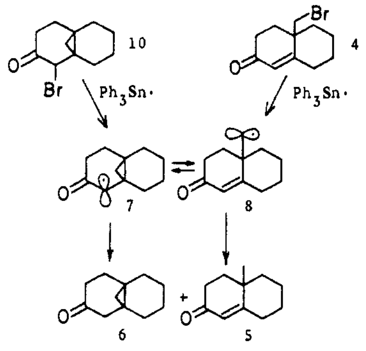
Scheme III. Ground State Generation of Equilibrating Radical Pair 7 and 8 with Ph$_6$Sn$_2$



tochemical efficiencies follow the trend expected for leaving group ability within the ester series.[14]

Scheme II depicts the molecular processes for the electron-transfer and displacement reactions adapted and extended from the original Stork mechanism.[2] The initial intermediate from internal nucleophilic displacement within the semi-enone leads to the α-keto, cyclopropylcarbinyl radical (**7**), an intermediate possessing considerable carbon radical character.[15] By analogy with other unsubstituted cyclopropylcarbinyl radicals, ring opening to the neopentyl radical **8** is expected to be very facile.[16] An alternative mechanism may involve direct formation of **8** from the triplet enone–amine exciplex.

The ring closure process from **8** back to **7** should be considerably more difficult, suggesting a large equilibrium constant for rearrangement ($K_{eq} >> 1$).[17] Hydrogen atom abstraction by **7** or **8** would then complete the reaction sequence to **5** and **6** analogous to an ECC route.[18] Alternatively, under reductive conditions, a subsequent second electron transfer to form the enolate **9**[19] and protonation completes the reaction sequence an ECE mechanism.[18]

In order to test the hypothetical intermediacy of the equilibrating radicals **7** and **8**, we have independently generated each radical from its precursor bromide (**4** and **10**) employing either (n-Bu)$_3$SnH or Ph$_6$Sn$_2$.[20] As illustrated in Scheme III and Table II, both bromides yield the same two products. Furthermore, the ratio of **5** to **6** is a sensitive function of the nature and concentration of the hydrogen atom source, whether it be (n-Bu)$_3$SnH, diethyl ether, isopropyl alcohol, or Et$_3$N$^{\bullet+}$, and the nature of the stannane derivative, clearly demonstrating both the intermediacy of the equilibrating pair of radicals and the hydrogen atom abstraction pathway.

Thus, the dissolving metal reductions from Stork's studies[2] continue to be a successful model for reductive electron-transfer processes as well as the initial stages of the photoinduced process. Of more general interest, however, is the observation that the photochemical reaction provides critical insight into the nature of the chemical reductions and further suggests the need for additional research on the mechanism of the ground-state electron-transfer process. The work here represents our continuing effort toward that goal.

Acknowledgment. The financial support of a research grant from the University of Kansas General Research Fund is gratefully acknowledged. We thank Professor Leo Paquette, The Ohio State University, for the timely suggestion of Ph$_6$Sn$_2$ for the investigations related to the equilibration experiments.

Registry No. 1 OTS, 741-43-5; **1** OMS, 71280-42-7; **1** O$_2$CCF$_3$, 103240-06-8; **1** Br, 103240-07-9; **5**, 826-56-2; **6**, 5689-11-2; **10**, 103240-08-0.

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(12) (a) The lower reduction potential for bromide **4** is in accord with results obtained for other δ-bromo-α,β-unsaturated carbonyl derivatives.[12b] (b) Nugent, S. T.; Baizer, M. M.; Little, R. D. *Tetrahedron Lett.* **1982**, 1339.

(13) The electrochemical and dissolving metal reductions of p-toluenesulfonate esters result in cleavage of the O–S bond to yield the alcohol. In contrast, methanesulfonate esters are not cleaved under similar conditions. Horner, L.; Singer, R.-J. *Chem. Ber.* **1968**, *101*, 3329. Within the 2-octalone series, the 10-propyl-3′-tosylate gave only the alcohol upon treatment with lithium in liquid ammonia.[2b]

(14) Noyce, D. S.; Virgilio, J. A. *J. Org. Chem.* **1972**, *37*, 2643.

(15) The electron density at carbon of a simple α-keto cyclohexyl radical is estimated to be 85% (Camaioni, D. M.; Walter, H. F.; Pratt, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 4057).

