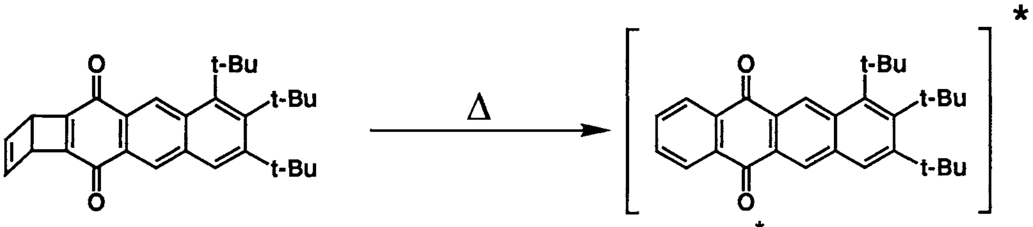
CHEMISTRY LETTERS, pp. 65-68, 1992.

Chemiexcitation of Naphthacenequinone Derivative *via* the Thermal Cycloreversion of the Corresponding *hemi*-Dewar-naphthacenequinone

Sadao MIKI,* Osamu KOBAYASHI, Hiroyuki KAGAWA,
Zen-ichi YOSHIDA,* and Hiroshi NAKATSUJI*
Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606

7,8,9-Tri-t-butyl-1,4-Dewar-5,12-naphthacenequinone (**1**) was synthesized. Upon thermolysis of **1** the formation of the detectable amount of naphthacenequinovalene (**3**) was observed. Singlet excited state of 7,8,9-tri-t-butyl-5,12-naphthacenequinone produced *via* the thermal cycloreversion of **1** is responsible for the formation of **3**.

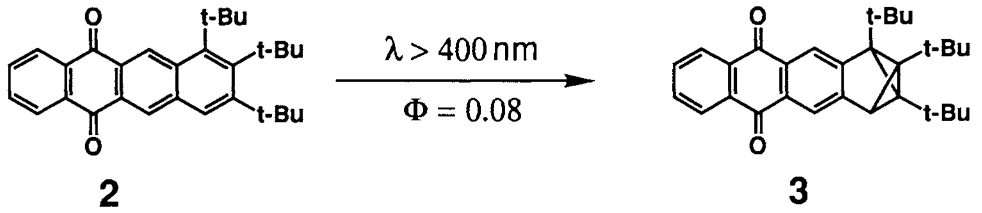
Formation of triplet benzene in the thermolysis of Dewar-benzene reported by Turro, Breslow and their co-workers[1a)] is the prototype example of a simple unimolecular chemiexcitation. In the series of our study on the light energy storage based on photosynthesis of strained molecules,[2)] we have been interested in this intriguing class of nonadiabatic valence isomerization as a type of releasing strain energy. In this context we have studied on the chemiexcitation in the thermal rearrangement of 7,8,9-tri-t-butyl-1,4-Dewar-5,12-naphthacenequinone (**1**), Eq.1.



1 **2***

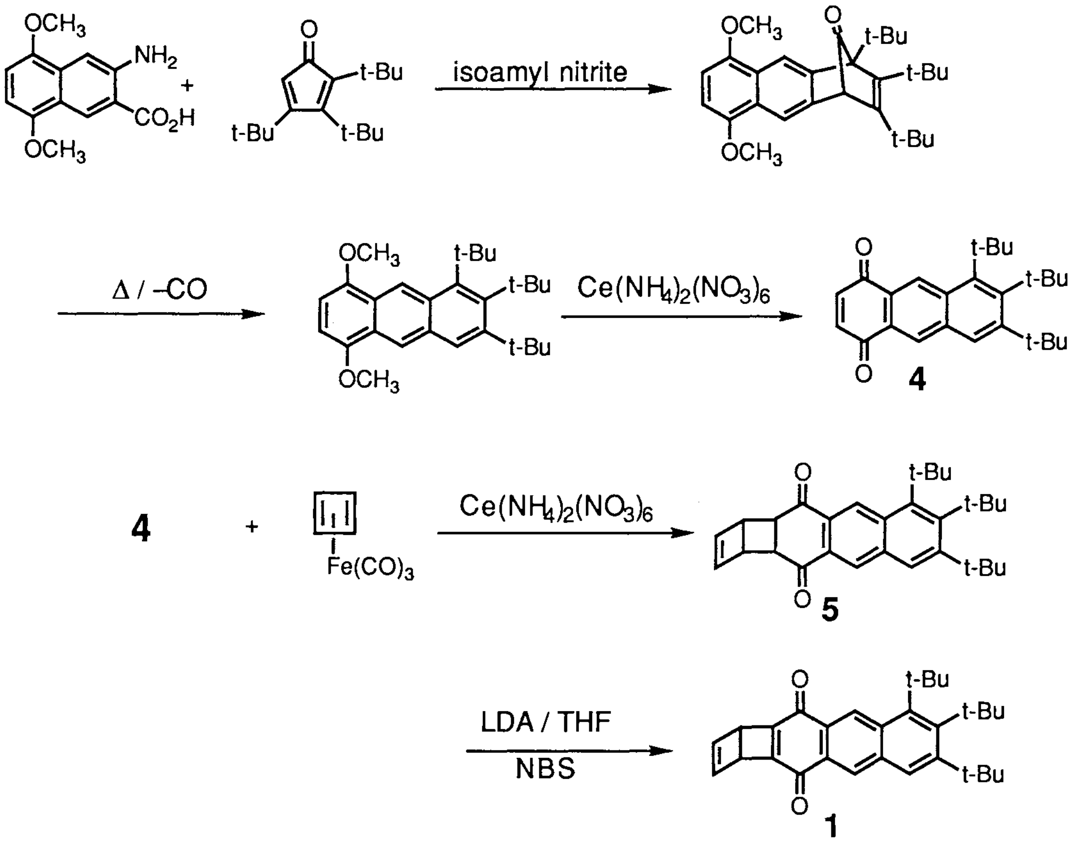
(1)

