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o-Quinonoid Heterocyclic Compounds: Naphtho[2,3-*c*]thiophene Revisited[†]

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Abstract

Naphtho[2,3-*c*]thiophene (**2**) has been synthesized in high yield *via* a facile base-catalyzed Pummerer reaction. Dilithiation and the reaction of the dilithiospecies with several electrophiles is reported. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords

dehydration; naphthalene; sulfoxide; thiophene;

Introduction

In contrast to the chemistry of benzo[*c*]thiophene (**1**) which has been well investigated, very little is known about that of naphtho[2,3-*c*]thiophene (**2**)[1,2]. It was first generated twenty-six years ago *via* acid-catalyzed Pummerer reaction on sulfoxide **3** and trapped by N-phenylmaleimide *in situ*[3,4]. Years later, it was obtained as a yellow solid on a cold finger by a pyrolytic reaction on sulfoxide **3**. It was claimed that it was very unstable, necessitating the determination of its nmr spectrum in $CDCl_3$ at low temperature[5].

About a decade ago, interest in naphtho[2,3-*c*]thiophene was regenerated by the publication of two theoretical papers[6,7]. These dealt with prediction of the properties of a conjugated polymer derived from **2**. One of these calculations predicted that the bandgap would be close to 0 ev whereas the other one gave a value of ~ 1.5 ev. A detailed optoelectronic study by

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[†] Dedicated to our colleague and friend Professor Madeleine M. Joullie in celebration of forty years of distinguished teaching and research at the University of Pennsylvania.

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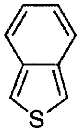
Ikenoue of polymerized **2** obtained by the acid alumina dehydration of sulfoxide **3** provided the experimental value of ~ 1.5 ev[8].

In this paper, we present recent results from our laboratories concerning the facile preparation in good yield of **2**. Further transformations of **2** are also described.



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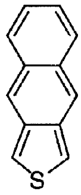

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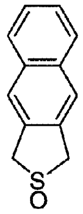

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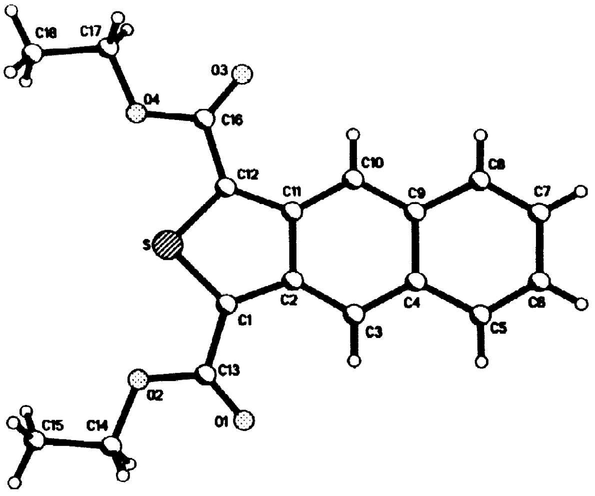


Figure 1. Crystal structure of compound **4**.

