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Photoinduced Skeletal Rearrangement of 1,1-Diphenylspiropentanes

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Abstract: Photoreactions of 1,1-diphenylspiropentanes have been investigated under various photochemical conditions. The exploratory studies have provided unprecedented examples of photochemically induced skeletal rearrangement of spiropentanes to methylenecyclobutanes.

Molecular rearrangements in the ground and excited states have been the subject of considerable attention in the chemistry of strained compounds.^{1a} Spiropentanes rank among the most remarkable strained compounds and both experimental and theoretical investigations have been made on their skeletal rearrangement to methylenecyclobutanes.^{1b-g} Despite the abundant studies on the thermally induced rearrangements, little work has been done on the photochemical rearrangement of spiropentanes. Although the parent spiropentane is known to undergo fragmentation reactions when photolyzed in the gas-phase,² no photochemical rearrangement has been observed. We have investigated photochemical reactions of 1,1-diphenylspiropentanes 1 by direct photolysis, triplet photosensitization with acetone ($E_T = ca$. 80 kcal mol⁻¹),³ and photoinduced electron transfer reaction with tetracyanoethylene (TCNE). These exploratory studies have provided unprecedented examples of photochemical skeletal rearrangement of spiropentanes.

In Table 1 are summarized the results of the direct photolyses of 1 and the sensitized photolyses of 1 with acetone.⁴ Upon direct photolyses (254 nm) of acetonitrile solutions containing 2.0×10^{-2} M of 1, three types of methylenecyclobutanes 2, 3, and 4 were obtained together with 1,1-diarylallenes 5. The skeletal rearrangement of 1 was also induced by irradiation (300 nm) of acetone solutions containing 2.0×10^{-2} M of 1. Intriguingly, the acetone sensitized photolysis of 1 selectively led to the formation of 2 and 3 in high yields. Control experi-

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spiro- pentane		Direct / yield ^c (%)				Sens. / yield ^c (%		
	2	3	4	5	recov.	2	3	recov.
1a	10	9	10	38	30	21	27	38
1 b	12	20	2	12	37	21	45	9

^a 6 ml acetonitrile solutions of 1 (2.0 x 10^{-2} M) were photolyzed with low pressure Hg lamps (254 nm) for 3 hours. ^b 6 ml acetone solutions of 1 (2.0 x 10^{-2} M) were photolyzed (300 nm) for 5 hours. ^c By 90 MHz ¹H-NMR.



ments showed that 2, 3 and 4 did not interconvert one another under the photolysis conditions.

Possible mechanisms for the photoreactions can be deduced with respect to the position of the diarylmethylene moiety of the photolysis products. As shown below, photolysis of 1 would cause the C1-C2 fission and the C1-C3 fission competitively to afford 1,3-diradicals 6 and 8, respectively. Migration of C4 accompanied by the C3-C4 bond cleavage of the intermediate 6 well explains the formation of 2 and 3, while intermediate 8 should be responsible for the formation of 4 through the ring opening of the cyclopropyl radical moiety to give 9 followed by the cyclization. As for the formation of 5, it is conceivable that fragmentation involving fission of both C3-C4 and C3-C5 bonds occurs to give 2,2-diphenylcyclopropylidene 10 as the third reaction pathway. Similar retro-1,2-addition to generate carbenes in the photolyses of cyclopropanes,^{5a} and facile ring opening of 10 have been reported elsewhere.^{5b, c}



A characteristic feature of the direct photolysis is lack of selectivity upon the initial bond fission. Presumably this is due to the excess vibrational energy of the photoexcited 1. In contrast, the acetone sensitized photolyses involve the selective C1-C2 bond fission to afford 2 and 3. In this case a mechanism involving diradicals 6 and 7 is feasible.

