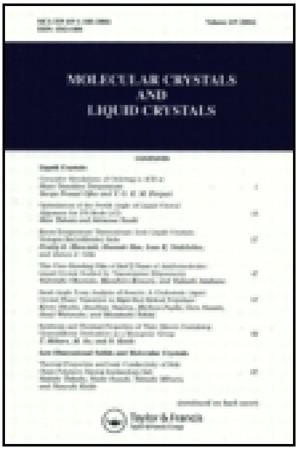

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Recent Advances in Organic Metals

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RECENT ADVANCES IN ORGANIC METALS

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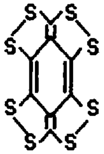
Abstract Recent advances in the synthesis of octathioquinodimethan (OTQ) culminating in the preparation of a perthiomethylated terephthalate, a methylated precursor of OTQ are presented.

INTRODUCTION

It is clear from previous papers in this conference and previous publications that in order to observe superconductivity in organic solids, one must have multiple chalcogen-chalcogen interactions[1]. This led us to design molecules whose periphery consists of group VI atoms (except oxygen). One example is octathioquinodimethane[2] (OTQ, 1):



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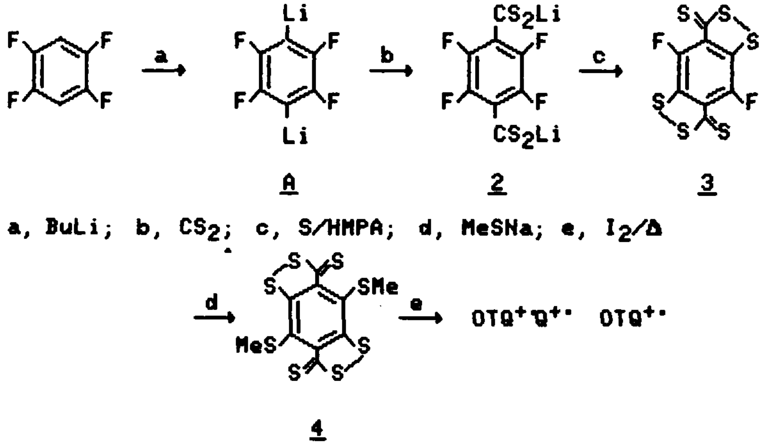
This molecule is interesting because its open shell derivatives may be stable either as a cation or anion so that it could be considered a good donor[2] and a relatively good acceptor. Furthermore, under the right circumstances, OTQ may undergo a neutral-to-ionic transition[3] which can be associated with an insulator-to-metal transition. For these reasons we decided to attempt to prepare this highly functional molecule. In this paper we present results of systematic introduction of up to eight sulfur atoms into a p-xylene.

RESULTS AND DISCUSSION

After several abortive attempts to prepare 1 in one step, it was decided to rationally incorporate all the sulfur atoms into a p-xylene framework. A potentially economic route is shown in Scheme I, below:

Scheme I



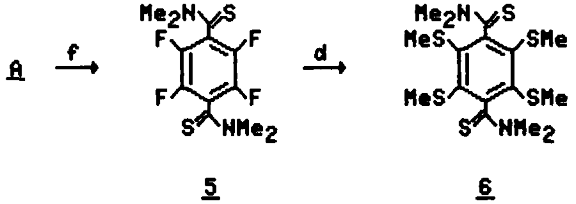
a, BuLi; b, CS$_2$; c, S/HMPA; d, MeSNa; e, I$_2$/Δ

The preparation of 2 was modeled after the preparation of its oxygen analog, tetrafluoro terephthalate[4], and the next two steps were based on previous experience with multithiolation of aromatic rings[5]; the last step required an oxidative dealkylation where we intended to take advantage of the volatility of methyl iodide to "drive" the reaction.

