Chemistry of Condensed Thiophenes. III. Acetylation of Triphenyleno[1,12-*bcd*]thiophene [1]

L. H. Klemm*, Eliot Hall [2], Wai M. Lee [3] and Long K. Tran [3]

Department of Chemistry, University of Oregon,
Eugene, Oregon 97403

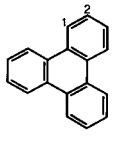
Received September 7, 1988

Dedicated to Professor Ernest Campaigne on the occasion of his 75th birthday

Friedel-Crafts reaction of triphenyleno[1,12-*bcd*]thiophene (**2**) by means of aluminum chloride, nitrobenzene, and a limited excess of acetyl chloride yielded 3-acetyl-**2** (78%) and 3,5-diacetyl-**2** (7%). Use of a large excess of acetyl chloride gave yields of 42% and 22%, respectively. Wolff-Kishner reduction of the acetyl compounds produced 3-ethyl-**2** (15%) and 3,5-diethyl-**2** (8%). Structures were assigned largely on the basis of ^{1}H nmr and ultraviolet absorption spectra of the products.

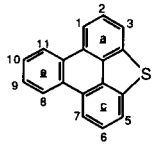
J. Heterocyclic Chem., **26**, 1241 (1989).

In a previous publication we reported the direct conversion of dodecahydrotriphenylene into a mixture of triphenylene (**1**) and triphenyleno[1,12-*bcd*]thiophene (**2**), in approximately equal amounts, by heterogeneous catalysis in a flow system at 540° with hydrogen sulfide as the carrier gas [4]. Nitration of enriched (*ca.* 95 mole %) samples of **2** with nitric acid/acetic anhydride gave 1-nitro, 3-nitro, and 1,7-dinitro derivatives [4]. In continuation of our studies on electrophilic substitution into **2**, we now report Friedel-Crafts acetylation of **2**, as well as Wolff-Kishner reduction of the acetyl derivatives produced.



1

a: 2-Ac



2

a: 3-Ac
b: 3,5-diAc
c: 3-Et
d: 3,5-diEt

Mixtures of **1** and **2** were acetylated by means of acetyl chloride and aluminum chloride in nitrobenzene at 0-22°. Two widely different molar ratios of reactants were used. First, an enriched sample of **2** (93 mole %) was treated with a limited excess of acetyl chloride (molar ratios of 1:2:acetyl chloride:aluminum chloride = 0.08:1:1.5:1.9) to produce 3-acetyltriphenyleno[1,12-*bcd*]thiophene (**2a**) in 78% yield and 3,5-diacetyltriphenyleno[1,12-*bcd*]thiophene (**2b**) in 7% yield. No recovered **2** was identified, while considerable unreacted **1** plus some monoacetylated **1** were found. It is, therefore, apparent that **2** undergoes acetylation far more readily than **1**. In a second experiment, a mixture of **1** and **2** (47 mole %), directly from a sulfur-bridging reaction, was treated with a large excess of acetyl chloride (molar ratios of 1.13:1:6.5:8.2) in a deliberate effort to increase the yield of **2b**. All **1** reacted to give 2-acetyltriphenylene (**1a**) in 81% yield, while **2** was converted into **2a** (42%) and **2b** (22%). Again, the marked activating effect of the heterosulfur atom in electrophilic substitution into the aromatic ring system is observed.

The structural assignment of **2a** is based on its ^{1}H nmr and ultraviolet absorption spectra. The former spectrum shows the presence of an AB system with a coupling constant of 8.2 Hz and no indication of long-range splitting-consistent with the presence of the acetyl group at either C-1 or C-3 in ring *a*, but inconsistent with location of the substituent in ring *e*. In the parent molecule **2** the chemical shifts for the bay region hydrogens occur at δ 8.75 for H-8 and H-11 and at 8.47 for H-1 and H-7 [4]. In **2a** the chemical shifts for three of these protons (H-7 at 8.48, H-8 and H-11 at 8.72) remain essentially unchanged. If the acetyl group were located at C-1, it should be twisted out of coplanarity with the aromatic ring and cause an appreciable upfield shift in the signal for H-11 [5]. Contrariwise, location of the acetyl group at C-3 should permit it to become coplanar with (*i.e.* to conjugate with) the aromatic π-system and to show little effect on the chemical shift of H-11. In fact, conjugation by the acetyl group is readily apparent upon comparison of the wavelengths and log ε values for all observed maxima at λ > 340 nm in **2a** {347 (4.15), 368 (3.92), and 387 (4.03)} and in **2** {341 (3.15), 348 (2.82), and 357 (2.85)} [6]. While the longest wavelength maximum is shifted bathochromically by 30 nm in **2a**, the Δ log ε of 1.18 indicates that an intense absorption band is involved in this shift.

