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The di-π-methane rearrangement induced in tris(2-benzo[*b*]thienyl)methane

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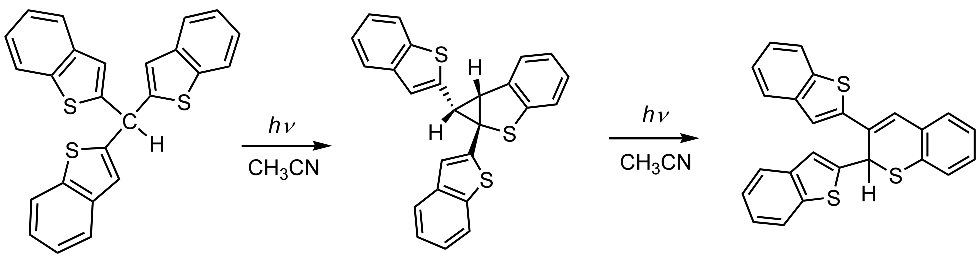
Abstract—Photoirradiation of tris(2-benzo[*b*]thienyl)methane in acetonitrile resulted in the unexpected formation of a cyclopropane compound, which is rationalized based on the di-π-methane rearrangement including two unsaturated bonds of the benzo[*b*]thiophene rings. © 2003 Elsevier Science Ltd. All rights reserved.

The di-π-methane rearrangement has been known to take place not only in divinylmethanes but also in the 'methane carbon' which bears an aryl group in place of a vinyl.[1] Thus, a Kekule double bond of aromatic rings can enter into the rearrangement as a π moiety. However, except for dibenzobarrelene,[2] no case has been described in which two aromatic rings participate in the rearrangement as di-π-moieties. The aromatic rings in dibenzobarrelene are fixed in a rigid framework without conformational freedom, being advantageous for the initial step to form a cyclopropane intermediate. We demonstrate herein for the first time that the di-π-methane rearrangement can be realized in a tri(aryl)-methane-type compound such as tris(2-benzo[*b*]-thienyl)methane (**1**). We found, furthermore, a novel photochemical transformation of the rearranged product into a thiopyran derivative.

An acetonitrile solution of compound **1** (ca. 0.5 mM) was irradiated with a high-pressure Hg lamp through a Pyrex filter under nitrogen at 0°C. Chromatography on silica gel of the resulting mixture gave cyclopropane compound **2** (19%) and thiopyran derivative **3** (46%) along with recovery of **1** (~30%) (Scheme 1). The two photoproducts were further purified by means of gel permeation chromatography (GPC). The structures of **2** and **3** have been deduced from spectral characterizations and determined unequivocally by X-ray structural analyses (Figs. 1 and 2).[3,4] The benzo[*b*]thiophene rings attached to the cyclopropane ring of **2** were revealed to be in a *trans* arrangement. It is evident from the NMR spectrum of the photoreaction mixture that compound **2** is present as such in the photoproducts and does not arise from the isolation procedure (Fig. 3(a)).

Cyclopropane **2** was easily converted to compound **3** (~95%) upon irradiation under the same conditions for the photoreaction of **1**. Therefore, **3** is the secondary photoproduct derived from the primary product, **2**. The



1 2 3

Scheme 1.

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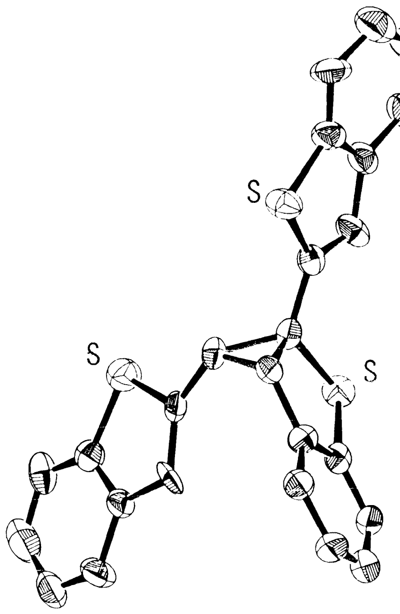


Figure 1. ORTEP representation of **2**.

