88. The Photorearrangements of a Naphthobarrelene-like System. Dependence on Excited-State Spin Multiplicity and Electronic Configuration, and Evidence for Biradical Intermediates

Preliminary communication[1])

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Summary

8-Benzoyl-9-deuterio-naphtho[*de*-2.3.4]bicyclo[3.2.2]nona-2,6,8-triene (**1**) rearranged quantitatively in a photochemical di-π-methane-type process to 2-, 6-, and 9-deuteriated 1-benzoyl-naphtho[*de*-2.3.4]tricyclo[4.3.0.0^{2,9}]nona-2,6-diene (**8a–c**). The phenylhydroxymethyl analogue **2** underwent a similar regioselective rearrangement to **9a–c**. The rearrangement **1**$\rightarrow$**8a–c** is proposed to proceed along three reaction paths evolving from two primary photochemical processes of naphthyl-vinyl and vinyl-vinyl bonding (**1**$\rightarrow$**3**+**6**). Evidence for a competition between several paths and involvement of biradical intermediates derives from changes in the isotopomeric composition with temperature, and from laser flash detection (λ_{exc} 353 nm) of a transient. The dependence of the quantum yield for product formation from **1** on excitation wavelength and sensitizer triplet energy leads to the conclusion that reaction to the primary biradicals occurs directly from the $S_1(n,\pi^*)$ and $T_2(n,\pi^*)$ states, and that reaction from $T_1(\pi,\pi^*)$ and from $S_2(\pi,\pi^*)$ proceed either directly or *via* T_2.

Zimmerman & Bender [2] have shown that triplet-excited 1,2- and 2,3-naphthobarrelenes undergo di-π-methane (DPM) rearrangements initiated by selective α-naphthyl-vinyl and vinyl-vinyl bonding, respectively. On direct irradiation of the 1,2-isomer, the two bonding modes become nearly equivalent and competition by cycloaddition of a double bond to the naphtho group prevails [3].

We now report on the photorearrangements of the bicyclo[3.2.2]nonanaphthalenes **1** [1] and **2**[3]). The two different labels R and D served, *inter alia*, to analyze the mechanistic details of the rearrangement paths which are overall similar to

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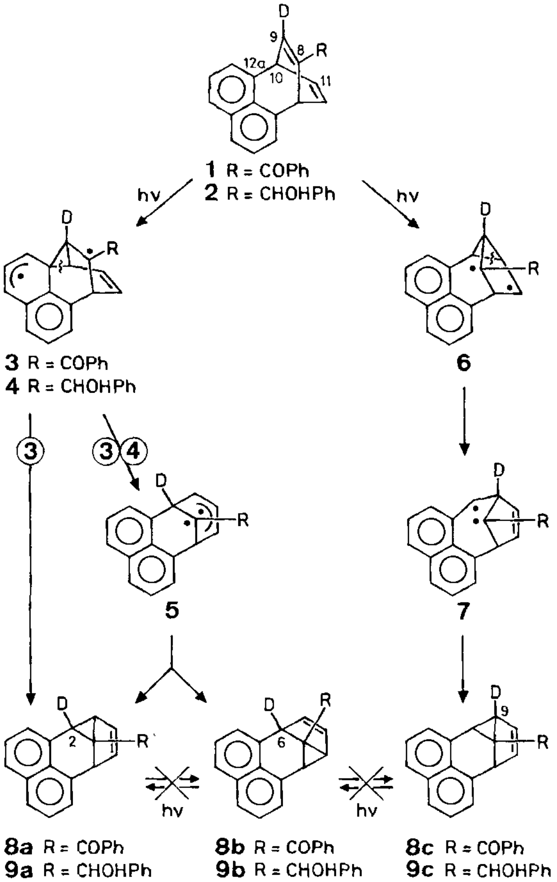
[3]) [a]) All compounds gave satisfactory elemental and spectral analyses. [b]) The nomenclature chosen in [1] is adopted here. For the nomenclature of **1** and **8** according to IUPAC rules see the *Summary*.

those of the naphthobarrelene→naphthosemibullvalene DPM rearrangements [2] [3]. Furthermore, evidence is presented on the dependence of the reaction on spin multiplicity and electronic configuration, and on the possible occurrence of discrete intermediates during the rearrangement of **1**.

