PUMMERER REACTION IN SYNTHESIS AND TRANSFORMATIONS OF HETEROCYCLIC COMPOUNDS (REVIEW)

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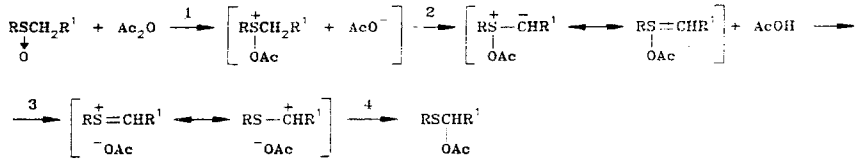
Data on the use of the Pummerer reaction in the synthesis and transformations of various heterocyclic compounds that contain oxygen, sulfur, and nitrogen as the heteroatoms are correlated.

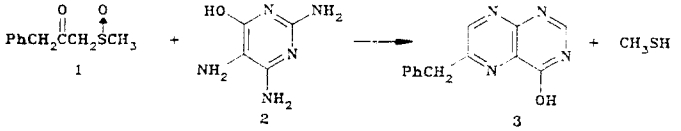
The Pummerer reaction, which is the reaction of sulfoxides with acid anhydrides, was discovered in 1909 [1]. The reaction includes four elementary steps



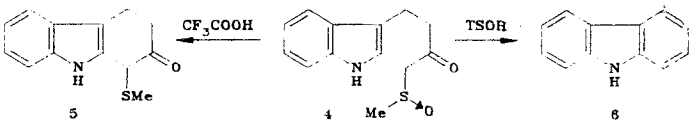
and is one of the promising pathways of the transformation of sulfoxides to other organosulfur compounds that contain diverse functional groups [2]. Recent research has shown that this reaction can be used successfully in the synthesis of various heterocyclic compounds that contain oxygen, sulfur, and nitrogen as the heteroatoms. In the present review we will attempt to correlate the available literature data on the use of the Pummerer reaction in the synthesis and transformations of heterocyclic compounds.

1. Utilization of the Pummerer Reaction in the Synthesis of Heterocyclic Compounds

1.1. Reactions of β-Keto Sulfoxides. An interesting method for the synthesis of substituted pteridines was described in [3]. Thus sulfoxide 1 reacts with 2,4,5-triamino-6-hydroxypyrimidine (2) in glacial acetic acid in the presence of sodium acetate to give 4-hydroxy-6-benzylpteridine (3):



β-Keto sulfoxides of the indole series such as 4 undergo cyclization under the influence of trichloroacetic acid, trifluoroacetic acid, and p-toluenesulfonic acid; depending on the reaction conditions, compounds of the tetrahydrocarbazole (5) and carbazole (6) series are formed [4, 5].



M. V. Lomonosov Moscow State University, Moscow 119899. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1299-1313, October, 1989. Original article submitted November 28, 1988.

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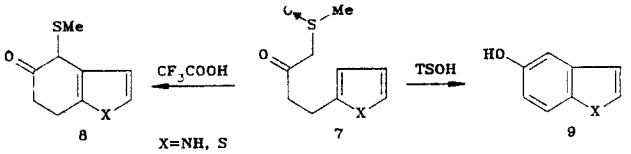
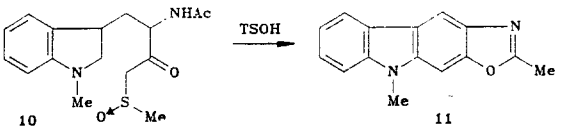
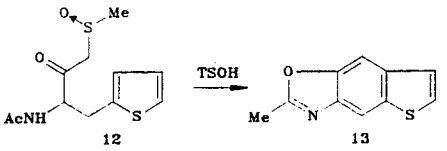
Similar transformations have also been accomplished for β-keto sulfoxides that contain pyrrole or thiophene fragments in their molecules [4]:



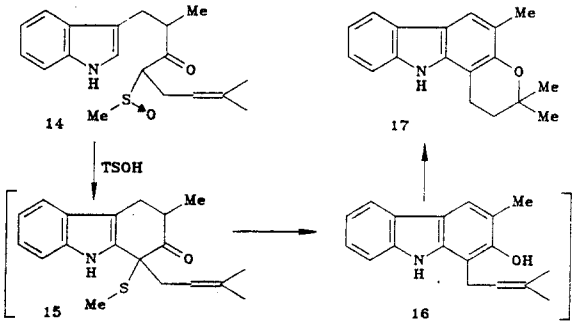
Sulfoxide 10 forms a polynuclear heterocyclic compound (11) of the oxazolocarbazole series in high yield (80%) under the influence of p-toluenesulfonic acid [5]:



Oxazolobenzothiophene 13 was similarly obtained from thiophene derivative 12 but in lower yield:

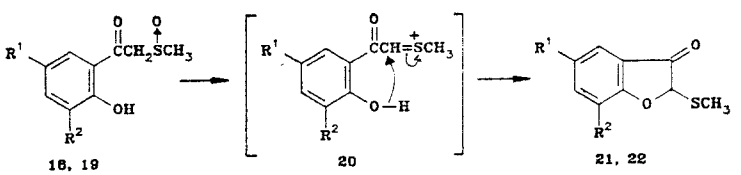


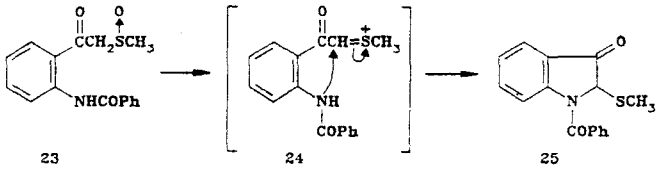
According to the data in [6], sulfoxide 14 can be used to obtain compounds of the pyranocarbazole series (17):



Despite the low yield (23%) of 17, the reaction is of considerable synthetic interest, since a tetranuclear condensed heteroring is formed in one step.

