Investigation of the reactions of pyrocatechol derivatives with $AlBr_3$ by NMR spectroscopy

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Alkylpyrocatechols are dealkylated by $AlBr_3$ in CH_2Br_2. The formation of stable carbenium ions (*tert*-butyl, methylcyclopentyl, and 1-adamantyl) was detected by ^1H NMR spectroscopy. Pyrogallol and 2,3-dihydroxynaphthalene are coordinated with $AlBr_3$ in the tautomeric keto form, and 2-mercapto-4-methylphenol forms a complex in the hydroxy form.

Key words: pyrocatechol derivatives, multiatomic phenols, complexes, $AlBr_3$, dealkylation.

It has been previously shown that in the presence of aluminum halides, naphthols and methylated phenols undergo tautomeric transformations with the migration of a proton of the hydroxy group to the ring.[1—4] The reactions of multiatomic phenols with Lewis acids in nonaqueous solutions are poorly studied. However, it is known that under the action of BF_3, resorcinol, 5-methylresorcinol, and phloroglucinol are transformed into complexes of the tautomeric keto form.[5]

In the present work, the reactions of $AlBr_3$ with pyrocatechol, 4-*tert*-butyl-, 4-cyclohexyl-, 4-(1-adamantyl)-, 3,5-di-*tert*-butyl-, 3,5-di-*tert*-butyl-6-(piperidyl-1-methyl)-, and 3,5-di(1-adamantyl)pyrocatechols, as well as with pyrogallol, 2,3-dihydroxynaphthalene, and 2-mercapto-4-methylphenol, in CH_2Br_2 were studied. Taking into account the rather high stability of tautomeric keto forms of hindered phenols,[6] we proposed that pyrocatechols with bulky substituents in the ring can give complexes in the tautomeric keto form.

Alkylpyrocatechols were added to a suspension of $AlBr_3$ in CH_2Br_2 (1 : 3) that was cooled to −30 °C. Solid complexes, which can be dissolved at 20 °C, were precipitated from the mixture. Deeply colored solutions of complexes were immediately formed from 2,3-dihydroxynaphthalene, pyrogallol, and 2-mercapto-4-methylphenol.

The ^1H NMR spectrum of the mixture of 4-*tert*-butylpyrocatechol with $AlBr_3$ at 20 °C (Fig. 1, spectrum *2*) exhibits one signal corresponding to the protons of the ring at δ 7.4 and a singlet corresponding to the protons of the Bu^t group at δ 4.13. The spectrum of the mixture of 3,5-di-*tert*-butylpyrocatechol with $AlBr_3$ has the same pattern. The strong downfield shift of the signal of the Bu^t group is evidently caused by the appearance of a positive charge on the tertiary C atom. The chemical shift of the *tert*-butyl cation obtained from Me_3CF through the action of SbF_5 is 4.15 ppm.[7] Elimination of the Bu^t group is also observed in the reaction of 3,5-di-*tert*-butyl-6-(piperidyl-1-methyl)pyrocatechol with $AlBr_3$.

The data of the ^1H NMR spectrum of the mixture of 4-cyclohexylpyrocatechol with $AlBr_3$ in CH_2Br_2 (see Fig. 1, spectrum *3*) testify that the cyclohexyl substituent is eliminated. The signals at δ 2.55, 4.06, and 4.30 ppm are apparently related to the methylcyclopentyl cation formed by isomerization of the secondary

