Tetrahedron Letters,Vol.25,No.22,pp 2403-2406,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

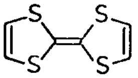
THE PREPARATION OF DERIVATIVES OF 2,2'-(2,6-NAPHTHALENEDIYLIDENE)BIS(1,3-DITHIOLE) (NBDT): NEW DONORS FOR ORGANIC METALS

Martin R. Bryce

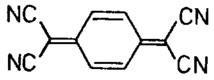
Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE, U.K.

Abstract: Routes from 2,6-bis(bromomethyl)naphthalene to compounds (3) and (4) are described. A complex between (4) and iodine has been obtained.

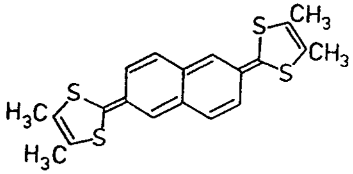
Since the discovery a decade ago of metallic conductivity in the complex of tetrathiafulvalene (1) and tetracyano-p-quinodimethane (2) (TTF-TCNQ) a large number of analogous donor and acceptor molecules have been prepared and many highly-conducting complexes are now known.[1] Derivatives of TTF with extended conjugation between the dithiole rings are currently receiving attention,[2] and we describe synthetic routes to derivatives of NBDT, specifically the tetramethyl derivative (3) (TM-NBDT) and the diphenyl derivative (4) (DP-NBDT) These molecules are of special interest as analogues of the well-known acceptor TNAP (5).[1,3]



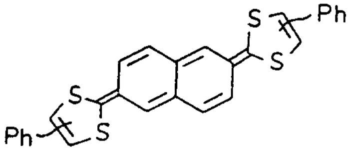
(1)



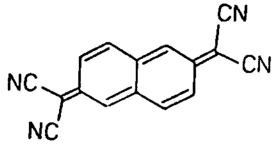
(2)



(3)

