

## Letters to the Editor

### The first example of the copper-free chloro- and hydrodediazonation of aromatic amines using sodium nitrite, $\text{CCl}_4$ , and $\text{CHCl}_3$

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One of the widely used methods for synthesis of chloroarenes is based on the reaction of aromatic diazonium salts with HCl or other sources of chloride ion in the presence of copper salts (Sandmeyer reaction).<sup>1</sup> In spite of considerable success in this type of transformations, this method as a whole does not satisfy modern trends of "green" organic synthesis because of the presence of copper or its salts, high acidity of the media, and use of lowered temperatures at the diazotization stage. Only a few examples for preparative copper-free diazotization—chlorination of anilines are known. Among them are diazotization—chlorination with potassium nitrite in HCl and in DMSO (see Ref. 2) and reactions of some arenediazonium tetrafluoroborates with chloroform in the presence of phase-transfer catalysts of crown ethers or poly(ethylene glycol) with moderate yields of chloroarenes.<sup>3,4</sup> Generally, the chemistry of diazonium salts is based on the use of highly polar media (most frequently, aqueous solutions),<sup>1</sup> whereas the diazotization of anilines and subsequent transformations of aromatic diazonium compounds in nonpolar solutions are poorly studied. The diazotization—chlorination of anilines with *tert*-butyl thionitrate in  $\text{CCl}_4$  (see Ref. 5) or with a  $\text{NaNO}_2/\text{Me}_3\text{SiCl}/\text{CCl}_4/\text{PhCH}_2\text{N}^+\text{Et}_3\text{Cl}^-$  system<sup>6</sup> can be ascribed to a few reac-

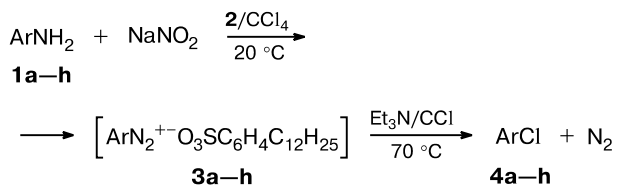
tions of this type. Chlorobenzene was formed in low yield by the thermal decomposition of a suspension of benzenediazonium chloride in  $\text{CCl}_4$ .<sup>7</sup>

We have recently<sup>8–13</sup> shown that *p*-toluenesulfonic acid as an acidic component provides mild conditions for the diazotization of aromatic and heterocyclic amines to form stable arenediazonium tosylates  $\text{ArN}_2^+\text{TsO}^-$  or the substitution products of the diazonium group for bromine, iodine, or tosylate group in the absence of copper salts. At the same time, arenediazonium tosylates are insoluble in nonpolar media and do not react with chlorides or HCl in the absence of copper salts with the formation of chloroarenes. However, as shown below, the properties of diazonium salts change drastically with a lipophilicity increase of the arylsulfonate counterion.

We found that aromatic amines **1a–h** readily undergo diazotization with sodium nitrite and *p*-dodecylbenzenesulfonic acid (**2**) in  $\text{CCl}_4$  at ambient temperature within 1.5–2 h with the complete conversion of the initial amines. The subsequent heating of the reaction mixture with triethylamine for 30–40 min results in the decomposition of intermediate diazonium salts **3a–h** and formation of the corresponding chloroarenes **4a–h** in high or moderate preparative yields (Scheme 1). The optimum molar

ratio of the reaction components is **1** : NaNO<sub>2</sub> : **2** : Et<sub>3</sub>N = 1 : 6 : 1 : 1.

Scheme 1



Ar = *p*-MeC<sub>6</sub>H<sub>4</sub> (**a**), 45%; *p*-C<sub>6</sub>H<sub>13</sub>C<sub>6</sub>H<sub>4</sub> (**b**), 88%; *p*-MeOC<sub>6</sub>H<sub>4</sub> (**c**), 51%; *p*-PhN=NC<sub>6</sub>H<sub>4</sub> (**d**), 89%; *p*-NCC<sub>6</sub>H<sub>4</sub> (**e**), 63%; *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**f**), 35%; *o*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**g**), 49%; *m*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (**h**), 54%.

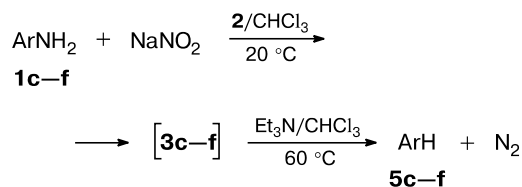
As far as we know, the observed transformations have no precedents in the chemistry of diazonium salts, and we found no data on the use of acid **2** as an acidic component of diazotization and of triethylamine as an agent inducing halodediazotation. The results of chlorodediazotation are general, since they involve amines with electron-donating substituents and different positions of the substituents in the benzene ring.

