of an active bromine cation by the reactions between anthracene and bromine in the dark. On this basis, the conversion of *cis* to *trans* isomers in the dark might then be represented by the series of reactions shown.

The isomerization would thus be a true chain reaction since the bromine cation is constantly regenerated after each conversion.

These results indicate that bromine cations, as well as bromine atoms, may cause rapid isomerization about an olefinic bond. This latter reaction, therefore, must be applied with reservation as a criterion for the presence of bromine atoms.

Summary

The reaction of bromine with anthracene in the dark has been found to catalyze the isomerization of ethyl maleate to ethyl fumarate.

The mechanism of this conversion has been formulated with a positively charged bromine ion as an intermediate.

The subsequent limitation of *cis–trans* isomerization as a criterion for the presence of bromine atoms is pointed out.

URBANA, ILLINOIS RECEIVED JULY 1, 1938

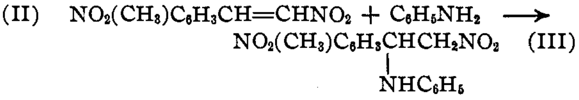
[A CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

The Action of Ammonia and Aromatic Amines on 4-Methylnitrostyrene and Related Compounds

BY DAVID E. WORRALL

Nitrostyrene has been shown[1] to react with aniline in a manner characteristic of α,β-unsaturated compounds, forming ultimately a saturated β-anilino derivative. That the additive capacity of the unsaturated system toward such substances is slight became apparent when it was discovered that comparatively few reacted in this way, if at all. An attempt[2] to facilitate the reaction by working with a substance incapable of polymerization, namely, bromonitrostyrene, was fruitless as the presence of halogen promoted the formation of Schiff bases. Similar results were obtained by Musante[3] working with nitrostyrenes containing methoxy or oxymethylene groups. A study has now been made of the effect of substituents on the alkylated nitrostyrene, $\mathrm{CH_3C_6H_4CH{=}CHNO_2}$ (I).

The ability to add organic bases is entirely lost on the introduction of a methyl group into the ring of nitrostyrene, although the tendency for polymerization or hydrolysis is not greatly changed. It is true that a condensation product of the amine and aldehyde is formed when I reacts with an alcoholic solution of phenylenediamine or benzidine, a reaction that may be interpreted as resulting from the decomposition of an intermediate addition product. Since no reaction takes place with anhydrous benzene as a solvent, it seems apparent that the product is rather the result of hydrolysis and condensation. The additive power of I is not increased by the introduction of bromine in the side chain, but the presence of a nitro group in the ring partially restores the lost reactivity. Addition compounds are formed with aniline and *p*-toluidine, but not with phenylhydrazine.



$$\text{(II)}\quad \mathrm{NO_2(CH_3)C_6H_3CH{=}CHNO_2 + C_6H_5NH_2 \longrightarrow NO_2(CH_3)C_6H_3\underset{\substack{|\\ NHC_6H_5}}{CH}CH_2NO_2}\quad \text{(III)}$$

p-Phenylenediamine reacts in a similar manner, both functional groups being involved. With ammonia the reaction is somewhat different inasmuch as the primary addition product reacts further with a second molecule of II.

$$\mathrm{2NO_2(CH_3)C_6H_3CH{=}CHNO_2 + NH_3 \longrightarrow IV}$$
$$\mathrm{(NO_2(CH_3)C_6H_3CH[CH_2NO_2])_2NH}$$

The introduction of bromine into the side chain of II again cuts down the ability to form addition compounds. No reaction takes place in the absence of water and with wet reagents only unchanged components or products resulting from hydrolysis or destructive decomposition are present.

The nitrostyrene (V) obtained from nitroethane and toluic aldehyde contains an alkyl group in the side chain next to the nitro group as well as in the ring. It shows no tendency to

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[1] Worrall, THIS JOURNAL, **49**, 1598 (1927). This particular substance was first prepared, in another manner, by Tönnies, *Ber.*, **20**, 2986 (1887), although the true structure was pointed out later by Wieland, *ibid.*, **36**, 2564 (1903).

[2] Worrall, THIS JOURNAL, **43**, 919 (1921).

