Design, Generation, and Characterization of a 1,5-Hexadiene Bearing Two Lophyl Radicals as a Probe of the Stepwise Mechanism for the Cope Rearrangement

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The mechanism of the Cope rearrangement of 1,5-hexadienes remains controversial. Two pathways for the rearrangement of 2,5-diphenyl-1,5-hexadiene have been debated over the past several decades. The first is a concerted route that takes place via a pericyclic transition state and the other is a stepwise process via a biradical intermediate or biradicaloid transition structure. In this study, we explored a new intramolecular trapping approach to examine the possible existence of the putative biradical that might intervene in the stepwise Cope rearrangement. For this purpose, a study was carried out in which a 1,5-hexadiene, bearing two lophyl radicals at C2 and C5 positions, moieties capable of trapping a putative biradical intermediate intramolecularly, was designed, generated, and characterized both experimentally and with density functional theory.

Since the time of the original report of the Cope rearrangement involving thermal isomerization of ethyl 2-allyl-2-cyano-3-methyl-3-pentenoate to yield ethyl 2-cyano-3,4-dimethyl-2,6-heptadienoate,[1] the mechanism of the reaction has been studied extensively using both experimental[2] and theoretical[3] tools. Gajewski[4] has proposed what appears to be the most plausible pathway for this process that involves a variable transition state. Specifically, Gajewski suggested the transition state for the Cope rearrangement changes depending on the positions and the types of substituents contained within the 1,5-hexadiene skeleton. This is best shown using the More O'Ferral Jenks diagram displayed in Figure 1. The parent 1,5-hexadiene (**1**) as well as other derivatives undergoes [3,3]-sigmatropic rearrangement in a concerted manner via a chair-type six-membered transition state ($\mathbf{2}_{\mathrm{TS}}$, solid arrow). However, when radical-stabilizing groups, such as a phenyl, are appended to the C2 and C5 positions of **1**, the Cope rearrangement may occur by a stepwise route via a singlet cyclohexane-1,4-diyl ($^{1}\mathbf{3}^{\bullet\bullet}$)-type intermediate (Figure 1, dashed arrow), which can be referred to as a cyclization (CY)–cleavage mechanism. As a matter of fact, Dewar[5] put forth the bold proposal earlier that reaction of 2,5-diphenyl-1,5-hexadiene (**4**) possibly proceeds through the intermediacy of a singlet biradical $^{1}\mathbf{6}^{\bullet\bullet}$, or a biradicaloid rather than a concerted pathway via transition state $\mathbf{5}_{\mathrm{TS}}$. Unfortunately, no direct evidence has been provided for the existence of biradical intermediates, such as $^{1}\mathbf{3}^{\bullet\bullet}$ or $^{1}\mathbf{6}^{\bullet\bullet}$, in the Cope rearrangement. This is a likely result of the expected short lifetimes of these transients. Consequently, biradicals $^{1}\mathbf{3}^{\bullet\bullet}$ or $^{1}\mathbf{6}^{\bullet\bullet}$ at this point can only be regarded as putative intermediates.[6]

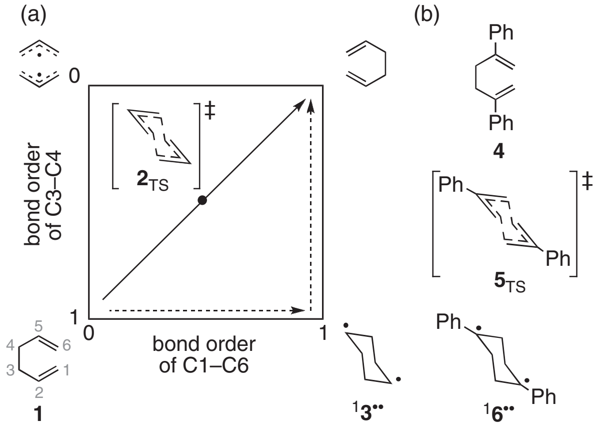

Figure 1. (a) A More O'Ferral Jenks diagram of the Cope rearrangement of 1,5-hexadiene (**1**). (b) The structure of **4**, the corresponding transition state $\mathbf{5}_{\mathrm{TS}}$, and a putative biradical intermediate $^{1}\mathbf{6}^{\bullet\bullet}$.

