Photochemistry of Diethynyl Sulfides: A Cycloaromatization for the Formation of Five-Membered Rings

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Supplementary Information

Photochemical reactions: A solution (0.4 mM) of the diethynyl sulfide was sparged with nitrogen, and the deaerated solution was irradiated in a quartz tube. Trapping agent, 1,4-cyclohexadiene (CHD) or γ-terpinene (terp), was added to the hexanes solutions prior to reaction. A Rayonet (model RPR 600-Mini) photochemical reactor equipped with a "merry-go-round" apparatus and eight 300 nm bulbs (RMR 3000) or eight 350 nm bulbs (RMR 3500) was used as the source. Yields were measured by gas chromatography against dodecane internal standard using a Shimadzu GC-17A with a flame ionization detector and are normalized for response. Product identification was achieved by GC-MS analysis using a ThermoQuest Trace GC equipped with a Finnigan Polaris/GCQ Plus Ion Trap MS by comparison to the retention times and mass fragmentation patterns of authentic samples (see syntheses below). NMR spectra were obtained with either a Varian Inova 400 or 500 spectrometer and referenced to residual $CHCl_3$ (7.26 ppm). Mass spectra of oligomerization products were collected with a Micromass Tof Spec 2E without matrix. IR spectra were measured with a Perkin Elmer Spectrum BX.

An authentic sample of 3,4-diphenylthiophene (**4a**) was synthesized according to the literature procedure[1] employing 2.2 eq of phenylmagnesium bromide. Authentic samples of 3,4-dipropylthiophene (**4b**) and 3-phenyl-4-propylthiophene (**4c**) were synthesized via Grignard crosscoupling of 3,4-dibromothiophene with phenylmagnesium bromide and propylmagnesium bromide. Pentanoic acid ethyl ester was synthesized by the reaction of valeric anhydride with ethanol. This was converted to the thionoester (**6b**) using Lawesson's reagent.[2] Phenyl-thioacetic acid *o*-ethyl ester (**6c**) was synthesized by reacting phenylacetyl chloride with ethanol followed by conversion to thionoester.[2] Pentanoic acid isopropyl ester was synthesized by the reaction of valeric anhydride with isopropanol and then converted to the thionoester (**6d**).[2] Butyl phenylethynyl sulfide (**9**) was synthesized according to the literature procedure.[3]

Preparation of bis(phenylethynyl) sufide (3a): Bis(phenylethynyl) sulfide[4,5] was purified by flash chromatography on silica gel (hexanes as eluent). UV-Vis (hexanes): 222 nm (ε = 26,700), 239 nm (ε = 29,600), 260 nm (ε = 25,200), and 282 nm (ε = 15,000).

Synthesis of dipentynyl sulfide (di-but-1-ynyl-sulfane, 3b) and phenylethynyl pentynyl sulfide (pent-1-ynylsulfanylethynyl-benzene, 3c): A solution of pentyne (0.690 mL, 6.99 mmol) and phenyl acetylene (0.383 mL, 3.49 mmol) in anhydrous ether (25 mL) was cooled to –78 °C. BuLi (1.6 M in hexane, 6.40 mL, 10.2 mmol) was added dropwise and the reaction mixture stirred for 1 hr. The mixture remained at –78 °C and a solution of SCl_2 (0.318 mL, 5.01 mmol) in anhydrous ether (10 mL) cooled to 0 °C was added dropwise via cannula. The solution was stirred for 1 hr and allowed to warm to room temp. The reaction mixture was then poured into a separatory funnel containing 50 mL of deionized water. The aqueous layer was removed and extracted with hexanes (2 × 50 mL). The organic layers were combined and washed with brine (2 × 100 mL) and dried over anhydrous sodium sulfate. Flash chromatography on silica gel (hexanes as eluent) provided the products as pale yellow oils. Yield **3b**: 143 mg (15.2%). IR (film): 2963 (s), 2933 (s), 2872 (m), 2198 (w), 1462 (m), 1380 (w), 1337 (m), 1324 (m), 1272 (m), 879 (w), 783 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.29 (t, *J* = 7.1 Hz, 2H), 1.55 (tq, *J* = 7.3, 7.3 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 96.00, 62.62, 22.05, 21.82, 13.47. MS (EI) *m/z* (relative intensity): 166 (M^+, 52), 137 (16), 123 (11), 103 (12), 97 (25), 95 (32), 91 (52), 77 (63), 69 (100). UV-Vis (hexanes): 213 nm (ε = 3,200), 225 nm (ε = 3,200), 245 nm (ε = 1,000). Yield **3c**: 216 mg (22.9%) (5% contamination with **3b**). IR (film): 2963 (s), 2932 (s), 2871 (m), 2197 (w), 2175 (w), 1595 (m), 1486 (s), 1442 (s), 1380 (w), 1337 (w), 1324 (w), 1272 (w), 754 (s), 689 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 - 7.44, 7.34 - 7.29 (m, 5H), 2.33 (t, *J* = 7.1 Hz, 2H), 1.58 (tq, *J* = 7.2, 7.2 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 131.72, 128.74, 128.22, 122.31, 96.60, 94.15, 73.15, 61.56, 22.08, 21.78, 13.51. MS (EI) *m/z* (relative intensity): 200 (M^+, 100), 184 (15), 171 (51), 165 (20), 152 (15), 127 (61), 115 (7), 93 (10), 89 (19), 69 (26). UV-Vis (hexanes): 223 nm (ε = 13,800), 236 nm (ε = 12,700), 247 nm (ε = 11,200), 258 nm (ε = 9,600).

