

Synthesis of Nitrotriphenyleno[1,12-*bcd*]thiophenes [1]

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Sulfur bridging to form triphenyleno[1,12-*bcd*]thiophene (**2**) in *ca.* 46% yield has been effected at 540° by direct addition of crystalline triphenylene (**1**) or dodecahydrotriphenylene (**4**) to a heterogeneous catalyst in a stream of hydrogen sulfide. Treatment of a reaction mixture of **1** and **2** with hydrogen peroxide-glacial acetic acid gives **2** sulfone **2d** and 1,4-triphenylenoquinone (**3**). Reduction of **2d** with lithium aluminum hydride in tetrahydrofuran leads back to **2** (80%), while reductive acetylation of **3** produces 1,4-diacetoxytriphenylene. Treatment of **2** with nitric acid in acetic anhydride at 65° gives a mixture of 1-nitro (30%), 3-nitro (47%), and 1,7-dinitro (11%) derivatives, separable by chromatography on alumina. Structures of these derivatives are assigned on the basis of ultraviolet-visible absorption and proton magnetic resonance spectra, as well as the chemical conversion 1-nitro-**2** → 1,7-dinitro-**2**. The substitution pattern in **2** is correlated with Hückel molecular orbital calculations on reactivity and with substitution in analogous polycyclic, condensed aromatic compounds.

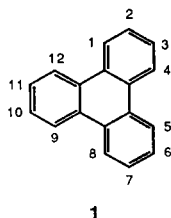
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In a previous publication we reported that passing a solution of triphenylene (**1**) in benzene through a heterogeneous catalyst at 500° in a stream of hydrogen sulfide gas gives sulfur bridging to form triphenyleno[1,12-*bcd*]thiophene (**2**) in 18% yield [4]. Unfortunately, the product mixture from this reaction contained considerable unreacted **1** as well as dibenzothiophene (from reaction of the solvent benzene) [5], both of which are difficult to separate from **2** by the usual methods of recrystallization and column chromatography. Originally we purified **2** *via* its sulfoxide **2e**, but this requires three additional steps of oxidation, column chromatography, and reduction (of the isolated sulfoxide back to **2**), plus recrystallization to remove dibenzothiophene. We now report studies aimed at simplification of both the sulfur-bridging process and the purification methodology.

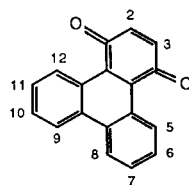
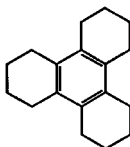
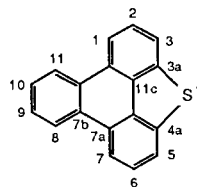
First, an alternative oxidation procedure on an original

sulfur-bridging reaction mixture bearing only 13 mole % of **2** was tried. Refluxing this mixture with hydrogen peroxide in glacial acetic acid produced 2-sulfone **2d** (42% yield), 1,4-triphenylenoquinone (**3**) (1.3%), and recovered 1-separable by crystallization plus chromatography on silica gel. Treatment of the sulfone with lithium aluminum hydride in tetrahydrofuran effected reconversion to **2** in 80% yield. While it is noteworthy that the sulfone can be deoxygenated readily, this procedure offers no improvement over the sulfoxide method for isolation of pure **2**. Structural determination and characterization of quinone **3**, including its reductive acetylation to **1c**, are presented later in this paper.

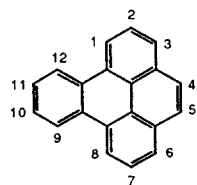
A markedly improved route to pure **2**, however, resulted from conducting the sulfur-bridging process without added solvent in a modification of the procedure used with phenanthrene as substrate [6]. In that method the phenan-

**1**

a, 1-nitro
b, 2-nitro
c, 1,4-diOAc

**3****4****2**

a, 1-nitro
b, 3-nitro
c, 1,7-dinitro
d, 4,4-dioxide
e, 4-oxide

**5**

a, 1-nitro
b, 3-nitro

threne was deposited on alumina pellets which were lowered into the furnace during the reaction proper. In the present case, instead, increments of powdered **1** were shaken onto the top of the catalyst column during the reaction proper. In fact, it was found that dodecahydrotriphenylene (**4**), a synthetic precursor of **1** [7], could be used as well as **1** itself. Thus, the chromia catalyst Harshaw Cr-0101T used effects both dehydrogenation of **4** [8] and sulfur bridging of **1**. Since hydrogen gas is a product of the sulfur-bridging reaction *per se*, it seems reasonable that the extra hydrogen formed from the conversion **4** → **1** in the catalytic reactor does not appreciably affect the insertion of a sulfur bridge. Thus, from **4** as the substrate and a reaction temperature of 540° there were obtained yields of 45% of **1** and 44% of **2** (but no recovered **4**), as based on pmr analysis [9]. Similarly from **1**, the yield of **2** was 47% under essentially the same reaction conditions. Not only are these yields of **2** considerably larger than we obtained before, but the isolation of **2** in 90-96 mole % purity (plus 4-10% of **1**), as based on pmr analysis, could be accomplished by simple crystallization of the crude reaction products.