The possibility of amine diazotization in nonpolar CCl<sub>4</sub> is determined, of course, by the lipophilic properties of acid **2** providing solubility in CCl<sub>4</sub> that is not typical of the known diazonium salts. Intermediate salts **3** were not isolated; however, their presence in the reaction mixture was proved by the quantitative formation of the azocoupling products with β-naphthol, which is a typical reaction of diazonium compounds. Heating of solutions of salts **3** (obtained at the first stage of the reaction) in CCl<sub>4</sub> in the absence of triethylamine for 4 h did not result in their complete conversion and gives low yields of the corresponding chloroarenes **4**. The addition of triethylamine induces the instant decomposition of salts **3a-h** with nitrogen evolving and the parallel formation of chloroarenes **4a-h**. The effect of pyridine resembles that of triethylamine but is less pronounced.

Although the detailed mechanism of the found chlorodediazotation reaction with CCl<sub>4</sub> and the initiating role of triethylamine were not studied, it is evident that these transformations are free-radical, which is confirmed by the GC/MS observation of hexachloroethane as a coupling product of trichloromethyl radicals in the reaction mixture.

The diazotization of anilines **1c-f** via Scheme 1 proceeds successfully in chloroform; however, the subsequent decomposition of intermediate salts **3c-f** proceeds via different route than that in CCl<sub>4</sub>, and the complete reduction (hydrodediazotation) occurs within 30–40 min instead of chlorodediazotation to form the corresponding arenes **5c-f** as the single products (Scheme 2), which were identified by gas chromatography.

Scheme 2



Note that hydrodediazotation in chloroform occurs with high selectivity, since no even trace amounts of the corresponding chloroarenes are observed in the products. As in the case of using CCl<sub>4</sub>, the decomposition of salts **3c-f** in chloroform is efficient only in the presence of triethylamine. The reactions of reduction of diazonium salts are significant for organic synthesis, and the discovered method of hydrodediazotation with the Et<sub>3</sub>N/CHCl<sub>3</sub> system is novel and also interesting from the preparative point of view.

Thus, we found that the diazotization of aromatic amines in the presence of lipophilic *p*-dodecylbenzenesulfonic acid for the first time allows this process to be carried out in nonpolar solvents CCl<sub>4</sub> and CHCl<sub>3</sub>. Under the action of triethylamine, the intermediate diazonium salts exhibit properties that are not typical of the known diazonium salts, undergoing chlorodediazotation in CCl<sub>4</sub> or reducing in chloroform.

Chloroform, CCl<sub>4</sub>, triethylamine (reagent grade) and 4-dodecylbenzenesulfonic acid (Aldrich) were used as received.

**Chlorodediazotation of amines 1a-h (general procedure).** The corresponding aniline (3 mmol) and NaNO<sub>2</sub> (18 mmol) were added to a solution of 4-dodecylbenzenesulfonic acid (**2**) (0.98 g, 3 mmol) in CCl<sub>4</sub> (10 mL). The solution was stirred at 20 °C for 1.5–2 h until the initial aniline disappeared (TLC, eluent C<sub>6</sub>H<sub>6</sub>–EtOH (9 : 1, vol.)). The reaction mixture was heated to 70 °C, and triethylamine (0.16 mL, 3 mmol) was added, resulting in instant nitrogen evolving. Then the mixture was kept for 30–40 min to the negative reaction with β-naphthol to the diazonium salt. Anhydrous Al<sub>2</sub>O<sub>3</sub> (0.9 g) was added to the reaction mixture, which was stirred for 15 min and filtered off. The filtered off Al<sub>2</sub>O<sub>3</sub> was washed with CCl<sub>4</sub> (20 mL), the combined solutions of CCl<sub>4</sub> was passed through a column with Al<sub>2</sub>O<sub>3</sub>, and the solvent was evaporated *in vacuo*. The resulted chloroarenes were identified by the <sup>1</sup>H, <sup>13</sup>C NMR and mass spectra and by comparing with authentic samples.

**Hydrodediazotation of amines 1c-f (general procedure).** The reactions were carried out and treated as described above using CHCl<sub>3</sub> instead of CCl<sub>4</sub>. The obtained solutions of arenes in CHCl<sub>3</sub> were analyzed by GC/MS, and the chromatograms indicates peaks of compounds **5c-f** only.

**Methoxybenzene (5c).** MS, *m/z*: 108 [M]<sup>+</sup> (100), 93 (15), 77 (60), 65 (58), 51 (12), 39 (18).

**1, 2-Diphenyldiazene (5d).** MS, *m/z*: 182 [M]<sup>+</sup> (34), 152 (9), 105 (19), 77 (100), 44 (33).

**Benzonitrile (5e).** MS, *m/z*: 103 [M]<sup>+</sup> (100), 77 (31), 50 (10), 44 (20), 40 (80).

**Nitrobenzene (5f).** MS, *m/z*: 123 [M]<sup>+</sup> (56), 107 (7), 93 (15), 77 (100), 65 (12), 51 (39), 43 (11).

This work was financially supported by State contracts P1296, 16.512.11.2127, and 16.512.11.2217.

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*Received April 13, 2011;  
in revised form September 6, 2011*