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4,5-Bis(methylene)-1,3-dithiole-2-ones from Brominated 4,5-Dimethyl-1,3-dithiole-2-ones: Precursors for Tetramethylene-Tetrathiafulvalenes

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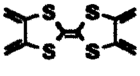
Abstract: *Treatment of di- and tetrabromo-1,3-dithiole-2-ones 7 and 8 with Et_4NI yields unsubstituted diene 4, trapped as its dimer or a cycloadduct; and dibromodiene 9. Treatment of 8 with DBU gives tribromodiene 10. Spectroscopic evidence indicates that tetramethylene-TTFs are formed by heating 9 and 10 with $P(OEt)_3$. Diels Alder adducts are formed by 9.*

1,3-Dithiole derivatives form a large, and important, group of organic metals precursors. New examples, of the tetrathiafulvalene (TTF) and related families in particular, are sought after, for use in the synthesis of conducting materials with enhanced 2D, and 3D interactions, and to broaden the range of available donor potentials. This creates the need for starting materials or intermediates which can give access to new derivatives.[1]

Herein we report the allylic bromination of dimethyl-1,3-dithiole-2-one and the generation and isolation of stable bis(methylene)-1,3-dithiole-2-ones from the brominated derivatives. The unusually stable dienes were used to prepare tetramethylene-tetrathiafulvalenes, and several Diels Alder adducts. Bis(methylene)-1,3-dithiole-and bromo 1,3-dithiole-2-ones have the potential to be useful for preparing TTFs and other 1,3-dithiole systems, via Diels Alder or substitution reactions, respectively. Tetramethylene-TTFs could be useful as intermediates for preparing TTFs, and, possibly, in their own right as novel, TTF-like, electron donors.

Tetramethylene-TTFs and bis(methylene)-1,3-dithioles have been the subject of two previous reports. Cowan *et al*[2] attempted to prepare tetramethylene-tetrathiafulvalene 1 by retro Diels-Alder reaction of bis(dioxothiacyclopenta)-TTF 2, with inconclusive results. However, a diene was generated and trapped from iminium ion 3, and, subsequently, Zard *et al*[3] reported the generation and trapping of bis(methylene)-1,3-dithiol-2-one 4 and its dimethyl derivative, by heating propargylic xanthates 5.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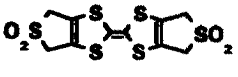
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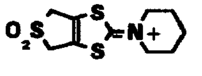
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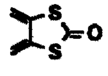
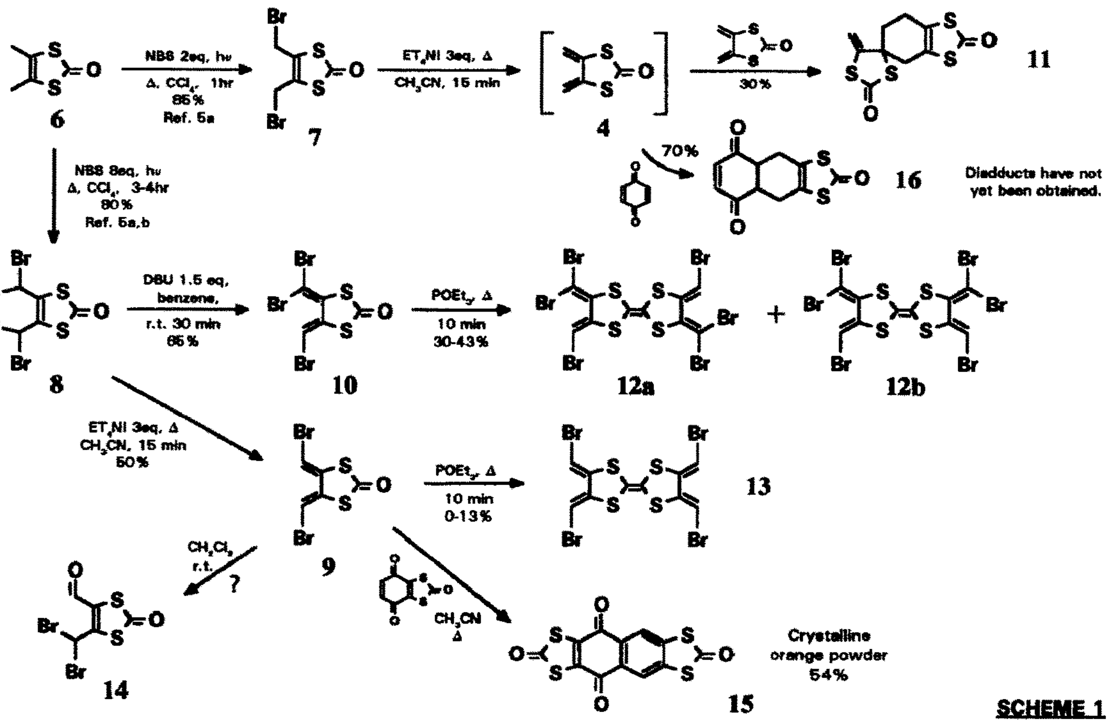

