Reaction of *O,O*-Dialkyl Dithiophosphoric Acid. III.[1] Reductive Cleavage Reactions of Nitrogen-Nitrogen Bond by *O,O*-Diethyl Dithiophosphoric Acid

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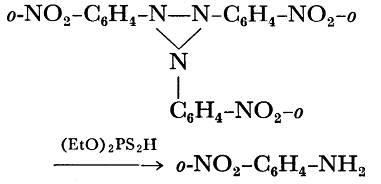
o-Nitroaniline was obtained when tri(*o*-nitrophenyl) triaziridine(I) was allowed to react with excess *O,O*-diethyl dithiophosphoric acid. It was found that azobenzene derivatives(IIa-e) are converted into the corresponding reduction products aniline derivatives(IVa-e) in the reaction with excess *O,O*-diethyl dithiophosphoric acid. Similarly, arylhydrazines (IIIa-c) were converted into the corresponding aniline derivatives (IVa,d,e) by the action of *O,O*-diethyl dithiophosphoric acid.

In a previous paper,[1] we reported on the reactions between *O,O*-dialkyl dithiophosphoric acid and various compounds having a semipolar linkage. Meanwhile, we have found that compounds having a less polarized nitrogen-nitrogen linkage or none at all, such as tri-(*o*-nitrophenyl)triaziridine(I), azobenzene(IIa—e), and arylhydrazine(IIIa—c), also readily react with *O,O*-diethyl dithiophosphoric acid to afford the corresponding reduction products. The reduction of tri(*o*-nitrophenyl)triaziridine(I) to *o*-nitroaniline, and the formation of *o*-nitroaniline from I appear to support the structure of I to be of triaziridine ring. The reduction of IIa—e to anilines and benzidine in the reaction with *O,O*-diethyl dithiophosphoric acid is also interesting, since there has been no report that azobenzene is reduced by organic reducing agents. Meanwhile in the N–N bond cleavage reaction of IIIa—c with *O,O*-diethyl dithiophosphoric acid, nucleophilic substitution on the nitrogen atom (Chart 3) appears to take place to afford anilines (IVa,d,e). This is one of only a few known examples of nucleophilic substitution on the nitrogen atom. This paper gives a detailed account of the N–N bond cleavage reaction with an acidic mercaptan, *O,O*-diethyl dithiophosphoric acid ($\mathrm{p}K_a=1.62$[3]).

Results and Discussion

*Reaction of Tri(*o*-nitrophenyl)triaziridine(I) with (EtO)$_2$PS$_2$H.* Recently, tri(*o*-nitrophenyl)triaziridine(I), a remarkably stable derivative of the triaziridine ring system,[4,5] has been prepared by the thermolysis of *o*-nitrophenyliminopyridinium betaine.[6] However, catalytic hydrogenation of I over PtO_2 or the reduction of I with Zn/AcOH afforded *o*-phenylenediamine,[6] *viz.*, both the nitro group and triaziridine ring were similtaneously reduced. The reaction of I with a large excess of $(EtO)_2PS_2H$ at 80°C for 24 hr[7] gave *o*-nitroaniline in a 12% yield and unreacted I (70%) as shown by Eq. (1). Thus $(EtO)_2PS_2H$ is the first selective reducing agent which cleaves the N–N bond of aziridine ring without reducing *o*-nitro group. This strongly suggests the structure of I to be of a three-membered triaziridine ring. Although we could neither detect nor isolate any such intermediate as 2,2′-dinitroazobenzene, the reduction pathway undoubtedly involves the cleavage of azo (–N=N–) and/or hydrazo (–NH–NH–) linkages. We therefore allowed azobenzene derivatives to react with $(EtO)_2PS_2H$ and found the reaction to proceed more easily than I. The conversion of I into *o*-nitroaniline is considered to follow the scheme shown in Chart 1. The initial step of the reaction between I and $(EtO)_2PS_2H$



(1)

