Communications

Unusual Photocyclization of a Naphthalene–Diphenylethylene Bichromophore. 1,2-Hydrogen Migration in a 1,4 Diradical

Summary: The naphthalene–diphenylethylene bichromophore **1** undergoes photochemical cyclization to cyclopropane derivative **8** by a process which appears to involve an unusual hydrogen migration in a 1,4 diradical.

Sir: Apart from cis–trans isomerization, the most prevalent intramolecular photochemical reaction of the β-alkylstyrenes and -1,1-diphenylethylenes which we have examined is cyclopropane formation via the 1,2-migration of a γ substituent to the β carbon;[1,2] in certain β-alkyldiphenylethylene cases a rare 1,2-vinyl hydrogen shift predominates.[3] We now report results of an investigation of the photochemistry of the bichromophoric molecule 4-methyl-4-(1-naphthyl)-1,1-diphenylpentene (**1**). The principal locus of electronic excitation in the lowest excited singlet state of **1** should be the naphthalene portion of the molecule. By contrast, in the other compounds investigated[1,3] the excitation energy was concentrated in the aryl olefin grouping. We find that (1) this change is accompanied by a marked change in photochemical behavior from that of the previous systems studied,[1–3] and (2) the reaction of **1** appears to involve an unusual conversion of a 1,4 diradical to a cyclopropylmethyl derivative via hydrogen migration.

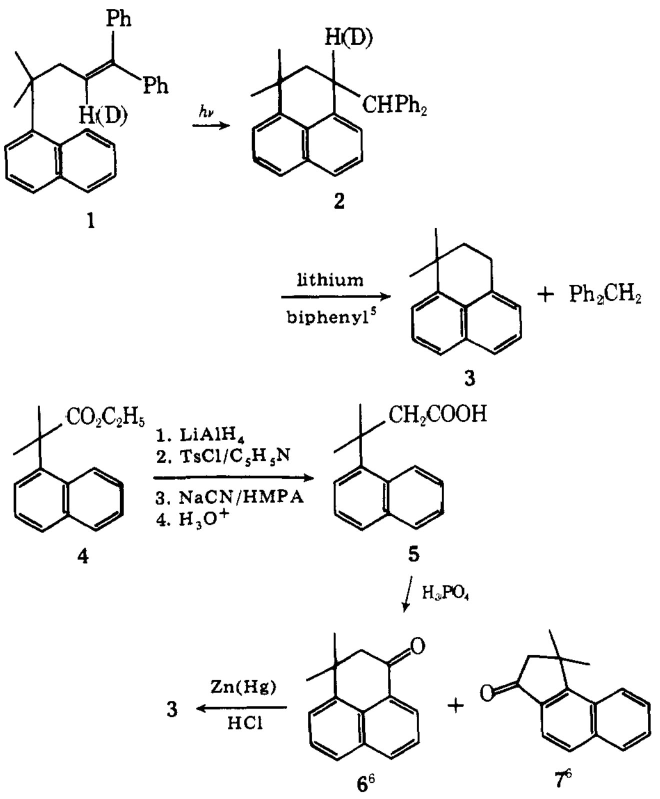
Irradiation[4] for 2 h of a solution of 0.520 g of **1** in 110 mL of cyclohexane resulted in the complete disappearance of **1** and the formation of one major product isolated in 60% yield. (See paragraph at end of paper regarding supplementary material.) The NMR spectrum of this product suggested either the 1,8-cyclized compound **2** or the analogous product in which cyclization had occurred at the 2 position of the naphthalene ring instead. That **2** was indeed the correct structure of the photoproduct was determined as outlined in Scheme I.

To aid in mechanistic studies **1d** containing >95% deuterium at C-2 was prepared and irradiated. NMR analysis of the resulting **2d** revealed that no migration of the deuterium had occurred in the transformation **1** → **2** (Scheme I). Thus, in contrast to the photochemistry of the 4-phenyl analogue of **1**,[3b] irradiation of **1** does not result in migration of a vinyl hydrogen. Benzophenone-sensitized irradiation of **1** gave no discernible product formation.

