Rev.* **2003**, *103*, 4077. (c) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207. (d) González, J. J.; Francesch, A.; Cárdenas, D. J.; Echavarren, A. M. *J. Org. Chem.* **1998**, *63*, 2854. (e) Lewis, K. D.; Matzger, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 9968.

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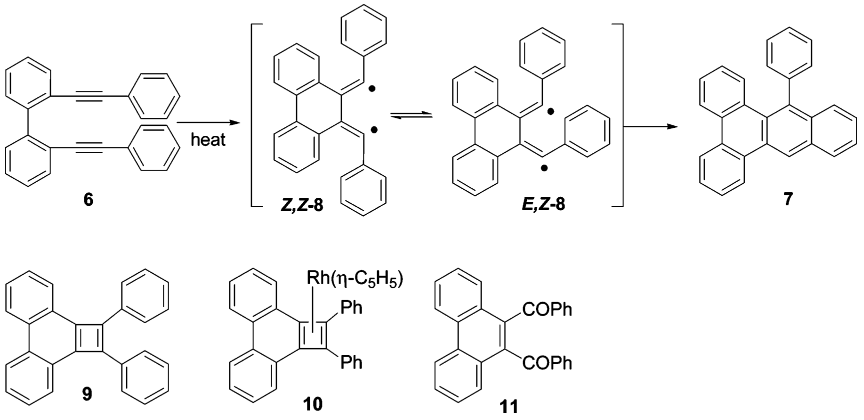
SCHEME 3



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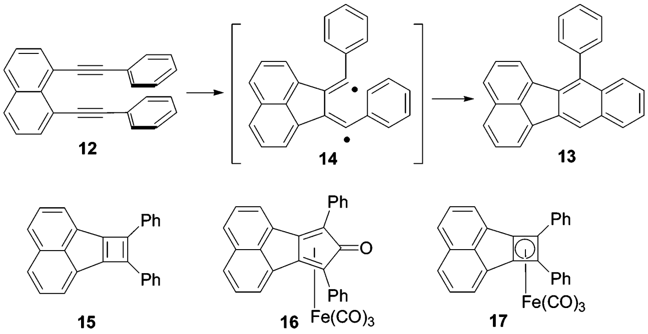

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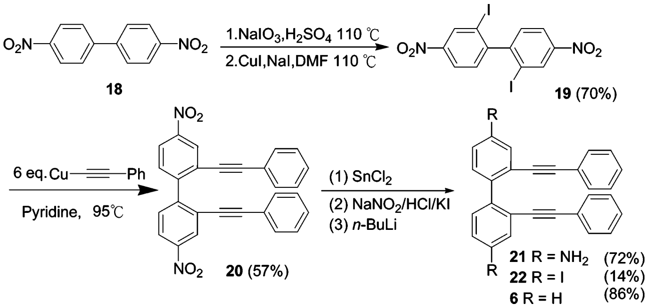

product **7** as a major product (Scheme 3).[5] Diradical intermediates **8** were proposed to account for the formation of **7**. No direct evidence for the formation of phenanthrocyclobutadiene derivative **9** was provided.

Although the reaction of **6** with (η^5-C_5H_5)Rh(CO)$_2$ led to an unequivocal η^4-C_4-ring complex **10**,[6] whether **10** was formed through the intermediate **9** is uncertain.[7] On the other hand, the reaction of **6** with air in the presence of $RhCl_3 \cdot H_2O$ and Aliquat 336 afforded **11** in 60% yield.[8] All of these reactions suggested that proximity interactions between two adjacent acetylene moieties were significant.

Similar thermal cyclization of 1,8-bis(phenylethylenyl)naphthalene (**12**) proceeded to give rise to polynuclear aromatic compound **13**. A diradical intermediate **14** was proposed for this reaction (Scheme 4). A repeated attempt to entrap the reactive cyclobutadiene intermediate **15** with iron pentacarbonyl only gave rise to the acecycloneirontricarbonyl (**16**) instead of cyclobutadieneirontricarbonyl (**17**).[9]

We hereby revisit the [2 + 2] thermal cycloaddition reactions. Trapping experiments for the reactive phenanthrocyclobutadiene intermediates were successfully carried out by using 2,3,4,5-tetraphenylcyclopentadienone as a trapping reagent.