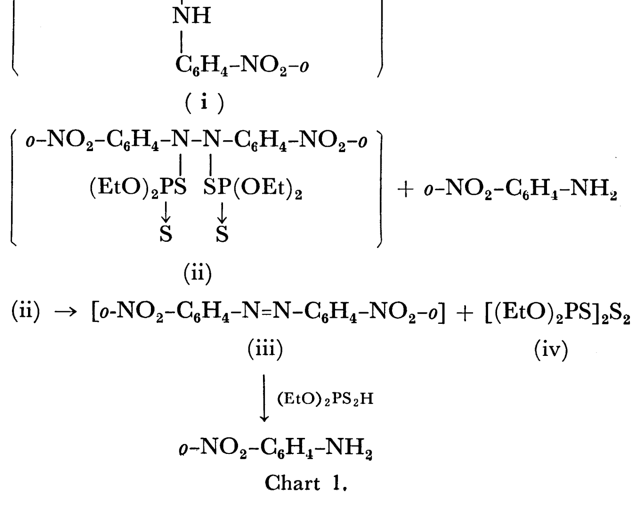


Chart 1.

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[1] Part II; S. Oae, A. Nakanishi, and N. Tsujimoto, *Tetrahedron*, **28**, 2981 (1972).

[2] Present Address: Faculty of Pharmaceutical Sciences, Osaka University, Toneyama, Toyonaka, Osaka.

[3] M. I. Kabachnik, S. T. Ioffe, and T. A. Mastryukova, *J. Gen. Chem. U.S.S.R.*, **25**, 653 (1955); *Chem. Abstr.*, **50**, 3850i (1956).

[4] M. Colonna and A. Risalti, *Gazz. Chim. Ital.*, **41**, 204 (1961).

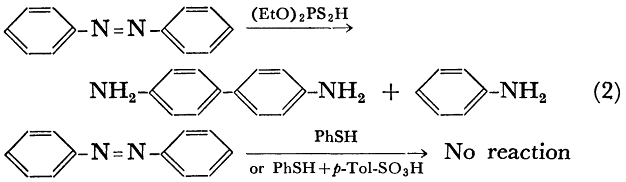
[5] M. S. Gibson, *Tetrahedron*, **18**, 1377 (1962).

[6] Y. Tamura, N. Tsujimoto, M. Ikeda, and K. Tomita, Abstracts of the Third International Congress of Heterocyclic Chemistry, Tohoku University, Sendai, Japan, 1971, p. 252.

[7] I did not react with conc. H_2SO_4 or thiophenol and was then recovered.

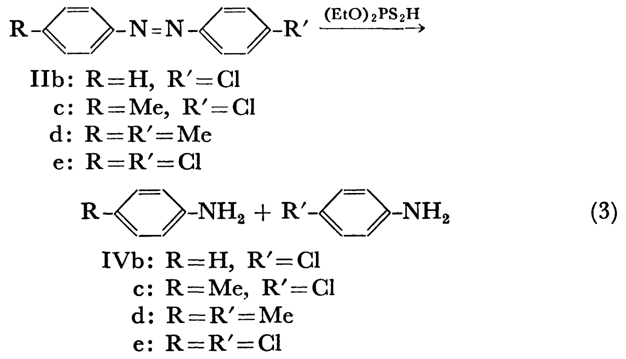
would be the formation of an intermediate(i), which reacts further with another mole of $(EtO)_2PS_2H$ to afford an intermediate(ii) and *o*-nitroaniline. (ii) then immediately changes to azobenzene(iii) and bis-[*O*,*O*-diethyl thiophosphoryl]disulfide(iv). (iii) is readily reduced to *o*-nitroaniline by $(EtO)_2PS_2H$ under the reaction conditions.

Reaction of Azobenzene(IIa—e) with (EtO)$_2$PS$_2$H. As anticipated 2,2'-dinitroazobenzene(iii) can be reduced smoothly with $(EtO)_2PS_2H$ to *o*-nitroaniline. It is well-known that azobenzene is reduced to the corresponding reduction product by treatment with such inorganic reducing agents as $Na_2S_2O_4$,[8] NH_2-$NH_2 \cdot H_2O/Cu$,[9] or HCl/Zn.[10] However, it is not known that azobenzene is reduced to aniline in the reaction with any organic reducing agent, such as acidic mercaptans. Actually the reaction between azobenzene(IIa) (1 mol) and $(EtO)_2PS_2H$ (10 mol) at 70°C for 24 hr gave benzidine and aniline (IVa) in the yields of 27% and 40%, respectively [Eq. (2)]. Since no reaction takes place when azobenzene is treated with a large excess of thiophenol either in the presence or absence of *p*-Tol-SO_3H, the reduction of azobenzene with $(EtO)_2PS_2H$ is caused by the inherently-built-in high acidity and nucleophilicity of the dithiophosphoric acid.