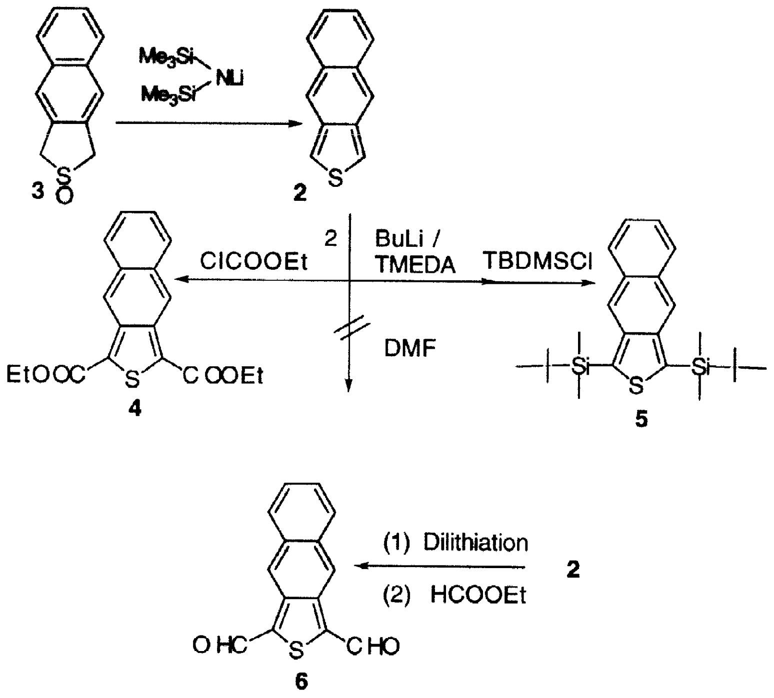
Results

The known sulfoxide **3** was treated in anhydrous THF with lithium hexamethyldisilazide solution at room temperature when dehydration occurred very quickly and the bright yellow, fluorescent **2** was formed. Upon work-up under an inert atmosphere **2** could indeed be isolated as a bright yellow solid, mp ~ 60 °C (dec). In contrast to the reported observation[5], the nmr spectrum of **2** could be determined in $CDCl_3$, benzene-d_6 or DMSO-d_6 at room temperature. While all the solutions degraded over time, (several days) that in $CDCl_3$ degraded within hours, probably due to traces of DCl generated in solution from the solvent.

It was found that **2** could be dilithiated by n-BuLi in the presence of TMEDA in THF. Reaction of the dianion with reactive electrophiles led to the isolation of several stable disubstituted derivative (**4**, **5**). In contrast, the reaction of the dianion from **2** with DMF did not lead to the expected dialdehyde **6** but gave intractable white powders. The dialdehyde **6** was obtained in extremely low yield by the reaction of the dianion with ethyl formate. (Scheme 1)

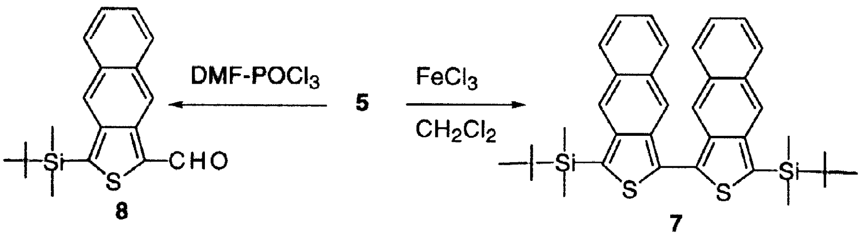
The diester **4** formed crystals suitable for X-ray analysis which was carried out; it represents the first example of structure determination in the naphtho[2,3-*c*]thiophene series. In contrast to the parent **2**, diester **4** was found to be very stable.

The structure of **4** was confirmed by X-ray crystallography (Figure 1). The observed bond lengths are clearly in accord with the expected 2,3-naphthoquinonoid structure. For example, the α,β bond length of the thiophene unit is 1.408 Å, while the β,β bond length is 1.445 Å.



Scheme 1. Synthesis of 2 and its transformations.

The *bis*-t-butyldimethylsilyl derivative **5** was also very stable. It underwent several interesting reactions. It was oxidized by anhydrous ferric chloride in methylene chloride to give a dimeric product **7** in 43 % yield. Reaction of **5** with DMF-$POCl_3$ replaced one silyl group by a formyl function leading to aldehyde **8** in 84 % yield. (Scheme 2).



Scheme 2. Transformations of **5**.

Conclusion

In conclusion, a viable synthesis of naphtho[2,3-*c*]thiophene (**2**) has been achieved, and it can be stored under an inert atmosphere in the solid state for several days. Although dilithiation was facile, the dianion appears to react only with reactive electrophiles. In contrast to **2**, the bis silyl derivative **5** is much more stable. Bissilyl derivative **7**, represents the first example of a dimeric naphtho[2,3-*c*]thiophene system.

Experimental

General

All melting points are uncorrected. NMR spectra (360 MHz) were determined in $CDCl_3$ unless otherwise stated and δ values are stated in ppm relative to TMS. All organic extracts were washed well and dried (anhyd Na_2SO_4). The crystallographic data on diester **4** are deposited with the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Naphtho[2,3-c]thiophene (2):

