SHORT PAPER

J. Chem. Research (S),
2002, 11–12

An efficient synthesis of 2-(3-methylbutoxy)-1,3-benzodithiole†

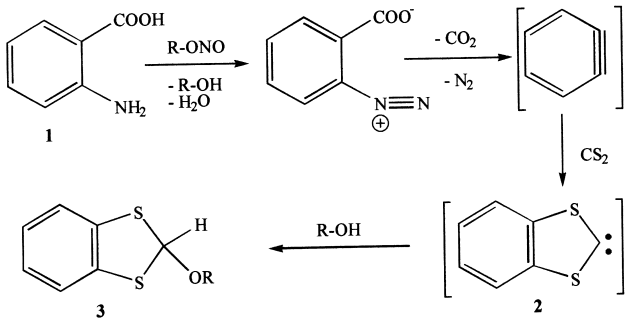
Abd El-Wareth Sarhan* and Taeko Izumi

Department of Chemistry and Chemical Engineering, Faculty of Engineering, Yamagata University, 3-16 Jonan 4-Chome, Yonezawa 992-8510, Japan

2-(3-Methylbutoxy)-1,3-benzodithiole has been synthesised in good yield by a modification of the method previously described by Nakayama.

Keywords: 1,3-benzodithioles, benzyne, carbon disulfide, cycloaddition

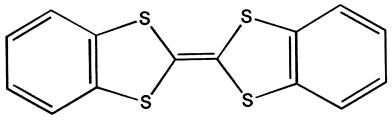
In 1969 Campbell and Rees reported that 2-methoxy-1,3-benzodithiole (**3**; R = CH_3) could be synthesised by the 1,3-dipolar cycloaddition of CS_2 with benzyne, generated from 1-aminobenzotriazole, followed by addition of methanol to the resultant 1,3-benzodithiole-2-carbene **(2)**.[1] Nakayama modified the reported method by using anthranilic acid **(1)** instead of 1-aminobenzotriazole to generate the benzyne, but the yield using this method was relatively low, 33–51% at best.[2] Increasing the temperature, using a long reaction time, or attempting vacuum distillation at slightly higher temperature, Nakayama's method leads to the formation of several products and a low yield of the 2-alkoxy-1,3-benzodithiole **(3)**.[3,4]



Scheme 1

The 1,3-benzodithiole-2-carbene **(2)** was also generated on vacuum pyrolysis of the thermally unstable compound **3** during the distillation process and this leads to the formation of the tetrathifulvalene derivative **(4)** as a major product.[5,6] Besides the 1,3-benzodithiole **(3)** and TTF **(4)**, an unidentified compound was obtained as orange crystals in low yield, along with the formation of polymeric materials. The structure of this compound is still under investigation.

Using Nakayama's procedure, the tetrathifulvalene **4** was obtained in considerable yield.[2] However, following the method described in the present work **4** was obtained as only a minor by-product (4.5%).



4

The structure of the tetrathiafulvalene (TTF) **4** was confirmed using IR, ^{1}H NMR, ^{13}C NMR and FAB-MS spectral analysis. Details of the analysis are described in the experimental section.

In this work we report the synthesis of 2-(3-Methylbutoxy)-1,3-benzodithiole (**3**; R = $CH_2CH_2CH(CH_3)_2$) with some modification of Nakayama's method described in Scheme 1. The importance of the 1,3-benzodithiole ring system **3** is as a precursor to many useful reagents, in particular by generation of the fluoroborate salt followed by direct transformation into the phosphonate ester.[7,8] Using the modified method described in this text, the 2-(methylbutoxy)-1,3-benzodithiole **(3)** can be obtained in 77% yield without any difficulties of purification, avoiding the formation of black polymeric materials and the dimerization product of the carbene **2** at high temperature, and vacuum distillation, which gives rise to the tetrathiafulvalene **(4)**. The addition of isoamyl nitrite to the refluxing reaction mixture, rather than having it all present from the outset, leads to the formation of a dark red colour and a reduced yield of the product **3**.

Using the modified method for synthesis of 1,3-benzodithiole derivative **3** the TTF **4** and an unknown compound were also obtained in very low yield.

In conclusion, we report here an efficient modification of a synthesis of a derivative of the 1,3-benzodithiole ring system which may serve as a useful precursor for the synthesis of several conducting materials.

Experimental

Solvents were distilled before use. Melting points were recorded on a Gallenkamp melting point apparatus. Infrared spectra (IR) were measured on a Hitachi 260-10 spectrometer (Hitachi Ltd, 1-5-1, Marunouchi, Chiyod-ku, Tokyo, Japan). ^{1}H NMR spectra were recorded at room temperature on a Varian Spectrometer at 200 MHz and 500 MHz; ^{13}C NMR were obtained at 50 and 125 MHz. Chemical shifts are given in δ units (ppm) relative to TMS as internal standard; *J* values are given in Hz. $CDCl_3$ was used as solvent. Mass spectra were obtained using a JEOL JMS-AX505HA (Nihon Denshi Ltd, 3-1-2, Musashino, Akishima-shi, Tokyo, Japan). Column chromatography was performed on silica gel 60 (230-400 Mesh ASTM). Anthranilic acid is commercially available.