(2)

The reaction with $(EtO)_2PS_2H$ was successfully applied to the reduction of a few substituted azobenzene derivatives (IIb—e) [Eq. (3)]. The results are listed in Table 1. In an attempt to trap an intermediate of this reaction an equimolar mixture of IIa and *O*,*O*-diethyl dithiophosphoric acid was kept at 0°C for 24 hr, and then 10% benzidine and 38% recovered IIa were obtained. Thus, neither intermediate nor aniline (IVa), a reduction product of azobenzene, could be obtained. However, benzidine and IVa are presumed to be formed *via* an initial formation of hydrazobenzene(Va) or its derivative. We therefore allowed Va to react with *O*,*O*-diethyl dithiophosphoric acid. The results are summarized in Table 2.



(3)

TABLE 1. YIELD OF ANILINE DERIVATIVES (IVb-e) BY TREATMENT OF AZOBENZENE DERIVATIVES (IIb-e) WITH EXCESS *O*,*O*-DIETHYL DITHIOPHOSPHORIC ACID AT 70°C

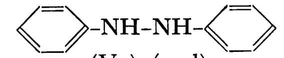
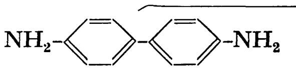
Aniline deriv.	Yield (%)
IVb	23[a]
IVc	50[b]
IVd	63
IVe	93

a) Yield was a mixture of aniline and 4-chloroaniline.
b) Yield was a mixture of 4-methylaniline and 4-chloroaniline.

A mixture of hydrazobenzene(Va) (1 mol) and excess *O*,*O*-diethyl dithiophosphoric acid was heated at 70°C for 24 hr. As in the case of IIa, benzidine and IVa were obtained in the 50% and 32% yields, respectively. IIa was obtained when less than two moles of $(EtO)_2PS_2H$ was used. In order to understand the process of formation of IIa, 4,4'-dichlorohydrazobenzene(Vb) (1 mol) was treated with $(EtO)_2$-PS_2H (1 mol); 4,4'-dichloroazobenzene(IIe) (50%) and 4-chloroaniline(IVe) (50%) were obtained. When $(EtO)_2PS_2H$ was used as an acid catalyst, the same reaction occurred (Table 3). This is in line with the observation[10] that in acid catalysis one molecule of hydrazo compound becomes oxidized to the azo compound, while another is reduced to two molecules of amine.

As regards the reaction mechanism for the conversion of IIa into benzidine and IVa, the sequence of reactions shown in Chart 2 is conceivable. The initial step of the reaction between II and *O*,*O*-diethyl dithiophosphoric acid would be the formation of an intermediate(v) similar to that[11] between azobenzene and an arenesulfinic acid which has also a similar pK_a

TABLE 2. REACTION OF HYDRAZOBENZENE(Va) WITH *O*,*O*-DIETHYL DITHIOPHOSPHORIC ACID AT 70°C

 (Va) (mol)	$(EtO)_2PS_2H$ (mol)	Yield of product (%)			
			(IVa)	(IIa)	Recov. (Va)
1	10	50	32	—	—
1	1	17	10	30	—
1[a]	1	10	9	37	7

a) The reaction mixture was kept at room temperature.

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[8] L. F. Fieser, "Organic Syntheses," Coll. Vol. II, p. 39 (1950).

[9] H. Kubota, T. Akita, and T. Yokojima, *Yakugaku Zasshi*, **78**, 1194 (1958).

[10] H. J. Shine, "Mechanism of Molecular Migrations," ed. by B. S. Thyagarajan, Vol. 2, p. 191, Interscience, New York (1969).

