TABLE I

p-PHENYLENEDIAMINE ADDITION COMPOUNDS[3]

-Nitrostyrene	Appearance	M. p., °C.	Formula	Analyses, % Calcd. C	H	Found C	H
2-Nitro	Brownish-red plates	147	$C_{22}H_{20}N_6O_8$	53.2	4.0	53.5	4.4
3-Nitro	Red microscopic cryst.	168	$C_{22}H_{20}N_6O_8$	53.2	4.0	52.9	4.3
4-Nitro	Yellow microsc. cryst.	172	$C_{22}H_{20}N_6O_8$	53.2	4.0	53.1	4.2
2-Methoxy-4-nitro	Orange plates	157–158	$C_{24}H_{24}N_6O_{10}$	51.8	4.3	52.1	4.2
2-Nitro-4-chloro	Golden plates	156–157	$C_{22}H_{18}Cl_2N_6O_8$	46.7	3.2	46.4	3.5

with concd. hydrochloric acid caused disappearance of color. The white microscopic crystals of the salt that promptly appeared were analyzed in one instance (3-nitro derivative) and found to agree with the calculated value.

α-Nitro-β-(*p*-toluidino)-β-(2-nitro-4-chlorophenyl)-ethane.—Obtained in the customary manner it crystallized from alcohol in the form of brownish-yellow plates, m. p. 136–137°, dec. It was observed to form a hydrochloric acid salt.

Anal. Calcd. for $C_{15}H_{14}ClN_3O_4$: C, 53.4; H, 4.2. Found: C, 53.1; H, 4.1.

No reaction was observed between toluidine and the other nitrostyrenes reacting with *p*-phenylenediamine. Negative results with both *p*-toluidine and *p*-phenylenediamine followed attempts at addition with the following: 2-methoxy, 4-methoxy, 2-nitro-4-methoxy, 2,4-dimethoxy, 2,4-dimethoxy-6-nitro, 3-methoxy-4-hydroxy, 3,4-oxymethylene and 4-chloronitrostyrenes. Furfurylidene also was without action.

Summary

p-Phenylenediamine forms addition compounds with the three mononitro, 2-methoxy-4-nitro and 2-nitro-4-chloronitrostyrenes. *p*-Toluidine acts similarly with 2-nitro-4-chloronitrostyrene. Neither substance reacts with other nitrostyrenes prepared from the common aldehydes.

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[3] In naming these substances they may be regarded as substituted phenyl derivatives of N,N′-[(α,α-diphenyl)-β,β′-dinitrodiethyl]-*p*-phenylenediamine.

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

The Action of Aromatic Amines on 4-Nitro-2-chloronitrostyrene

BY DAVID E. WORRALL

In a recent investigation relating to the additive capacity of substituted nitrostyrenes,[1] it was disclosed that the 2-nitro-4-chloro derivative represented an unusually active combination as measured by *p*-toluidine and *p*-phenylenediamine. The isomeric 2-chloro-4-nitro compound (II) has been found to be much more reactive, so the present communication is concerned with a study of this capacity toward a variety of organic bases containing mobile hydrogen.

II is decidedly more reactive in some respects than nitrostyrene itself. It forms, for example, addition compounds with *o*- and *m*-toluidines as well as *p*-anisidine. On the other hand, it does not react, at least under similar experimental conditions, with aniline or β-naphthylhydrazine, both of which add to nitrostyrene. It is believed that the failure to obtain similar compounds with II is the consequence of an increased tendency for destructive oxidation–reduction reactions originating in the nitro groups. This also explains the formation of black tars when II is heated with hydrazine or hydroxylamine and the rapid destruction of the ammonia addition product by alcohol.

Experimental

α-Nitro-β-(2-chlorophenyl)-ethylene (I).—Obtained by the action of triethylamine[2] it crystallized from alcohol as long yellow needles, m. p. 48°.

Anal. Calcd. for $C_8H_6ClNO_2$: C, 52.3; H, 3.3. Found: C, 52.1; H, 3.5.

α-Nitro-β-(2-chloro-4-nitrophenyl)-ethylene (II).—The product from the nitration of 10 g. of I separated from alcohol in the form of slender pale yellow needles, m. p. 149–150°, yield 7.5 g.

Anal. Calcd. for $C_8H_5ClN_2O_4$: C, 42.0; H, 2.2. Found: C, 41.9; H, 2.5.

α-Bromo-α-nitro-β-(2-chloro-4-nitrophenyl)-ethylene (III).—Five grams of II after bromination was treated with alcoholic potassium acetate producing after crystallization from alcohol 3.5 g. of yellow prismatic needles, m. p. 132–133°.

