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DEDIAZONIZATION OF ARYLDIAZONIUM TOSYLATES IN THE PRESENCE OF TRIFLUOROMRTHYLSULFIDE ANIONS

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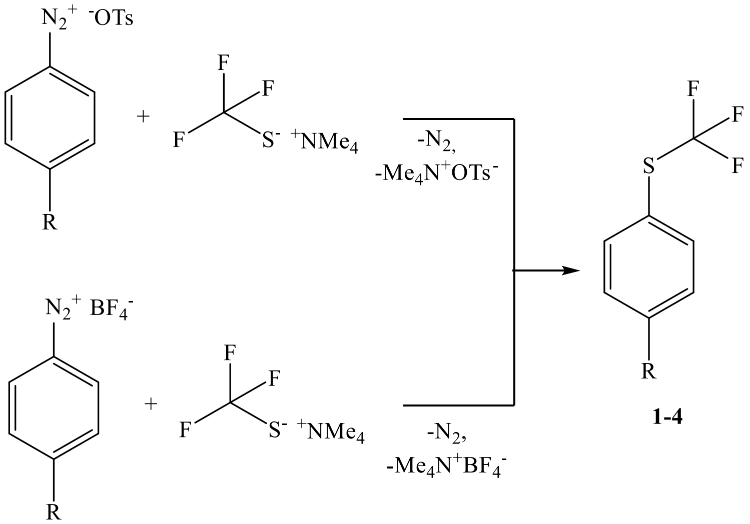
The high reactivity of aromatic diazonium salts necessitates their use immediately after preparation, so these compounds are often not isolated from solutions in their individual state (halides, nitrates, sulfates, perchlorates, etc.). Aryldiazonium salts with complex anions are more stable (BF_4^-, PF_6^-, SbF_6^-, $CuCl_4^{2-}$, $ZnCl_3^-$, $SnCl_6^{2-}$, $HgCl_3^-$), but their practical applications, with the exception of tetrafluoroborates, do not meet the modern requirements of "green chemistry" [1].

Another group of diazonium salts is known that could potentially serve as stable, “diazonium” building blocks. These include aromatic diazonium salts with arylsulfonate anions $Ar^1N_2^+Ar^2SO_3^-$. A limited number of such salts have been known for quite some time, but they were obtained only indirectly, namely by ion exchange from aryldiazonium chlorides $ArN_2^+Cl^-$, and from the chemical properties only azo coupling reactions and the synthesis of individual azo dyes have been studied sporadically [2]. An important advantage of the aryldiazonium tosylates obtained by us is their good solubility in water, alcohols, acetone, acetic acid, dimethyl sulfoxide, dimethylformamide, and acetonitrile. The solubility of these diazo compounds in water opens up the possibilities of syntheses involving them in aqueous and aqueous-organic media.

In order to study the reactivity of aryldiazonium tosylates, we studied the dediazonization of these diazo compounds under the conditions of the Gattermann-Sandmeyer reaction and compared these arylating reagents with the corresponding aryldiazonium tetrafluoroborates.

It was found that 4-methyl-, 4-chloro-, 4-bromo- and 4-nitrophenyldiazonium tosylates interact with tetramethylammonium trifluoromethylsulfide in a water-acetone (1:1) medium with the formation of products of substitution of the diazo group for the trifluoromethylsulfide group [3, 4] - aryltrifluoromethylsulfides **1-4**. Compounds **1-4** were also obtained by countersynthesis starting from aryldiazonium tetrafluoroborates. In both cases, the same dediazonization products are formed, which is confirmed by the determination of their physicochemical constants.

The use of diazonium tosylates in this reaction provides a number of advantages, in particular, the dediazonization temperature is slightly increased (by 10-15^{0}C), nitrogen release occurs more evenly, and the proportion of azo coupling products and other competing processes in the reaction mixtures decreases. It has also been established that the yields of aryltrifluoromethyl sulfides under these conditions increase by 15-20%.



1-4

The yields of dediazonization products are higher under copper-catalysis conditions (74% (compound **1**), 80% (**2**), 81% (**3**), 85% (**4**)). When the reaction is carried out in the absence of a catalyst, the yields of trifluoromethyl sulfides decrease by 25-40% due to the competing processes of azo coupling and transformations of the anionoid reagent. At the same time, the nitrogen release temperature increases by 10-20^{0}C.

Thus, aryldiazonium tosylates are milder, but at the same time highly reactive compounds that can be used as effective arylating reagents in dediazonization reactions in the presence of nucleophiles. These reagents will be especially useful in reactions with unsaturated compounds in the presence of strong nucleophiles (anionarylation reactions), since their conduct requires a fairly low temperature, sometimes reaching below –30^{0}C, which requires active cooling of the reaction mixtures. In particular, the reactions of thiocyanato-, O-alkyldithiocarbonato- and N,N-diethyldithiocarbamatoarylation in most cases occur vigorously at low temperatures and are strongly exothermic. Reducing the reaction rate will positively affect the regioselectivity of these reactions and allows for their kinetic control.

According to the data of experimental studies, the synthesized compounds proved to be quite effective in terms of antibacterial and antifungal action.

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SYNTHESIS AND GROWTH-REGULATORY ACTIVITY OF 2-ARYLBUTENE-1,4-DIOIC ACIDS

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Saturated and unsaturated dicarboxylic acids are important in modern crop production as growth promoters and plant protection agents. Their use contributes to increased yields, improved stress resistance, and reduced dependence on chemical pesticides. In particular, succinic acid helps to increase yield, improve