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Photoaddition Reactions of Acetylene and Butadiyne Derivatives to Benzodithiophene[†,1]

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Abstract: The photochemical $[2\pi + 2\pi]$ cycloaddition of dimethyl acetylenedicarboxylate to benzo[1,2-*b*:4,5-*b′*]-dithiophene has been used to synthesize substituted cyclobuta[*b*]thieno[2,3-*f*][1]benzothiophene. The first $[2\pi + 2\pi]$ photocycloaddition reaction of a series of butadiynes to benzodithiophene is reported to yield regioselective and acetylene-substituted cyclobutene derivatives containing an aromatic thiophene moiety.

In the classic review about thiophene, Wynberg[2] wrote, “To many chemists thiophene is merely one member of the inexhaustible supply of heterocyclic compounds.” Despite being known for 100+ years, it has never found large-scale industrial use save in some semisynthetic pencillins.[2] Today, due mostly to their efficient electrochemical polymerization, thiophene-containing building blocks play major roles in the development of new materials ranging from conducting polymers,[3] organic semiconductors,[4] and polymeric liquid crystals.[5] The fascinating photochemistry of thiophenes, some of which was also first reported by Wynberg,[6] remains largely unexplored. For instance, thiophene possesses the unique ability to undergo photochemical cycloaddition reactions with acetylenes.[7] This can be used as a convenient pathway in the transformation of a thiophene to a benzene moiety. We report herein the first in a series studies that explore photochemical approaches in the synthesis of oligo[*n*]acenes,[8] polycyclic aromatic hydrocarbons of the Clar type,[8] and molecular subunits of graphite.[9]

Intermolecular photoaddition reactions of acetylenes to heteroaromatic compounds such as furan, thiophene, and pyrrole have been previously reported.[10] The photochemical reaction of thiophene and dimethyl acetylenedicarboxylate (**1**) affords a $[4\pi + 2\pi]$ Diels−Alder adduct that undergoes instant extrusion of sulfur yielding dimethyl phthalate as the sole reaction product.[7] Benzo[*b*]thiophene (BT) undergoes cycloaddition reactions with **1**, methyl propiolate, and methyl phenylpropiolate affording adducts that differ from the expected simple $[2\pi + 2\pi]$ photoadduct.[11,12] The primary adduct of **1** to BT undergoes a secondary photorearrangement under the reaction conditions.[13] Interestingly, this rearranged photoadduct is thermally unstable and yields naphthalene 1,2-dimethyl carboxylate upon pyrolysis.[12]

We have investigated the photochemical $[2\pi + 2\pi]$ cycloaddition of **1** to benzo[1,2-*b*:4,5-*b′*]dithiophene (**2**), Scheme 1. Irradiation of **1** and **2** at 300 nm for 16 h yields one product. As expected, the reaction proceeds directly to the secondary photoadduct **4** as observed by ^{1}H NMR. Product **4** was isolated in 16% yield, and unreacted starting material **2** was recovered. Gas chromatographic analysis of **4** shows $m/z = 300$ [M$^+$ − 32], which is attributed to the thermal rearrangement product (detector temperature = 270 °C) yielding dimethyl naphtho[2,3-*b*]thiophene-5,6-dicarboxylate (**5**),[14] in agreement with previous literature reports.[12,15,16]

Photocycloaddition of conjugated poly-ynes to alkenes yields cyclobutene adducts and minor quantities of bicyclopropyl adducts.[17] Diphenyl-1,3-butadiyne (**6a**) undergoes photoaddition to various alkenes such as 2,3-dimethylbut-2-ene,[18] dimethyl fumarate,[19] acrylonitrile, and ethyl vinyl ether[20] affording regioselective and site-selective cyclobutene derivatives, cyclopropyl, and oxirane adducts. The proposed reaction pathways involved a cumulene-type triplet excited state, a polar triplet structure of the 1:1 cyclobutene adduct, and carbene intermediates in the case of cyclopropyl and oxirane adducts.[18,19]

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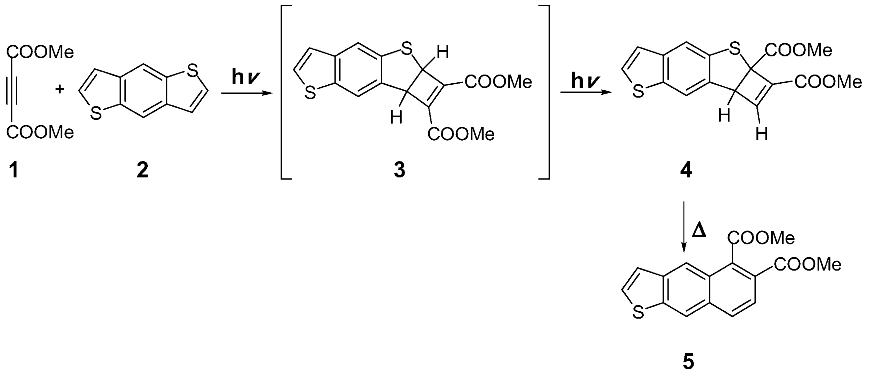
SCHEME 1. Photoaddition of Dimethyl Acetylenedicarboxylate (1) to Benzo[1,2-*b*:4,5-*b*′]dithiophene (2)