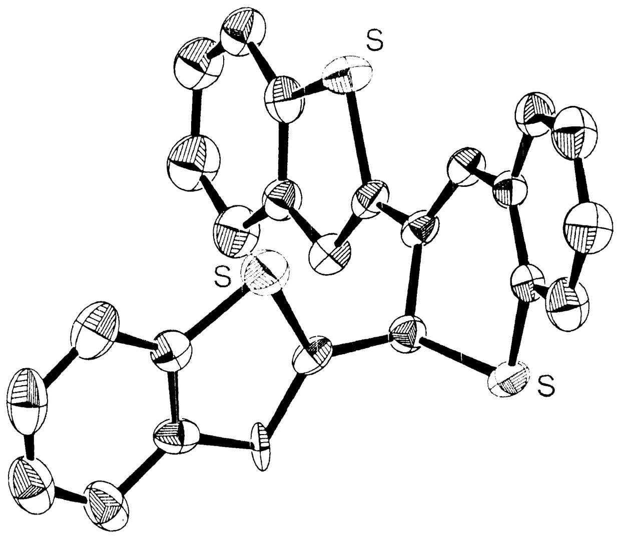


Figure 2. ORTEP representation of **3**.

isomerization of **1** to **2** is rationalized based on the di-π-methane rearrangement including the two benzo[*b*]thiophene rings in **1** (Scheme 2). In order to ascertain the mechanism, the deuterated derivative of **1** was prepared, in which the hydrogen at C-1 was deuterated. The ^{1}H NMR spectrum of the photoproducts from deuterated **1** showed clearly the lack of some signals that are observed in the product mixture from non-deuterated **1** (Fig. 3). For product **2** the singlet signal at 3.33 ppm is absent. This signal is assigned, based on the 2D NMR spectroscopy (HMQ, HH-COSY, and DNOH), to the *tert*-position that bears the benzothiophene ring. The results of deuterated **1** are consistent with the di-π-methane rearrangement which involves no hydrogen migration. On the other hand, for the secondary photoproduct **3**, the signal at 5.44 ppm is absent, implying the deuterium migrates during the photoprocess from **2** to **3**. Thus photolysis of **2** is interpreted by the homolytic cleavage of the cyclopropane bond to generate a 1,3-diradical species, followed by the hydrogen migration to produce a double bond in a six-membered ring.

Intra- and intermolecular photocyclizations, in particular, $[2\pi+2\pi]$ cycloadditions have been frequently observed in benzo[*b*]thiophene derivatives.[5] The unsaturated bond of the benzo[*b*]thiophene ring is more alkene-like than that of benzene. Therefore, it is reasonable that the former is more susceptible to the di-π-

