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Thermal isomerization of dewarbenzene derivatives

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A R T I C L E I N F O

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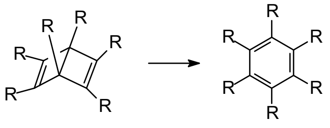
A B S T R A C T

The rates of thermal conversion of seven simple dewarbenzene derivatives to their corresponding benzene isomers were measured. Relatively minor substituent changes were found to have profound effects; isomerization rates increased with the number and strength of electron-withdrawing moieties. Surprisingly, the rate of thermal isomerization for one derivative was the same in fluid solution as in a solid polymer matrix, suggesting that this reaction has a low volume of activation. Other preliminary experiments suggest that the putative intermediate has some polar character. These data may provide some insights into the reaction mechanism.

Dewarbenzenes (**1**) are highly strained valence isomers of benzenes (**2**) that have been studied in detail for many years. The isomerization of dewarbenzene to benzene is highly exothermic (ca. 60 kcal/mol);[1–3] nevertheless many dewarbenzene derivatives show remarkable kinetic stability, presumably because the direct pericyclic isomerization is forbidden by orbital symmetry. Indeed, the fully substituted derivative hexamethyldewarbenzene (**1a**) is sufficiently thermally stable that it can be obtained commercially.



1 **2**

Much of the interest in this class of compounds lies in their rich photochemistry. For example, the isomerization of dewarbenzenes to the corresponding benzenes can be sensitized, and, under favorable conditions, effective quantum yields substantially greater than unity can be achieved. Two mechanisms for this photoinitiated chain reaction have been identified, one propagating via a cation radical intermediate,[4,5] and the second via a triplet excited state,[1,6] depending on the sensitizer used.

Because dewarbenzenes have significantly different physical properties than their benzene isomers, a number of researchers have attempted to apply this conversion to imaging technology. For example, Marsella et al.[7] demonstrated the unsensitized photo-conversion of an oily film of dimethyl tetramethyldewarphthalate (**1c**) to crystalline dimethyl tetramethylphthalate (**2c**). Our interest in dewarbenzenes stems from a refractive index imaging scheme known as Quantum Amplified Isomerization (QAI),[8,9] in which the photosensitized conversion of dewarbenzenes to benzenes is carried out within a solid polymer matrix. This scheme was demonstrated by the recording of diffraction gratings via holographic exposure of polymers containing dewarbenzene derivatives.[8,9] QAI using dewarbenzenes is an attractive candidate for imaging applications in photonics and holography for several reasons:

- Under favorable conditions, more than one product molecule is formed per photon absorbed, therefore high sensitivity media can be produced.
- The refractive index difference between the dewarbenzene reactant and the corresponding benzene product is ample for many applications.
- The molecular volumes of the reactant and product are similar, therefore very low dimensional changes accompany the recording process, important for high-resolution imaging.
- The reactants and products are generally stable under ambient conditions.

This last point is the subject of the current work, as thermal isomerizations of unsubstituted dewarbenzene,[10] hexamethyldewarbenzene (**1a**)[2,3] and of related, more complicated compounds[11,12] have been observed. Because a practical imaging medium might encounter temperature excursions above ambient, it seemed desirable to investigate the thermal stability of simple dewarbenzene derivatives, especially to determine the effect of structure. Therefore, we undertook a study of the rates of thermal isomerization of seven relatively simple dewarbenzene derivatives (**1b**–**h**, Table 1) in solutions of nonpolar solvents. We compared our results to the literature data for hexamethyldewarbenzene (**1a**). Additionally, we measured the rate of isomerization of one example (**1c**) in a more polar solvent and in a rigid polymer matrix, poly(methyl methacrylate) (PMMA) to learn more about the nature of the thermal isomerization reaction.