In an investigation of electrophilic substitution into **2** we treated this substrate with nitric acid/acetic anhydride at 65° for 12 hours and separated the product mixture into three main components, *viz.* 1-nitrotriphenyleno[1,12-*bcd*]thiophene (**2a**), 3-nitrotriphenyleno[1,12-*bcd*]thiophene (**2b**), and 1,7-dinitrotriphenyleno[1,12-*bcd*]thiophene (**2c**) (yields, 30%, 47%, and 11%, respectively) by column chromatography on alumina (*R_f* values, alumina/toluene: **1**, 0.60; **2**, 0.60; **2a**, 0.39; **2c**, 0.25; **2b**, 0.16).

Locations of the nitro groups on the parent ring system **2** were established by a combination of (a) spectral methods, (b) chromatographic data, (c) chemical interconversion, **2a** → **2c**, and (d) correlation with literature data

for various nitroarenes. Because of the symmetry of **2** there are only five possible mononitro derivatives, *i.e.* ones with a substituent in the 1, 2, 3, 8, or 9 position. Based on the concept of steric hindrance to coplanarity of the nitro group with the triphenylenothiophene ring system one can subdivide these five possible isomers into two major categories, *viz.* (1) bay-region 1 and 8 derivatives, where steric interference with a juxtaposed bay-region hydrogen atom (at C-11 and C-7, respectively) should cause marked twisting of the planar nitro substituent out of coplanarity with the aromatic ring structure and (2) non-bay-region 2, 3, and 9 derivatives, where steric hindrance to uniplanarity in the nitro derivative should be relatively small. Comparison of the ultraviolet-visible spectra of **2** and its isolated nitro derivatives permitted initial categorization of **2a-2c** in this manner (Table I).

Examination of Table I shows that mononitro compound **2a** and dinitro compound **2c** have electronic spectra very similar in shape to one another and to the spectrum of **2** itself. This occurs because their nitro groups are all located in bay regions where they are sterically prevented from attaining conjugation with the aromatic ring portion. Mononitro derivative **2b**, on the other hand, shows marked bathochromic shifts (*ca.* 50 nm) of its first (shortest wavelength) β -band and of its longest wavelength maximum, consistent with the presence of conjugation between the nitro group and the aromatic π -electronic system of **2**. This implies effective uniplanarity in the molecule. As a model for comparison of electronic spectra in **2a** and **2b** one has 1- and 2-nitrotriphenylenes **1a** and **1b**, respectively [11]. 1-Nitrotriphenylene, with a bay-region nitro group analogous to that in **2a**, exhibits only one maximum at 258 nm plus a shoulder at 280 nm similar (albeit with much less fine structure) to that of **1**

Table I

Ultraviolet-Visible Absorption Spectral Maxima for **2** and Its Nitro Derivatives [a]

Compound: Maxima:	2 [b]		2a [c]		2b [d]		2c [c]	
	λ	log ϵ	λ	log ϵ	λ	log ϵ	λ	log ϵ
	233 sh	4.53	227	4.61			227	4.56
	243	4.58	245	4.63			248	4.63
β -bands	254	4.49	256	4.56			260 sh	4.53
	264	4.41	266	4.55				
	280	4.40	280 sh	4.36	286	4.47		
			293 sh	4.22	299	4.42	301	4.21
	304 [e]	4.02	302 sh	4.15	311 sh	3.96		
	357 [f]	2.85			359 sh	3.96	359	3.82
			367 sh	3.49	375	4.01		
					399	3.97		
					415	3.95		

[a] λ is given in nm; sh denotes a shoulder. [b] From reference [4], solvent: 95% ethanol. Assignment of β -bands is based on the system of E. Clar for **5** [10]. [c] Solvent: absolute ethanol (benzene-free). [d] Solvent: toluene. [e] Three other maxima at 317, 341, and 348 also occur for **2** between 304 and 357 nm. [f] An α -band.