Results and Discussion

Preparation of 4,4′-Disubstitued 2,2′-Bis(phenylethynyl)biphenyls. Iodination of 4,4′-dinitrobiphenyl (**18**)[10] was achieved with a two-step sequence reaction of iodonium salt formation[11] followed by nucleophilic aromatic substitution[12] with CuI/NaI to afford **19** in 70% yield (Scheme 5). Since the Sonogashira coupling of **19** with phenylacetylene would be influenced by a side reaction of palladium-catalyzed intramolecular cyclization,[13] copper phenylacetylide was therefore used instead as the reagent in the Castro coupling reaction to give **20** in 57% yield.[14] The nitro groups of **20** were reduced by $SnCl_2 \cdot 2H_2O$ to give diamine **21** in 72% yield.[15] Compound **21** was subjected to diazotization−iodination conditions using HCl/$NaNO_2$/KI as reagents to

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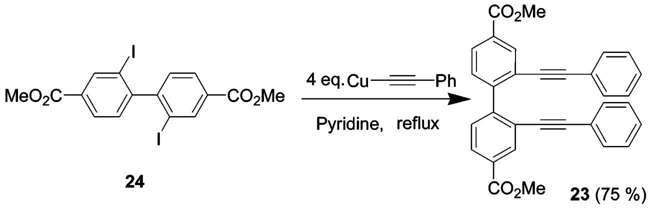
SCHEME 6



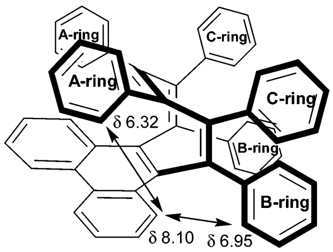
afford diiodo compound **22**.[16] Although the percent yield of this step is relatively low, the product was easily purified by liquid chromatography to create yellowish crystals. The iodide group was then removed by iodo−lithium exchange, followed by protonation of the corresponding aryllithium intermediate to give **6**.[17]

Carbomethoxy-substituted **23** was prepared by a similar coupling reaction of the corresponding 2,2′-diiodobiphenyl **24** with copper phenylacetylide in 75% yield (Scheme 6).[18]

Thermal Cyclization and Trapping Reaction of 4,4′-Disubstituted 2,2′-Bis(phenylethynyl)biphenyls with 2,3,4,5-Tetraphenylcyclopenta-2,4-dienone. Although benzocyclobutadiene had been trapped by many reactive dienes such as cyclopentadiene, furan, and 1,3-diphenylisobenzofuran,[19] an attempted trapping experiment of **9** with 1,3-diphenylisobenzofuran was proved to be unsuccessful.[19e] Since 2,3,4,5-tetraphenylcyclopenta-2,4-dienone (**25**) had been proved as a good trapping reagent for benzocyclobutadiene, we therefore adopted **25** as the trapping reagent for **9**.[20] In a typical trapping experiment (Scheme 7), a mixture of 2,2′-bis(phenylethynyl)-biphenyls (**6**) and an excess amounts of **25** under neat conditions under nitrogen was heated at 260−270 °C for 4 h. Two major products were isolated by liquid chromatography on silica gel. The first product was identified as the polynuclear aromatic adduct **7,** which has been reported in other studies.[5b] The second major product isolated in 12% yield was identified with an ^{1}H NMR spectrum with a relatively symmetrical pattern. On the basis of the ^{1}H,^{1}H−COSY experiment, the aromatic resonance signals was assigned into four groups: (1) δ 8.74 (d, 2H), 8.10 (d, 2H), 7.60 (t, 2H), 7.44 (t, 2H); (2) 7.20 (t, 2H), 7.14 (t, 4H), 7.07 (d, 4H); (3) 6.95 (m, 6H), 6.87 (t, 4H); (4) 6.81 (t, 2H), 6.68 (t, 4H), 6.32 (d, 4H). These ^{1}H NMR patterns were in good agreement with structure **26**, in which one group of phenanthrene protons and three groups of phenyl protons were expected. Similar cyclooctatetraene products **27** and **28** were found in the other trapping experiments. The yield percentage of diiodo derivative **27** was relatively high in the trapping reaction. On the contrary, for unknown reasons no cyclooctatetraene products were isolated in the reactions of **20** and **21** under similar conditions.

