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Stereoselective Tandem Cyclization of 1,1-Diphenyl-1,n-alkadienes via Photoinduced Electron Transfer Reaction

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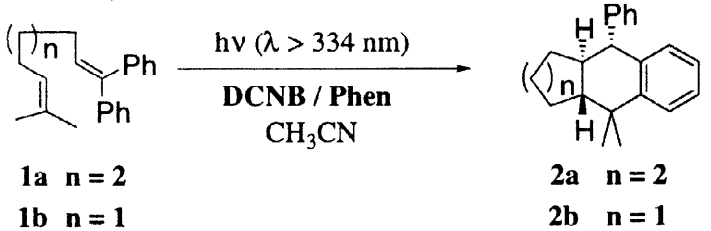
Abstract: The photoinduced electron transfer reaction of 1,1-diphenyl-1,n-alkadienes in the presence of phenanthrene and 1,4-dicyanobenzene as a sensitizer and an electron acceptor, respectively gave intramolecular tandem cyclization products in highly stereocontrolled manner.

Keywords: Intramolecular Cyclization; 1,1-Diphenyl-1,n-alkadienes; Photoinduced Electron Transfer

Photoinduced electron transfer reactions are now recognized as versatile methods for generating radical cation species from electron-rich olefins and aromatic compounds. [1] We are currently investigating the synthetic application of radical cations generated from 1,1-diphenylethylene-based substrates by using the photosensitized electron transfer reaction. [2] Herein we wish to disclose the highly stereoselective intramolecular tandem cyclization of 1,1-diphenyl-1,n-alkadienes by photoinduced electron transfer in the presence of phenanthrene (**Phen**) and 1,4-dicyanobenzene (**DCNB**) as sensitizer and electron acceptor (Scheme 1).

As shown below, by utilizing the present photoinduced tandem cyclization, we could construct 5/6/6-fused ring systems as well as 6/6/6-fused ones in one step with high stereoselectivity at the newly formed stereogenic centers.

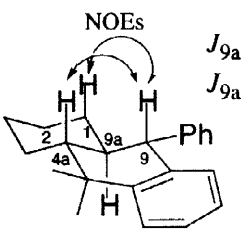
Irradiation of an acetonitrile solution of 1,1-diphenyl-8-methyl-1,7-nonadiene (**1a**, 1 x 10^{-2} M), in the presence of **DCNB** (2.5 x 10^{-2} M) and **Phen** (1 x 10^{-2} M) through an aqueous $CuSO_4$ filter solution (> 334 nm) under argon atmosphere afforded stereoselectively 4a,9a-*trans*-9,9a-*trans*-1,2,3,4,4a,9,9a,10-octahydro-10,10-dimethyl-9-phenylanthracene (**2a**) in 45% yield.[3] **DCNB** and **Phen** were completely recovered. In the absence of **DCNB** or **Phen**, no reaction took place and the starting material was recovered.



1a n = 2
1b n = 1

2a n = 2
2b n = 1

Scheme 1



$J_{9aH\text{-}9H}$ = 10.2 Hz
$J_{9aH\text{-}4aH}$ = 11.5 Hz

Figure 1: Relative stereochemistry of **2a**.