4


5 R = H, Me

We have found an alternative route to the bis(methylene)-1,3-dithiole system. Reaction of 4,5-dimethyl-1,3-dithiole-2-one 6 and N-bromosuccinimide in refluxing carbon tetrachloride, yielded the allylic bromides 4,5-bis(bromomethyl)-1,3-dithiole-one 7 and 6,6,7,7-tetrabromo-4,5-dimethyl-1,3-dithiole-2-one 8, according to Scheme 1. The parent diene 4, and 4,5-bis(bromomethylene)-1,3-dithiole-2-one 9 were generated using a procedure similar to that used by Cava *et al*[4] to generate *α,α'-o*-quinodimethane, but slightly modified to shorten reaction times. Thus treatment of 7 or 8 with tetraethylammonium iodide in refluxing acetonitrile, in the absence of dienophiles, yielded dimer 11 and diene 9 respectively. The reactions were monitored by tlc, and the products isolated by chromatography.[5] Both crystallised from their chromatograhic solvent: 11 as oblong prisms; and 9 as long, colorless, needles that were too thin for X-ray crystal structure determination. Diene 9 gradually disappears if left in solution, but a new product appears which crystallises as triangular prisms. Spectroscopic data[7]



SCHEME 1

suggests that it possesses structure **14**, but it's mode of formation is not known. As long as the reaction time is short this compound forms to a limited extent during the preparation of **9**, but complicates subsequent reactions if it forms more quickly than the diene can react. Tribromodiene **10** was prepared by adding diazabicycloundecene (DBU) dropwise to a solution of **8** in benzene, removing the DBU·HBr precipitate, and filtering the mother liquor through silica gel. Evaporation leaves the product **10** as a colorless crystalline powder. This compound is particularly stable, can be stored at room temperature; and does not decompose in solution, as does **9**. It can withstand heating from our laser at 676 nm, and we have obtained a Raman spectrum using this wavelength.

The dienes are expected to possess the least sterically hindered *E,E* and *E* structures as drawn. Their ^{1}H NMR spectra each consist of one singlet,[7] *i.e.* neither is detectably a mixture of isomers, hence presumably only the most favoured isomer has formed. The singlet position is shifted 0.9 ppm downfield in **10**; a deshielding effect of similar magnitude to that observed for an H close in space to Cl, but separated by five bonds, in chloro substituted pyrroloquinoxalines;[8] which suggests that **10** forms as the *E* isomer. This assignment is also comparable to those made in a study of several isomeric chloro substituted *cis*-fixed dienes.[9]

When tribromodiene **10** was warmed in triethylphosphite[1] a microcrystalline mustard-yellow powder precipitated. This material has limited solublility, and we have been unable to grow crystals. The ^{13}C MAS NMR spectrum contains broad features, and an irreversible transformation at 197 °C, was observed using differential scanning calorimetry. The multiplet which would be expected, if this compound is tetramethylene-TTF **12**, was observed by FAB mass spectrometry, the results of which are shown in Figure 1. The multiplet centered around 721 amu may be due to fragmentation of a larger molecule formed during heating of the spectrometer probe. Elemental analyses values for C, Br and S are close to those expected for $C_{10}H_2Br_6S_4$, although the value for H is approximately 20% too high.[7]

Comparison of the IR spectra of **10** and **12**, shown in Figure 2, reveal that the C=O stretching band is missing in the spectrum of the product; but that the diene C=C bands are present in the same position as they appear in the spectrum of **10**. The C-H stretching frequencies are also very similar: 3126 cm^{-1} and 3128 cm^{-1} for **10** and the product respectively. A decrease of approximately 100 cm^{-1} would be expected if the H was attached to an