Synthesis of phenyl-thioacetic acid *o*-isopropyl ester (6a): Phenyl-thioacetic acid *o*-isopropyl ester was synthesized via photochemical reaction of **3a** in isopropanol. A solution of **3a** (110 mg, 0.469 mmol) in isopropanol (400 mL) was sparged with nitrogen and irradiated (300 nm) for 20 hrs. Thionoester **6a** was isolated via flash chromatography on silica gel (hexanes as eluent). Yield: 17.6 mg (16.0%). IR (film): 3029 (w), 2978 (m), 2928 (m), 1495 (m), 1453 (m), 1372 (m), 1354 (m), 1302 (s), 1257 (s), 1205 (s), 1173 (s), 1090 (vs), 959 (w), 761 (m), 719 (m), 696 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.24 (m, 5H), 5.59 (sep, *J* = 6.2 Hz, 1H), 4.00 (s, 2H), 1.31 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 219.91, 136.16, 129.01, 128.42, 126.95, 75.79, 65.84, 20.89. MS (EI) *m/z* (relative intensity): 194 (M^+, 10), 152 (21), 135 (4), 119 (9), 91 (100), 65 (13).

Preparation and photochemistry of 2,5-diiodo-3,4-diphenylthiophene: 3,4-Diphenylthiophene was dissolved in dry ether and deprotonated with 1.6M BuLi. After heating to reflux for two hours, the dianion was quenched with iodine after cooling. The product was rotovapped to dryness and recrystallized from ethanol. Irradiations at 300nm were performed in hexanes in quartz tubes with no added trapping agent as alluded to in footnote 12 of the manuscript.

Preparation of trans,trans-bis(2-phenylvinyl) sulfide, and trans-(2-phenylvinyl)-2-phenylethynyl sulfide: Lithium-halogen exchange on β-bromostyrene (0.492 mL, 3.84 mmol) was performed according the literature procedure.[6] Phenylacetylene (0.205 mL, 1.87 mmol) was added via syringe to the lithiostyrene mixture and stirred for one hour. SCl_2 (0.120 mL, 1.89 mmol) was added analogous to the above procedure for **3a** and **3b**. The product mixture was filtered through a pad of silica gel (hexanes as eluent) and used in the photochemical experiment alluded to in the manuscript.

Irradiation of bis(phenylethynyl) sulfide (**3a**) at 300 nm.

Solvent	**4a** (% yield)	**5** (% yield)	**6a**, **c**, or **e** (% yield)
hexanes (1.5 mM CHD)	16	33	—
hexanes (1.7 mM CHD)	16	33	—
hexanes (1.9 mM CHD)	16	33	—
hexanes (2.2 mM CHD)	16	34	—
hexanes (2.7 mM CHD)	14	30	—
hexanes (3.1 mM CHD)	14	32	—
hexanes (3.5 mM CHD)	14	31	—
hexanes (8.5 mM CHD)	12	32	—
hexanes (13 mM CHD)	11	31	—
hexanes (21 mM CHD)	9.0	30	—
hexanes (42 mM CHD)	5.8	28	—
hexanes (85 mM CHD)	3.3	26	—
hexanes (218 mM CHD)	3.4	24	—
hexanes (1.5 mM terp)	11	32	—
hexanes (1.7 mM terp)	14	33	—
hexanes (1.9 mM terp)	13	32	—
hexanes (2.1 mM terp)	13	32	—
isopropanol	8.3	34	20 (**6a**)
ethanol	11	29	22 (**6c**)
methanol	3.6	20	10 (**6e**)
t-butanol	1.6	3.6	—

Irradiation of bis(phenylethynyl) sulfide (**3a**) at 350 nm.

Solvent	**4a** (% yield)	**5a** (% yield)	**6a** or **c** (% yield)
hexanes (1.8 mM CHD)	15	30	—
hexanes (2.2 mM CHD)	15	30	—
hexanes (2.6 mM CHD)	14	30	—
hexanes (3.0 mM CHD)	14	30	—
isopropanol	6.6, (8.7 BORSM)	28, (38 BORSM)	15 (**6a**), (20 BORSM)
ethanol	4.8, (9.8 BORSM)	12, (25 BORSM)	8.4 (**6c**), (16.9 BORSM)

BORSM = based on recovered starting material

Irradiation of dipentynyl sulfide (**3b**) at 300 nm.

Solvent	**4b** (% yield)	**6b** or **d** (% yield)
hexanes (7.7 mM CHD)	2.0	—
isopropanol	—	1.3 (**6b**)
ethanol	—	7.6 (**6d**)

Irradiation of phenylethynyl pentynyl sulfide (**3c**) at 300 nm.

Solvent	**4c** (% yield)	**5a** (% yield)	**6a-d** (% yield)
hexanes (0.5 mM CHD)	2.8	25	—
hexanes (1.7 mM CHD)	2.7	25	—
hexanes (2.1 mM CHD)	2.5	24	—
hexanes (2.5 mM CHD)	2.9	26	—
hexanes (3.0 mM CHD)	3.0	26	—
hexanes (3.4 mM CHD)	2.8	25	—
isopropanol	1.9	21	2.6, 1.4 (**6a**, **6b**)
ethanol	—	12	2.2, 2.9 (**6c**, **6d**)

Irradiation of butyl phenylethynyl sulfide (**9**) at 300 nm.

Solvent	**5a** (% yield)	**6a** (% yield)
isopropanol	1.4	17

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