The Single Electron Transfer Induced Degenerate Methylenecyclobutane Rearrangement through an Allylically Stabilised 1,4-Cation Radical

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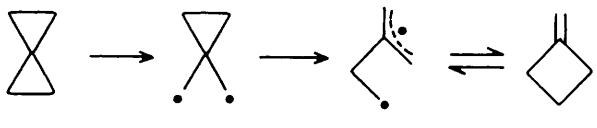
Upon irradiation under 1,4-dicyanonaphthalene- or 9,10-dicyanoanthracene-sensitized conditions, 3,3-diaryl-1-dideuteriomethylenecyclobutanes underwent degenerate methylenecyclobutane rearrangement through allylically stabilized 1,4-cation radicals which could be successfully intercepted by molecular oxygen.

Because of the low barriers to internal rotation and cyclization of biradicals, it is usually difficult to identify such species as true intermediates in thermal unimolecular rearrangements of neutral molecules. For instance, allylically stabilized 1,4-biradicals (**3**) are typical hypothetical biradicals which, it is postulated, may or may not intervene in the thermal degenerate methylenecyclobutane (MCB) and spiropentane (SP)–MCB rearrangement (Scheme 1). In contrast, radical cation species can often be identified easily as intermediates in single electron transfer induced rearrangements by chemical capture; for example, we have already reported the trapping with molecular oxygen of the trimethylenemethane cation radical, a key intermediate of the single electron transfer induced degenerate methylenecyclopropane rearrangement.[2—5]

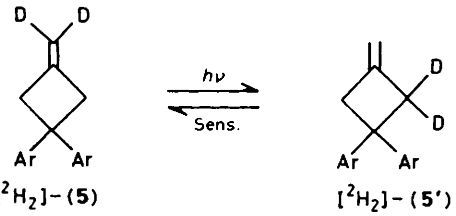
As an extension of our studies on the structure and reactivity of radical cation intermediates generated in a single electron transfer pathway, we have investigated the photoinduced electron transfer reactions of diaryl-substituted MCB and SP derivatives in order to discover whether or not similar rearrangements occur *via* 1,4-cation radical species analogous to (**3**). We found that the single electron transfer pathway did indeed occur, with 1,4-cation radicals intermediates which could be captured by molecular oxygen. We report here the single electron transfer induced degenerate methylenecyclobutane rearrangements of [$^2H_2$]-(**5**) (Scheme 2).

The luminescence of 1,4-dicyanonaphthalene (DCNA) and 9,10-dicyanoanthracene (DCA) was efficiently quenched by the derivatives (**5a**) ($E_{1/2}^{ox}$ 2.17 V *vs.* S.C.E.),† (**5b**) ($E_{1/2}^{ox}$ 1.89 V), and (**5c**) ($E_{1/2}^{ox}$ 1.56 V), except for that of DCA by (**5a**).‡ Upon irradiation§ of a solution of [$^2H_2$]-(**5a**) (0.2 mmol) and DCNA (0.001 mmol) in acetonitrile (10 ml) under argon degenerate rearrangement slowly occurred, affording an 88 : 12 mixture of [$^2H_2$]-(**5a**) and -(**5a′**) after 10 h irradiation, whereas, the rearrangement was not observed under DCA-sensitized conditions even upon prolonged irradiation. However, the more electron-donating [$^2H_2$]-(**5b**) and -(**5c**) underwent degenerate rearrangement under DCA-sensitized conditions. In conjunction with the exothermicity of the electron transfer from (**5**) to the excited sensitizers (Table 1), a single electron transfer mechanism is likely for the observed degenerate rearrangement. The intermediacy of allylically stabilized 1,4-cation radicals was substantiated by trapping with molecular oxygen.



(**1**) (**2**) (**3**) (**4**)

Scheme 1



[$^2H_2$]-(**5**) [$^2H_2$]-(**5′**)

Scheme 2. a; Ar = Ph
b; Ar = *p*-MeC_6H_4
c; Ar = *p*-$MeOC_6H_4$

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† Half-wave oxidation potentials were measured by cyclic voltammetry at a platinum electrode in acetonitrile with 0.1 M tetraethylammonium perchlorate as supporting electrode. S.C.E. = saturated calomel electrode.

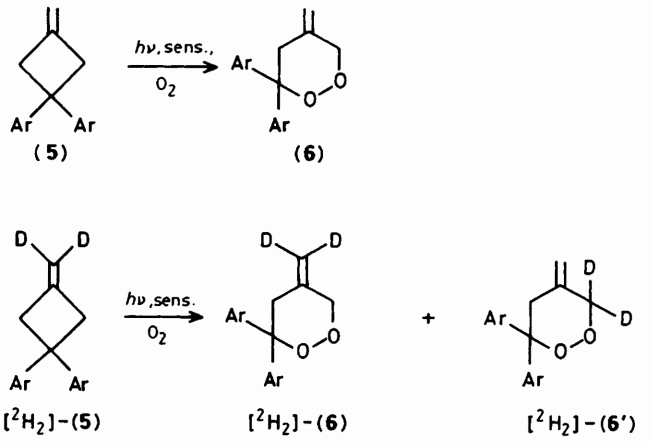
‡ Quenching experiments were carried out in aerated acetonitrile at 20 °C. The Stern–Volmer slopes ($k_q\tau$) for (**5a—c**) were 64.1, 85.1, 105.7 dm^3 mol^{-1}, respectively, for DCNA and those for (**5b**) and (**5c**) were 42.0 and 168.2 dm^3 mol^{-1}, respectively, for DCA.

