3,5-Diphenyl-4-(4-methylphenyl)-isoxazole was obtained from VII by the action of hot alcoholic potash as needles, m. p. 198°.

Anal. Calcd. for $C_{22}H_{17}NO$: C, 84.9; H, 5.5. Found: C, 84.7; H, 5.5.

5-(4-Bromophenyl)-4-(4-methylphenyl)-3-phenylisoxazolone Oxide.[9]—A suspension of 3 g. of *p*-bromophenylnitromethane and VII in 50 cc. of alcohol was saturated with ammonia. The product after an hour was dissolved in alcohol separating as feathery needles, m. p. 182–183°; yield 2.5 g.

Anal. Calcd. for $C_{22}H_{18}NO_2Br$: C, 64.7; H, 4.4. Found: C, 65.1; H, 4.6.

5-(4-Bromophenyl)-4-(4-methylphenyl)-3-phenylisoxazole.—Obtained from the isoxazolone oxide it separated from alcohol in hair-like needles, m. p. 175°.

Anal. Calcd. for $C_{22}H_{16}BrNO$: C, 67.7; H, 4.1. Found: C, 67.6; H, 4.3.

Summary

It has been shown that the presence of an alkyl group in the aromatic ring of nitrostyrene prevents addition reactions with ammonia and aromatic amines, but does not stop polymerization. An alkyl group in the side chain partially blocks the addition reaction and completely stops the tendency to polymerize. Halogen has a similar effect. Both reactions are suppressed by a phenyl group in this position. The presence of a nitro group in the ring partially restores the addition tendency, but has no noticeable influence on polymerization.

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[9] It has been assumed that this substance resulted rather than the isomeric 3-(4-bromophenyl)-5-phenyl derivative; see Kohler and Richtmyer, THIS JOURNAL, **50**, 3092 (1928).

[A CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

The Action of *p*-Toluidine and *p*-Phenylenediamine on Substituted Nitrostyrenes

BY DAVID E. WORRALL AND FREDERIC BENINGTON

It was shown in a previous communication[1] that the tendency of a nitrostyrene to form an addition compound with an aromatic amine, which is rather limited in the mother substance, may be modified by the introduction of certain groups into the molecule. In the hope of finding a more active combination, a number of unsaturated nitro compounds have been prepared and a study made of their additive power. *p*-Toluidine and *p*-phenylenediamine, most powerful of the primary aromatic amines for reactions of this type, were selected to test the reactivity.

The results clearly indicate that an addition reaction between an aromatic amine and a substituted nitrostyrene is relatively uncommon and even more circumscribed than with the parent substance. No reaction takes place with the unsaturated nitro compounds prepared from aldehydes containing hydroxy, methoxy or methylene oxy groups. The presence of a nitro group in the ring on the contrary enhances the additive capacity and even may restore the lost activity of a substituted nitrostyrene. Halogen also has a favorable influence as the most active substance in the list contains a chlorine as well as a nitro substituent. *p*-Phenylenediamine is more reactive than *p*-toluidine with these particular substances.

α-Nitro-β-(2-methoxyphenyl)-ethylene.—This substance, prepared by condensing *o*-methoxybenzaldehyde with nitromethane in the presence of triethylamine,[2] separated from alcohol in the form of yellow prismatic crystals, m. p. 50°.

Anal. Calcd. for $C_9H_9NO_3$: C, 60.3; H, 5.0. Found: C, 60.1; H, 5.1.

α-Nitro-β-(2-methoxy-4-nitrophenyl)-ethylene.—The product obtained by the action of fuming nitric acid crystallized from alcohol as yellow plates, m. p. 175–176°.

Anal. Calcd. for $C_9H_8N_2O_5$: C, 48.2; H, 3.6. Found: C, 48.7; H, 3.9.

The isomeric 2-nitro-4-methoxy compound obtained in a similar manner formed microscopic canary yellow crystals from alcohol, m. p. 145–146°.

Anal. Calcd. for $C_9H_8N_2O_5$: C, 48.2; H, 3.6. Found: C, 47.9; H, 3.8.

The following procedure was used in testing the addition ability of the nitrostyrenes with *p*-phenylenediamine and *p*-toluidine. To a filtered solution containing the correct amount of the base in alcohol was added 1 g. of the unsaturated compound. The mixture was heated until all of the solid phase had disappeared, adding more solvent if necessary. The addition product usually appeared within a few minutes. No good solvent was found for the phenylenediamine derivatives although they are somewhat soluble in acetone. The crude products were purified by thorough extraction with hot alcohol. The 2-nitro and 3-nitro derivatives may have contained traces of colored impurities. All melted with decomposition and were dissolved readily by alcoholic potash. Shaking

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[1] THIS JOURNAL, **60**, 2841 (1938).

[2] Worrall, *ibid.*, **56**, 1556 (1934).

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.