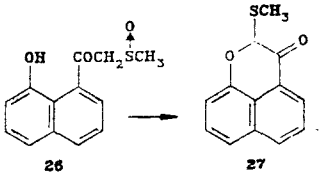
The Pummerer reaction of β-keto sulfoxides of the aromatic series that contain, in the ortho position relative to the sulfinyl fragment, substituents that are capable of intramolecular nucleophilic attack of the intermediates (20, 24) of the Pummerer reaction opens up extensive possibilities in the synthesis of heterocyclic compounds [7]. Thus the corresponding furanones 21 and 22 and 3-indolone 25 were obtained by heating sulfoxides 18, 19, and 23 in benzene in the presence of trifluoroacetic acid.



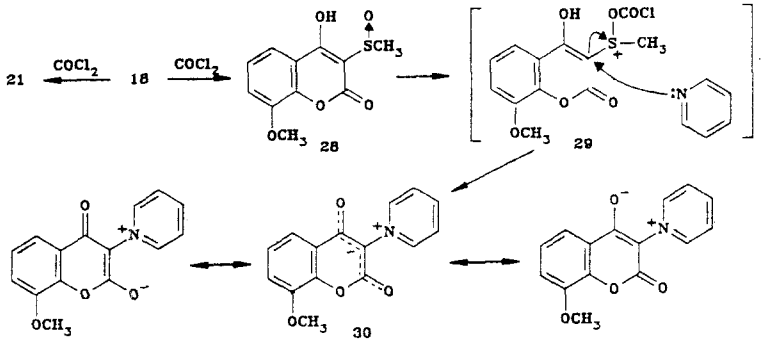


18, 21 R^1, R^2=H, MeO; 19, 22 R^1, R^2=Cl, H

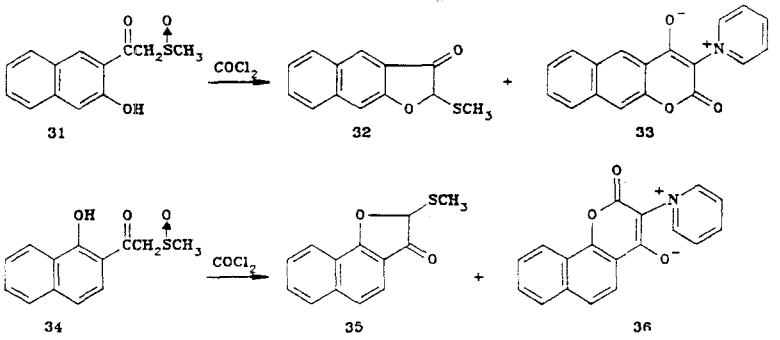
Compound 27 was obtained in 64% yield under similar conditions [7]:



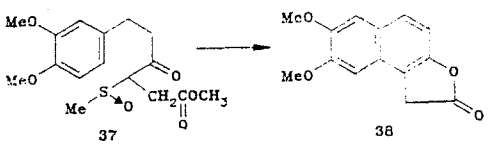
If phosgene is used in place of trifluoroacetic acid and pyridine is used as the solvent, stable inner salt 30 is formed instead of furanone 21 as a result of the reaction of β-keto sulfoxide 18 [8]. In the opinion of Connor and Sorenson [8], its formation is associated with the primary cyclization of sulfoxide 18 to 4-hydroxy-3-(methylsulfinyl)coumarin (28) and nucleophilic attack on intermediate 29 by pyridine:



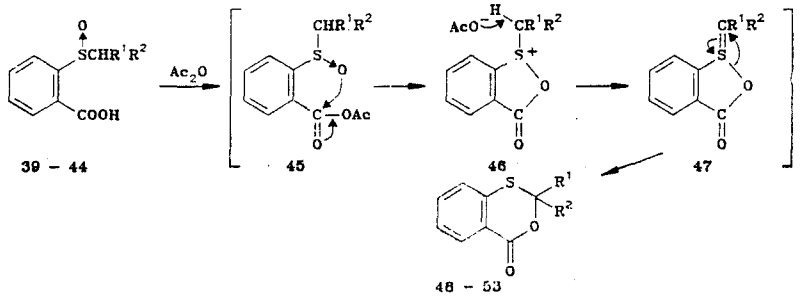
Similar results were obtained for sulfoxides 31 and 34:



If there is a substituent in the α position relative to the sulfur atom in the β-keto sulfoxide molecule, cyclization in the presence of p-toluenesulfonic acid leads to the formation of 2,3,5,6-substituted naphthalenes [9]. Thus heating sulfoxide 37 in benzene leads to the formation of the corresponding lactone 38 in 60% yield:



1.2. Reactions of o-Carboxyphenyl Sulfoxides. It is apparent from the data presented above that the cyclization of β-keto sulfoxides under the conditions of the Pummerer reaction, as a rule, does not lead to the formation of heterocycles that contain a sulfur atom. The synthesis of many sulfur-containing heterocyclic compounds was accomplished by Numata and Oae [10] by intramolecular cyclization of o-carboxyphenyl sulfoxides 39-44:

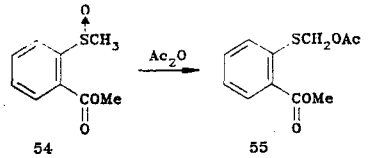


39 - 44 → 45 → 46 → 47 → 48 - 53

39, 48 R^1, R^2=H; **40, 49** R^1, R^2=H, Me; **41, 50** R^1, R^2=H, Et; **42, 51** R^1, R^2=H, Ph; **43, 52** R^1, R^2=H, *p*-ClC_6H_4; **44, 53** R^1, R^2=Me

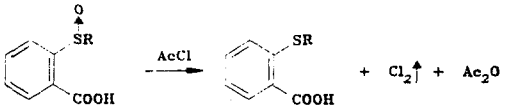
In the opinion of Numata and Oae [10], the assumption of the intermediate formation of five-membered, cyclic, acyloxy sulfonium salt 46, which, after splitting out of a proton and 1,2 migration of the hydroxy oxygen atom of the carboxy group from the sulfur atom to the carbon atom, is converted to the cyclic compound, is the most likely one to explain the 39–44 → 48–53 transformation.