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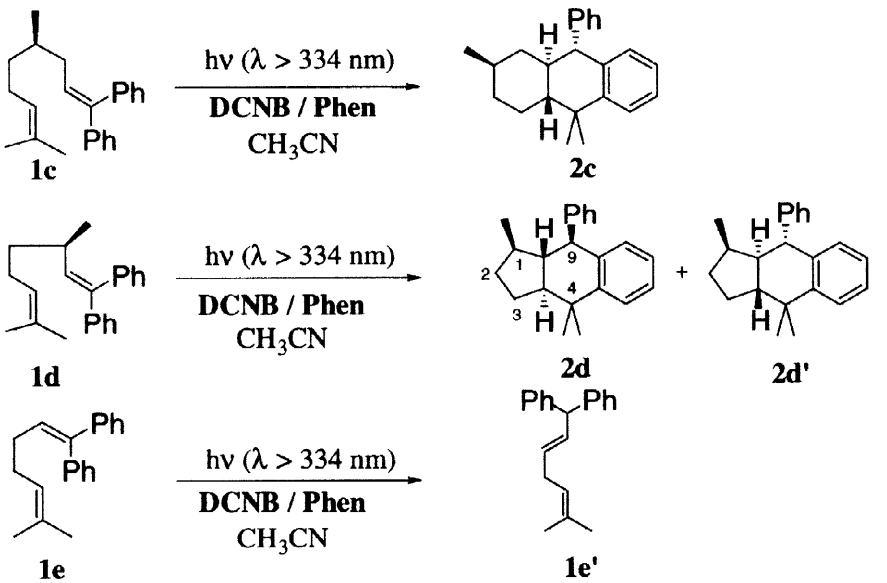
Similar irradiation of 1,1-diphenyl-7-methyl-1,6-octadiene (**1b**) in the presence of **DCNB** and **Phen** gave stereoselectively 3a,9a-*trans*-9,9a-*trans*-4,4-dimethyl-2,3,3a,4,9,9a-hexahydro-9-phenylbenz[f]indene (**2b**) in 57% yield (Scheme 1).

The planer structures of **2a** and **2b** were determined by the analyses of ^{1}H NMR, ^{13}C NMR, H-H COSY, C-H COSY, IR, and mass spectra.[4] The stereochemistry of **2a** rests on NOE evidence and ^{1}H-^{1}H coupling constants as shown in Figure 1. The stereochemistry of **2b** was confirmed by X-ray crystallography.[5]

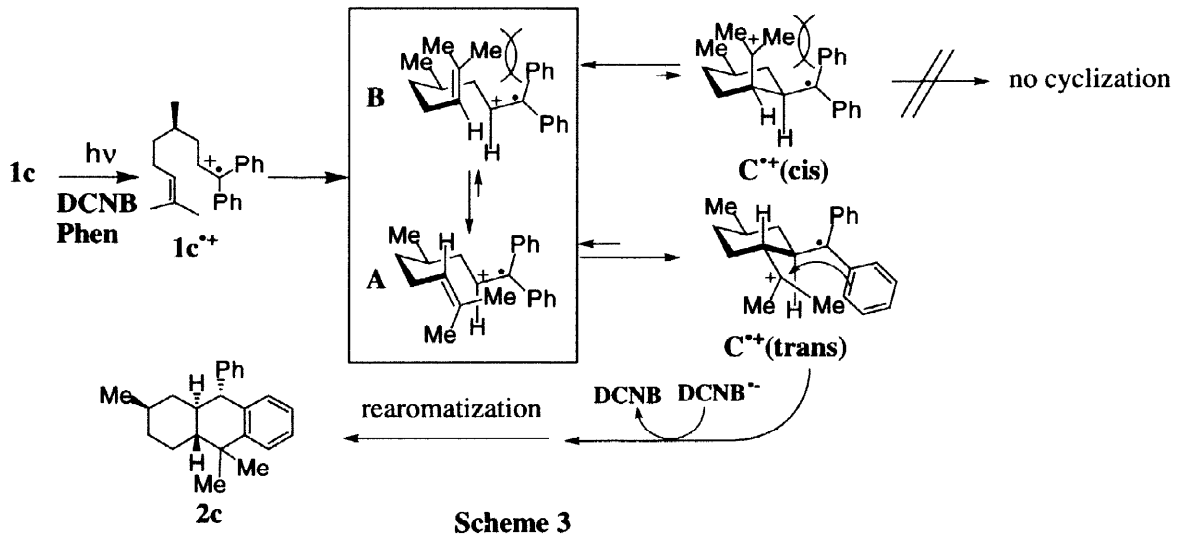
On irradiation of **1c** under similar conditions, 4a,9a-trans-9,9a-trans-2,9a-cis-1,2,3,4,4a,9,9a,10-octahydro-2,10,10-trimethyl-9-phenylanthracene (**2c**) was obtained in 71% yield as a sole product, while **1d** gave two stereoisomers **2d** and **2d'** in 25% and 5% yields respectively. The stereochemistry of **2c**, **2d** and **2d'** was determined by the extensive analyses of their ^{1}H NMR spectra.[4] On the other hand, the irradiation of **1e** under the similar conditions underwent only 1,3-shift of hydrogen to give the isomer **1e'** (Scheme 2).