[11] W. Bradley and J. D. Hannon, *J. Chem. Soc.*, **1962**, 2713.

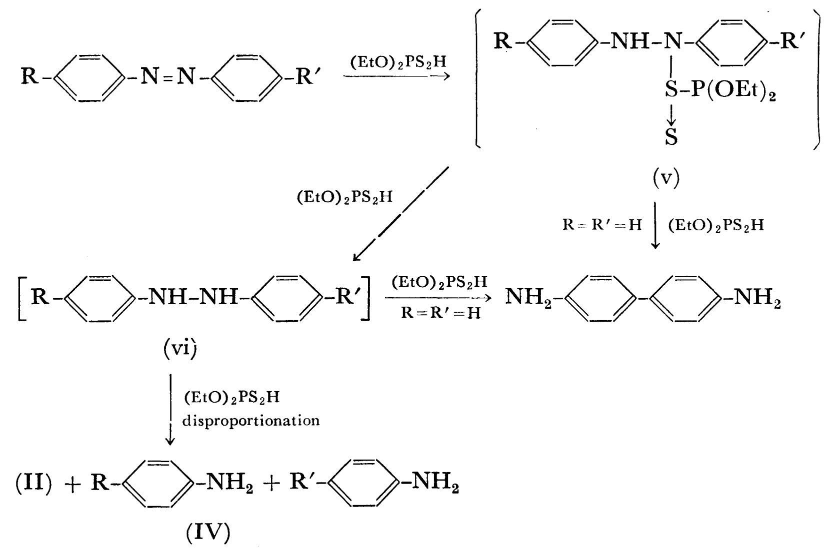

Chart 2.

Table 3. Reaction of 4,4′-dichlorohydrazobenzene(Vb) with *O,O*-diethyl dithiophosphosphoric acid at room temperature[a]

$(EtO)_2PS_2H$ (mol)	(Vb) (mol)	Reaction time	Yield (%) of product (IIe)	Yield (%) of product (IVe)
1	1	24 hr	50	50
0.2	1	7 day	50	50

a) An equimolar mixture of 4-chloro-4′-methylhydrazobenzene(Vc) and *O,O*-diethyl dithiophosphoric acid gave IIc(50%), IVc(25%), and IVe(25%). There was no cross-over of amine group between 4-chloroaniline and 4-methylaniline during the course of reaction.

Table 4. Reaction of arylhydrazine(IIIc) with *O,O*-diethyl dithiophosphoric acid

Hydrazine deriv.	Yield (%) of an-line deriv.
IIIa	51
IIIb	65
IIIc	60

value 1—1.5.[12] Then the intermediate(v), upon reaction with another mole of $(EtO)_2PS_2H$, gives benzidine or hydrazobenzene derivatives(vi), which, however, could not be isolated. Hydrazobenzene (vi) would either be reduced with $(EtO)_2PS_2H$ to aniline or rearrange to benzidine or undergo acid catalyzed disproportionation[10] to give II and IV.

Reaction of Arylhydrazine (IIIa—c) with $(EtO)_2PS_2H$. Since hydrazobenzene was found to be cleaved readily by $(EtO)_2PS_2H$, we applied this procedure for the N–N bond cleavage of arylhydrazine(IIIa—c). When a mixture of phenylhydrazine(IIIa) (1 mol) and $(EtO)_2PS_2H$ (10 mol) was heated at 70°C for 24 hr, aniline (IVa) was obtained in a 51% yield. In an alternative procedure to prepare IVa, an equimolar mixture of IIIa and $(EtO)_2PS_2H$ in ether was kept at room temperature to give hygroscopic phenylhydrazinium *O,O*-diethyl dithiophosphate (viia). The structure of viia was identified by NMR and IR spectra (Tables 5,6). The salt (VIIa) was then heated under refluxing in benzene to yield IVa. Similarly, other arylhydrazines (IIIb, c) were also reduced to the corresponding aniline derivatives (IVd, e), as listed in Table 4. These reactions are assumed to proceed *via* the formation of an intermediate salt (vii) prior to the formation of the reduction product VI and *S*-amino-*O,O*-diethyl dithiophosphate (VIII). Compound (VIII) is so unstable that, upon being kept standing, it is converted into bis[*O,O*-diethyl thiophosphoryl]disulfide (VI).[1]

These reduction reactions of azobenzenes (IIa—e) and arylhydrazines (IIIa—c) with *O,O*-diethyl dithiophosphoric acid are interesting examples of nucleophilic substitution on the nitrogen atom.