The cyclization described above occurs only when the sulfoxide contains a free carboxy group in the ortho position relative to the sulfinyl fragment [11]. Thus heating sulfoxide 54 in excess acetic anhydride leads to the formation of the normal product (55) of the Pummerer reaction:



54 → 55

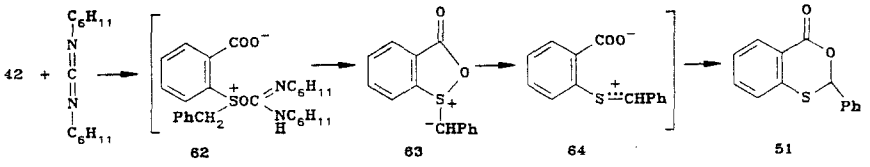
Cyclization products also are not formed when acetic anhydride is replaced by another acylating agent, viz., acetyl chloride; the corresponding o-carboxyphenyl sulfides 59-61 are isolated in good yields when this is done [12].



56 - 58 → 59 - 61

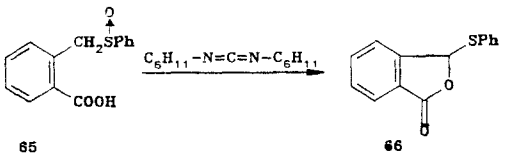
56, 59 R=Me; **57, 60** R=Et; **58, 61** R=CH_2Ph

In [13, 14] it was shown that N,N-dicyclohexylcarboxydiimide or p-toluenesulfonic acid can be used successfully as the reagent in the Pummerer reaction that causes cyclization of o-carboxyphenyl sulfoxides; depending on the solvent used, the yields of the final reaction products range from 19% to 98%.



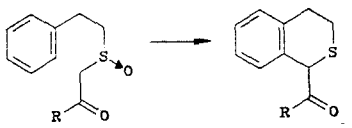
42 → 62 → 63 → 64 → 51

This reaction [13] has also been used for the synthesis of 3-phenylthiophthalide (66) from sulfoxide 65:



65 66

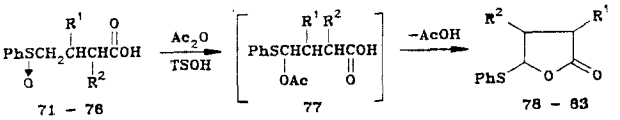
According to the data in [15], acylmethyl phenyl sulfoxides 67 and 68 also readily undergo intramolecular cyclization under the influence of p-toluenesulfonic acid to give the corresponding thiochromans 69 and 70 in high yields (80-90%).



67, 68 69, 70

67, 69 R=EtO; 68, 70 R=Ph

2,3-Disubstituted 4-phenylbutyric acids 71-76 form 1-(3-phenylthio-4,5-disubstituted)-furanones 78-83 when they are refluxed with acetic anhydride in toluene in the presence of p-toluenesulfonic acid [16].

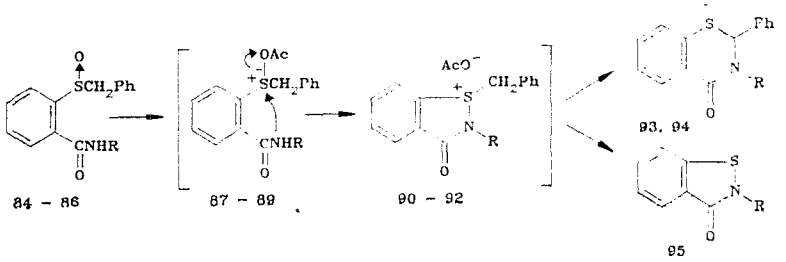


71 - 76 77 78 - 83

71, 78 R^1, R^2=H; 72, 79 R^1, R^2=H, Ph; 73, 80 R^1, R^2=H, Me; 74, 81 R^1, R^2=H, Et; 75, 82 R^1, R^2=Me, H; 76, 83 R^1=R^2=$CH_2CH{=}CH_2$

The reaction does not take place in the absence of p-toluenesulfonic acid. Benzene or xylene can be used as the solvent in place of toluene; this does not have a substantial effect on the yields of cyclic compounds.

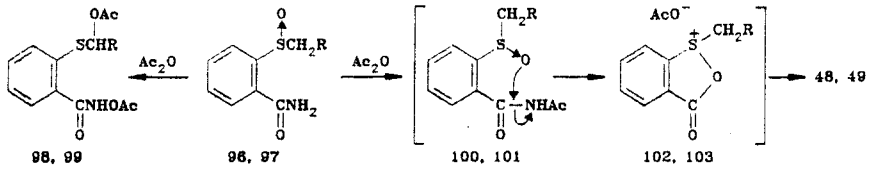
1.3. Synthesis of Oxathiaza- and Thiazaheterocyclic Compounds. o-Aminocarbonylphenyl sulfoxides 84-86 also undergo intramolecular cyclization under the influence of acetic anhydride; depending on the structure of the sulfoxides, six-membered (87, 88) or five-membered (89) heterocycles are formed [11]:



84 - 86 87 - 89 90 - 92 93, 94 95

84, 87, 90, 93 R=Ph; 85, 88, 91, 94 R=Me; 86, 89, 92, 95 R=H

Nitrogen-containing heterocycles are not formed in the case of sulfoxides with an unsubstituted amido group (96, 97) under similar conditions, but rearrangement to acetoxymethyl o-acetylaminocarbonylphenyl sulfides (98, 99) and benz-2,4-oxathian-1-ones (48, 49) occurs. The yields of 98 and 99 are 90%, while the yields of 48 and 49 do not exceed 5%, which constitutes evidence for the occurrence of the reaction for sulfoxides 96 and 97 under severe conditions (140°C, 2 h) primarily via an intermolecular scheme. Oae and Numata [11] link the intramolecular pathway of the formation of 48 and 49 with the intermediate formation of a cyclic acyloxy sulfonium salt:

