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Reaction of Iminophosphoranes with a Diazonium Salt: Synthesis of Wholly Aromatic Aminophosphonium Salts

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Synopsis. *N*-Phenyliminotriphenylphosphorane reacts with benzenediazonium tetrafluoroborate to form wholly aromatic *N,N*-diphenylaminotriphenylphosphonium tetrafluoroborate. This synthetic method can be applied to prepare a cationic polymer having the aminophosphonium structure.

Highly polarized iminophosphoranes undergo a variety of nucleophilic reactions.[1] Several decades ago, Staudinger found that they react with alkyl halides to yield aminophosphonium halides.[2] This nucleophilic substitution has been applied for the preparation of *N,N*-dialkylaminotriphenylphosphonium salts,[3,4] and the hydrolysis of these aminophosphonium salts has been investigated to prepare amines carrying bulky alkyl groups.[5] Since aryl halides do not react with iminophosphoranes, no *N,N*-diarylaminophosphonium salt can be synthesized by this method, and no other reaction has been reported for the preparation of wholly aromatic aminophosphonium salts. We report in the present paper that *N*-phenyliminotriphenylphosphorane reacts with a benzenediazonium salt to give such an aromatic aminophosphonium salt.

Results and Discussion

Phosphonium ylids, i.e., Wittig reagents couple directly with diazonium salts: methoxycarbonylmethylenetriphenylphosphorane reacts with benzenediazonium tetrafluoroborate to yield a phosphonium salt which can be converted into a phenylazo-substituted new ylid upon treatment with an aqueous base.[5] Cyclopentadienylidenetriphenylphosphorane also reacts with benzenediazonium chloride, but electrophilic aromatic substitution of the phenylazo group takes place on the cyclopentadienyl ring.[6]

$$(C_6H_5)_3P{=}NC_6H_5 + C_6H_5N_2^{\oplus}BF_4^{\ominus} \longrightarrow (C_6H_5)_3\overset{\oplus}{P}{-}N(C_6H_5)_2BF_4^{\ominus} + N_2$$

Table 1. Reaction of *N*-Phenyliminotriphenylphosphorane with Benzenediazonium Tetrafluoroborate[a)]

Run	Solvent(condition)[b)]	Reaction time/h	Yield/%
1	Acetonitrile(homo)	23	83
2	DMF (homo)	19	51
3	Benzene (hetero)	13	79
4	Benzene (hetero)	24	84

a) The reaction conditions are described in the experimental section. b) The reaction mixtures are homogeneous(homo) or heterogeneous(hetero).

We have found that *N*-phenyliminotriphenylphosphorane reacts with benzenediazonium tetrafluoroborate with an elimination of nitrogen to afford wholly aromatic *N,N*-diphenylaminotriphenylphosphonium tetrafluoroborate (Table 1). In polar solvents, such as acetonitrile or DMF, the reaction proceeded homogeneously, while the reaction was heterogeneous in benzene because both the diazonium salt and the phosphonium salt formed are less soluble in the solvent. The reaction, however, occurred readily even in the less polar benzene and the IR and NMR spectra of the products were identical with those of the products obtained in the polar solvents. When the orange-colored aminophosphonium salt was dissolved in methanol together with dimethoxybenzene, the spectrophotometric observation showed no definite evidence for the formation of a charge-transfer complex. The results suggest that the positive charge is not dispersed over the aminophosphonium molecule but, rather, localized on the phosphorus atom.

A few polymers carrying phosphonium structures have been reported,[7,8] whereas a number of anion-exchange resins with ammonium structures are available. Therefore, the above-mentioned reaction was applied in order to introduce the aminophosphonium structure into a polymer: poly(*N*-phenylimino-*p*-styryldiphenylphosphorane (P-1) was converted into a

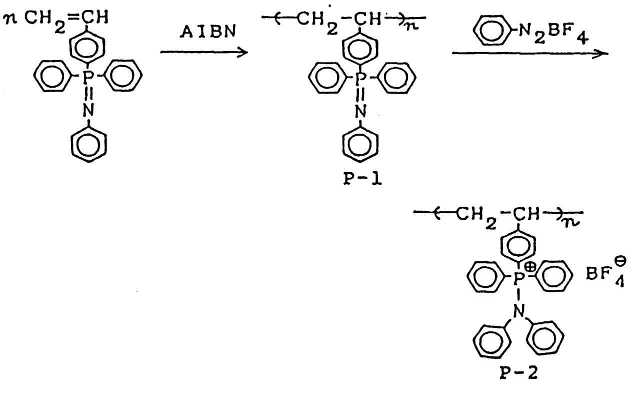

Table 2. Reaction of P-1 with Benzenediazonium Tetrafluoroborate[a)]

Run	Solvent	Temp/°C	Reaction time/h	Conversion/%
1	DMF	40	26	82
2	DMF	60	24	79
3	Benzene	60	24	72
4[b)]	Benzene	60	20	70

a) The reaction conditions are described in the experimental section. b) The concentration of reactants was half compared with that for the other runs.

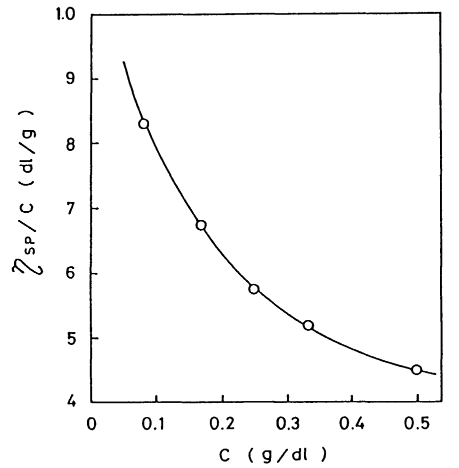

Fig. 1. Solution viscosity of P-2 (Run 3 in Table 2). The viscosity was measured in methanol at 30 °C.