On direct and sensitized irradiations, **1** gave isotopomers of a single product, **8a–c**[3]). A sensitized irradiation of **2** afforded in 40% yield products **9a–c**[3]). The other products were shown by NMR. not to be regioisomers of **9**. Under the conditions of formation, the isotopic isomers were not interconvertible. Reaction conditions, quantum yields and deuterium distribution in the products are given in the *Table*[4]).

The regioselective rearrangements[5]) to 1-substituted tricyclo[4.3.0.0^{2,9}]nonanaphthalenes[3b]) demand, in the formulation of any mechanism, that either the 10, 11- or 10, 12a-single bond of the starting compound is broken and that in each case both



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4) For the deuterium analyses, the proton signals at C(2), C(6) and C(9) were integrated by 270-MHz ^{1}H-NMR. As these signals were sufficiently separated only in 7,8-dihydro-**8**, samples of **9** were oxidized to **8** which was then catalytically hydrogenated prior to NMR. measurements. ^{2}H-NMR. (15.4 MHz, FT.) confirmed that deuterium was exclusively attached to C(2), C(6) and C(9).

5) For regioselective control by directing groups in other arobarrelenes, see [4].

Table. *Quantum Yields of Product Formation and Deuterium Distribution in the Products* **8** *and* **9**[a])

Run no.	Compound	Excitation wavelength, nm	Temperature, K	Sensitizer (E_T, kcal/mol)	Proposed initial **1*** and **2*** states populated	Φ[b])	% Deuterium[c])		
							C(2) (=% **8a**)	C(6) (=% **8b**)	C(9) (=% **8c**)
1	**1**[d])	313	298	-	$S(\pi,\pi^*)$	0.52	58	33	8
2	**1**[e])	366	77	-	$S(n,\pi^*)$	n.d.	72	10	17
3	**1**[f])	366	298	-	$S(n,\pi^*)$	0.90	54	32	15
4	**1**[d])	366	298	-	$S(n,\pi^*)$	1.02	58	31	10
5	**1**[d])	405	298	-	$T(n,\pi^*)$	0.48	64	28	8
6	**1**[d])	436	278	-	$T(\pi,\pi^*)$	0.001	n.d.	n.d.	n.d.
7	**1**[d])	436	298	-	$T(\pi,\pi^*)$	0.011	60	30	10
8	**1**[d])	436	348	-	$T(\pi,\pi^*)$	0.016	n.d.	n.d.	n.d.
9	**1**[d])	366	298	benzophenone (68.9)	$T(n,\pi^*)$	0.57[g])	61	31	7
10	**1**[d])	366	298	thioxanthone (65.5)	$T(n,\pi^*)$	0.54[g])	57	34	10
11	**1**[d])	366	298	phenanthrene (61.9)	$T(\pi,\pi^*)$	<0.05[g])	64	29	7
12	**2**[d])	366	298	benzophenone (68.6)	$T(\pi,\pi^*)$	0.029	39[h])	39[h])	23[h])

[a]) Degassed solutions. [b]) Actinometry in runs 1-4 and 9-12 as described in [6]; for runs 5-8 the excitation wavelength was isolated by line filters and ferrioxalate actinometry was employed; product analysis of all runs by GLC. at several conversions; Φ values given are extrapolated to zero conversion, experimental error ±5% (runs 5-8 and 11: ±30%). [c]) Experimental error ±5%. [d]) 7×10^{-3}M in benzene. [e]) 7×10^{-3}M in EPA. [f]) 7×10^{-3}M in *t*-butyl alcohol. [g]) Values corrected for 10% direct absorption. [h]) =% **9a**, **9b** and **9c**, respectively.

