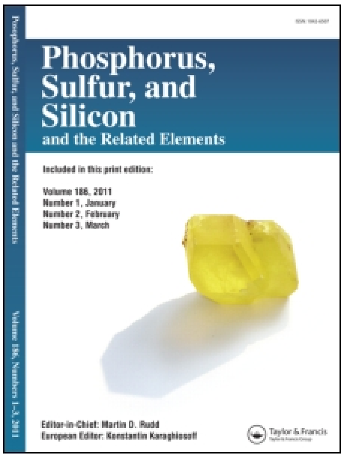

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Valters, Raimonds , Karlivans, Gatis , Bace, Ausma and Gulbis, Juris(1997) 'Synthesis of [b]-Fused Benzo[d]furano Heterocycles', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 411 — 412

To link to this Article: DOI: 10.1080/10426509708545573
URL: http://dx.doi.org/10.1080/10426509708545573

Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 411–412
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Synthesis of [b]-Fused Benzo[d]furano Heterocycles

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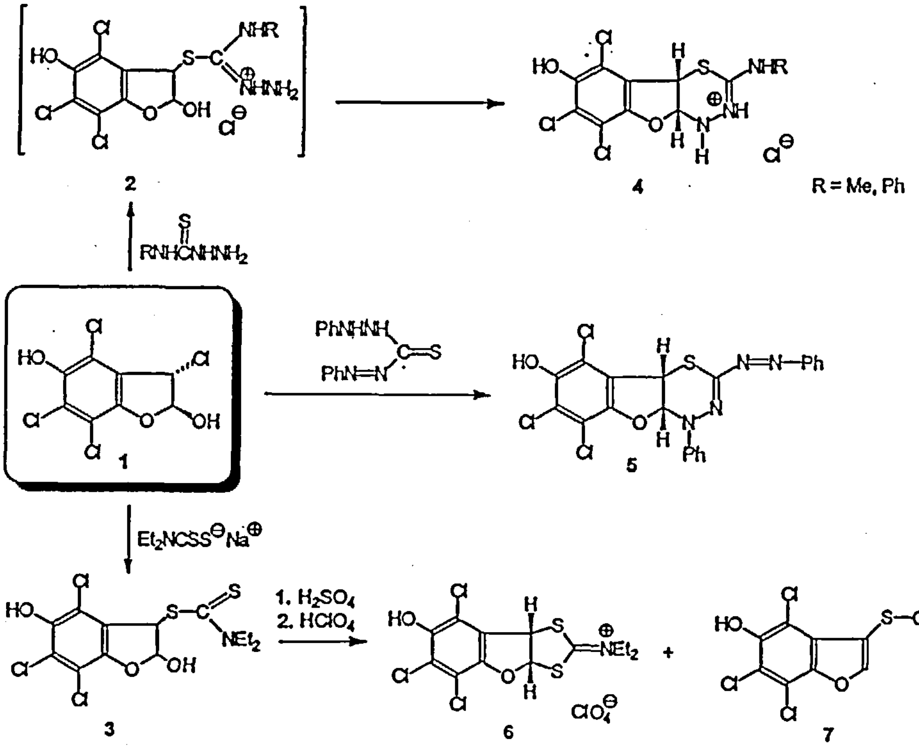
In the reactions of 3,4,6,7-tetrachloro-2,5-dihydroxy-2,3-dihydrobenzo[b]furan with 4-methyl and 4-phenyl thiosemicarbazides, dithizone and sodium N,N-diethyldithiocarbamate the [b]fused benzo[d]furano heterocycles have been synthesized.

KEY WORDS 1,3,4-thiadiazines ,1,3 dithiole, and thiazole, fused with benzofuran ring.

Recently, we have presented a general method[1] for the synthesis of trichloro-1,4-benzoquinonylsubstituted sulfur containing heterocycles in the reactions of furan **1** with thioureas (selenoureas), thiosemicarbazides and other sulfur containing bifunctional compounds. The presence of electron donor heterocycle and the C--C linked quinonoid acceptor in the molecule of these compounds creates an intense intramolecular charge transfer. The initial furan **1** is easy obtainable in two step synthesis[2,3] from tetrachlorobenzoquinone.

In continuation we have found that furan **1** in reactions with 4-methyl and 4-phenyl thiosemicarbazides produced hydrochlorides of 6,7,9-trichloro-8-hydroxy-2-methyl(or phenyl)amino-4a,9b-dihydro-*4H*-1,3,4-thiadiazino[5,6-b]benzo[d]furanes **4** (R = Me or Ph). We suppose that the fused heterocycles **4** are formed after the cyclization of the intermediate **2** which is the product of nucleophilic substitution of chlorine atom in the molecule of furan **1** and could not be isolated. Similarly the reaction with dithizone led to the compound **5**. In the reaction of furan **1** with sodium N,N-diethyldithiocarbamate the furan **3** have been isolated. Its cyclization in conc. sulfuric acid led to the mixture of the salt of 5,6,8-trichloro-2-(N,N-diethylimmonio)-7-hydroxy--3a,8b-dihydro-1,3-dithiolo[4,5-b]benzo[d]-furan (isolated as perchlorate **6**) and 4,6,7-trichloro-3-(N,N-diethyldithiocarbamoyl)-5-hydroxybenzo[b]furan **7**.

Previously we have shown[4] that 5-(3,4,6-trichloro-2,5-dihydroxyphenyl)-3-methylthiazoline-2-thione in the presence of hydrochloric acid isomerized into 5,6,8-trichloro-7-hydroxy-3-methyl-2,3,3a,8b-tetrahydrothiazolo[4,5-b]benzo[d]furan-2-thione **8** as a result of the intramolecular addition of the phenolic hydroxyl to the C=C bond of the thiazoline ring. The spin coupling constants (^3J = 5 - 7.5 Hz) between the 4a,9b protons in the compounds **4, 5** and 3a,8b protons in **6, 8** prove cis-fusion of the rings.



The oxidative cleavage of the dihydrofuran ring (**4, 5, 6, 8**) using chemical[5] and electrochemical[6] methods have been investigated but we did not succeed in obtaining the corresponding trichlorobenzoquinonylsubstituted heterocycles.

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