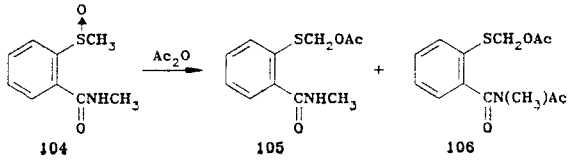


98, 99 96, 97 100, 101 102, 103

48, 90, 92, 100, 102 R=H; 49, 91, 93, 101, 103 R=Me

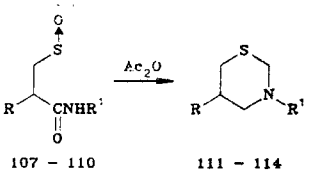
Whereas acylation of the carbonyl or aminocarbonyl grouping with the formation of intermediates of the 45 and 100 and 101 type occurs in the first step for 39-44 and 96 and 97, in the case of 84-86 the oxygen atom of the sulfinyl group primarily undergoes acylation, and amino sulfonium salts 90-92 are formed. Subsequently, in the case of nucleophilic attack by the acetate anion on the benzyl carbon atom one observes the formation of five-membered heteroring 95 and benzyl acetate, while deprotonation with a subsequent 1, 2 shift leads to six-membered heterocyclic derivatives 93 and 94.

If there is no benzyl substituent in the o-aminocarbonylphenyl sulfoxide molecule with a substituted amido group (sulfoxide 104), the reaction with acetic anhydride proceeds with the formation of only acetoxy-substituted compounds 105 and 106:



104 105 106

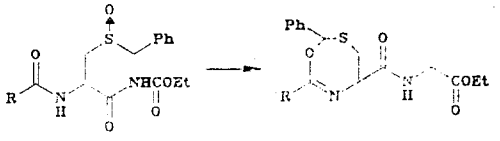
The Pummerer reaction can also be used to obtain heterocyclic compounds that are not condensed with an aromatic ring [17]. Thus sulfoxides 107-110 undergo cyclization on heating in acetic anhydride to give thiazine derivatives 111-114:



107 - 110 111 - 114

107, 111 R, R'=H; 108, 112 R, R'=H, CH_3; 109, 113 R, R'=H, $CH(CH_3)_2$; 110, 114 R, R'=H, CH_2OEt

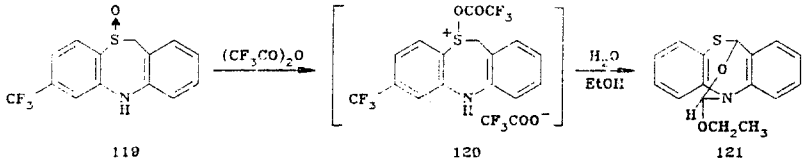
In contrast to 107-110, sulfoxides 115 and 116 undergo cyclization to give seven-membered heterocycles of the oxathiazepine series 117 and 118.



115, 116 117, 118

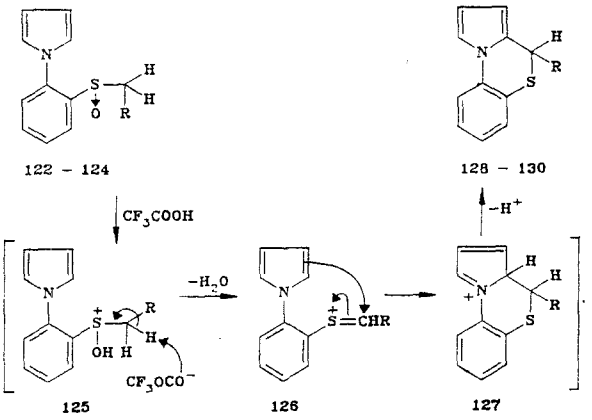
115, 117 R=H; 116, 118 R=CH_3

Yale [18] has used the Pummerer reaction to obtain bridged tetracyclic compound 121; the reaction proceeds only in the presence of trifluoroacetic anhydride.



119 120 121

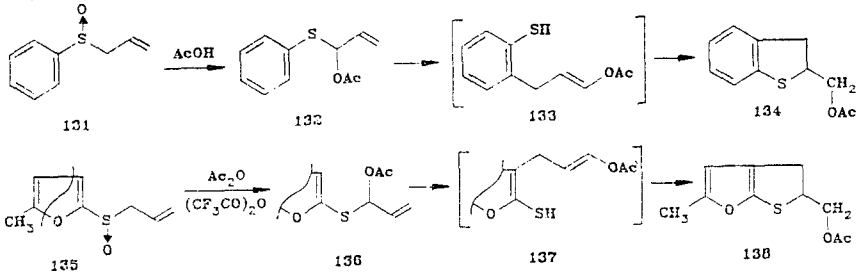
According to the data presented in [19], trifluoroacetic acid can give rise to intramolecular cyclization of 122-124. 4-Substituted pyrrolo[2,1-c]-1,4-benzothiazines 128-130 are obtained as a result of the reaction:



Bates and coworkers [19] note that the reaction cannot be realized if electron-donor groups (CH_3, C_6H_5), which decrease the CH acidity of the α position of the starting sulfoxide, act as substituent R in sulfoxides 122-124.

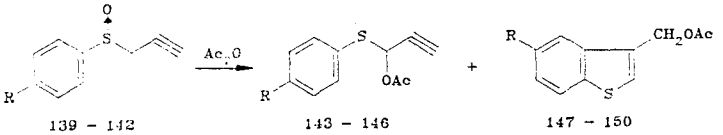
1.4. Alkenyl Aryl Sulfoxides in the Synthesis of Heterocyclic Compounds. There are a relatively small number of studies in which the production of compounds that contain thiophene fragments from allyl aryl (hetaryl) sulfoxides by the action of electrophilic agents that are usually employed in the Pummerer reaction is described.

