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Photochemical Reactions of Aromatic Compounds. XXIX.[1] Photochemical and Thermal Cycloreversions of 1,2,2a,8b-Tetrahydrocyclobuta[*a*]naphthalenes

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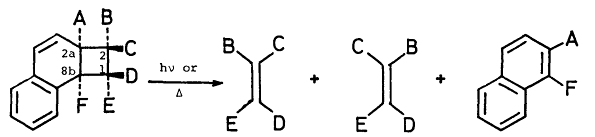
Synopsis. Photochemical and thermal cycloreversions of 1,2,2a,8b-tetrahydrocyclobuta[*a*]naphthalenes were investigated. The cycloreversion in the excited singlet state was completely stereospecific; a concerted mechanism was assigned. The benzophenone-sensitized and thermal decomposition gave a mixture of *cis*- and *trans*-olefins, but favored stereoretention. The mechanisms are discussed in terms of singlet and triplet 1,4-biradicals.

The [2+2] cycloreversions of cyclobutane compounds have been of theoretical and mechanical interest in relation to the Woodward-Hoffmann rule[2] and 1,4-biradical intermediates.[3] We wish to report here on the stereochemical features of photochemical and thermal cycloreversions of 1,2,2a,8b-tetrahydrocyclobuta[*a*]naphthalenes **1a**—**d**.



1 2 3 4

	A	B	C	D	E	F
a:	H	H	CH_3	OC_6H_5	H	CN
b:	H	CH_3	H	OC_6H_5	H	CN
c:	CN	H	CH_3	OCH_3	H	H
d:	CN	CH_3	H	OCH_3	H	H

The direct or benzophenone-sensitized photolysis of **1a**—**d** quantitativlly gave **2a**—**d**, **3a**—**d**, and **4**. The results are listed in Table 1. The olefin formation by the direct photolysis of **1a**, **b** occurred with >95% stereospecificities, whereas the cycloreversion in the presence of ferrocene or in neat 1,3-pentadiene was completely stereospecific. Since ferrocene and 1,3-pentadiene are well-known to be good triplet quenchers, the formation of small amounts of **3a**, **b** in the absence of such compounds probably occurs by means of a triplet mechanism. Similarly, the direct photolysis of **1c** or **1d** in the presence of ferrocene gave only **2c** or **2d** each. In the excited singlet state, therefore, the cycloreversions proceed *via* a $_\sigma 2_s + _\sigma 2_s$ concerted mechanism.

On the other hand, the benzophenone-sensitized decomposition of **1a**, **b** occurred with only a partial stereoretention. In recovered **1a**, **b**, the epimers could not be detected. The results suggest that triplet biradicals, ^{3}**4c** and ^{3}**5t**, undergo the C_1–C_2 bond rotation in competition with the intersystem crossing to singlet biradicals (Scheme 1).[4]

The thermal decomposition of **1a**—**d** at 300±10 °C gave **2a**—**d**, **3a**—**d**, and **4**> in 80% yields, with high stereospecificities. It should be noted that the stereoretention of the *cis* configuration in **1a**, **c**→**2a**, **c** predominanted over that of the *trans* configuration in **1b**, **d**→**2b**,**d**;[6] usually the retention of the *trans* configuration predominates over that of the *cis* configuration in thermolyses of cyclobutane[5a,5c,7] and oxetane[8] compounds. The C_2–C_3 bond cleavage of singlet biradicals is spin-allowed and favored by the aromatization of the dihydronaphthyl residue. Moreover, the sterically crowded nature of ^{1}**4c** reinforces the bond cleavage which overcomes the C_1–C_2 bond rotation, whereas ^{1}**5t** undergoes the bond rotation to a significant extent

TABLE 1. PHOTOCHEMICAL AND THERMAL CYCLOREVERSIONS OF **1a**—**d**[a)]

			1a		**1b**		**1c**		**1d**	
			2a[b)]	**3a**[c)]	**2b**[c)]	**3b**[b)]	**2c**[d)]	**3c**[e)]	**2d**[e)]	**3d**[d)]
Photolysis	Direct	A[f,g)]	95±1	5±1	98±1	2±1	—	—	—	—
		C[f,h)]	95±1	5±1	99	1	—	—	—	—
		P[i)]	>99	<1	100	0	—	—	—	—
		F[j)]	100	0	100	0	100	0	100	0
	Sens[k)]	A[f,g)]	55±1	45±1	78±1	22±1	—	—	—	—
Thermolysis[l)]		300 °C	95±2	5±2	76±2	24±2	90±3	10±3	80±3	20±3
		350 °C	90	10	76	24	—	—	—	—
		480 °C	88	12	75	25	—	—	—	—

a) Averaged for each three runs. b) *cis*-1-Phenoxypropene. c) *trans*-1-Phenoxypropene. d) *cis*-1-Methoxypropene. e) *trans*-1-Methoxypropene. f) Extrapolated at zero-time irradiation. g) Acetonitrile solution. h) Cyclohexane solution. i) In neat 1,3-pentadiene; conversion, <10%. j) Acetonitrile solution in the presence of ferrocene; conversion, <10%. k) Sensitized by benzophenone. l) The thermolyses were carried out in the inlet part of a GC-2C machine.