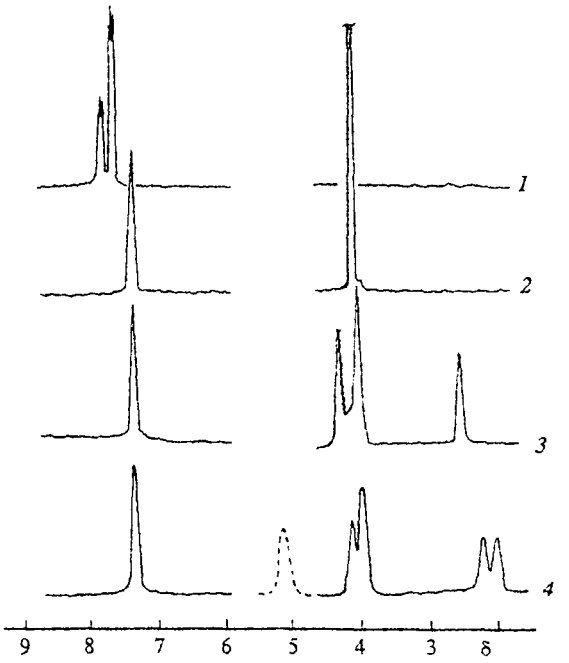

Fig. 1. ^1H NMR spectra of solutions of mixtures: pyrocatechol (*1*), 4-*tert*-butylpyrocatechol (*2*), 4-cyclohexylpyrocatechol (*3*), and 4-(1-adamantyl)pyrocatechol (*4*) with $AlBr_3$ (1 : 3) in CH_2Br_2 at 20 °C.

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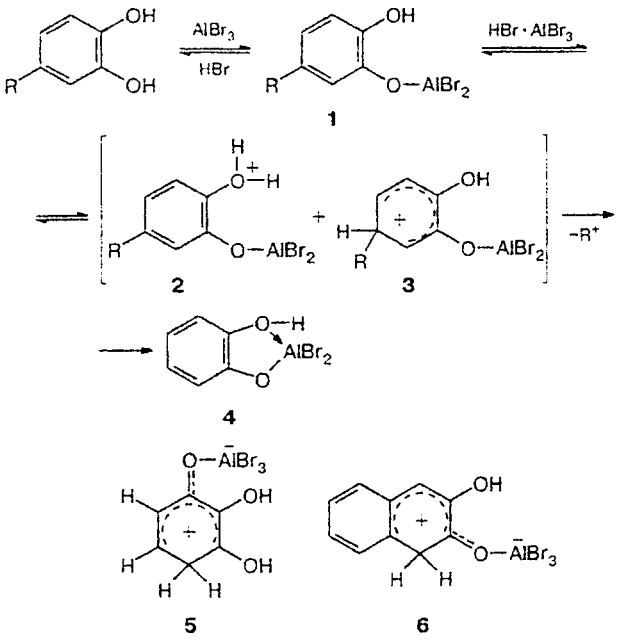
cyclohexyl cation. Signals at δ 2.45, 3.98, and 4.20 are observed in the spectrum of the methylcyclopentyl cation in $SO_2ClF \cdot SbF_5$ at −70 °C.[8]

The ^1H NMR spectra of the products of the reactions of 4-(1-adamantyl)- and 3,5-di(1-adamantyl)pyrocatechols with $AlBr_3$ also contain a single signal corresponding to the protons of the ring (δ 7.4) and a series of signals at δ 2.10 and 4.10 (see Fig. 1, spectrum *4*) probably corresponding to the adamantyl cation (δ 2.37, 4.10, and 5.12 in $HSO_3F \cdot SbF_5$).[9] In our case, the signal at δ 5.12 overlaps with the signal of the solvent in the 4.7—5.4 ppm region.

The results obtained can be explained as follows. The complex initially formed between the hydroxy form of pyrocatechols and $AlBr_3$ adds a proton in the *ipso*-position and is transformed into a complex of the keto form. The bipolar complex is stabilized by the elimination of a stable carbenium ion to form a chelate salt. Another way of dealkylating pyrocatechols suggests the formation of aluminate **1** with the elimination of HBr. The appearance of the acidic system $HBr \cdot AlBr_3$ in the solution results in the protonation of the aluminate at both the oxygen and carbon atoms of the ring (see Scheme 1). When the pyrocatechol ring contains a bulky substituent, fragmentation occurs giving a carbenium ion and chelate salt **4**. When nonsubstituted pyrocatechol is used, the process ceases at the stage of oxonium ion **2**.