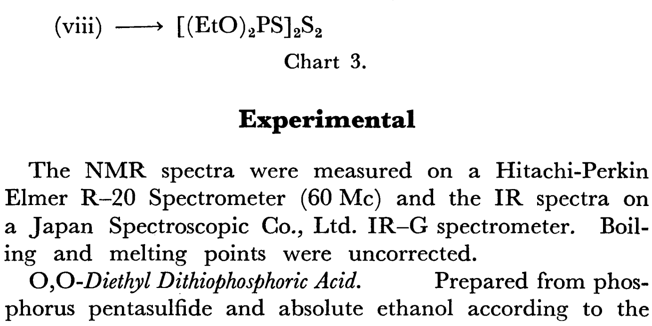

Chart 3.

Experimental

The NMR spectra were measured on a Hitachi-Perkin Elmer R–20 Spectrometer (60 Mc) and the IR spectra on a Japan Spectroscopic Co., Ltd. IR–G spectrometer. Boiling and melting points were uncorrected.

O,O-Diethyl Dithiophosphoric Acid. Prepared from phosphorus pentasulfide and absolute ethanol according to the procedure of Kabachnik and Mastryukova,[13] bp 64—66°C/

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[12] P. Rumph and J. Sadet, *Bull. Soc. Chim. Fr.*, **1958**, 450.

[13] M. I. Kabachnik and T. A. Mastryukova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 121 (1953); *Chem. Abstr.*, **48**, 3244e (1954).

2 mmHg(lit,[13] bp 81.5—82.5°C/5 mmHg).

Tri(o-nitrophenyl)triaziridine. Prepared from the thermolysis of *N-o*-nitrophenyliminopyridinium betaine at 140—150°C,[6] mp 132—133°C(lit,[6] mp 132—133°C).

Azobenzene(IIa). Prepared by the usual method,[14] mp 66—67°C (lit,[14] mp 66—67.5°C from ethanol).

4-*Chloroazobenzene(IIb).* Prepared from azoxybenzene and phosphorus trichloride according to the procedure of Vozza,[15] mp 89°C from ethanol (lit,[15] mp 87—88°C).

4,4′-*Disubstituted Azobenzene(IIc-e).* Prepared from the reaction between zinc chloride double salt of *p*-substituted benzene diazonium chloride and the corresponding Grignard reagent according to the procedure of Nomura.[16]

4-Chloro-4′-methylazobenzene(IIc), mp 152—153°C (lit,[17] mp 153°C)

4,4′-Dimethylazobenzene(IId), mp 140—141°C (lit,[18] 140—141°C)

4,4′-Dichloroazobenzene(IIe), mp 177—178°C (lit,[18] mp 177—178°C)

Hydrazobenzene(Va-c). Prepared from the corresponding azobenzene using 80% hydrazine hydrate and copper powder according to the procedure of Kubota, *et al.*[9]

Hydrazobenzene(Va), mp 124—126°C(lit,[19] mp 126°C)

4,4′-Dichlorohydrazobenzene(Vb), mp 123—124°C(lit,[19] mp 124°C)

4-Chloro-4′-methylhydrazobenzene(Vc), mp 123—124°C (lit,[17] mp 124°C)

Aryhydrazine(IIIa-c). Pure arylhydrazines were obtained by either distillation or recrystallization of commercial compounds.