(16) A rate constant of 10^6 s^{-1} for ring opening of a cyclopropylcarbinyl radical to a homoallylic radical has been reported (Friedrich, E. C.; Holmstead, R. L. *J. Org. Chem.* **1972**, *37*, 2550).

(17) The equilibrium constant between the α-carbonyl, cyclopropyl radical **7** and the 10-methylene-2-octalone radical **8** can be estimated at $K_{eq} = 10^3$ by using data for the rates for cyclopropylcarbinyl ring opening (10^6 s^{-1})[16] and 10^3 s^{-1} for homoallyl radical ring closure (Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734). This analysis overestimates th K_{eq} value since **8** is stereoelectronically better suited for such a ring closure step whereas the value used for this estimate was obtained for an acyclic homoallyl radical.

(18) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcell Dekker: New York, 1969.

(19) Furthermore, the enolate of **6** is not converted to **5** under the reaction conditions.[3]

(20) (a) Kuivila, H. G.; Pian, C. C. H. *J. Chem. Soc., Chem. Commun.* **1974**, 369. (b) Menapace, L. W.; Kuivila, H. G. *J. Am. Chem. Soc.* **1964**, *86*, 3047.

(21) Russell, G. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Chapter 7, pp 312–313.

Cycloreversion of Quadricyclane Derivative via Triplet State. Adiabatic vs. Biradicaloidal Mechanism

Hideo Nishino, Susumu Toki, and Setsuo Takamuku*

The Institute of Scientific and Industrial Research
Osaka University, 8-1 Mihogaoka
Ibaraki, Osaka 567, Japan

Received December 30, 1985

Photochemically induced interconversion between norbornadiene and quadricyclane has been the focus of considerable attention in connection with the storage of solar energy.[1] A variety of sensitization methods have been applied to the valence isomerization of norbornadiene and its derivatives, including direct photolysis, triplet sensitization, complexation with metal ions, and donor–acceptor interaction.[2]

For triplet excitation, it has been reported that norbornadiene in a triplet state isomerizes efficiently to a ground state of quadricyclane through a biradicaloidal intermediate on the basis of photochemical investigation of the corresponding cyclic azoalkanes.[3] In the present paper, on the other hand, we have found that a naphthalene derivative of quadricyclane isomerizes inversely to the corresponding norbornadiene derivative via the triplet in a very high yield, and the cycloreversion has been substantiated to be an adiabatic process by convincing experimental supports. Furthermore, it might be pointed out that the conformation of the olefinic moiety of the norbornadiene in the relaxed triplet state, i.e., planar or twisted, is one of the important factors which control the reaction mechanism, i.e., adiabatic or biradicaloidal.

Benzophenone(BP) sensitization of NN and QN has been carried out by a nanosecond pulse radiolysis of the degassed benzene solution.[4,5] The transient absorption spectra recorded

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(1) Jones, G., II; Chiang, S.-H.; Thanh Xuan, P. T. *J. Photochem.* **1979**, *10*, 1. Scharf, H.-D.; Fleischhauser, J.; Leisman, H.; Ressler, I.; Schleker, W.; Weitz, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 652.

(2) Hammond, G. S.; Wyatt, P.; DeBoer, C. D.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, *86*, 2532. Roquitte, B. C. *J. Phys. Chem.* **1965**, *69*, 2475. Kaupp, G.; Prinzbach, H. *Chimica* **1968**, *22*, 502. Kaupp, G.; Prinzbach, H. *Liebigs Ann. Chem.* **1969**, *725*, 52. Johns, G., II; Schwarz, W.; Malla, V. *J. Phys. Chem.* **1982**, *86*, 2286. Kaupp, G.; Prinzbach, H. *Helv. Chim. Acta* **1969**, *52*, 956. Schwarz, W.; Dangel, K.-M.; Jones, G., II; Bargon, J. *J. Am. Chem. Soc.* **1982**, *104*, 5686. Yoshida, Z. *J. Photochem.* **1985**, *29*, 27. Ingen, J. W. F.; Tiegem, C. H. C.; Cramer, W. A. *J. Chem. Phys.* **1970**, *53*, 3665.

(3) Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7388. Turro, N. J.; McVey, J.; Ramamurthy, V.; Lechtken, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 572.