The ^{1}H nmr spectrum of the diacetyl derivative **2b** exhibits only one singlet for both acetyl groups, an AB system for four aromatic protons (J = 8.1 Hz) in rings *a* and *c*, and two signals for two protons each at δ 8.67 (H-8 and H-11) and 7.77 (H-9 and H-10) in ring *e*. Moreover, the infrared spectrum of **2b** contains only a single carbonyl absorption band. It is , therefore, apparent that the acetyl groups must occupy equivalent positions in rings *a* and *c*. The *ortho* coupling constant of 8.1 Hz indicates that **2b** is either 1,7-diacetyl-**2** or 3,5-diacetyl-**2** (as shown). The latter assignment is selected on the basis of (a) the small difference (Δδ = −0.05) in the chemical shift for H-8 (and H-11) from that in parent molecule **2** and (b) strong evidence for conjugation by the acetyl groups with the parent π-elec-

tronic system. First, compound **2b** is intensely yellow in color, while **2a** is only faintly cream-colored. The low solubility of **2b** in ethanol precluded use of this solvent for determination of an ultraviolet spectrum. However, in spectral grade dimethyl sulfoxide **2b** showed strong absorption bands at 361 and 378 nm (log ϵ 4.24).

It is of interest to compare positions of substitution for **2** in nitration and acetylation. Both reactions may be considered to follow *ortho-para* orientation rules with respect to the ring-activating sulfur atom. However, for nitration the *ortho*/*para* ratio found was *ca.* 1:1 [4], while in the present acetylation study only *ortho* substitution occurred. Analogous results have been reported for triphenylene (**1**) where nitration produces nearly equal amounts of the 1- and 2-nitro isomers [7,8] while acetylation occurs only at the sterically less-hindered 2-position [9,10].

The availablility of acetyl derivatives **2a** and **2b** prompted us to investigate their conversions into ethyl derivatives by means of the Wolff-Kishner reaction. These reductions gave small yields of white crystals of 3-ethyltriphenyleno-[1,12-*bcd*]thiophene (**2c**) (15%) and 3,5-diethyltriphenyleno[1,12-*bcd*]thiophene (**2d**) (8%), respectively. While no by-products were isolated in these reductions, the odor of hydrogen sulfide was readily detected upon acidification of the alkaline reaction mixtures. Surprisingly, the ^{1}H nmr spectrum of **2c** (but not of **2d**) exhibited a singlet at δ 1.44 for the presence of two protons per molecule of **2c**. Tentatively, we assigned this singlet to the presence of a mole of complexed hydrogen sulfide in the initial sample. Elemental analysis of the sample (after drying at 78° *in vacuo*), in fact, indicated that one-tenth of a mole of hydrogen sulfide still remained in the crystals.

The ultraviolet absorption spectrum of **2d** in 95% ethanol resembles closely that of the parent molecule **2** (measured in the same solvent [6]) in the wavelength range of 220-345 nm, but with corresponding maxima displaced bathochromically by 1-5 nm in the diethyl compound. A greater difference is observed in the range of 345-365 nm, where two maxima at 348 and 357 nm (log ϵ 2.84 $\pm$ 0.02) in **2** are replaced by one maximum at 362 nm (3.44) in **2d**. Although the ultraviolet spectrum of **2c** was obtained in carbon tetrachloride it is also closely similar to the spectrum of **2d**. These ultraviolet spectra, as well as the corresponding ^{1}H nmr spectra, show clearly that the triphenyleno[1,12-*bcd*]thiophene ring system remains intact in the Wolff-Kishner products.