In the investigation described below, we have explored a new intramolecular trapping approach that is designed to determine the possible existence of putative biradicals as intermediates in the Cope rearrangement. We reasoned that a 1,5-hexadiene which contains radical-type substituents at the C2 and C5 positions (i.e., $\mathbf{7}^{\bullet\bullet}$, Scheme 1) would be capable of undergoing the Cope rearrangement in a stepwise manner via a 1,4-cyclohexanediyl intermediate like $^{1}\mathbf{3}^{\bullet\bullet}$. In this case, the intermediate would be a tetraradical $\mathbf{8}^{\bullet\bullet\bullet\bullet}$ that could be trapped intramolecularly by bond alternation (BA) to give a 1,4-dimethylenecyclohexane (**9**). Below, we describe the design, generation, and characterization of the 1,5-hexadiene $\mathbf{10}^{\bullet\bullet}$ (Chart 1), a species that contains two lophyl radical substitu-

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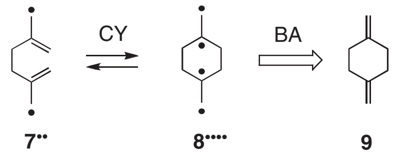


Scheme 1. An intramolecular trapping model of a putative $^{1}\mathbf{3}^{\bullet\bullet}$-type intermediate ($\mathbf{8}^{\bullet\bullet\bullet\bullet}$) in the Cope rearrangement of 1,5-hexadiene derivative $\mathbf{7}^{\bullet\bullet}$. BA and CY refer to bond alternations and cyclization, respectively.

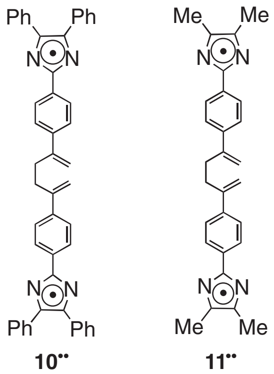
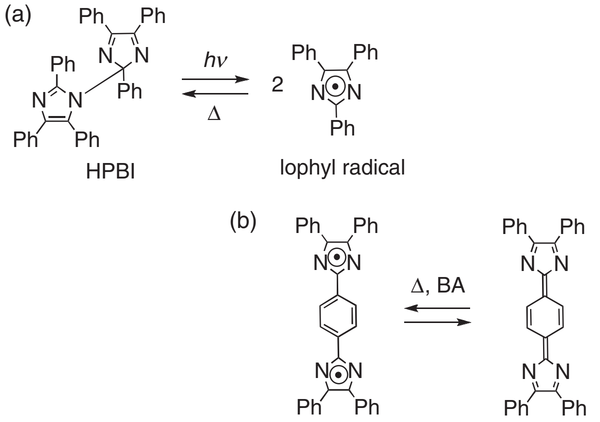


Chart 1. Structures of $\mathbf{10}^{\bullet\bullet}$ and $\mathbf{11}^{\bullet\bullet}$ in their cisoid form.

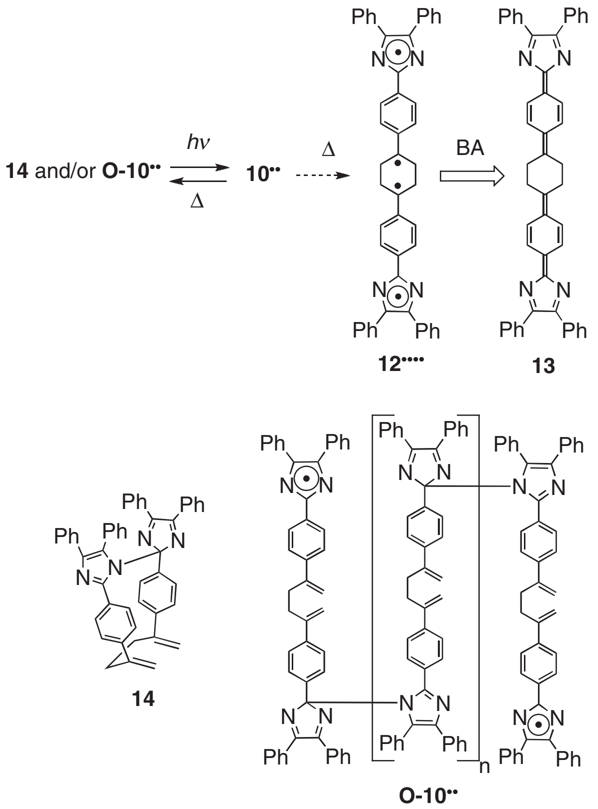


Scheme 2. The chemical behavior of (a) the lophyl radical and (b) tetraphenyl-*p*-diimidazolylbenzene.

ents (Scheme 2a) at C2 and C5 positions, which could serve as a probe for the nonconcerted mechanism of the Cope rearrangement. We also describe the results of density functional theory (DFT) calculations[7] that were used to ascertain the properties of a biradical related to $\mathbf{10}^{\bullet\bullet}$ as well as other intermediates derived from this species.

