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DIVERGENT REARRANGEMENT PATHWAYS IN THE ELECTRON-TRANSFER INDUCED SPIROPENTANE-METHYLENECYCLOBUTANE REARRANGEMENT: ROLE OF CIP AND SSIP

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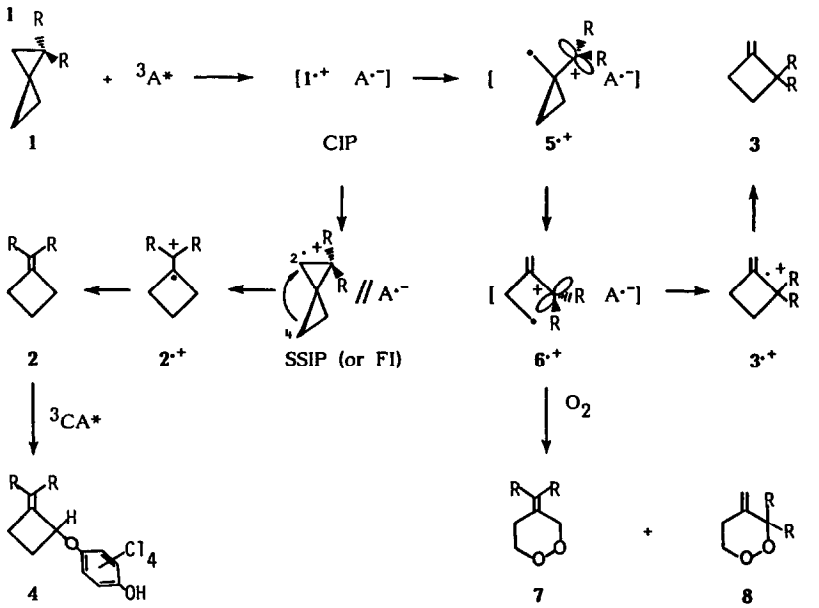
Summary: Photogenerated 1,1-diarylspiropentane cation radicals competitively rearranged to the more thermodynamically stable 1-(diarylmethylene)cyclobutanes and the less stable 2,2-diaryl-1-methylenecyclobutanes in a concerted and stepwise manner, respectively.

Doering had proposed that the thermal unimolecular rearrangement of spiropentane (SP) to methylenecyclobutane (MCB) occurs via two successive bond cleavages, involving cyclopropyl-1,1-biscarbinyl and allylically stabilized 1,4-biradicals.[1] However, the possibility of the concerted rearrangement of SP to MCB was proposed later.[2] Herein we report the SP-MCB rearrangement of photogenerated 1,1-diarylspiropentane cation radicals, in which two different processes compete, i.e., the rearrangement to 1-(diarylmethylene)cyclobutanes occurs predominantly in a concerted manner, whereas a sequential rearrangement pathway gives rise to 2,2-diaryl-1-methylenecyclobutanes.

Scheme 1



(a: R=p-MeOC$_6$H$_4$; b: R=p-MeC$_6$H$_4$; c: R=C$_6$H$_5$)

The phosphorescence of anthraquinone (AQ, $E^{red}_{1/2}$=-0.94 V vs. S.C.E) was efficiently quenched by **1a** ($E^{ox}_{1/2}$=1.17 V vs. S.C.E),[3] **1b**($E^{ox}_{1/2}$=1.42V vs. S.C.E)[3] and **1c**($E^{ox}_{1/2}$=1.67V vs. S.C.E),[3] at rates of k_q=1.3x10^{10}, 8.1x10^9 and 2.5x10^9 $M^{-1}s^{-1}$, respectively, in acetonitrile. Upon irradiation[4] of AQ with **1a** in acetonitrile, **2a**[5] and **3a**[5] were isolated in 33 and 26% yields, respectively, after 79% conversion of **1a**. Similarly, **2** and **3** were obtained either under the 2,4,7-trinitrofluorenone (TNF, $E^{red}_{1/2}$= -0.42 V vs. S.C.E) or under the *p*-chloranil (CA, $E^{red}_{1/2}$= +0.01 V vs. S.C.E)-sensitized conditions as shown in Table 1. However, under the CA-sensitized conditions a significant amount of **4**[5] was isolated as a secondary CA-adduct in acetonitrile and dichloromethane.[6a] The intriguing facets in photoinduced electron-transfer (PET) reactions of **1** are: i) the **2** to **3** ratio increases with an increase in solvent polarity[6b]; ii) the ratio of the sum of **2** and **4** to **3** in acetonitrile under the CA-sensitized conditions is markedly large as compared with that under the TNF- or AQ-sensitized conditions.