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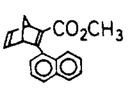
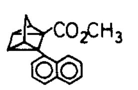
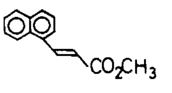
at various times after an 8-ns pulse irradiation are shown in Figure 1, along with those of related compounds, **1** and **2**



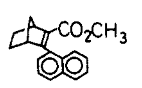
NN



QN



1



2

In both systems, a transient absorption band with λ_{max} at 530 nm, which is assigned to a BP triplet, was observed immediately after the pulse. The T–T absorption band of BP decays according to a pseudo-first-order kinetics followed by a simultaneous formation of a 500-nm band in both systems.[6] The reciprocal lifetime of the T–T absorption band of BP at 540 nm was plotted against the concentration of NN or QN in order to obtain the second-order rate constant of the triplet energy transfer; $k(^3\mathrm{BP}^* + \mathrm{NN}) = 2.0 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, $k(^3\mathrm{BP}^* + \mathrm{QN}) = 1.8 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, respectively. The lifetime of the 500-nm band from NN and QN was identical within experimental error (NN, 5.6 μs, and QN, 5.9 μs), suggesting the formation of a common intermediate.

Methyl *trans*-3-(1-naphthyl)propenoate(**1**) provided a T–T absorption band, λ_{max} 480 nm with a lifetime of 4.2 μs. A naphthylnorbornene derivative **2**, which is a cisoid planar model of **1**, also gave completely the same spectra to that of **1**, λ_{max} 480 nm but a longer lifetime, 16 μs. The longer lifetime of **2** is reasonably explained by the constraints which affect the capability of the triplet to twist about the double bond.[7,8] These observations suggest that the stable conformation of the triplet state of a naphthylethylene moiety is a planar transoid at the olefinic double bond, and a rigid planar cisoid also provides the similar absorption band with a longer lifetime due to the restriction. The fact is consistent with the findings by Tokumaru and his co-workers.[9]

The similarity of the 500-nm band obtained from NN and QN to the T–T absorption bands of **1** and **2** which are the model compound of NN indicates that the 500-nm band can be assigned to a triplet state of NN. The 20-nm red shift of the 500-nm band may be caused by the interaction with the proximately faced double bond.

Further evidences which support the above conclusion are obtained: (a) The 500-nm band can be quenched at nearly the same rate starting from either isomer by the following quenchers: oxygen (k_q, NN 2.2×10^9; QN $1.8 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$), perylene ($E_T$ = 35.1 kcal/mol, k_q, NN 2.9×10^9; QN 2.3×10^9), and azulene (E_T = 39.8 kcal/mol, k_q, NN 1.5×10^9; QN 2.0×10^9). Since the quenching was not observed by pyrene with a high E_T value (48.2 kcal/mol), the available triplet energy of the transient species, that is, the energy gap between the relaxed T_1 and S_0 surface was estimated to be around 40 kcal/mol. The fact excludes the possibility of the species to be a 1,3-biradicaloidal intermediate. (b) Upon γ-irradiation to a benzene solution of QN (1×10^{-4}M), isomerization of QN to NN took place with a high efficiency; the 100-eV yield for the isomerization (QN to NN) was 3.3 while the reverse reaction (NN to QN) was not detected under the similar reaction conditions.[10]

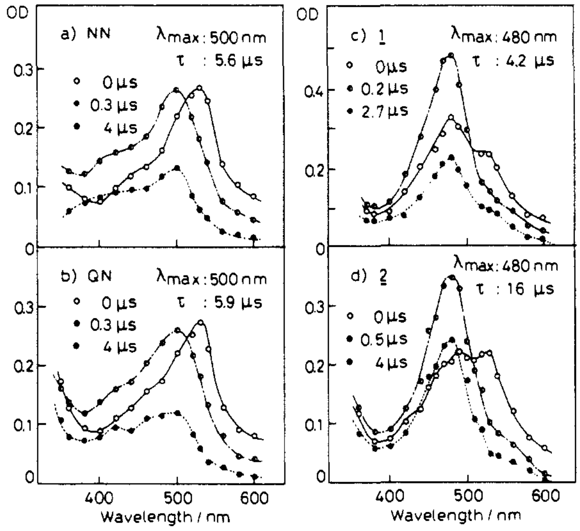


Figure 1. Transient absorption spectra obtained at various times after an 8-ns pulse irradiation of benzene solutions of (a) benzophenone (20 mM) and NN (1 mM), (b) benzophenone (20 mM) and QN (1 mM), (c) benzophenone (21 mM) and **1** (2 mM), and (d) benzophenone (20 mM) and **2** (1 mM) at room temperature. Absorbed dose was 0.57 kGy per pulse.