The rearrangement of allyl phenyl sulfoxide (131) at 130°C in the presence of glacial acetic acid leads to 1-acetoxyallyl phenyl sulfide (132) and 2-acetoxymethyl-2,3-dihydrobenzothiophene (134) [20], while the reaction of sulfoxide 135 in a mixture of acetic and trifluoroacetic anhydrides gives sulfide 136 and a condensed heterocycle – 2-acetoxymethyl-5-methyl-2,3-dihydrothieno[2,3-b]furan (138) [21].



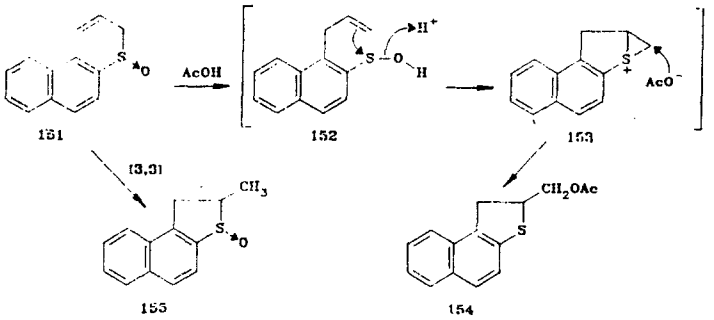
The formation of 134 and 138 indicates the stepwise character of the transformation of sulfoxides 131 and 135, in the first step of which the Pummerer reaction occurs; this is followed by conversion of sulfides 132 and 136 via the scheme of a concerted [3, 3]-sigmatropic shift to intermediate thiols 133 and 137 and their cyclization with the formation of heterocycles 134 and 138, respectively.

The corresponding 1-acetoxypropyn-2-yl phenyl sulfides 143-146 and 5-R-3-acetoxymethylbenzo[b]thiophenes 147-150 are formed by the action of excess acetic anhydride on sulfoxides 139-142 [22]:



139, 143, 147 R=CH_3; **140, 144, 148** R=H; **141, 145, 149** R=Cl; **142, 146, 150** R=NO_3

The authors note that the introduction of an electron-donor substituent into the aromatic ring significantly increases the yields of 143-146, while the introduction of an electron-acceptor substituent promotes the primary formation of benzothiophenes 147-150.



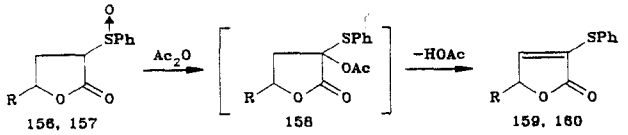
According to the data in [23], 2-acetoxymethyl-1,2-dihydronaphtho[2,1-b]thiophene (154) is formed when sulfoxide 151 is heated in DMF in the presence of acetic acid. Cyclic sulfoxide 155 is formed in the absence of acid.

The authors link the formation of dihydronaphthothiophene 154 with the transformation of episulfonium acetate 153, which is formed as a result of [3,3]-sigmatropic rearrangement of sulfoxide 151 by the action of acetic acid on it.

2. Pummerer Reaction in the Transformations of Heterocyclic Compounds

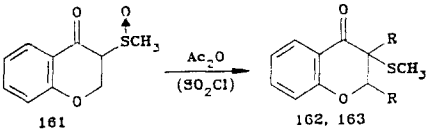
The use of the Pummerer reaction in the chemistry of heterocyclic compounds is not restricted only to the creation of heterocyclic structures; a significant number of studies have been devoted to its use for the modification of systems that are already available.

According to the data in [24], the Pummerer reaction of 1-phenylsulfinyllactones 156 and 157 with the subsequent elimination of acetic acid from the intermediately formed 158 leads to the formation of 1-phenylthiobutenolides 159 and 160 in high yields (80-90%).



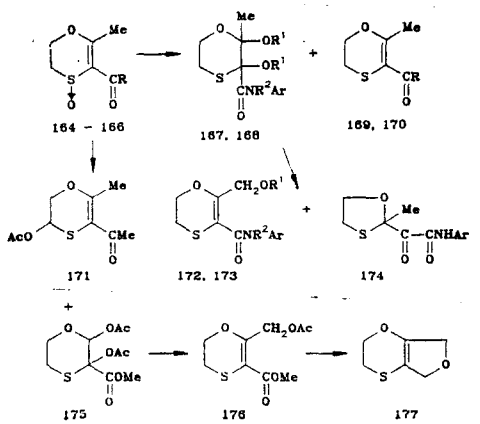
156, 159 R=H; 157, 160 R=CH_3

The behavior of sulfoxides $RS(O)CH_3$, which contain complex heterocyclic fragments as substituent R, was studied in [25], in which 3-methylsulfinyl-substituted quinolines, chromones, and chromones were subjected to the action of acetic anhydride and sulfuryl chloride. The



162 R=OAc; 163 R=Cl

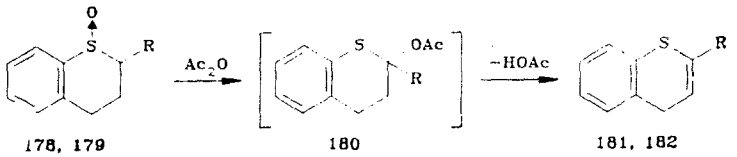
formation of an unsaturated heterocyclic system from a saturated system was observed in all cases. The authors note the anomalous behavior of sulfoxide 161, which forms diacetate 162 or dichloride 163, depending on the reagent used.



164, 169 R=NHAr; **165, 170** R=NMeAr; **167** R^1, R^2=CF_3CO, H; **168, 173** R^1, R^2=Ac, H; **172** R^1=R^2=CF_3CO

The formation of diacetates and bis(trifluoroacetates) in the Pummerer reaction is also indicated in studies by King [26, 27], which were devoted to the transformations of substituted oxathianes 164-166.

