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FACILE SYNTHESIS OF UNSYMMETRICAL BENZOTETRATHIAFULVALENES VIA CLEAVAGE OF THE CORRESPONDING HEXATHIOORTHOOXALATES

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ABSTRACT: Unsymmetrical hexathioorthooxalates of types (1) and (2) undergo elimination of dialkyl disulfide on heating in an organic solvent; the reaction, which is catalyzed by acid, proceeds without fission of the central C–C bond and provides the first general, high yield synthesis of unsymmetrical benzotetrathiafulvalenes of types (3) and (4).

As we have shown in the preceding communication, unsymmetrical hexathioorthooxalates of types (1) and (2) are readily synthesized by reaction of appropriate trithioorthoformate anions with cyclic trithiocarbonates followed by alkylation *in situ*.[1] We now show that such compounds undergo thermal decomposition by cleavage of the non-cyclic C–S bonds to yield the corresponding tetrathiafulvalenes of types (3) and (4), important examples of tetrakis(alkylthio)ethylenes.

Much has been written about the pyrolysis of hexakis(organylthio)ethanes (5). In particular, the reactions are radical in nature and lead primarily to tetrakis(organylthio)ethylenes (6) and disulfides (7) (Eq. 1).[2] The detailed mechanism of the reaction depends on the organic groups, R. For example, hexakis(phenylthio)ethane (5, R=Ph) is converted into the corresponding ethylene (6, R=Ph) by a mechanism involving total cleavage of the C–C bond at some point, as indicated by cross-over experiments.[3] This could involve initial C–C cleavage (step a, Scheme 1) or initial C–S cleavage (step b) followed by further breakdown of the substituted ethyl radical (step b_1), as has been shown in related systems.[2] Hindered hexakis(alkylthio)ethanes such as (5, R=cyclohexyl) behave in a similar manner.[3] However, only partial crossover occurs with (5, R=isopropyl) and no crossover at all occurs with hexakis(methylthio)ethane (5, R=Me), suggesting pathway b. Unfortunately, even in the last case,

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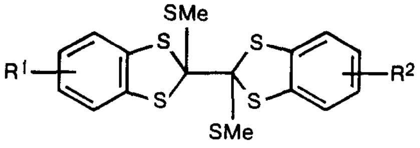
exchange of MeS groups for SCD_3 occurs in a mixed sample because the reaction of methylthiyl radicals with tetrakis(methylthio)ethene (6, R=Me) is reversible. Thus, even when C–C bond cleavage does not occur, exchange of organylthio groups appears likely to prevent the clean formation of unsymmetrical tetrathioethenes from unsymmetrical hexakis(organylthio)ethanes.

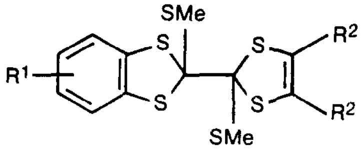
We have investigated the pyrolysis of the compounds of types (1) and (2)[1] because of the importance of the products which might result, *viz.* unsymmetrical tetrathiafulvalenes (3) and (4).[4] The steric hindrance about the central C–C bond in (1) and (2) should be less than in (5, R=Me), while the cyclic nature of four of the C–S bonds should favor their being retained during the reaction. Thus, it was not entirely unreasonable to hope that the products (3) and (4) might predominate.[5] Indeed, pyrolysis of (1, R^1=H, R^2=Me) led to (3, R^1=H, R^2=Me)[6] contaminated by no more than trace amounts of the symmetrical analogues (3, R^1=R^2=H) and (3, R^1=R^2=Me), as evidenced by mass spectrometry. The convenience and success of this method is in sharp contrast to the 15% yield of the same product obtained in the previous synthesis only after extensive and tedious crystallization.[7]

There are several features of interest about the reaction to convert (1) into (3). Firstly, although very pure samples of compounds (1) decompose to (3) only slowly in refluxing CCl_4, the presence of small quantities of impurities (particularly ones which cause a pink coloration – presumably dithiolium salts) causes a vast increase in the rate of decomposition, so that it can be difficult to obtain ^{13}CNMR spectra of impure samples of (1) in CCl_4 at 35°. Secondly, *identical* samples of (1, R^1=R^2=H) decompose at different rates in different solvents in the order 1,2-dichloroethane>CCl_4>toluene. Thirdly, the rate of reaction is greatly increased by addition of a small quantity of toluene-4-sulfonic acid. We interpret these results as suggestive of a polar mechanism (electrophile-induced removal of MeS^- as a first step), which can dominate the usual radical pathway if appropriate catalytic conditions exist. Finally, prolonged heating of pure samples of (1), when decomposition is slow, sometimes results in formation of significant quantities of another compound, isomeric with (1). We shall report on these compounds at a later date.