Table. 1. Photoreactions of **1** under the AQ-, TNF- and CA-Sensitized Conditions[a]

		yields and conversions (%)											
		in CH_3CN			in CH_2Cl_2			in $CHCl_3$			in C_6H_6		
		1a	**1b**	**1c**	**1a**	**1b**	**1c**	**1a**	**1b**	**1c**	**1a**	**1b**	**1c**
	2	33	19	13	17	13	t[b]	15	t[b]	t[b]	12	0	0
AQ	**3**	26	29	29	41	31	18	48	20	11	44	4	2
	con.	79	61	59	68	59	28	81	35	18	86	13	4
	2	31	18	14	13	9	7				8	6	0
TNF	**3**	20	20	12	34	23	14				32	23	10
	con.	61	51	30	67	41	29				51	41	17
	2	3	8	18	6	18	6				0	0	5
CA	**3**	2	t[b]	4	t[b]	10	13				40	32	31
	4	45	72	49	12	44	47				0	t[b]	5
	con.	100	100	100	100	99	94				100	100	97

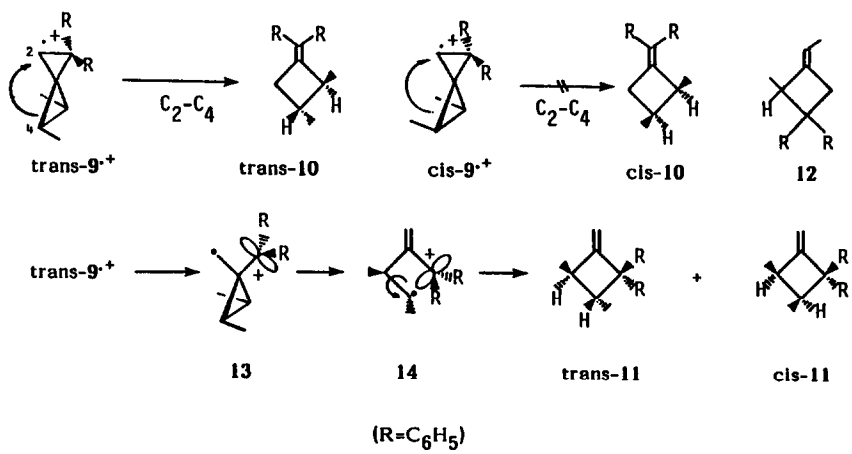
[a] A 5 ml solution of **1** (0.08 mmol) and AQ (0.01 mmol), TNF (0.01 mmol) or CA (0.08 mmol) was irradiated for 30 min (AQ), 20 min (TNF) and 60 min (CA), [b] less than 2%.

Because **2** and **3** failed to interconvert under the sensitized conditions employed and the separation of photogenerated ion radical pairs is assumed to be facilitated by an increase in solvent polarity, an increase in the **2** to **3** ratio with an increase in solvent polarity suggests that **2** and **3** are formed independently after and before the separation of photogenerated ion radical pairs, respectively. After the separation to the solvent-separated ion radical pairs (SSIP) or free ion radicals (FI), the direct C_4 to C_2 migration occurs in $\mathbf{1}^{\cdot+}$ so as to give the more thermodynamically stable $\mathbf{2}^{\cdot+}$ than $\mathbf{3}^{\cdot+}$ which could be formed by the alternative sterically unfavorable migration to C_1. Because the separation to SSIP or FI would be most facilitated in the combination of $\mathbf{1}^{\cdot+}$ with the more localized $CA^{\cdot-}$ among three sensitizer anion radical counterparts, the exclusive formation of **2** in acetonitrile under the CA-sensitized conditions can be well accounted for by a mechanism through SSIP or FI. In contrast, $\mathbf{1}^{\cdot+}$ subsequently collapse within contact ion radical pairs (CIP) to $\mathbf{5}^{\cdot+}$ and $\mathbf{6}^{\cdot+}$ in which charge and spin are localized,[7] keeping a tight ion pair interaction which is important for the stabilization of CIP in the less polar solvents. Because of the steric reasons, the diarylmethylene moiety of $\mathbf{6}^{\cdot+}$ is orthogonal to the C_2-C_3 bond. The formation of the less thermodynamically stable **3** thus requires only the rotation of the C_4 methylene group, but not