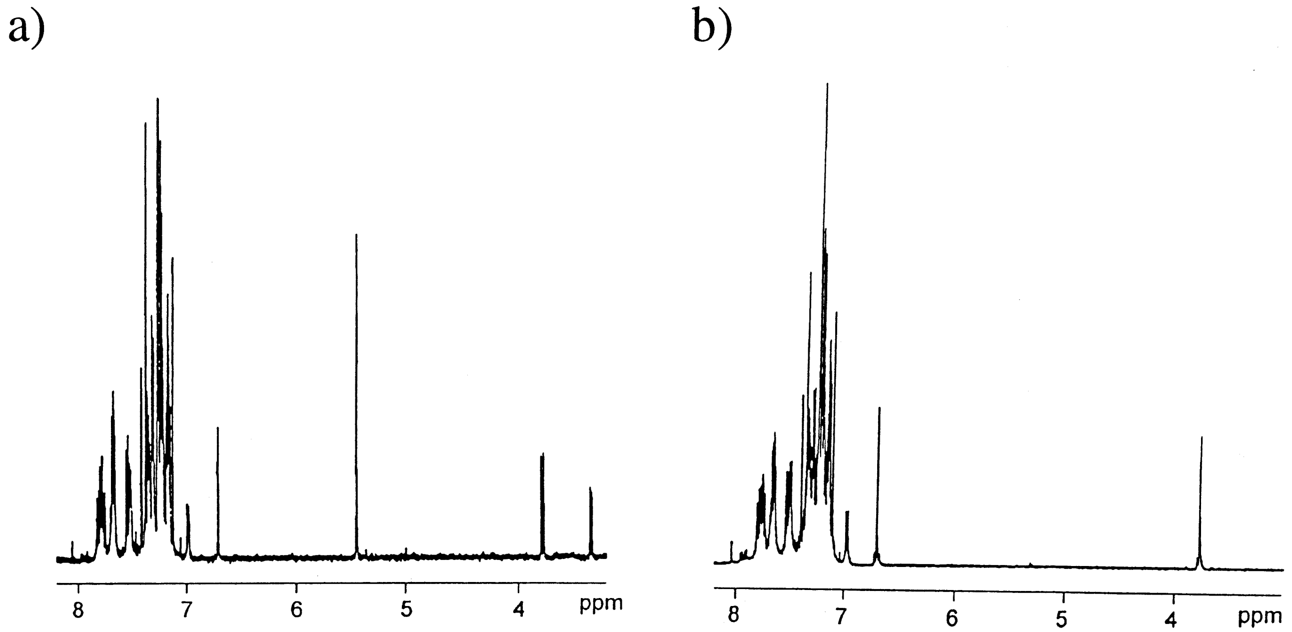
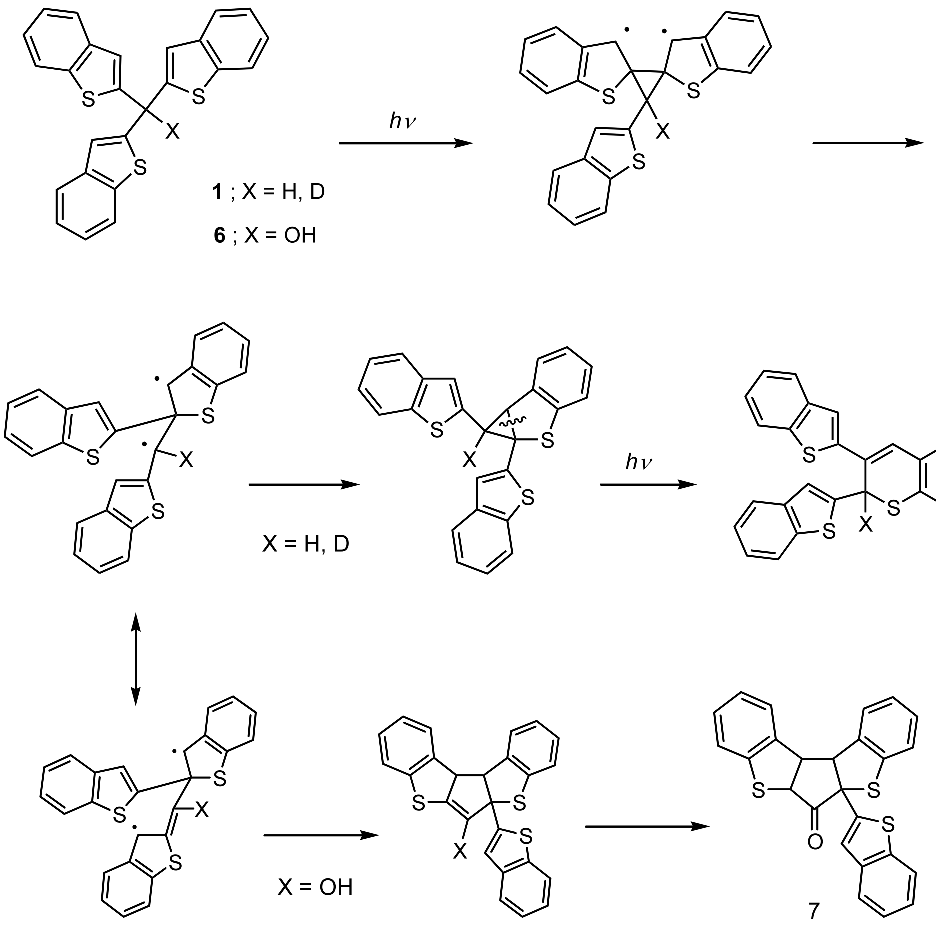


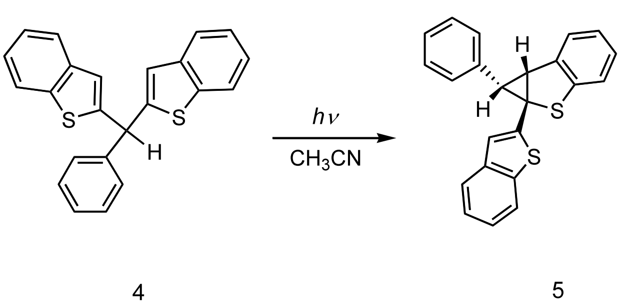
Figure 3. NMR spectra of the photoproducts from **1** (a) and deuterated **1** (b).