The structural identification was further supported by X-ray crystallographic analysis. Single crystals of **28** were successfully created by slow evaporation of the solvent from a corresponding chloroform solution (Figure 1). The tub-shape cyclooctatetraene skeleton (C_4−C_5, C_{19}−C_{24}) was clearly shown. In addition, the product containing a phenanthrene ring (C_1−C_{14}), two **A**-rings (C_{37}−C_{42} and C_{43}−C_{48}), two **B**-rings (C_{25}−C_{30} and C_{55}−C_{60}), and two **C**-rings (C_{31}−C_{36} and C_{49}−C_{54}) was the same as proposed before. The geometry of the tub-shape eight-membered ring was normally shaped with four sets of carbon−carbon π bonds localized between C_4−C_5, C_{19}−C_{20}, C_{21}−C_{22}, and C_{23}−C_{24}. The bond lengths were 1.364(5), 1.354(5), 1.353(6), and 1.342 (5), respectively.

The relative orientation of the phenyl groups and the phenanthrene group clearly explained the NMR pattern of **26** described in the previous section. The important finding to mention is the fact that the forth group of the aryl signals of **26** were abnormally upfield shifted to δ = 6.32−6.81 ppm. According to the crystal structure of **28**, we concluded that the phenyl protons on ring **A** were placed right over the phenanthrene units, so therefore the phenyl protons fell into a shielded region that arise from the diamagnetic anisotropic field of the phenanthrene moiety. This led to the unusual upfield shifts.



26

In addition to that, strong NOE enhancements between the phenanthrene doublet at 8.10 with the phenyl doublets at 6.32 and 6.95 were observed in the NOESY spectrum of **26**, which indicated that protons on the A-rings, B-rings, and phenanthrene were spatially close to each other. This was consistent with the prediction based on the tub-shape structure.

Mechanistic Aspects. Benzocyclobutadiene is a well-known reactive antiaromatic dienophile that would form Diels−Alder cycloadducts with the reactive cyclopentadienones, even under very mild conditions.[20,21] As shown in Scheme 8, bridged ketones were formed accordingly as the adduct under the reaction conditions.[20] The thermal stabilities of the bridged ketone cycloadducts were different, depended on the substituents on the cyclopentadienone. For example, adducts **31** and **32** were stable and could be identified at room temperature. Thermal decarbonylation in diglyme at 160 °C gave **34** and **35** as its products. Adduct **33** from acecyclone, on the other hand, was decarbonylated directly under the reaction conditions to form cyclooctatetraene **36.** When cyclobutadiene **9** was formed from the intramolecular acetylene−acetylene cyclization of **6** at high temperature, **9** was trapped in a similar fashion by **25** to give bridged ketone cycloadduct **37** (Scheme 9). However, due to the steric repulsions between the phenyl rings, it was expected

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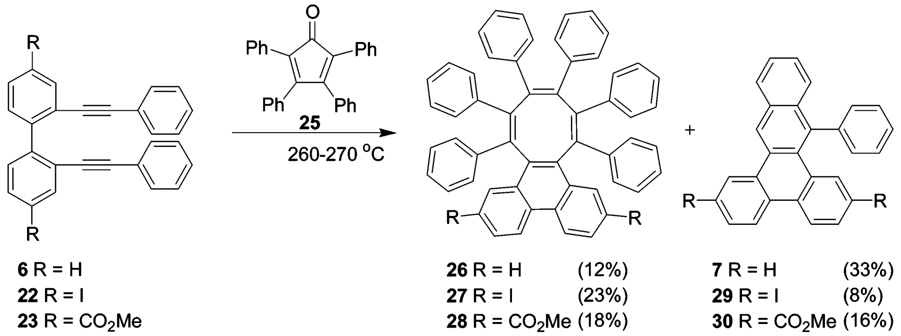
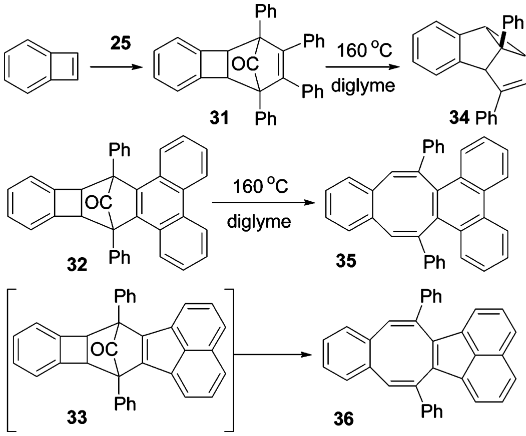
SCHEME 7