Scheme 2

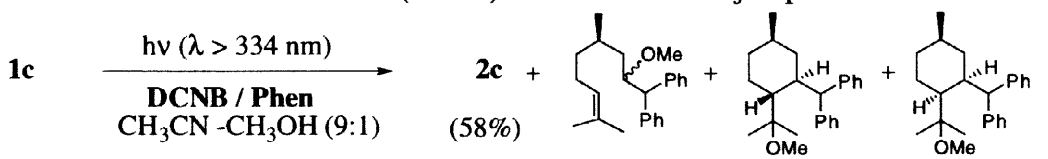
Scheme 3 shows a plausible mechanism for these reactions. **Phen**-sensitized irradiation of **1c** in the presence of **DCNB** provides a reactive radical cation intermediate **1c**$^{\cdot+}$. [6] The intramolecular cyclization of the intermediate **1c**$^{\cdot+}$ may proceed exclusively via a stable chair-like 6-membered transition state **A** to give a distonic radical cation **C**$^{\cdot+}$**(trans)**. The consecutive trap of the resulting cation with the aromatic ring followed by back electron transfer from **DCNB**$^{\cdot-}$ and rearomatization lead to the final product **2c**.[7]

The minor intermediate **C**$^{\cdot+}$**(cis)** that may be present in an equilibrium concentration may not cyclize owing to severe steric congestion in the transition state of the second cyclization.



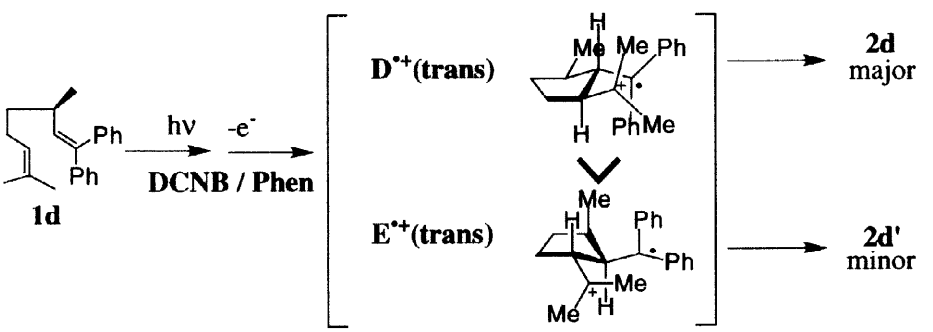
Scheme 3

This inference was confirmed by a trapping experiment (Scheme 4). Thus the irradiation of **1c** in the presence of methanol as a nucleophile gave **2c** (58%) as a major product together with *anti*-Markovnikov methanol adducts **3c** (8%) and monocyclization products **4c(trans)** (3%) and **4c(cis)** (2%), indicating that the cyclization of **C$^{\cdot+}$(trans)** is very rapid and therefore the formation of **2c** via **C$^{\cdot+}$(trans)** becomes the major process.



Scheme 4

Similarly, the intramolecular cyclization of **1d** may proceed mainly via the intermediate **D$^{\cdot+}$ (trans)** formed through a stable transition state, leading to **2d** as the major product (Scheme 5).



Scheme 5

Further application and scope and limitation for these intramolecular cyclization reaction are now in progress.

