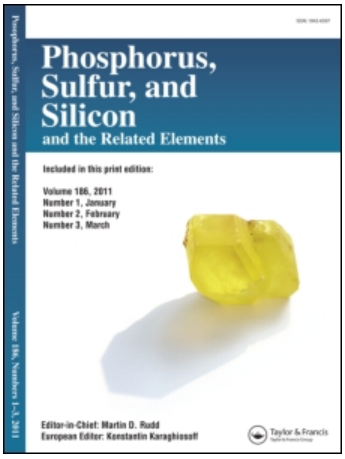

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STUDIES ON BENZO[C]THIOPHENES

Wolfgang Volz[a]; Jürgen Voss[a]
[a] Institut für Organische Chemie der Universität Hamburg, Hamburg 13, FRG

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Communication

STUDIES ON BENZO[C]THIOPHENES

WOLFGANG VOLZ and JÜRGEN VOSS*
Institut für Organische Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, FRG

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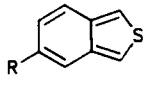
Attempts for the synthesis of 5-tert-butylbenzo[c]thiophene **1c** are described. The preparation of pure **1c** by heating of sulfoxide **5** with alumina failed. However **1c** could be generated *in situ* and trapped with *N*-phenylmaleimide **6**. Under the conditions of mass spectroscopic measurements the cycloadducts of **1c** with **6** underwent a retro-Diels-Alder reaction which proves the existence of free **1c** in the gas-phase.

Key words: Diels-Alder reaction; benzo[c]thiophene; electronic substituent-effect; oxidation; mass spectroscopy.

INTRODUCTION

Unsubstituted benzo[c]thiophene **1a**, first prepared by R. Mayer *et al.*[1] in 1962, represents a reactive compound which is stable only at low temperature. In case of substitution in the 1- or 3-position by eletron-withdrawing groups pronounced stabilization of the heterocyclic system is observed. For example, 1,3-diarylbenzo[c]thiophenes are very stable at room temperature.[2] On the other hand 1,3-unsubstituted benzo[c]thiophenes are substantially more reactive. During the last decades only few systematic investigations on benzo[c]thiophenes have been performed although certain derivatives are used as *o*-chinodimethane-precursors.[3] In 1968 H. Wynberg *et al.*[4] prepared the 5-carboxymethylbenzo[c]-thiophene **1b** which is stabilized by the electron-withdrawing carboxymethylgroup and is stable at room temperature for two days (at −20°C for 1 month).

In this paper we describe the influence of an electron-donating substituent, i.e. a tert-butyl group at **1c**.

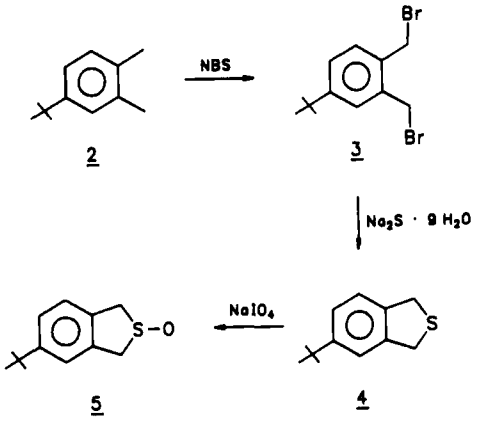


1a R = H
1b R = CO_2Me
1c R = tBu

Scheme 1

RESULTS AND DISCUSSION

1,2-Bis(bromomethyl)-4-tert-butylbenzene **3** was prepared by bromination of 4-tert-butyl-1,2-dimethylbenzene **2**[5] and converted into 5-tert-butyl-1,3-dihydro-benzo[c]thiophene **4** with sodium sulfide in aqueous ethanol. The isolation and purification was carried out by steam distillation. The cyclic sulfide **4** is a very unstable solid which decomposes very fast at room temperature. Therefore, it was



