Wittig Reaction of 1,3-Benzodithiol-2-ylidenetriphenylphosphorane with Carbon Disulfide

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(Received March 10, 1981)

Synopsis. 1,3-Benzodithiol-2-ylidenetriphenylphosphorane reacted with carbon disulfide to give 1,3-benzodithiole-2-thione, dibenzotetrathiafulvalene, and an unidentified crystalline red compound in addition to triphenylphosphine sulfide. The same products were also obtained by treatment of 1,3-benzodithiol-2-ylthiocarbonyl chloride with base.

Recent findings concerning the highly-conductive charge transfer salt of tetrathiafulvalene (TTF) with tetracyanoquinodimethan (TCNQ) have created a wide and extensive interest in the design of organic donors and acceptors.[1] Thus, the syntheses of compounds of types **1**[2] and **2**[3] have appeared recently; in compounds **1**, TTF system is extended by insertion of a quinonoid unit and compound **2** is isoelectronic with TCNQ. In this connection, the synthesis of organic donor like **3** is of current interest. We report here some findings found during the attempted synthesis of **3**.

There are abundant examples of dimerization of thioketenes which yield 1,3-dithietans.[4] Therefore, dimerization of the thioketene **4**, which would be produced by the Wittig reaction of carbon disulfide with 1,3-benzodithiol-2-ylidenetriphenylphosphorane (**5**) (conveniently obtainable by treatment of **6** with butyllithium),[5] was chosen as our synthetic strategy to **3**.

A stirred suspension of **6** in tetrahydrofuran was treated with a slight excess of butyllithium and then carbon disulfide was added at −78 °C. The mixture was gradually warmed to room temperature and then refluxed. Chromatographic purifications gave 1,3-benzodithiole-2-thione (**7**) (9—25%), dibenzotetrathiafulvalene (**8**) (15—20%), and a red crystalline compound **9** (5—9%) in addition to triphenylphosphine sulfide (44—65%). The reaction was repeated several times and gave reproducible results. Although the occurrence of triphenylphosphine sulfide is suggestive of the formation of the expected thioketene **4**, no products, which correspond to the dimer of **4**, were isolated. The red compound **9** has a molecular formula of $C_{15}H_8S_5$ on the basis of mass spectrum and elemental analysis (a tentative structure is given in the Experimental section).

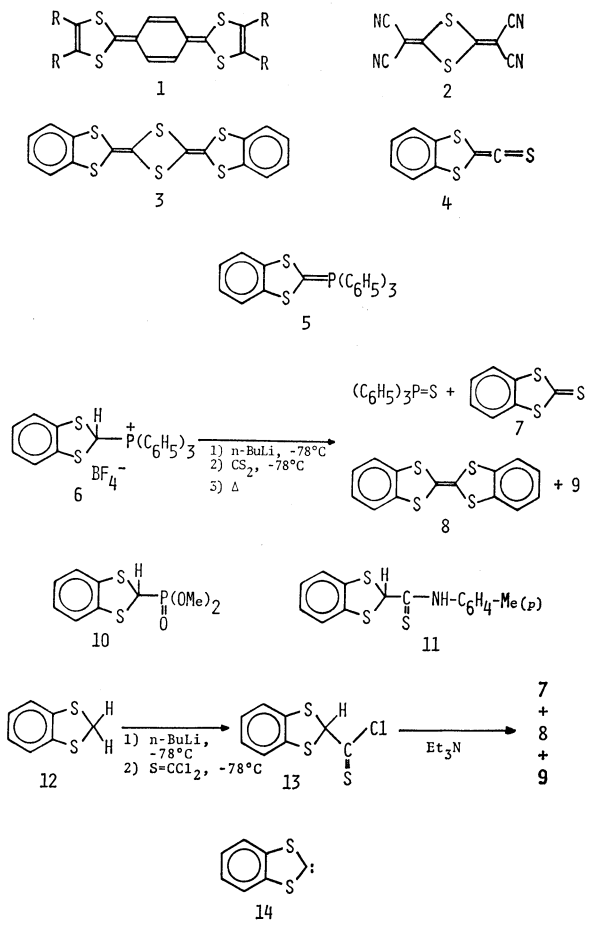
The use of compound **10**[5] instead of **6** gave an intractable mixture.

As to the mechanism of the formation of **7** and **8**, initial formation of **7** from **5** and carbon disulfide followed by reaction of **7** and **5** which yields **8**, was ruled out since control experiment showed that compound **7** is unreactive toward **5**.

Attempted trapping of **4** with amine was fruitless. The Wittig reagent **5**, prepared as above, was allowed to react with carbon disulfide and then a solution of *p*-toluidine in tetrahydrofuran was added at −78 °C. Workup of the mixture by column chromatography did not give the expected adduct **11**, but afforded compounds **7**, **8**, and **9** in decreased yields. The result indicates that either the final products, **7**, **8**, and **9**, are produced by a mechanism which does not involve **4** as the intermediate or **4** fails to react with *p*-toluidine and is readily converted to the final products under the conditions.

Generation of **4** by other method was next tried. 1,3-Benzodithiole (**12**) was lithiated by butyllithium[6] and allowed to react with thiophosgene at −78 °C, and then the resulting **13** was dehydrochlorinated by triethylamine. Purification of the mixture by column chromatography yielded **7** (2%), **8** (28%), and **9** (2%). The use of DBU as the base gave a similar result. The formation of the same products, **7**, **8**, and **9**, by two different reactions is strongly suggestive of the presence of the common intermediate **4**.