References and Notes

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[4] **2a**; colorless cubes: mp 140.0-140.5 ℃. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.41 (dd, J = 7.9, 1.3 Hz, 1 H), 7.32-7.18 (m, 3 H), 7.15-7.08 (m, 3 H), 6.93 (ddd, J = 7.9, 7.9, 1.3 Hz, 1 H), 6.60 (br d, J = 7.9 Hz, 1 H), 3.56 (d, J = 10.2 Hz, 1 H), 2.01-1.97 (m, 1 H), 1.83-1.60 (m, 4 H), 1.45 (ddd, J = 11.5, 11.5, 3.3 Hz, 1 H), 1.40 (s, 3 H), 1.31-0.90 (m, 4 H), 1.26 (s, 3 H) ppm. ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 146.79(s), 146.77(s), 138.82(s), 129.85(d), 129.67(d), 128.21(d), 126.17(d), 125.98(d), 125.77(d), 125.18(d), 54.42(d), 47.47(d), 40.67(d), 37.02(s), 33.02(t), 27.91(q), 27.52(q), 27.01(t), 26.73(t), 26.10(t) ppm. IR (KBr) 2960, 2850, 1490, 760, 740, 700 cm^{-1}. HR-MS (EI) found: *m/z* 290.2045. Calcd for $C_{22}H_{26}$ (M^+): 290.2034.

2b; colorless cubes: mp 100.0-101.0 ℃. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.42 (br dd, J = 7.9, 0.9 Hz, 1 H), 7.35-7.11 (m, 6 H), 6.97 (br dd, J = 7.9, 7.9 Hz, 1 H), 6.72 (br d, J = 7.9 Hz, 1 H), 3.70 (d, J = 10.6 Hz, 1 H), 1.95 (dddd, J = 10.6, 10.6, 10.6, 6.3 Hz, 1 H), 1.91-1.44 (m, 6 H), 1.40 (s, 3 H), 1.37-1.26 (m, 1 H), 1.26 (s, 3 H) ppm. ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 147.89(s), 146.65(s), 139.91(s), 129.89(d), 128.99(d), 128.29(d), 126.28(d), 126.03(d), 125.98(d), 125.33(d), 55.03(d), 52.49(d), 45.28(d), 37.31(s), 31.47(t), 29.55(q), 26.22(q), 25.78(t), 22.32(t) ppm. IR (KBr) 2950, 2860, 1480, 760, 750, 700 cm^{-1}. HR-MS (EI) found: *m/z* 276.1890. Calcd for $C_{21}H_{24}$ (M^+): 276.1878.

2c; colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.44 (dd, J = 8.1, 1.3 Hz, 1 H), 7.34-7.10 (m, 6 H), 6.98 (ddd, J = 7.9, 7.1, 1.3 Hz, 1 H), 6.63 (ddd, J = 7.9, 1.3, 1.1 Hz, 1 H), 3.58 (d, J = 10.6 Hz, 1 H), 2.02 (dddd, J = 12.9, 3.1, 3.1, 3.1 Hz, 1 H), 1.77-1.84 (m, 2 H), 1.66 (dddd, J = 12.8, 3.6, 3.6, 2.4 Hz, 1 H), 1.44(s, 3 H), 1.40-1.46 (m, 1 H), 1.29 (s, 3 H), 1.21-1.32 (m, 2 H), 0.98 (dddd, J = 12.8, 11.7, 11.7, 3.1 Hz, 1 H), 0.84 (d, J = 6.4 Hz, 1 H), 0.70 (ddd, J = 12.8, 11.7, 11.7 Hz, 1 H) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 146.79(s), 146.78(s), 138.88(s), 129.90(d), 129.70(d), 128.22(d), 126.13(d), 125.97(d), 125.76(d), 125.18(d), 54.35(d), 47.01(d), 41.69(t), 40.47(d), 36.95(s), 35.23(t), 32.10(d), 28.03(q), 27.49(q), 26.88(t), 22.56(q) ppm. IR (KBr) 3050, 3025, 2925, 1600, 1490, 1450, 1380, 760, 700 cm^{-1}. HR-MS (EI) found: *m/z* 304.2180. Calcd for $C_{23}H_{28}$ (M^+): 304.2191.

