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Novel intramolecular photocyclization of tris(2-benzo[*b*]thienyl)methyl alcohol

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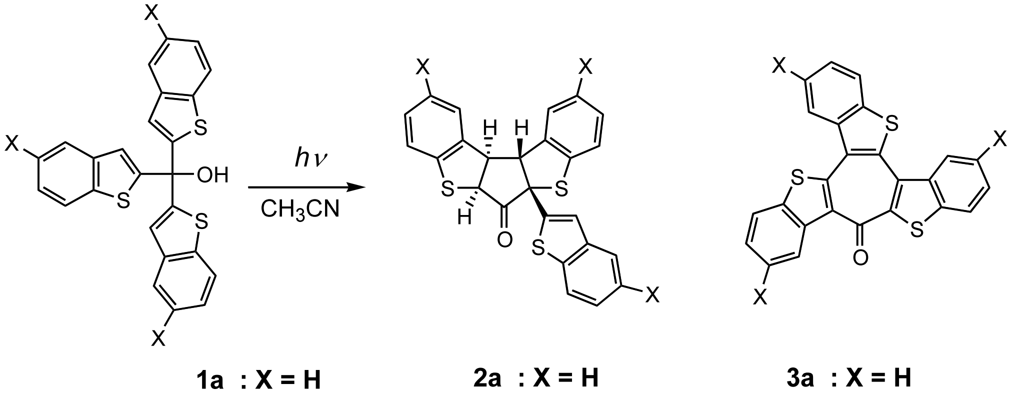
Abstract—Photoirradiation of tris(2-benzo[*b*]thienyl)methyl alcohol in acetonitrile afforded a cyclopentanone compound and a benzo[*b*]thiophene-condensed tropone derivative. The former is interpreted to originate via the di-π-methane rearrangement using the unsaturated bonds in two thiophene rings, while the latter via trimerization of the unsaturated bonds in three thiophene rings. © 2002 Elsevier Science Ltd. All rights reserved.

Thiophene compounds show versatile photoreactivity and wide mechanistic perspectives. The photoisomerization that results in a positional change of the carbon atoms in the thiophene ring has been studied in great detail.[1] An unsaturated bond of thiophene derivatives exhibits photoreactivity as an ethylene or a 2π-electron moiety. Thus, inter- or intra-molecular [π2s+π2s] cycloadditions are frequently encountered, particularly in benzo[*b*]thiophene.[2] Photoinduced electrocyclization of 1,2-di(2-thienyl)ethylenes to give a cyclohexadiene framework has been attracting considerable attention in relation to photochromic materials.[3]

We herein report novel intramolecular photocyclization of tris(2-benzo[*b*]thienyl)methyl alcohol (**1a**) to afford five- and seven-membered products. The latter compound is particularly interesting because its formation suggests the participation of the three unsaturated bonds of the benzo[*b*]thiophene rings.

An acetonitrile solution of compound **1a** (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 cyclopentanone **2a** (43%) and benzo[*b*]thiophene-condensed tropone



1a : X = H
1b : X = CH_3

2a : X = H
2b : X = CH_3

3a : X = H
3b : X = CH_3

Scheme 1.

Keywords: photocyclization; benzo[*b*]thiophene ring; di-π-methane rearrangement; tropone derivative; π-trimerization.

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derivative **3a** (23%) along with recovered **1a** (~30%) (Scheme 1)