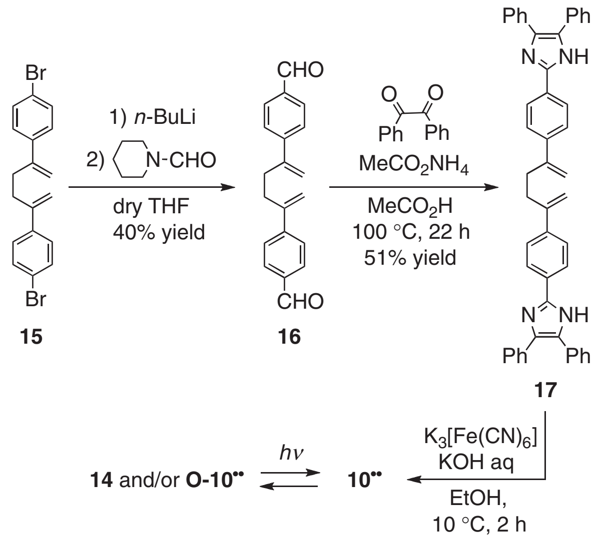
Results and Discussion

Molecular Design. In the system we have devised, the lophyl radical is employed as a radical-type substituent at the C2 and C5 positions of 1,5-hexadiene. Generally, the lophyl radical can be reversibly generated by C–N bond cleavage of a hexaphenylbiimidazolyl (HPBI),[8] a representative of T-type photochromic compounds (Scheme 2a). It is known that the tetraphenyl-*p*-diimidazolylbenzene π-type biradical, shown in Scheme 2b, exists in thermal equilibrium with its quinoid closed-shell form.[9] The double BA that occurs in this system is a key component of the intramolecular trapping process that we envisage for detection of a putative $^{1}\mathbf{3}^{\bullet\bullet}$-type intermediate in the Cope rearrangement. Guided by this observation, we have developed a strategy in which a similar BA would convert a tetraradical $\mathbf{12}^{\bullet\bullet\bullet\bullet}$, potentially formed from $\mathbf{10}^{\bullet\bullet}$, into a closed-shell species **13** (Scheme 3). The intramolecularly linked HPBI **14** was selected as the precursor of $\mathbf{10}^{\bullet\bullet}$. In addition, the oligomeric form $\mathbf{O\text{-}10}^{\bullet\bullet}$, a compound containing an intermolecularly substituted by HPBI, could also be utilized as a precursor of $\mathbf{10}^{\bullet\bullet}$. We anticipated that UV irradiation would promote homolytic C–N bond cleavage reactions of these starting materials to form $\mathbf{10}^{\bullet\bullet}$ (Scheme 3). The stepwise degenerate Cope rearrangement of $\mathbf{10}^{\bullet\bullet}$ would then take place via tetraradical intermediate $\mathbf{12}^{\bullet\bullet\bullet\bullet}$, which would be trapped intramolecularly by BA to give a 1,4-dimethylenecyclohexane derivative **13**. Fundamental features of this strategy have been explored in the investigation described below.



Scheme 3. The expected reaction mechanism for $\mathbf{10}^{\bullet\bullet}$ obtained from **14** and/or $\mathbf{O\text{-}10}^{\bullet\bullet}$.

Synthesis of 14 and/or $\mathbf{O\text{-}10}^{\bullet\bullet}$. As shown in Scheme 4, substrate **14** and/or $\mathbf{O\text{-}10}^{\bullet\bullet}$ was synthesized starting with 2,5-bis(4-bromophenyl)-1,5-hexadiene (**15**).[10] Bis-formylation of **15** by treatment with *n*-BuLi followed by *N*-formylpiperidine produced 2,5-bis(4-formylphenyl)-1,5-hexadiene (**16**), which was converted to **17** by condensation with benzil in the presence of $MeCO_2NH_4$.[9e] Two-electron oxidation of **17** using $K_3[Fe(CN)_6]$ gave **14** and/or $\mathbf{O\text{-}10}^{\bullet\bullet}$ via formation and coupling of the lophyl-type biradical $\mathbf{10}^{\bullet\bullet}$.[8i] Although we have not yet been successful in purifying **14** and/or $\mathbf{O\text{-}10}^{\bullet\bullet}$, the structure(s) of this substance has been assigned by using the characterization methods described below.



Scheme 4. Synthesis of **14** and/or **O-10**$^{\bullet\bullet}$.

Evidence for the Formation of 14 and/or O-10$^{\bullet\bullet}$**. ^{1}H NMR and MS Analysis:** The ^{1}H NMR spectrum of a mixture obtained by oxidation of **17** does not contain any peaks that can be assigned to **14**.[11,12] Although it is not clear at this stage, this could be a consequence of the selective formation of **O-10**$^{\bullet\bullet}$ from **10**$^{\bullet\bullet}$. However, the presence of a peak at $m/z = 669$, among countless others, in the MS (FAB) spectrum[12] of the mixture arising by oxidation of **17** suggests that either or both **14** ($C_{48}H_{36}N_4 = 668.29$) and **O-10**$^{\bullet\bullet}$ have been produced.

