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A FACILE *IN-SITU* DIAZO-COUPLING REACTIONS UNDER TWO-PHASE CONDITIONS CATALYZED BY TETRAKIS[3,5-BIS(TRIFLUOROMETHYL)PHENYL]BORATE ION

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Abstract:

In-situ diazo-coupling and *N*- and *C*-nitrosations under CH_2Cl_2-aq.H_2SO_4 two-phase systems have proved to be catalyzed by TFPB ion.

The use of the normal diazotization of aromatic amines with sodium nitrite in aqueous mineral acids is limited in the cases of weakly basic amines such as 2,4-dinitroaniline because of their poor solubility in aqueous media and the decomposition of the labile diazonium ions by hydrolysis.[1] Furthermore the diazo-coupling under acidic conditions is frequently accompanied by some undesired results, for example, the complete dealkylation of alkoxybenzene or -naphthalene substrates in coupling.[2] The example of anionic phase-transfer catalysis are recently shown in diazo-coupling reactions by using stable arenediazonium tetrafluoroborates, in which lipophilic organic anions such as tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(TFPB)[3,4] or dodecylbenzenesulfonate[5] ions incorporate diazonium ions from solid or aqueous phase into organic phase in the form of ion pairs and promote diazo-coupling. We report here that TFPB ion catalyzes the diazotization of aromatic amines in organic phase under two-phase conditions and the subsequent diazo-coupling occurs very effectively enough to overcome the above obstacles in diazotization and diazo-coupling by the normal method.

After enough stirring a two-phase system of CH_2Cl_2 containing sodium TFPB and 0.5 mol l^{-1} aqueous H_2SO_4 containing $NaNO_2$, the aqueous phase was separated out from the CH_2Cl_2 phase in which cationic nitrosating species(E^+) could be incorporated in the form of an ion pair with TFPB. 4-Nitroaniline(1) was added to the CH_2Cl_2 solution for diazotizing 1 to diazonium ion(2) and then 9-ethylcarbazole(3) was added for *in-situ* diazo-coupling to yield 9-ethyl-3-(4-nitrophenylazo)carbazole(4) and oxonium TFPB(5).

As shown in Table, the efficacy of TFPB is apparent for turning the PTC cycle(Runs 1,2 and 3). Runs 2 and 3 indicate that the nitrosating species(E^+)

incorporated from the aqueous phase stoichiometrically in the form of an ion pair with TFPB is *not* a nitrosonium ion(NO^+) because a catalytic amount of TFPB is enough for promoting the diazotization.

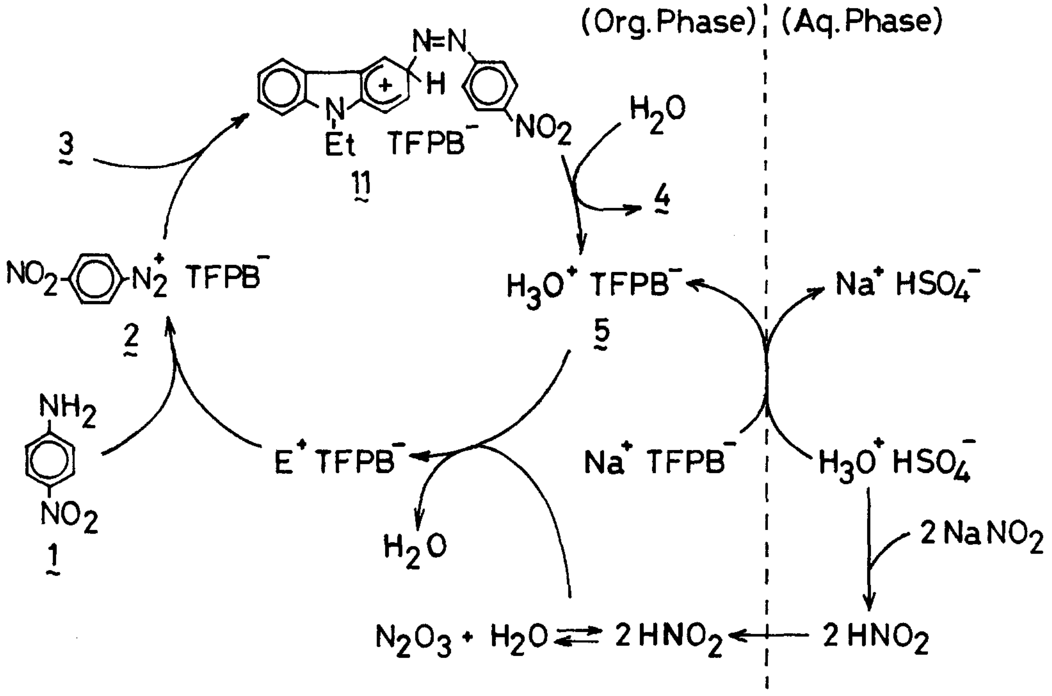
Table: *In-situ* diazotization and diazo-coupling[a)]

Run	TFPB mmol	$NaNO_2$ mmol	1 mmol	3 mmol	4 mmol
1	-	1.30	0.084	0.064	-
2	0.032	1.32	0.084	0.064	0.060
3	0.024	1.41	0.110	0.115	0.098

a) CH_2Cl_2(10 ml)-0.5 mol l^{-1} H_2SO_4(10 ml)