Synthesis of 2-(3-methylbutoxy)-2H-1,3-benzodithiole **(3)**: *Method A:* A sample of anthranilic acid (**1**; 21 g, 0.15 mol) was added portion wise over a period of 40 min. to a stirred and gently refluxing solution of isoamyl nitrite (21 g, 0.18 mol), 3-methylbutanol (26.5 g, 0.3 mol) and carbon disulfide (75 ml) in 1,2-dichloroethane/chloroform (300 ml; 1:1). After the addition was completed, the mixture was refluxed for further 1 hour. The resultant red reaction mixture was evaporated under vacuum and the residue was washed with water (5 × 100 ml), and dried with sodium sulfate. Solvent and excess of reagents were removed under reduced pressure and the red viscous oily residue was chromatographed on silica gel (300 g.) using hexane as eluent to give in the first fractions a pale yellow oil, **3** (R = $CH_2CH_2CH(CH_3)_2$) (28.6 g, 77%). Increasing the polarity of the eluent (hexane/$CHCl_3$ 7:3) gave the tetrathiafulvalene **4** as yellow brown

* To receive any correspondence. e-mail: sarhan@chem.yz.yamagata-u.ac.jp

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

crystals (2.1 g., 4.5%). From later fractions, orange crystals (1.2 g) of an unknown compound were isolated.

Method B: As described in method A, but instead of 1,2-dichloroethane, only chloroform was used. The reaction mixture was worked up and chromatographed using silica gel and hexane to isolate the 1,3-benzodithiole **3**; R = $CH_2CH_2CH(CH_3)_2$ in 62% yield.

2-(3-Methylbutoxy)-1,3-benzodithole (**3**): IR (KBr) ν 3058m, 2954s, 2867m, 1563m, 1446s, 1384m, 1120s, 1066s, 1027s, 740s cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ 7.35–7.30 (m, 2H, aromatic-H), 7.09–7.04 (m, 2H, aromatic-H), 6.76 (s, 1H-2), 3.45–3.39 (t, *J* = 6.6 Hz, OCH_2), 1.70–1.50 (m, 1H, $CH(CH_3)_2$), 1.44–1.34 (q, 2H, *J* = 6.6 Hz, CH_2CH), 0.855–0.822 (d, *J* = 6.6 Hz, 6H, 2 CH_3). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 136.94 (C-3a, C-7a), 125.85 (C-4, C-7), 122.44 (C-5, C-6), 90.56 (C-2), 63.3 (OCH_2), 38.36 (CH), 25.49 (CH_2), 23.07 (2 CH_3). FAB-MS *m*/*z* (%) = 240 (54) [M^+].

Tetrathiafulvalene (TTF, **4**): M.p. 234–236 °C, Lit[6]. M.p. 234 °C, 4.5% yield. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.26–7.24 (m, 4H, aromatic-H), 7.12–7.10 (m, 4H, aromatic-H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.81 (4 aromatic-C), 126.07 (4 aromatic-CH), 122.04 (aromatic-CH), 110.76 (2 C = C). FAB-MS *m*/*z* (%) = 304 (48) [M^+].

A third product, orange crystals, (1.2 g), m.p. 91–93 °C, was also isolated. IR (KBr) ν 3066m, 1658s, 1563s, 1432s, 1257s, 1112s, 1058s, 925s, 892s, 740s, 671s cm^{-1}. ^1H-NMR ($CDCl_3$, 500 MHz) δ 7.48–7.11 (m, 8H, aromatic-H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.5 (4 aromatic-C), 127.30 (1 C), 126.36 (4 aromatic-CH), 121.78 (4 aromatic-CH).

This work was partially supported by a Grant-Aid for Scientific Research No. 12650844 from the Ministry of Education, Sciences, Sports and Culture (Japan). We thank Mr S. Murakami, technical assistant for mass spectral analysis.

Received 15 August 2001; accepted 6 November 2001
Paper 01/1014

References

1 C.D. Campbell and C.W. Rees, *J. Chem. Soc.* [C] 1969, 742.
2 J. Nakayama, *Chem. Commun*. 1975, 38.
3 J. Nakayama, *Chem. Commun*. 1974, 166.
4 L. Friedman and F.M. Logullo, *J. Org. Chem*., 1969, **34**, 3089.
5 G.S. Bajwa, K.D. Berlin and H.A. Pohl, *J. Org. Chem*., 1976, **41**, 145.
6 W.R.H. Hurtley and S. Smiles, *J. Chem. Soc*., 1926, 2263.
7 J. Nakayama, K. Fujiwara and M. Hoshino, *Chem. Lett*., 1975, 1099.
8 K. Akiba, K. Ishikawa and N. Inamoto, *Bull. Chem. Soc. Jpn*., 1978, **51**, 2674.