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PRELIMINARY NOTE

Diazotization of pentafluoroaniline by means of anion-catalyzed phase transfer catalysis in a hydrophobic organic solvent

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SUMMARY

Anion-catalyzed phase-transfer catalysis was successfully applied to diazotization of pentafluoroaniline in a dichloromethane-aqueous sulfuric acid two-phase system. The resulting diazonium group was coupled in situ with anisole, 1-methoxynaphthalene, and mesitylene, and replaced in situ with bromo, hydryl, and phenyl substituents under a two-phase condition.

Diazotization of pentafluoroaniline has been recommended to be carried out in nonaqueous media or concentrated mineral acid, otherwise the coupling product always contains a hydroxyl group on the perfluorophenyl ring at the position para to the azo group [1].

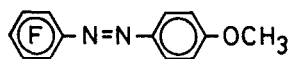
Recently we reported that tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) ion catalyzed the diazotization of aromatic amine in the organic phase of a dichloromethane-aqueous sulfuric acid two-phase system and accelerated the subsequent diazo coupling with various coupler components in the same phase [2].

We have now found that pentafluoroaniline is diazotized by this technique and that the resulting diazonium group was coupled in situ with phenolic ethers and an aromatic hydrocarbon and replaced in situ with some substituents under a two-phase condition. For example, aqueous sodium nitrite (1.17 mmol in 1

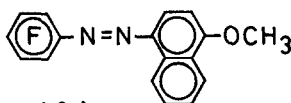
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ml of water) was added during 5 min to a cold (0°C on an ice-water bath) stirred two-phase mixture of dichloromethane (20 ml) containing pentafluoroaniline (0.84 mmol), anisole (1.4 mmol) and NaTFPB (0.028 mmol) and aqueous sulfuric acid (31 mmol in 3 ml of water). After the two-phase mixture was kept stirring for 3 hours, the organic layer was washed with aqueous sodium chloride and chromatographed on a silica-gel column. A fraction eluted by dichloromethane gave 4-(pentafluorophenylazo)anisole (**1**) [3] (0.67 mmol, 80% yield), mp 101.5 - 102.5°C (from ethanol), which was characterized by elemental analysis (Found: C, 51.60; H, 2.34; N, 9.38%) and $^1\text{H-NMR}$ (CDCl_3 , TMS) δ = 3.80 (s, 3H), 6.89 (d, 2H) and 7.79 ppm (d, 2H). When the solution was allowed standing for a day at room temperature, the signals due to the cis isomer appeared at 3.76, and 6.84 ppm, and the cis/trans molar ratio from ^1H -signal intensities was 1 : 2.2.

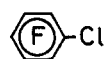
4-(Pentafluorophenylazo)-1-methoxynaphthalene (**2**), mp 221.5 - 223°C, and pentafluorophenylazo-2,4,6-trimethylbenzene (**3**), mp 153 - 154.5°C, were afforded in a similar manner and isolated in 75 and 44% yields, respectively, by column chromatography. No p-hydroxyperfluorophenylazo compounds [1] nor diazoamino ones [4] were found in the products and the O-methyl group on the coupler component was retained in the product [5]. **2**: Found: C, 57.99; H, 2.62; N, 7.89%. $\text{C}_{17}\text{H}_9\text{F}_5\text{N}_2\text{O}$ requires C, 57.96; H, 2.57; N, 7.95%. $^1\text{H-NMR}$: (CDCl_3 , TMS) δ = 3.99, 4.11 (-OCH₃), 6.92, 7.50 - 7.80, 7.98, 8.20 - 8.40, 8.75 - 8.90 ppm (aromatic). $^{19}\text{F-NMR}$: (CDCl_3 , C_6F_6) δ = -1.16 (m, 14.8F), 1.05 (m, 2F), 5.25 (t, 1F), 7.41 (t, 7.4F), 10.76 (m, 14.8F), and 14.50 ppm (m, 2F). Cis/trans ratio from ^{19}F -signal intensities was 1 : 7.4. **3**: Found: C, 57.18; H, 3.56; N, 8.63%. $\text{C}_{15}\text{H}_{11}\text{F}_5\text{N}_2$ requires C, 57.33; H, 3.52; N, 8.91%. $^1\text{H-NMR}$: (CDCl_3 , TMS) δ = 2.31 (s, 3H), 2.42 (s, 6H), and 6.86 ppm (s, 2H). $^{19}\text{F-NMR}$: (CDCl_3 , C_6F_6) δ = -1.0 (m, 2F), 7.3 (t, 1F), and 10.5 ppm (m, 2F).



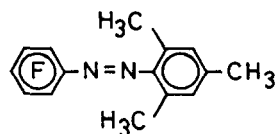
(1)



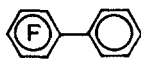
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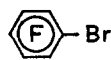
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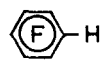
(3)



(4)



(6)



(7)

The present anion-catalyzed phase-transfer catalysis technique was also applied to the in situ replacement of the diazonium group. An aqueous sodium nitrite (1.29 mmol in 2 ml of water) was added during 5 min to a cold (0°C) two-phase mixture of dichloromethane (25 ml) containing pentafluoroaniline (0.91 mmol), NaTFPB (0.042 mmol) and benzene (10 ml) and aqueous sulfuric acid (60 mmol in 10 ml of water) containing cupric sulfate (0.77 mmol) and cuprous chloride (0.12 mmol). After the mixture was kept stirring at room temperature for 100 min, the organic phase was analyzed by GLC. The products were assigned by the comparisons of retention times in GLC and ^{19}F -NMR spectra with those of the authentic specimen to be pentafluorobiphenyl (4), mp 108.0 - 110.5°C [6], (60%) and pentafluorochlorobenzene (5)* (5%). When the reaction was carried out in a similar manner except with the addition of three--times molar amounts of potassium bromide in place of benzene, the major products were pentafluorobromobenzene (6)* (19%) and pentafluorobenzene (7) [7] (30%), hydrogen of which was regarded to be from dichloromethane [7].

The present two-phase technique has the advantage of no need to use troublesome hydrofluoric acid, and yet can afford a reasonable yield comparable to those by conventional methods, providing a promising convenient method for the preparation of pentafluorobenzenediazonium ion and various in situ derivatives from the diazonium ion. Further applications of this technique are under way in this laboratory.

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*Authentic samples were commercially available.