Photochromic Behavior and Absorption Spectra: The HPBI-like photochromic behavior of the mixture obtained by $K_3[Fe(CN)_6]$ treatment of **17** (ca. 1.0×10^{-3} M) in benzene is displayed in Figure 2. The benzene solution was initially a pale greenish yellow color (Figure 2, left). Upon UV (350 nm) irradiation with a Rayonet reactor (5 W × 16) for 1 min, the color of the solution turned to deep purple (Figure 2, center), a change that is ascribed to the formation of **10**$^{\bullet\bullet}$. On standing for 5 min in the dark at room temperature, the color of the solution gradually returned to pale greenish yellow (Figure 2, right). This photochromic change demonstrates that the mixture obtained from **17** contains a species like **14** and/or **O-10**$^{\bullet\bullet}$ that possesses the HPBI moiety.

The spectral changes associated with the photochromic behavior of the mixture obtained from **17** (ca. 1×10^{-5} M) in benzene are displayed in Figure 3. The beginning pale greenish yellow benzene solution has an absorption band at $\lambda_{AB} < 470$ nm. Upon 350-nm irradiation for 1 min, the color of the solution turned to deep purple concomitant with an increase and decrease of the respective absorption bands at 580 and 380 nm. On standing in the dark at room temperature for 5 min, the solution returned to pale greenish yellow in association with a decrease and increase in the absorption bands at 580 and 380 nm, respectively. The <470-nm and 380- and 580-nm absorption bands are assignable to the chromophores present in **14** and/or **O-10**$^{\bullet\bullet}$ and **10**$^{\bullet\bullet}$, respectively. Support for the assignments of the 380- and 580-nm bands comes from inspection of the absorption spectroscopic properties of the structurally related model compound[12] **18** and the radical[12] **19**$^{\bullet}$ (Scheme 5), which possess absorption bands at <440 nm, and 369 and 569 nm, respectively (Figure 4). Furthermore, the results of time-dependent DFT calculation suggest that **19**$^{\bullet}$ should have electronic transitions at 408 and 625 nm.

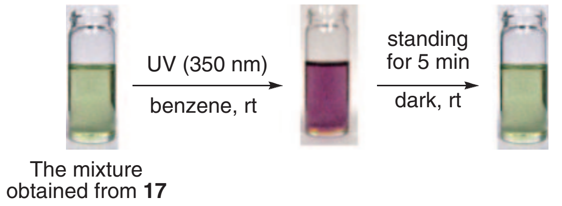


Figure 2. Photochromic behavior of the mixture obtained by oxidation of **17** (ca. 1.0×10^{-3} M in benzene), which suggests that **10**$^{\bullet\bullet}$ forms via **14** and/or **O-10**$^{\bullet\bullet}$. Photos taken before (left) UV light irradiation, (center) 1 min after UV light irradiation, and (right) after successively standing for 5 min in the dark.

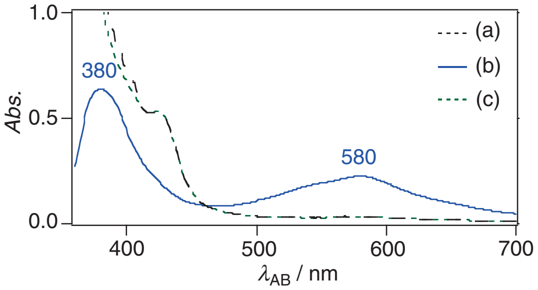
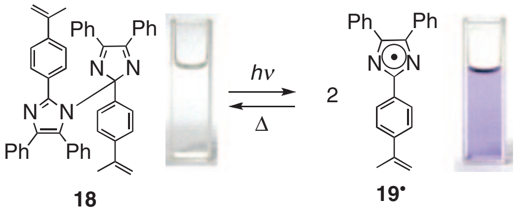


Figure 3. (a) Absorption spectra of a benzene solution of the mixture obtained from **17** (ca. 1×10^{-5} M), (b) after UV (350 nm) light irradiation for 1 min at room temperature, and (c) after successively standing in the dark for 5 min.



Scheme 5. Photochromic behavior of **18**.

These results strongly suggest that (1) **10**$^{\bullet\bullet}$ is formed by oxidation of **17**, (2) thermal recombination of **10**$^{\bullet\bullet}$ produces **14** and/or **O-10**$^{\bullet\bullet}$, and (3) **10**$^{\bullet\bullet}$ is generated from **14** and/or **O-10**$^{\bullet\bullet}$ via a photochemical process.

ESR Spectroscopy and the Photochromic Behavior: The mixture obtained from $K_3[Fe(CN)_6]$ treatment of **17** was subjected to ESR spectroscopic analysis to provide additional evidence for the formation of **10**$^{\bullet\bullet}$. Prior to photoexcitation, a toluene solution containing the mixture is not ESR active. However, after photoexcitation with a 500 W Xe arc lamp at 77 K, broad ESR signals were obtained, as shown in Figure 5. The *g* value of 2.0027 for the broad band is in good agreement with published data[8d] for the parent lophyl radical. Interestingly, no signal assignable to the forbidden transition originating from a triplet biradical was observed. However, this was not incompatible with the structure of the lophyl-type biradical **10**$^{\bullet\bullet}$ where two radicals are mutually separate, implying no