the bulkier diarylmethylene group. This sequential rearrangement process resembles that confirmed in the degenerate rearrangement of 2,2-diaryl-1-methylenecyclopropane cation radicals through the trimethylenemethane cation radical intermediate.[8] Evidence that oxygenation products such as **7**[5] and **8**[5] were formed only under conditions[9] where **3** is formed in moderate yields support **6**$^{\cdot+}$ as the direct precursor of **3**.

In support of this mechanism are the stereochemical results derived from PET reactions of *trans*- and *cis-anti*-4,5-dimethyl-1,1-diphenylspiropentane (trans-**9** and cis-**9**).[10] If this mechanism is correct, the rearrangement to 1-(diarymethylene)cyclobutanes would occur with high stereoselectivity, whereas stereorandomization would be expected for the rearrangement to 2,2-diaryl-1-methylenecyclobutanes. Under the CA-sensitized conditions in acetonitrile, trans-**9** gave trans-**10** (30%) together with the **4**-type CA-adduct (10%) and **12** (17%).[5] The AQ-sensitized reaction of trans-**9** in acetonitrile afforded trans-**10**, trans-**11**, and cis-**11** in 14, 11, and 4% yields, respectively together with **12** (9%) after 65% conversion.[5] Evidence that the CA-sensitization of trans-**9** did not give either cis- or trans-**11** in acetonitrile while the AQ-sensitization of trans-**9** gave those together with trans-**10** further supplements the arguments that two independent rearrangement pathways are operative in PET reactions of 1,1-diarylspiropentanes. The high stereoselective formation of trans-**10** from trans-**9** can be explained by the concerted [σ2a+σ2s] pathway with retention at C_2 and retention at C_4.[2] The retention pathway at C_2 and C_5 can afford trans-**10** in a similar way, but this pathway does not operate because of significant steric repulsion.[2] In fact, cis-**9** was reluctant to give cis-**10**, but instead the successive C_1-C_3 and C_4-C_5 bond cleavage[11] led to **12** under the CA- and AQ-sensitized conditions regardless of solvent polarity. The non-stereoselective formation of cis- and trans-**11** can be well explained by a sequential mechanism through **13** and **14** as shown in Scheme 2. The results shown here thus provided a characteristic rearrangement of cation radicals in which rearrangement sequence is changed by the degree of the donor-acceptor interaction in photogenerated ion radical pairs.

Scheme 2



References and Notes

(1) Doering, W von E; Gilbert, J. C. *Tetrahedron, Suppl.*, **1966**, *7*, 397.
(2) Gajewski, J. J.; Burka, L. T. *J. Am. Chem. Soc.*, **1972**, *94*, 8865.
(3) measured by cyclic voltammetry at a platinum electrode in dry acetonitrile with 0.1M

tetraethylammonium perchlorate as supporting electrode.

(4) 2 kW xenon lamp through a Toshiba cutoff filter UV-37 (350-nm) at 15-20°C.