Anal. Calcd. for $C_8H_4BrClN_2O_4$: C, 31.2; H, 1.3. Found: C, 31.1; H, 1.6.

In a similar manner I was changed into the monobromo derivative, yellow needles melting at 60–61°.

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[1] Worrall and Benington, THIS JOURNAL, **60**, 2844 (1938).

[2] Worrall, THIS JOURNAL, **56**, 1556 (1934). No polymer formation observed.

TABLE I

β-DERIVATIVES OF α-NITRO-β-(2-CHLORO-4-NITROPHENYL)-ETHANE

Substance	Formula	Cryst. form	M. p., °C.	Analyses, %			
				Calcd.		Found	
				C	H	C	H
o-Toluidino	$C_{15}H_{14}ClN_3O_4$	Golden narrow plates	117–118	53.6	4.2	53.7	4.3
m-Toluidino	$C_{15}H_{14}ClN_3O_4$	Golden narrow plates	127–128	53.6	4.2	54.1	4.4
p-Toluidino	$C_{15}H_{14}ClN_3O_4$	Golden narrow plates	130–131	53.6	4.2	54.0	4.5
p-Anisidino	$C_{15}H_{14}ClN_3O_5$	Yellow plates	88–89	51.2	4.0	50.8	4.1
Phenylhydrazino	$C_{14}H_{13}ClN_4O_4$	Orange prisms	133–134	49.9	3.9	49.6	4.0
p-Tolylhydrazino	$C_{15}H_{15}ClN_4O_4$	Golden plates	127–128	51.3	4.3	51.3	4.5
DERIVATIVES OF (α,α'-DI-(2-CHLORO-4-NITROPHENYL)-β,β'-DINITRODIETHYL)							
Ammonia	$C_{16}H_{13}Cl_2N_5O_8$	Pale yellow narrow plates	118–119	40.5	2.8	40.4	3.1
p-Phenylenediamine	$C_{22}H_{18}Cl_2N_6O_8$	Brownish-yellow platelets	201–202	46.7	3.2	46.9	3.5
Benzidine	$C_{28}H_{22}Cl_2N_6O_8$	Yellow microscopic	137–138	52.4	3.4	52.7	3.6

Anal. Calcd. for $C_8H_5BrClNO_2$: C, 36.6; H, 1.9. Found: C, 37.0; H, 2.2.

N,N'-(α,α'-Di-(2-chlorophenyl)-β,β'-dinitrodiethyl)-*p*-phenylenediamine.—*p*-Phenylenediamine, but not *p*-toluidine, formed an addition compound with I, separating from an alcohol solution of the components as irregular yellow plates melting with decomposition at 147–148°.

Anal. Calcd. for $C_{22}H_{20}Cl_2N_4O_4$: C, 55.6; H, 4.2. Found: C, 56.1; H, 4.5.

α-Bromo-α-nitro-β-(2-chloro-4-nitrophenyl)-β-*p*-toluidino-ethane.—III reacted in alcohol with *p*-toluidine producing gold yellow platelets, m. p. 138°, dec. A slight odor of monobromonitromethane was noticed.

Anal. Calcd. for $C_{15}H_{13}BrClN_3O_4$: C, 44.3; H, 3.1. Found: C, 43.5; H, 3.3.

No addition reactions were observed with aniline or *m*-toluidine, but *p*-phenylenediamine produced tiny brownish needles. This material which melted indefinitely with marked decomposition gave a poor analysis and was not examined further.

A uniform procedure was used with II. Five-tenths gram of the nitro compound was weighed out carefully, together with the equivalent amount of the base and a few cc. of alcohol. The mixture was heated until solution was completed. The reaction, if it went at all, usually started in a few minutes. The phenylenediamine reaction started in less than one minute, while the *o*-toluido compound did not form for an hour. The products were recrystallized from alcohol, except those obtained with the diamines which were thoroughly washed with hot alcohol. The substance obtained from ammonia, using dry benzene as a solvent,[3] was decomposed rapidly by alcohol; therefore it was crystallized from a benzene-ligroin mixture. All of the above-mentioned addition products melted with decomposition.

Negative results ensued with aniline, *m*-anisidine, β-naphthylamine, β-naphthyl- and *m*-tolylhydrazines, and *m*-phenylenediamine. Destructive decomposition occurred with hydroxylamine, hydrazine, and piperidine.

Summary

4-Nitro-2-chloronitrostyrene is unusually reactive with aromatic amines and for the first time (with a nitrostyrene) addition compounds have been obtained with *o*- and *m*-toluidines as well as *p*-anisidine.

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[3] THIS JOURNAL, **60**, 2843 (1938).