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RADICAL ARYLATION OF THIOBENZANILIDES BY ARYLDIAZONIUM SALTS IN THE PRESENCE OF FERROCENE

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ESR spectroscopy was used to show that the decomposition of aryldiazonium tetrafluoroborides by the action of catalytic amounts of ferrocene (FC) gives the corresponding aryl radicals [1]. The use of this source of aryl radicals was proposed for the arylation of thioamides and thioureas [2].

In the present work, we studied this reaction for aromatic thioamides. The polar nature of the substituents of both the aniline fragment of the thioamides and in the aryldiazonium ring was altered. The reaction was carried out in acetone solution at 20°C and equimolar thioamide–diazonium salt ratio in the presence of 10 mole % FC. Arylation under these conditions takes 1.5-2 h and the conversion of the thioamides is 90-95%. The results are given in Table 1.

Several features were noted in comparing the experiments given in Table 1. Firstly, the reaction has pronounced chain nature. The yield of the reaction products, S-arylisothioamides, is 6-8 moles per mole FC. This supports our previous mechanistic scheme for this reaction [2], in which FC is initially oxidized by the aryldiazonium cation to the ferricinium cation (FC^+) with simultaneous generation of the aryl radical and then FC^+ is again reduced to FC by the intermediate radical adduct (I)

$$ArN_2^+BF_4^- + FC \rightarrow Ar^{\cdot} + N_2 + BF_4^- + FC^+$$

$$Ar^{\cdot} + PhCNHAr' \rightarrow PhC(S)\dot{C}HNHAr'$$

$$PhC(S)\dot{C}HNHAr' \rightarrow PhC(\dot{S}Ar)=NHAr' \quad (I)$$

$$(I) + FC^+ \rightarrow PhC(SAr)=NAr' + FC + H^+$$

We should note the virtually complete absence of products of the arylation of FC under these conditions. Perevalova et al. [3] have reported that arylferrocenes are formed in significant yield in the reaction of FC with aryldiazonium salts but a special experiment showed that even if FC is taken in amounts equimolar to the diazonium salt and thioamide, the yield of diazonium salt did not exceed 3-5%. This result supports the previously noted high efficiency of thiocarbonyl compounds as traps for free aryl radicals [4].

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TABLE 1. Arylation of Thioamides $C_6H_5C(=S)NH_6H_4X$-p by Aryldiazonium Tetrafluoroborides p-$YC_6H_4N_2BF_4$ in the Presence of 10 mole % FC in Acetone at 20°C over 2 h

Expt. No.	X	Y	Yield of S-arylisothioamide, %	Expt. No.	X	Y	Yield of S-arylisothioamide, %
1*	H	H	65	5 †	OMe	OMe	73
2	H	OMe	80	6 †	OMe	NO_2	78
3 †	H	NO_2	78	7 †	NO_2	NO_2	<30
4	OMe	H	81				

* See our previous work [2].

† In the absence of FC.

The second feature noted for these reactions is the finding that arylation by the p-nitrophenyldiazonium salt also proceeds readily in the absence of catalyst. This behavior is related to the relative ease of reduction of aryldiazonium cations containing electron-withdrawing groups [5]. In these cases (experiments 5 and 6), the thioamide itself may apparently act as the reducing agent. This process may be described by a scheme involving electron transfer from the thioamide to the aryldiazonium cation

$$Ph{-}\underset{\underset{S}{\|}}{C}{-}NHAr + NO_2C_6H_4N_2^+BF_4^- \rightarrow \left[Ph{-}\underset{\underset{S}{\|}}{C}{-}NHAr\right]^{+\cdot} + NO_2C_6H_4^{\cdot} + N_2 + BF_4^-$$

(II)

$$Ph{-}\underset{\underset{S}{\|}}{C}{-}NHAr + NO_2C_6H_4^{\cdot} \rightarrow Ph{-}\underset{\underset{SC_6H_4NO_2}{|}}{\dot{C}}{-}NHAr$$

$$Ph{-}\underset{\underset{SC_6H_4NO_2}{|}}{\dot{C}}{-}NHAr + (II) \rightarrow Ph{-}\underset{\underset{SC_6H_4NO_2}{|}}{C}{=}N{-}Ar + Ph{-}\underset{\underset{S}{\|}}{C}{-}NHAr + H^+$$

The aryl radical formed in the first step adds to the thioamide sulfur atom and the intermediate radical adduct is oxidized by radical-cation (II) with the formation of the final product and the initial thioamide, thereby providing for a kinetic chain. The possibility of generating aryl radicals from aryl diazonium salts containing electron-withdrawing substituents upon their reaction with thioureas and thiosemicarbazides was shown in our previous work by ESR spectroscopy [6].

As expected, the reaction of p-nitrophenyldiazonium with thiobenz-p-nitroanilide (experiment 7) also proceeds in the absence of FC. However, in this case, despite the complete conversion of the starting compounds, the yield of the corresponding S-arylisothioamide is extremely low. In addition, benz-p-nitroanilide and dinitrodiphenyl disulfide are also formed in significant amounts as well as small amounts of p-nitroaniline. This reaction course is in good accord with the results obtained previously for the arylation of thiobenz-p-nitroanilide by other aryl radicals [2] and indicates a third general feature for these reactions, namely, that aromatic isothioamides containing electron-withdrawing substituents in the aniline ring are readily hydrolyzed under the reaction conditions.

Thus, we may assume that the radical arylation of aromatic thioamides not containing electron-withdrawing substituents in the aniline ring by the aryldiazonium salt–ferrocene system is a convenient method for the synthesis of S-arylisothiobenzanilides. This reaction makes isothioamides containing various aryl groups at the sulfur atom readily available. Previously, the reaction of the corresponding imidoyl chlorides $Ar{-}CCl{=}NAr'$ with substituted thiophenols was used for the preparation of such compounds [7]; thiophenols are much less available than the corresponding anilines required for the preparation of the diazonium salts.