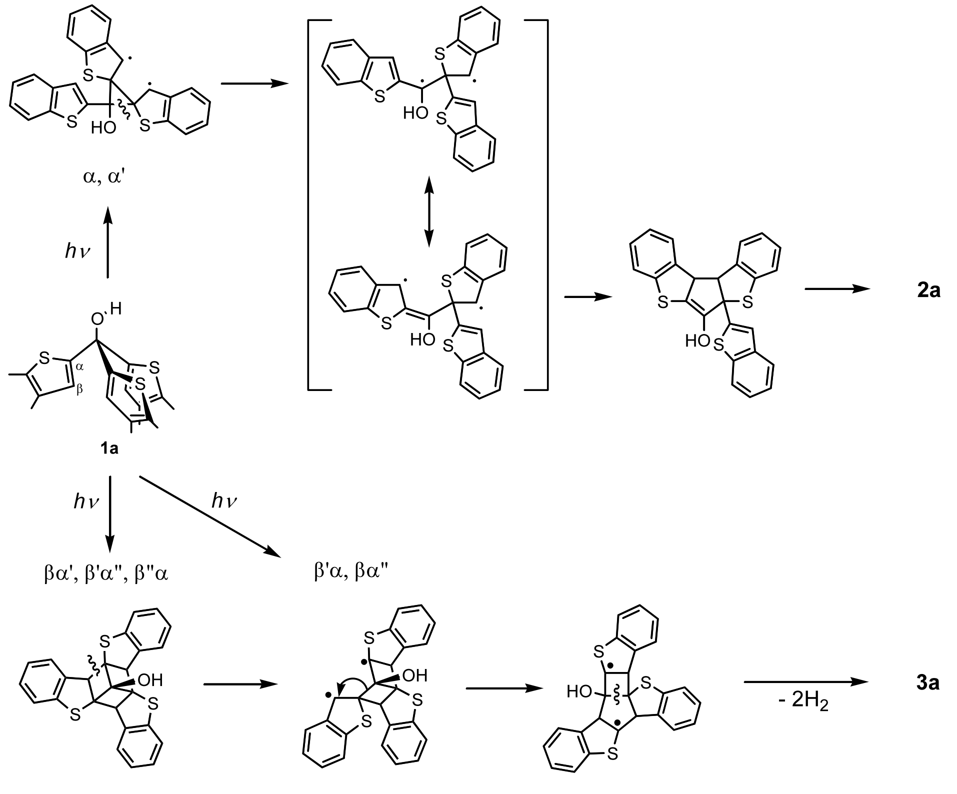
The structure of **2a** and **3a** has been deduced from elemental analysis and spectral data.[5,6] The IR spectrum of **2a** shows a carbonyl band at 1741 cm^{-1} characteristic of cyclopentanone rings. The ^{13}C NMR spectrum exhibits the signals due to a carbonyl carbon (203.8 ppm), a quaternary carbon, and three methine carbons along with 20 aromatic carbons. The coupling pattern of the methine proton signals (3.98, 4.25 and 5.09 ppm) is consistent with occurrence in the cyclopentanone ring of **2a**. The configuration of the ring junction could be deduced based on the NOE measurements.[7]

Compound **3a**, a pale yellow solid, exhibits the ^{13}C NMR signal at 179.5 ppm and the significant IR absorption band at 1653 cm^{-1}. In the mass spectrum of **3a**, only two peaks are distinguished; one is due to the molecular ion and the other at $m/z = 396$ is attributed to the loss of a CO fragment. The ^{1}H NMR spectrum can be interpreted by means of the presence of three *o*-di-substituted benzene rings, implying that the β-position of the three thiophene rings is substituted. Based on these observations, the structure was identified as a tropone derivative fused to three benzo[*b*]thiophene rings.[8] In the ^{1}H NMR spectrum of **3a** a doublet signal appears in a remarkably low field of 9.05 ppm. Thus, one proton should be situated close to the carbonyl group and experience anisotropic shift. The two signals occur also in low field at 8.20 and 8.13 ppm. This observation indicates the existence of two protons closely facing the aromatic ring. Upon the addition of a shift reagent, Eu(fod)$_3$, only the doublet signal at 9.05 ppm moved remarkably to lower field, while the other signals were not affected. Besides **3a**, there are three other possibilities accounting for the pattern of benzo[*b*]thiophene-fusion.[9] However, none of them can rationalize the spectral characteristics.