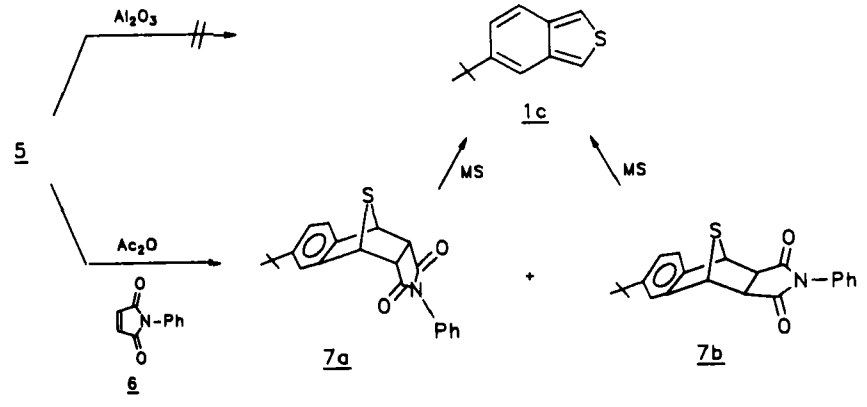
Scheme 2

oxidized immediately with sodium periodate to 5-tert-butyl-1,3-dihydro-benzo[c]thiophene-2-oxide **5**. The sulfoxide **5** is a colourless crystalline solid, stable for months at room temperature.

Finally 5-tert-butylbenzo[c]thiophene **1c** was to be produced according to M. P. Cava's[6] method by heating the sulfoxide **5** with alumina under reduced pressure. However, only a semi-solid mixture of decomposition products could be obtained which turned black at room temperature and access of air. Obviously, **1c** is even less stable than the unsubstituted benzo[c]-thiophene **1a**.

Because we failed to isolate pure **1c**, we generated this compound *in situ* and trapped it with *N*-phenylmaleimide **6**. The sulfoxide **5** was refluxed in acetic anhydride in the presence of the dienophile **6**. After working-up the endo- and exo-Diels–Alder adducts **7a** and **7b** of 5-tert-butylbenzo[c]thiophene with **6** could be isolated and separated by column chromatography. The endo/exo-ratio was about 2:1. The structures of **7a** and **7b** were assigned on the basis of their ^{1}H-NMR spectra. The protons in the α-position of the imide carbonyls show a strong deshielding due to the neighbouring sulfur bridge in the endo-product **6**.

Under the conditions of mass spectroscopic measurements **7a** and **7b**



Scheme 3

underwent retro-Diels–Alder reaction. The 100%-peak exhibits a molecular weight of 190.0819. This corresponds to the free monomeric 5-tert-butylbenzo[c]thiophene **1c**.

Thus, the donor-substituted **1c** which cannot be isolated but only trapped after generation exists as a stable molecule in the gas phase.

EXPERIMENTAL

General: Melting points (uncorrected): Elektrothermal melting point apparatus. IR spectra: Perkin–Elmer FT-IR 1720-X. NMR spectra: Bruker WH 270. ^{1}H- and ^{13}C-NMR spectra were recorded with tetramethylsilane as internal standard. Mass spectra: VG Analytical 70-250S.

5-Tert-butyl-1,3-dihydrobenzo[c]thiophene (**4**).[7] A solution of 15 g (47 mmol) 1,2-bis(bromomethyl)-4-tert-butylbenzene **3** in 120 ml of ethanol was added dropwise over a period of 5 hours under nitrogen to a stirred suspension of 50 g (0.2 mol) sodium sulfide nonahydrate in 500 ml of 80% aqueous ethanol. The mixture was stirred for 2 hours at room temperature and then treated with 300 ml of dichloromethane. Water was added and the aqueous phase extracted three times with dichloromethane. The combined organic phases were evaporated. Steam distillation gave 5.9 g (65%) of a white solid which darkened on standing in the air at room temperature.

m.p. 40–42°C. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.31 (s, 9H, t-Bu), 4.23 (s, 4H, CH_2), 7.2 (m, 3H, ArH). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 31.50 (CH_3), 34.54 (q.CMe_3), 37.73, 38.22 (C-1, C-3), 121.47, 124.02, 124.19 (C-4, C-6, C-7), 137.44 (C-7a), 140.34 (C-3a), 150.07 (C-5). IR (neat): 2965, 1579, 1458, 1438, 1406, 1363, 1202, 901, 820, 714 cm^{-1}. MS (70 eV): m/e = 192 (61%, M^+), 177 (100%, M^+—CH_3), 135 (32%, M^+—tBu), 131 (18%).