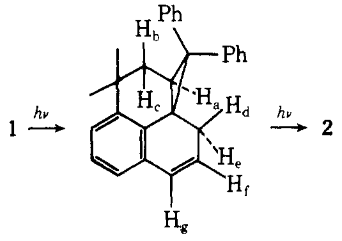
Though **2** was the only product isolated from **1** in our initial photolyses, analyses of reaction solutions obtained after photolysis of **1** for very brief periods revealed the transient appearance and disappearance of another compound. This thermally labile compound never comprised more than ~10% of the reaction mixture, a result of its efficient further photochemical transformation to **2**. However, by careful chromatography of product mixtures resulting from short periods of irradiation of several samples of **1** we were able to isolate sufficient quantities of pure intermediate, mp 138.8–139.5 °C, to permit characterization.

The UV spectrum of the intermediate showed a broad, unstructured long wavelength absorption band having λ_{max} at ~270 nm (ε 5550) on the edge of a stronger band having λ_{max} at 239 nm. The transformation of the naphthalene chromophore of **1** to a 1,2-dihydronaphthalene structure was thereby indicated.[7] The mass spectrum (80 eV) showed a parent ion at *m/e* 362 (rel intensity 6) and a base peak at *m/e* 169 (M − Ph$_2$CCHCH$_2$). These data, together with the fact that irradiation of the intermediate provided **2** in ~80% yield, suggested the compound to be either cyclopropane **8** or cyclobutane **9**. The formation of cyclobutane adducts through both inter-[7a,8] and intramolecular[7b] photochemical reactions of naphthalene derivatives with olefins has been noted frequently in the recent literature.

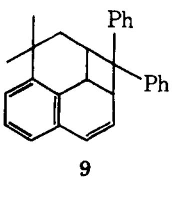
Scheme I



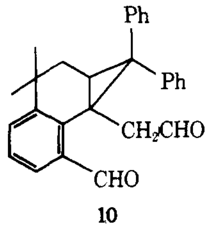
However, 270-MHz NMR analysis revealed the transient compound to have the more unusual structure **8**. The NMR spectrum showed δ 1.03 (s, 3, CH$_3$), 1.20 (s, 3, CH$_3$), three 1 H dd's at 2.33 (*J* = 4.3, 10.3 Hz), 1.78 (*J* = 4.3, 13.0 Hz), and 2.09 (*J* = 10.3, 13.0 Hz) assigned to H$_{a-c}$,[9] a 1 H dd at 1.61 (*J* = 17.3, 5.9 Hz) and a 1 H d (each peak of which is a poorly defined apparent triplet) at 2.58 (*J* = 17.3 Hz) arising from H$_d$ and H$_e$,[9] 5.97 (m, 1, H$_f$), 6.73 (dd, 1, H$_g$, *J* = 10.0, 2.5 Hz), and



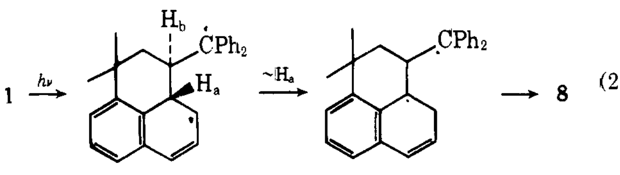
8 (1)



9



10



11 (2)

6.80–7.43 (m, 13, arom) ppm. Particularly noteworthy points about this spectrum are (a) H_{a-c} are coupled to each other but show no observable coupling to any other hydrogens, and (b) the large coupling constant (17.3 Hz) between H_d and H_e indicates that they are geminal.[10]

Chemical evidence that the product isolated does have structure **8** was provided by its ozonolysis to a dialdehyde (**10**), the NMR spectrum of which showed two distinctive aldehyde signals: a singlet at δ 10.67 and a doublet of doublets ($J = 2.2$, 2.5 Hz) at 9.15. (We did not isolate **10** in pure form; the NMR spectrum was taken of the crude ozonolysis reaction product.) The dialdehyde that would be obtained from **9** would not show this splitting pattern for the aldehyde hydrogens. Structure **8** is the one compatible with all our evidence.

