

Synthesis of a Weitz-type Organosulphur π -Donor with a Cumulenonic Bond: 1,2-Bis(2,6-diphenyl-4*H*-thiopyran-4-ylidene)ethene

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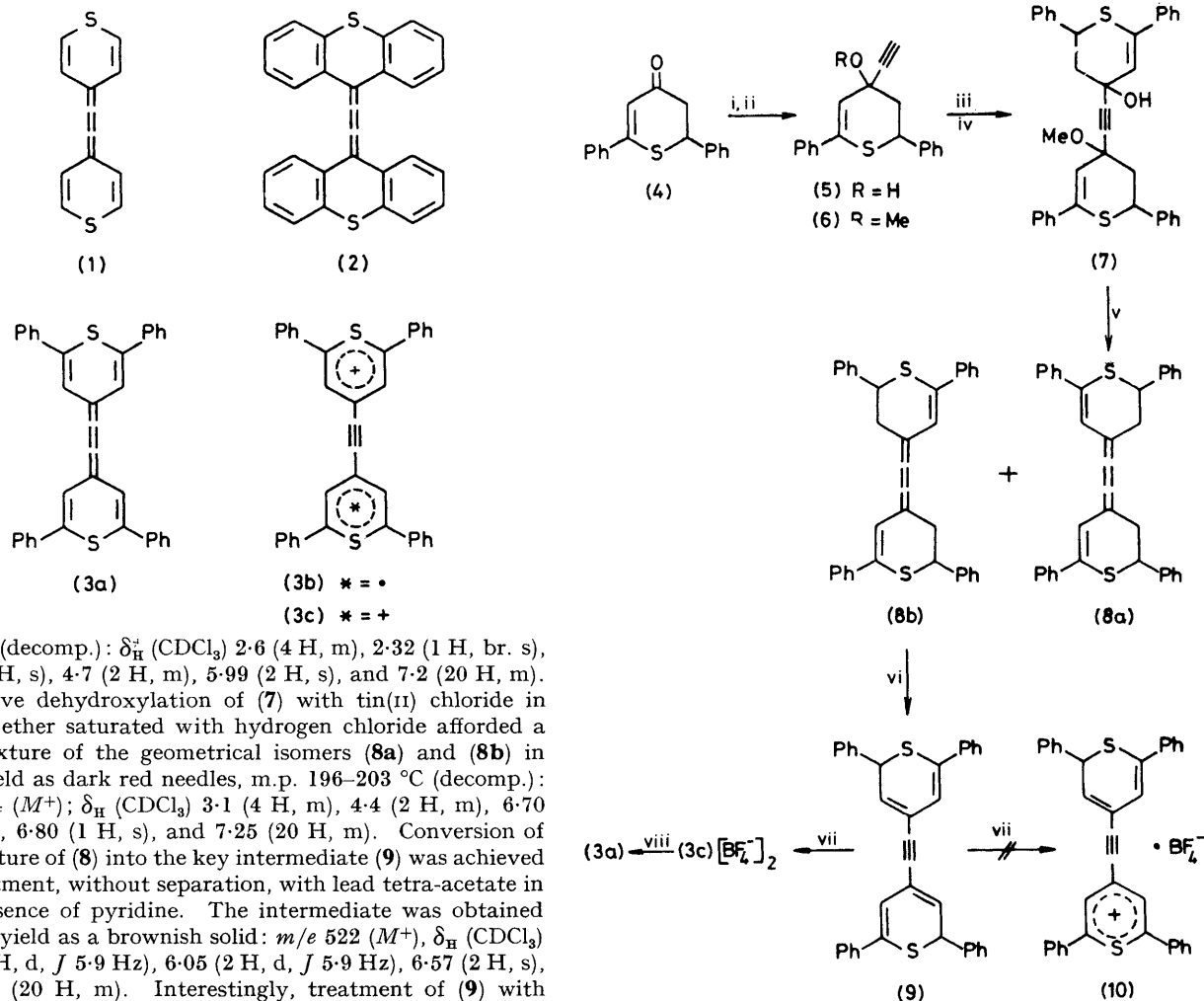
Summary The new, title organosulphur π -donor and its bistetrafluoroborate have been synthesised from 2,6-diphenyl-2,3-dihydrothiopyran-4-one *via* the key intermediate 1,2-bis(2,6-diphenyl-2*H*-thiopyran-4-yl)ethyne.

