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Novel Naphthalene Derivatives Undergoing Thermal Valence Isomerization to *hemi*-Dewar-naphthalene

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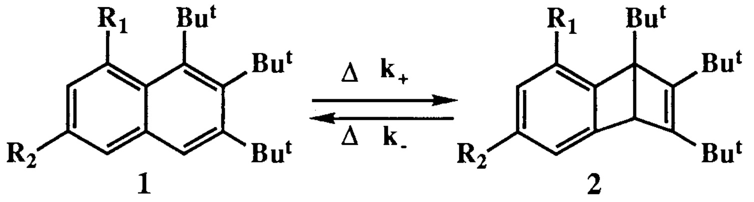
1,2,3-Tri-t-butyl-8-methyl- (**1a**), 1,2,3-tri-t-butyl-6-methyl-8-bromo- (**1b**), and 1,2,3-tri-t-butyl-8-bromo-naphthalene (**1c**) were synthesized. They underwent thermally forbidden electrocyclic reaction to give *hemi*-Dewar-naphthalenes (**2a,b,c**). Interconversion between **1** and **2** was thermally reversible. Energy profiles for the reactions were determined.

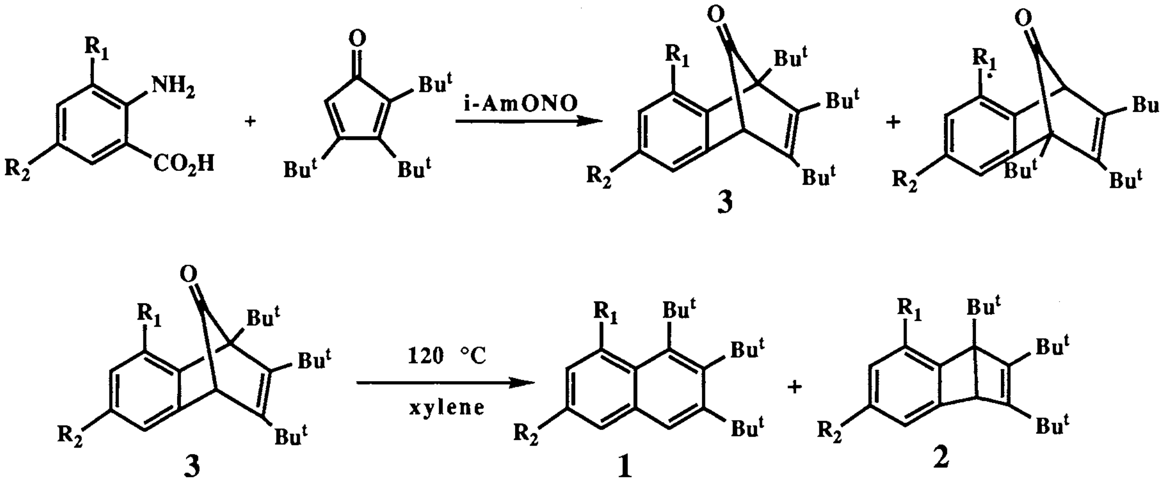
Valence isomerizations of benzene derivatives and annelated arenes have been a subject of much interest and widely studied.[1)] However, the formation of valence isomers *via* isomerization from their parent aromatics known so far generally involves their excited states, and no examples of thermal isomerization of benzenoid aromatic compound to afford their valence isomers have not been reported to our knowledge, although they were postulated in the rearrangement of aromatic compounds in some unusual conditions.[2)] Ground state valence isomerizations of aromatic compounds are grouped in so-called "forbidden reaction" in most and possess energetic constraint. In this paper we wish to report our finding on novel naphthalene derivatives (**1a,b,c**) which undergo thermal velence isomerization to give *hemi*-Dewar-naphthalene derivatives (**2a,b,c**).