SCHEME 8



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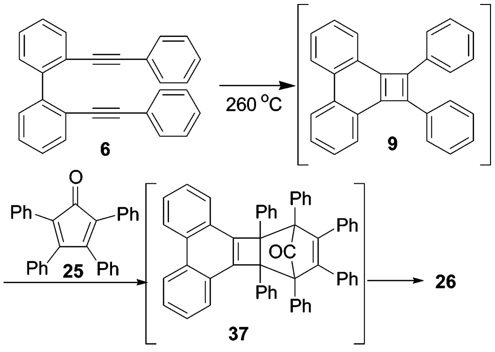
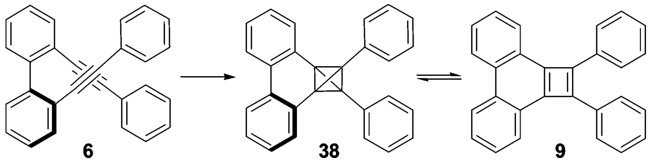


SCHEME 10



that thermal decarbonylation would subsequently occur at high temperature and give rise to **26**. In other words, the present results of the trapping reactions imply that the formation of **9** from **6** is feasible under thermal conditions.

The mechanism for the formation of **9** from **6** was not immediately obvious; nevertheless, the bisallenlic process in the Sondheimer cyclization was unlikely because it required an intermediate that can break down the aromaticity in the biphenyl unit. The formation of **9** directly through [2 + 2] cycloaddition or through a tetrahedrane intermediate **38**, on the other hand, was feasible at high temperature due to the proximity of the acetylene units (Scheme 10).[5a,b] Of course, the possibility of having the diradical intermediate *Z*,*Z*-**8** trapped by **25** to lead to the same product cannot be completely eliminated.

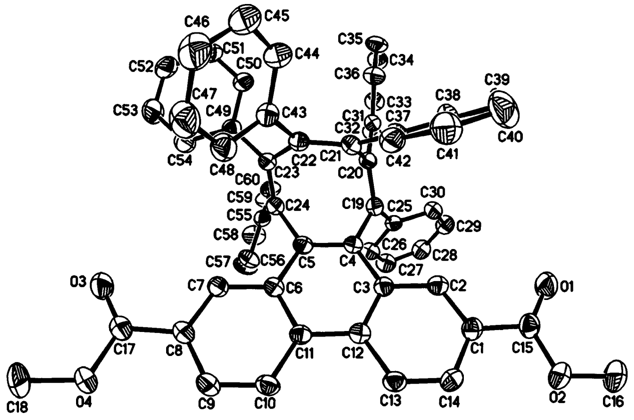


FIGURE 1. ORTEP diagram of **28**.

All these unsolved questions lead us to further investigate the involving mechanism. To compare the results, we adopted **22** as a probe to carry out a series of mechanistic studies under different conditions at a lower temperature of 150 °C in PhOPh. The results are summarized in Tables 1 and 2. Although the percent yields of **27** were lower in comparison, the amounts of unidentified products were reduced under these conditions. To examine if any diradical intermediates were involved in the Diels−Alder cycloaddition reaction, we employed 2,4,6-tri-*tert*-butylphenol (TBP) as a radical scavenger to test the assumption. The results are denoted in the last entry of Table 1. If the diradical intermediates were involved in the bimolecular cycloaddition process, the diradicals would be trapped by the scavengers, and therefore, the cycloaddition with **25** would be suppressed. However, our experimental results in Table 1 revealed that the presence of scavenger did not alter the isolated yields of **27**, leading to a contradictory implication against the diradical mechanisms. The almost identical isolated yields of **29** in all three cases are worthy of note. The presence of **25** did not inhibit the formation of **29**, indicating that **27** and **29** were formed in noncompetitive fashion. These unusual results urged us to follow the reaction kinetics in detail.

