88.5–90 °C; R_f 0.22 (methanol); ^{1}H NMR ($CDCl_3$) δ 7.21 (t, 1 H), 7.03 (d, 1 H), 7.02 (d, 1 H), 6.70 (dd, 1 H), 3.81 (s, 3 H), 3.31 (m, 1 H), 2.71 (m, 2 H), 2.52 (dd, 1 H), 2.40 (ddd, 1 H), 2.25 (s, 3 H), 2.20–1.30 (m, 10 H); mass spectrum, *m/e* (relative intensity) 275 (M^+, 78), 258 (38), 187 (12), 167 (31), 121 (16), 71 (100), 57 (37). Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 73.97; H, 9.15; N, 4.81.

2-Methyl-4aα-(3-methoxyphenyl)-1,2,3,4,4a,5,6,7,8,8aβ-decahydro-6α-isoquinolinol (6). This compound was prepared as above from 1.0 g (3.7 mmol) of **20**. Purification was performed by column chromatography (methanol) to yield 0.82 g (82%) of crystalline product that recrystallized from hexane: mp 116–117 °C (lit.[9] mp 117–117.5 °C); R_f 0.23 (methanol); ^{1}H NMR ($CDCl_3$) δ 7.26 (t, 1 H), 7.13 (d, 1 H), 7.11 (br t, 1 H), 6.72 (dd, 1 H), 4.02 (br s, 1 H), 3.80 (s, 3 H), 2.78 (ddd, 1 H), 2.72 (dd, 1 H), 2.54 (m, 2 H), 2.32 (m, 1 H), 2.27 (s, 3 H), 2.09–1.42 (m, 8 H), 0.80 (br s, 1 H); mass spectrum, *m/e* (relative intensity) 275 (M^+, 34), 260 (7), 204 (33), 167 (16), 121 (19), 91 (20), 71 (100), 57 (79). Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 73.92; H, 9.06; N, 5.09.

2-Methyl-4aα-(3-methoxyphenyl)-1,2,3,4,4a,5,6,7,8,8aα-decahydro-6β-isoquinolinol (7). A solution of 1.0 g (3.7 mmol) of **19** and **21** in 50 mL anhydrous ethanol/acetic acid (1:1) was hydrogenated over PtO_2 at a hydrogen pressure of 60 psi for 16 h. At the end of this period, the catalyst was filtered off, and the solvent was removed under reduced pressure to afford 0.96 g of crude product. Purification was performed by column chromatography with methanol eluent, yield 0.73 g (73%): R_f 0.30 (methanol); ^{1}H NMR ($CDCl_3$) δ 7.25 (t, 1 H), 7.04 (d, 1 H), 7.00 (t, 1 H), 6.73 (dd, 1 H), 3.80 (s, 3 H), 3.67 (m, 1 H), 2.62 (m, 3 H), 2.50 (ddd, 1 H), 2.32 (s, 3 H), 2.25 (ddd, 1 H), 2.08 (d, 2 H), 1.86–1.32 (m, 7 H); mass spectrum, *m/e* (relative intensity) 275 (M^+, 20), 258 (16), 187 (10), 167 (14), 121 (12), 91 (92), 71 (100), 57 (28). Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 74.36; H, 8.93; N, 4.87.

2-Methyl-4aα-(3-methoxyphenyl)-1,2,3,4,4a,5,6,7,8,8aα-decahydro-6α-isoquinolinol (8). This compound was prepared as above from 1.0 g (3.7 mmol) of **20**. Purification was performed by column chromatography with methanol solvent, affording 0.68 g (68%) of **16**, which could be recrystallized from benzene, mp 95–96 °C (lit.[9] mp 95–97 °C), or from hexane/ethyl acetate (4:1), mp 104–106 °C: R_f 0.25 (methanol); ^{1}H NMR ($CDCl_3$) δ 7.27 (t, 1 H), 6.99 (d, 1 H), 6.95 (br t, 1 H), 6.75 (dd, 1 H), 3.92 (m, 1 H), 3.82 (s, 3 H), 2.64 (br d, 1 H), 2.46 (d, 1 H), 2.26 (m, 3 H), 2.11 (s, 3 H), 2.09–1.66 (m, 6 H), 1.35 (m, 3 H); mass spectra, *m/e* (relative intensity) 275 (M^+, 37), 258 (8), 204 (58), 187 (14), 121 (19), 91 (13), 71 (97), 58 (47), 44 (100). Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 74.29; H, 9.30; N, 5.18.