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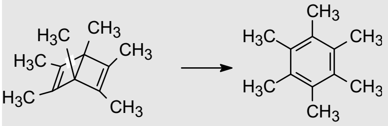
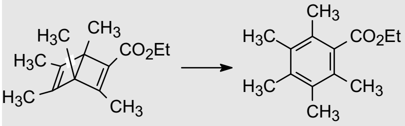
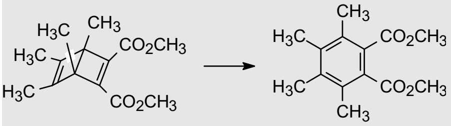
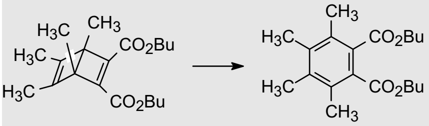
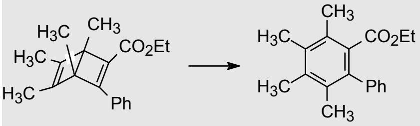
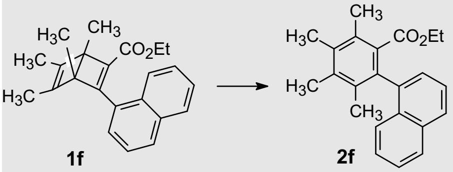
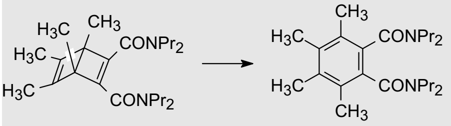
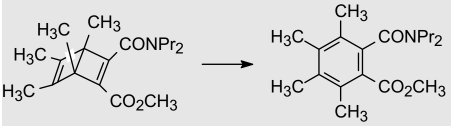
Table 1
Arrhenius parameters for the thermal isomerization of dewarbenzenes **1** to benzenes **2**

Reaction	Solvent	E_a (kcal mol^{-1})	A (s^{-1})	# of T's[b]	T Range (°C)	Half life@ 20 °C (years)
 **1a** **2a**	None	37.2[a]	1.1×10^{15}[a]	–	–	>1000
 **1b** **2b**	Toluene *o*-Xylene	25.6 25.6	3.7×10^{9} 3.5×10^{9}	2 5	90–110 90–130	70 76
 **1c** **2c**	Toluene	24.0	1.3×10^{10}	7	50–110	1.4
 **1d** **2d**	Toluene	25.1	3.9×10^{9}	2	90–110	2.9
 **1e** **2e**	*o*-Xylene	23.0	6.26×10^{7}	4	100–130	47
 **1f** **2f**	*o*-Xylene	22.6	1.91×10^{8}	4	80–130	8.8
 **1g** **2g**	Toluene	Very stable[c]	Very stable[c]	2	90–110	>100
 **1h** **2h**	Toluene	26.1	3.0×10^{11}	3	70–110	22

[a] Data from Ref. 2.
[b] Number of different temperatures studied.
[c] Rate of thermal isomerization was too slow to measure accurately, even at the highest temperature examined.

The dewarbenzene and benzene derivatives discussed herein contain four methyl groups and two variable substituents. This substitution pattern is a consequence of the use of readily available 2-butyne as starting material,[13,14] although a few other substituents at these positions have been reported in the literature.[11,12] Dewarbenzene esters **1b**–**f** were prepared by adaptation of the known method.[14] Compounds **1b**,[8] **1c**,[15] and the methyl ester analogous to **1e**[16] have been reported previously. Diamide **1g** was prepared by simple transformations of **1c**, and amide-ester **1h** similarly via the 'half acid' synthesized by the procedure of Niwayama.[17]

The thermal stability of dewarbenzenes **1b**–**h** was evaluated by heating solutions of the compounds under argon at various temperatures, sampling periodically, and analyzing by reverse phase

