Novel Thermally Induced Rearrangement of a Propargylallene to a Furofuran Derivative in the Solid State

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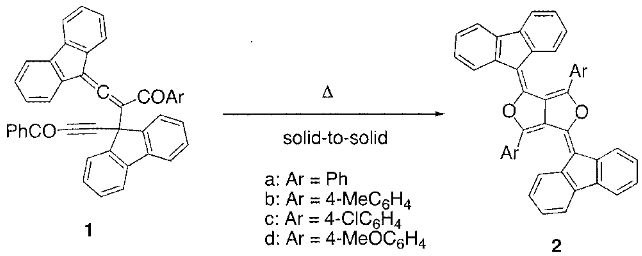
When colorless prisms of propargylallene **1** were heated at 192–200 °C, **1** changed to dark copper-brown crystals of furofuran derivative **2** without any melting. The solid-state mechanism of the reaction was studied by DSC, FT-IR and X-ray analyses.

Introduction

In recent years there has been increasing interest in solid-state organic reactions in the absence of a solvent due to their simple operation, energy-saving, and avoidance of solvent wastes, hazards and toxicity.[1] However, thermally induced organic reactions from solid to solid have been little explored,[2] although relatively many examples of solid-to-solid photoreactions have been reported.[3] Here we report a novel, thermally induced rearrangement of 3-(fluoren-9-ylidenyl)-2-[9-(3-oxo-3-phenylprop-1-ynyl)-9*H*-fluoren-9-yl]-1-phenylpropenones (**1**) into 1,4-bis(fluoren-9-ylidenyl)-3,6-diphenyl-1*H*,4*H*-furo[3,4-*c*]furans (**2**) in the solid state.



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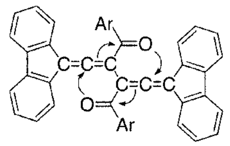

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Results and Discussion

When colorless prisms of 3-(fluoren-9-ylidenyl)-2-[9-(3-oxo-3-phenylprop-1-ynyl)-9*H*-fluoren-9-yl]-1-phenylpropenone (**1a**) [4] were heated at 198 °C, **1a** changed to dark copper-brown crystals of 1,4-bis(fluoren-9-ylidenyl)-3,6-diphenyl-1*H*,4*H*-furo[3,4-*c*]furan (**2a**) quantitatively. This reaction occurs without any melting. A differential scanning calorimetry (DSC) measurement of the crystal of **1a** showed a sharp exothermic peak at 198 °C due to the transformation of **1a** into **2a** (Figure 1).

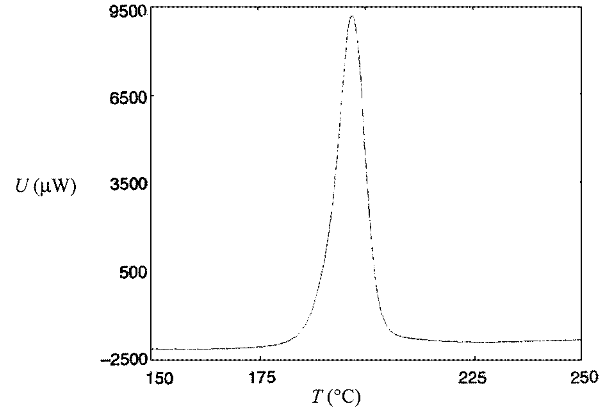

Figure 1. DSC diagram of **1a** at a heating rate of 10 °C/min; ΔH value for exothermic peak at 198 °C is ca. 152 KJ/mol

The melting temperature of **2a** is significantly higher (>300 °C) than the reaction temperature. Similarly, heating colorless crystals of **1b**−**1d** at around 200 °C gave the corresponding compounds **2b**−**2d** in quantitative yield also without any melting. DSC measurement of **1b**−**1d** showed exo-