General Procedure for the Synthesis of the 6-Oxodecahydroisoquinolines 3 and 4. A solution of 8.7 mL of DMSO in 25 mL of methylene chloride was added dropwise to 5.1 mL of oxalyl chloride in 130 mL of methylene chloride under nitrogen, and a temperature of −55 °C was maintained. After the addition was complete, the reaction was stirred for 2 min at this temperature. A solution of isoquinolinol (15.0 g, 0.055 mol) in 52 mL of methylene chloride was added dropwise to this mixture, and a temperature of −55 °C was maintained. The resulting mixture was then stirred an additional 15 min at −55 °C. Triethylamine (36 mL) was added, and the reaction mixture was allowed to warm to room temperature. Water (250 mL) was added dropwise to the mixture, and the layers were separated. The organic layer was washed two times with brine, dried over K_2CO_3, and concentrated under reduced vacuum. Purification was achieved by either column chromatography or recrystallization.

2-Methyl-4aα-(3-methoxyphenyl)-1,2,3,4,4a,5,6,7,8,8aβ-decahydroisoquinoline (3). This compound was prepared as described above from 15.0 g (0.055 mol) of **5** or 15.5 g (0.056 mol) of **6**. The resulting solids were recrystallized from hexane/ethyl acetate (1:1) to yield 13.7 g (91%) from **5** and 14.2 g (92%) from **6**: mp 90–92 °C; mp 93.5–94.5 °C (hexane/benzene, 1:1; lit.[9] mp 94–95 °C); R_f 0.23 (methanol); ^{1}H NMR ($CDCl_3$) δ 7.22 (t, 1 H), 6.98 (m, 2 H), 6.71 (dd, 1 H), 3.79 (s, 3 H), 2.93 (d, 1 H), 2.84 (dd, 1 H), 2.68 (t, 1 H), 2.59 (d, 1 H), 2.53–2.20 (m, 5 H), 2.33 (s, 3 H), 2.13–1.84 (m, 4 H); mass spectrum, *m/e* (relative intensity) 273 (M^+, 100), 258 (11), 202 (13), 165 (28), 150 (32), 71 (72), 57 (65), 44 (40); IR ($CDCl_3$) 1709.05 (C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.97; H, 8.68; N, 5.39.

2-Methyl-4aα-(3-methoxyphenyl)-1,2,3,4,4a,5,6,7,8,8aα-decahydro-6-oxadecahydroisoquinoline (4). This compound was prepared as above from 1.90 g (0.0069 mol) of **7** and 1.40 g (0.005 mol) of **8**. The resulting viscous oils were purified by column chromatography with methanol solvent to yield **4**, 1.60 g (84%) from **7** and 1.20 g (86%) from **8**. Material crystallized on standing: mp 66–67.5 °C (hexane); R_f 0.46 (methanol); ^{1}H NMR ($CDCl_3$) δ 7.24 (t, 1 H), 7.00 (m, 2 H), 6.75 (dd, 1 H), 3.79 (s, 3 H), 2.90–2.46 (m, 6 H), 2.36 (s, 3 H), 2.36–2.10 (m, 4 H), 1.86–1.64 (m, 2 H), 1.58 (m, 1 H); mass spectrum, *m/e* (relative intensity) 273 (M^+, 21), 258 (5), 202 (6), 165 (6), 115 (9), 96 (8), 79 (100), 57 (36), 44 (67); IR ($CDCl_3$) 1706.16 cm^{-1} (C=O). Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.39; H, 8.77; N, 4.94.

Registry No. **3**, 61528-04-9; **4**, 61528-05-0; **5**, 61528-21-0; **6**, 61528-20-9; **7**, 61528-23-2; **8**, 61528-24-3; **9**, 73224-22-3; **11**, 118864-98-5; **11**·HCl, 118724-76-8; **12**, 118864-99-6; **12**·HCl, 118916-31-7; **13**, 118724-77-9; **14**, 118724-78-0; **15**, 118724-79-1; **16**, 118724-80-4; **17**, 118724-81-5; **18**, 118724-82-6; **19**, 118724-83-7; **20**, 118724-84-8; **21**, 118724-85-9; **22**, 88055-58-7.