HPLC. Biphenyl was added to each solution as an internal standard. An automated reactor (Anachem SK233, including a Gilson robotic liquid handler) was used for these experiments, assuring consistency in reaction conditions and the timing of the analyses. We did not explore temperatures above 130 °C because of the limitations of the reactor. However, compounds requiring such high temperatures to observe isomerization would be considered sufficiently stable for practical purposes. Plots were constructed using the integrated HPLC peak areas, and first-order kinetics were observed. Rate constants were obtained by nonlinear curve-fitting of the relative reactant concentration versus time to a decaying exponential. Reliable numerical fits could be obtained with the reactant data, but equivalent information derived from the rise of the product concentration was confounded by large uncertainty in the calculations. This problem was purely numerical, in that the curve fitting algorithm for a rising exponential to maximum was essentially over-parameterized. The standard errors in rate constant and projected maximum concentration were large, as a range of these values could fit the data equally well. Therefore only data from the reactant was used in subsequent analyses.

Arrhenius data are summarized in Table 1. In addition, the table shows the estimated half lives at 20 °C for each compound, a value that is perhaps relevant to the eventual use of these compounds. Specifically, the spontaneous conversion of **1**→**2** would reduce shelf life and image permanence in practical imaging media because contrast in QAI depends on creating locally increased concentrations of **2** versus **1** photochemically. This apparent instability is a concern, considering the other desirable properties of these compounds for QAI. For example, **1c** is probably too unstable for a practical system, but **1b** may provide an acceptable combination of thermal stability and photochemical reactivity.

The thermal stability of these dewarbenzene derivatives seemed to decrease with the strength and number of electron-withdrawing substituents. For example, compound **1c** with two ester groups was less stable than **1b** with one ester group. Amides **1g**–**h** were found to be more stable than the corresponding compound bearing two esters (**1c**). Indeed, compound **1g** with two amides isomerized so slowly even at 110 °C that accurate rate measurements could not be obtained. Among the compounds studied, hexamethyldewarbenzene (**1a**) is apparently the most thermally stable; however, **1a** gradually decomposes when exposed to air. Compounds **1b**–**h** appear to be more stable in air, probably because the electron-withdrawing substituents increase their oxidation potentials compared to **1a**.

Chemical reactions are usually significantly slower in solid media compared to fluid solutions. For practical QAI imaging media, one might hope that the thermal isomerization of dewarbenzene derivatives would be inhibited in rigid media. Surprisingly, analysis of solid films of **1c** in PMMA (10 wt %) that were stored in a 60 °C oven (50% RH) showed *approximately the same rate of thermal isomerization to* **2c** *as for toluene solutions at the same temperature* (Fig. 1). These results can be rationalized as follows: Dewarbenzenes **1** and benzenes **2** have similar molecular volumes; for example, molecular mechanics calculations predict 240 Å^3 for **1c**, and 237 Å^3 for **2c**.[18] The conversion **1**→**2** may involve a relatively low volume of activation. Only a very small local rearrangement of the polymer binder may be necessary during the isomerization to accommodate the new shape of **2** compared to **1**, including the transition state. Therefore, the reaction appears to be insensitive to local viscosity, and proceeds readily even in solid media.

The intermediates in the photosensitized isomerization of dewarbenzenes via the cation radical and triplet mechanisms have been studied both experimentally and theoretically.[5,6,25–28] The mechanistic details of the thermal isomerization are less clear,[10,29,30] but the above mentioned insensitivity to local viscosity has obvious bearing. In addition, some other preliminary experiments may provide insight into the putative intermediate. Dimethyl ester **1c** appears to isomerize thermally more rapidly than the dibutyl ester **1d** (Fig. 2). Also, the rate of thermal isomer-