In the kinetic studies, we compared the decay rate of **22** in the presence and in the absence of **25**. The two parallel experiments were run simultaneously. To calibrate the amount

TABLE 1. Effects of Radical Scavenger TBP on the Cycloaddition Reaction of 22 (0.088 M) with 25 in PhOPh at 150 °C

			isolated yield (%)	
entry	**25** (equiv)	TBP (equiv)	**27**	**29**
1				50
2	8		18	55
3	11	3	17	51

TABLE 2. Chemical Kinetics Data for the Intramolecular Cyclization of 22 (0.070 M) and the Cycloaddition Reaction of 22 (0.070 M) with 25 (5.5 equiv) in PhOPh at 145 °C

	without **25**		with **25**		
time (min)	**22**[a]	**29**[a]	**22**[a]	**29**[a]	**27**[a]
0	100	0	100	0	0
40	74	9	69	10	2
110	31	51	31	47	7
210	10	60	9	63	10

[a] Against the internal standard **24** (0.052 M).

of all the components in the reaction mixture, we adopted **24** as an internal standard. The amounts of **22**, **27**, and **29** were determined on the basis of their integrations at $\delta = 8.00$ (d, $J = 1.5$ Hz, 2H), 8.41 (d, $J = 1.7$ Hz, 2H), and 9.00, 9.01(2s, 2H) ppm, respectively, against the standard at $\delta = 8.63$ (s, 2H) ppm. These signals corresponded to the aromatic protons adjacent to the iodo groups. The experiments were run at 145 °C under argon in order to avoid any interference from oxygen.[8] The reaction mixtures were sampled using a syringe and were dissolved in $CDCl_3$ for ^1H NMR measurements. The results are summarized in Table 2. Some critical observations based on the experimental results can be concluded as follows: (1) the rates of decay of **22** were very close in both cases; (2) the rates of formation of **29** were almost identical in two experiments; and (3) the presence of **25** did not suppress formation of **29**.

Semiempirical Calculations. To explore the plausible reaction intermediates, semiempirical PM5 calculations[22] were carried out in order to estimate the heats of formation of the related structures. According to other studies, compounds **6**, **7**, **9**, **38**, **39**, and the diradical intermediates **8** are targets for evaluation. The closed-shell structures of **6**, **7**, **9**, **38**, and **39** could be optimized by Hartree−Fock methods, and the estimated heats of formation ($\Delta H_f°$) of 186, 114, 175, 245, and 184 kcal/mol were respectively calculated (Figure 2). Perhaps due to the large ring-strains of the tetrahedran skeleton, the calculated $\Delta H_f°$ of **38** is 59 kcal/mol higher than that of diyne **6**. Due to the high heat of formation of **38**, involvement of **38** as an intermediate in the reactions was unlikely. The estimated $\Delta H_f°$ of **9** and **39**, on the other hand, were slightly lower than that of **6** by 11 and 2 kcal/mol, respectively. We attribute the relatively high $\Delta H_f°$ of **6** to the weak carbon−carbon π bonds of the acetylene groups.[23] Although **7** was thermodynamically more stable than **6** by 72 kcal/mol, it seemed to be formed from **6** in stepwise fashion. The most likely intermediate was **39**, which could be formed either through a concerted or stepwise diradical mechanism from **6**.

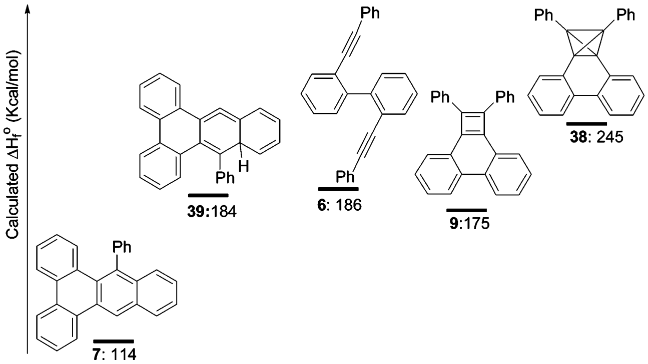


FIGURE 2. Relative plot of the calculated heats of formation of compounds **6**, **7**, **9**, **38**, and **39**.