Electron-Transfer Induced Rearrangement of Spirofluorenebicyclo[6.1.0]nonatriene to Spirofluorenebarbaralane

Tsutomu Miyashi,*[†] Yasutake Takahashi,[†] Akinori Konno,[†] Toshio Mukai,[†,‡] Heinz D. Roth,*[§,∥] Marcia L. Schilling,[§] and Christopher J. Abelt[§,⊥]

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan, and AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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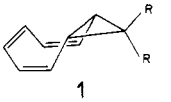
Bicyclo[6.1.0]nonatriene (1) and its derivatives are among the most thoroughly investigated hydrocarbon systems. A multiplicity of thermal and photochemical rearrangements are observed, and substituents at C-9 affect the course of the rearrangement in remarkable fashion.[1] We are interested in the structure and the potential rearrangements of radical cations.[2] Accordingly, we investigated the photoinduced electron transfer reactions of spirofluorenebicyclo[6.1.0]nonatriene (**1a**)[3] and 9,9-diphenylbicyclo[6.1.0]nonatriene (**1b**).[4] In polar solvents, **1a** undergoes a novel rearrangement, chiefly to spirofluorenebarbaralane (**2a**), a type of rearrangement without precedent in radical cation chemistry.



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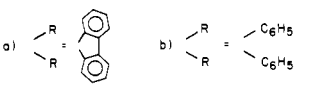

The fluorescence of 9,10-dicyanoanthracene (DCA) was efficiently quenched by either **1a** (k_q = 1.4 × 10^{10} mol^{-1} dm^3 s^{-1}, $E_{1/2}^{ox}$ = 1.52 V vs SCE)[5] or **1b** (k_q = 1.8 × 10^{10}

[†] Tohoku University.
[‡] Current address: College of Industry, Nihon University, Kohriyama 963, Japan.
[§] AT&T Bell Laboratories.
[∥] Current address: Department of Chemistry, Rutgers University, New Brunswick, NJ 08903.
[⊥] Current address: Department of Chemistry, The College of William and Mary, Williamsburg, VA 23185.

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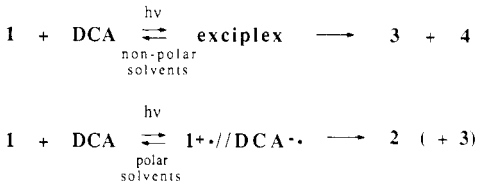
Table I. Photosensitized Rearrangement of 1a and Free Energy Change (ΔG) under Various Sensitized Conditions

sens[b]	$E^{red}_{1/2}$ (V vs SCE)	ΔG,[a] kJ/mol	solv	yields, % 2	3	4	con
DCA	−0.98	−43.1	CH_3CN	47	16	6	90
DCA	−0.98	−22.0	CH_2Cl_2	14	21	12	47
DCA	−0.98	+59.8	C_6H_6	2	13	11	26
DCN	−1.30	−95.4	CH_3CN	23	8	2	50
TCA	−0.45	−95.8	CH_3CN	22	8	2	40
TCNAQ	−0.25	−98.7	CH_3CN	40		2	100
CA	+0.01	−119.7	CH_3CN	11	4		54
TNF	−0.42	−87.9[c]	CH_3CN	16	43		79
TNF	−0.42	−66.9	CH_2Cl_2	6	39		73
TNF	−0.42	+16.7	C_6H_6		31		54

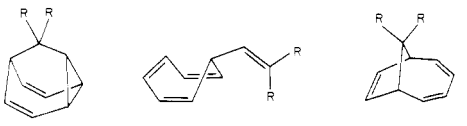
[a] Calculated from $\Delta G = 96.48[E^{ox}_{1/2}$ (1a) $- E^{red}_{112}$(sens) $+ (2.6/\epsilon) - 0.13] - E_{0\text{-}0}$(sens) kJ/mol. [b] DCA, 9,10-dicyanoanthracene; DCN, 1,4-dicyanonaphthalene; TCA, 2,6,9,10-tetracyanoanthracene; TCNAQ, 2,6-dichloro-11,11,12,12-tetracyano-9,10-anthraquinodimethane;[12] CA, chloranil; TNF, 2,4,7-trinitrofluorenone. [c] $E_{0\text{-}0}$ was estimated from its end absorption (450 nm).