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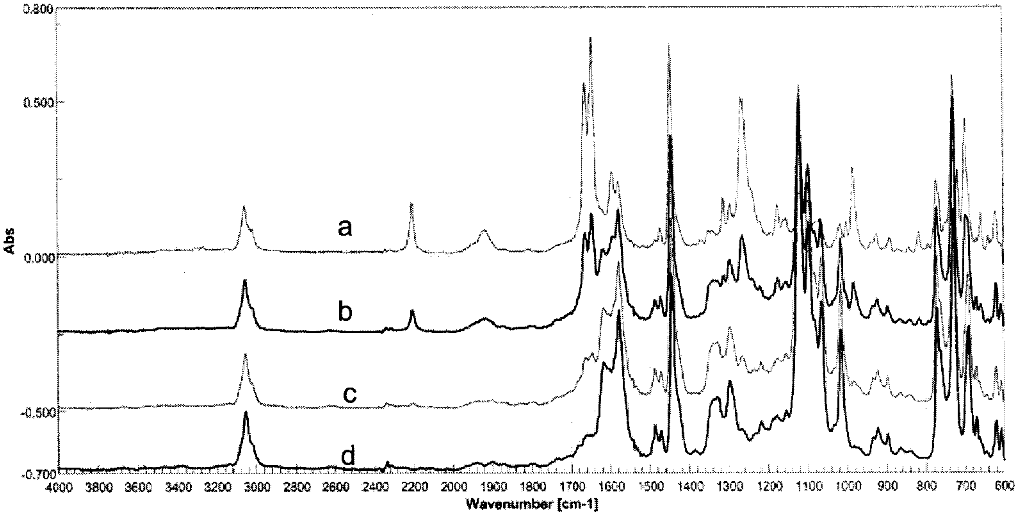


Figure 2. FT-IR spectra for **1a** after heating at 198 °C for 0 sec (a), 50 sec (b), 100 sec (c) and 200 sec (d) in the solid state

thermic peaks at 200, 198 and 192 °C, respectively. These data indicate that the transformation of **1** to **2** occurs without detectable melting prior to rearrangement.

These thermal rearrangements probably involve two solid-to-solid reactions. The propargylallene **1** is probably rearranged to the symmetrical diallene intermediate **3**, which gives furofuran derivative **2** through an 8π-electron thermal cyclization reaction. When the IR spectrum of a single crystal of **1a** was measured continuously every 50 seconds at 198 °C, the signals at $\tilde{\nu}$ = 2210 cm^{-1} (C≡C), 1922 cm^{-1} (C=C=C), and 1660 and 1646 cm^{-1} (C=O) gradually decreased and finally disappeared, and new signals at 1133, 1100 and 1069 cm^{-1} (C−O−C) corresponding to **2a** appeared (Figure 2).

However, the signals corresponding to the intermediate **3a** were not detected. This may be due to the facile thermal cyclization of the intermediate **3a** under these conditions. Thermal rearrangement of **1a** to **2a** in xylene solution has been described previously,[4] although the structures of **1a** and **2a** have not been fully characterized.

Single-crystal structures of **1a** and **2a** were obtained and compared.[5] Compound **1a** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit and four molecules in the unit cell, while **2a** is centrosymmetric orthorhombic (*Pbcn*) with 1/4 molecules in the asymmetric unit and $Z = 4$ (Figure 3). The cell volume of the thermolysed product **2a** is smaller than that of the unthermolysed material **1a.** This is reflected in a greater calculated density indicating closer packing of the furofuran derivative. The packing of **1a** and **2a** varies significantly, as illustrated in Figure 4, and, while the fluorene moieties approach co-planarity in both structures, a