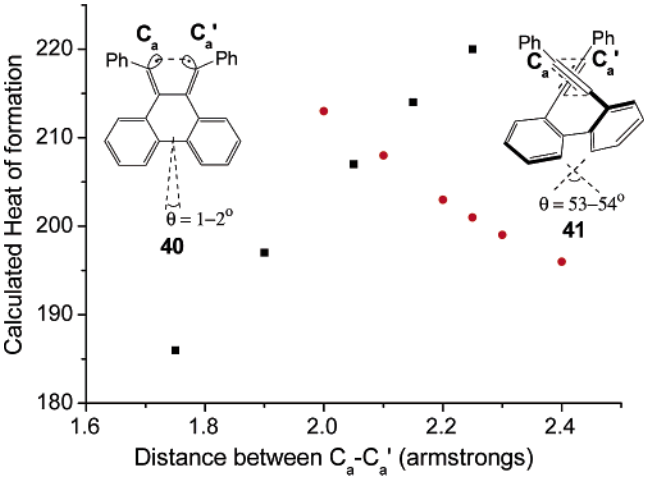


FIGURE 3. Estimation of the energy of *Z,Z*-**8** by mapping the $C_a-C_{a'}$ bond formation from **6** and the $C_a-C_{a'}$ bond cleavage of **9**.

Although there was a possibility of involvement of the diradical **8** in the reaction, direct calculation for the heat of formation of the diradicals are complicated. Therefore, we attempted to estimate the energy of the diradicals by mapping the reaction profile. In this approach, formation of *Z,Z*-**8** from **9** was mapped by locking the $C_a-C_{a'}$ bond length (L) at a specified value and optimized the remaining structural parameters by PM5 methods. The calculated $\Delta H_f°$'s that corresponded to each specific L were plotted in Figure 3. As expected, the $\Delta H_f°$ increased when L increased gradually. When L was kept shorter than 2.0 Å, the optimized geometry fell into a distorted cyclobutadiene-like structure **40**, with the dihedral angle θ around $2 \pm 1°$ for the nearly coplanar biphenyl moiety. On the other hand, when L was set around 2.1 Å, two structures with similar heats of formation could be identified. One was in the form of **40** while the other was in the form of **41**. When L was locked at a distance larger than 2.2 Å, the distorted diynelike skeleton **41** became energetically charged. In these cases, the biphenyl unit was twisted, with the dihedral angle $\theta \approx 53-54°$. A reaction profile could therefore be constructed. When the phenylacetylene carbons C_a and $C_{a'}$ of **41** became close to a certain short distance around 2.1 Å, a crossover from **41** to **40** was expected. The form of diradical *Z,Z*-**8** occurred as a

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[22] The calculations were carried out by using the package software of CAChe developed by Oxford Molecular Ltd. and Fujitsu Ltd.

[23] (a) Zavitas, A. A. *J. Phys. Chem. A* **2003**, *107*, 897. (b) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook*; Linstrom, P. J., Mallard, W. G., Eds.; NIST Standard Reference Database 69; National Institute of Standards and Technology: Gaithersburg, MD 20899, July 2001 (http://webbook.nist.gov). (c) Luo, Y. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC: Boca Raton, 2003.

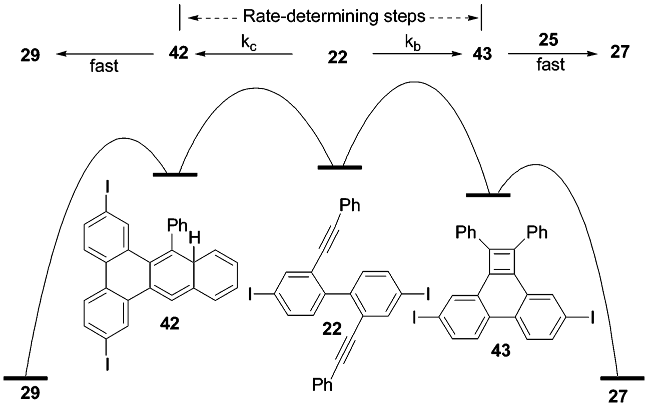

FIGURE 4. Tentatively proposed mechanisms for the Dessy−White intramolecular cycloadditions of **22**.