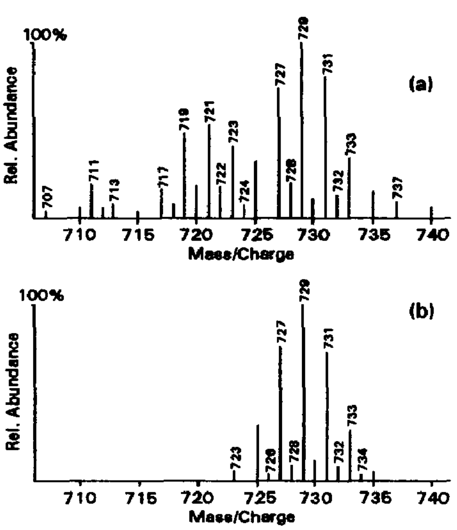


FIGURE1: FAB mass spectrum of compound 12
(a) Ions observed above 700 amu
(b) Simulated spectrum for the molecular ion region of $C_{10}H_2Br_8S_4$

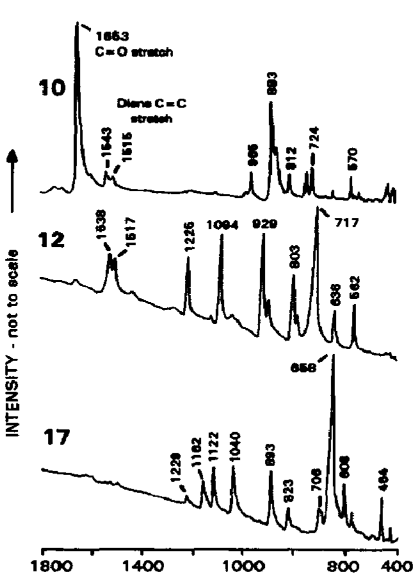


FIGURE 2: IR spectra of compounds 10, 12 & 17

sp^3 centre. The analytical, and mass and IR spectral data are compelling evidence supporting the assignment of the reaction product as **12a** and/or **12b**, both structures being possible. The yield (~ 35%) is similar to that of many TTFs obtained from the reaction of 1,3-dithiole-2-chalcogenones and trialkylphosphites.[1]

A yellow, or brown microcrystalline powder can also be obtained by warming **9** in triethylphosphite for several minutes, followed by evaporation to a thick syrup and tituration with CH_2Cl_2. The poor yield, which ranges from 0 - 13%, is due to the decreased stability of **9** in solution. On the basis of IR evidence, which parallels that for **12**, we have assigned this compound as tetramethylene-TTF **13**. However, the analytical data[7] is not as good, probably due to impurities, and this assignment must be considered to be less certain than for **12**.

We have attempted to isolate the parent diene **4**, so that it, also, might be used to react with triethylphosphite to provide **1**, but it polymerises too rapidly, and we have only been able to obtain dimer **11**. However, as reported in Ref. 2, **4** readily yields Diels Alder adducts; and we have observed that, under the same conditions that we use for **4**, diene **9** also forms cycloadducts. These lose HBr, yielding products such as **15**. Such adducts can be specifically targeted for use in the preparation of TTFs, or other desired systems. For example, we are attempting to modify **15**, and to obtain diadducts, *e.g.* from **16**, to give access to bis(TTFs) and dithiolene polymers.[10] We have not yet obtained a cycloadduct from **10**, and a similar poor reactivity would be expected of **12**.

The Br atoms must be the stabilising influence in dienes **9** and **10**, and tetramethylene-TTFs **12** and **13**, *i.e.* in comparison to **4**, but their presence would also be expected to result in electron-deficient compounds, with poor donor properties. It may be for this reason that our initial attempts to prepare charge-transfer complexes from both **12** and **13**, *e.g.* with I_2 and TCNQ, have been unsuccessful. Poor donor potentials might, however, be an advantage with regard to cycloadduct formation, reducing the likelihood of charge-transfer complex formation with dienophiles.

Attempted oxidation of either **12** or **13** by excess Br_2 in refluxing dichloromethane, yielded very small, black, needles, which were insoluble in common solvents. Their IR spectra reveal that the diene C=C feature has disappeared and that the C-H stretching frequency has decreased by 100 cm^{-1}. The spectrum of the product obtained from **12** (**17**) is shown in Figure 2. Although the C=C and C-H stretches would be expected to move to lower wavenumbers if oxidation had occurred, elemental analysis of this product indicates an approximate formula $C_{10}H_2Br_{12\text{-}13}S_4$. There is no evidence of polybromides in its' Raman spectrum. These observations suggest that Br_2 has added to the diene double bonds, possibly to give a TTF, or a tetrathioethylene.

Synthesis of tetramethylene-TTF derivatives, with better donor properties, by replacement of the Br; *e.g.* by way of Lithium-halogen exchange, may be possible, however, preparation of new dienes, from other alkyl substituted 1,3-dithiole-2-ones, is an approach that appears more likely to succeed, and our current efforts are aimed at making progress in this direction.