A similar photoreaction was induced also in methyl-substituted derivative **1b**, giving rise to **2b** (33%) and **3b** (30%).[10] The photoproduct **3b** exhibits a simpler ^{1}H NMR spectrum in the aromatic region than **3a**, supporting further the condensed-tropone structure of the photoproduct.

The inter-conversion between **2a** and **3a** was not induced under the photolysis conditions. Thus, the photoproducts are not the precursor to each other. The isomerization of **1a** to **2a** is interpreted based on the di-π-methane rearrangement which involves the two benzo[*b*]thiophene rings in **1a**; a resonance structure of the 1,3-diradical, which is formed via the 1,4-diradical intermediate of the di-π-methane rearrangement, could make its cyclization possible to give a cyclopentene framework (Scheme 2). The resulting cyclic enol can be transformed to its keto form **2a**.[11] 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.[12,13]

As for the formation of a novel product **3a**, the bond formations between the α and β carbons among three thiophene rings are most plausible as an initial photoprocess. The resulting 1,6-diradical intermediate of a bicyclo[2.2.0]hexane backbone could undergo rear-



Scheme 2.

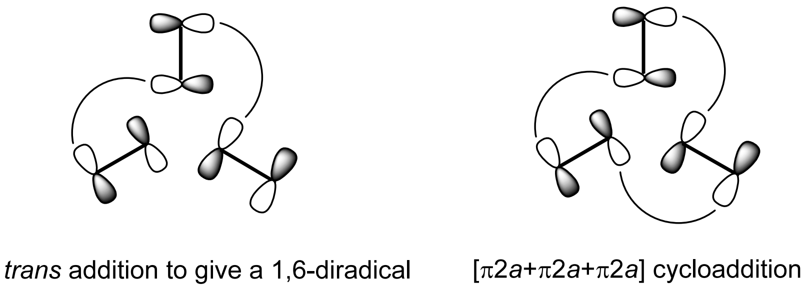
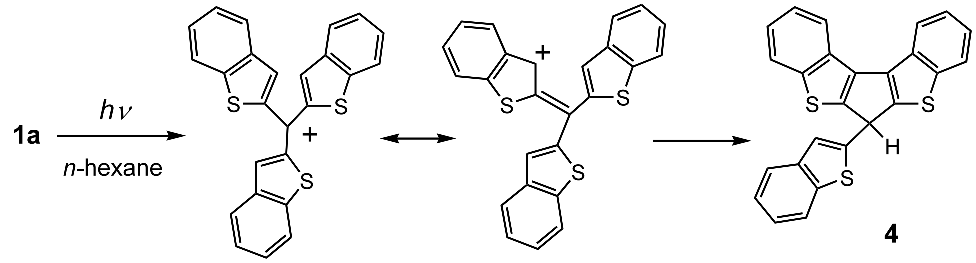


Figure 1.



Scheme 3.

rangement, ring expansion, and oxidation finally to produce **3a**. The initial trimerization of three unsaturated bonds of the thiophene rings should take place as *trans* addition because of the spacial requirement for bonding between the α and β carbons in the adjacent thiophene rings (Fig. 1). Otherwise, concerted [π2a+π2a+π2a] cycloaddition can be assumed (Fig. 1), which is photochemically allowed but has not been reported so far.[4]

The three unsaturated bonds of each benzo[*b*]thiophene ring are considered to arrange side-by-side as depicted in Scheme 2, because the attractive interaction between the C–O and C–S bonds makes their gauche conformation favorable.[14,15] In such spacial situation, the bond formation between the α and β positions among the three or two benzo[*b*]thiophene rings would be possible to give **3a** as well as that between the α and α positions which gives rise to **2a**.

