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BIS-1,3-DITHIOLE CHEMISTRY: SYNTHESIS OF COMPOUNDS CONTAINING THE 4,4'BIS-(1,3-DITHIOLE) UNIT

J. R. Andersen*†, V. V. Patel, and E. M. Engler*
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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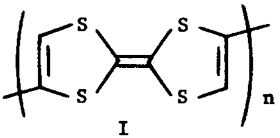
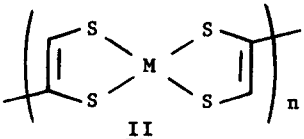
Recently, 1,3-dithiole and 1,3-dithiolium systems[1] gained in interest because of their use as precursors for tetrathiafulvalenes (TTF's) and transition metal bis-dithiolene complexes - compounds which have been found to display a variety of interesting physical properties[2,3]. We describe here the synthesis of dimeric 1,3-dithioles[4], since they appeared to be the obvious choice as precursors for the polymeric homologs of TTF (I) and metal bis-dithiolenes(II).



I



II

The synthetic procedures used are outlined in the Scheme. Treatment of 1,4-dibromo-2,3-butanedione with dithiocarbamates in CH_2Cl_2 resulted in instantaneous formation of the expected oxoesters III in quantitative yields. These were in turn cyclized in conc. H_2SO_4[5] and the resulting colorless imonium salts IV were isolated in 50-60% yield as tetrafluoroborates[6] (Table). The typical procedures[7,8] for converting these kinds of imonium salts to derivatives suitable for coupling to TTF's could not be carried out on IV-a and b since they were too insoluble to react. However, in the case of IV-c, where the dissymmetric substitution improves the solubility, reduction by $NaBH_4$ could be achieved to yield the apparently thermally unstable V (R_1=CH_3; R_2=C_2H_5) as a yellow oil. NMR($CDCl_3$, δ) 6.48 (singlet, 1H) 6.36 and 6.32 (two singlets due to hindered rotation about the C-N bonds, 1H) 2.72 (quartet, 2H; J=7Hz) 2.34 (singlet, 3H) and 1.20 (triplet, 3H; J=7Hz).

On treatment of a cold (0^o) methanolic solution of V with 70% $HClO_4$ a slightly yellow precipitate was formed. The synthetic route, together with the UV spectrum (λ_{max}, CF_3COOH: 252 nm vs. 260 nm for the monomeric 1,3-dithiolium cation) indicated, that the product was 4,4'-bis-(1,3-dithiolium) perchlorate, VI. Because of the explosive nature of dithiolium perchlorates[9], and since the product was very insoluble, no further characterization was attempted. Further-

TABLE

Properties of 4,4'-bis-(1,3-dithiole-2-imonium) tetrafluoroborates (IV).

		NMR(CF_3COOD, δ)	mp. °C
$R_1/R_2=(CH_2)_5$	IV-a	8.92 singlet, 1H 4.68 broad singlet, 4H 2.32 broad singlet, 6H	273-75d.
$R_1=R_2=CH_3$	IV-b	9.10 singlet, 1H 4.36 singlet, 6H	288-90d.
$R_1=CH_3;R_2=C_2H_5$	IV-c	9.10 singlet, 1H 4.70 quartet, 2H; J=7Hz 4.26 singlet, 3H 1.84 triplet, 3H; J=7Hz	276-78d.

more, because of the insolubility, we have not so far been able to couple[10] VI to yield I.

While the bis-imonium derivatives, IV, did not appear useful for elaborating the polymeric systems I and II, another bis-dithiole derivative - 4,4' bis-(1,3-dithiole-2-one) VIII - appeared more promising. Reaction of 1,4-dibromo-2,3-butanedione with potassium O-isopropyldithiocarbonate in CH_2Cl_2 gave the oxoester VII as yellow crystals, mp. 48-49° (hexane). NMR($CDCl_3$, δ) 5.70 (septet, 1H; J=6Hz) 4.34 (singlet, 2H) and 1.40 (doublet, 6H; J=6Hz). VII was cyclized in conc. H_2SO_4 and was isolated after addition to ice-water[4]. Crystallization from EtOH gave VIII in ca. 10% overall yield as long, colorless needles, mp. 214-15°. NMR(DMSO-d_6(sat.), δ) 7.46 (singlet); IR(KBr)C=O stretch: 1640cm^{-1}; m/e:234.