mol^{-1} dm^3 s^{-1}, $E_{1/2}{}^{ox} = +1.49$ V vs SCE).[5] DCA-sensitized irradiation of **1a** at wavelengths > 370 nm resulted in the formation of **2a** as the major product (47%)[7] together with smaller yields of **3a** (16%) and **4a** (6%),[8] whereas the analogous sensitized irradiation of **1b** gave **3b** as a sole product. The remarkable skeletal rearrangement of **1a** to **2a** stands in contrast to the results of direct photolysis or thermal reaction[8] of **1a**, in which formation of **3a** or **4a** was observed. Obviously, the electron-transfer sensitization changes the course of the reaction. The new rearrangement also occurred with other electron-acceptor sensitizers; the results are shown in Table I.

Scheme I



As shown in the table, the formation of **2a** is favored in polar solvents such as acetonitrile, whereas the formation of **3a** or **4a** was not strongly affected by solvent polarity. Indeed, the quantum yield of **2a** decreased to one-hundredth, when the solvent was changed from acetonitrile ($\epsilon = 37$) to benzene ($\epsilon = 2.3$). In contrast, the quantum yields of **3a** and **4a** were reduced to only one-fourth and half, respectively.



2 3 4

The intriguing effect of solvent polarity on product distribution is ascribed to the involvement of two different intermediates with different degrees of charge separation. In polar media, a (solvent-separated) radical ion pair is invoked that would give rise to **2a**; in nonpolar solvents, an exciplex is suggested that would produce an alternative product, **3a**. The possible intermediacy of an exciplex is supported by the observation of a broad emission band (λ_{max} = 505 nm) upon irradiation of DCA and **1a** in benzene, while no such emission was observed in acetonitrile. Thus it seems most likely that an exciplex is responsible for the formation of **3a** and **4a**, whereas a radical ion is the major contributor in the formation of **2a**.

The intermediate in the conversion of **1a** to **2a** poses several interesting problems: the nature of the bonding between the three carbons of the cyclopropane moiety; its stereochemical and conformational preferences; and its

(1) Vogel, E.; Kiefer, H. *Angew. Chem.* **1961**, *73*, 54. LaLancette, E. A.; Benson, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 1941. Staley, S. W.; Henry, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1239, 787. Boche, G.; Boehme, H.; Martens, D. *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 594. Barborak, J. C.; Su, T.-M.; Schleyer, P. v. R.; Boche, G.; Schneider, G. *J. Am. Chem. Soc.* **1971**, *93*, 279. Masamune, G.; Baker, P. M.; Hojo, K. *J. Chem. Soc., Chem. Commun.* **1969**, 1203. Radlick, P.; Fenical, W. *J. Am. Chem. Soc.* **1969**, *91*, 1560. Radlick, P.; Alford, G. *J. Am. Chem. Soc.* **1969**, *91*, 6259. Radlick, P.; Fenical, W.; Alford, G. *Tetrahedron Lett.* **1970**, 2707. Anastassiou, A. G.; Orfanos, V.; Gebrian, J. H.; *Tetrahedron Lett.* **1969**, 4491. Anastassiou, A. G.; Cellura, A. P.; Ciganek, E.; *Tetrahedron Lett.* **1970**, 5267. Anastassiou, A. G.; Griffith, R. C. *J. Am. Chem. Soc.* **1971**, *93*, 3083; *Tetrahedron Lett.* **1973**, 3067. Schoenleber, D. *Chem. Ber.* **1969**, *102*, 1789. Klaerner, F.-G. *Tetrahedron Lett.* **1971**, 3611; *Angew. Chem.* **1972**, *84*, 892. Glock, V.; Wette, M.; Klaerner, F.-G. *Tetrahedron Lett.* **1985**, *26*, 1441. Sohn, M. B.; Jones, M., Jr.; Fairless, B. *J. Am. Chem. Soc.* **1972**, *94*, 4774. Paquette, L. A.; Epstein, M. J.; *J. Am. Chem.* Soc. **1973**, *95*, 6717. Brown, J. M.; Ogilvy, M. M. *J. Am. Chem. Soc.* **1974**, *96*, 292. Lewis, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **1975**, *97*, 651.

