

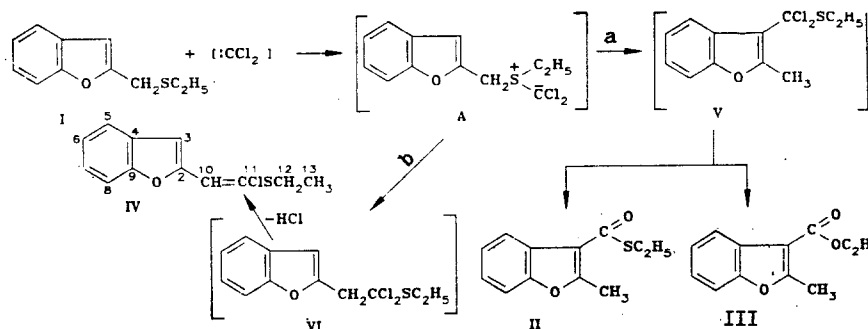
FORMATION OF 2,3-DISUBSTITUTED BENZOFURANS IN THE REACTION OF DICHLOROCARBENE WITH A 2-ALKYLTHIOMETHYLBENZOFURAN

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Carbenes, generated under different conditions, react with substituted furans and benzofurans to give functionally-substituted five- and six-membered heterocycles [1, 2] and substituted olefins [3].

On reacting 2-ethylthiomethylbenzofuran (I) with dichlorocarbene, generated by phase-transfer catalysis (80% NaOH, 55°C, TEBAB, chloroform), the products were found to contain the 2,3-disubstituted benzofurans (II) and (III), and the unsaturated sulfide (IV). Compounds (II-IV) appear to be formed by reaction of the ylid A in two ways, namely 2,3-sigmatropic rearrangement involving the C₍₂₎-C₍₃₎ bond of the furan ring (a), and Stevens rearrangement with migration of the benzofurfuryl residue (b), the resulting intermediates (V) and (VI) undergoing further reactions.



Alcoholysis (by the alcohol present in the chloroform as stabilizer) of the unstable dichloro-sulfide (V) affords (II) and (III). The sulfide (IV) consists of a mixture of the E- and Z-isomers, the ^{13}C NMR spectra of which differ in that the chemical shifts of the carbon atoms involved in the double bond in Z-(IV) are smaller than in E-(IV).

The reaction between dichlorocarbene and 2-ethoxymethylbenzofuran, which cannot form an ylid, affords (GC-MS) the product of the addition of dichlorocarbene to the C₍₂₎-C₍₃₎ bond of the furan ring (~3% of the reaction mixture).

The elemental analyses for (II)-(IV) were in agreement with the calculated values.

Ethyl 2-Methyl-3-benzofurancarboxylate (III, C₁₇H₁₂O₃). Yield 46%, bp 109-111°C (10 mm). PMR spectrum (CCl₄): 1.30-1.65 (3H, t, CH₃), 2.7-2.9 (3H, s, CH₃), 4.1-4.6 (2H, q, OCH₂), 7.0-7.4 and 7.7-8.0 ppm (4H, m, arom. C₆H₄). Mass spectrum, m/z (I_{rel}, %): 204 (M, 90), 175 (28), 174 (100), 159 (10), 158 (88), 146 (3), 130 (21), 102 (21), 91 (6), 77 (37), 63 (7).

Z-2-(2-Chloro-2-ethylthiovinyl)benzofuran (IV). ^{13}C NMR spectrum (CDCl₃): 154.09 (C₍₂₎); 111.03 (C₍₃₎); 128.65 (C₍₄₎); 121.31 (C₍₅₎); 120.00 (C₍₆₎); 123.06 (C₍₇₎); 107.36 (C₍₈₎); 151.50 (C₍₉₎); 125.08 (C₍₁₀₎); 130.42 (C₍₁₁₎); 27.90 (C₍₁₂₎); 14.36 ppm (C₍₁₃₎).