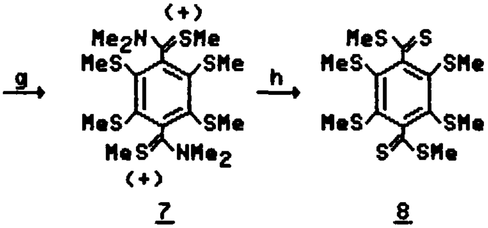
The first problem arose with the dithiocarbonation; unlike the reaction of 1,4-dilithio-2,3,5,6-tetrafluorobenzene with carbon dioxide[4], the reaction with carbon disulfide gave disappointingly low yields of both lithium tetrathioterephthalate and lithium tetrafluorodithiobenzoate [characterized as their methyl esters, 2Me (5%) and BMe (10%), respectively]. Others have made similar observations[6]. The reasons for this outcome are not obvious since the reaction mixture contained uncharacterized deeply colored oils which could have resulted from decomposition (polymerization, etc) of thiolates formed from thiophilic addition . Nonetheless we investigated the next step by the *in situ* trapping of 2 with sulfur, followed by intramolecular nucleophilic substitution of the adjacent fluoride atoms. Indeed, 3 was prepared in this manner for the first time but since the yields of the sequence tetrafluorobenzene → 3 were so meager, we did not have enough material to continue with this approach. However, even if the yield of 3 is low, it still constitutes a quick entry into a benzo-bis-1,2-dithiol-3-thione system[7] and is probably worth pursuing in terms of yield optimization. The obvious side product from this reaction, trifluorobenzo-1,2-dithiole-3-thione (3A) was also isolated and charaterized spectroscopically.

The next approach relied on a slight variation starting with A:

Scheme II



f, $Me_2NC(S)Cl$; g, MeI; h, H_2S/Pyr.

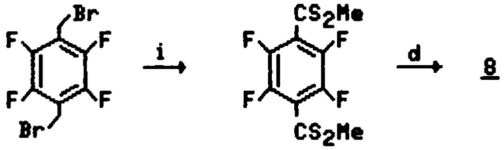


While the yields of 5 were considerably better than those of 2Me, they were still not respectable. Furthermore, in attempts to prepare N,N'-dimethyl-2,3,5,6-tetrafluorothio-benzamide 5A) by the prsumed monolithiation of tetrafluorobenzene[8], relatively higher yields of 5 were obtained; indicating that these lithiation-alkylation reactions in both Schemes are more complex than initially surmised and that 5A could be deprotonated very efficiently by 1-lithio-2,3,5,6-tetrafluorobenzene. To test this hypothesis we allowed 5A to react with LDA, followed by quenching with N,N-dimethyl thiocarbamoyl chloride; indeed, this procedure afforded the best yield of 5.

Surprisingly, the prepapration of 6 and 7 was uneventful under rather mild conditions. This enticement to success was obliterated by the utter failure of the sulfo-deamination step; the only isolable material from the reaction of 8 with hydrogen sulfide in pyridine was its precursor, 6. A possible explanation for this observation is that, in fact, the resonance structure drawn for 7 in Scheme II is the predominant one with little or no charge on the nitrogens due to steric inhibition of resonance; as a rsult, the sulfur atoms are forced to bear the full load of a positive charge and are demethylated. In addition, the thioacyl atoms which must be attacked by HS^- to afford 9, are burried in a sea of large, lone pair-bearing atoms.

Had we been able to obtain 8, we would have attempted to convert it to $OTQ^{+\cdot}$ *via* an oxidative demethylation. Another route to 8 is shown below:

Scheme III



9 2Me

i, S/MeO⁻/MeOH; MeI quench

Whereas in Scheme I we produced 2Me only in very low yields, in the above scheme the yield of the desired ester was respectable. This remarkably mild thiolation reaction was used previously for the preparation of tetrathio terephthalate[9] and is also extendable to the preparation of 2,3,5,6-tetrachloro tetrathioterephthalate[10]. The next step in the above sequence gave us some difficulty, particularly in the work up. Some of the problems were ameliorated when it was observed that upon quenching the reaction mixture with methyl iodide, the yield of 8 was improved and some 2Me could be recovered; indicating that at some stage during the nucleophilic aromatic substitution reaction, demethylation of the thioesters had taken place and the resulting bis dithiocarboxylate was then rendered less reactive to further attack by methyl mercaptide. The above also implied that the fully thiomethylated tetrathio terephthalate had suffered demethylation.

SUMMARY

In this publication we have presented the preparation of a number of terephthalate derivatives. Even though none of the yields were optimized (e.g., in the preparation of 5, stepwise lithiation should afford much higher yields), a relatively efficient preparation of a most highly functionalized benzene ring; tetrakis(thiomethyl) dimethyl tetrathioterephthalate (8) was achieved in only two steps. The physical and chemical properties of 8 are currently under investigation; we are intersted in 1) converting it to OTQ by multiple oxidative demethylation, 2) doubly methylating it to convert it to a symmetric dication that may have intersting electrochemical as well as solid state properties.

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