(2) (a) Takahashi, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6511–6513. (b) Miyashi, T.; Takahashi, Y.; Mukai, T.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 1079–1080. (c) Miyashi, T.; Wakamatsu, K.; Akiya, T.; Kikuchi, K.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 5270–5271.

(3) Duerr, H.; Kober, H. *Justus Liebigs Ann. Chem.* **1970**, *740*, 74.

(4) Cantrell, T. S.; Silverton, J. V. *J. Org. Chem.* **1979**, *44*, 4477.

(5) Half-wave oxidation potentials were measured by cyclic voltammetry at a Pt electrode in acetonitrile with 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

(6) Solutions were irradiated with light from a 2-kW xenon lamp at 15–20 °C. A Toshiba cutoff filter L-39 (370 nm) was used except for the DCN-sensitization and the direct excitation of the EDA complex, where UV-33 (300 nm) and L-42 (400 nm) were employed, respectively.

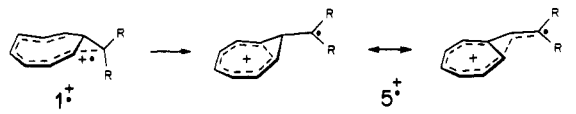
(7) Satisfactory elemental analyses were obtained for all new compounds. **2a**: mp 185 °C; *m/z* (100 °C, 25 eV) 268 (M^+, 100), 267 (43), 253 (21); IR ν_{max} (KBr) 3030, 2990, 2930, 1616, 1473, 1444, 1290, 977 cm^{-1}; ^{1}NMR (90 MHz, CCl_4), δ 2.20 (2 H, t, J = 6.3 Hz), 4.32 (4 H, t, J = 6.3 Hz), 5.89 (2 H, t, J = 6.3 Hz), 6.93–7.26 (4 H, m), 7.53 (4 H, m). **3a**: mp 90–93 °C; *m/z* (80 °C, 13.5 eV) 268 (M^+, 100), 267 (75); ^{1}H NMR (90 MHz, CCl_4) δ 3.25 (1 H, ddd, J = 8.4, 5.1, 5.1 Hz), 5.40 (2 H, dd, J = 9.6, 5.1 Hz), 6.40 (2 H, ddd, J = 9.6, 3.3, 3.3 Hz), 6.87 (2 H, dd, J = 3.3, 3.3 Hz), 7.07 (1 H, d, J = 8.4 Hz), 7.16–7.45 (5 H, m) 7.70 (3 H, m). **3b**: mp 84–85 °C; ^{1}H NMR (90 MHz, CCl_4) δ 2.36 (1 H, ddd, J = 9.9, 5.6, 1.5 Hz), 5.16 (2 H, dd, J = 9.3, 5.6 Hz), 6.06 (2 H, dddd, J = 9.3, 3.0, 3.0, 1.5 Hz), 6.24 (1 H, d, J = 9.9 Hz), 6.48 (2 H, dd, J = 3.0, 3.0 Hz), 7.17 (10 H, m). **6a**: mp 298 °C dec; *m/z* (140 °C, 25 eV) 396 (M^+, 11), 268 (100), 253 (49); IR ν_{max} (KBr) 3020, 2230, 1475, 1443, 1385, 1040, 983 cm^{-1}; ^{1}H NMR (90 MHz, DMSO-d_6) δ 1.11 (2 H, br d, J = 7.5 Hz), 1.53 (4 H, m), 4.45 (2 H, m), 7.5–8.0 (8 H, m). **7a**: mp 191–194 °C dec; *m/z* (120 °C, 25 eV) 396 (M^+, 8.8), 268 (100), 253 (29), 252 (30); IR ν_{max} (KBr) 3050, 2240, 1647, 1448, 778, 743, 725 cm^{-1}; ^{1}H NMR (90 MHz, DMSO-d_6) δ 2.08 (3 H, m), 4.55 (2 H, m), 6.56 (2 H, dd, J = 3.6, 4.6 Hz), 6.68 (1 H, br d, J = 9.0 Hz), 7.37 (4 H, m), 7.83 (4 H, m). **8a**: mp 198 °C dec; *m/z* (120 °C, 25 eV) 300 (M^+, 50), 284 (73), 256 (100); IR ν_{max} (KBr) 3040, 1447, 1335, 1100, 970, 890, 753 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.01 (2 H, dd, J = 6.9, 6.9 Hz), 1.83 (4 H, m), 5.07 (2 H, m), 7.35 (4 H, m) 7.73 (4 H, m); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 14.10 (d), 23.16 (d), 40.43 (s), 71.46 (d), 120.22 (d), 123.83 (d), 127.50 (d), 127.91 (d), 139.94 (s), 150.42 (s). **9a**: mp 265 °C dec; *m/z* (160 °C, 25 eV), 396 (M^+, 100), 268 (68), 216 (51), 190 (46); IR ν_{max} (KBr), 3050, 3000, 2230, 1445, 762, 735 cm^{-1}; ^{1}H NMR (90 MHz, DMSO-d_6) δ 2.34 (2 H, br s), 3.27 (2 H, br s), 4.21 (2 H, m), 6.6–6.9 (3 H, m), 7.2–7.5 (5 H, m), 7.8–8.1 (2 H, m).