RECENT interest in π -donors¹ such as tetrathiafulvalene (TTF) and $\Delta^{4,4}$ -bithiopyran (BTP), which are regarded as Weitz-type multistage redox systems² having relatively low ionization potentials, has provided the impetus for the synthesis of a variety of structurally modified TTF's and BTP's. In addition to symmetrical- and unsymmetrical-type modifications, several insertion-type analogues³ have been investigated in order to extend the conjugation of these π -frameworks. We have recently described the preparation of a tetrabenzo-annelated derivative (**2**) of the cumulene insertion-type BTP system (**1**), in which two terminal π -systems are connected by sp-carbons.⁴ The cumulenonic bond in (**2**) makes it possible to modify the structure of BTP-type donors without introducing steric

hindrance between the terminal groups. However, because a stable aromatic sextet is created upon oxidation to the radical cation (**3b**) or the dication (**3c**), the tetraphenyl derivative, 1,2-bis(2,6-diphenyl-4*H*-thiopyran-4-ylidene)ethene (**3a**), is a better donor than (**2**). We now report the synthesis of (**3a**) according to the route shown in the Scheme.[†]

We selected the dihydro-derivative (**9**) of the final product (**3a**) as a key precursor for our synthesis, reasoning that it might be converted into (**3a**) by an appropriate dehydrogenation procedure. The ethynyl alcohol (**5**), prepared in 86% yield by ethynylation of (**4**) with lithium acetylide in tetrahydrofuran (THF), was converted into its methyl ether (**6**) (in 88% yield), colourless solid, m.p. 53–55 °C: m/e 306 (M^+); ν (neat) 3267 ($\equiv\text{C-H}$) and 2100 ($\text{C}\equiv\text{C}$); δ_{H} (CDCl_3 , Me_4Si as internal standard) 2.6 (2 H, m), 2.73 (1 H, s), 3.44 (3 H, s), 4.8 (1 H, m), 5.97 (1 H, s), and 7.2 (10 H, m). The lithium salt of (**6**) was treated with (**4**) to give the acetylene (**7**) in 57% yield as a pale yellow solid, m.p. 61.5–

[†] All new compounds gave satisfactory elemental analyses.