§ Solutions were irradiated with light from a 2 kW xenon lamp through a Toshiba cutoff filter UV-33 (300 nm) for DCA and TCA sensitizations, and UV-37 (350 nm) for DCNA and AQ sensitizations at 15—20 °C.

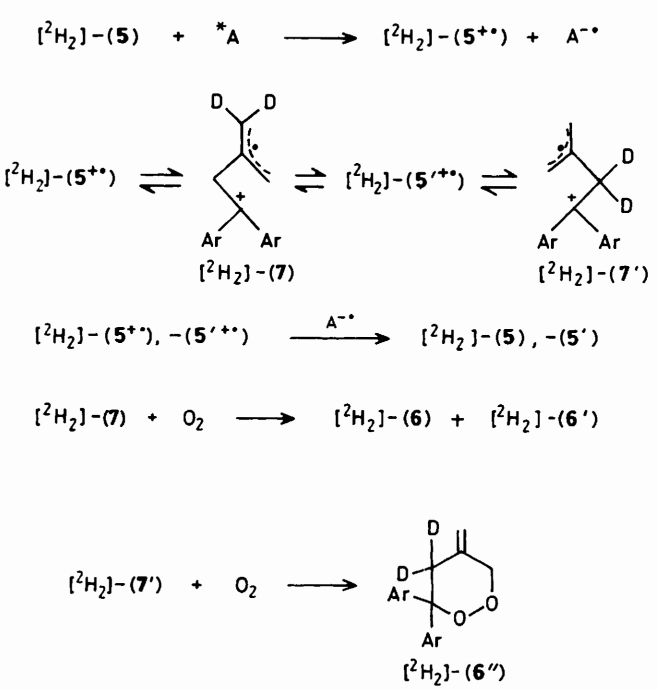
Table 1. Calculated ΔG values and yields (%) of (**6**).

	(**5a**)			(**5b**)			(**5c**)		
Sens.	ΔG^a	(**6a**)	Con.^{b}	ΔG^a	(**6b**)	Con.^{b}	ΔG^a	(**6c**)	Con.^{b}
DCNA	−7.8	11	36	−14.2	56	100	−21.8	11	42
TCA	−7.8	2	6	−14.2	81	95	−21.9	14	38
DCA	+4.8	0	6	−1.8	65	100	−9.4	19	84
AQ	+7.6	0	17	+1.2	5	68	−6.4	15	93

[a] kcal/mol; 1 cal = 4.184 J. Calculated from the Rehm–Weller equation.[7] [b] Con.: conversion (%) of (**5**) after 1 h irradiation.



Scheme 3



Scheme 4. A = sensitizer.

Trapping experiments were performed by irradiating an oxygen-saturated acetonitrile solution of (**5**) and the sensitizer for 1 h (Scheme 3). The yields of 1,2-dioxanes (**6a**—**c**)¶ from (**5a**—**c**) under DCNA-, 2,6,9,10-tetracyanoanthracene (TCA)-, DCA-, or anthraquinone (AQ)-sensitized conditions are shown in Table 1. Oxygenation of [^{2}H]-(**5**) gave further insight into the intermediacy of 1,4-cation radicals. The observed ratio of the hydrogen content, $H_2C{=}:{-}CH_2{-}O{-}O{-}:{-}CH_2{-}C(Ar)_2$, of the labelled 1,2-dioxane isolated after 38% conversion of [$^2H_2$]-(**5b**) under TCA-sensitized conditions was found to be 1 : 1 : 1.8, indicating the exclusive formation of a 1 : 1 mixture of [$^2H_2$]-(**6b**) and -(**6b**′). Similar results were also obtained in oxygenation of [$^2H_2$]-(**5a**) and -(**5c**), under DCNN- and TCA-sensitized irradiation conditions, respectively. It is noteworthy that electron-acceptor sensitizers which facilitated the rearrangement also facilitated the oxygenation. These results thus clearly indicate that an allylically stabilized 1,4-cation radical is the common intermediate for both the degenerate rearrangement and the oxygenation.

A plausible electron-transfer mechanism to account for these results is shown in Scheme 4. The initial reductive quenching of the sensitizer singlet or triplet state by [$^2H_2$]-(**5**) affords the radical cations [$^2H_2$]-($5^{+\bullet}$) which undergo ring cleavage to form [$^2H_2$]-(**7**). The fact that the degenerate rearrangement is slower than the oxygenation may be ascribed to rapid back electron transfer from the sensitizer anion radicals to [$^2H_2$]-($5^{+\bullet}$) and/or to the relatively high rotational barrier in [$^2H_2$]-(**7**), which would be *ca.* 7 kcal/mol on the basis of 1,4-biradical barriers.[6] The fact that the molecular oxygen trapping of [$^2H_2$]-(**7**) to give [$^2H_2$]-(**6**) and -(**6**′) nevertheless occurred much more rapidly than the rearrangement indicates that oxygen very efficiently captured the initially formed 1,4-cation radicals [$^2H_2$]-(**7**) as they were generated. In fact neither the degeneracy in the recovered labelled starting materials nor the formation of [$^2H_2$]-(**6**″) expected from [$^2H_2$]-(**7**′) could be observed under oxygenation conditions.