SCHEME 2. Photoaddition of Butadiynes (6a−d) to Benzo[1,2-*b*:4,5-*b*′]dithiophene (2)

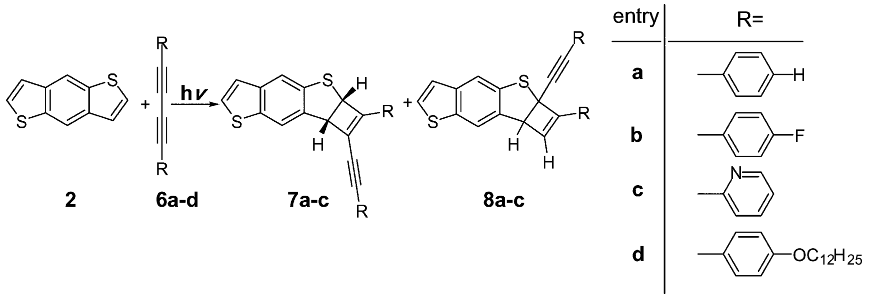


TABLE 1. Comparison of ^{1}H NMR Data of Photoproducts 7 and 8

	^{1}H NMR signal of **7**		^{1}H NMR signal of **8**	
diyne	H$_1$[a]	H$_2$[a]	H$_3$[a]	H$_4$[a]
6a	4.54 *d* 4.4	4.72 *d* 4.4	4.64 *s*	5.91 *s*
6b	4.52 *d* 4.4	4.63 *d* 4.4	4.62 *s*	5.81 *s*
6c	4.47 *d* 4.4	5.12 *d* 4.4	[b]	[b]
6d	[b]	[b]	[b]	[b]

[a] Chemical shift δ (ppm), multiplicity (*d*, *s*), coupling constant *J* (Hz). [b] No corresponding peaks were observed.

Our studies involved the $[2\pi + 2\pi]$ photocycloaddition reaction of **2** to a series of electron-poor and electron-rich butadiynes (**6a**−**d**). This reaction yielded two major products identified as cyclobutene derivatives **7** and **8** as confirmed using ^{1}H NMR spectroscopy, Table 1.

The photoreactions of **2** to diphenylbuta-1,3-diyne (**6a**), bis(4′-fluorophenyl)buta-1,3-diyne (**6b**),[21] bis(2′-pyridyl)-butadiyne (**6c**)[22] were successfully carried out. The electron-rich diyne, bis(4′-dodecyloxy)buta-1,3-diyne (**6d**),[23] does not undergo photoaddition to **2**. All results are summarized in Scheme 2, Table 1.

The UV−vis absorption spectrum of a mixture of **2** and **6a** is a superposition of the individual spectra of **2** and **6a**; we can therefore rule out a ground-state complex in the reaction pathway.[24] The molar decadic extinction coefficient of **2** is 3−5-fold higher than that of **6a** in the spectral region between 300 and 350 nm.[25,26] Since we irradiate at 300 nm and the most efficient product formation occurs when **2** is used in excess, we deduce that **6a** is the reactive species in the photoreaction. Alternatively, **2** and **6a** might form an excited-state complex, but this assumption has to be investigated further.[16]

The 0−0 band of **2** was assigned at 489 nm and corresponds to a triplet energy of 59 kcal/mol.[27] The triplet energy of **6a** is 58 kcal/mol.[28] The yield of the photoproduct as observed by NMR was slightly increased in the presence of iodoethane, while the presence of piperylene ($E_T = 57$ kcal/mol; triplet quencher)[7] decreased the yield of photoproduct, suggesting a photoreaction via the triplet excited state of **2**.

Photoadduct **7a** was isolated by column chromatography and characterized. The isolated yield of photoproduct **7a** is 4%. When photolyzed separately, **2** and **6a**[29] do not undergo photodecomposition under the reaction conditions as observed by ^{1}H NMR. Unreacted **2** and **6a** can be recovered after photolysis.