(8) Jones, M., Jr.; Ando, W.; Hendrick, M. E.; Kulczycki, A., Jr.; Howley, P. M.; Hummel, K. F.; Malament, D. S. *J. Am. Chem. Soc.* **1972**, *94*, 7469.

mode of reaction. One-electron oxidation of the cyclopropane group often gives rise to "trimethylene" radical cations.[9] In the present case, the observed rearrangement requires cleavage of one cyclopropane bond (C_8–C_9) and bond formation between C_9 and C_5, amounting to a major conformational change. A possible mechanism is shown in Scheme I.

Some insight into the nature of the radical cation preceding **2a** is provided by the CIDNP effects observed during the irradiation of chloranil with **1a** in acetone-d_6, in which **2a** was the only polarized product.[11] The bridgehead protons (2.1 ppm) show emission whereas the olefinic protons (6.0 ppm) and those alternating between cyclopropane and olefinic character (4.4 ppm) show enhanced absorption. However, the polarization differs from that generated in an authentic sample of **2a**. The signal at 4.4 ppm shows much weaker enhancement, and the doublet at 7.65 ppm (fluorene *o*-H) appears in enhanced absorption. These differences are consistent with the involvement of at least one additional intermediate as a short-lived precursor to $\mathbf{2a}^{\bullet+}$.[11]

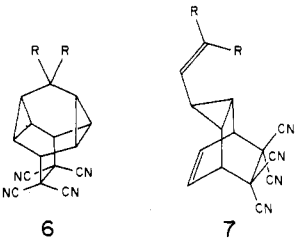
The observed CIDNP effects rule out that $\mathbf{1a}^{\bullet+}$ is responsible for the altered polarization of **2a**, since its involvement in the spin-sorting process would cause polarization for regenerated **1a**, which we did not observe. Although our results are not sufficient to identify the intermediate, we note that a singly linked species, such as $\mathbf{5a}^{\bullet+}$, is an attractive candidate to explain the rearrangement.



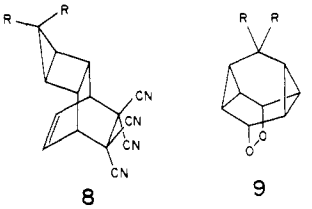
To some extent, $\mathbf{5a}^{\bullet+}$ might play a role in the formation of **3a** as indicated by the moderate, but not negligible, solvent polarity dependence. On the other hand, an exciplex intermediate may maintain more or less the boat configuration of **1a**, giving rise mainly to **3a** and **4a**, or regenerating **1a**, because of a lower degree of charge separation.

The difference between the rearrangements of **1a** and **1b** can be explained in terms of a lower rate of the bond formation of $\mathbf{1b}^{\bullet+}$ to give $\mathbf{2b}^{\bullet+}$ probably because of relatively larger steric hindrance of the diphenylmethyl group compared to the planar fluorenyl group.