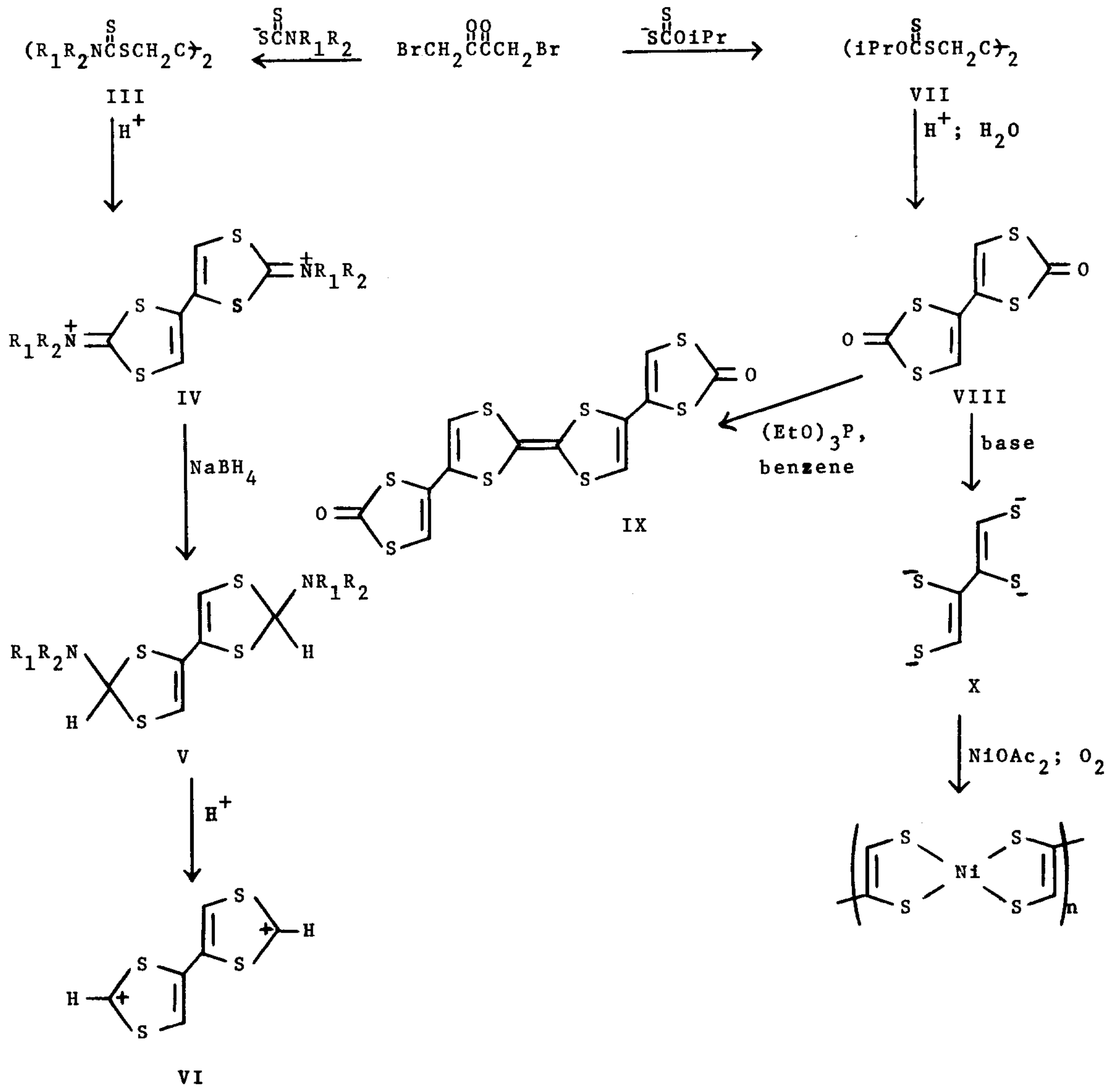
Attempts to polymerize VIII with $(EtO)_3P$ in refluxing benzene (48 hours) gave only the dimerized product[11], the TTF derivative IX, as a brick-red powder, mp. 275-77°d. IR(KBr) C=O stretch: 1640cm^{-1}. UV-Vis (λ_{max},$CHCl_3$): 295, 325 (sh) and 410 nm.

IX does not form a charge transfer salt with TCNQ, probably because of its reduced electron donating properties as compared to TTF. Two reversible one-electron redox couples were observed at 0.73 and 0.90V (DMF, 0.1M TEAP; volts vs. SCE). TTF gave under the same conditions the values 0.49 and 0.75V[12].

4,4'-bis-(1,3-dithiole-2-one) VIII appears to be a useful precursor to II. For example, reaction of VIII with strong base (MeLi in THF or NaOMe in MeOH) generated the unstable intermediate tetrathiolate X, which was reacted with $NiOAc_2$. The resulting dark homogenous reaction mixture was then treated with O_2 to precipitate the neutral, black nickel bis-dithiolene polymer (II; M=Ni). Preliminary measurements show the characteristic nickel bis- dithiolene absorption in the infrared[3]; however, this absorption is considerably broadened and shifted to slightly lower energy compared to the monomeric system (λ_{max}, DMF: 0.9 <u>vs.</u> 0.85μ for the parent nickel bis-dithiole). Another, unusually low energy absorption was also observed at λ_{max} <u>ca.</u> 1.8μ.

We are currently pursuing a more complete characterization of the nickel bis-dithiolene polymer and will report our results at length.

SCHEME



References and Notes

† IBM Postdoctoral Fellow. Permanent address: Chemistry Dept., Research Establishment RISØ, DK-4000, Denmark.

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11. A similar observation was seen for thiapendione, see ref. 4c.

12. The authors wish to thank F. B. Kaufman and D. C. Green for performing the electro-chemical measurements.