(5) Satisfactory elemental analyses were obtained for all new compounds in this report. **2a**: mp 118.5°C; ^{1}H NMR (90 MHz, CCl_4), δ 2.00 (2H, q, J=7.5 Hz), 2.86 (4H, t, J=7.5 Hz), 3.74 (6H, s), 6.68 (4H, m), 6.99 (4H, m). **2b**: mp 64-65°C; ^{1}H NMR (90 MHz, CCl_4), δ 2.00 (2H, q, J=7.8 Hz), 2.30 (6H, s), 2.87 (4H, t, J=7.8 Hz), 6.85-7.04 (8H, m); ^{13}C NMR (50.2 MHz, $CDCl_3$), δ 17.33 (t), 21.12 (q), 32.18 (t), 128.71 (d), 132.59 (s), 135.62 (s), 137.89 (s), 139.87 (s). **2c**: mp 58-58.5°C; ^{1}H NMR (90 MHz, CCl_4), δ 2.02 (2H, q, J=7.5 Hz), 2.90 (4H, t, J=7.5 Hz), 6.93-7.32 (10H, m); **3a**: oil; ^{1}H NMR (90 MHz, CCl_4), δ 2.63 (4H, br.s), 3.73 (6H, s), 4.83 (1H, m), 4.96 (1H, m), 6.70 (4H, m), 7.10 (4H, m). **3b**: oil; ^{1}H NMR (90 MHz, CCl_4), δ 2.27 (6H, s), 2.60 (4H, br.s), 4.83 (1H, m), 4.95 (1H, m), 6.87-7.16 (8H, m). **3c**: oil; ^{1}H NMR (90 MHz, CCl_4), δ 2.63 (4H, br.s), 4.88 (1H, m), 4.98 (1H, m), 6.92-7.28 (10H, m). **4a**: mp 152-152.5°C (decomp); ^{1}H NMR (90 MHz, CCl_4), δ 2.10-2.80 (3H, m), 3.40-3.80 (1H, m), 3.71 (3H, s), 3.73 (3H, s), 5.70 (1H, br.s), 5.77 (1H, m), 6.40-7.10 (8H, m). **4b**: mp 145-149°C (decomp); ^{1}H NMR (90 MHz, CD_2Cl_2), δ 2.10-2.86 (3H, m), 2.27 (3H, s), 2.31 (3H, s), 3.33-3.90 (1H, m), 5.63 (1H, m), 5.83-6.06 (1H, m), 6.67 (2H, m), 6.87 (2H, m), 7.04 (4H, s); ^{13}C NMR (50.2 MHz, CD_2Cl_2), δ 21.28 (q), 21.40 (q), 25.97 (t), 31.42 (t), 80.91 (d), 118.87 (s), 127.95 (s), 128.58 (d), 128.91 (d), 128.99 (d), 129.09 (d), 135.18 (s), 136.91 (s), 136.98 (s), 137.43 (s), 137.66 (s), 139.37 (s), 144.96 (s), 146.11 (s). **4c**: mp 132-137°C (decomp.); ^{1}H NMR (200 MHz, CD_2Cl_2), δ 2.20-2.38 (1H, m), 2.42-2.58 (1H, m), 2.60-2.76 (1H, m), 3.60-3.78 (1H, m), 5.82 (1H, s), 5.92-6.00 (1H, m), 6.78-6.90 (2H, m), 7.04-7.42 (8H, m); ^{13}C NMR (50.2 MHz, $CDCl_3$), δ 26.00 (t), 31.12 (t), 80.84 (d, 118.87 (s), 126.97 (s), 127.58 (d), 127.90 (d), 128.38 (d), 129.09 (d), 129.19 (d), 136.44 (s), 139.53 (s), 139.56 (s), 140.40 (s), 144.89 (s), 146.15 (s). **7a**: not separated; ^{1}H NMR (90 MHz, $CDCl_3$), δ 2.62 (2H, t, J=5.7 Hz), 3.77 (6H, s), 4.32 (2H, t, J=5.7 Hz), 4.76 (2H, s), 6.7-7.3 (8H, m). **7b**: not separated; ^{1}H NMR (90 MHz, $CDCl_3$), δ 2.30 (3H, s), 2.32 (3H, s), 2.60 (2H, t, J=5.7 Hz), 4.30 (2H, t, J=5.7 Hz), 4.73 (2H, s), 6.9-7.3 (8H, m). **7c**: mp 88-89°C; ^{1}H NMR (90 MHz, CCl_4), δ 2.57 (2H, t, J=5.7 Hz), 4.21 (2H, J=5.7 Hz), 4.63 (2H, s), 6.93-7.38 (10H, m). **8a**: not separated; ^{1}H NMR (90 MHz, $CDCl_3$), δ 2.55 (2H, br.t, J=6.0 Hz), 3.77 (6H, s), 4.42 (2H, t, J=6.0 Hz), 4.48 (1H, m), 5.20 (1H, m), 6.7-7.3 (8H, m). **8b**: not separated; ^{1}H NMR (90 MHz, $CDCl_3$), δ 2.32 (6H, s), 2.47 (2H, br.t, J=6.0 Hz), 4.40 (2H, t, J=6.0 Hz), 4.45 (1H, m), 5.17 (1H, m), 6.8-7.3 (8H, m). **8c**: mp 126.0-127.5°C; ^{1}H NMR (90 MHz, CCl_4), δ 2.50 (2H, br.t, J=6.0 Hz), 4.36 (2H, t, J=6.0 Hz), 4.40 (1H, m), 5.13 (1H, m), 7.09-7.33 (10H, m). trans-**10**: oil; ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.85 (3H, d, J=7.0 Hz), 1.15 (3H, d, J=7.0 Hz), 1.97 (1H, dddq, J=5.0, 6.0, 7.0, 8.7 Hz), 2.33 (1H, dd, J=6.0, 16.5 Hz), 2.80 (1H, ddq, J=2.8, 5.0, 7.0 Hz), 3.25 (1H, ddd, J=2.8, 8.7, 16.5 Hz), 7.20 (10H, m). trans-**11**: oil; ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.88 (3H, d, J=6.5 Hz), 1.15 (3H, d, J=6.5 Hz), 2.52 (1H, dddq, J=9.3, 6.5, 3.0, 2.6 Hz), 2.78 (1H, dq, J=9.3, 6.5 Hz), 4.95 (1H, d, J=3.0 Hz), 5.03 (1H, d, J=2.6 Hz), 7.2 (10H, m). cis-**11**: oil; ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.72 (3H, d, J=7.0 Hz), 1.03 (3H, d, J=7.0 Hz), 3.08 (1H, dddq, J=9.4, 7.0, 3.0, 2.6 Hz), 3.36 (1H, dq, J=9.4, 7.0 Hz), 5.19 (1H, d, J=2.6 Hz), 5.26 (1H, d, J=3.0 Hz), 7.2 (10H, m). **12**: mp 39.5-41.5°C; ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.82 (3H, d, J=7.9 Hz), 1.66 (3H, dddd, J=6.5, 2.5, 2.5, 1.0 Hz), 3.06 (1H, dddq, J=15.0, 2.5, 2.5, 1.0 Hz), 3.52 (1H, dddq, J=15.0, 2.5, 2.5, 1.0 Hz), 3.73 (1H, dddqq, J=7.0, 2.5, 2.5, 1.0, 1.0 Hz), 5.18 (1H, dddq, J=6.5, 2.5, 2.5, 1.0 Hz), 7.23 (10H, m); ^{13}H NMR (50.2 MHz, $CDCl_3$), δ 13.08 (q), 14.96 (q), 41.63 (t), 48.26 (d), 51.14 (s), 112.63 (d), 125.68 (d), 125.71 (d), 127.07 (d), 127.65 (d), 127.89 (d), 128.16 (d), 141.59 (s), 144.59 (s), 150.44 (s).