Scheme 2.

rearrangement than the latter. In fact, bis(2-benzo[*b*]thienyl)phenylmethane (**4**), in which one of the benzo[*b*]thiophene rings of **1** is replaced by a phenyl group, was found to undergo the di-π-methane rearrangement without intervention of the π bond in the phenyl substituent: photolysis of **4** afforded cyclopropane compound **5** in 25% yield (Scheme 3). The structure of **5** was determined by X-ray crystal analysis.[6] The formation of the thiopyran compound corresponding to **3** was also suggested by occurrence of the characteristic ^{1}H NMR signal around 5.5 ppm (~10%).

Recently, we have reported the formation of a cyclopentanone compound **7** upon irradiation of tris(2-benzo[*b*]thienyl)methyl alcohol (**6**).[7] The formation of **7** was interpreted based on the 1,3-diradical intermediate of the di-π-methane rearrangement, which could undergo cyclization to a five-membered ring owing to the delocalization of the radical center. This type of rearrangement should be classified as a tri-π-methane rearrangement[8] rather than the di-π-methane rearrangement. Bonding between two C-1 carbon atoms of two aryl rings has been proposed as a special case of the di-π-methane rearrangement for photoinduced α,α-elimination of triphenylmethane derivatives.[9,10] In the case of the photolysis of **1**, products due to the tri-π-methane rearrangement were not obtained. The significant difference in the photoreaction paths between the methane form **1** and alcohol form **6** cannot be rationalized at this stage. The mechanistic details, including the excited state associated with the reaction paths, are under investigation to elucidate the photochemical characteristics of tris(2-benzo[*b*]thienyl)methane derivatives.



Scheme 3.

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3. For **2**: mp 172∼173°C. ^{1}H NMR ($CDCl_3$) δ 3.33 (1H, d, $J=9.0$ Hz), 3.77 (1H, d, $J=9.0$ Hz), 6.71 (1H, s), 6.97 (1H, dd, $J=7.5$, 7.0 Hz), 7.15∼7.26 (4H, m), 7.30∼7.38 (2H, m), 7.41 (1H, s), 7.48∼7.55 (2H, m), 7.68 (1H, d, $J=7.5$ Hz), 7.74 (1H, d, $J=7.0$ Hz), 7.80 (1H, d, $J=8.0$ Hz).

   For **3**: mp 241∼243°C. ^{1}H NMR ($CDCl_3$) δ 5.43 (1H, s), 7.10∼7.41 (11H, m), 7.51 (1H, dd), 7.62∼7.70 (2H, m), 7.7 (1H, dd).
4. X-Ray data: for **2**: $M=412.58$, $C_{25}H_{16}S_3$, orthorhombic, space group $Fdd2$ (#43), $a=25.621(9)$, $b=52.792(5)$, $c=5.685(3)$ Å, $V=7688$ (5) Å^3, $Z=16$, $D_{calcd}=1.069$ g cm^{-3}, $R=0.052$, $R_W=0.046$.

   For **3**: $M=412.58$, $C_{25}H_{16}S_3$, monoclinic, space group $P2_1/n$ (#14), $a=5.970(3)$, $b=16.275(3)$, $c=20.391(2)$ Å, $\beta=97.17(2)$°, $V=1965(1)$ Å^3, $Z=4$, $D_{calcd}=1.394$ g cm^{-3}, $R=0.062$, $R_w=0.062$. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 195167 for **2** and CCDC 195168 for **3**. A copy of the data can be obtained, free of charge, from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].
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6. X-Ray data: for **5**: $M=356.48$, $C_{23}H_{16}S_2$, monoclinic, space group $C2/c$ (#43), $a=25.446(15)$, $b=5.930(3)$, $c=24.519(14)$ Å, $\beta=107.96(10)$°, $V=7688(5)$ Å^3, $Z=8$, $D_{calcd}=1.345$ g cm^{-3}, $R=0.036$, $R_w=0.09$. Crystallographic data (excluding structure factors) for the structure of **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 195169.
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