FERROCENE-FERRICINIUM CATION, A REDOX SYSTEM INITIATING RADICAL REACTIONS OF ARYLDIAZONIUM SALTS

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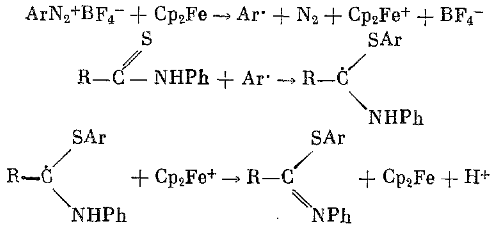
Copper salts are usually used for the production of aryl radicals from aryldiazonium salts. However, this catalyst has several disadvantages, in particular, it is sparingly soluble in the usual organic solvents, and therefore an aqueous or aqueous or aqueous–acetonic required to carry out the reaction. The catalyst also limits the possible application of this method for the preparation of aryl radicals, for example, for the arylation of thioamides, since the arylation products, isothioamides, readily hydrolyze in the presence of copper salts [1].

We found that aryl radicals are readily produced from aryldiazonium borofluorides by the action of catalytic amounts of ferrocene in both acetone and benzene. The formation of the aryl radicals (Ar = C_6H_5, p-CH_3-OC_6H_4) during the reaction of ArN_2BF_4 with Cp_2Fe was recorded by the EPR method using RNO spin traps (R = t-Bu; 2,3,5,6-Me_4C_6H; 2,4,6-t-$Bu_3C_6H_2$). The parameters of the EPR spectra of the spin adducts obtained agree with those described in the literature.

The aryldiazonium–ferrocene system is also very suitable from the preparative point of view. Thus, in the arylation of thiobenzanilide and diphenylthiourea using this system, S-arylisothioamide and S-aryldiphenylisothiuronium, respectively, are formed in a yield of 50-60%. The reaction can be described by the scheme



R = PhNH, Ph

It was also shown by the EPR method using spin traps that aryl radicals are formed from ArN_2BF_4 when Cr, Mo, Mn, Re, or Fe carbonyls are used as catalysts.

LITERATURE CITED

1. B. V. Kopylova, I. O. Bragina, I. I. Kandror, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 719 (1980).

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