[3] Musante, *Gazz. chim. ital.*, **67**, 579 (1937).

polymerize or form addition compounds. The introduction of bromine into the side chain on carbon next to the ring has no effect but nitration produces a substance again capable of reacting, by addition, with *p*-toluidine. The presence of the methyl group in the side chain, however, has a hindering effect as the nitro derivative does not form an addition compound with *p*-phenylenediamine.

The introduction of a phenyl group into the side chain produces a nitrostilbene, a substance showing no tendency to react by addition or polymerization. It is converted by alcoholic ammonia into an isoxazolone oxide.[4]

Experimental

α-Nitro-β-[4-methylphenyl]-ethylene I.—While toluic aldehyde may be condensed with nitromethane through the action of alkali,[5] it was found more convenient in working with smaller quantities (0.25 to 0.5 g. mole) to use a modification of the method of Knoevenagel.[6] The two components were heated under a reflux condenser by steam in the presence of 5% of the equivalent amount of amylamine for forty minutes. The yield by either method after crystallization from two volumes of alcohol was slightly better than 60%. A much better yield was obtained on heating with alcoholic amylamine but the product was contaminated with a small amount of polymer difficult to remove. I separated from alcohol in long light yellow needles, m. p. 102°.

Anal. Calcd. for $C_9H_9NO_2$: C, 66.3; H, 5.5. Found: C, 66.0; H, 5.5.

A gelatinous precipitate difficult to filter separated from a warm alcohol solution of I in the presence of ammonia or an aliphatic amine. Considerable discoloration may take place especially with ammonia. No good solvent was found for the polymer which dried out after thorough washing with hot alcohol to a white powder. It gradually decomposed above 230°.

Anal. Calcd. for $(C_9H_9NO_2)x$: C, 66.3; H, 5.5. Found: C, 66.5; H, 5.6.

Ammonia did not react with a dry benzene solution of I. Amylamine in the absence of solvents reacted vigorously, producing a tar from which 4-methylbenzalamylamine and nitromethane were isolated and identified.

I gave no evidence of reacting with aniline. On long standing the oily residue was found to consist of a mixture of unchanged components. Similar results were obtained with phenylhydrazine and *p*-toluidine. No reaction took place between I and *p*-phenylenediamine dissolved in dry benzene even after the mixture had been heated to boiling and then kept at room temperature for a day. Unchanged amine separated out. These same substances did react in warm alcohol, but as the product was insoluble in alcoholic potash and was unchanged on heating with this same reagent, it was not an addition product but a Schiff base. Recrystallized from glacial acetic acid, it appeared as tiny brownish-yellow needles, m. p. 188–189°.

Anal. Calcd. for $C_{22}H_{20}N_2$: C, 84.6; H, 6.4. Found: C, 84.3; H, 6.5.

Similar results were obtained with benzidine.

α-Nitro-β-(4-methylphenyl)-ethylene Dibromide.—Ten grams of I was brominated in chloroform by heating for an hour under a reflux condenser. The oily residue after removal of solvent hardened on cooling. A small portion was crystallized from ligroin, separating in colorless tablets, m. p. 79–80°.

Anal. Calcd. for $C_9H_9O_2NBr_2$: Br, 49.5; Found: Br, 49.3.

α-Nitro-α-bromo-β-[4-methylphenyl]-ethylene.—The crude dibromide reacted spontaneously and smoothly with a warm alcohol solution of potassium acetate. After standing for a short time the new substance was isolated, separating from alcohol as lustrous yellow plates, m. p. 67–67.5°.

Anal. Calcd. for $C_9H_8BrNO_2$: Br, 33.1. Found: Br, 32.8.

It did not polymerize in the presence of alcoholic ammonia, neither was it observed to react with *p*-toluidine or *p*-phenylenediamine. The corresponding chlorine derivative obtained in a similar manner as narrow yellow plates melting at 78–78.5° was also non-reactive.

Anal. Calcd. for $C_9H_8ClNO_2$: C, 54.7; H, 4.1. Found: C, 54.3; H, 4.2.