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5. Tlc: **7**, **8**, **9**, **10** & **14** distinctive blue, **11** slow pink\brown spot when developed by spraying with EtOH/conc. H_2SO_4/anisaldehyde 92:5:3 and charring. Solvent: ethyl acetate (EA)/pet. ether (PE) 1:5; except **9** EA / PE 1:20 . Chromatography: silica gel 60, Merck 9385; **11** EA/PE 1:5; **9** benzene/PE 1:5. $Na_2S_2O_3$ was carefully used in work up to remove halogen coloration.
6. (a) Reflux over a 250 watt heat lamp. (b) Benzoyl peroxide required on some occasions.
7. Analytical data: ^1H NMR δ(ppm,TMS/$CDCl_3$); IR (cm^{-1}, KBr disc); E.I. maspec (m/z) highest mass, % intensity relative to most abundant ion; in all cases. **7** $C_5H_4Br_2OS_2$; *mw:* 304.002; *maspec:* 302,304,306 1:2:1, 30%; *^1H NMR:* 4.37 s. **8** $C_5H_2Br_4OS_2$; *mw:* 461.786; *maspec:* 457,459,461,463,465 1:3:5:3:1, $[M-1]^+$ 17%; *^1H NMR:* 6.78 s. **9** $C_5H_2Br_2OS_2$; *mw:* 301.986; *calculated (%): C* 19.89; *H* 0.67; *S* 21.23; *Br* 52.92; *found (%): C* 20.11; *H* 0.72; *S* 21.38; *Br* 53.09; *maspec:* 300,302,304 1:2:1, 43%; *^1H NMR:* 6.86 s; *IR:* 3065 mw; 1699 mw; 1647 vs; 1610 sh; 1558 m; 1497 w; 1235 mw; 1121 m; 951 m; 911 w; 850 s; 770 mw; 753 s; 748 ms; 656 mw; 613 m; 557 w; 554 mw; 425 ms. **10** $C_5HBr_3OS_2$; *mw:* 380.878; *maspec:* 378,380,382,384 1:3:3:1, 39%; *^1H NMR:* 7.76 s. **11** $C_{10}H_8O_2S_4$; *mw:* 288.404; *maspec:* 288 m, 73%; *^1H NMR:* 5.46 dd, 2H J_{AB} 2.4 Hz; 3.18 t, 1H; 2.69 m, 1H; 2.58 m, 1H. **12ab** $C_{10}H_2Br_6S_4$; *mw:* 729.756; *calculated (%): C* 16.46; *H* 0.27; *S* 17.57; *Br* 65.69; *found (%): C* 16.55; *H* 0.33; *S* 17.87; *Br* 65.71. **13** $C_{10}H_4Br_4S_4$; *mw:* 571.972; *calculated (%): C* 21.00; *H* 0.70; *S* 22.42; *Br* 55.88; *found (%): C* 21.61; *H* 1.01; *S* 21.40; *Br* 55.78; *IR:* 3066 ms; 1555 vs; 1217 vs; 1116 vs; 1039, 1021 m; 880 m; 782 wm; 753, 725 s; 689 s; 658 m; 607 wm. **14** $C_5H_2Br_2O_2S_2$; *mw:* 317.986; *calculated (%): C* 18.88; *H* 0.63; *S* 20.16; *Br* 50.25; *found (%): C* 19.02; *H* 0.58; *S* 20.30; *Br* 51.22; *^1H NMR:* 9.91 s, 1H; 7.35 s, 1H; *maspec:* 316,318,320 1:2:1, 10%. **15** $C_{12}H_2O_4S_4$; *mw:* 338.376; *maspec:* 338 m, 100%; *IR:* 1715, 1701 s; 1645 vs; 1564 ms; 1524 m; 1317 m; 1296 s; 1261 m; 1410 m; 853 m; 721 m; 429, 422 m. **16** $C_{11}H_8O_3S_2$; *mw:* 252.294; *maspec:* 252 m, 100%; *^1H NMR:* 6.77 s; 3.50 m; 2.75 broad m; ratio 1:1:2. *IR:* 1722 sh; 1691 sh; 1680 vs; 1635 s; 1595 s; 1436, 1429 m; 1347 m; 1265 ms; 1090 ms; 865 ms; 844 m; 421 m; 406 m. **18** *found (%): C* 9.52; *H* 0.19; *S* 10.34; *Br* 79.96.
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