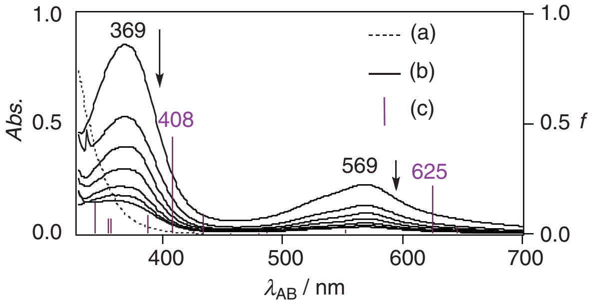


Figure 4. (a) Absorption spectra of a benzene solution of **18** (1×10^{-5} M). (b) Time-dependent changes of the absorption spectra of a benzene solution of **18** after UV (350 nm) irradiation for 1 min at room temperature. The spectra were recorded at 5 min intervals over a 30 min period. (c) A bar graph showing the electronic transitions of the radical **19•**, which was obtained by using time-dependent DFT calculation [UB3LYP/6-31G(d,p)].

The mixture obtained from **17** $\xrightarrow[\text{toluene, 77 K}]{\text{UV (350 nm)}}$ **10••**

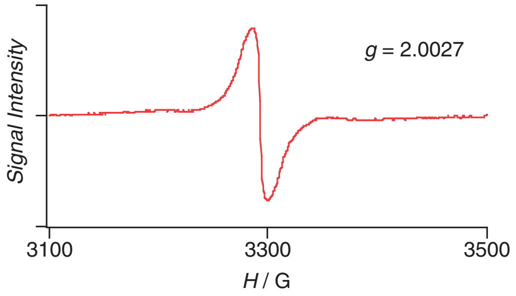
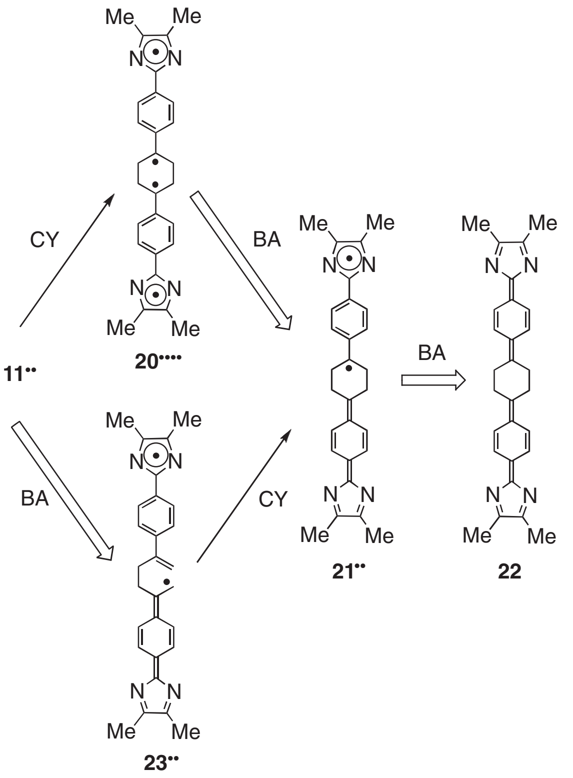


Figure 5. An ESR spectrum of a degassed toluene matrix of the mixture obtained by oxidation of **17** (ca. 4 mM) after UV irradiation for 2 min with a Xe lamp at 77 K. Center field = 3260 G, sweep time = 5 min, microwave frequency = 9.204 GHz.

significant interaction between the two radical moieties. Thus, these findings suggest that **10••** is formed upon irradiation of the mixture formed from **17**.

Theoretical Analysis. To gain further insight into the mechanism expected for reactions **14** and/or **O-10••**, DFT calculations were carried out by using the (U)B3LYP/6-31G(d,p) method.[7] The calculations were actually performed on tetramethyl derivatives (e.g., **11••**), which are simplified models in which four phenyl groups (e.g., in **10••**) are replaced by four methyls. As shown in Scheme 6, we expected that if **11••** were to undergo cyclization the resulting tetraradical intermediate **20••••** would be trapped intramolecularly by double BA to give the stable closed shell species **22**. Interestingly, the results of the calculations suggest that reaction of **11••** would proceed via the monoquinoidal biradical **21••**. Although an alternative pathway via a biradical **23••** is formally possible, it can be ruled out since **23••** does not appear to make a significant contribution to the electronic structure of **11••**. Below, we present a description and discussion of the results of calculations[13] on the stepwise reaction of **11••** that produces **22** via biradical **21••** taking multiplicity into consideration.



Scheme 6. The expected reaction mechanism for **11••**.

Hexadienes 11••: Interestingly, the transoid forms of the triplet and singlet biradicals ^{3}**11••** and ^{1}**11••** (Figure 6) have nearly the same energies (Figure 7). This result is in accord with experimental observation that biradical **10••** is formed as an intermediate in the reaction of **14** and/or **O-10••**.