5-Tert-butyl-1,3-dihydrobenzo[c]thiophene-2-oxide (**5**).[8] A solution of 5.9 g (31 mmol) freshly prepared **4** in methanol was added to a solution of 6.6 g (31 mmol) sodium periodate in 150 ml of water/methanol (1:1). The mixture was stirred overnight and filtered. After evaporation the residue was treated with water and extracted five times with dichloromethane. The combined extracts were dried over sodium sulfate. Evaporation gave a yellow oil which was recrystallized from ethyl acetate/petrol ether 60/70 to give 3.9 g (60%) of colourless crystals. m.p. 61–63°C. Anal. calc. for $C_{12}H_{16}SO$: C 69.19, H 7.74, S 15.39. Found: C 69.12, H 7.74, S 15.43. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.33 (s, 9H, t-Bu), 4.05–4.33 (m, 4H, CH_2), 7.30–7.38 (m, 3H, ArH). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 31.40 (CH_3), 34.74 (q.CMe_3), 59.06, 59.54 (C-1, C-3), 123.45, 125.70, 126.11 (C-4, C-6, C-7), 132.01, 134.95 (C-3a, C-7a), 151.89 (C-5). IR (KBr): 2961, 1497, 1418, 1364, 1268, 1126, 1047, 819 cm^{-1}. MS (70 eV): m/e = 208 (44%, M^+), 160 (100%, M^+—SO), 145 (70%).

Endo- and exo-6-tert-butyl-1,4-epithio-N-phenyl-1,2,3,4-tetrahydronaphthalene-2,3-dicarboximide (**7a**, **7b**).[6] 0.96 g (4.6 mmol) of sulfoxide **5** and 0.87 g (5 mmol) of *N*-phenylmaleimide **6** were refluxed in 20 ml acetic anhydride for 90 minutes. Evaporation of the dark solution under reduced pressure gave a residue which was recrystallized from toluene. Separation of the two isomers was achieved by column chromatography (80 g silica gel; dichloromethane). The first fraction (R_f = 0.56) contained the exo-isomer **7b** (274 mg, 16%) which formed white plates after recrystallization from methanol.

m.p. 198–199°C. Anal. calc. for $C_{22}H_{21}NO_2S$: C 72.70, H 5.82, N 3.85, S 8.82. Found C 72.70, H 5.88, N 3.86, S 8.77. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.31 (s, 9H, t-Bu), 3.45 (s, 2H, COCH), 4.98 (s, 2H, S-CH), 7.0–7.6 (m, 8H, ArH). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 31.41 (CH_3), 34.86 (q.CMe_3), 51.57, 51.65 (C-2, C-3), 56.00, 56.59 (S-CH), 117.83, 123.38, 128.99 (C-5, C-7, C-8), 119.80 (C-4′), 126.62 (C-2′), 129.28 (C-3′), 131.92 (C-8a), 143.16 (C-4a), 146.15 (arom. N-C), 150.40 (arom. C-tBu), 175.28 (C=O). IR (KBr): 2961, 1776, 1718, 1498, 1382, 1184, 795, 751 cm^{-1}. MS (70 eV): m/e = 363 (44%, M^+), 190 (100%, **1c**), 175 (48%).

Then the endo-isomer **7a** was eluted (R_f = 0.37; 503 mg, 30%). White crystals from methanol.

m.p. 188–190°C. Anal. calc. for $C_{22}H_{21}NO_2S$: C 72.70, H 5.82, N 3.85, S 8.82. Found C 72.42, H 5.97, N 3.88, S 8.80. ^{1}H-NMR ($CDCl_3$, 250 MHz): δ = 1.27 (s, 9H, tBu), 4.17 (m, 2H, COCH), 4.95 (m, 2H, S-CH), 6.35–6.47 (m, 2H, arom. N-C-CH), 7.10–7.30 (m, 6H, ArH). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): δ = 31.43 (CH_3), 34.87 (q.CMe_3), 53.20, 53.24 (C-2, C-3), 55.20, 55.78 (S-CH), 119.00, 121.16, 124.21, 128.83 (C-5, C-7, C-8, C-4′), 126.55 (C-2′), 128.90 (C-3′), 131.05 (C-8a), 139.95 (C-4a), 142.63 (arom. N-C), 150.91 (arom. C-tBu), 173.66, 173.74 (C=O). IR (KBr): 2965, 1773, 1713, 1499, 1385, 1181, 832, 746, 694, 602, 510 cm^{-1}. MS (70 eV): m/e = 363 (38%, M^+), 190 (100%, **1c**), 175 (53%).

The HRMS of the endo-product **7b** showed a peak at 190.0819 (calc. for **1c**: 190.0816).

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