62.0 °C (decomp.): $\delta_{\text{H}}^{\text{a}}$ (CDCl_3) 2.6 (4 H, m), 2.32 (1 H, br. s), 3.45 (3 H, s), 4.7 (2 H, m), 5.99 (2 H, s), and 7.2 (20 H, m). Reductive dehydroxylation of (7) with tin(II) chloride in diethyl ether saturated with hydrogen chloride afforded a 1:1 mixture of the geometrical isomers (8a) and (8b) in 85% yield as dark red needles, m.p. 196–203 °C (decomp.): m/e 524 (M^+); δ_{H} (CDCl_3) 3.1 (4 H, m), 4.4 (2 H, m), 6.70 (1 H, s), 6.80 (1 H, s), and 7.25 (20 H, m). Conversion of the mixture of (8) into the key intermediate (9) was achieved by treatment, without separation, with lead tetra-acetate in the presence of pyridine. The intermediate was obtained in 80% yield as a brownish solid: m/e 522 (M^+), δ_{H} (CDCl_3) 4.82 (2 H, d, J 5.9 Hz), 6.05 (2 H, d, J 5.9 Hz), 6.57 (2 H, s), and 7.3 (20 H, m). Interestingly, treatment of (9) with triphenylmethyl tetrafluoroborate gave, instead of the monocation (10), the acetylenic dication (3c)[BF_4^-] $_2$ in 39% yield as an orange solid, m.p. 188–190 °C (decomp.). The D_{2h} symmetrical structure of (3c)[BF_4^-] $_2$ was characterized by ^1H and ^{13}C n.m.r. spectroscopy ($\text{CF}_3\text{CO}_2\text{D}$, Me_4Si as internal standard): δ_{H} (100 MHz) 7.6–8.2 (20 H, m) and 9.05 (4 H, s); δ_{C} (22.5 MHz) 102 (C-7), 135 (C-3), 144 (C-4), 174 (C-2), and 130, 133, 135, and 137 p.p.m. (C_6H_5). Finally, (3c)[BF_4^-] $_2$ was treated with a large excess of triethylamine ‡ to give the desired cumulene (3a) § in 45% yield as dark violet needles with a metallic lustre, m.p. 211–213 °C (decomp.): m/e 520 (M^+); δ_{H} ($\text{CS}_2 + \text{C}_6\text{D}_{12}$) 6.58 (4 H, s) and 7.33 (20 H, m); λ_{max} (CH_2Cl_2) 553 nm (log ϵ , 4.99), 284 sh (4.36), 258 sh (4.58), and 242 (4.69); Raman, ν 2022 cm^{-1}

SCHEME. Reagents. i, $\text{LiC}\equiv\text{CH}$, THF; ii, NaH-MeI , THF; iii, $\text{Bu}^{\text{a}}\text{Li}$ in hexane, THF; iv, (4); v, SnCl_2 , HCl -diethyl ether; vi, $\text{Pb}(\text{OAc})_4$ -pyridine, benzene; vii, $\text{Ph}_3\text{C}^+\text{BF}_4^-$, CH_2Cl_2 ; viii, Et_3N , CH_2Cl_2 .

($\text{C}=\text{C}=\text{C}$). The cyclic voltammogram ¶ of (3a) exhibited two reversible one-electron oxidation waves at $E_1 + 0.14$ and $E_2 + 0.49$ V (100 mV s^{-1} scan) which shows that it is far easier to oxidize than the corresponding tetrabenzocumulene analogue (2) ($E_1 + 0.43$, $E_2 + 0.65$ V), 4 as would be expected.

In a preliminary experiment, (3a) reacted with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene solution to give the 3:4 complex as a dark brown solid, m.p.

‡ When reduction of the dication (3c) [BF_4^-] $_2$ was attempted with a large excess of zinc dust in acetonitrile or dichloromethane, only a minute amount of the desired cumulene (3a) was detected by t.l.c.

§ After completion of this synthesis, the authors became aware of a recent paper by Hünig *et al.* (B. Hagenbruch, K. Hesse, S. Hünig, and G. Klug, *Liebigs Ann. Chem.*, 1981, 256) which describes the synthesis of a butatriene derivative with a cross-conjugated double bond. The compound (3a) presented in our communication could also be prepared, though in very low yield, from 2,6-diphenylthiopyran-4-one by Hünig's method.

¶ The cyclic voltammetry on (3a) was carried out in dichloromethane (3.2×10^{-4} M) at -60 °C under nitrogen with added Et_4NClO_4 (0.1 M) vs. Ag/AgCl with a glassy carbon electrode as the working electrode; the values are corrected to the standard calomel electrode.

182—184 °C (decomp.); λ_{max} (CH_2Cl_2) 1115 nm ($\log \epsilon$, 3.79), 806 (4.09), 598 sh (4.32), 508 (4.68), and 351 (4.87).

The synthetic procedure apparently provides a general method for synthesising a variety of cumulene-inserted systems having unsymmetrical terminal groups.

We are grateful to Professor S. Ikeda, Dr. I. Watanabe, and Mr. N. Ogawa of our department for the cyclic voltammetry measurement.

(Received, 28th July 1981; Com. 915.)

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