Phenylhydrazine(IIIa), bp 140°C/20 mmHg(lit,[20] bp 137—138°C/18 mmHg)

4-Methylphenylhydrazine(IIIb), mp 64—66°C(lit,[21] mp 65—66°C)

4-Chlorophenylhydrazine(IIIc), mp 88—89°C(lit,[22] mp 88°C)

Reaction of Tri(o-nitrophenyl)triaziridine with $(EtO_2)PS_2H$. Tri(*o*-nitrophenyl)triaziridine(500 mg) was reacted with 5 g of $(EtO)_2PS_2H$ at 80°C. After 24 hr aqueous Na_2CO_3 was added to this reaction mixture of remove excess $(EtO)_2PS_2H$. The reaction products were extracted with $CHCl_3$ from *aq.* Na_2CO_3 solution, and then chromatographed(silica gel column) with benzene-hexane(1 : 1) to give bis[*O,O*-diethyl thiophosphoryl] disulfide, 90 mg of *o*-nitroaniline(12%), and 560 mg of recovered tri(*o*-nitrophenyl)triaziridine(70%).

Reaction of Azobenzene(IIa) with Excess $(EtO)_2PS_2H$. A mixture of IIa(1.82 g, 0.01 mol) and $(EtO)_2PS_2H$(18.6 g, 0.1 mol) was heated at 70°C for 24 hr. Excess Na_2CO_3 was added to the reaction mixture and the product was extracted with benzene. After removal of benzene at atmospheric pressure, the residue was chromatographed through a silica gel column with $CHCl_3$ as an eluent to give benzidine, 0.40 g, 27%, mp 113—115°C (lit,[23] mp 115—120°C) and aniline(IVa), 0.74 g, 40%. These compounds were identified by comparing their IR spectra and melting points with those of the corresponding authentic samples. In this reaction small amounts of three other unidentified liquids were also obtained.

Reaction of Azobenzene Derivatives(IIb-c) with excess $(EtO)_2PS_2H$. A mixture of IIb-e(0.01 mol) and $(EtO)_2PS_2H$-(0.1 mol) was heated at 70°C until the reaction mixture changed in to a clear solution. The mixture was treated with excess Na_2CO_3 and extracted with benzene. The benzene solution was extracted with 10% aqueous HCl and the aqueous layer was concentrated under reduced pressure to obtain HCl salts of aniline derivatives (IVb-e). A small amount of water was added to the crude salts of IVb-e and neutralized with Na_2CO_3 and then extracted with benzene. The benzene layer was dried over $MgSO_4$ and concentrated under atmospheric pressure to give aniline derivatives(IVb-e), which were found to be identical with the authentic samples in melting points and IR spectra. The amounts of IVb and IVc were estimated by comparison with the mixture of authentic samples. The yields are summarized in Table 1.

Reaction of an Equimolar Mixture of Azobenzene(IIa) and $(EtO)_2PS_2H$. To a solution of IIa(1.82 g, 0.01 mol) in ether(5 ml) was added dropwise a solution of $(EtO)_2PS_2H$ (1.86 g, 0.01 mol). The mixture was allowed to stand at 0°C overnight. The white precipitates were collected and washed thoroughly with ether to give crude *O,O*-diethyl dithiophosphate of benzidine. The crude salt of benzidine was neutralized with aqueous Na_2CO_3 and then extracted with benzene. The benzene solution was dried over $MgSO_4$ and upon removal of the benzene benzidine, 0.19 g, 10%, mp 113—116°C(lit,[23] mp 115—120°C), was obtained. The ether filtrate was concentrated to give orange crystals, which were recrystallized from ethanol to give recovered azobenzene, 0.7 g, 38%, mp 64—66°C(lit,[14] mp 66—67.5°C).

Reaction of Hydrazobenzene(Va) with Excess $(EtO)_2PS_2H$. A mixture of Va(1.84 g, 0.01 mol) and $(EtO_2)PS_2H$(18.6 g, 0.1 mol) was heated at 70°C for 24 hr. Excess Na_2CO_3 was added to the reaction mixture and the mixture was extracted with benzene. After removal of the benzene at atmospheric pressure, the residue was chromatographed through a silica gel column with $CHCl_3$ as an eluent to give benzidine, 0.92 g, 50%, mp 113—116°C(lit,[23] mp 115—120°C) and aniline(IVa)(0.60 g, 31%), which were found to be identical with the corresponding compounds.