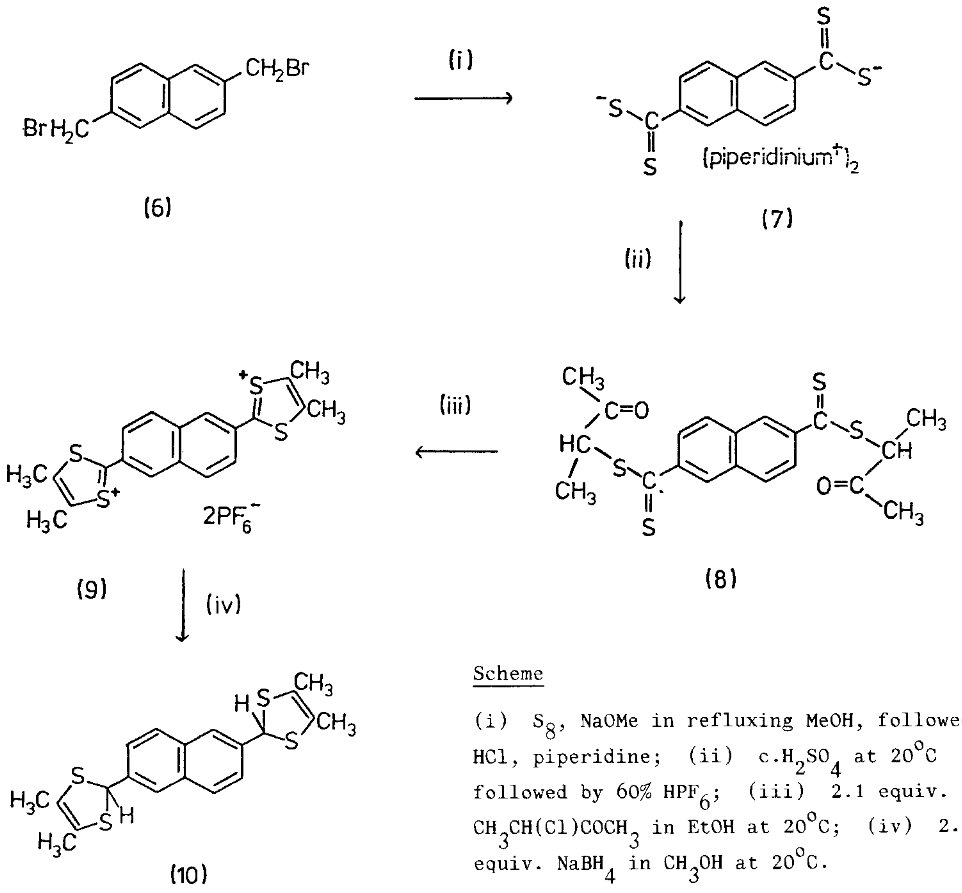


(4)



(5)

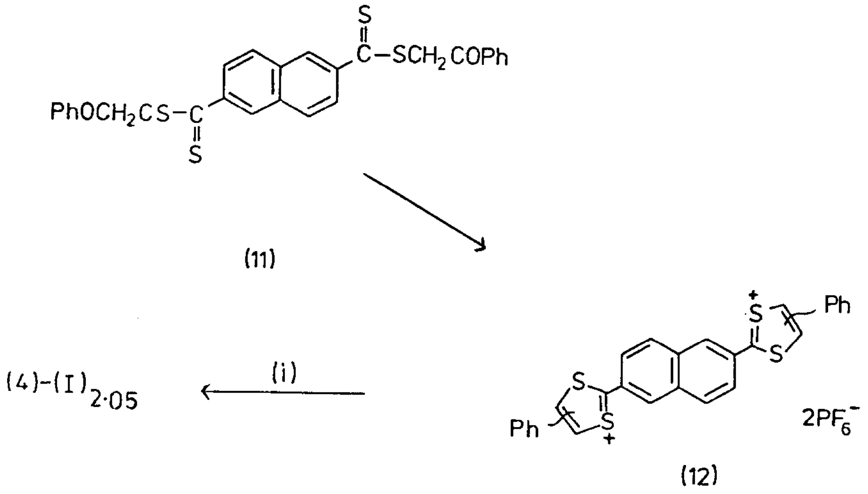
The route to compound (3) is outlined in the Scheme; all steps have literature precedents.[4] Treatment of 2,6-bis(bromomethyl)naphthalene (6) with sulphur and sodium methoxide yielded compound (7), isolated as the dipiperidinium salt.[5] Reaction of (7) with 3-chlorobutanone afforded compound (8)[6] which readily cyclised to yield dication (9).[7] Reduction of (9) with sodium borohydride gave dihydro-derivative (10).[8] Attempted dehydrogenation of (10) to compound (3) using triethylamine gave no identifiable products, and reaction of (10) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) yielded a highly insoluble brown powder, identified from i.r., e.s.r. and u.v. spectral data[9] and microanalytical data as a 1:1 salt of the quinol radical anion and the TM-NBDT radical cation.



Scheme

(i) S_8, NaOMe in refluxing MeOH, followed by HCl, piperidine; (ii) c.H_2SO_4 at 20°C followed by 60% HPF_6; (iii) 2.1 equiv. $CH_3CH(Cl)COCH_3$ in EtOH at 20°C; (iv) 2.1 equiv. $NaBH_4$ in CH_3OH at 20°C.