We cannot distinguish between the stepwise and concerted mechanisms at this stage. In any event, the intramolecular co-occurrence of the α-α′ bonding and the β′-α, β-α″ bonding is a novel aspect in the photochemistry of thiophenes. The formation of **3a** requires the elimination of four hydrogens. Concomitant dehydrogenation is considered to occur in the photoreaction and not during the work-up procedure, because the appearance of the NMR signals due to **3a** was observed upon irradiation of a CD_3CN solution of **1a** in an NMR tube.

The triarylmethyl-type *tert*-alcohols have been known to undergo nucleophilic photosubstitution.[16] Compound **1a** should generate a stable carbocation due to thiophene substitution.[17,18] Thus, **1a** was irradiated in methanol. However, no photosolvolysis took place to give the methoxy derivative, but again **2a** and **3a** were obtained in 45 and 22% yields, respectively. In contrast, irradiation in *n*-hexane resulted in the formation of a cyclopentadiene compound **4** (41%)[19] and neither **2a** nor **3a** was obtained. It seems most likely that **4** is formed via the *tert*-carbocation and subsequent ring-closure by intramolecular electrophilic attack (Scheme 3). In fact, when treated with *p*-toluenesulfonic acid, compound **1a** was thermally converted to **4** in almost quantitative yield. 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.

Acknowledgements

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5. For **2a**: mp 211–212°C. ^{1}H NMR ($CDCl_3$) δ 3.98 (1H, t, $J=8.0$ Hz), 4.25 (1H, d, $J=8.0$ Hz), 5.09 (1H, d, $J=8.0$ Hz), 7.33∼7.14 (10H, m), 7.42 (1H, s), 7.64 (1H, d, $J=7.1$ Hz), 7.69 (1H, d, $J=7.\ 1$ Hz); ^{13}C NMR ($CDCl_3$) δ 54.2, 58.7, 64.9, 72.4, 122.1, 122.5, 122.8, 122.7, 123.7, 124.4, 124.6, 124.7, 124.9, 125.2, 125.8, 128.9, 129.2, 138.2, 139.1, 139.3, 139.4, 140.5, 141.1, 143.1, 203.8; MS (m/z) 428 (M^+, 31%), 266 (100%); IR (KBr) 1741 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ε) 292 (26000), 303 (2900) nm. Anal. calcd for $C_{25}H_{16}OS_3$: C, 70.09; H, 3.74; S, 22.43. Found: C, 70.13; H, 3.98, S, 22.04.
6. For **3a**: mp 223–224°C. ^{1}H NMR ($CDCl_3$) δ 7.38 (2H, t, $J=7.5$ Hz), 7.48–7.58 (4H, m), 7.89 (1H, d, $J=8.0$ Hz), 7.95 (1H, d, $J=8.0$ Hz), 8.01 (1H, d, $J=8.5$ Hz), 8.13 (1H, d, $J=8.5$ Hz), 8.20 (1H, d, $J=8.5$ Hz), 9.05 (1H, d, $J=7.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 121.5, 122.4, 122.9, 123.7, 124.2, 126.4, 126.7, 126.8, 126.9, 127.2, 127.4, 127.5, 128.8, 130.3, 132.7, 135.5, 137.8, 138.0, 138.1, 138.3, 139.4, 141.2, 144.3, 148.5, 179.5; MS (m/z) 424 (M^+, 100%), 396 (67%); IR (KBr) 1653, 1578 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ε) 327 (3500), 417 (19000) nm. Anal. calcd for $C_{25}H_{12}OS_3$: C, 70.75; H, 2.83, S, 22.64. Found: C, 70.56; H, 2.76; S, 22.44.
7. NOE-enhancement was not observed between the methine protons in 3- and 4-positions of the cyclopentanone ring.
8. The carbonyl absorption of 1653 cm^{-1} seems to fall at low frequencies as a conjugated cyclic ketone. We assume that the substitution of the three sulfur atoms in the tropone framework causes reduction in the frequency due to resonance contribution. This is also suggested by the ^{13}C NMR: the chemical shift of 179.5 ppm corresponds to that of the carbonyl carbons in esters rather than cyclic ketones.
9. Besides **3a**, there are three other possibilities, **A**, **B** and **C**, for the pattern of benzo[*b*]thiophene-fusion. However, none of them can rationalize the spectral characteristics. For **A** and **B** the chemical shifts of two face-to-face aromatic protons should occur in lower field than that observed because of their remarkable proximity. Furthermore, the NOE measurements of **3a** gave no evidence for the presence of closely-neighboring protons. For **C** two protons facing the carbonyl group should exhibit almost the same chemical shift because of the nearly equivalent environment.
10. For **2b**: ^{1}H NMR ($CDCl_3$) δ 2.33 (3H, s), 2.35 (3H, s), 2.38 (3H, s), 3.89 (1H, dd, $J=8.1$, 8.4 Hz), 4.17(1H, d, $J=8.1$ Hz), 5.04 (1H, d, $J=8.4$ Hz), 6.98∼7.18 (7H, m), 7.31 (1H, s), 7.41 (1H, s), 7.55 (1H, d, $J=8.1$ Hz); ^{13}C NMR($CDCl_3$) δ 20.9, 21.0, 21.3, 54.1, 58.8, 64.8, 72.5, 121.6, 122.1, 122.4, 123.6, 125.5, 125.7, 126.2, 129.5, 129.8, 133.9, 134.7, 134.9, 135.5, 135.7, 137.0, 139.4, 140.8, 141.3, 143.3, 204.1; IR (KBr) 1740 cm^{-1}.