Reaction of an Equimolar Mixture of Hydrazobenzene (Va) and $(EtO)_2PS_2H$ *at 70°C.* To a solution of Va(1.84 g, 0.01 mol) in ether (5 ml) was added dropwise a solution of $(EtO)_2PS_2H$ (1.86 g, 0.01 mol). The mixture was heated at 70°C overnight. The white mass was collected and washed thoroughly with ether to give crude *O,O*-diethyl dithiophosphate of benzidine. The crude salt of benzidine was neutralized with aqueous Na_2CO_3 and then extracted with benzene. The benzene solution was dried with $MgSO_4$ and the benzene was removed to give benzidine, 0.32 g, 17%, mp 112—116°C(lit,[23] 115—120°C). The ether filtrate was concentrated to give an orange residue. The residue was chromatographed through a silica gel column with $CHCl_3$ as an eluent to give aniline(0.19 g, 10%) and azobenzene (IIa), 0.55 g, 30%, mp 65°C(lit,[14] mp 66—67.5°C).

Reaction of an Equimolar mixture of Hydrazobenzene(Va) and $(EtO)_2PS_2H$ *at 0°C.* To a solution of Va(1.84 g, 0.01 mole) in ether (5 ml) was added dropwise a solution of $(EtO)_2PS_2H$ (1.86 g, 0.01 mol). The mixture was allowed to stand at 0°C overnight. Treatment of the reaction mixture in a manner similar to that described above gave benzidine (0.18 g, 10%), mp 112—116°C(lit,[23] mp 115—120°C),

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[14] H. E. Bigelow and D. B. Robinson, "Organic Syntheses," Coll. Vol. III, p. 103 (1955).

[15] J. F. Vozza, *J. Org. Chem.*, **34**, 3219 (1969).

[16] Y. Nomura, This Bulletin, **34**, 1648 (1961).

[17] H. Wieland, *Ber.*, 48, 1110 (1915).

[18] K. Nakagawa and T. Tsuji, *Chem. Pharm. Bull.*, **11**, 296 (1963).

[19] P. Grammatcakis, *Bull. Soc. Chem. Fr.*, 951 (1951).

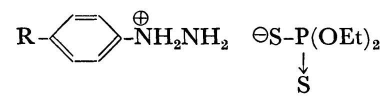
[20] G. H. Goleman, "Organic Syntheses," Coll. Vol. 1, p. 442 (1941).

[21] E. Fisher, *Ber.*, **9**, 890 (1876).

[22] H. Voswinckel, *ibid.*, **34**, 2351 (1901).

[23] N. Zinin, *Ann.*, **137**, 376 (1866).

TABLE 5. NMR SPECTRA OF ARYLHYDRAZINIUM *O,O*-DIETHYL DITHIOPHOSPHATE



Comp.	Chemical shift (in $CDCl_3$ from ext. TMS, ppm)				Coupling constant (Hz)		
	Ethyl group		Amine-H	Aromatic-H	Methyl group	$J_{CH_3-CH_2-}$	J_{CH_2-O-P}
IIIa	1.15 (6H, t)	4.00 (4H, q, d)	8.15 (4H, s)	7.20—7.40 (5H, m)	—	7	11
IIIb	1.31 (6H, t)	4.12 (4H, q, d)	8.36 (4H, m)	7.20—7.25 (4H, m)	2.41	7	11
IIIc	1.20 (6H, t)	3.98 (4H, q, d)	8.60 (4H, s)	7.18—7.40 (4H, m)	—	7	11

aniline(IVa) (0.18 g, 9%), and azobenzene(IIa), 0.67 g, 37%, mp 65°C(lit.[14] mp 66—67.5°C) while recovering hydrazobenzene(Va), 0.13 g, 7%, mp 123—126°C(lit,[19] mp 126°C).

Reaction of an Equilimolar Mixture of 4,4′-Dichlorohydrazobenzene (Vb) and $(EtO)_2PS_2H$. To a solution of Vb (2.52 g, 0.01 mole) in ether (10 ml) was added dropwise a solution of $(EtO)_2PS_2H$(1.86 g, 0.01 mol). The mixture was allowed to stand at room temperature for 24 hr, and the ether was removed to give crystals which were then washed with ethanol to give 4,4′-dichloroazobenzene(IIe), 1.25 g, 50% mp 176—177.5°C (lit,[18] mp 177—178°C). The ethanol filtrate was condensed and neutralized with aqueous Na_2CO_3 and then extracted with benzene. After removal of the benzene at atmospheric pressure, the residue was recrystallized from ether to give 4-chloroaniline(IVe), 1.27 g, 50%, 71—72°C (lit,[24] mp 72.5°C).