Electron transfer (ET) from donors to acceptors occurs upon photoirradiation of their electron donor-acceptor (EDA) complexes.⁶ Accordingly, photolysis of EDA complexes is a straightforward method for ET reactions. Spiropentanes 1 are good electron donors and form EDA complexes with tetracyanoethylene (TCNE) in methylene chloride. The irradiation (λ >390 nm) of the characteristic charge-transfer (CT) absorption bands^{7a} induced the skeletal rearrangement of 1. In methylene chloride 1a afforded 2a (44%) as a major product and 3a (7%) as a minor product (Table 2).^{4,7b} In the case of the reaction of 1b, TCNE cycloadducts 11b (17%) and 12b (8%) were obtained together with lower yields of 2b and 3b. The structure of 11b was unequivocally de-

Table 2. Photoreaction of the EDA complexes of 1 and TCNE^{*a*}

donor	solvent	yield (%) ^b						
	(time / h)	2	3	11	12	13	recov.	
1 a	CH ₂ Cl ₂ (20)	44	7	0	0	0	35	
1 a	CH ₃ CN (20)	38	0	0	0	0	60	
1 b	CH_2Cl_2 (6)	4	2	17	8	34	25	
1 b	CH ₃ CN (6)	19	0	4	ť	11	48	

^a 4 ml methylenechloride solutions of 1 and TCNE (0.20 mmol each) were irradiated by using a 2 kW xenon lamp (λ >390 nm). ^b Analyzed by 90 MHz ¹H-NMR. ^c Less than 2%.



 $(Ar = 4-MeOC_6H_4)$

termined by X-ray crystallography (Fig. 1). A novel 2: 1 adduct 13b was also produced. Control experiments showed that 2 and 3 did not interconvert each other under comparable conditions and that 12b was not obtained by analogous CT photolysis of 2b or 3b with TCNE.

Related studies on the ET reactions of various strained hydrocarbons⁸ have revealed that the strained σ bonds can be weakened or cleaved by ET. The observed rearrangement of 1 to 2 can be explained as a result of C1-C2 bond fission of 1^{*+} in a photogenerated ion pair [1^{*+}, TCNE^{*-}] followed by migration of the C4 (or C5) onto C2 (eq. 1a). Back ET from TCNE^{*-} to resulting 2^{*+} leads to 2. Similar skeletal rearrangement involving the initial C1-C2 bond fission followed by C4 (C5) migration was observed for parent spiropentane cation radical.⁹ Photosensitized ET reaction of 1 also resulted in the rearrangement.^{4a} In the present case formation of 13b suggests that cation radical 1b^{*+} may undergo an additional type of rearrangement employing C4 migration onto the 4-methoxyphenyl ring to give 14 as shown in eq. (2). Deprotonation followed by the reaction with TCNE is a possible pathway for the formation of 13b.

It is noteworthy that product distribution was affected by solvent polarity. In acetonitrile exclusive formation of 2a from 1a was observed. Similarly, 2b was produced in complete preference to 3b with suppressed yield formation of cycloadducts 11b and 12b (Table 2). Favored formation of 2 can be due to the higher thermodynamic stability of 2^{*+} relative to 3^{*+} . Calculations based on the redox potentials of 2, 3, and TCNE¹⁰ suggest that ion pairs [$2a^{*+}$, TCNE^{*-}] and [$2b^{*+}$, TCNE^{*-}] are more stable than ion pairs [$3a^{*+}$, TCNE^{*-}] and [$3b^{*+}$, TCNE^{*-}] by 0.55 and 0.30 eV, respectively. In this respect cation radical transformation as shown in in eq. (1b) seems unlikely.

Solvent polarity plays an important role in many ET photoreactions and photogenerated ion pairs sometimes show diverse reactivities depending on the solvent polarity.¹¹ In a polar solvent, acetonitrile, solvation of the photogenerated ion pair $[1^{++}, \text{TCNE}^{--}]$ would result in elongation of the interionic distance. Under the circumstances migration of the C4 (or C5) of 1^{++} onto C2 to give 2^{++} (eq. 1a) is expected to proceed with diminished electronic and steric effects due to pairing TCNE⁺⁻.