Compound **2** has been identified in samples of lubricating oil and coal liquids and its alkyl derivatives may also be present in various fractions from fossil fuels [11-14].

EXPERIMENTAL [15]

Acetylation of Triphenyleno[1,12-*bcd*]thiophene (**2**).

(a) With a Limited Excess of Acetyl Chloride.

A solution of 0.7 ml (9.8 mmoles) of acetyl chloride and 1.67 g (12.5 mmoles) of anhydrous aluminum chloride in 2 ml of dry nitrobenzene was added dropwise over a period of two minutes to a stirred solution of 1.71 g of purified **2** (93 mole % **2**, 6.23 mmoles; 7 mole % triphenylene, **1**, by ^{1}H nmr analysis) in 50 ml of nitrobenzene at 0°. The blood red mixture was stirred for 14 hours at 0-22° and then treated with excess 18% hydrochloric acid and steam distilled to remove nitrobenzene. A chloroform extract of the residual solid plus liquid was washed with additional 18% hydrochloric acid and then water, dried (sodium sulfate), and chromatographed on a column of 185 g of silica gel with chloroform as eluent to give these fractions: #1, 350 ml, R_f 0.51, recovered **1**; #2, 150 ml, R_f 0.43, 2-acetyltriphenylene (**1a**); #3, 200 ml, mixed **1a** and 3-acetyltriphenyleno[1,12-*bcd*]thiophene (**2a**), R_f 0.24, 0.32 g of solid (75 mole % **2a** by ^{1}H nmr); #4, 715 ml, **2a** only, 1.22 g, mp 188-193°; #5, 600 ml, 3,5-diacetyltriphenyleno[1,12-*bcd*]thiophene (**2b**), R_f 0.20, 0.14 g (7%), mp 303-313°. The combined yield of **2a** from fractions 3 and 4 is 1.46 g (78%).

Recrystallization of **2a** from 2-butanone gave cream-colored, matted needles, mp 193-194°; ir: 1659 (s, carbonyl), 1562, 1380, 1352, 1271, 1257, 750 (s) cm^{-1}; ^{1}H nmr: δ 8.72 (split pseudotriplet, J = 8.4, *ca.* 2 Hz, 2H, H-8 and H-11), 8.48 (d, $J_{6,7}$ = 7.8 Hz, H-7), 8.38 (dd, AB system, J_{AB} = 8.2 Hz, $\Delta\delta$ = 23.9 Hz, H-1 and H-2) [16], 8.17 (d, $J_{5,6}$ = 7.6 Hz, H-5), 7.92 (t, H-6), 7.78 (d of split t, $J_{9,10}$ = 5.2 Hz, $J_{8,10}$ = $J_{9,11}$ = 1.3 Hz, H-9 and H-10), 2.88 (s, Ac); ms: m/e 300 (M^+, 48), 285 ([M - Me]$^+$, 81), 257 ([M - Ac]$^+$, 100), 256 (81), 43 (Ac^+, 41); uv (toluene): λ max 283 nm (log ϵ 4.37), 302 (4.52), 334 shoulder (4.05), 347 (4.15), 368 (3.92), 387 (4.03).

Anal. Calcd. for $C_{20}H_{12}OS$: C, 79.97; H, 4.02; S, 10.67. Found: C, 79.88; H, 4.02; S, 10.78.

(b) With a Larger Excess of Acetyl Chloride.