Reaction of 4,4′-Dichlorohydrazobenzene(Vb) with $(EtO)_2PS_2H$ *as Acid Catalysis.* To a solution of Vb(2.52 g, 0.01 mol) in ether(10 ml) was added dropwise a solution of $(EtO)_2PS_2H$(0.37 g, 0.002 mol). The reaction mixture was allowed to stand at room temperature for 7 days. Treatment of the reaction mixture in a manner similar to that described above gave 4,4′-dichloroazobenzene(IIe) (1.25 g, 50%) and 4-chloroaniline(IVe) (1.27 g, 50%), which were identical with the corresponding authentic samples.

Equimolar Reactions between 4-Chloro-4′-methylhydrazobenzene (Vc) and $(EtO)_2PS_2H$. To a solution of Vc (2.32 g, 0.01 mol) in ether(10 ml) was added dropwise an etheral solution of $(EtO)_2PS_2H$(1.86 g, 0.01 mol). The mixture was allowed to stand at room temperature for 24 hr. Ether was removed to give orange crystals. The crystals were washed with ethanol to give 4-chloro-4′-methylazobenzene (IIc) (1.15 g, 50%), mp 152—153°C(lit,[17] mp 153°C). There is no crossover of aniline group between 4-chloroaniline and 4-methylaniline during the course of reaction. The ethanol filtrate was condensed and neutralized with aquoeus Na_2CO_3 and then extracted with benzene. After removal of the benzene at atmospheric pressure, the residue containing 4-chloroaniline and 4-methylaniline was determined spectrometrically.

TABLE 6. IR SPECTRA OF ARYLHYDRAZINIUM *O,O*-DIETHYL DITHIOPHOSPHATE

Comp.	ν_{max}^{KBr} (cm^{-1})					
IIIa	3250,	1025,	1010,	940,	920,	680
IIIb	3220,	1030,	1015,	940,	680,	660
IIIc	3250,	1020,	1005,	940,	900,	660

General Procedure for the Reaction of Arylhydrazine(IIIa-c) with Excess $(EtO)_2PS_2H$. A mixture of IIIa–c(0.01 mol) and $(EtO)_2PS_2H$(0.01 mol) was heated at 70°C until the reaction mixture changed into a clear solution. The mixture was treated with excess Na_2CO_3 and extracted with benzene. The benzene solution was extracted with 10% aqueous HCl and dried over $MgSO_4$ and then condensed to give a colorless oil(1.5—2.0 g), which was identical with the authentic sample, bis[*O,O*-diethyl thiophosphory]disulfide.[25] Aqueous HCl solution (10%) was concentrated under reduced pressure to give HCl salt of aniline derivatives (IVa, d, e). A small amount of water was added to the crude salts of IVa,d,e and neutralized with Na_2CO_3 and then extracted with benzene. The benzene solution was dried over $MgSO_4$. Removal of benzene gave aniline derivatives (IVa,d,e). The yields of IVa,d,e are given in Table 4.

Reaction of an Equimolar of Arylhydrazine(IIIa–c) and $(EtO)_2PS_2H$. To a solution of IIIa–c(0.01 mol) in ether(10—50 ml) was added dropwise an ether solution of $(EtO)_2PS_2H$(0.01 mol). The mixture was allowed to stand at room temperature for several hours. The precipitates were collected and recrystallized from ether to give arylhydrazinium *O,O*-diethyl dithiophosphate quantitatively. These products were hygroscopic white needles and identified by their NMR and IR spectra listed in Table 5 and 6. A solution of arylhydrazinium *O,O*-diethyl dithiophosphates in benzene was heated under refluxing for 1—2 days. After removal of the benzene at atmospheric pressure, the residue was distilled or recrystallized to give aniline derivatives (IVa,d,e) (50—70% yield).

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