C(9) and C(8) are involved in the formation of two permanent new single bonds. In the most plausible stepwise formulation, the *major* route for **1** and **2** is initial naphthyl-vinyl bonding to **3** and **4**, respectively, which can only furnish **8a**+**8b** and **9a**+**9b**, respectively. A stepwise sequence alone from **4** *via* **5** would give the final products with equal probability in each case for symmetry reasons (neglecting the asymmetric deuterium substitution in **5**). This condition is indeed met for **2**→**9a**+**9b**. The predominance of **8a** over **8b** shows that in the benzoyl case either an additional path to **8a** competes with the stepwise route, or that the (*E*)- and (*Z*)-isomers of **5** are populated in unequal amounts and remain trapped within the lifetime of the intermediate. Thus, on one hand, the electrophilic nature of the α-keto radical in **3** could provide a driving force (which is lacking in **4**) for a direct conversion **3**→**8a** by displacing C(12a) at C(10) in a cyclopropane cleavage concomitant with regio-specific cyclization (an $S_{\mathrm{H}}2\mathrm{i}$ reaction)[6]). On the other hand, the benzoyl conformers of excited **1** could give rise to (*E*)/(*Z*) mixtures of **3** and **5** in unknown ratios. If the (*E*)-**5**⇄(*Z*)-**5** interconversion is slow relative to the formation of **8a** and **8b**, the distribution of these isomers could simply reflect the isomeric composition of **5**. In either case, the involvement of intermediates appears mandatory.

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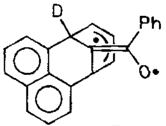
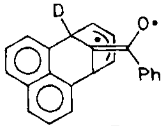
[6]) An allowed overall concerted ${}_{\sigma}2_{a(\text{or s})}+{}_{\pi}2_{a}+{}_{\pi}10_{s(\text{or a})}$ photoreaction could also account for **1**→**8a**, whereas **1**→**8b** would require a photochemically forbidden ${}_{\sigma}2_{a(\text{or s})}+{}_{\pi}2_{a(\text{or s})}+{}_{\pi}2_{s}+{}_{\pi}10_{a}$ photoprocess (involving both double bonds). This latter path is followed, however, in the *thermal* (>200°) rearrangement **1**→**8** [5].



(*E*)-**5**



(*Z*)-**5**

Any route to the *minor* products **8c** and **9c** must involve **7** rather than **5** and, therefore, include an eventual 9,11-bonding step. The most economic path⁷) is initiated by direct vinyl-vinyl bonding **1**,**2** → **6**. The proportion of the isotopic isomers **8a–c** was independent of the mode of excitation (*Table:* runs 1, 4, 5, 7, 9–11) but varied slightly with solvent (run 3) and more strongly with temperature (run 2), which is compatible with a competition between several reaction paths evolving from one or several excited states with similar reaction properties.

The dependence of the quantum yield of **1** on excitation wavelength and sensitizer triplet energy indicates that reaction can occur directly from *at least* one singlet and one triplet excited state as shown in the *Figure*. The results with 405 and 436 nm (runs 5–8) suggest that with these wavelengths two different triplet states are populated. The lower-lying one is probably the phosphorescent naphthalene-like $T(\pi,\pi^*)$ state (E_T 58.2 kcal/mol, τ_p 1.56 s, at 77 K)⁸). The quantum yields obtained from this state increase with temperature (E_a *ca.* 8 kcal/mol). The unity quantum yield upon singlet $n \rightarrow \pi^*$ excitation in benzene precludes, within experimental error, $S \rightarrow T$ intersystem crossing prior to reaction, whereas intersystem crossing and endothermic internal conversion to the upper triplet (of presumed n,π^* configuration) remain alternatives to direct reactions from $S(\pi,\pi^*)$ and $T(\pi,\pi^*)$, respectively. Laser flash measurements in benzene showed that the triplets of all sensitizers used (runs 9–11) were quenched by **1** at similar rates close to diffusion control [$(2.8\text{–}4.2) \times 10^9$ $\text{M}^{-1}\text{s}^{-1}$], and the fall-off in rates with chrysene (E_T 56.6 kcal/mol), 1-acetonaphthone (56), and benzil (50.9) indicates [8] E_T *ca.* 59 kcal/mol for the lowest triplet of **1** in agreement with phosphorescence. Yet, the quantum yields obtained with benzophenone and thioxanthone on one hand and with phenanthrene on the other are distinctly different. The former (runs 9 and 10) coincide with those on direct irradiation at 313 and 405 nm (runs 1 and 5), whereas the latter (run 11) falls into the category of the 436 nm irradiations (runs 6–8). These results place the $T(n,\pi^*)$ state in the range of *ca.* $60 < E_T < 63$ kcal/mol.