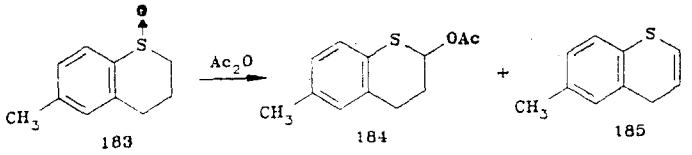
Benzothiopyrans 181 and 182 are formed from thiochroman S-oxides 178 and 179 by the action of excess acetic anhydride [28, 29].



178, 179 180 181, 182

178, 181 R=H; 179, 182 R=CH_3

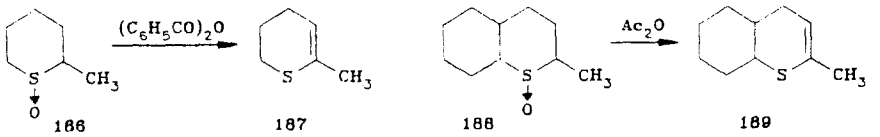
2-Acetoxy-6-methylthiochroman (184) and a product of elimination of acetic acid – 6-methyl-4H-benzothiopyran (185) – in a ratio of 5:1 are formed by the action of acetic anhydride on 6-methyl-1-thiochroman sulfoxide (183) [30].



183 184 185

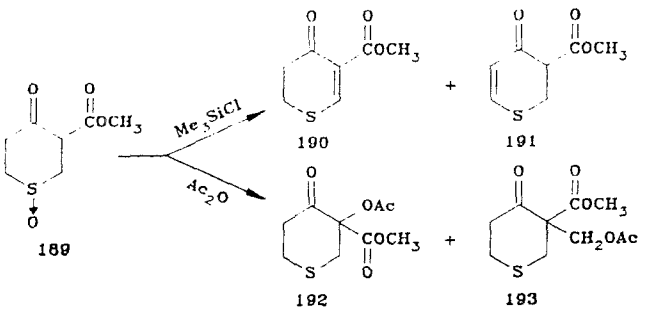
Karaulova and coworkers [30] link such a significant change in the stability of the 2-acetoxy derivative when a methyl group is introduced into the 6 position with the +I effect of the alkyl substituent, which is transmitted to the sulfur atom in the para position; this decreases the effect of the latter on the adjacent methylene group.

2-Methyl-5,6-dihydrothiopyran (187) is formed in high yield by the action of benzoic acid anhydride in refluxing benzene [31] on 2-methyltetrahydrothiopyran 1-oxide (186), while 2-methyl-1-thiadecalin (189) was obtained from 2-methyl-1-thiadecalin sulfoxide (188) by the action on it of acetic anhydride [30]:



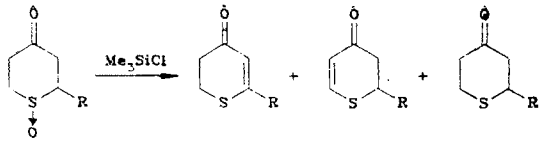
186 187 188 189

Trimethylchlorosilane was used in [32] as a reagent for the synthesis of unsaturated sulfides from sulfoxides, as a result of which enones 190 and 191 were obtained from 3-carbomethoxythian-4-one S-oxide (189). At the same time, elimination processes are not observed in the action of Ac_2O, and a mixture of acetoxy-substituted compounds 192 and 193 is formed.



189 190 191 192 193

4-Thianone S-oxide (194) forms sulfide 196 in high yield, while sulfoxide 195 reacts with the formation of a mixture of 197-199.

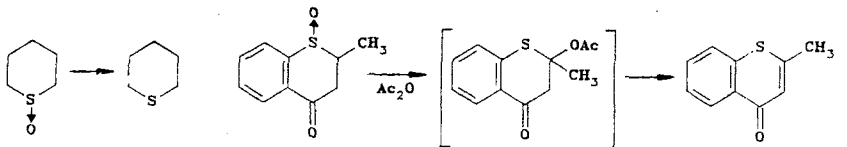


194, 195 196, 197 198 199

194, 196 R=H; 195, 197 – 199 R=n-Bu

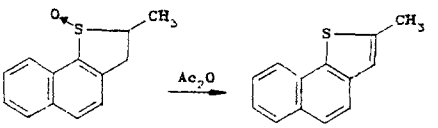
An unsaturated sulfide could not be obtained only from unsubstituted tetrahydrothiopyran 1-oxide (200), which, under the influence of trimethylchlorosilane, is reduced only to tetrahydrothiopyran (201) in 56% yield.

Under the influence of acetic anhydride sulfoxide 202 forms a product (204) of elimination of acetic acid from the intermediately formed 2-acetoxy-substituted compound [29].



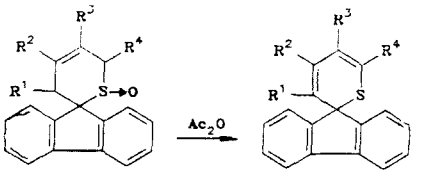
200 201 202 203 204

2-Methyl-2,3-dihydronaphtho[1,2-b]thiophene 1-oxide (205) forms 2-methylnaphtho[1,2-b]-thiophene (206) in high yield (up to 80%) under the same conditions [33].



205 206

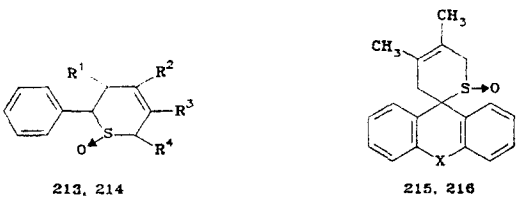
Under the influence of acetic anhydride spiran dihydrothiopyran S-oxides 207-209 form substituted thiopyrans 210-212 [31].



