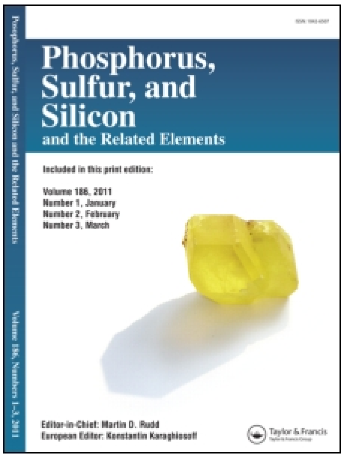

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A GENERAL METHOD FOR THE SYNTHESIS OF TRICHLORO-1,4-BENZOQUINONYLSUBSTITUTED SULFUR CONTAINING HETEROCYCLES

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Abstract On the basis of easily obtainable 3,4,6,7-tetrachloro-2,5-dihydroxy-2,3-dihydrobenzo[b]furan as an universal synthone a general method for the synthesis of a large variety of trichlorobenzoquinonylsubstituted sulfur or selenium containong heterocycles has been elaborated. An intense intramolecular charge transfer between the electrondonating heterocycle and electronaccepting quinone moiety in the molecules of the synthesized compounds has been detected.

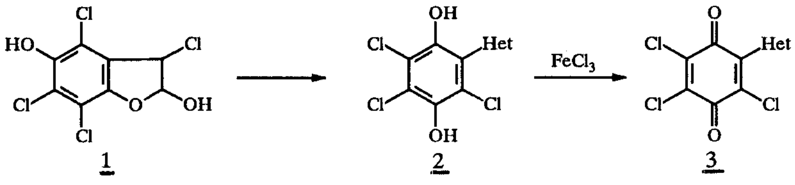
INTRODUCTION

Extensive treatments of chemical and physical properties of quinonoid compounds are available[1,2]. Recently some of quinone derivatives are intensively studied because many of them have found an application as electronaccepting components in the synthesis of ion-radical salts and charge transfer complexes, which can be used as materials in molecular electronics. There are many wellknown methods[3] for the synthesis of benzoquinones fused with a heterocycle but there is no a general method in the literature allowing to obtain 1,4-benzoquinones C-C linked to the heterocycle moiety.

The aim of the present work is to synthesize chloro-substituted 1,4-benzoquinones C-C linked to the sulfur or selenium containing heterocycle. The presence of electrondonor (S-heterocycle) and quinonoid acceptor in the molecule of these compounds creates an intense intramolecular charge transfer.