    For **3b**: ^{1}H NMR ($CDCl_3$) δ 2.42 (6H, s), 2.56 (3H, s), 7.28–7.45 (3H, m), 7.75 (1H, d, $J=8.4$ Hz), 7.82(1H, d, $J=8.4$ Hz), 7.88 (1H, d, $J=8.1$ Hz), 7.95 (1H, s), 8.02 (1H, s), 8.86 (1H, s); ^{13}C NMR ($CDCl_3$) δ 21.4, 21.5, 21.8, 121.0, 121.9, 122.5, 126.7, 126.8, 127.4, 128.5, 128.6, 128.7, 129.2, 130.2, 132.3, 133.4, 133.9, 135.3, 135.8, 136.4, 136.6, 138.2, 138.3, 138.4, 138.6, 144.8, 148.7, 179.6; IR (KBr) 1654, 1577 cm^{-1}.
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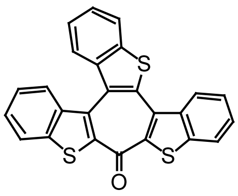
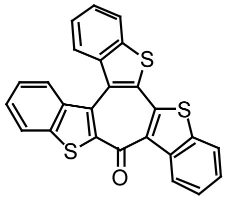
19. For **4**: mp 234–235°C. ^{1}H NMR($CDCl_3$) δ 5.57 (1H, s), 7.32 (2H, t, $J=8$ Hz), 7.34 (1H, s), 7.40 (2H, t, $J=8$ Hz), 7.57(2H, t, $J=8$ Hz), 7.70 (1H, d, $J=8$ Hz), 7.74 (1H, d, $J=8$ Hz), 7.90 (2H, d, $J=8$ Hz), 8.48 (2H, d, $J=10$ Hz); ^{13}C NMR ($CDCl_3$) δ 46.9, 122.2, 122.4, 123.4, 123.5, 124.0, 124.3, 124.4, 124.9, 131.9, 138.3, 139.5, 139.7, 142.0, 144.4, 148.7; MS (m/z) 410 (M^+); UV (CH_2Cl_2) λ_{max} (ε) 387 (2100), 402 (2500) nm.



A



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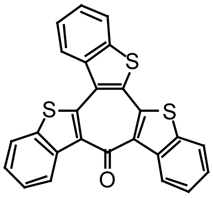

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