(1)

a; $R_1 = CH_3$, $R_2 = H$
b; $R_1 = Br$, $R_2 = CH_3$
c; $R_1 = Br$, $R_2 = H$

In the course of our study on polycyclic aromatic compounds with large molecular congestion, we have encountered an unusual reaction of benzonorbornadienone derivative (**3b**) when it was subjected to thermal decarbonylation. As shown in Scheme 1, thermolysis of **3b** at 120 °C in xylene afforded an unusual product, *hemi*- Dewar-naphthalene derivative (**2b**) in the yield of 18% in addition to normal decarbonylation product (**1b**) in 72% yield. It was considered at first that the formation of **2b** was caused by photolysis of **1b** by ambient light, but the same result was obtained when all the experimental procedures were performed in a dark room under a red safety lamp. After separating **1b** and **2b** by chromatography **1b** and **2b** were heated independently, and each reaction gave mixture of **1b** and **2b** with an identical stationary composition. Thus, the formation of **2b** in the thermolysis of **3b** is in doubtless the result of the thermal valence isomerization of the primary decarbonylation product **1b**, and interconversion between them is thermally reversible. The feature was also the case of pairs of valence isomers **1a**/**2a** and **1c**/**2c**.



a; $R_1 = CH_3$, $R_2 = H$ b; $R_1 = Br$, $R_2 = CH_3$ c; $R_1 = Br$, $R_2 = H$

Scheme 1.

Naphthalene derivatives (**1**)[3] were synthesized according to Scheme 1. *Hemi*-Dewar-naphthalenes (**2**)[3] were obtainable by irradiating a mixture of **1** and **2** without separation with a high-pressure Hg-lamp through a $CuSO_4$ solution filter.

Thermolyses of **1** and **2** were performed in d_8-toluene sealed in NMR sample tubes, and the tubes were entirely dipped in a thermostated ethylene glycol bath so that no temperature gradient existed between the bath and the internal reaction mixture. The samples were subjected to ^{1}H-NMR analysis for composition of **1** and **2** at appropriate time intervals. Kinetic analysis was performed according to Eq.2 assuming that both the forward and the reverse reactions are first order :

$$-\frac{d[1]}{dt} = \frac{d[2]}{dt} = k_+[1] - k_-[2] = Kk_-[1] - k_-[2] \qquad (2)$$

where k_+ and k_- are first order rate constants for the forward and reverse reactions as indicated in Eq.1, and K is equilibrium constant defined as $K = [2]/[1]$ and is correlated to k_+ and k_- by $K = k_+/k_-$. The equilibrium constants were determined based on the composition of **1** and **2** in the sample after heating it long enough that change in the composition was no more observed. In practical runs, it was easier to follow the reaction kinetically starting from **2** than from **1**, because the equilibrium lies to the side of **1**. Therefore, rate constants were obtained from kinetic analyses of the reactions starting from **1**. Equilibriums attained both from **1** and from **2** were identical for each case. Rate constants and equilibrium constants determined for various temperatures are reported in Table 1.

Activation enthalpies (ΔH_+^a, ΔH_-^a) and enthalpy separations (ΔH) between **1** and **2** depicted in Fig. 1 were determined based on the temperature dependency of kinetic constants and equilibrium constants (Table 2).

Table 1. Rate Constants and Equilibrium Constants for the Thermal Rearrangements between **1** and **2** at Various Temperatures[a)]

Reaction	Temperature °C	Equilibrium constants(K)	Rate constants $k_+ / 10^4\ s^{-1}$	$k_- / 10^4\ s^{-1}$
1a $\rightleftarrows$ **2a**	100	0.25	0.055	0.22
	120	0.31	0.47	1.5
	140	0.38	3.2	8.6
1b $\rightleftarrows$ **2b**	100	0.21	0.045	0.16
	120	0.27	0.32	1.2
			(0.33)	(1.2)
	140	0.35	2.0	5.8
1c $\rightleftarrows$ **2c**	120	0.46	0.44	0.95
			(0.45)	(0.98)

a) Values in parentheses are obtained from thermolysis of **1**. For other values, see text.