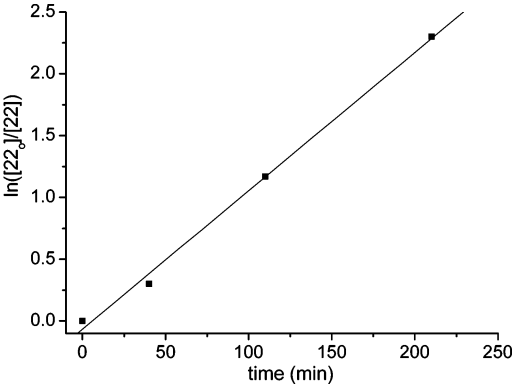

FIGURE 5. Linear correlation plot of $\ln([\mathbf{22}]_o/[\mathbf{22}]_t)$ versus reaction time.

transition state or a short-life reactive intermediate in the reaction profile, with an energy about 20 kcal/mol higher than that of **6**.

Aspects from the Kinetics Study. The above experimental results serve as very useful information for constructing a view of reaction mechanisms. First of all, as mention before, since **27** and **29** were formed in noncompetitive fashion, the assumption of formation of **27** and **29** through competition of a common intermediate should be eliminated. To explain for the above observations, we tentatively propose a mechanism as shown in Figure 4.

Two parallel electrocyclic reactions of **22** occurred to lead to highly reactive **42** and **43** that would further react quickly to yield the final products. The electrocyclic reactions were irreversible and rate-determining. According to this mechanism, a first-order decay of **22**, expressed as $-d[\mathbf{22}]/dt = (k_b + k_c)[\mathbf{22}]$, was expected. Transformation of the rate equation into the integrated form gave $\ln([\mathbf{22}]_o/[\mathbf{22}]_t) = (k_b + k_c)t$, in which $[\mathbf{22}]_o$ and $[\mathbf{22}]_t$ were the concentrations of **22** at time equal to 0 and *t*, respectively. This prediction was consistent with the linear correlation in the plot of $\ln([\mathbf{22}]_o/[\mathbf{22}]_t)$ versus reaction time shown in Figure 5. Since the decay of **22** was a result of the intramolecular processes, the decay rate should be constant, regardless of the presence or absence of the Diels−Alder trapping reagent **25**.

The percent yield of **29**, on the other hand, was governed by the constant rate ratio of $k_c/(k_b + k_c)$. Therefore, the formation of **29** would not be affected by the Diels−Alder trapping reaction. Since phenanthrocyclobutadiene **43** was the key intermediate involved in the Diels−Alder reaction step, formation of the adduct **27** would not be interrupted by TBP, the radical scavenger.

In summary, our results provided a mechanistic point of view for the Dessy−White intramolecular acetylene−acetylene [2 + 2] cycloaddition reaction. The reaction may involve formation of a phenanthrocyclobutadiene intermediate from two proximate acetylene groups at high temperature.

Experimental Section

Preparation and Identification of 6, 19−23, 28, and 30. The corresponding synthetic procedures and characterization data are reported in the Supporting Information.