The fact that TFPB ion incorporates nitrosating species into organic phase was also confirmed by *N*- and *C*-nitrosations catalyzed by TFPB ion under two-phase systems. A two-phase system of CH_2Cl_2 containing diphenylamine and 5 mol% of sodium TFPB and an equal volume of 0.5 mol l^{-1} aqueous H_2SO_4 containing equimolar $NaNO_2$ was stirred at 0 °C for 15 min to yield *N*-nitrosodiphenylamine(65%). On the other hand, a two-phase reaction of 9-ethylcarbazole(3) with 1 mol% of sodium TFPB and 1.1 times molar quantity of $NaNO_2$ at room temperature for 24 h gave 9-ethyl-3-nitrocarbazole(6)(76%), and a similar reaction of 2-naphthol(7) at 0 °C for 3.3 h gave 1-nitro-2-naphthol(8) (17.7%) accompanying 1,2-naphthoquinone(9)(25.4%)[6]. The reaction of 7 was followed by monitoring HPLC of the reaction mixture and the intermediary formation of 1-nitroso-2-naphthol(10) was confirmed. The result that an authentic sample of 10[7] was transformed into a mixture of 8 and 9 under a two-phase condition of CH_2Cl_2-0.5 mol l^{-1} aqueous H_2SO_4 containing $NaNO_2$ without sodium TFPB, suggests that initially formed nitroso-compounds, 10 and 9-ethyl-3-nitrosocarbazole, have been readily oxidized to the corresponding nitro-compounds, 8 and 6, respectively, and a part of 10 has been hydrolyzed to 9 under the two-phase conditions.

According to these results, the mechanism of the *in-situ* diazo-coupling reactions catalyzed by TFPB ion under the two-phase conditions can be considered as follows. Under the PTC condition TFPB ion incorporates oxonium ion in the form of an ion pair[8] and excess nitrous acid in the aqueous phase can be transfered into the CH_2Cl_2 phase and equilibrate with dinitrogentrioxide(N_2O_3) and water[9]. The nitrosating species(E^+) must be a protonated HNO_2 or $HN_2O_3^+$ generated in the organic phase which diazotizes 1 to 2. Deprotonation by water from an intermediate(11) in the diazo-coupling of 2 with 3 regenerates oxonium TFPB(5) in the organic phase which catalyzes the PTC cycle until 1 or 2 is consumed.



In-situ diazo-coupling under two-phase system

The effectiveness and the simplicity of this *in-situ* diazo-coupling under two-phase conditions compared with general methods are cleary demonstrated in the following cases. After stirring 2,4-dinitroaniline(0.63 mmol) in a two-phase system of CH_2Cl_2(20 ml)-5 mol l^{-1} aqueous H_2SO_4(20 ml) with $NaNO_2$(0.55 mmol) and sodium TFPB(1 mol%) for 15 min at 25 °C, the carbazole(3)(0.55 mmol) was added and the reaction mixture was stirred for 4 h at 25 °C, which gave 3-(2,4-dinitrophenylazo)-9-ethylcarbazole(42% isolated by column chromatography over silica-gel). In contrast to this system, laborious isolation of an unstable 2,4-dinitrobenzenediazonium sulfate after diazotization in conc.H_2SO_4 and diazo-coupling with carbazole in dioxane under anhydrous conditions gives only a lower yield of the coupling product(28%).[10] A similar two-phase reaction of 1-methoxynaphthalene with equimolar 1 and $NaNO_2$ with sodium TFPB (0.2 mol%) in CH_2Cl_2(25 ml)-0.5 mol l^{-1} aqueous H_2SO_4(10 ml) gave 1-methoxy-4-(4-nitrophenylazo)naphthalene(12)(80%), while diazo-coupling in homogeneous conditions in aqueous acetic acid is always accompanied by complete demethylation from the methoxyl group of 12 by hydrolysis.[11]

The present two-phase and *in-situ* diazo-coupling without any cautions for avoiding the decomposition of the diazonium salts or substrates in acidic aqueous media must be practical for the preparation of various azo-dyestuffs and further applications of this system will be shown in a future report.

References and Notes

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4. Sodium TFPB as a hydrate with 2.5 H_2O can be readily prepared similarly to sodium tetraphenylborate[12] by treating a Grignard reagent of 3,5-bis(trifluoromethyl)phenyl iodide[13] or bromide(commercially available from Yarsley Research Lab. Ltd. or Showa Denko, K. K.) with 1/6 times molar amount of boron trifluoride in ether and refluxing the reaction mixture for 12 h(ca. 75% yield). Sodium TFPB·2.5 H_2O is soluble in nonpolar solvents(up to 10^{-3} and 5.7×10^{-5} mol l^{-1} in CH_2Cl_2 and benzene, respectively), but practically insoluble in water and remarkably stable under a two-phase system of CH_2Cl_2-5 mol l^{-1} aqueous H_2SO_4 and even in a homogeneous methanol-conc.H_2SO_4(80/20 v/v) system for one month at room temperature. On the contrary, sodium tetraphenylborate is quite soluble in water, insoluble in CH_2Cl_2, and readily decomposed under acidic and oxidative conditions.[14]
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