The preceding reaction was modified by adding a solution of 2 ml (28 mmoles) of acetyl chloride and 4.75 g (35.6 mmoles) of aluminum chloride in 15 ml of nitrobenzene to a stirred solution of 2.23 g of a mixture of **1** (53 mole %, 4.88 mmoles) and **2** (4.33 mmoles) in 50 ml of nitrobenzene. After 20 hours the mixture was processed as before to give a chloroform extract plus a brown solid (0.27 g) which collected between the aqueous and organic phases. This solid (mp 300-330°), identified as **2b** by ^{1}H nmr, was recrystallized from dimethyl sulfoxide to give either prisms or needles. Chromatography of the chloroform-soluble portion yielded a mixture of **1a** (81% yield) and **2a** (42%), analyzed by ^{1}H nmr, as well as an additional 50 mg (total yield 22%) of **2b**. Further recrystallization of **2b** from dimethyl sulfoxide gave canary yellow prisms, mp 329-330.5°; ir: 1665 (carbonyl), 1573, 1262 cm^{-1}; ^{1}H nmr: δ 8.67 (2 overlapping d, 2H, H-8 and H-11), 8.38 (dd, AB system, $J_{1,2}$ = $J_{6,7}$ = 8.1 Hz, $\Delta\delta$ = 27.2 Hz, H-1, H-2, H-6, H-7) [16], 7.77 (2 overlapping d, 2H, H-9 and H-10), 2.83 (s, 2 Ac groups); ms: m/e 342 (M^+, 76), 328 (27), 327 ([M - Me]$^+$, 100), 284 ([M - Me -Ac]$^+$, 36), 256 ([M - 2Ac]$^+$, 38), 43 (ac^+, 22); uv (spectral grade dimethyl sulfoxide): λ max 319 nm (log ϵ 4.61), 361 (4.24), 378 (4.24).

Anal. Calcd. for $C_{22}H_{14}O_2S$: C, 77.17; H, 4.12. Found: C, 76.93; H, 4.01.

3-Ethyltriphenyleno[1,12-*bcd*]thiophene (**2c**).

A stirred mixture of 0.61 g (2 mmoles) of monoacetyl derivative **2a**, 0.42 g (7.5 mmoles) of potassium hydroxide pellets, 0.3 ml (6.2

mmoles) of hydrazine hydrate, and 15 ml of triethylene glycol was refluxed for 2 hours while the temperature gradually rose to 185°. Volatile components were removed by slow distillation at 185° while more triethylene glycol was added to maintain a constant liquid volume. The cooled reaction mixture was treated with excess 18% hydrochloric acid and extracted with chloroform. Evaporation of the water-washed, dried (sodium sulfate) organic layer gave a brownish-yellow residue.

The residue was adsorbed onto 6 g of silica gel which was placed atop a column of 50 g of alumina (bottom portion) and 40 g of silica gel. Elution with benzene/cyclohexane (1:1) gave 97.1 mg (15%) [17] of **2c**, mp 105-110°. Recrystallization from benzene gave white needles, mp 115.5-117.5°; ir: 1432, 1384, 756 cm^{-1} [18]; ^1H nmr: δ 8.60 (close dd, 2H, H-8 and H-11), 8.33 (2 overlapping d, 2H, probably H-1 and H-7), 7.97 (d, 1H, probably H-5), 7.75 (t, 1H, H-6), 7.56-7.67 (m, 3 aromatic H), 3.02 (q, 2H, methylene group), 1.44 (s, 2H, complexed hydrogen sulfide?) [19], 1.4 (t, 3H, Me group); ms: m/e 286 (M^+, 55), 284 (25), 272 (32), 271 ([M - Me]$^+$, 100), 269 (33), 134.5 (29); uv (carbon tetrachloride): λ max 259 nm (log ϵ 4.48), 270 (4.52), 286 (4.54), 310 (4.11), 316 shoulder (4.08), 324 (4.14), 345 (3.35), 361 (3.20). A sample dried at 78° *in vacuo* was submitted for elemental analysis.

Anal. Calcd. for $C_{20}H_{14}S \cdot 1/10H_2S$: C, 82.88; H, 4.94; S, 12.17. Found: C, 82.89; H, 4.73; S, 11.81.

3,5-Diethyltriphenyleno[1,12-*bcd*]thiophene (**2d**).