(maxima at 257 and 284 nm) [12]. However, the spectrum of 2-nitrotriphenylene exhibits long-wavelength maxima at 312 and 335 nm ($\log \epsilon$ 3.93 and 3.94), not seen in the spectrum of **1a**. Similarly, **2b** has long-wavelength maxima at 399 and 415 nm ($\log \epsilon$ 3.97 and 3.95). The large bathochromic shift of 80-87 nm in these long-wavelength maxima on going from **1b** to **2b** may be ascribed to the enhanced conjugation which the sulfur atom in system **2** provides. One might also expect 1- and 3-nitrobenzo[*e*]pyrenes **5a** and **5b** to be suitable models for spectral comparison, since **2** is a thienolog of **5** [13]. However, this does not prove to be the case. The spectra of **5a** and **5b** are not greatly different in the long-wavelength region (maxima at 376 and 373 nm, respectively) [14]. While the rationale for this situation is uncertain [15], we suggest that *peri*-interaction between the nitro group and H-4 in **5b** may be sufficient to cause greater deviation from coplanarity in **5b** than in **2b** (no *peri* hydrogen) and result in dissimilar degrees of conjugation in these two molecules.

The R_f values of the nitro derivatives (*vide supra*) are consistent with the assigned structures and with the proposal that the parent ring system should be adsorbed preferentially flatwise (on alumina or silica gel) with the nitro group(s) coplanar to the aromatic rings where possible [16]. Thus, the 3-nitro derivative **2b** has a lower R_f value than the 1-nitro derivative **2a**. In addition, the dinitro derivative (with two bay-region substituents) is more strongly adsorbed than **2a** [16]. The relative adsorbabilities of the mononitrotriphenylenes and mononitrobenzo[*e*]pyrenes also fit these generalizations in that **1b** > **1a** and **5b** > **5a** in adsorbability [11,14,17].

Finally, specific structural assignments were made to **2a** and **2b** on the basis of pmr spectral data. The method used consists of (a) comparison of changes in chemical shifts ($\Delta\delta$) for selected protons which result from the conversions **2** \rightarrow **2a** and **2** \rightarrow **2b**, and (b) correlation of these $\Delta\delta$ values in system **2** with the analogous values in system **5**, *i.e.* for **5** \rightarrow **5a** and **5** \rightarrow **5b** [14,19,20]. In this analysis we are not concerned with the signals for H-4 and H-5 in system **5**, since they have no counterpart in system **2**. It should be noted that the structural assignments for **5a** and **5b** have been clearly established by extensive experimental investigation [14,19]. First, as expected, signals for the bay region hydrogens in **2** and **5** occur farthest downfield (δ = 8.47 for H-1 and H-7, 8.75 for H-8 and H-11 in **2**; 8.81 for H-1 and H-8, 8.76 for H-9 and H-12 in **5**) perhaps due to repulsive van der Waals interaction [21]. In the transformation **2** \rightarrow **2a** one of the signals for a bay region hydrogen disappears and the others are shifted upfield ($\Delta\delta$ = -0.05 for H-7 and H-8, -0.53 for H-11). The large upfield shift for the H-11 signal is consistent with the introduction of an out-of-plane nitro group at C-1. This is corroborated by a small change $\Delta\delta$ = 0.07-0.15 in the signal

for the ortho proton H-2 [15]. Correspondingly the transformation **5** \rightarrow **5a** shows $\Delta\delta$ = -0.52 for H-12 and +0.24 for ortho proton H-2. In the case of **2** \rightarrow **2b** all signals for bay region hydrogens are still present and are shifted *downfield* by 0.06 to 0.33 ppm. In fact, all non-bay region hydrogen signals are also shifted downfield similarly, but with a large value of $\Delta\delta$ = 0.69 occurring for ortho hydrogen H-2. This effect on the chemical shift of H-2 is a typical amount [15]. Again for the conversion **5** \rightarrow **5b** all proton signals are shifted downfield with $\Delta\delta$ = 0.76 for ortho proton H-2 and $\Delta\delta$ = 0.11-0.23 for the other signals.

The pmr spectrum for dinitro derivative **2c** is surprisingly simple in appearance in that it consists of two overlapping doublets at 8.28 and also at 7.73 ppm, plus the signal for an AB spin system at 8.13. Thus, it is clear that the nitro groups must occupy positions of symmetry in parent structure **2**. The presence of the AB system provided only two possible substitution patterns, *viz.* 1,7 and 3,5. Although the ultraviolet-visible absorption spectrum and the R_f value left little doubt that the correct structure must be 1,7-dinitrotriphenyleno[1,12-*bcd*]thiophene, it seemed desirable to corroborate this assignment by chemical evidence. This was accomplished by conducting further nitration on the 1-nitro derivative **2a** and on the 3-nitro derivative **2b**. Only **2a** produced some **2c**. No identified products were obtained from **2b**.