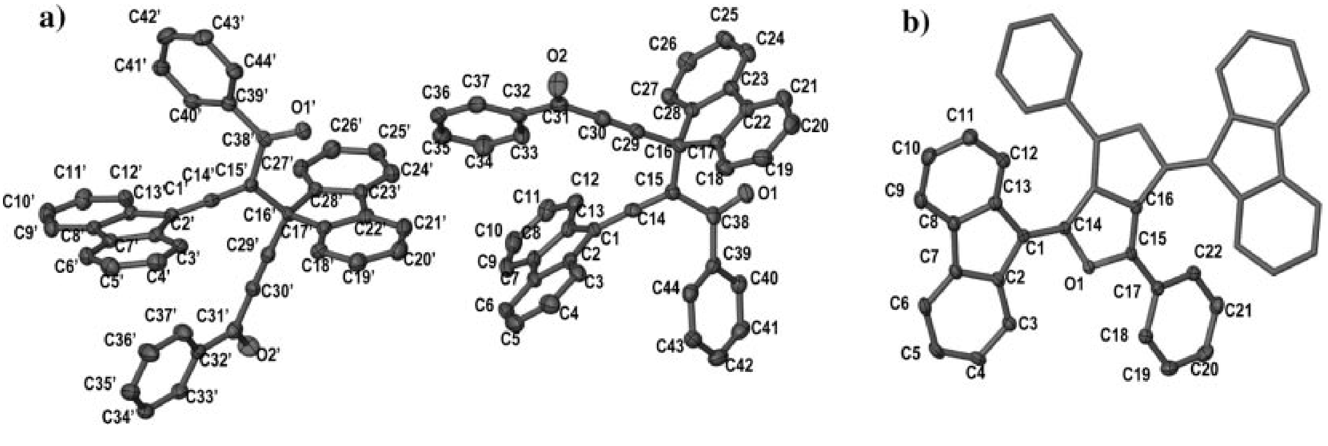


Figure 3. Molecular diagrams of a) **1a** and b) **2a**. Atoms of the asymmetric unit are depicted as ellipsoids at the 50% probability level and the symmetry generated portion of **2a** is depicted in stick mode. The dihedral angles defining the twist of the fluorene moieties relative to each other in an individual molecule are 10.5(2)° and 11.7(2)° for **1a** (in the order depicted left to right) and 35.99(4)° for **2a**, while the pendant phenyl rings, which are almost perpendicular to the fluorine moiety plane in **1a** are, by virtue of the new bonds formed, approximately co-planar with those in **2a** (although to minimize steric interaction between H22 and H21 with H12($-x$, y, $-z + 3/2$) and H11($-x$, y, $-z + 3/2$) the entire molecule adopts a twisted shape

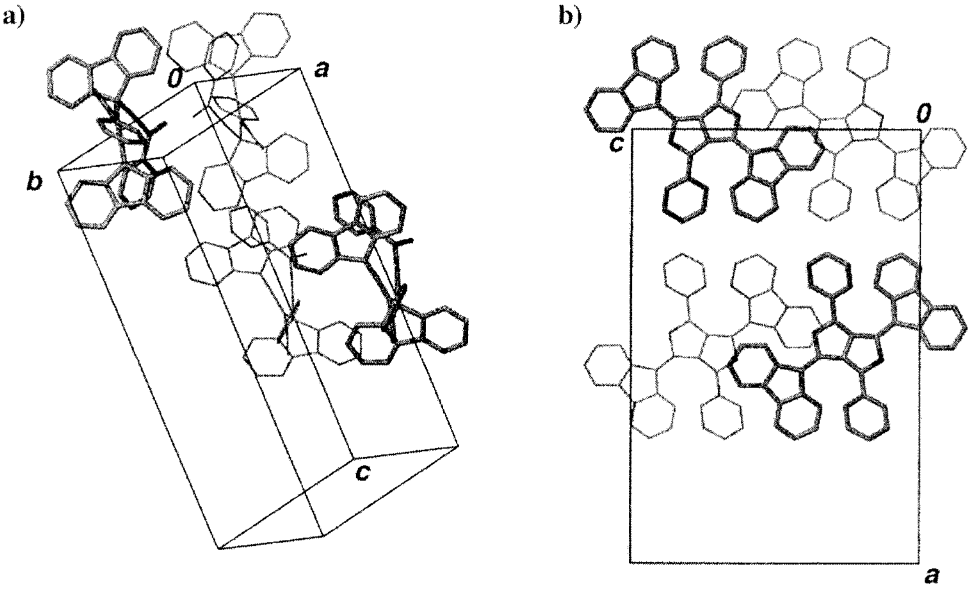
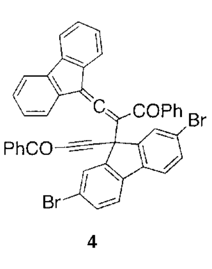