2d; colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$): δ7.39 (brd, J = 7.4 Hz, 1 H), 7.31-7.10 (m, 6 H), 6.95 (br dd, J = 7.9, 7.9 Hz, 1 H), 6.67 (br d, J = 7.9 Hz, 1 H), 3.74 (d, J = 10.9 Hz, 1 H), 1.99-1.69 (m, 3 H), 1.61 (ddd, J = 11.3, 10.9, 8.6 Hz, 1 H), 1.49 (ddd, J = 11.3, 11.3, 8.9 Hz, 1 H), 1.38 (s, 3 H), 1.28 (s, 3 H), 1.28-1.18 (m, 1 H), 0.40 (d, J = 6.3 Hz, 3 H) ppm. ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 147.58(s), 146.50(s), 140.55(s), 129.97(d), 129.53(d), 128.25(d), 126.15(d), 126.10(d), 125.87(d), 125.33(d), 55.10(d), 53.79(d), 51.30(d), 39.81(d), 37.36(s), 33.04(t), 29.41(q), 26.10(q), 24.27(t), 20.96(q) ppm. IR (KBr) 3030, 2950, 1600, 1480, 1460, 760, 740, 700 cm^{-1}. HR-MS (EI) found: *m/z* 290.2056. Calcd for $C_{22}H_{26}$ (M^+): 290.2034.

2d'; colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.38 (dd, J = 7.8, 1.3 Hz, 1 H), 7.34-7.11 (m, 6 H), 6.97 (ddd, J = 7.8, 7.8, 1.3 Hz, 1 H), 6.64 (br d, J = 7.8 Hz, 1 H), 3.66 (d, J = 9.4 Hz, 1 H), 2.17 (ddd, J = 11.3, 7.0, 7.0 Hz, 1 H), 2.10-2.01 (m, 3 H), 1.81 (m, 1 H), 1.50-1.35 (m, 1 H), 1.40 (s, 3 H), 1.35 (s, 3 H), 1.30-1.18 (m, 1 H), 0.78 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 146.75(s), 145.21(s), 139.10(s), 129.74(d), 129.47(d), 128.32(d), 126.02(d), 125.96(d), 125.36(d), 125.12(d), 51.08(d), 49.14(d), 49.12(d), 39.08(d), 36.00(s), 34.36(q), 31.96(t), 27.48(q), 26.72(t), 22.17(q) ppm. IR (KBr) 3030, 2950, 1600, 1490, 1450, 760, 740, 700 cm^{-1}. HR-MS (EI) found: *m/z* 290.2070. Calcd for $C_{22}H_{26}$ (M^+): 290.2034.

[5] The cell dimensions were determined by a least squares fit on 25 reflections ($28° < 2\theta < 30°$) using the MoKα (λ = 0.71073 Å) radiation and are a = 9.483(2), b = 11.042(2), c = 9.394(2) Å, α = 104.14(2)°, β = 101.45(2)°, γ = 114.03(2)°, and V = 820.4(3) Å^3. The crystal system, the space group, and Z value are triclinic, P1, and 2, respectively. The reflections were collected up to $2\theta \leqq 55°$ at 25℃, thus 3769 unique reflections were obtained. The structure was solved by a direct method with the program SHELXS-86 and refined by a full-matrix least squares method with the program SHELXL-97. All unique reflections were used for the refinement. After the final refinement, the structure was converged to R(F) = 0.044, wR(F^2) = 0.132, and S = 1.08 ($I > 2\sigma I$). No significant peaks were observed in the final difference maps ($\Delta\rho_{min}$ = -0.21 and $\Delta\rho_{max}$ = 0.17 e•Å^{-3}). SHELXS-86: Sheldrick, G. M.; *Acta Crystallogra. Sect. A*, **1990**, A46, 467. SHELXS-97: Sheldrick, G. M.; "SHELX-97," a program package for the crystal structure determination. Univ. of Göttingen, Germany, 1997.

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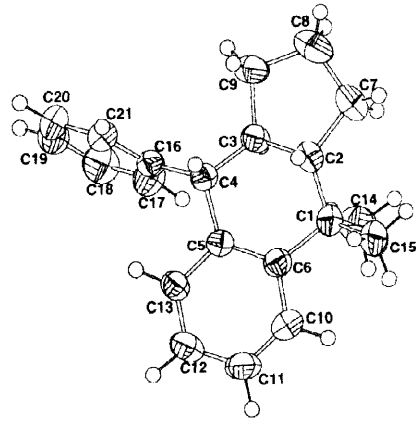

ORTEP drawing of **2b**.