Tetraradicals 20••••: If the singlet biradical ^{1}**11••** undergoes the first step of a nonconcerted Cope rearrangement, the tetraradical intermediate ^{1}**20••••** would be generated. However, attempts to optimize the molecular structures of ^{1}**20••••** and its triplet counterpart ^{3}**20••••** result in the formation of **22** and ^{3}**21••**, respectively. In contrast, optimization of the quintet tetraradical ^{5}**20••••** converges nicely to yield an energy relative to that of the transoid ^{1}**11••** [E_{rel}(^{5}**20••••**)] of +32.4 kcal mol^{-1} (Figure 7). Thus, E_{rel}(^{3}**20••••**) and E_{rel}(^{1}**20••••**), evaluated by using single point calculations on the Cartesian coordinates of ^{5}**20••••**, were found to be +16.8 and +2.5 kcal mol^{-1}, respectively.

Monoquinoidal Biradicals 21••: Optimization of ^{1}**21••** results in the generation of **22** (Figure 7). In contrast, optimization of ^{3}**21••** converges successfully to give an energy [E_{rel}(^{3}**21••**)] of +11.9 kcal mol^{-1}. E_{rel}(^{1}**21••**) was evaluated by using a single point calculation on the Cartesian coordinates of ^{3}**21••** as −2.5 kcal mol^{-1}.

Trapped Molecule 22: The energy of **22** relative to the singlet transoid biradical ^{1}**11••** is calculated to be −7.5 kcal mol^{-1}.

The theoretical results presented above suggest that ^{1}**11••** undergoes cyclization to give ^{1}**20••••** without a significant activation energy and that ^{1}**20••••** readily participates in BA to give **22** via ^{1}**21••**. Thus, the findings show that intramolecular trapping by facile double BA reactions of a putative biradical

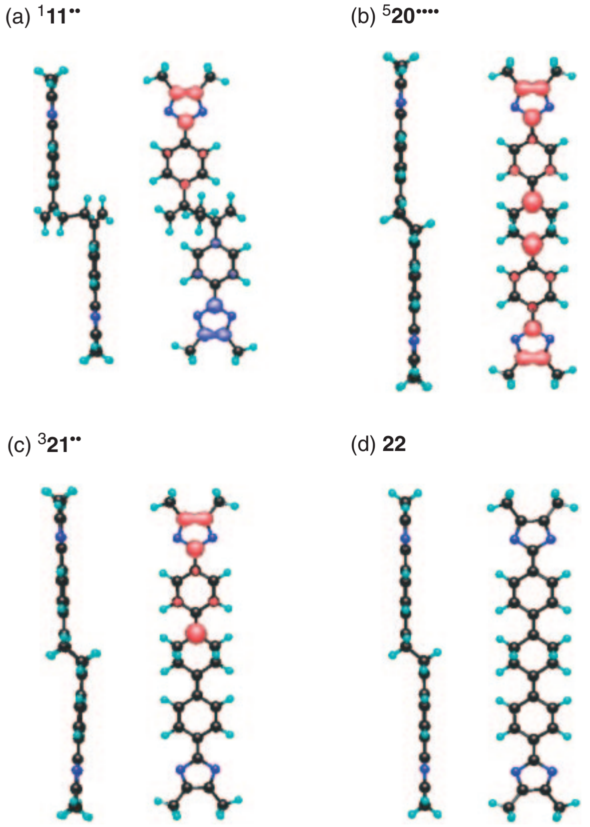


Figure 6. Molecular structures and spin densities of (a) $^{1}\mathbf{11}^{\bullet\bullet}$, (b) $^{5}\mathbf{20}^{\bullet\bullet\bullet\bullet}$, (c) $^{3}\mathbf{21}^{\bullet\bullet}$, and (d) **22**, optimized by using the (U)B3LYP/6-31G(d,p) method. Left; side views, right; front views. See Ref. 14.

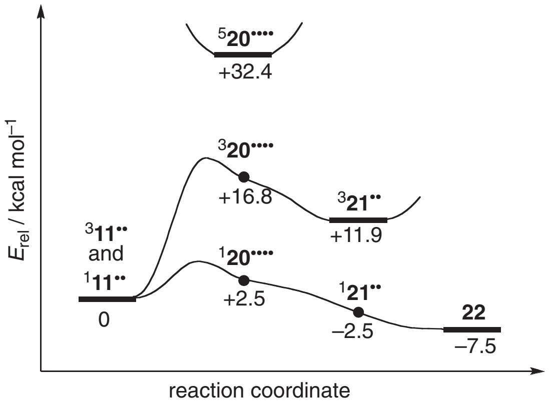


Figure 7. Outline of energy diagram for the putative stepwise Cope rearrangement of $\mathbf{11}^{\bullet\bullet}$ and a possible intramolecular trapping of $\mathbf{20}^{\bullet\bullet\bullet\bullet}$ to give **22** via $\mathbf{21}^{\bullet\bullet}$. Relative energies were calculated by using the (U)B3LYP/6-31G(d,p) method.[7,13]

intermediate in the Cope rearrangement can be achieved. Consequently, the observations suggest that the tetraphenyl derivative $^{1}\mathbf{10}^{\bullet\bullet}$ would be a suitable probe to examine the possible operation of the debated stepwise Cope rearrangement mechanism taking place via a putative biradical intermediate.