Figure 4. Packing diagrams of a) **1a** and b) **2a** viewed approximately perpendicular to the fluorine moieties for comparison. Clearly a large degree of motion is required in the solid state to effect the intramolecular reaction transforming **1a** into **2a.** The predominant intermolecular interaction in **1a** is the CH···π interaction, while in **2b** π···π interactions are most important

large concerted movement of the central part of the molecule is required to transform **1a** into **2a**. This large shift in molecular shape probably accounts for the decomposition of a single crystal to a powder even though no melting is observed during the solid-solid transformation of **1a** into **2a**.

In order to determine the intramolecularity of the solid-state rearrangement, we prepared the unsymmetrical propargylallene derivatives (**4** and **5**) by cross-coupling reactions. The thermal reaction of **4** and **5** afforded the same product **6**, and no other products resulting from the intermolecular reaction were obtained. These results indicate that the rearrangement proceeds probably intramolecularly in the crystals.



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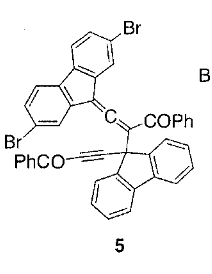

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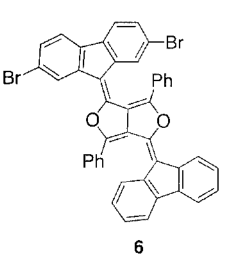

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Experimental Section

General Remarks: ^1H NMR spectra were recorded in $CDCl_3$ on a JEOL Lambda 300. IR spectra were recorded with a JASCO FT-IR 200 spectrometer. UV spectra were measured on a Shimadzu MPS-2000 spectrometer. DSC traces were recorded on a Seiko DSC-22 system. All melting points were determined using a Yanaco micro melting-point apparatus and are uncorrected.

Thermal Rearrangement of 1 to 2: Heating of 100 mg of **1a−d**[4] in the solid state at 198 °C for 30 min afforded 100 mg of **2a−d** in 100% yield. Recrystallization of these from CH_2Cl_2 gave pure **2a−d** as dark copper-brown prisms.

2a: Mp 293−295 °C. IR (Nujol): $\tilde{\nu}$ = 1133, 1100 (C−O) cm^{-1}. UV ($CHCl_3$): λ_{max} (ε) = 258 nm (84800), 327 (66700), 398 (7160), 607 (46100). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.54−8.53 (m, 26 H) ppm. $C_{44}H_{26}O_2$ (586.19): calcd. C 90.08, H 4.47; found C, 90.21, H 4.75.

2b: Mp 295−296 °C. IR (Nujol): $\tilde{\nu}$ = 1128, 1095 (C−O) cm^{-1}. UV ($CHCl_3$): λ_{max} (ε) = 258 nm (61900), 303 (101000), 606 (113000). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.59−8.53 (m, 24 H), 2.42 (s, 6 H) ppm. $C_{46}H_{30}O_2$ (614.22): calcd. C 89.88, H 4.92; found C, 90.06, H 5.15.

2c: Mp 292−294 °C. IR (Nujol): $\tilde{\nu}$ = 1131, 1099 (C−O) cm^{-1}. UV ($CHCl_3$): λ_{max} (ε) = 257 nm (111000), 332 (99200), 403 (10900), 611 (57400). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.53−8.46 (m, 24 H) ppm. $C_{44}H_{24}Cl_2O_2$ (654.12): calcd. C 80.61, H 3.69; found C, 80.44, H 3.99.

2d: Mp 243−245 °C. IR (Nujol): $\tilde{\nu}$ = 1124, 1097 (C−O) cm^{-1}. UV ($CHCl_3$): λ_{max} (ε) = 259 nm (66000), 336 (33000), 612 (13700). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.62−8.51 (m, 24 H), 3.83 (s, 6 H) ppm. $C_{46}H_{30}O_4$ (646.21): calcd. C 85.43, H 4.68; found C, 85.49, H 4.47.