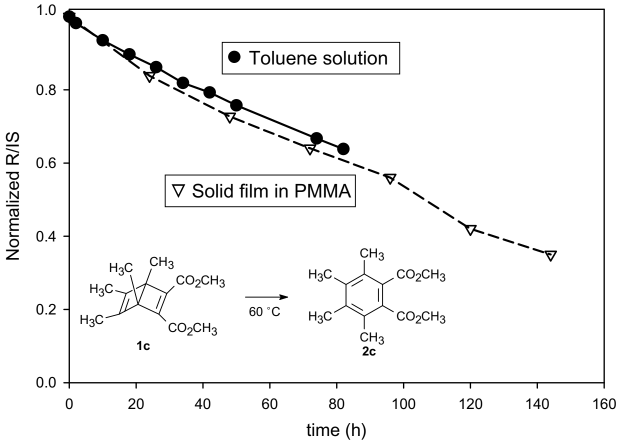


Figure 1. Decrease in concentration of **1c** in toluene solution and in a solid PMMA polymer film at 60 °C. Data are plotted as normalized HPLC peak areas. Lines are drawn as an aid to the eye.

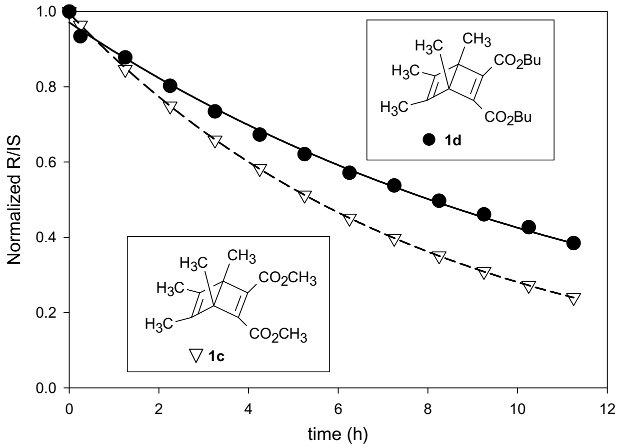


Figure 2. Effect of alkyl group on the thermal isomerization rate of dewarbenzene diesters **1c** and **1d** in toluene solution at 90 °C. Data are plotted as normalized HPLC peak areas. Lines show nonlinear fits to decaying exponentials, corresponding to the rate parameters.

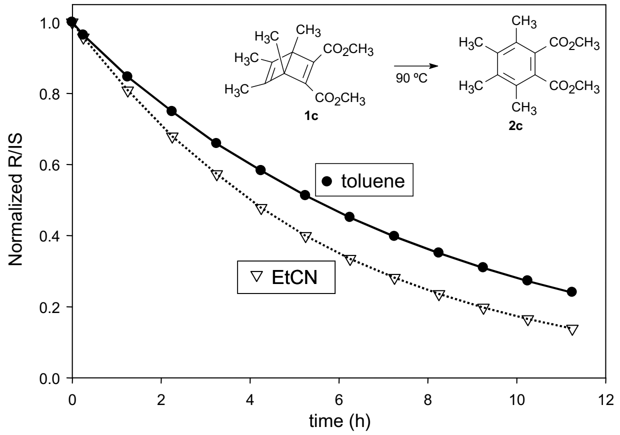


Figure 3. Effect of solvent on the thermal isomerization rate of **1c**. Data are plotted as normalized HPLC peak areas. Lines show nonlinear fits to decaying exponentials, corresponding to the rate parameters.

ization of **1c** was greater in more polar propionitrile compared to toluene (Fig. 3). These data suggest that the intermediate may have some polar character.[31]

These combined results demonstrate that substitution by even moderately strong electron-withdrawing groups on the dewarbenzene skeleton causes surprisingly large increases in the thermal isomerization rates. Furthermore, the data suggest that the thermal isomerization mechanism for dewarbenzenes of the type studied herein proceeds through a polar intermediate state of similar geometry to the reactant and product. Presumably, the polar substituents of **1b**–**h** provide access to intermediates of reduced symmetry on the reaction surface that significantly reduce the barrier to isomerization compared to hexamethyldewarbenzene (**1a**).

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