In the case of the rearrangement of Dewar-benzene the population of singlet excited benzene is not allowed by energetic constraint. The thermolysis of **1**, on the other hand, is anticipated to release *ca.* 334 kJ/mol[3)] in activation and reaction enthalpy. This amount of energy is sufficient to yield the singlet state of **2**. Thus the system of Eq.1 possesses the following characteristic feature : (1) both the S_1 and T_1 of the valence isomer (**2**) possess a lower energy content than the transition state for the thermal isomerization; (2) although not very strong the valence isomer fluoresces upon excitation; (3) as mentioned later, excited singlet state of **2** is reactive to give tri-t-butyl-naphthacenequinovalene (**3**), Eq.2. The features of (2) and (3) are also different from the previously studied cases.[1)] Thus, the formation of the singlet excited state of **2** could be expected *via* nonadiabatic isomerization of **1**, and it might be detectable by the direct chemiluminescence and/or by the formation of **3**.



(2)

The *hemi*-Dewar-naphthacenequinone was synthesized according to Scheme 1. The addition of cyclobutadiene released from its iron carbonyl complex to 5,6,7-tri-t-butyl-1,4-anthraquinone (**4**) afforded 2,3-dihydro-2,3-cyclobuteno-5,6,7-tri-t-butyl-1,4-anthraquinone (**5**) in quantitative yield. The oxidation of the dianion generated by the treatment of **5** with LDA gave **1**.4) Special cautions were paid to prevent photolysis of reaction materials by ambient light, and all the synthetic procedures were performed in a dark room under a red safety lamp by using apparatus made of colored glass. Especially, **5** was rigorously purified prior to use in the last step. Tri-t-butylnaphthacenequinone (**2**) was prepared by the reaction of 2,3,4-tri-t-butylcyclopenta-2,4-diene-1-one with 2-amino-3-carboxyanthraquinone in the presence of isoamyl nitrite followed by decarbonylation. Spectroscopic data for the key compounds are summarized in Table 1.



Scheme 1.

Table 1. Melting points, ^{1}H-NMR and mass spectroscopic data of **1**, **2**, **3** , and **5**

Compounds	Mp	^{1}H-NMR (CDCl$_3$)$^{a)}$	Exact MS
	°C	δ ppm (TMS)	m/z $M^{+\cdot}$ (calcd)
1	---b)	8.96 (1H, s), 8.28 (1H, s), 7.57 (1H, s) 6.60 (2H, br.s), 4.47 (2H, br.s) 1.67 (9H, s), 1.46 (9H, s), 1.38 (9H, s)	---c)
2	223	9.26 (1H, s), 8.56 (1H, s) 8.41-8.31 (2H, m), 7.86-7.72 (2H, m) 7.65 (1H, s), 1.73 (9H, s), 1.51 (9H, s) 1.40 (9H, s)	426.25313 (426.25602)
3	218 (dec.)	8.38-8.23 (2H, m), 8.14 (1H, s) 7.81-7.70 (2H, m), 7.85 (1H, s) 2.38 (1H, s), 1.56 (9H, br.s) 1.23 (18H, s)	426.25650 (426.25602)
5	145	9.04 (1H, s), 8.36 (1H, s), 7.59 (1H, s) 6.17 (2H, m), 3.98 (2H, m), 3.84 (2H, m) 1.69 (9H, s), 1.47(9H, s), 1.35 (9H, s)	428.26879 (428.27168)

a) Measured at 90 MHz b) see Ref. 4. c) The *hemi*-Dewar-naphthacenequinone is too thermolabile to vaporize without isomerization in mass chamber.

Irradiation of the degassed solution of **2** in chloroform with a high pressure Hg-lamp coupled with a Toshiba L 42 glass filter (>420 nm) gave the naphthacenequinovalene (**3**) in quantitative yield. The quantum yield for the photochemical formation of **3** from **2** was determined to be 0.08.