Conclusion

In conclusion, the studies described above have resulted in the design, synthesis, and characterization of $\mathbf{10}^{\bullet\bullet}$, a species that possesses two lophyl radical substituents at the C2 and C5 positions of a 1,5-hexadiene structural framework, and have shown that this species should serve as a useful probe of the controversial stepwise mechanism for the Cope rearrangement. The results of DFT calculations on the simpler model $\mathbf{11}^{\bullet\bullet}$ suggest that $\mathbf{10}^{\bullet\bullet}$, generated from **14** and/or $\mathbf{O\text{-}10}^{\bullet\bullet}$, would undergo an exergonic Cope rearrangement via $\mathbf{12}^{\bullet\bullet\bullet\bullet}$ (i.e., a $^{1}\mathbf{3}^{\bullet\bullet}$-type intermediate).

At this time, we have not yet succeeded in isolating and purifying **14** and/or $\mathbf{O\text{-}10}^{\bullet\bullet}$. However, we have observed that the mixture obtained by oxidation of **17** displays HPBI/lophyl radical-like photochromic behavior and that photoexcitation of the mixture, perhaps containing either or both **14** and $\mathbf{O\text{-}10}^{\bullet\bullet}$, displays an ESR signal assignable to $\mathbf{10}^{\bullet\bullet}$. These findings strongly suggest that we will be able to prepare and purify **14** and/or $\mathbf{O\text{-}10}^{\bullet\bullet}$. We are now attempting to capture $\mathbf{12}^{\bullet\bullet\bullet\bullet}$ by demonstrating the formation of **13** and/or its derivative(s) in the thermal reaction of **14** and/or $\mathbf{O\text{-}10}^{\bullet\bullet}$. We believe that successful execution of this challenging effort will yield a new strategy to study the controversial stepwise mechanism for the Cope rearrangement and related sigmatropic reactions.[10,16,17]

Experimental

General. Melting points were obtained with a Yanako (MP-500) and are reported uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer. ^{1}H NMR spectra at 195 K were recorded on a JNM-ECX400 spectrometer. Mass spectrometric data (MS) were collected using SHIMADZU GC-17A (EI) and JEOL JMS-700 (FAB) instruments. Elemental analyses were performed at Kanazawa University, Advanced Science Research Center, Research Institute for Instrumental Analysis. UV–vis spectra were recorded on a spectrometer adjunct to a JASCO FP-6300 spectrofluorometer. The ESR spectrum was recorded using a spectrometer (JEOL, JES-RE2X) equipped with a 500 W Xe lamp (USHIO, UI-501C).

Materials. All solvents were distilled before use. THF was dried with CaH_2 and then $LiAlH_4$. An extra pure grade of $MeCO_2H$ was treated with $KMnO_4$ and distilled prior to use. Benzene was fractioned from CaH_2 and then Na. Toluene was distilled and dried over 4 Å molecular sieves. All reagents were purchased from Tokyo Chemical Industry Co. or Nacalai tesque. These reagents were purified as much as possible.

2,5-Bis(4-formylphenyl)-1,5-hexadiene (16). To a stirred solution of **15** (1.18 g, 3 mmol) in dry THF (25 mL) under argon at −78 °C was added dropwise *n*-BuLi (1.6 M in hexane, 6.0 mL, 9.3 mmol) and stirred at −78 °C for 20 min. *N*-Formylpiperidine (1.4 mL, 12 mmol) was added and the reaction mixture was stirred at −78 °C for 30 min. After 30 min, the mixture was slowly warmed to room temperature and then stirred at room temperature for 2 h before being quenched by the addition of aq. NH_4Cl. After usual work-up, column chromatography (SiO_2) was performed with *n*-hexane–$MeCO_2Et$ (10:1) as the eluent, giving a solid which was recrystallized from *n*-hexane–$CHCl_3$ (3:1) to give 432 mg (40%) of **16** as colorless cubes; mp 92.5–94.0 °C. ^1H NMR (300 MHz, $CDCl_3$): δ_{ppm} 2.68 (s, 4H), 5.16 (s, 2H), 5.40 (s, 2H), 7.52 (AA′BB′, $J = 4.5$ Hz, 4H), 7.85 (AA′BB′, $J = 4.5$ Hz, 4H), 10.0 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_{ppm} 34.2 (2C), 115.6 (2C), 126.7 (2C), 126.7 (4C), 129.8 (4C), 135.4 (2C), 147.0 (2C), 191.5 (2C). IR (KBr): ν 1702 (s, C=O) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) 290 (20, M^+), 171 (14), 158 (25), 130 (100, C_9H_6O), 115 (75), 91 (68). Anal. Calcd for $C_{20}H_{18}O_2$ (290.4): C, 82.73; H, 6.25%. Found: C, 82.28; H, 6.27%.