Thermal Rearrangement of 4 and 5 to 6: The propargyl allenes **4** and **5** were prepared by a similar method to **1**.

4: Pale-yellow prisms; thermal rearrangement occurred upon heating at 202 °C (DSC). IR (Nujol): $\tilde{\nu}$ = 2111 (C≡C), 1923 (C=C=C), 1671, 1637 (C=O) cm^{-1}. UV ($CHCl_3$): λ_{max} (ε) = 258 nm (84800), 327 (66700), 398 (7160), 607 (46100). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.05−8.01(m, 24 H) ppm. $C_{44}H_{24}Br_2O_2$ (742.01): calcd. C 70.99, H 3.25; found C, 71.18, H 3.40.

5: Yellow prisms; thermal rearrangement occurred upon heating at 178 °C (DSC). IR (Nujol): $\tilde{\nu}$ = 2203 (C≡C), 1939 (C=C=C), 1670, 1636 (C=O) cm^{-1}. UV ($CHCl_3$): λ_{max} (ε) = 260 nm (82600). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.15−7.94 (m, 24 H) ppm.

$C_{44}H_{24}Br_2O_2$ (742.01): calcd. C 70.99, H 3.25; found C, 71.05, H 3.57.

Heating of 100 mg of **4** or **5** in the solid state at 180 °C for 30 min afforded 100 mg of **6** in 100% yield. Recrystallization of these from CH_2Cl_2 gave pure **6** as dark copper-brown prisms.

6: Mp 292−293 °C. IR (Nujol): $\tilde{\nu}$ = 1124, 1111 (C−O) cm^{-1}. UV ($CHCl_3$): λ_{max} (ε) = 268 (98500), 327 (66800), 611 (44100). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.50−8.66 (m, 24 H) ppm. $C_{44}H_{24}Br_2O_2$(742.01): calcd. C 70.99, H 3.25; found C, 70.70, H 3.15.

X-ray Crystallographic Study: Data were collected on an Enraf−Nonius Kappa CCD diffractometer at 123 K using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å, and ω scans). Structures were solved by direct methods using the program SHELXS-97[6] and refined by full-matrix least-squares refinement on F^2 using the programs SHELXL-97[6] and X-Seed.[7] Non-hydrogen atoms were refined anisotropically and hydrogen atoms inserted in geometrically determined positions with temperature factors fixed at 1.2-times that of the parent atom.

Crystal Data for 1a: $C_{44}H_{26}O_2$, M_r = 586.65, triclinic, space group $P\bar{1}$, a = 9.5480(1), b = 14.6578(1), c = 22.9710(2) Å, α = 89.926(1), β = 87.470(1),γ = 72.791(1)°, V = 3067.70(5) Å^3, Z = 4, D_{calc} = 1.270 g·cm^{-3}, μ(Mo-K_α) = 0.077 mm^{-1}. Of 25479 reflections measured, 14264 were unique (R_{int} = 0.082), with 4373 having $I > 2\sigma(I)$, R indices [$I > 2\sigma(I)$] R_1 = 0.0556, wR_2 = 0.0788, GoF on F^2 = 0.809 for 829 refined parameters and 0 restraints.

Crystal Data for 2a: $C_{44}H_{26}O_2$, M_r = 586.65, orthorhombic, space group $Pbcn$, a = 25.5602(2), b = 6.7881(1), c = 16.9459(1) Å, V = 2940.20(5) Å^3, Z = 4, D_{calc} = 1.325 g·cm^{-3}, μ(Mo-K_α) = 0.080 mm^{-1}. Of 11823 reflections measured, 3597 were unique (R_{int} = 0.078), with 2090 having $I > 2\sigma(I)$, R indices [$I > 2\sigma(I)$] R_1 = 0.0472, wR_2 = 0.0911, GoF on F^2 = 0.927 for 208 refined parameters and 0 restraints.

CCDC-203829 (**1a**) and -203830 (**2a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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