Table I. Rate Constants for the Triplet Energy Transfer from Various Sensitizers to NN and QN in Benzene

sensitizer	λ,[a] nm	E_T,[b] kcal mol^{-1}	k_q, M^{-1} s^{-1} NN	k_q, M^{-1} s^{-1} QN
benzophenone	540	68.6	2.0×10^9	1.8×10^9
biphenyl	370	65.7	1.9×10^9	1.6×10^9
naphthalene	420	60.9	1.7×10^9	8.6×10^8
1-methylnaphthalene	420	59.6	1.5×10^9	6.8×10^8
acenaphthene	420	59.2	1.5×10^9	6.0×10^8
p-terphenyl	420	58.4	1.3×10^9	6.0×10^8
fluoranthene	420	54.2	5.2×10^8	1.2×10^7

[a] Triplet monitoring wavelengths. [b] Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970.

On the basis of the above experimental observations one can conclude an adiabatic cycloreversion via the triplet state. The efficiency of the reaction presumed to be very high from the γ-radiolysis and also the results of Figure 1, that is, the yield of the NN triplet obtained by the T–T absorption spectra in the BP sensitization of QN was identical with that of NN, indicating that the isomerization is quantitative ($^3\mathrm{QN}^* \rightarrow {}^3\mathrm{NN}^*$, $\phi = 1.0$).

Although a few adiabatic cycloreversion via a singlet excited state have been previously reported,[11] triplet states of arylcyclobutanes are normally expected to undergo diabatic cycloreversion via a 1,4-biradical intermediate.[12] Thus, the present observation seems to be a novel and exceptional case.[13]

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(4) The L-band linear accelerator at Osaka University was used as the source of electron pulse. The energy was 28 MeV and the pulse width was selected as 8 ns. The dose was 0.74 kGy per pulse. A 450-W xenon pulse lamp (OPG-450, Osram), a monochromater (Nikon G-250), a photomultiplier (R 928), and a programmable digitizer (Tektronix 7912 AD) were used. NN was synthesized by Diels–Alder reaction of cyclopentadiene and methyl 3-(1-naphthyl)propiolate (bp 122–123 °C (0.07 torr)), which was synthesized by the method of Wojack et al. (Wojack et al. *Chem. Ber.* **1938**, *71*, 1372), in a stainless steel autoclave at 150 °C for 27 h in benzene, and was purified by column chromatography on silica gel (mp 94.5–95 °C). QN was obtained by the photolysis of NN in acetonitrile through a Pyrex filter and was recrystallized from hexane (mp 112.5–113 °C). **1** was synthesized by the method of Koe et al. (Koe et al. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 327) and **2** was obtained by the hydrogenation of NN with palladium on charcoal in ethanol and was recrystallized from hexane (mp 105.5–106.0 °C). The spectral data of NN, QN, **1**, and **2** are consistent.

(5) It has been well established that pulse radiolysis of an aromatic liquid such as benzene or toluene produces significant yields of triplet of the solute (Kitamura, T.; Toki, S.; Takamuku, S.; Sakurai, H. *Chem. Lett.* **1980**, 145. Gorman, A. A.; Gould, I. R.; Hamblett, I. *J. Am. Chem. Soc.* **1981**, *103*, 4533. Reference 8).

(6) Without benzophenone the similar absorption spectra with λ_{max} 500 nm and $\tau = 6.0 \pm 0.1$ μs was also obtained immediately after the pulse.

(7) Caldwell, R. A.; Singh, M. *J. Am. Chem. Soc.* **1982**, *104*, 6121. Caldwell, R. A.; Cao, C. V. *J. Am. Chem. Soc.* **1982**, *104*, 6174.

(8) Gorman, A. A.; Hamblett, I.; Irbine, M.; Raby, P.; Standen, M. C.; Yeates, S. *J. Am. Chem. Soc.* **1985**, *107*, 4404.

(9) Arai, A.; Sakuragi, H.; Tokumaru, K.; Sakaguchi, Y.; Nakamura, J.; Hayashi, H. *Chem. Phys. Lett.* **1983**, *98*, 40.