2,5-Bis[4-(4,5-diphenylimidazolyl-2-yl)phenyl]-1,5-hexadiene (17). A solution of hexadiene **16** (150 mg, 0.5 mmol), benzil (250 mg, 1.2 mmol) and $MeCO_2NH_4$ (1.1 g, 15 mmol) in 5.0 mL of $MeCO_2H$ was stirred at 100 °C for 22 h. The reaction mixture was cooled to room temperature and poured into a mixture of iced-water. The resulting solids were separated by filtration, washed with aq. $NaHCO_3$, EtOH, and water. Recrystallization from THF gave 170 mg (0.26 mmol, 51% yield) of **17** as a colorless solid; mp 284–286 °C. ^1H NMR (300 MHz, DMSO-d_6): δ_{ppm} 2.70 (s, 4H), 5.14 (s, 2H), 5.47 (s, 2H), 7.20–7.58 (m, 24H), 8.07 (AA′BB′, $J = 4.2$ Hz, 4H), 12.71 (s, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ_{ppm} 33.3 (2C), 112.7 (2C), 124.9 (4C), 125.7 (4C), 126.8–129.0 (m, 26C) 129.1 (4C), 139.5 (2C), 144.9 (2C), 146.1 (2C). IR (KBr): ν 3370 (s, N–H), 1603 (s, C=N) cm^{-1}. MS (FAB): *m*/*z* 671 [$(M + H)^+$]. Anal. Calcd for $C_{48}H_{38}N_4$ (670.31): C, 85.94; H, 5.71; N, 8.35%. Found: C, 80.11; H, 5.72; N, 7.29%.

1,5-Hexadiene Fused by HPBI (14) and/or Its Oligomer (O-10$^{\bullet\bullet}$). All manipulations were carried out in the dark. To a solution of **17** (134 mg, 0.2 mmol) in 2 M KOH–EtOH (200 mL) under an argon atmosphere was added a solution of $K_3[Fe(CN)_6]$ (1.3 g, 3.8 mmol) in water (20 mL). The reaction mixture was vigorously stirred at 10 °C for 2 h. The organic layer was separated, exhaustively washed with water and concentrated in vacuo giving a residue which was recrystallized from benzene–MeCN (4:1) to give 20 mg (0.03 mmol, 15% yield) of crude **14** and/or **O-10**$^{\bullet\bullet}$ as a pale greenish yellow solid; dp 254–260 °C. ^1H NMR (400 MHz, toluene-d_8): No peaks were observed except for those associated with the solvent. For the detail, see the text and the Supporting Information. IR (KBr): ν 3056, 2968, 1603 (s, C=N), 1492, 1445, 968 cm^{-1}. MS (FAB): *m*/*z* 669 [$(M + H)^+$]. Anal. Calcd for $C_{48}H_{36}N_4$ (668.29): C, 86.20; H, 5.43; N, 8.38%. Found: C, 77.67; H, 5.86; N, 6.99%.

ESR Study. A tube containing a 5 mL toluene solution of the mixture obtained by oxidation of **17** (ca. 4 mM) in a J-Young tube was degassed by using three freeze (77 K)–pump (0.1 mmHg)–thaw (room temperature) cycles and then sealed the tube at 77 K. The sample was irradiated with a 500 W Xe lamp for 2 min in close contact with the sample tube.

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Supporting Information

^1H NMR and MS (FAB) spectra of the compound obtained from **17**. The detail of synthesis of **18** and ESR spectrum of **19**$^{\bullet}$. Results of the DFT calculation for **11**$^{\bullet\bullet}$, **19**$^{\bullet}$, **20**$^{\bullet\bullet\bullet\bullet}$, **21**$^{\bullet\bullet}$, and **22**. These data and materials are associated with this article can be found, in the online version, at http://www.csj.jp/journals/bcsj/.

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11 Judging from the ^{1}H NMR of **18**, for example, $\delta_{\text{ppm}} = 5.0$–$5.5$ (olefin) and 7.0–9.0 (phenyl), etc. are expected for the ^{1}H NMR of **14**.

12 See the Supporting Information for details.

13 The zero-point corrections were not made for the relative energies discussed in the manuscript because the zero-point energies for $^{1}\mathbf{20}^{\bullet\bullet\bullet\bullet}$, $^{3}\mathbf{20}^{\bullet\bullet\bullet\bullet}$, and $^{1}\mathbf{21}^{\bullet\bullet}$ were not obtained owing to their energetically semistable properties.

14 Figure 6 was drawn by using *WinMOPAC ver 3.9*.[15]

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