Thermolysis of **1** was performed in a degassed CDCl$_3$ solution sealed in an NMR sample tube in dark at 30 °C for 12 h. Direct ^{1}H-NMR analysis at 400 MHz revealed that the starting material disappeared completely and two products appeared, small amount of tri-t-butylnaphthacenequinovalene (**3**) in addition to the main product **2**. The formation of **3** indicates the existence of nonadiabatic chemiexcitation process in the cycloreversion of **1**. Although attempts to determine the absolute yield of **3** were unsuccessful, it was estimated to be not less than 0.1% judging from the comparison of the ^{1}H-NMR signals for t-butyl protons of **3** with those of **2**. Based on this value and the quantum yield (0.08) for the photoreaction (Eq.1), the efficiency of the chemiexcitation to produce excited state of **2** responsible for the formation of **3** is estimated to be not less than 1%. As shown in Fig.1, fluorescence of **2** can be observed by usual measurement. However, attempts to detect chemiluminescence under thermolysis of **1** were unsuccessful. The photochemical reaction of Eq.1 could not be quenched with triplet quenchers such as cyclohexadiene,anthracene and trans-stilbene. On the other hand, the fluorescense of **2** was quenched by N,N-dimethylaniline with $k_q\tau$=2.5 M^{-1}, and correspondingly the reaction of Eq.1 was quenched in the same condition. These results suggest that **3** is produced *via* the singlet excited state of **2**. Thus it seems likely that the singlet excited state of **2** is produced *via* nonadiabatic valence isomerization of **1**.

Further studies including a theoretical treatment of the reaction are in progress.

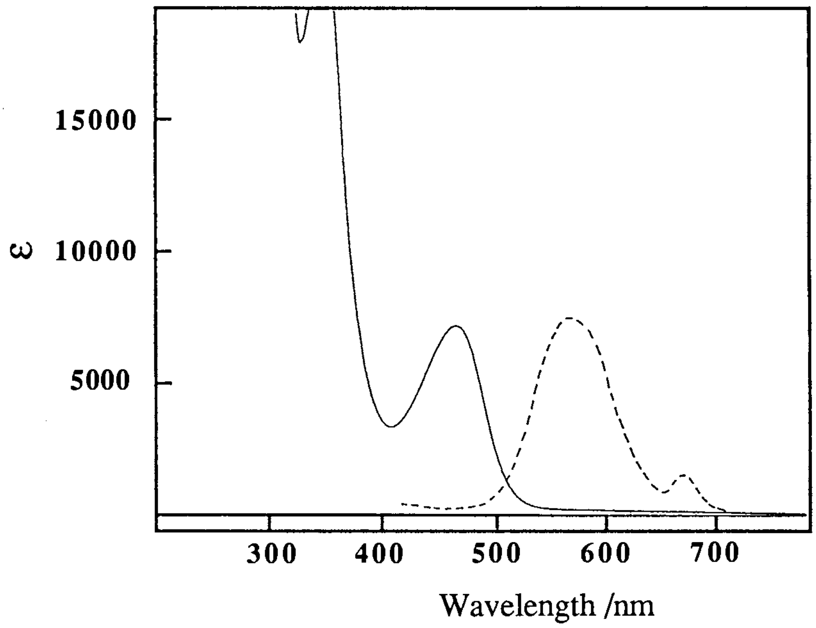


Fig. 1. Absorption (—) and emission (---) spectra of **1** in acetonitrite.

The present work is supported by a Grant-in-Aid Scientific Research on Priority Area from Ministry of Education,Science and Culture Japan, Project 02203234 and Project 03203238.

References

1) a) P. Lechtken, R. Breslow, A.H. Schmidt, and N. J. Turro, *J. Am. Chem. Soc.*, **95**, 3025 (1973) ; b) M.J.S. Dewar, S. Kirschner, and H. W. Kollmar, *ibid.*, **96**, 7579 (1974) ; c) N. J. Turro, G. Schuster, J. Pouliquen, R. Pettit, and C. Mauldin, *ibid.*, **96**, 6797 (1974).

2) Z. Yoshida, *J. Photochem.*, **29**, 27 (1985) ; S. Miki, K. Matsuo, M. Yoshida, and Z. Yoshida, *Tetrahedron Lett.*, **29**, 2211 (1988) ; S. Miki, T. Maruyama, T. Ohno, T. Tohma, S. Toyama, and Z. Yoshida, *Chem. Lett.*, **1988**, 861.

3) In the case of *hemi*-Dewar-anthraquinone, the reaction enthalpy for the cycloreversion has been determined to be 263 kJ/mol by a DSC measurement. The activation enthalpy for the isomerization has been determined to be 109 kJ/mol.

4) Attempts to purify **1** resulted in rearrangement to **2**. However, samples of **1** subjected to use contained **2** as a sole impurity.

(Received October 1, 1991)