(10) Benzene solutions of QN and NN (1×10^{-4} M) were irradiated with a ^{60}Co γ-ray source up to a dose of 0.49 kGy at room temperature. The changes of UV absorption spectra after irradiation were analyzed by a Hitachi-323 spectrophotometer in order to determine the interconversion.

(11) Yamamoto, S.; Hoshino, M.; Imamura, M. *Chem. Phys. Lett.* **1983**, *98*, 615. Smothers, W. K.; Saltier, J. *J. Am. Chem. Soc.* **1983**, *105*, 2794. Hasegawa, E.; Okada, K.; Mukai, T. *J. Am. Chem. Soc.* **1984**, *106*, 6852.

(12) Takamuku, S.; Schnabel, W. *Chem. Phys. Lett.* **1980**, *69*, 399. Kohashi, T.; Ikawa, H.; Kondo, R.; Morita, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3013.

(13) As adiabatic reactions of triplet states, photoisomerization of anthrylethylenes (Karatsu, T.; Arai, T.; Sakuragi, H.; Tokumaru, K. *Chem. Phys. Lett.* **1985**, *115*, 9) and photocyclization of 2-vinylbiphenyls (Lazare, S.; Lapouyade, R.; Bonneau, R. *J. Am. Chem. Soc.* **1985**, *107*, 6604) have been reported.

An adiabatic reaction is expected only when the reaction is exothermic and no large energy barrier is present between the reactant and the product. In order to confirm the exothermicity of the reaction, the triplet energies of NN and QN were estimated by the measurement of the rate constants for the triplet energy transfer from various sensitizers to NN and QN by the similar pulse radiolysis technique. Although the precise consideration of the energy-transfer mechanism is under progress, the results shown in Table I make possible the estimation of the triplet energies of NN and QN, which are approximately 56 and 60 kcal/mol, respectively. Considering the strain energy of QN, which is estimated to be about 22 kcal/mol on the analogy to that of quadricyclane, the present cycloreversion of the triplet QN becomes exothermic by about 26 kcal/mol.

Now, let us consider the factors which control the reaction mechanism, adiabatic or biradicaloidal. In the case of a norbornadiene (N)–quadricyclane (Q) system, a 1,3-biradicaloidal species was estimated as the most stable common intermediate although the isomerization from Q to N is exothermic by 10 kcal/mol. The most distinguished difference between norbornadiene (N) and the naphthalene derivative (NN) is the conformation of the relaxed triplet state of the olefinic moiety. The most stable conformation of the triplet of simple olefins is twisted and the spin densities are localized at the olefinic double bond. Therefore, the olefinic double bond in the N triplet is also twisted and reactive to the other, proximately faced double bond giving a 1,3-biradical intermediate through the addition reaction. On the other hand, the naphthylethylene moiety of NN triplet is mainly planar at the relaxed state, thus the reactivity of the olefinic carbon atoms is reduced owing to the delocalization of the spin density to the naphthyl group. Thus, the NN triplet becomes the most stable form of the possible isomers.

Such a consideration of the conformation–reactivity relations of triplet olefins may lead to a better understanding of the potential energy surface of the reaction. Further investigation is in progress.

Acknowledgment. We are grateful to the members of the Radiation Laboratory of this institute for their running the linear accelerator. We are also indebted to the members of the Material Analysis Center of this institute for the analysis of the materials used.

Retinal and Rhodopsin Analogues Directed toward a Better Understanding of the H.T.-*n* Model of the Primary Process of Vision[†]

A. E. Asato, M. Denny, and R. S. H. Liu*

Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822

Received February 10, 1986

Consideration of the effect of the medium (protein) on the direction of photoisomerization of polyenes has led to the proposal of a new mechanism for geometric isomerization,[1] which involves simultaneous rotation of two adjacent formal single and double bonds resulting in conformational as well as configurational isomerization. This process requires a small reaction volume, therefore it is particularly suitable for isomerizations in restricted cavities such as protein binding sites. Hence, it was shown that the process is compatible with all published experimental facts concerning the primary processes of vision[1] and bacteriorhodopsin.[2,3] This mechanistic process[1,2] has been dubbed H.T.-*n* (hula-twist at center *n*, also known as C.T.-n, concerted twist at center n).[1,2]