Scheme 1



The ^1H NMR spectrum of nonsubstituted pyrocatechol with $AlBr_3$ differs in the aromatic region from the spectra of the alkylpyrocatechol complexes, because it consists of two split signals at δ 7.55 and 7.75 with a ratio of intensities of 3 : 1 (see Fig. 1, spectrum *1*). It can be assumed that these signals correspond to oxonium ion **2**. In fact, the signal at δ 7.7 is observed for the oxonium ion obtained by the protonation of anisole in the $HF \cdot BF_3$ system at −80 °C.[10]

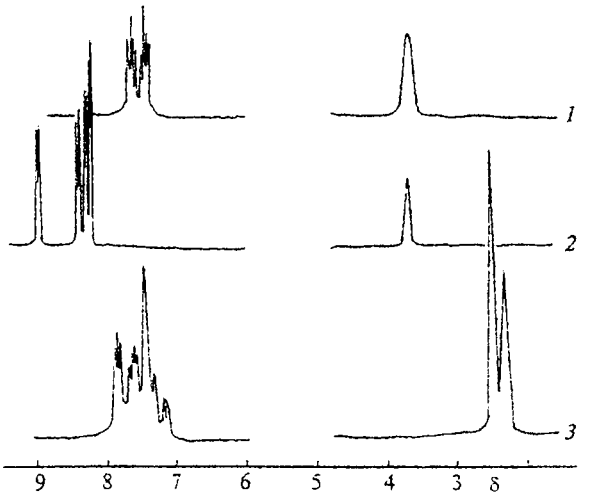


Fig. 2. ^1H NMR spectra of solutions of mixtures of pyrogallol (*1*), 2,3-dihydroxynaphthalene (*2*), and 2-mercapto-4-methylphenol (*3*) with $AlBr_3$ (1 : 3) in CH_2Br_2 at 20 °C.

Thus, under the experimental conditions, for the pyrocatechol derivatives studied, no complexes of the tautomeric keto forms were detected. Pyrogallol and 2,3-dihydroxynaphthalene with excess $AlBr_3$, on the other hand, form rather stable complexes of the keto form. According to the positions of the signals (δ 3.65, 7.38, and 7.58) (Fig. 2, spectrum *1*), structure **5** corresponds to the pyrogallol complex. Structure **6** can be assigned to 2,3-dihydroxynaphthalene (signals at δ 3.70, 9.02, and 8.24—8.42).

It was of interest to investigate the effect of the replacement of the hydroxy group by a thio group on the direction of the formation of complexes with *para*-cresol, which, as is known, forms only complexes of the hydroxy form.[1] The ^1H NMR spectrum of the products of the reaction of 2-mercapto-4-methylphenol with $AlBr_3$ (see Fig. 2, spectrum *3*) contains no signals that could be assigned to the methylene groups of the ring. The existence of two signals of Me groups at δ 2.3 and 2.5 is likely associated with the formation of two complexes, in one of which $AlBr_3$ is linked to the O atom, and in the other of which it is bound to the S atom.

Thus, the reactions of pyrocatechol derivatives with $AlBr_3$ are accompanied by relatively smooth dealkylation. The introduction of an additional hydroxy group into the pyrocatechol molecule or coupling with the aromatic ring are stabilizing factors in the formation of complexes of the tautomeric keto forms.

Experimental

^{1}H NMR spectra were recorded on a Bruker AM-400 instrument (399.13 MHz) at 20 °C using CH_2Br_2 as the internal standard (5 ppm).

4-*tert*-Butyl and 3,5-di-*tert*-butylpyrocatechols were synthesized by a known procedure.[11] The method of preparation of 3,5-di-*tert*-butyl-6-(piperidyl-1-methyl)pyrocatechol and 4-cyclohexylpyrocatechol is similar to that described in Ref. 12. 4-Adamantyl- and 3,5-diadamantylpyrocatechols were obtained by a known procedure.[13] Melting and boiling points of pyrocatechol, pyrogallol, 2,3-dihydroxynaphthalene, and 2-mercapto-4-methylphenol corresponded to the published data. $AlBr_3$ and CH_2Br_2 (chemical purity grade) were used.

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