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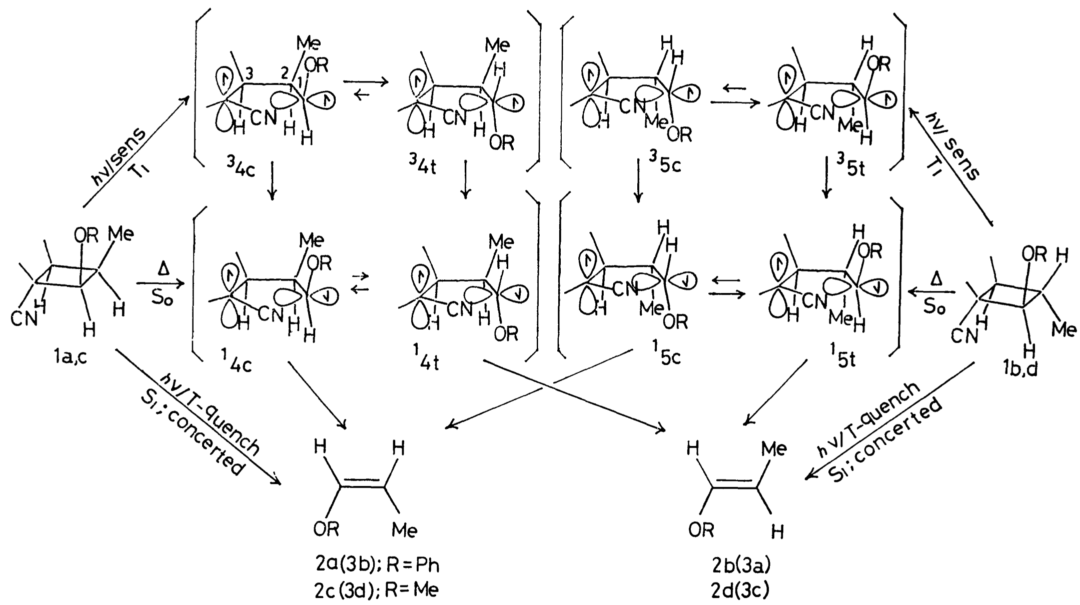

Scheme 1.

because of the smaller steric repulsion. Alternatively, a biradicaloid transition-state mechanism[3b,3f] offers an attractive speculation; a concerted mechanism could contribute more to the cycloreversion of **1a**, **c** than to that of **1b**,**d**.[8b,9]

Experimental

Materials. *cis*- and *trans*-*endo*-1-Phenoxy-2-methyl-1,2,2a,8b-tetrahydrocyclobuta[*a*]naphthalene-8b-carbonitriles **1a** (mp 138.5—139.5 °C) and **1b** (mp 97.5—98.5 °C) were obtained by the photocycloaddition of *cis*- and *trans*-1-phenoxypropenes to 1-naphthonitrile[10] respectively. Similarly, **1c** (mp 65—66 °C) and **1d** (mp 127.5—129 °C) were prepared according to the method reported previously.[11] These materials, benzophenone, and ferrocene were recrystallized from methanol. The 1,3-pentadiene was distilled from sodium under a nitrogen atmosphere.

Photolyses. Solutions of **1a**—**d** (2 mg/cm^3) in cyclohexane, acetonitrile, or 1,3-pentadiene were prepared. Solutions of **1a**—**d** (2 mg/cm^3) and ferrocene (2 mg/cm^3) or benzophenone (1 mg/cm^3) in acetonitrile were also prepared. Each solution (2 cm^3) was placed in a Pyrex tube, bubbled with a pure nitrogen stream, and irradiated with a high-pressure mercury arc at 20±2 °C, using a merry-go-round apparatus. In benzophenone-sensitized runs, a hexane solution of naphthalene (13 g/dm^3, 1 cm path length) was used as the light filter. During the course of the irradiation, the photolysates were analyzed by VPC at 5-min intervals.

Thermolyses. Pyrex tubes, in which **1a** or **1b** (10—20 mg) was placed, were degassed ($<10^{-3}$ mmHg), sealed, and heated on a metal bath maintained at 300±10 °C for 2—3 h. The decomposition was completed. 1-Naphthonitrile and a mixture of *cis*- and *trans*-1-phenoxypropenes were formed in *ca.* 90 and 80% yields respectively. More conveniently, the thermolyses were carried out by introducing 0.5—1.0 μl portions of acetonitrile solutions of **1a**—**d** into a Shimadzu GC-2C gas chromatograph, the inlet part of which was maintained at a constant temperature (300—480 °C).

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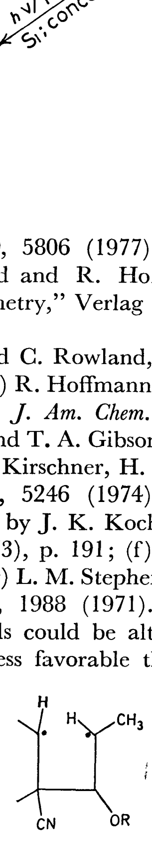
4) The **6** biradicals could be alternative intermediates, but are energetically less favorable than **4** and **5**.



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6) Under the conditions of the thermolyses, the isomerization of **2a**—**d** and **3a**—**d** is negligible.

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