Norwegian workers noted that only nitroarenes bearing a bay region nitro group show a mass spectral peak for loss of OH from the molecular ion [11,14]. We did observe a very small peak at ($M - 17$) for **2a**, but found no peak at either ($M - 17$) or ($M - 34$) for **2c**. The mass spectra of **2b** and **2c** at a source temperature of 200°, however, exhibited large peaks for ($M - 76$) and ($M - 77$); 49% and 96% for **2b**, 50% and 59% for **2c**. It seems possible that these peaks result from the loss of benzyne and phenyl radicals, respectively, from retro-Diels-Alder fragmentation of the molecular ion. Further investigation of mass spectral fragmentation patterns of **2a-2c** as a function of source temperature and ionizing voltage seems warranted.

Electrophilic substitution at positions 1 and 3 of triphenylenothiophene **2** is expected on the basis of ortho, para orientation by a ring-activating sulfur atom. Quantitatively, molecular orbital calculations (Table II) show nearly identical reactivity indices for these two positions. The experimental observation that one obtains a ratio of mononitro isomers of **2b:2a** = 1.6:1.0 seems inconsistent with the HMO calculations until one takes into account the simultaneous formation of 1,7-dinitro-**2** in 11% yield. Assuming that the bay region nitro group in **2a** is twisted so far out of coplanarity with the aromatic ring that the deactivating effect of the nitro group on further electrophilic substitution is negligible one can calculate a revised

observed reactivity ratio of 1-substitution:3-substitution = $(30 + 2 \times 11)\%:47\% = 1.1:1.0$. Thus, it appears that steric hindrance to substitution at C-1 is either counterbalanced by resonance activation by the sulfur atom or is of no real pertinence.

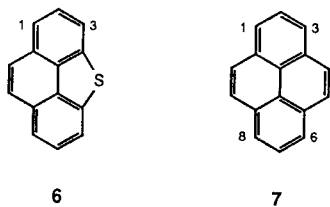
Table II

Calculated Reactivity Indices for Compound **2** [a]

Position r	S_r^{elec}	S_r^{nucl}
1	2.19	0.80
2	1.01	0.79
3	2.24	0.85
3a	0.89	0.66
4	6.49	0.42
7a	0.99	0.77
7b	0.84	0.79
8	0.97	0.92
9	0.93	0.87
11c	1.51	0.62

[a] S_r is given in units of β_c^{-1} and represents superdelocalizability toward electrophilic or nucleophilic attack, as based on simple HMO theory with $\alpha_s = \alpha_c$ and $\beta_{c-s} = 0.9 \beta_{c-c}$ [22,23].

It is of interest to compare the ratios of isomers formed on nitration of analogous polycyclic aromatic hydrocarbons and condensed thiophenes by means of nitric acid in acetic acid or acetic anhydride. Triphenylene (**1**) produces a 1:1 ratio of the two possible mononitro derivatives [11,24]. With benzo[*e*]pyrene (**5**) as reactant, the ratio of isomers **5a**:**5b** formed varies from 1:1 to 1.78:1 depending on the ratio of nitric acid to hydrocarbon used [14,25]. Recently we reported that phenanthro[4,5-*bcd*]thiophene (**6**) undergoes nitration at C-1 and C-3 to give variable



isomeric ratios of $1.2 \pm 0.6:1$ [6]. The benzolog of **6**, pyrene (**7**), gives only 1-nitro-**7** plus further nitration at the analogous positions 3, 6, and 8 [11,26,27]. In summary, it is apparent that the pairs of isosteric, *peri*-condensed compounds **2** plus **5** and **6** plus **7** show closely similar substitution patterns on nitration. In fact, even the transformation **1** \rightarrow **2** does not alter this pattern. Thus, while it is convenient to consider that the sulfur atom in **2** and **6** directs an entering nitro group to an ortho or para position, the observed orientation in these five compounds may be influenced largely by the overall geometries of the molecules rather than by other factors.

As noted previously, treatment of a mixture of triphenylene (**1**) and **2** from sulfur bridging with hydrogen peroxide

in glacial acetic acid gives a low yield (1.3%) of quinone **3**. To establish that the source of **3** is actually **1** (rather than **2**) pure triphenylene was also oxidized in the same manner to give a somewhat better yield (7%). This unstable 1,4-quinone was characterized by spectral methods and by reductive acetylation with zinc and acetic anhydride to 1,4-diacetoxytriphenylene (**1c**). Charles *et al.* reported the isolation of a trace of **3** from treatment of **1** with *m*-chloroperbenzoic acid in a two-phase system, but they gave no data on its chemical or physical properties [28]. On the other hand, 1,2-triphenylenedione has been known for a number of years [29].