The diphenyl derivative (4) has been approached by a directly analogous route. Thus treatment of (7) with phenacyl bromide yielded compound (11)[10] which cyclised to dication (12).[11] Reaction of bis(dithiolium) dications with lithium iodide is a known route for the formation of donor-iodine complexes, possibly via electron transfer from iodide anion to form the radical cation of the donor.[4] TM-NBDT dication (9) was added to lithium iodide in acetone to yield a dark solution, but no product could be isolated. However, under the same conditions, dication (12) yielded an iodine complex as a black powder, for which analytical data suggested a stoichiometry (DP-NBDT) $(I)_{2.05}$. The large bathochromic shift in the u.v. spectrum of this complex (λ_{max} 655 and 1030 nm) confirms the presence of the highly conjugated structure of DP-NBDT (4) as opposed to an aromatic structure such as (12). Preliminary conductivity measurements on this iodine complex of DP-NBDT suggest the material is an insulator [σ_{rt} (compressed powder) $< 10^{-5}$ $(\Omega\ cm)^{-1}$]. Studies on the use of TM-NBDT and DP-NBDT as donors for TCNQ and TNAP will be reported separately.



(i) excess LiI in refluxing acetone.

References and Notes

1. For recent reviews and monographs see J.B. Torrance, *Accounts Chem. Res.*, 1979, **12**, 79; 'The Physics and Chemistry of Low Dimensional Solids', ed. L. Alcacer, D. Reidel, Dordrecht, Holland, 1980; 'Extended Linear Chain Compounds', Vols. 1-3, Plenum, London, 1982 and 1983; M.R. Bryce and L.C. Murphy, *Nature*, 1984, in press.
2. D.J. Sandman, G.D. Zoski, W.A. Burke, G.P. Hamill, G.P. Caesar, A.D. Baker, *J. Chem. Soc. Chem. Commun.*, 1981, 829; T. Kawase, H. Awaji, S. Yoneda and Z. Yoshida, *Heterocycles*, 1982, **18**, 123; M.R. Bryce, *J. Chem. Soc. Chem. Commun.*, 1983, 4; Z. Yoshida, T. Kawasi, H. Awaji, I. Sugimoto, T. Sugimoto and S. Yoneda, *Tetrahedron Lett.*, 1983, **24**, 3469; Z. Yoshida, T. Kawase, H. Awaji and S. Yoneda, *Tetrahedron Lett.*, 1983, **24**, 3473.
3. D.J. Sandman and A.F. Garito, *J. Org. Chem.*, 1974, **39**, 1165.
4. Y. Ueno, M. Bahry and M. Okawara, *Tetrahedron Lett.*, 1977, 4607; J.-M. Fabre, E. Torreilles and L. Giral, *Tetrahedron Lett.*, 1978, 3703.
5. Satisfactory analytical data were obtained for all new compounds unless otherwise stated. Compound (7), 50% yield, orange crystals, m.p. 152-155°C; ν_{max} 1000 cm^{-1} (CSS^-).
6. Compound (8), 50% yield, red needles, m.p. 181-183°C; ν_{max} 1695 (C=O) and 1190 cm^{-1} (C=S); δ_H ($CDCl_3$) 1.63 (d, 6H), 2.36 (s, 6H), 4.95 (q, 2H), 7.5-8.5 (m, 6H).
7. Compound (9), 62% yield, brown powder, m.p. > 300°C; δ (CF_3CO_2H) 2.75 (s, 12H), 8.1-8.7 (m, 6H); λ_{max} (CH_3CN) 325, 442 nm.
8. Compound (10), brown powder which could not be obtained analytically pure; δ_H [$(CD_3)_2SO$] 1.80 (s, 12H), 5.60 (s, 2H), 7.5-8.0 (m, 6H).
9. ν_{max} 1554 cm^{-1} (phenoxyl radical band), C=O absent; e.s.r. (powder) singlet, g 2.0003. λ_{max} (CH_3CN) 785, 640, 430, 330 nm

   See Y. Ueno, A. Nakayama and M. Okawara, *J. Chem. Soc. Chem. Commun.*, 1978, 74.
10. Compound (11), 60% yield, red crystals, m.p. 184-187°C, ν_{max} 1690 (C=O) and 1205 (C=S) δ_H ($CDCl_3$) 7.4-8.5 (m).
11. Compound (12), 74% yield, brown powder, m.p. > 300°C; λ_{max} (CH_3CN) 249, 339, 463 nm.

(Received in UK 30 March 1984)