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Facile Conversion of the t-Butylthio Group of 1,3,4,6-Tetrakis(t-butylthio)thieno[3,4-c]thiophene into Other Alkylthio Groups Initiated by Protonation

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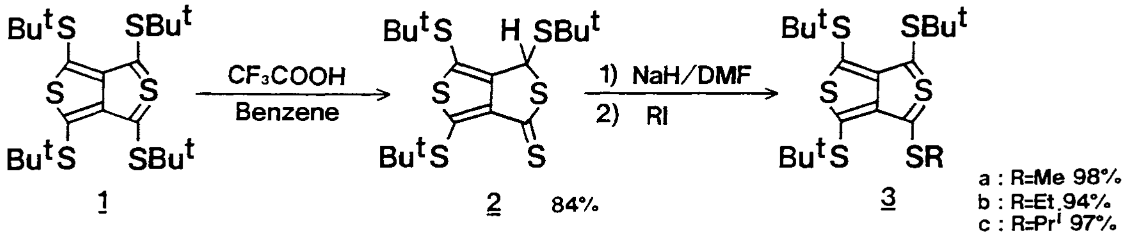
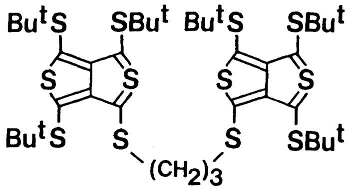
The t-butylthio group of 1,3,4,6-tetrakis(t-butylthio)thieno[3,4-c]thiophene was converted into other alkylthio groups by treatment with trifluoroacetic acid, followed by alkylation with alkyl iodides.

The thieno[3,4-c]thiophene system is attractive as one of the nonclassical condensed thiophenes.1) However, only a few examples1,2) have been known because of the difficulty in preparing the system. We aimed to develop the novel method for converting the t-butylthio group of 1,3,4,6-tetrakis(t-butylthio)thieno[3,4-c]thiophene (1) into other alkylthio groups and now report our findings that 1 is converted into 1,3-dihydro-3,4,6-tris(t-butylthio)thieno[3,4-c]thiophene-1-thione (2) by reaction with trifluoroacetic acid (TFA), and the treatment of 2 with sodium hydride and then alkyl iodides gives the 1-alkylthio-3,4,6-tris(t-butylthio)thieno[3,4-c]thiophenes (3) in high yields.



A typical procedure is as follows : TFA (1.2 mmol) was added under nitrogen to a solution of 1 (0.40 mmol) in benzene (20 ml) and the mixture was stirred at 35 °C for 4 h. The solvent was evaporated and the residue was chromatographed on silica gel to give 2 as reddish purple solid in 84% yield [mp 129.5-130.5 °C (dec.); ^1H NMR ($CDCl_3$) δ 1.42 (9H, s), 1.45 (9H, s), 1.57 (9H, s), and 5.67 (1H, s)]. This reaction is considered to proceed through the addition of proton to the 1-position of the thieno[3,4-c]thiophene ring, followed by the cleavage of the t-Bu-S bond.

A solution of 2 (0.2 mmol) in dimethylformamide (DMF) (1 ml) was added under nitrogen to a suspension of sodium hydride (0.4 mmol) in DMF (5 ml) at room temperature. The mixture was stirred for 0.5 h and then methyl iodide (0.4 mmol) was added. After stirring for 0.5 h, the mixture was poured into water, extracted with dichloromethane, and concentrated to give 1-methylthio-3,4,6-tris(t-butylthio)thieno[3,4-c]thiophene (3a) as red solids in 98% yield [mp 105-106 °C; ^{1}H NMR ($CDCl_3$) δ 1.32 (9H, s), 1.34 (9H, s), 1.37 (9H, s), and 2.61 (3H, s); UV/Vis(hexane) λmax 256 (log ε 4.27), 303 (3.96), and 515 nm (4.06); MS m/z 450 (M^+); Anal. Found: C,50.46; H,6.68%. Calcd for $C_{19}H_{30}S_6$: C,50.62; H,6.71%]. Other derivatives (3b and 3c) were prepared by similar methods in high yields.$^{3)}$ When 1,3-diiodopropane (0.1 mmol, 0.5 equiv.) was used as an alkylating reagent, the thieno[3,4-c]thiophene derivative (4) linked by a trimethylene chain was formed in 80% yield.$^{3)}$ The visible spectra of 3a-3c and 4 in hexane solution showed the characteristic absorptions due to the thieno[3,4-c]thiophene ring at 515, 508, 508, and 510 nm, respectively. All new compounds gave satisfactory spectral data and elemental analyses.



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The above results provide the novel method for the conversion of the t-butylthio group of 1 into other alkylthio groups.

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References
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3) 3b: 94% yield; mp 121-122 °C; ^{1}H NMR ($CDCl_3$) δ 1.32 (9H, s), 1.34 (9H, s), 1.34 (3H, t, J=7.3 Hz), 1.37 (9H, s) and 3.02 (2H, q, J=7.3 Hz); UV/Vis (hexane) λmax 257 (log ε 4.27), 303 (4.02), and 508 nm (4.10); 3c: 97% yield; mp 154-155 °C (dec.); ^{1}H NMR ($CDCl_3$) δ 1.31 (6H, d, J=6.5 Hz), 1.33 (9H, s), 1.34 (9H, s), 1.37 (9H, s), and 3.44 (1H, sep, J=6.5 Hz); UV/Vis (hexane) λmax 256 (log ε 4.28), 302 (4.05), and 508 nm (4.17); 4: mp 109-110 °C; ^{1}H NMR ($CDCl_3$) δ 1.32 (18H, s), 1.34 (18H, s), 1.35 (18H, s), 2.04 (2H, quintet, J=7.3 Hz), and 3.16 (4H, t, J=7.3 Hz); UV/Vis (hexane) λmax 256 (log ε 4.52), 302 (4.27), and 510 nm (4.26).

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