207 – 209 210 – 212

207, 210 $R^1=R^4=H$, $R^2=R^3=CH_3$; **208, 211** $R^1=R^4=CH_3$, $R^2=R^3=H$; **209, 212** $R^1=R^2=R^3=R^4=H$

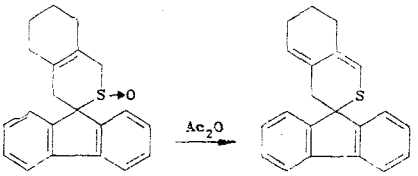
The corresponding thiopyrans were also obtained from sulfoxides 213-216.



213, 214 215, 216

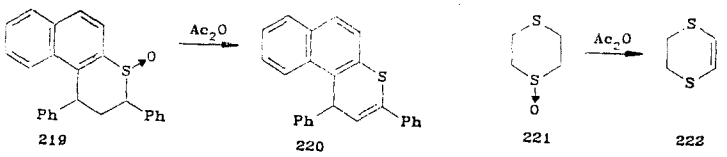
213 $R^1=R^4=H$, $R^2=R^3=CH_3$; **214** $R^1=R^4=CH_3$, $R^2=R^3=H$; **215** X=O; **216** X=S

A peculiarity of the reaction of sulfoxide 217 with acetic anhydride is the formation (in 38% yield) of thiopyran 218 with two conjugated double bonds in different rings [34].



217 218

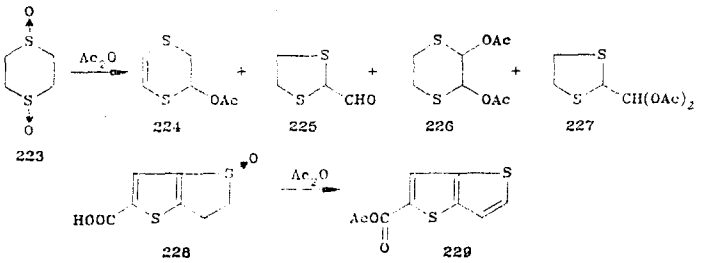
Sulfoxide 219 forms 2,4-diphenylnaphtho[1,2-b]thiopyran (220) under the influence of the same reagent [24]:



219 220 221 222

Interesting data on the reaction of 1,4-dithiane 1-oxide (221) and 1,4-dithiane 1,4-dioxide (223) with acetic anhydride were presented in [35]. Thus 1,4-dithiene (222) was obtained in 53% yield from 221. In contrast to 221, disulfoxide 223 reacts nonselectively and forms 2-acetoxy-1,4-dithi-5-ene (224), 2-formyl-1,3-dithiolane (225), 1,3-dithiolan-2-yldiacetoxymethane (227), and 2,3-diacetoxy-1,4-dithiane (226).

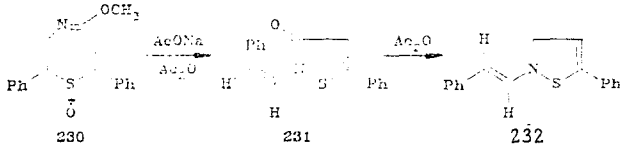
This method proved to be convenient for the synthesis of 5-carboacetoxythieno[3,2-b]thiophene (229) from 5-carboxy-2,3-dihydrothieno[3,2-b]thiophene 1-oxide (228).



223 224 225 226 227 228 229

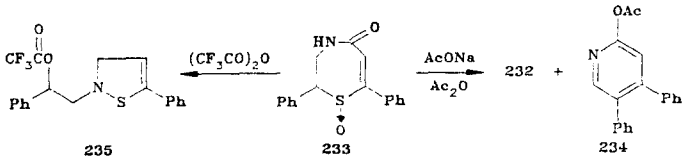
An example of the reaction of 3-acetylbenzothiazoline sulfoxides on heating with acetic anhydride, as a result of which benzothiazines are formed, is presented in [36]. The reaction proceeds with expansion of the heteroring and is undoubtedly of considerable synthetic interest. The reaction can also be carried out without heating if trifluoroaetic anhydride is used in place of acetic anhydride.

According to the data in [37], the Pummerer reaction of 2,7-diphenyl-5-methoxy-2,3-dihydro-1,4-thiazepine 1-oxide (230) under the influence of sodium acetate in acetic anhydride leads to 3-oxo-5-phenyl-cis-N-styrylisothiazole (231), which undergoes quantitative isomerization to trans form 232 on heating in excess acetic anhydride.



230 231 232

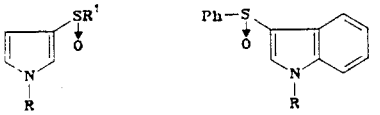
Under the same conditions sulfoxide 233 also forms trans isomer 232; however, the yield of the latter does not exceed 6%, and the 2-acetoxy-4,5-diphenylpyridine (234) constitutes the principal mass (68%).



235 233 232 234

When sulfoxide 233 is heated with trifluoroacetic anhydride in methylene chloride, it forms N-[2-(trifluoroacetoxy)-2-phenylethyl]-3-oxoisothiazole (235) in good yield.

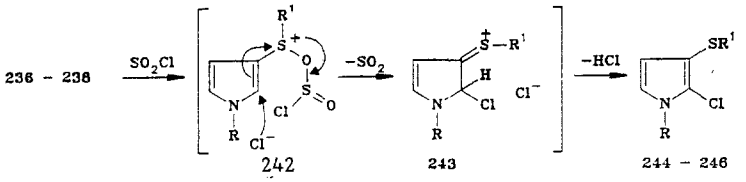
In [38] the Pummerer reaction is used to obtain 2,3-substituted pyrroles and indoles. 3-Pyrrolyl and 3-indolyl sulfoxides 236-241 have been subjected to reaction with thionyl chloride