EXPERIMENTAL [30]

Starting Materials.

1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydrotriphenylene (**4**) was prepared by condensation of cyclohexanone [31], mp 216-224°; pmr: δ 2.59 (s, 12 H- α), 1.79 (s, 12 H- β), used directly in sulfur-bridging reactions.

A mixture of 10 g of recrystallized **4** (mp 230-232°) and 1 g of 30% palladium-on-charcoal was heated over a period of seven hours to 310°, where it was maintained 18 hours longer. The mixture was cooled and processed in the manner used for dehydrogenation of octahydrotriphenylene [32], yield 8.2 g (82%) of triphenylene (**1**), mp 196-199° (lit 196.5-197.5°) [32]; pmr: δ 8.67 (2 overlapping d, 6 H- α), 7.67 (2 overlapping d, 6 H- β) [33].

Sulfur-bridging Reactions.

(a) Run with Solvent.

The general procedure of Klemm and Lawrence was used [4], but with a solution of 5.7 g of **1** in 300 ml of warm benzene and 150 g of Harshaw Cr-0101T (chromia/alumina/magnesia) as the catalyst. The effluent yielded 1.6 g of solid product which showed two components by vpc (Dow 710 silicone fluid on 100-120 mesh Chromosorb WHP at 248°): **1** (retention time 3.3 minutes) and **2** (9.6 minutes), molar ratio 1.0:2.3. Extraction of the spent catalyst with chloroform gave 3.9 g of solid product in the molar ratio **1**:**2** = 1.0:0.15. The tlc of these products showed the presence of two other components, not detected by vpc.

Two g of the product obtained from extraction of the catalyst was refluxed with a mixture of 4 ml of 30% hydrogen peroxide and 40 ml of glacial acetic acid for 45 minutes. The cooled solution was diluted with water and extracted with chloroform. The extract was washed with 5% aqueous sodium hydroxide, dried (magnesium sulfate), and rotoevaporated. The residue was chromatographed on 60-200 mesh silica gel to give three fractions: #1, eluted with carbon tetrachloride, recovered **1**; #2, eluted with chloroform; and #3, eluted with chloroform-methanol (3:1). Recrystallization (carbon tetrachloride) of product from fraction 2 gave 25 mg (ca. 1.3% for the oxidation step) of 1,4-triphenylenedione (**3**), as orange needles, mp 186-192°; ir (chloroform): 1650 cm^{-1} (quinone) [34]; pmr: δ 9.29 (d, $J_{5,6} = J_{11,12} = 8.3$ Hz, 2H, H-5 and H-12), 8.76 (d, $J_{7,8} = J_{9,10} = 8.3$ Hz, 2H, H-8 and H-9), 7.80 and 7.75 (2 overlapping t, 4H, H-6, H-7, H-10, H-11), 6.97 (s, 2H, H-2 and H-3) [35]; uv (95% ethanol): λ max (log ϵ) 249 (4.62), 273 sh (3.98), 2.93 sh (3.70), 305 sh (3.62), 417 broad (3.51); ms: (170°) *m/e* 260 (34), 259 (26), 258 (M^+ , 100), 202 ($M^+ - 2CO$, 27), 176 ($M^+ - C_6H_2O_2$, 23), 105 (25).

A sample was recrystallized from acetone and dried for 3 hours at 120° *in vacuo*, mp 198.5-199.5°.

Anal. Calcd. for $C_{18}H_{10}O_2 \cdot 1/10H_2O$: C, 83.13; H, 3.95. Found: C, 83.13; H, 3.82. Exact mass: Calcd. for $C_{18}H_{10}O_2$: 258.068. Found: 258.068.

Chromatographic fraction #3 was separated further by thick layer chromatography (silica gel/chloroform) into 4 zones. Product from the third zone (from the starting line) gave, after recrystallization from acetone, 70 mg (ca. 42% yield for the oxidation step) of sulfone **2d**, mp

324-326° (lit 325-327°) [4]. Similar oxidative workup of the effluent product from the bridging reaction gave considerably more **2d**.

To a refluxing solution of 280 mg of **2d** in 100 ml of peroxide-free THF was added 0.1 g (excess) of lithium aluminum hydride (LAH). The reaction was continued until tlc (silica gel/chloroform) indicated that all **2d** (R_f 0.2) had reacted. Ethyl acetate was added to react with unused LAH and the solution was rotoevaporated. The residue was treated with water and extracted with chloroform. Evaporation of the chloroform gave 200 mg (80%) of **2**, mp 184-185° (lit 190-191°) [4]; pmr: δ 8.75 (2 overlapping d, H-8 and H-11), 8.47 (d, $J_{1,2} = J_{6,7} = 8.3$ Hz, H-1 and H-7), 8.07 (d, $J_{2,3} = J_{5,6} = 8.0$ Hz, H-3 and H-5), 7.88 (t, H-2 and H-6), 7.76 (2 overlapping d, H-9 and H-10).