The preceding reduction procedure was repeated with a mixture of 200 mg (0.58 mmole) of diacetyl compound **2b**, 0.4 g (10 mmoles) of sodium hydroxide pellets, 0.4 ml (8.3 mmoles) of hydrazine hydrate, and 10 ml of triethylene glycol. The orange chloroform extract showed the presence of two components by tlc (silica gel/chloroform), R_f 0.48 (unidentified) and 0.77 (assigned to **2d**). Column chromatography using 20 g of silica gel and elution with chloroform gave **2d** in fraction #3 (15 ml) and a mixture of the two components in fraction #4 (20 ml). The solid from fraction #3 recrystallized from ethanol as rosettes of white needles of **2d**, mp 130-130.5° 15 mg (8%); ir: 2965, 1429, 1383, 821, 757 cm^{-1}; ^1H nmr: δ 8.70 (dd, 2H, H-8 and H-11), 8.43 (d, $J_{1,2} = J_{6,7} =$ 8.3 Hz, H-1 and H-7), 7.72 (m, 4 aromatic H), 3.14 (q, $J_{Et} = 7.8$ Hz, 4H, 2 methylene groups), 1.53 (t, 6H, 2 methyl groups); ms: m/e 315 (29), 314 (M^+, 100), 300 (28), 299 ([M - Me]$^+$, 97), 284 ([M - 2Me]$^+$, 56), 142 ([M - 2Me]$^{++}$, 34); uv (95% ethanol): λ max 237 nm shoulder (log ϵ 4.61), 246 (4.71), 255 shoulder (4.58), 269 (4.66), 282 (4.71), 309 (4.23), 322 (4.25), 344 (3.49), 362 (3.44).

Anal. Calcd. for $C_{22}H_{18}S$: C, 84.03; H, 5.77. Found: C, 84.30; H, 5.50.

REFERENCES AND NOTES

[1] Paper I: L. H. Klemm, R. Tsuchiya, E. K. L. Wong, M. P. Stevens, J. J. Lu and C. E. Klopfenstein, *J. Heterocyclic Chem.*, **24**, 357 (1987). For Paper II see reference [4].

[2] Postbaccalaureate research assistant, 1987.

[3] Postbaccalaureate teaching and research assistant, 1987-1988.

[4] L. H. Klemm, E. Hall, L. Cousins and C. E. Klopfenstein, *J. Heterocyclic Chem.*, **24**, 1749 (1987).

[5] Compare data for the 1- and 3-nitro derivatives of **2** [4].

[6] L. H. Klemm and R. F. Lawrence, *J. Heterocyclic Chem.*, **16**, 599 (1979).

[7] A discussion of this result is presented in reference [4].

[8] L. H. Klemm, E. Hall and S. K. Sur, *J. Heterocyclic Chem.*, **25**, 1427 (1988).

[9] N. P. Buu-Hoï and P. Jacquignon, *J. Chem. Soc.*, 941 (1953).

[10] C. C. Barker, R. G. Emmerson and J. D. Periam, *ibid.*, 448 (1955).

[11] R. C. Kong, M. L. Lee, Y. Tominaga, R. Pratap, M. Iwao, R. N. Castle and S. A. Wise, *J. Chromatogr. Sci.*, **20**, 502 (1982).

[12] G. Grimmer, J. Jacob and K.-W. Naujack, *Fresenius' Z. Anal. Chem.*, **306**, 347 (1981).

[13] M. Nishioka, D. G. Whiting, R. M. Campbell and M. L. Lee, *Anal. Chem.*, **58**, 2251 (1986).

[14] M.-A. Poirier and B. S. Das, *Fuel*, **63**, 361 (1984).

[15] Unless otherwise noted, infrared spectra were determined on potassium bromide wafers by means of a Nicolet 5-DXB FTIR instrument; ultraviolet spectra by means of a Beckman DU-7 spectrophotometer; and ^1H nmr spectra in deuteriochloroform, by means of a General Electric QE-300 instrument. Electron-impact mass spectra were obtained at 70 eV by Dr. Richard Wielesek of this laboratory on a VG 12-250 instrument. Elemental analyses were conducted by Desert Analytics, Tucson, Arizona.

[16] L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry", Pergamon Press, New York, NY, 1959, p 89.

[17] Yield calculated for a 1:1 molecular complex of **2c** with hydrogen sulfide.

[18] Unfortunately, the ir spectrum of this sample was not investigated at wave numbers greater than 2000 cm^{-1}.

[19] This signal was not observed in the ^1H nmr spectrum of diethyl compound **2d**.