We have applied the reaction to a range of compounds of types (1) and (2). The results are recorded in the Table, which demonstrates that this approach can be used as a general method for synthesis of unsymmetrical benzotetrathiafulvalenes of types (3) and (4). In only one case have we ever observed more than trace quantities of a symmetrical tetrathiafulvalene from an unsymmetrical precursor, and there may have been special circumstances in this case. Otherwise, the synthesis proceeds in a highly satisfactory manner to produce high yields of benzotetrathiafulvalenes. This is the first general synthesis of unsymmetrical benzotetrathiafulvalenes which proceeds in high overall yield.[8] Metallation of the parent tetrathiafulvalene[9] has not been demonstrated in the benzo series, while the reactions of triphenylphosphoranes with dithiolium salts[10] proceed only in low yield. Thus, the reaction should be highly useful. We are currently investigating its application to the synthesis of functionally substituted benzotetrathiafulvalenes.



(1)



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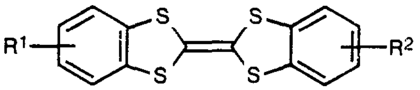
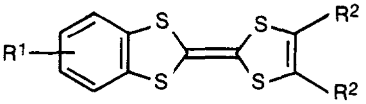
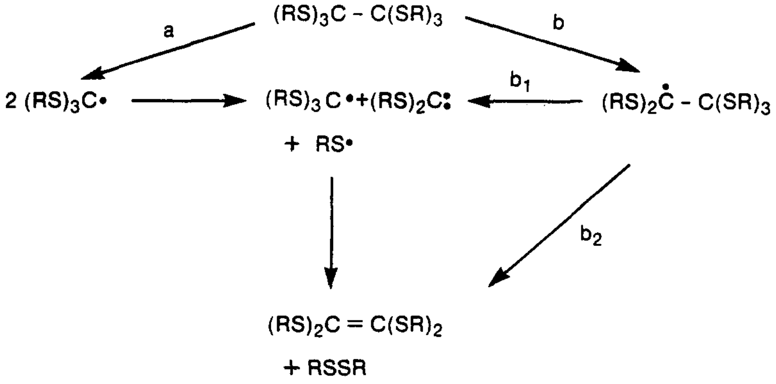


(3)



(4)

$$\underset{(5)}{(RS)_3C-C(SR)_3} \xrightarrow{\Delta} \underset{(6)}{(RS)_2C=C(SR)_2} + \underset{(7)}{RSSR} \qquad [1]$$



Scheme I

ACKNOWLEDGMENT

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TABLE I

Syntheses of Tetrathiafulvalenes (3) and (4)

Starting Material (1) or (2)	R^1	R^2	Product[a] (3) or (4)	Yield[b]
(1)	H	H	(3)	95%
(1)	H	Me	(3)	75%
(1)	Me	Me	(3)[c]	86%
(1)	H	Cl	(3)	98%
(1)	Me	Cl	(3)[c]	82%
(2)	H	Me	(4)	89%
(2)	Me	Me	(4)	81%
(2)	Me	–[d]	(4)	40%
(2)	H	–[d]	(4)	–[e]

[a] All products were characterized by mass spectrometry (including high resolution), ^{1}HNMR, microanalysis, and, where solubility permitted, ^{13}CNMR.

[b] Yield of crystallized material; more product could generally be observed in the mother liquors.

[c] These products are presumably mixtures of two isomeric components, but they could not be separated chromatographically on silica nor seen as separate signals in the NMR spectra (100 MHz for ^{1}H; 25.1 MHz for ^{13}C).

[d] $R_2=(CH_2)_3$.

[e] Not determined.

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6. In order to prove that the products were in fact tetrathiafulvalenes and not isomeric materials, for example containing dithiane (6-membered) rings rather than dithiole rings, the compound (3, $R^1=R^2=H$) obtained from (1, $R^1=R^2=H$) was compared with an authentic sample of dibenzotetrathiafulvalene and shown to be identical in all respects.
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