(b) Run With **4** and Without Solvent.

The general procedure was the same as used previously, but with the following modifications. The dropping funnel was replaced by a length of flexible, translucent plastic tubing attached to the top of the reactor tube at one end and to the mouth of a pyrex addition flask at the other. The reactor tube was packed with 150 g of Harshaw Cr-0101T catalyst and then (on top of it) a zone of pyrex glass beads 3 cm high. The addition flask was charged with 3.66 g of finely powdered dodecahydrotriphenylene (**4**) and the catalyst was conditioned in a stream of hydrogen sulfide gas at 540° (reaction temperature) for a period of 2 hours. Then the addition flask was periodically raised and shaken to introduce small increments of **4** into the reactor over a period of 2 more hours. Forty-five minutes later (when evolution of hydrogen gas had ceased, as evidenced by observing the collapse of bubbles in the aqueous potassium hydroxide gas trap) the reaction was stopped. From the effluent was obtained 1.47 g of solid, mp 160-172°, consisting of a molar ratio of **2**:**1** = 1.0:1.3 (as indicated by pmr). Sublimate from the cool, lower part of the reactor tube was also collected; 1.13 g, mp 146-158°, molar ratio **2**:**1** = 1.0:1.4. The used catalyst was not removed from the reactor, but was reconditioned and treated with a second batch of 4.45 g of **4** in the same manner to give 1.14 g of solid, mp 159-168°, molar ratio 1.0:1.3, from the effluent and 3.53 g, mp 109-159°, molar ratio 1.0:0.9, from the reactor tube. None of the products showed pmr evidence for the presence of unreacted **4** or other impurities, though elemental sulfur would not be detected; combined yields, 44% of **2**, 45% of **1** [36].

To increase the percentage of **2** in this mixture the crude product was recycled through fresh catalyst and then recrystallized from benzene or benzene-ethanol, as exemplified in part (c).

(c) Run With **1** and Without Solvent.

The general procedure varied slightly from that given in part (b) in that 9.76 g of **1** was used, the reactor tube was larger in diameter (same length of catalyst bed, but packed with 290 g of catalyst), the sample was added over a period of 7 hours, heating was continued 2 hours longer, and only a single pass was made through the reactor. The effluent and reactor tube yielded 7.1 g of solid, mp 136-150°, in a molar ratio of **2**:**1** = 2.3:1.0. Recrystallization from benzene-ethanol allowed removal (by crystal picking) of 0.19 g of elemental sulfur; calculated yield of **2**, 5.0 g (45%). Further crystallizations gave samples containing 90-96 mole % **2**, used directly in nitration reactions.

Oxidation of Pure **1** to Quinone **3**.

A solution of 3.06 g (13.4 mmoles) of triphenylene (**1**) in a mixture of 15.8 ml (0.15 mole) of 30% hydrogen peroxide and 125 ml of glacial acetic acid was refluxed for 55 minutes. The bright orange solution was poured into ice/water and extracted with chloroform. The organic layer was washed with water, dried (sodium sulfate), and rotoevaporated onto 14.7 g of silica gel (J. T. Baker, 60-200 mesh). This impregnated adsorbent was placed atop a column of 101 g of fresh silica gel and eluted, first with carbon tetrachloride and then with chloroform. Recovered **1** (1.59 g; R_f 0.80, silica gel/chloroform) was eluted first. Combined fractions (336 mg) of R_f 0.34-0.47 were rechromatographed with chloroform to yield 249 mg (7%) of crude **3**, mp 182-198°, used directly in the following reductive acetylation reaction.

1,4-Diacetoxytriphenylene (**1c**).