Fig. 1. Molecular structure of 11b. Crystal data: a = 20.867(2), b = 11.875(1), c = 16.883(3) Å; β = 95.29(3), V = 4165.7(9) Å³; monoclinic, C2/c, Z = 8, D_{calcd} = 1.303 g cm⁻³, final R = 5.42%.





In methylene chloride shorter interionic distance between 1^{•+} and TCNE^{•-} would bring about certain degree of electronic and steric effect upon fission of the C1-C2 bond of 1^{•+}. It is likely that a 1,3-diradical similar to 6 may be generated to some extent through the C1-C2 bond cleavage of 1^{+} followed by back ET from pairing TCNE^{••}. The results of direct photolysis of 1 suggest that hypothetical diradical 6 leads to the formation of 2 and 3 through 7 without significant selectivity. It should be referred to that 1b afforded cycloadducts 11b and 12b whereas 1a does not. A simple explanation for this is that methoxy substituents would enhance the reactivity of 6 and 7. Diradicals 6b and 7b may be more reactive than 6a and 7a to be trapped by TCNE leading to 11b and 12b.

In summary, spiropentanes 1 are found to be photoreactive. The present studies have provided unprecedented examples of photochemically induced skeletal rearrangement of spiropentanes to methylenecyclobutanes.

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- a) Eox values of 1a and 1b are +1.67 and +1.17 V (vs. SCE in CH₃CN), respectively. The absorption 7 maxima of the EDA complexes in CH₂Cl₂ are: 1a, λ_{max} 406, λ_{sh} 486 nm; 1c, λ_{max} 398, 598 nm. b) 11b, mp. 230 - 231 °C. Mass (100 °C, 25 eV) 408 (M+, 87%), 279 (100). IR (KBr) 2930, 2830, 2230 (CN), 1607, 1510, 1260, 1180, 1030 cm⁻¹. ¹H-NMR (90 MHz, CDCl₃) 0.97 (4H, br s), 3.11 (2H, br s), 3.83 (6H, s), 6.90 (4H, m), 7.33 (4H, m). 12b, mp. 153 -154 °C. Mass (100 °C, 25 eV) 408 (M⁺, 12%), 281 (100). IR (KBr) 2930, 2820, 2280 (CN), 2240 (CN), 1605, 1510, 1440, 1240, 1170, 1027 cm⁻¹. ¹H-NMR (200 MHz, CDCl₃) 2.53 (2H, A₂B₂, J = 3.5, 7.0 Hz), 2.66 (2H, A₂B₂, J = 3.5, 7.0 Hz), 3.22 (2H, s), 3.80 (3H, s), 3.82 (3H, s), 6.88 (4H, m), 7.05 (4H, m). 13b, mp. 176 -177 °C (decomp.). FAB Mass (NBA matrix) 688 (M++2, 3%), 687 (M++1, 7), 686 (M+, 7), 343 (5), 280 (27), 279 (100). IR (KBr) 2930, 2830, 2250 (CN), 2220 (CN), 1640, 1610, 1570, 1510, 1460, 1305, 1280. 1250, 1175, 1110, 1035 cm⁻¹. ¹H-NMR (200 MHz, CDCl₃) 2.59 (4H, dd, J = 5.5, 8.5 Hz), 2.92 (4H, dd, J = 5.5, 8.5 Hz), 3.06 (4H, s), 3.78 (6H, s), 3.83 (6H, s), 6.59 (4H, br s), 6.73 (2H, s), 6.93 -7.10 (8H, m).
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- 10 E_{ox} values of **2a**, **2b**, **3a**, and **3b** are +1.46, +1.19, +2.01, and +1.49 V (vs. SCE, in MeCN), respectively. E_{red} of TCNE is + 0.22 V (vs. SCE, in MeCN). Mattey, J. Angew. Chem. Int. Ed. Engl. **1987**, 26, 825-845; Kavarnos, G. J.; Turro, N. J. Chem.
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