236 - 238 239 - 241

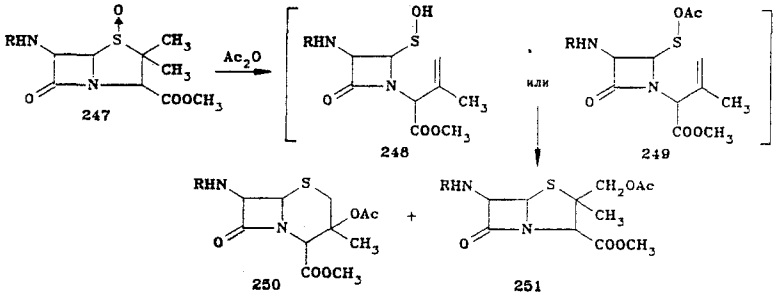
236—238 $R^1 = p\text{-}CH_3C_6H_4$; **236** R=H; **237** $R=CH_3$; **238** $R=CH_2Ph$; **239** R=H; **240** $R=CH_3$; **241** $R=CH_2Ph$

and the reaction itself, according to the data in [38], proceeds via the following scheme:



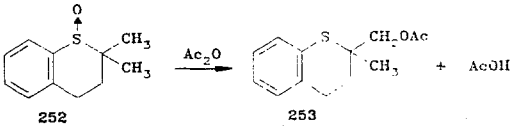
236 - 238 242 243 244 - 246

The transformations (under the conditions of the Pummerer reaction) of cyclic sulfoxides with geminal substitution in the α position relative to the sulfur atom are of considerable interest in the synthesis of β-lactam antibiotics. The formation of two acetoxy-substituted compounds 250 and 251 is observed when sulfoxide 247 is heated in acetic anhydride [39]. Morin and coworkers [39] assume tnat the process takes place with opening of the heteroring and the intermediate formation of sulfenic acid 248 or its derivative 249:



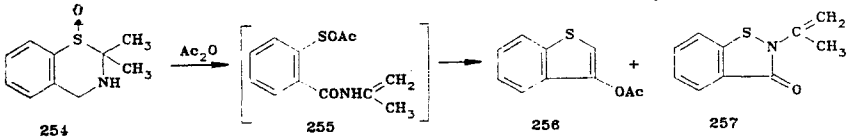
247 248 или 249 250 + 251

A similar mechanism is evidently also realized when 2,2-dimethylthiochroman S-oxide (252) is heated with acetic anhydride; this leads to the corresponding acetoxymethyl-substituted thiochroman 253 [40]:



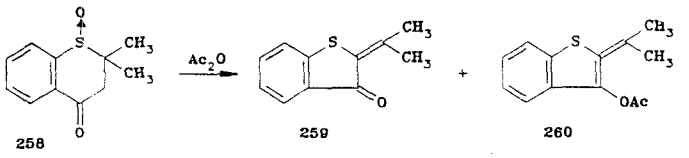
252 253

At the same time, in the case of sulfoxide 254, which contains a nitrogen atom as the second heteroatom in the heteroring, the reaction proceeds with contraction of the heteroring [41]:

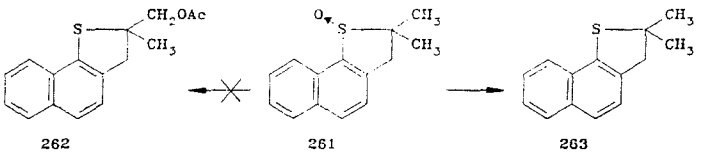


254 255 256 257

Contraction of the heterocyclic system is also observed in the case of sulfoxide 258 [29]:

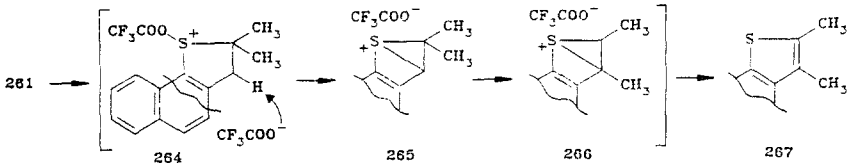


Only one compound – 2,2-dimethyl-2,3-dihydronaphtho[1,2-b]thiophene (263) – was isolated instead of the expected 2-acetoxymethyl-2-methyl-2,3-dihydronaphtho[1,2-b]thiophene as a result of the reaction of sulfoxide 261 under the influence of acetic anhydride [33]:



The mechanism of this unusual reduction of the sulfinyl group to a sulfide group remains unclear.

Under the influence of trifluoroacetic anhydride, sulfoxide 261 forms 2,3-dimethylnaphtho [1,2-b]thiophene (267) [33]:



One of the possible steps in the reaction in this case is 1,2 migration of the methyl group.

Thus the correlated literature data provide evidence for the great synthetic possibilities of the Pummerer reaction, which can be used both to obtain new heterocyclic systems and for functionalization of already available heterocyclic compounds.

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HETEROORGANIC DERIVATIVES OF FURAN.

69.* ANALYSIS OF ELECTRON STRUCTURES OF 2-FURYLTRIETHOXYSILANE AND 1'-(2-FURYL)-SILATRANE BY THE MO LCAO CNDO/2 METHOD

A. K. Kozyrev, R. G. Kutlubaev,
N. P. Erchak, and E. Lukevits

UDC 530.145:547.722:546.287

The electron structures (charges on the atoms, additive populations of the atomic orbitals, and multiplicities of the chemical bonds) of 2-furyltriethoxysilane, 1'-(2-furyl)silatrane, and the starting triethanolamine were analyzed by the MO LCAO CNDO/2 method taking into account the d orbitals. The localized molecular orbitals and the hybrid atomic orbitals that form them were constructed by the Polak projection method.

We have previously investigated the electron structures of furan (I) and trimethyl(2-furyl)silane (II) [4]. In the present research we calculated the electron-density matrixes for 2-furyltriethoxysilane (III), 2-furylsilatrane (IV), and the starting triethanolamine (V).

The description of the electron structures of the indicated compounds was accomplished using characteristics such as the charges on the atoms, the additive populations of the atomic orbitals (AO), and the multiplicities of the chemical bonds — the Wiberg indexes. The structures of the individual bonds in the molecules were investigated by construction of the

*see [1-3] for Communications 66-68.

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