EXPERIMENTAL

The PMR spectra were taken on a Bruker WP-200-SY spectrometer in deuteroacetone. The chemical shifts are given in the δ scale with TMS as internal standard. The mass spectra were taken on a DS-60 mass spectrometer.

Reaction of Thiobenz-p-anisidide with Phenyl Tetrafluoroboride. a) A solution of 0.19 g (1 mmole) FC in 10 ml acetone was added dropwise in an argon stream to a solution of 2.4 g (10 mmoles) thioamide and 1.9 g (10 mmoles) diazonium salt in 30 ml acetone and stirred for 2 h at 20°C. After distilling off the acetone, the residue was dissolved in 100 ml $CHCl_3$, washed with saturated aq. $NaHCO_3$ and water and dried over $MgSO_4$. Thin-layer chromatography showed that this treatment does not cause hydrolysis of the reaction products.

After distilling off the solvent, the residue was recrystallized from ethanol to yield 2.6 g S-phenyl-N-p-methoxyphenylisothiobenzamide, mp 59-60°C identified by undepressed mixed melting point with an authentic sample and identical IR spectrum to this sample [8].

b) The experiment was carried out analogously in the presence of 1.9 g (10 mmoles) FC. The mother liquor obtained after recrystallization of the product was subjected to column chromatography on silica gel with hexane eluent to give 1.7 g (90%) EC and 0.1 g of a mixture of phenyl- and diphenylferrocenes identified by thin-layer chromatography relative to authentic samples.

S-p-Nitrophenyl-N-phenylisothiobenzanilide was obtained analogously by the reaction of thiobenzanilide with $p\text{-}NO_2C_6H_4N_2BF_4$ but in the absence of FC, mp 78-79.5°C (from ethanol) [9].

S,N-bis(p-methoxyphenyl)isothiobenzamide was obtained analogously by the reaction of thiobenz-p-anisidide with $p\text{-}CH_3OC_6H_4N_2BF_4$ in the presence of 10 mole % FC, mp 96°C (from ethanol). Found: C 72.05; H 5.56; N 4.22; S 9.07%. Calculated for $C_{21}H_{19}NO_2S$: C 72.18; H 5.48; N 4.01; S 9.17%. PMR spectrum: 3.61 s (3H, OCH_3), 3.73 s (3H, OCH_3), 6.4-7.4 m (13H, aromat. protons).

S-p-Nitrophenyl-N-p-methoxyphenylisothiobenzamide was obtained analogously by the reaction of thiobenz-p-anisidide with $p\text{-}NO_2C_6H_4N_2BF_4$ in the absence of FC, mp 107-108°C (from ethanol). Found: C 66.24; H 4.42; N 7.38; S 8.99%. Calculated for $C_{20}H_{16}N_2O_3S$: C 65.92; H 4.44; N 7.69; S 8.80%. PMR spectrum: 3.81 s (3H, OCH_3), 6.9-8.1 m (13H, aromat. protons).

S-p-Methoxyphenyl-N-phenylisothiobenzamide was obtained analogously by the reaction of thiobenzanilide with $p\text{-}CH_3OC_6H_4N_2BF_4$ in the presence of 10 mole % FC as a light yellow oil (after column chromatography on silica gel with 20:1 benzene–ethanol eluent). Found: C 74.40; H 5.39; N 4.42; S 11.13%. Calculated for $C_{20}H_{17}NOS$: C 75.20; H 5.37; N 4.38; S 10.04%. PMR spectrum: 3.70 s (3H, OCH_3), 6.7-7.9 m (14H, arom. protons). Mass spectrum, m/z: 319 (M^+, 0.3%), 180 ($M^+ - SC_6H_4OCH_3$, 100%), 139 ($SC_6H_4OCH_3$, 26%).

The reaction of 2 g (7.8 mmoles) thiobenz-p-nitroanilide with 1.85 g (7.8 mmoles) $p\text{-}NO_2C_6H_4N_2BF_4$ in the absence of FC was carried out and worked up as described above. After distilling off the chloroform, the residue was subjected to column chromatography on silica gel with 20:1 hexane–ethanol eluent to give 1.25 g (50%) benz-p-nitroanilide and 0.03 g p-nitroaniline identified by undepressed mixed melting point with authentic samples. Also, 0.9 g of a yellow crystalline substance was obtained which had the following elemental analysis after recrystallization thrice from acetic acid: C 55.24; H 3.03; N 9.88; S 12.77%.

Mass spectrometry indicated that this substance is a mixture of S,N-bis(p-nitrophenyl)isothiobenzamide (A) and dinitrodiphenyl disulfide (B), m/z: (M_A^+, 0.2%), 225 ($M_A^+ - SC_6H_4NO_2$, 99%), 308 (M_B^+, 100%). The elemental analysis data correspond to 64% A and 36% B. Calculated: C 55.32; H 3.15; N 10.35; S 12.89%.

CONCLUSIONS

1. The radical chain thiophilic arylation of thiobenzanilide and thiobenz-p-anisidide by phenyl- and p-methoxyphenyldiazonium tetrafluoroborides was carried out using ferrocene as the catalyst. The corresponding S-arylisothiobenzanilides were obtained in high yield.

2. p-Nitrophenyldiazonium tetrafluoroboride arylates these thiobenzanilides in the absence of ferrocene, presumably also by a radical mechanism; the thioamide is the catalyst for decomposition of the aryldiazonium cation.

3. S-Arylisothiobenzanilides containing electron-withdrawing substituents on the aniline ring undergo hydrolysis under the reaction conditions.

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