The most likely pathway for the formation of **8** from **1** involves initial bonding between C-8 of the naphthalene ring and C-2 of the double bond to form 1,4 diradical **11** followed by hydrogen migration and ring closure (eq 2).[11] We note, though, that such a mechanism ascribes exceedingly novel behavior to **11**, for the normal modes of reaction of 1,4 diradicals are either fragmentation to olefins or cyclization to cyclobutanes.[12,13] However, inspection of molecular models helps to elucidate why such an unusual reaction course is followed in the present case. Thus, the sterically most favorable mode of initial vinyl–naphthyl bonding is that which results in diradical **11** having H_a and H_b trans to each other. Closure of **11** to a cyclobutane would involve considerable strain; the p orbitals which must join to form the four-membered ring cannot become optimally aligned for bonding. Likewise, fragmentation of **11** to **1** is hindered by poor overlap between the newly formed bond and the p orbital on C-7 of the naphthalene ring; cleavage to starting olefin therefore does not totally dominate the chemistry of **11**.[14] On the other hand, in **11** the bond to H_a on the naphthalene C-8 is nearly parallel to the adjacent p orbital on C-7, an arrangement optimal for migration of this hydrogen. Thus with the normal fragmentation and cyclization processes hindered, an unusual hydrogen migration prevails.

The migration of hydrogen to an adjacent radical center such as that postulated in eq 2 has not been observed to occur in monoradicals.[15,16] In the present case, however, we are dealing with a diradical, and the following points should be noted. (1) The conversion of **11** to **8** may be a concerted process—the homologue of the commonly observed conversion of a 1,3 diradical to an olefin.[17] Simultaneous carbon–carbon bond formation would lower the normally high barrier to migration. (2) The ^1S state of a diradical species such as **11** has considerable zwitterionic character.[18] It is possible that a polarization[19] of **11** in its ^1S state considerably enhances hydrogen migration relative to a similar migration in a monoradical.

The high yield, facile conversion of cyclopropane **8** to **2** is not unusual. Analogous reactions have been found by Griffin and others to occur with good efficiency upon irradiation of numerous 2-alkylarylcyclopropanes.[2b,20]

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Supplementary Material Available. The experimental details of this work (13 pages). Ordering information is given on any current masthead.

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(2) The first examples of the 1,2 shifts that we have studied were provided by Griffin; see, e.g., (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Close, *J. Am. Chem. Soc.*, **87**, 1410 (1965); (b) H. Kristinsson and G. W. Griffin, *ibid.*, **88**, 378 (1966); (c) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *tetrahedron Lett.*, 2951 (1965).

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(4) A Hanovia 450-W medium-pressure mercury arc, equipped with a Corex filter, was used.

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(6) Ketones **6** and **7** (Scheme I) were readily differentiated on the basis of their UV and IR spectra; see D. G. Hawthorne and Q. N. Porter, *Aust. J. Chem.*, **19**, 1909 (1966), and N. H. Cromwell and G. V. Hudson, *J. Am. Chem. Soc.*, **75**, 872 (1953).

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(9) We have not assigned signals to the individual hydrogens H_a, H_b, and H_c or to H_d and H_e.

(10) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds", Wiley, New York, N.Y., 1967, pp 131 ff; L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, New York, N.Y., 1969.

(11) The reaction could well involve prior formation of an intramolecular exciplex; however, we have no evidence for such exciplex formation. The fluorescence spectrum (room temperature, cyclohexane) of **1** is identical with that of 2-methyl-2-(1-naphthyl)-propan-1-ol (**13**), though the emission quantum yield of **1** is only 30% of that of **13** (nondegassed samples).

(12) See, e.g., (a) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971); (b) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, J. M. McGrath, H. N. Schott, and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 7506 (1972).

(13) Disproportionation via 1,5-hydrogen transfer is a major process of 1-hydroxy 1,4 diradicals.[12b]

(14) Diradical **11** may well undergo reversion to **1**; such a process would not be detected. However, the transformation of **1** to **8** is qualitatively an efficient one. This efficiency is indicative of some difficulty in the cleavage process.

(15) One may regard the process shown in eq 2 as a [1,6] as well as a [1,2] shift of hydrogen to a radical center.

(16) J. W. Wilt, in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 378.

(17) R. G. Bergman, in ref 16, p 191.

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A Synthesis of Betalamic Acid

Summary: N-Benzylnorteloidinone (**6**) available by Robinson–Schöpf synthesis was converted to the ortho ester **7** with methyl orthoformate; catalytic debenzylation followed by addition of allylmagnesium bromide gave **9** which was transformed to the *O*-benzoylhydroxylamine **10** with benzoyl peroxide; acetylation and deprotection gave diol **12**, which on two consecutive oxidations furnished the aldehyde **14**; betalamic acid dimethyl ester was obtained from **14** by oxidation with lead tetracetate in methanol; and the latter was converted to betanidin trimethyl ester following a known procedure.