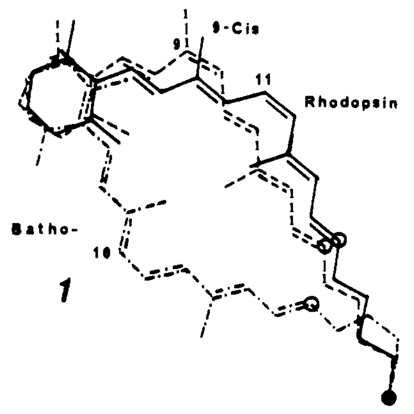
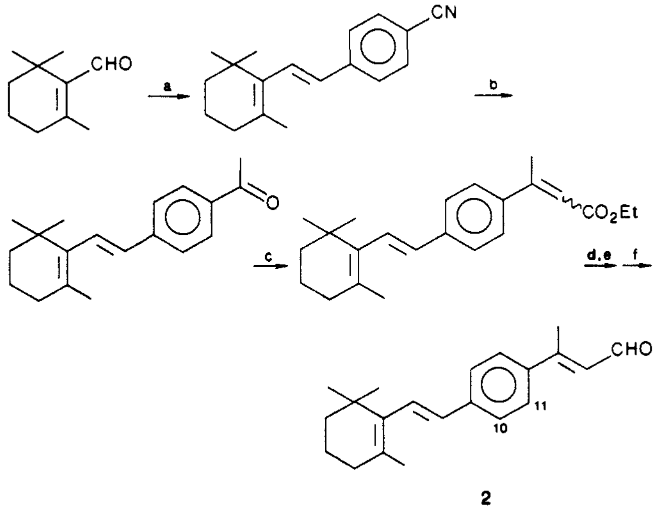


Figure 1. H.T.-*n* model for the primary processes of vision.[1,2] The 11-*cis*-retinylidene chromophore of rhodopsin (—) bonded to the butyl amine of Lys-296 via a protonated Schiff base linkage. The imino nitrogen is marked by a circle. Its photochemical conversion to bathorhodopsin (---), or the reverse, can be accomplished by the H.T.-11 process, i.e., concerted rotation of the 10,11- and the 11,12-bonds. The conversion of 9-*cis*-rhodopsin (---) to bathorhodopsin, or the reverse, can be accomplished by the H.T.-10 process, i.e., concerted rotation of the 9,10- and 10,11-bonds. It should be emphasized that only the substituent on carbon *n* is transposed from one side of the polyene chain to the other in such a H.T.-*n* process.

Scheme I



[a](a) LDA in THF; *p*-cyanobenzylphosphonate; (b) MeMgCl/THF reflux; (c) $Me_3SiCH_2CO_2Et$, LDA/THF-hx; (d) DIBAL; (e) MnO_2; (f) preparative HPLC.

Some of the important consequences from applying the H.T.-*n* process to vision are summarized in Figure 1. The chromophore of the primary photoproduct bathorhodopsin has the all-trans,10-s-cis structure 1. Photochemical interconversions of the 11-cis and the 9-cis chromophores by way of bathorhodopsin[4] proceed via the H.T.-11 and H.T.-10 processes. We have now carried out a study of several ring-fused retinal analogues designed to test these implications.

All analogues involve minor structural modifications, adding no more than two carbon atoms. First, the aromatic retinal

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[†] Bioorganic Studies of Visual Pigment Analogues. 5. For previous paper in the series, see: ref. 9.

(1) Liu, R. S. H.; Asato, A. E. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 259–263.

(2) (a) Liu, R. S. H.; Mead, D.; Asato, A. E. *J. Am. Chem. Soc.* **1985**, *107*, 6609–6614. (b) Liu, R. S. H.; Browne, D., *Acc. Chem. Res.* **1986**, *19*, 42–48.

(3) Recent vibrational spectroscopic studies reached opposite conclusions concerning the conformation of the retinyl chromophore in the primary photoproduct: (a) Smith, S. O.; Hornung, I.; van der Steen, R.; Pardoen, J. A.; Braiman, M. S.; Lugtenburg, J.; Mathies, R. A. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 967–971. (b) Gerwert, K.; Siebert, F. *EMBO J.* **1986**, *5*, 805–811.

(4) Yoshizawa, T.; Wald, G. *Nature (London)* **1963**, *197*, 1279–1286.