The absorption spectrum of **7a** in ethanol (Figure 1) exhibits a broad structureless absorption band around 300−350 nm. This band is similar to the charge-transfer absorption band as observed in the unrearranged photoproduct of **1** and benzo[*b*]thiophene.[13]

The photoaddition reaction is regioselective. An X-ray crystal structure[30] of **7a** reveals that the photoaddition

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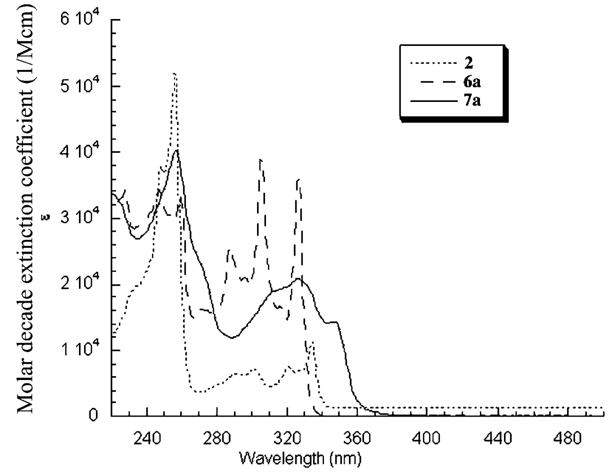

FIGURE 1. Absorption spectrum of **2**, **6a**, and **7a** in ethanol.

reaction proceeds in a syn configuration.[31] Future studies will explore the transformation of photoadduct **7a** into a phenyl acetylene-substituted naphtho[2,3-*b*]thiophene via the photochemical rearrangement followed by a thermal desulfurization.

In summary, we have shown the successful photoaddition of dimethyl acetylenedicarboxylate (**1**) to benzodithiophene (**2**). A new reaction, the photoaddition of benzo[1,2-*b*:4,5-*b*′]dithiophene (**2**) to butadiynes, is introduced. This photoreaction leads to new, regioselective acetylene-substituted cyclobutene derivatives.

Experimental Section

All photochemical reactions were carried out in NMR tubes (ϕ 5 mm; cutoff = 300 nm) purged with dry argon. Photoreactions were carried out for 16 h in a Rayonet photochemical reactor using 16 lamps (300 nm, 21 W each). UV-grade benzene was dried by azeotropic distillation and stored over molecular sieves under argon.

Dimethyl Cyclobuta[*b*]thieno[2,3-*f*][1]benzothiophene-5a,6[7a*H*]-dicarboxylate (4): yield, 16%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (3H, s), 3.85 (3H, s), 6.90 (1H, d, $J = 1.2$ Hz), 7.20 (1H, d, $J = 5.4$ Hz), 7.40 (1H, d, $J = 5.4$ Hz), 7.58 (1H, s) 7.70 (1H, d, $J = 0.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 165.1, 160.8, 146.6, 140.8, 139.2, 138.5, 137.2, 130.4, 127.8, 123.2, 119.0, 117.4, 59.4, 53.6, 52.2. Anal. Calcd for $C_{16}H_{12}S_2O_4$: C, 57.81; H, 3.64; S, 19.29. Found: C, 57.62; H, 3.76; S, 19.44. Mp = 154−155 °C.

6-Phenyl-7-(phenylethynyl)-5a,7a-dihydrocyclobuta[*b*]thieno[2,3-*f*][1]benzothiophene (7a): yield 4%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97 (1H, d, $J = 4.4$ Hz), 5.15 (1H, d, $J = 4.4$ Hz), 7.16 (1H, d, $J = 5.5$ Hz), 7.33−7.42 (7H, m), 7.51−7.54 (3H, m), 7.71−7.73 (2H, m), 7.85 (1H, d, $J = 0.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.6, 140.5, 140.2, 137.0, 133.6, 132.4, 132.2, 129.4, 129.2, 128.9, 128.8, 127.1, 126.6, 123.2, 123.0, 122.8, 119.1, 117.7, 97.4, 83.9, 57.4, 49.0. Crystallization from $CHCl_3$/pentane gave white needles, mp 202 °C. MS *m*/*z* (%): 392 (12) [M], 358 (3), 290 (11), 202 (6), 190 (100). Anal. Calcd for $C_{26}H_{16}S_2 \cdot 1H_2O$: C, 76.06; H, 4.42; S, 15.62. Found: C, 76.02; H, 4.08; S, 16.03. HRMW ($C_{26}H_{16}S_2$): calcd mass, 392.069644; found mass, 392.069408.

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Supporting Information Available: Spectroscopic data of **2** and **6a**−**d**, copies of ^{1}H and ^{13}C NMR of compounds **4** and **7a**, and X-ray structure data refinement and ORTEP of **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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