As shown in Table 2, the enthalpy separations (ΔH) between **1** and **2** were astonishingly small for this class of pair of valence isomers.[4)] This is due to the heavy molecular congestion around C_1,C_2 and C_8 in **1** which may be released on going of the reaction of **1** to **2**. Because of this small enthalpy difference, detectable amount of **2** could be populated in the equilibrium mixture. One other reason for **1** to undergo thermal isomerization to **2** should be a large out-of plane bending deformation of C_1 which possibly exists in **1**. This bending deformation of C_1 should make it possible for C_1 and C_4 to close together in a distance short enough for bond making in

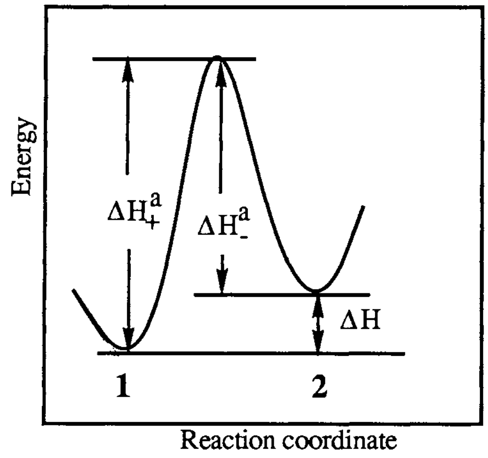


Fig. 1. Energy profile for the interconversion between **1** and **2**.

Table 2. Enthalpy Separations (ΔH) and Activation Enthalpies (ΔH_{+}^{a}, ΔH_{-}^{a}) for the Interconversion between **1** and **2**

System	ΔH	ΔH_{+}^{a}	ΔH_{-}^{a}
	$kJ\ mol^{-1}$	$kJ\ mol^{-1}$	$kJ\ mol^{-1}$
1a/2a	13	132	119
1b/2b	16	131	115

vibrationally excited states of low energy. In case of usual naphthalenes, such state may possess too large energy to be attained thermally. The t-butyl group at C_3 plays an important role in the thermal isomerization of **1** to **2**. In the case of 1,2-di-t-butyl-8-methylnaphthalene [5)] which is devoid of t-butyl group at C_3 position, no formation of detectable amount of *hemi*-Dewar isomer was observed in its thermolysis.

In summary, the present case represents a rare example of thermal rearrangement of benzenoid aromatics to afford highly strained valence isomer. Although energy profile determined for the interconversion between **1** and **2** reveals feasibility of the thermal valence isomerization of **1** to **2**, the electronic structure of the transition state for this " forbidden reaction " remains to be studied. Thus, further studies on the reaction including theoretical treatment are in progress.

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3) Selected spectral properties of **1a,b,c** and **2a,b,c**. **1a** ; ^{1}H-NMR (CDCl$_3$) $\delta = 1.39$ (9H, s), 1.46 (9H, s), 1.55 (9H, s), 2.73 (3H, s), 7.01 (1H, d), 7.08 (1H, dd), 7.33 (1H, s), and 7.41(1H, d). **2a** ; ^{1}H-NMR (CDCl$_3$) $\delta = 1.07$ (9H, s), 1.15 (9H, s), 1.16 (9H, s), 2.34 (3H, s), 3.72 (1H, s), and 6.91-7.01 (3H, m). **1b** ; ^{1}H-NMR (CDCl$_3$) $\delta = 1.46$ (9H, σ), 1.49 (9H, s), 1.51(9H, s), 2.34 (3H, s), 7.22 (1H, s), 7.27 (1H, s), and 7.31 (1H, s). **2b** ; ^{1}H-NMR (CDCl$_3$) $\delta = 1.10$ (9H, s), 1.14 (9H, s), 1.19 (9H, s), 2.27 (3H, s), 3.71 (1H, s), 6.83 (1H, s), and 7.04 (1H, s). **1c** ; ^{1}H-NMR (CDCl$_3$) $\delta = 1.48$ (9H, s), 1.50 (9H, s), 1.53 (9H, s), and 6.84-7.52 (4H, m). **2c** ; ^{1}H-NMR (CDCl$_3$) $\delta = 1.13$ (9H, s), 1.15 (9H, s), 1.21 (9H, s), 3.76 (1H, s),and 6.91-7.19 (3H, m).
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5) 1,2-Di-t-butyl-8-methylnaphthalene (**4**) was prepared by elimination of trimethylsilyl group from 1,2-di-t-butyl-3-trimethylsilyl-8-methylnaphthalene (**5**) by treatment with tetrabutylammonium fluoride. **5** was prepared by decarbonylation from a Diels-Alder adduct of the type of **3** obtained by the reaction of 2,3-di-t-butyl-3-trimethylsilylcyclopenta-2,4-diene-1-one (**6**) with 3-methyl-1,2-dehydrobenzene. For **6**, see Ref.6.
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