RESULTS AND DISCUSSION

We have elaborated a general method for the synthesis of such compounds on the basis of 3,4,6,7-tetrachloro-2,5-dihydroxy-2,3-dihydrobenzo[b]furan (1) (cis/trans ratio 17:83 in DMSO-d_6, ^{1}H-NMR), which can be obtained[4,5] in two step synthesis starting from tetrachloro-1,4-benzoquinone. Furan (1) represents the cyclic hemiacetal of (3,4,6-trichloro-2,5-dihydroxyphenyl)-α-chloroacetaldehyde. In reactions with thiourea and its variously substituted derivatives[6] as well as with selenoureas[7] furan (1) produced corresponding (3,4,6-trichloro-2,5-dihydroxyphenyl)substituted heterocycles (2a-c) with excellent yields (80-95%). The title compounds (3a-c) were obtained by oxidation of (2a-c) with ferric chloride in aqueous DMF. Apparently, the reaction 1 $\rightarrow$ 2 proceeds via substitution of the chlorine atom with sulfur (or selenium) in the first stage and further opening of the hemiacetal ring with subsequent closure of the corresponding heterocycle. When this reaction was carried out with N,N,N'-trisubstituted thioureas[8,9] the intermediate (4) was isolated and its recyclization proceeded in conc. sulfuric acid leading to the thiazolium salts (2d). Treatment of the salts (2d, R = Me, Ph) with hydrogen sulfide led to the corresponding thiazoline-2-thiones (2e), which were obtained also in the reaction between furan (1) and triethylammonium N-methyl of N-phenyldithiocarbamates[9]. The reaction of furan (1) with sodium N.N-diethyldithiocarbamate led to the substitution product (5), however, after its cyclization in conc. sulfuric acid the mixture of compounds (6) and (7) were obtained. Therefore the compound (2f) could not be synthesized in such a way. The structure of products obtained in the reactions of furan (1) with thiosemicarbazides depends on the substitution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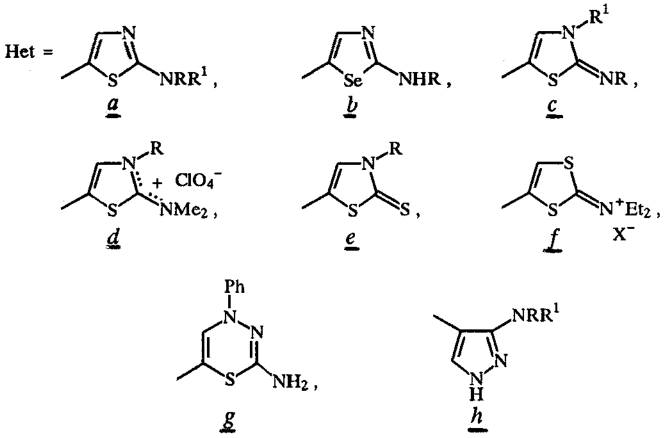
Het =
N
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NRR1 ,
a
N
Se
NHR ,
b
R1
N
S
NR ,
c
R
N
+ ClO4-
S
NMe2 ,
d
R
N
S
S ,
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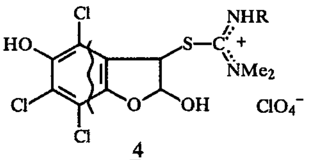

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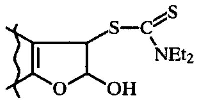

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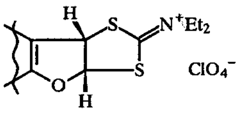

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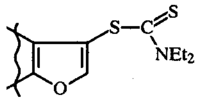

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pattern in thiosemicarbazide moiety: unsubstituted thiosemicarbazide produced the mixture of compounds (2a, R = H, R^1 = NH_2) and (2c, R = H, R^1 = NH_2), 4-phenylthiosemicarbazide in acetone solution gave the compound (2c, R = N=CMe_2, R^1 = Ph), the reaction with 1-phenylthiosemicarbazide, carried out in ethanol solution, led[10] to 4H-1,3,4-thiadiazine derivative (2g), but with 4,4-dialkylthiosemicarbazides the reactions proceeded with extrusion of sulfur and the formation[11] of pyrazole derivatives (2h). The quinones (3a-e,g,h) are deeply colored: from red to blue or violet. The longwave band in their electronic spectra can be associated with charge transfer from the electrondonating to the electronaccepting part of the molecule. That was confirmed by molecular orbital calculations in PPP approach. On the table below one can see that increasing electrondonating ability of the heterocyclic substituent at benzoquinone moiety gives rise to the longwave shift of this band.

TABLE

Longwave Band in Electronic Spectra of Trichlorobenzoquinonylsubstituted Heterocycles (3) in Ethanol

Het	R	R^1	λ_{max}, nm (log ε)
a	H	H	597 (3.67)
a	H	Me	620 (3.73)
a	H	MeCO	513 (3.53)
b	H	-	650 (3.60)
b	Ph	-	668 (3.94)
c	Ph	Ph	660 (3.48)
c	Me_2C=N	Ph	702 (3.48)
d	Me	-	537 (3.56)+
e	Me	-	578 (3.50)
g	-	-	482 (3.93)
h	Et	Et	593 (2.80)

+ In MeCN solution

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