(6) a) At low conversions, **4** was not detected by NMR. Control experiment showed that photoreaction of **2** with CA gave **4** in high yield. Under the CA-sensitized conditions, the 2:1 CA-**1a** adduct was also isolated in 40 and 58% yields, respectively, in acetonitrile and dichloromethane together with **2a**, **3a** and **4a**. b) Dielectric constant: 37.5 (CH_3CN, 20°C), 8.93 (CH_2Cl_2, 25°C), 4.81($CHCl_3$, 20°C), 2.27 (C_6H_6, 25°C).

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(9) A solution of **1** and AQ, TNF or CA in acetonitrile or dichloromethane was pressurized with oxygen (20 kg/cm^2) and irradiated. Under the AQ-sensitization in dichloromethane **1a** gave **7a** and **8a** in 7 and 8% yields, respectively, together with **3a** (27%). The AQ-sensitization in acetonitrile and TNF-sensitization in dichloromethane gave similar results. Under the CA-sensitized conditions in acetonitrile, however, **1a-1c** did not give any oxygenation product.

(10) Jones, W. M.; Grasley, M. H. *J. Am. Chem. Soc.*, **1963**, *85*, 2754. The cis isomer reported by Jones was a 8:1 mixture of anti-cis - (mp 30.5-31°C) and syn-cis- (mp 62-63°C) isomers. We separated both and used the anti-cis isomer (cis-**9**) for this work afetr the confirmation of stereochemistry by means of the NOE examination.

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