Thermal Cycloaddition Reactions of 4,4′-Disubstituted 2,2′-bis(phenylethynyl)biphenyls with 2,3,4,5-Tetraphenylcyclopenta-2,4-dienone. 9-Phenyldibenz[*a,c*]anthracene (7) and 9,10,11,12,13,14-Hexaphenylcycloocta[*l*]phenanthrene (26). A General Procedure under Neat Conditions. Reaction of 2,2′-bis(phenylethynyl)biphenyl (**6**) (0.12 g, 0.35 mmol) with **25** (1.42 g, 3.71 mmol) was carried out under nitrogen at 260−270 °C for 4 h. The mixture was purified by column chromatography on silica gel using toluene/hexane (1:10) as the eluent to produce **7** (rf = 0.59) and **26** (R_f = 0.18). Compound **7** was isolated as a slightly greenish solid (0.04 g, 33%). The spectra were identical with literature data:[5c] mp 228−230 °C (lit.[5c]mp 229 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.12 (s, 1H), 8.72 (d, J = 8.6 Hz, 1H), 8.48 (d, J = 8.6 Hz, 1H), 8.43 (d, J = 6.9 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.64−7.52 (m, 7H), 7.44−7.37 (m, 4H), 6.98 (dt, J_d = 1.4 Hz, J_t = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.3, 137.3, 132.3, 131.9, 131.7, 131.3, 130.7, 130.5, 129.3, 128.3, 127.7, 127.6, 127.4, 127.3, 126.9, 126.8, 126.1, 125.9, 125.4, 124.0, 123.23, 123.21, 122.0; HRMS (EI) *m/z* calcd for $C_{28}H_{18}$ 354.1409, found 354.1399. Compound **26** is a white solid (0.03 g, 12%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.74 (d, J = 8.0 Hz, 2H), 8.10 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.0 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.5 Hz, 2H), 7.14 (t, J = 8.0 Hz, 4H), 7.06 (d, J = 7.5 Hz, 4H), 6.96−6.92 (m, 6H), 6.87 (t, J = 7.5 Hz, 4H), 6.81 (t, J = 7.5 Hz, 2H), 6.68 (t, J = 8.0 Hz, 4H), 6.32 (d, J = 7.5 Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 143.7, 143.0, 140.1, 139.7, 139.0, 138.8, 138.2, 131.2, 130.5, 130.4, 130.2, 130.0, 128.1, 128.0, 127.6, 127.2, 127.1, 126.7, 126.4, 126.2, 126.1, 122.7; HRMS (EI) *m/z* calcd for $C_{56}H_{38}$ 710.2974, found 710.2950.

2,7-Diiodo-9-phenyldibenz[*a,c*]anthracene (29) and 2,7-Diiodo-9,10,11,12,13,14-hexaphenylcycloocta[*l*]phenanthrene (27). Reaction of **22** (0.12 g, 0.20 mmol) with **25** (0.48, 1.25 mmol) was carried out in diphenyl ether (1.5 mL) under nitrogen at 270 °C for 4 h. The mixture was cooled to room temperature and washed with hexane. The insoluble solid was filtered, collected, and washed with acetone to obtain insoluble **29** as a greenish solid (0.01 g, 8%): mp 304−306 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.01 (s, 1H), 9.00 (s, 1H), 8.13−8.04 (m, 3H), 7.88−7.84 (m, 2H), 7.74 (d, J = 8.7 Hz, 1H), 7.67−7.56 (m, 5H), 7.47−7.45 (m, 1H), 7.38 (d, J = 7.4 Hz, 2H). The amounts of the isolated products are not enough to provide a high-quality ^{13}C NMR spectrum. However, the pattern and the high-resolution mass spectrum support the assignment. HRMS (EI): *m/z* calcd for $C_{28}H_{16}I_2$ 605.9341, found 605.9341. The filtrate was collected, concentrated under reduced pressure, and purified by column chromatography on silica gel using CH$_2$Cl$_2$/hexane (1:3) as the eluent to produce **27** (R_f = 0.23) as a white solid (0.04 g, 23%): ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.41 (d, J = 1.8 Hz, 2H), 8.36 (d, J = 8.8 Hz, 2H), 7.84 (dd, J = 1.7, 8.7 Hz, 2H), 7.20 (t, J = 7.1 Hz, 2H), 7.14 (t, J = 7.4 Hz, 4H), 7.02 (d, J = 6.9 Hz, 4H), 6.99−6.96 (m, 2H), 6.94−6.85 (m, 10H), 6.75 (t, J = 7.7 Hz, 4H), 6.34 (d, J = 7.2 Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 144.6, 142.7, 139.6, 139.2, 138.5, 138.1, 137.8, 137.0, 135.1, 132.9, 130.3, 130.3, 129.9, 128.9, 128.2, 127.9, 127.44, 127.35, 126.8, 126.5, 124.2, 92.9; HRMS (EI) *m*/*z* calcd for $C_{56}H_{36}I_2$ 962.0906, found 962.0884.

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Supporting Information Available: Synthetic procedures for **6**, **19**−**23**, **28**, and **30**; ^{1}H and ^{13}C NMR spectra of **6**, **7**, **19**−**23**, **26**−**28**, and **30**; H spectrum of **29**; ^{1}H−^{1}H COSY, NOESY, HMBC, and HSQC spectra of **26**; CIF data of **28**; and PM5 coordinates of **6**, **7**, **9**, **38**, and **39**. This material is available free of charge via the Internet at http://pubs.acs.org.

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