¶ Satisfactory elemental analyses were obtained for all new compounds. (**6a**): m.p. 133—134.5 °C; *m/z* (80 °C, 13.5 eV), 252 (M^+, 0.2%), 250 (7.0), 236 (4.7), 235 (7.2), 234 (7.4), 221 (2.7), 206 (2.0), 205 (4.4), 183 (31.7), 182 (100), 181 (9.2), 176 (1.8), 175 (4.9), 158 (1.6), and 105 (25.4); i.r., $\nu_{max.}$ (KBr), 2890, 1660, 1492, 1450, 1335, 1041, 990, 755, 740, 698, and 625 cm^{-1}; ^{1}H n.m.r. (90 MHz, CCl_4), δ 3.13 (2H, br.s, 5-H), 4.50 (2H, br.s, 3-H), 4.87 (2H, m, $=CH_2$), and 7.05—7.20 (10H, m, Ar-H). (**6b**): m.p. 120.5—122 °C; *m/z* (80 °C, 10 eV), 280 (M^+, 3.8%), 248 (21.2), 234 (9.0), 233 (40.9), 211 (41.2), 210 (74.0), 195 (18.0), 190 (11.7), 189 (87.4), 172 (11.6), 156 (43.8), 120 (9.5), and 119 (100); i.r., $\nu_{max.}$ (KBr), 3010, 2900, 1659, 1510, 1442, 1183, 1060, 995, 910, 860, 780, and 558 cm^{-1}; ^{1}H n.m.r. (300 MHz, $CDCl_3$), δ 2.38 (6H, s, Me), 3.28 (2H, s, 5-H), 4.69 (2H, s, 3-H), 5.0 (1H, s, $=CHH$), 5.08 (1H, s, $=CHH$), 7.18, and 7.20 (8H, Ar-H); ^{13}C n.m.r. (75 MHz, $CDCl_3$), δ 21.15 (Me), 41.65 (C-5), 76.49 (C-3), 86.94 (C-6), 111.78 ($=CH_2$), 126.34, 128.84, 138.52, 140.45 (Ar-C), and 136.99 (C-4). (**6c**): m.p. 82.5—84 °C; *m/z* (80 °C, 10 eV), 312 (M^+, 3.5%), 294 (9.35), 280 (19.2), 266 (4.9), 265 (22.1), 243 (23.1), 242 (56.7), 205 (26.4), 189 (19), 188 (100), 173 (23.4), 172 (55.7), and 135 (55.3); i.r., $\nu_{max.}$ (KBr), 2960, 2820, 1607, 1580, 1510, 1460, 1440, 1339, 1313, and 1242 cm^{-1}; ^{1}H n.m.r. (300 MHz, $CDCl_3$), δ 3.20 (2H, s, 5-H), 3.79 (6H, s, OMe), 4.63 (2H, s, 3-H), 4.95 (1H, s, CHH), 5.0 (1H, s, $=CHH$), 6.85, and 7.30 (8H, Ar-H); ^{13}C n.m.r. (75 MHz, $CDCl_3$), δ 41.88 (C-5), 55.21 (OMe), 76.55 (C-3), 86.78 (C-6), 111.67 ($C{=}CH_2$), 113.44, 127.89, 138.61, 158.63 (Ar-C), and 135.53 (C-4).

These results thus unequivocally prove the intermediacy of allylically stabilized 1,4-cation radicals in the single electron transfer induced degenerate MCB rearrangement.

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References

1 Recent review on hypothetical biradical pathways in the thermal unimolecular rearrangements: J. A. Berson, in 'Rearrangements in Ground and Excited States,' ed. P. de Mayo, Academic Press, New York, 1980, p. 311, and references cited therein.

2 Y. Takahashi, T. Miyashi, and T. Mukai, *J. Am. Chem. Soc.*, 1983, **105**, 6511.

3 K. Okada, K. Hisamitsu, Y. Takahashi, T. Hanaoka, T. Miyashi, and T. Mukai, *Tetrahedron Lett.*, 1984, 5311.

4 T. Miyashi, Y. Takahashi, T. Mukai, H. D. Roth, and M. L. M. Schilling, *J. Am. Chem. Soc.*, 1985, **107**, 1079.

5 T. Miyashi, M. Kamata, and T. Mukai, *J. Am. Chem. Soc.*, 1986, **108**, 2755.

6 G. A. Seagal, *J. Am. Chem. Soc.*, 1974, **96**, 7892; P. B. Derban and D. S. Santilli, *ibid.*, 1980, **102**, 8363.

7 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.