To a stirred suspension of sulfoxide **3**[3] (0.1 g, 0.49 mmol) in dry THF (15 mL) under N_2 was added 1.25 mL of 1 M LHMDS solution (THF). The mixture was stirred at rt for 30 min. It was poured into ice water (degassed) and N_2 gas was bubbled through this till bright yellow solid (**2**) was formed, which was filtered and dried under N_2. Yield 0.06 g (66%); mp ~ 60 °C (dec). ^{1}H-NMR 7.70 s (2H), 7.35 dd (2H, J=9.72, 3.6 Hz), 6.93 s (2H), 6.79 dd (2H, J=10.1, 3.24 Hz). ^{1}H-NMR (C_6D_6) 7.91 s (2H), 7.56 dd (2H, J=9.72, 3.24 Hz), 7.47 s (2H), 7.00 dd (2H, J=10.08, 324 Hz). ^{13}C-NMR 138.0, 131.3, 129.1, 124.6, 119.4, 115.0. MS (m/e)184 (m^+, 100%), 152 (23), 139 (59), 117 (27), 104 (29). UV-VIS (hexane) λ_{max} (nm) 460 (log ε 2.77), 469 (2.67), 432 (2.72), 408 (2.49), 328 (2.50), 312 (2.50), 250 (4.12), 227 sh (3.57). HRMS Calcd: 184.03467. Found: 184.03281.

1,3-Di(ethoxycarbonyl)naphtho[2,3-c]thiophene (4):

A stirred suspension of sulfoxide **3** (0.2 g, 1 mmol) in 40 mL of dry THF under N_2 was treated with 2.5 mL of 1 M LHMDS solution (THF). The mixture was stirred for 30 min. It was then cooled to - 78 °C followed by addition of TMEDA (0.45 mL, 3 mmol) and BuLi (1 mL, 2.5 mmol). The reaction mixture was maintained at the same temp for another 30 min and ethyl chloroformate (0.38 mL, 4 mmol) was added and stirred for 1 h. It was poured over crushed ice. The crude product was extracted into CH_2Cl_2 (3x30 mL) to give 0.325 g (74%) of product as an orange-red solid. Mp 209-210 °C (MeOH). ^{1}H-NMR 9.08 s (2H), 7.87 dd (2H, J=9.72, 3.24 Hz), 7.34 dd (2H, J=10.08, 3.24 Hz), 7.54 q (J=7.2 Hz), 1.51 t (J=7.2 Hz). UV-VIS (CH_2Cl_2) λ_{max} (nm) 524 (log ε=3.91), 496 (3.90), 277 (3.59), 361 (3.54), 332 (3.58), 278 (4.90), 242 (4.55), 217 (4.19). MS (m/e) 328 (m^+, 95%), 300 (43), 283 (13), 272 (100), 228 (34), 211 (10), 199 (17), 184 (31), 171 (31), 139 (33), 127 (12), 112 (12). Anal. Calcd: C, 65.83%; H, 4.92%; S, 9.76%. Found: C, 65.89%; H, 4.98%; S, 9.84%.

1,3-Di(t-butyldimethylsilyl)naphtho[2,3-c]thiophene (5):

To a stirred suspension of sulfoxide **3** (0.2 g, 1 mmol) in 30 mL of dry THF under N_2 was added 2.5 mL of 1 M LHMDS solution (THF) and the mixture was stirred at rt for 30 min. Then it was cooled to - 78 °C followed by addition of TMEDA (0.45 mL, 3 mmol) and 2.5 M BuLi (1 mL, 2.5 mmol). After maintaining at the same temp for 30 min, TBDMSCl (0.6 g, 4 mmol) in dry THF (20 mL) was added. The reaction mixture was slowly warmed to rt and poured into ice water containing NH_4Cl. The crude product was extracted into Et_2O (3x40 mL). The residue from ether was then purified by passing through a short column of basic alumina (eluent: hexane). Yield 0.267 g (65.4%); mp 121-122 °C. ^{1}H-NMR 3.38 s (2H), 7.76 dd (2H, J=9.72, 2.96 Hz), 7.19 dd (2H, J=9.21, 2.69 Hz), 0.995 s (18H), 0.621 s (12H). UV-VIS (CH_2Cl_2) λ_{max} (nm) 476 (log ε=3.84), 447 (3.80), 315 (3.35), 262 (4.86), 218 (4.08). MS (m/e) 412 (m^+, 16%), 355 (100), 341 (6), 298 (7), 283 (10), 241 (5), 209 (8), 165 (7), 149 (20). Anal. Calcd: C, 69.82%; H, 8.81%; S, 7.77%. Found: C, 69.98%; H, 8.94%; S, 7.57%.