The foregoing crude quinone **3** was refluxed briefly with a mixture of 25 ml of acetic anhydride, 15 mg of sodium acetate, and 0.55 g of zinc dust until the color changed from orange to yellow. The hot solution was filtered to remove unreacted zinc (washed with hot glacial acetic acid), diluted with 15 ml of water, and refluxed for 15 minutes to hydrolyze the solvent. More water was added to give incipient precipitation from the boiling mixture and the solution was allowed to cool in an inert atmosphere. The precipitated solid was dissolved in chloroform and combined with a chloroform extract of the filtrate. The washed (water), dried (sodium sulfate) organic solution was concentrated and chromatographed with silica gel/chloroform to yield three fractions: #1, R_f 0.53, discarded; #2, R_f 0.18, collected as the product; and #3, R_f 0.04, discarded. Recrystallization of fraction #2 from carbon tetrachloride gave 44 mg (13% from **3**) of white needles, mp 149.5-151°, raised to 150.5-151° on recrystallization; ir: 1755 (ester carbonyl), 1190 cm^{-1} ; pmr: δ 9.02 (d, $J_{5,6} = J_{11,12} = 8.4$ Hz, H-5 and H-12), 8.64 (d, $J_{7,8} = J_{9,10} = 7.7$ Hz, H-8 and H-9), 7.67 and 7.60 (2 overlapping t, 4H, H-6, H-7, H-10, H-11), 7.32 (s, H-2 and H-3), 2.47 (s, 6H, 2 methyl groups); ms: (140°) m/e 344 (M^+ , 5), 260 ($M^+ - 2\text{CH}_2 = \text{C}=\text{O}$, 100), 202 ($M^+ - 2[\text{CH}_2 = \text{C}=\text{O} + \text{HCO}]$, 58), 176 (32), 44 (44), 43 (Ac^+ , 76) [37]. Compound **1c** was not obtained in analytically pure form.

Nitration of **2**.

To a stirred solution of 1.06 g of triphenyleno[1,12-*bcd*]thiophene (mp 185-189°, 95 mole % **2**, 3.92 mmoles; 5 mole % **1** [38]) in 140 ml of acetic anhydride was added dropwise (over a period of 65 minutes) 0.4 ml (6.4 mmoles) of 70% nitric acid (density 1.42 g/ml). The stirred mixture was heated at 65° for 12 hours until tlc (alumina/toluene) no longer showed the presence of **2**. The mixture was poured onto ice and extracted with chloroform. This extract was washed successively with water, excess 5% aqueous sodium hydroxide, and water, dried (sodium sulfate) and rotoevaporated to leave 1.14 g of solid. A portion (270 mg) of this solid was chromatographed on a column (2.5 x 30 cm, packed *in vacuo*) of alumina (Baker, 50-200 micron) to give four fractions (first three eluted with toluene; last one, with chloroform): #1, R_f 0.60, recovered **1**; #2, 0.39, 1-nitrotriphenyleno[1,12-*bcd*]thiophene (**2a**); #3, 0.25, 1,7-dinitrotriphenyleno[1,12-*bcd*]thiophene (**2c**); #4, 0.16, 3-nitrotriphenyleno[1,12-*bcd*]thiophene (**2b**). Further studies on these compounds are detailed in the following paragraphs.

1-Nitrotriphenyleno[1,12-*bcd*]thiophene (**2a**).

This compound was recrystallized from chloroform-carbon tetrachloride to yield (from the total **2** used in the nitration) 351 mg (30%) of yellow needles, mp 191.5-192°; ir: 1515 and 1357 (nitro group), 1427, 755 cm^{-1} ; pmr: δ 8.69 (dd, $J_{8,9} = 8.1$ Hz, $J_{8,10} = 1$ Hz, H-8), 8.42 (d, $J_{6,7} = 7.9$ Hz, H-7), 8.22 (dd, $J_{10,11} = 8.4$ Hz, $J_{9,11} = 1$ Hz, H-11), 8.05 (d, $J_{5,6} = 7.9$ Hz, H-5), 8.03 and 7.95 (2 d, $J_{2,3} = 8.2$ Hz, H-2 and H-3), 7.89 (t, H-6), 7.78 and 7.66 (dt, $J_{9,10} = 7.6$ Hz, H-9 and H-10); ms: (140°) m/e 303 (M^+ , 40), 273 ($M^+ - \text{NO}$, 58), 257 (44), 256 ($M^+ - \text{HNO}_2$, 59), 245 ($M^+ - [\text{NO} + \text{CO}]$, 100), 213 (40), 211 (42) [39]. A COSY nmr investigation of **2a** gave results consistent with the assigned structure.

A sample for microanalysis was recrystallized from chloroform-carbon tetrachloride and then from benzene-ethanol, and finally sublimed at 160° (0.025 mm), mp 193.0-193.5°.

Anal. Calcd. for $\text{C}_{18}\text{H}_9\text{NO}_2\text{S}$: C, 71.27; H, 2.99; N, 4.62; exact mass, 303.035. Found: C, 70.98; H, 3.05; N, 4.31; exact mass, 303.035.

3-Nitrotriphenyleno[1,12-*bcd*]thiophene (**2b**).