E-2-(2-Chloro-2-ethylthiovinyl)benzofuran (IV). ^{13}C NMR spectrum (CDCl₃): 154.09 (C₍₂₎); 111.03 (C₍₃₎); 128.75 (C₍₄₎); 121.64 (C₍₅₎); 121.50 (C₍₆₎); 123.00 (C₍₇₎); 107.17 (C₍₈₎); 151.65 (C₍₉₎); 124.80 (C₍₁₀₎); 131.50 (C₍₁₁₎); 28.93 (C₍₁₂₎); 14.97 ppm (C₍₁₃₎).

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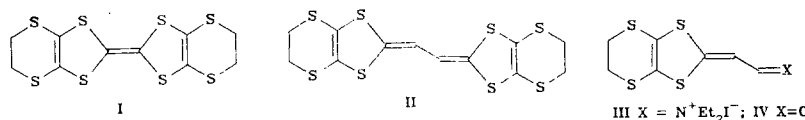
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SYNTHESIS AND PROPERTIES OF ETHANEDIYLIDENE-2, 2'-BIS (4, 5-ETHYLENEDITHIO-1, 3-DITHIOLE), A VINYLOG OF BEDT-TTF

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The discovery of superconductivity in cation-radical salts of bis-(ethylenedithio) tetrathiafulvalene (BEDT-TTF) (I) at temperatures of 1.4–11.0°K has prompted the synthesis of a number of its analogs in order to assess the effect of the structure of the electron donor on the electrophysical properties of its salts. Although some ethanediylidene-2, 2'-bis(1, 3-dithioles), which are vinylogs of tetrathiafulvalene, have been reported [1, 2], the 4, 5-ethylenedithio-compound, a vinylog of BEDT-TTF (II), is not known.



2-Ethylthio-4, 5-ethylenedithio-1, 3-dithiolium fluoroborate reacts with triethylamine and iodine [3] to give 50% of the iodide (III) as orange crystals, mp 166–168°C (from ethanol), PMR spectrum (CDCl₃): 1.37 (3H, t), 1.49 (3H, t), 3.67 (2H, q), 3.96 (2H, q), 3.44 (4H, s), 6.90 (1H, d), 8.61 ppm (1H, d). Hydrolysis of (III) gave a quantitative yield of the aldehyde (IV) as orange crystals, mp 125–126°C (from petroleum ether), IR spectrum (paraffin grease): 1600, 1520, 1050 cm⁻¹, UV spectrum (EtOH), λ_{max} (log ε): 415 (4.24), 290 (3.88), 274 nm (3.72), PMR spectrum (CDCl₃): 3.36 (4H, s), 6.60 (1H, d), 9.36 ppm (1H, d).

To a vigorously stirred suspension of 10 mmole of (4, 5-ethylenedithio-1, 3-dithio-1, 3-dithiol-2-yl)tributylphosphonium perchlorate (obtained as in [4]) in 20 ml of THF was added at –80 to –85°C 10 mmole of sodium tert-butoxide, followed by the dropwise addition over 20 min of a solution of 10 mmole of the aldehyde (III) in 20 ml of THF. After 20 min, the cooling was withdrawn, and after one hour the solid which had separated was filtered off and washed with water and ethanol to give 82% of (II), obtained as shining bronze leaflets on recrystallization from benzonitrile, mp > 250°C (decomp.). IR spectrum (paraffin grease): 1490, 1400, 1275, 960, 920, 880, 805 cm⁻¹. UV spectrum (dioxane), λ_{max} (log ε): 430 (4.15), 408 nm (4.13). The oxidation potentials were determined by cyclic voltammetry in acetonitrile, E₁^{Ox} = 0.36 V; E₂^{Ox} = 0.59 V (the values for (I) were 0.56 and 0.84 V respectively) (rel. s.c.e). Compound (II) is therefore a more powerful donor than (I). Oxidation of (II) with phenyliodosodiacetate in the presence of toluene-p-sulfonic acid gave the violet ditosylate (λ_{max} in acetonitrile, 503 nm). Reaction of (II) with tetracyanoquinodimethane in carbon disulfide afforded shining green crystals of the 1:2 complex, the properties of which will be reported elsewhere. The elemental analyses of the compounds obtained were in agreement with the calculated values.

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