*Naphtho[2,3-c]thiophene 1,3-dicarboxaldehyde (**6**):*

A stirred suspension of sulfoxide **3** (0.3 g, 1.5 mmol) in 30 mL of dry THF under N_2 was treated with 2.9 mL of 1.3 M LHMDS solution (THF). The mixture was stirred for 30 min. It was cooled to - 78 °C, and dilithiated by the addition of TMEDA (0.67 mL, 4.4 mmol) followed by BuLi (1.8 mL, 4.5 mmol). The reaction mixture was maintained at the same temp for 30 min, treated with excess of ethylformate (2.4 mL, 30 mmol) and immediately quenched with acetic acid. Standard work up followed by chromatographic purification led to the isolation of 0.02 g of dialdehyde **6**. Mp 124-126 °C. ^{1}H-NMR 10.16 s (2H), 9.05 s (2H), 7.94 dd (2H, J=9.79, 3.13 Hz), 7.47 dd (2H, J=9.86, 3.10 Hz). UV-VIS (CH_2Cl_2) λ_{max} (nm) 540 (log ε 3.68), 299 (4.49), 252 (4.44), 217 (4.18). MS (m/e) 240 (m^+, 100%), 212 (21), 184 (38), 154 (19), 139 (10). HRMS Calcd: 240.024501. Found: 240.023517.

*Ferric Chloride Oxidation of **5** to give (**7**):*

A stirred solution of substrate (0.1 g, 0.24 mmol) in dry CH_2Cl_2 (10 mL) was treated with anhyd $FeCl_3$ (0.05 g, 0.31 mmol). The mixture was stirred at rt under N_2 for 20 min and diluted with more CH_2Cl_2 (30 mL). The organic layer was washed with water and dried (Na_2SO_4). Removal of solvent followed by chromatographic separation of the residue on silica gel (eluent: hexane) gave 0.02 g of starting material and 0.025 g **7** (43%). Mp 176-177 °C. ^{1}H-NMR 8.59 s (2H), 8.35 s (2H), 7.78 d (2H, J=8.46 Hz), 7.69 d (2H, J=8.37 Hz), 7.19 m (4H), 1.08 s (18H), 0.68 s (12H). MS (m/e) 594 (m^+, < 5%), 555 (< 5%), 429 (10), 355 (10), 341 (18), 304 (80), 273 (50), 227 (84), 212 (16), 197 (27), 181 (24), 167 (18), 153 (21), 127 (55), 123 (60). UV-VIS (CH_2Cl_2) λ_{max} (nm) 488 (log ε = 3.53), 464 (3.57), 259 (4.51), 232 (4.67), 219 (4.37). HRMS Calcd: 594.2266. Found: 594.2232.

*Conversion of **5** to aldehyde (**8**):*

Vilsmeier reagent prepared from 0.084 mL DMF and 0.102 mL $POCl_3$ in dry CH_2Cl_2 (10 mL) was added to a solution of the disilyl derivative **5** (0.15 g, 0.36 mmol). The mixture was stirred at rt for 1 h and was poured into $NaHCO_3$ solution. The sticky precipitate was extracted into CH_2Cl_2 (2x20 mL). The residue from the extract was chromatographed on silica (eluent: 1:1 CH_2Cl_2; hexane) to give aldehyde **8**, 0.1 g (84% yield). Mp 64-66 °C. ^{1}H-NMR 10.2 s (1 H), 9.12 s (1H), 8.41 s (1H), 7.91 d (1H, J=8.5 Hz), 7.86 d (1H, J=8.50 Hz), 7.40 t (1H, J=8.15 Hz), 7.34 t (1H, J=8.0 Hz). MS (m/e) 326 (m^+, 18%), 314 (22), 299 (25), 271 (32), 269 (49), 241 (10), 214 (24), 200 (10), 189 (40), 154 (35), 149 (29), 147 (100), 126 (50). UV-VIS (CH_2Cl_2) λ_{max} (nm) 491 (log ε = 3.75), 313 (4.12), 273 (4.50), 253 (4.38), 235 (4.42), 219 (4.24). Anal. Calcd for $C_{19}H_{22}OSSi \bullet H_2O$: C, 66.23%; H, 7.03%;

S, 9.31%. Found: C, 66.11%; H, 6.62%; S, 9.37%. HRMS Calcd: 326.1161. **Found:** 326.1133.

Acknowledgments

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