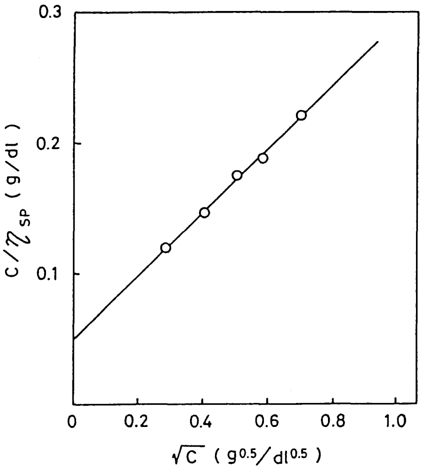

Fig. 2. The Fouss plot of the data of Fig. 1.

polymeric phosphonium salt (P-2) by the reaction with benzenediazonium tetrafluoroborate. The reaction proceeded in less polar benzene as well as in DMF (Table 2). Fig. 1 shows the solution viscosity behavior of P-2 (Run 3 in Table 2), suggesting the characteristic of ionic polymers. The linearity of the Fuoss plot[9] indicates that the physicochemical properties of the polymer are very similar to those of typical ionic polymers (Fig. 2). We previously reported the introduction of the iminophosphorane structure into cross-linked polystyrene beads, which can be utilized to prepare a phosphonium resin whose affinity for anions is different from that of ammonium resins. P-2 is therefore of interest from the viewpoint of chromatografic anion-selectivity.

Experimental

Materials. All reagent grade chemicals were used without further purification. *N*-Phenyliminotriphenylphosphorane and *N*-phenylimino-*p*-styryldiphenylphosphorane were synthesized by the reaction of the corresponding phosphines(*p*-styryldiphenylphosphine was kindly supplied by Hokko Chemical Industry Ltd.) and phenyl azide,[11,12] and freshly prepared benzenediazonium tetrafluoroborate was used.

Diphenylaminotriphenylphosphonium Tetrafluoroborate. Homogeneous Reaction. A solution of benzenediazonium tetrafluoroborate (2 mmol) in acetonitrile (10 ml) was added dropwise to a solution of *N*-phenyliminotriphenylphosphorane (2 mmol) in the solvent (10 ml). The solution turned red with the evolution of nitrogen at room temperature. After the solution was kept at 60 °C for 23 h, the solvent was removed by evaporation and benzene was added to solidify the only residue. The solid product was collected by filtration (yield 83%, Run 1 in Table 1) and was recrystallized from benzene. The IR spectrum of the product was identical with that of the product obtained by the heterogeneous reaction described below.

Heterogeneous Reaction. Benzenediazonium tetrafluoroborate (5 mmol) was added to a solution of *N*-phenyliminotriphenylphosphorane (5 mmol) in benzene (20 ml). The heterogeneous mixture was kept at 60 °C with stirring for 24 h, turning red with evolution of nitrogen. After the reaction mixture was cooled and kept at room temperature for 4 h, the precipitated product was collected (yield 84%, Run 4 in Table 1) and recrystallized from benzene, mp 170 °C. Found: C, 69.4; H, 5.0; N, 3.0; P, 6.2%. Calcd for $C_{30}H_{25}BF_4NP$: C, 69.7; H, 5.0; N, 2.7; P, 6.0%.

Poly(*N*-phenylimino-*p*-styryldiphenylphosphorane)(P-1). *N*-Phenylimino-*p*-styryldiphenylphosphorane (3.2 mmol) was polymerized with α,α'-azobis(isobutyronitrile)(AIBN) (1.6×10^{-5} mol) in benzene (4 ml) at 65 °C for 6 h; the polymer formed was precipitated in methanol and collected by filtration, conversion 71%. Found: C, 82.2; H, 5.8; N, 3.7; P, 8.0%. Calcd for $C_{26}H_{22}NP$: C, 82.3; H, 5.8; N, 3.7; P, 8.2%.

Poly(diphenylamino-*p*-styryldiphenylphosphonium tetrafluoroborate) (P-2). Homogeneous Reaction. A solution of benzenediazonium tetrafluoroborate (1.4 mmol) in DMF (10 ml) was added dropwise to a solution of P-1 (1.4 mmol, based on the monomer unit) in the solvent (10 ml). The evolution of nitrogen was observed and the solution turned red at room temperaure as in the case of monomeric compounds described above. After the solution was kept at 60 °C for 24 h, the phosphonium polymer formed was precipitated in a large excess of ether. The conversion into the phosphonium structure in P-2 was determined on the basis of a conductometric titration with silver nitrate in DMF-H_2O (9 : 1): 79% (Run 2 in Table 2).

Heterogeneous Reaction. Benzenediazonium tetrafluoroborate (1.4 mmol) was added to a solution of P-1 (1.4 mmol, based on the monomer unit) in benzene (10 ml). The heterogeneous mixture was kept at 60 °C for 24 h, turning red with evolution of nitrogen. After the reaction mixture was cooled to room temperature, the precipitated polymer was filtered and purified by reprecipitation from DMF/ether, conversion 72% (Run 3 in Table 2).

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