The crude **2b** (588 mg, 96% pure by pmr, *i.e.* 47% yield) from chromatography was recrystallized from chloroform to give yellow needles, mp 252-253°; ir: 1574, 1514 and 1326 (nitro group), 1308, 757, 743 cm^{-1} ; pmr (deuteriochloroform-carbon tetrachloride): (360 MHz [40]) δ 8.812 (dt, $J_{8,9} = J_{10,11} = 8.1$ Hz, $J_{8,10} = J_{9,11} = 1.5$ Hz, H-8 and H-11); converted to a singlet on double irradiation at 7.888 ppm, 8.804 (d, $J_{1,2} = 8.6$ Hz, H-1),

8.612 (d, $J_{6,7} = 7.9$ Hz, H-7), 8.572 (d, H-2), 8.236 (d, $J_{5,6} = 7.9$ Hz, H-5), 8.024 (t, H-6; converted to a doublet on double irradiation at 8.236 ppm), 7.888 (symmetric m, $J_{9,10} = 7.2$ Hz [41], H-9 and H-10); pmr (hexadeuteriodimethylsulfoxide): (360 MHz [40]) δ 8.252 (ddd, $J_{8,9} = J_{10,11} = 7.9$ Hz, $J_{8,10} = J_{9,11} = 1.4$ Hz, H-8 and H-11), 8.246 (d, $J_{1,2} = 8.6$ Hz, H-1), 8.083 (d, $J_{6,7} = 7.9$ Hz, H-7), 8.035 (d, H-2), 7.714 (d, $J_{5,6} = 7.9$ Hz, H-5), 7.353 (t, H-6), 7.214 (symmetric m, H-9 and H-10); ms: (200°) (quadrupole [42]), m/e 303 (M^+ , 10), 273 ($M^+ - NO$, 100), 243 (23), 227 (49), 226 ($M^+ - C_6H_5$, 96), 224 (24), 215 (28) [43].

Anal. Calcd. for $C_{18}H_5NO_2S$: C, 71.27; H, 2.99; N, 4.62. Found: C, 70.99; H, 2.80; N, 4.47.

1,7-Dinitrotriphenyleno[1,12-*bcd*]thiophene (2c).

This compound was recrystallized from toluene to give 151 mg (11%) of light yellow, translucent prisms, mp 293.5-299°; ir: 1527 and 1358 (nitro groups), 827, 792, 736 cm^{-1} ; pmr: δ 8.28 (2 overlapping d, 2H, H-8 and H-11), 8.13 (dd, AB system, $J_{2,3} = J_{5,6} = 8.4$ Hz, $\Delta\delta = 6.5$ Hz, H-2, H-3, H-5, H-6 [44]), 7.73 (2 overlapping d, 2H, H-9 and H-10); ms: (200°) (quadrupole [42]), m/e 348 (M^+ , 100), 318 ($M^+ - NO$, 24), 301 ($M^+ - HNO_2$, 25), 272 (50), 271 ($M^+ - C_6H_5$, 59), 256 (37), 244 (30), 243 ($M^+ - [C_6H_4 + HCO]$, 65), 211 (47).

Anal. Calcd. for $C_{18}H_6N_2O_4S$: C, 62.07; H, 2.31. Found: C, 62.03; H, 2.12.

Further Nitration of Mononitro Compounds 2a and 2b.

A solution of 110 mg (0.36 mmole) of 1-nitro compound 2a in 50 ml of acetic anhydride was treated with 0.041 ml (0.062 mmole) of 68% nitric acid (density 1.41 g/ml) and the mixture was maintained at 85° for 6 days, during which time a total additional 0.3 ml of nitric acid was added. The reaction mixture was poured into 100 ml of ice/water. The chloroform extract of this aqueous mixture was washed with excess 20% aqueous sodium bicarbonate and then with water, dried (sodium sulfate), and evaporated onto 3 g of aluminum oxide. This solid was placed atop a column (2.5 cm i.d. x 17 cm) of fresh alumina and eluted first with toluene and then with toluene/chloroform. Tlc showed the presence of 4 components: R_f 0.45 (recovered 2a); R_f 0.31 (18.1 mg, 14%) collected as 1,7-dinitro compound 2c; R_f 0.21 and 0, unidentified. The second component was identical with the dinitro compound isolated from direct nitration of 2, as indicated by tlc and nmr.

Similarly a sample of 112 mg of 3-nitro compound 2b was heated with nitric acid in acetic anhydride for 9 days and processed in the foregoing manner. Chromatography showed the presence of only 2 components: recovered 2b (20.9 mg, mp 246-269°, identified by tlc and nmr) and unidentified byproduct, R_f 0.

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