Similar skeletal rearrangements were observed when the electron donor–acceptor (EDA) complex of **1a** with tetracyanoethylene (TCNE), was irradiated. This system has charge-transfer (CT) absorption maxima at 402 and 568 nm in dichloromethane, which can be ascribed to the interaction of the fluorene moiety with TCNE. This assignment follows (a) from the similarity of the above CT absorption to that exhibited by fluorene itself with TCNE (λ_{max} 420, 560 nm) and (b) from its lack of compatibility with the much weaker CT band of the system bicyclo[6.1.0]nonatriene/TCNE (λ_{max} 400, 490 nm). Irradiation (>400 nm) of **1a**/TCNE in dichloromethane under argon gave rise to two TCNE adducts, **6a** and **7a**, in 44 and 27% yields,[7] respectively, at 89% conversion.



Similarly, irradiation of **1a**/TCNE in nitromethane gave **6a** (8%) and **7a** (7% at 35% conversion). In contrast, the thermal reaction of **1a** with TCNE in refluxing acetonitrile gave **8a** as sole product in 80% yield. The striking difference between photochemical and thermal reactions further supports the operation of a photoinduced electron-transfer mechanism. The cycloadducts **6a** and **7a** could be secondary products from the dark reaction of TCNE with **2a** and **3a** or they could be formed by direct interaction of the TCNE radical anion with $\mathbf{1a}^{\bullet+}$ or a rearranged radical cation.



Of particular interest is the fact that irradiation of **1a**/TCNE in oxygen-saturated nitromethane gave reduced yields of **6a** (3%) and **7a** (3%), together with an endo peroxide (**9a**, 11% yield at 24% conversion), which was also obtained directly from **2a** in excellent yield. Since the yields of **6a** and **7a** are reduced in favor of **9a**, but their ratio is not changed substantially, it is likely that molecular oxygen has intercepted (an) intermediate(s) on the pathway to **6a** and **7a**, the most likely species being $\mathbf{1a}^{\bullet+}$ and/or $\mathbf{5a}^{\bullet+}$. Additional work is in progress to further delineate the mechanism of the light-induced adduct formation with TCNE and to probe the details of the interesting photooxygenation reaction.

Registry No. **1a**, 114672-75-2; **1b**, 118864-83-8; **2a**, 114552-66-8; **3a**, 118724-11-1; **3b**, 100064-25-3; **4a**, 39520-18-8; **6a**, 118724-12-2; **7a**, 118724-13-3; **8a**, 118724-14-4; **9a**, 118760-91-1; DCA, 1217-45-4; DCN, 3029-30-9; TCA, 80721-78-4; TCNAQ, 106580-24-9; CA, 118-75-2; TNF, 129-79-3; TCNE, 670-54-2.

(9) Roth, H. D.; Schilling, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 7953–7958; *Can. J. Chem.* **1983**, *61*, 1027–1035; *J. Am. Chem. Soc.* **1983**, *105*, 6805–6808. Roth, H. D.; Schilling, M. L.; Schilling, F. C. *J. Am. Chem. Soc.* **1985**, *107*, 4152–4158.
(10) Haddon, R. C.; Roth, H. D. *Croat. Chem. Acta* **1984**, *57*, 1165–1176.
(11) Roth, H. D.; Schilling, M. L.; Abelt, C. J.; Miyashi, T.; Takahashi, Y.; Konno, A.; Mukai, T. *J. Am. Chem. Soc.* **1988**, *110*, 5130–5136.
(12) Childs, R. F.; Brown, M. A.; Anet, F. A. L.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2175–2183.
(13) Nishizawa, Y.; Suzuki, T.; Yamashita, Y.; Miyashi, T.; Mukai, T. *J. Chem. Soc. Jpn.* **1985**, 904.

Synthesis, Redox Behavior, and Spin-Trap Properties of 2,6-Di-*tert*-butylnitrosobenzene (DTBN)

V. Cerri,† C. Frejaville, F. Vila, A. Allouche,§ G. Gronchi,‡ and P. Tordo*

SREP, CNRS UA 126, Université de Provence, av. Normandie-Niemen, 13393 Marseille cedex 13, France

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Introduction

The spin-trap technique is now one of the most powerful tools to investigate the role of transient paramagnetic

†UER de Pharmacie Université d'Aix-Marseille 2.
‡Ecole Supérieure de Chimie de Marseille.
§Laboratoire des Méthodes Spectroscopiques, CNRS UA 773, Université de Provence.

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