One of possibilities as to the mechanism of the formation of the final products is the decomposition of **4** to the carbene **14** and carbon monosulfide since **14**, generated by addition of carbon disulfide to benzyne, is known to give **8** by dimerization and **7** by an uncertain mechanism.[7]



Experimental

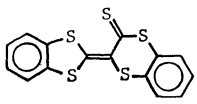
Reaction of 1,3-Benzodithiol-2-ylidenetriphenylphosphorane (5) with Carbon Disulfide. To a stirred suspension of 4.02 g (8 mmol) of **6**[5] in 200 ml of anhydrous tetrahydrofuran (THF) was added a 15% solution of butyllithium in hexane (6.0 ml, 9.2 mmol) under nitrogen at −78 °C. After stirring of 1.5 h, 0.76 g (10 mmol) of carbon disulfide in 7 ml of THF was added at −78 °C. The mixture was stirred for 0.5 h at −78 °C, gradually warmed to room temperature, and then refluxed for 2 h. The solvent was removed under reduced pressure and the residue was extracted with 200 ml of dichloromethane, washed with water, dried on sodium sulfate, and evaporated. The resulting reddish brown mass was chromatographed on a silica-gel column (Merck, Art 7734, 100 g). Elution with carbon tetrachloride gave 0.26 g (21.5%) of dibenzotetrathiafulvalene (**8**), mp 244—246 °C (lit,[8] mp 235—236 °C), 0.36 g (24.5%) of 1,3-benzodithiole-2-thione (**7**), mp 165—166 °C (lit,[9] mp 164 °C), and 82 mg (6%) of a dark red compound (**9**), mp 220—221 °C (from benzene). Elution of the column with benzene gave 1.03 g (44%) of triphenylphosphine sulfide, mp 158—159 °C.

The reaction was repeated several times and the yields of **7**, **8**, and **9** varied in the range of 15—25%, 9—25%, and 5—9%, respectively.

The red compound **9** has the following properties: ^{1}H NMR (CS_2) δ 5.94—6.35 (complex m); UV ($CHCl_3$) λ_{max} (log ε) 242 (4.4), 261sh (4.3), 287sh (4.0), 383 (3.7), and 480 nm (4.3); IR (KBr) 1450, 1380, 1270, 990, 960, and 740 cm^{-1}; MS *m/e* 348 ($C_{15}H_8S_5$, M^+, 100%), 304 (M^+—CS), 283, 208, 196, 164, 152, 120, 108, 96, and 69. Found: C, 51.68; H, 2.31; S, 45.79%. Calcd for $C_{15}H_8S_5$: C, 51.74; H, 2,32; S, 45.95%.

When compound **9** was heated at 200—220 °C for 2 h without solvent, it was converted into a mixture of compounds **7** and **8**. Attempted reduction with sodium borohydride resulted in the decolorization of **9**.

On the basis of these results, the following tentative structure was given for **9**.



Attempted Reaction of 5 with 7. To a stirred solution of **5**, prepared from 1.51 g (3 mmol) of **6** as described above, was added a solution of 0.55 g (3 mmol) of **7** in 25 ml of THF at −78 °C. The mixture was stirred for 0.5 h at −78 °C, gradually warmed to room temperature, and then refluxed for 3 h. Chromatographic purification gave 23 mg (5%) of **8** and a nearly quantitative yield of **7**.

When a solution of **5**, prepared at −78 °C in THF, was gradually warmed and then refluxed without any additive, a 10% yield of **8** was obtained.

It is therefore concluded that **8**, formed by attempted reaction of **5** with **7**, is produced by decomposition of **5**, but not by reaction of **5** with **7**, and thus the phosphorane **5** is unreactive toward **7**.

Attempted Trapping of 4 by p-Toluidine. The phosphorane **5**, prepared from 1.51 g (3 mmol) of **6** in THF, was allowed to react with carbon disulfide (0.28 g, 3.75 mmol) at −78 °C. After stirring of 2 h, a solution of *p*-toluidine (0.32 g, 3 mmol) in THF (5 ml) was added at −78 °C under nitrogen. The mixture was stirred for 2 h at −78 °C and then gradually warmed to room temperature. Chromatographic purification gave 43 mg (2.8%) of **8**, 23 mg (1.3%) of **7**, 82 mg (4.7%) of **9**, and 0.57 g (64%) of triphenylphosphine sulfide. *p*-Toluidine was recovered nearly quantitatively.

Attempted Generation of 4 from 1,3-Benzodithiole (12). Compound **12** was conveniently prepared by reduction of 1,3-benzodithiolylium tetrafluoroborate[10] with sodium borohydride in THF. A 15% solution of butyllithium in hexane (7.8 ml, 12 mmol) was added through a syringe to a stirred solution of **12** (1.54 g, 10 mmol) in THF (120 ml) under nitrogen at −78 °C.[6] Stirring was continued for 2 h and then a solution of thiophosgene (1.15 g, 10 mmol) in THF (1 ml) was added all at once. The mixture was stirred for 1 h at −78 °C and then 2 ml of triethylamine was added. After 0.5 h of stirring, the mixture was warmed to room temperature and then evaporated. The resulting dark red residue was extracted with dichloromethane (200 ml), washed with water, dried, and evaporated. Chromatographic purification of the residue gave 0.42 g (28%) of **8**, 40 mg (2%) of **7**, and 30 mg (2%) of **9**.

The use of DBU as the base instead of triethylamine yielded **7** (3%), **8** (0.3%), and **9** (4%).

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