With laser flash techniques (λ_{exc} 353 nm) two transients from **1** were detected. One was observed only at < 215 K in isopropyl alcohol, ether/isopentane/ethanol 5:5:2 (EPA), and glycerol triacetate, and it was identified as $T(\pi,\pi^*)$ (τ 3×10^{-8} s at 150 K in EPA). Its absorption spectrum (maxima at 380 and 430 nm) was similar to that of the $T \rightarrow T$ absorption of 2,3-dihydrophenalene. This spectrum disappeared on passing above 215 K in the flash experiments. In its place, a new transient spectrum with a single maximum at 380 nm built up. The same spectrum was observed also in

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⁷) Alternative routes to **8c** and **9c** would involve naphthyl bonding to C(8), followed by an 11(10 → 9) vinyl shift and cleavage of the initially formed bond, or the concerted equivalent thereof. Our experiments do not differentiate between these paths.

⁸) Phosphorescence data measured in EPA and methylcyclohexane glasses. Spectral position and shape of this emission were essentially identical to those of **2** and to the previously published data of 2,3-dihydrophenalene [7].

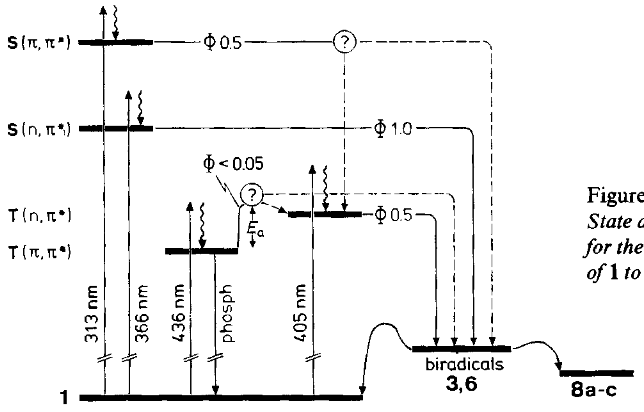

Figure.
State and reaction diagram for the DPM. rearrangement of **1** *to* **8a-c**

benzene at 280-350 K, with τ *ca.* 1.5×10^{-8} s. An excited-state nature of **1** for this species was excluded on the basis of both an extinction coefficient $< 2000\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ at ambient temperature9), and a *Stern-Volmer* slope of only $1.1\ \mathrm{M}^{-1}$ for the quenching of the unsensitized DPM reaction at room temperature with 1,3-cyclohexadiene at 366 nm. The properties of this transient strongly suggest that its observation constitutes direct evidence - which would be the first in a DPM-type rearrangement - that reaction from $S(n,\pi^*)$ involves at least one intermediate such as the proposed biradicals **3** and **5-7**10))11)).

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9) Unity quantum yield of the formation of this species was taken for the determination of the extinction coefficient. Values for ε of $T \rightarrow T$ transitions are significantly greater for, *e.g.*, benzophenone and naphthalene [9].

10) The occurrence of a biradical intermediate has also been observed in preliminary ESR. investigations of **1** (EPA, 77 K, 366 nm).

11) The result correlates with the demonstration by *Zimmerman et al.* [3b] that the independently generated triplet biradical corresponding to **6** preferentially leads to the DPM rearrangement product of 2,3-naphthobarrelene.