α-Nitro-β-[2-nitro-4-methylphenyl]-ethylene.—The product obtained by nitrating 25 g. of I using fuming acid and maintaining the temperature slightly below 20° was recrystallized from alcohol: yield 23 g.; m. p. 121–122°, after several crystallizations. It was identified as the 3-nitro derivative of I by an analysis and an examination of the oxidation product, obtained by the action of potassium permanganate, which did not depress an authentic sample of 3-nitro-*p*-toluic acid. The substance previously prepared by Hanzlik and Bianchi[7] by the nitration of *p*-methylcinnamic acid and recorded as melting at 117–118° probably contained some of the 2-nitro isomer. The original filtrate yielded 8.5 g. of material melting at 70–75°. By repeated crystallizations a small quantity of tiny pale yellow needles was obtained that had a constant melting point, 96–97°.

Anal. Calcd. for $C_9H_8N_6O_4$: C, 51.9; H, 3.8. Found: C, 51.5; H, 3.9.

It was unchanged by nitric acid while the melting point was depressed by the 3-nitro isomer. It seems safe to conclude that the substance was the 2-nitro derivative of I, although it still may have contained some of the isomer.

α-Nitro-β-anilino-β-[3-nitro-4-methylphenyl]-ethane III was obtained by heating, until solution was complete, the two components in the presence of alcohol. Crystals gradually formed on standing. III separated from alcohol as small yellow prisms, m. p. 98–99°. As with all of these addition compounds, some decomposition took place at the melting point which accordingly varies depending upon the rate of heating. III was soluble in alcoholic potash.

Anal. Calcd. for $C_{15}H_{15}N_8O_4$: C, 59.8; H, 5.0. Found: C, 59.5; H, 5.0.

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(4) Worrall, THIS JOURNAL, **57**, 2299 (1935).

(5) *Org. Syntheses*, **9**, 66 (1929).

(6) Worrall, THIS JOURNAL, **56**, 1556 (1934).

(7) Hanzlik and Bianchi, *Ber.*, **32**, 2287 (1899).

α-Nitro-β-toluidino-β-[3-nitro-4-methylphenyl]-ethane.—Prepared in a similar manner it separated from alcohol as bright yellow sparkling plates, m. p. 135–136°, dec.

Anal. Calcd. for $C_{16}H_{17}O_4N_3$: C, 61.0; H, 5.4. Found: C, 60.7; H, 5.4.

N,N′-(α,α′-[3-Nitro-4-methylphenyl]-β,β′-dinitro-diethyl)-*p*-phenylenediamine.—Yellow crystals quickly formed on heating II and *p*-phenylenediamine in alcohol until dissolved. No good solvent was found although the substance crystallized from acetone as tiny pale yellow plates, melting with decomposition at 152–153°. It was dissolved readily by alcoholic potash.

Anal. Calcd. for $C_{24}H_{24}N_6O_8$: C, 55.0; H, 4.6. Found: C, 55.4; H, 4.8.

II readily formed a polymer with alcoholic ammonia, an amorphous powder melting with decomposition at 198–200°. It was not examined further.

α,α′-([3-Nitro-4-methylphenyl]-β,β′-dinitrodiethyl)-amine, IV.—It was obtained by dissolving 2 g. of II in 100 cc. of dry benzene which was then saturated with dry ammonia. The mixture after standing for several hours in a closed container was allowed to evaporate spontaneously to a small bulk. The nodular crystalline aggregates that appeared were crystallized from alcohol. This must be done cautiously and in small lots as the substance is destroyed easily by hot alcohol solutions. Small colorless flat needles melting at 147° with decomposition were obtained. IV was insoluble in alcoholic potash and was not observed to form a salt with acids, although it was soluble in concd. hydrochloric acid.

Anal. Calcd. for $C_{18}H_{19}N_5O_8$: C, 49.9; H, 4.4. Found: C, 50.1; H, 4.5.

α-Nitro-β-bromo-β-[3-nitro-4-methylphenyl]-ethylene.—Ten grams of the bromine derivative of I was nitrated, the product crystallizing from a moderately large volume of alcohol in clumps of small pale yellow needles, m. p. 105°.

Anal. Calcd. for $C_9H_7BrN_2O_4$: C, 37.6; H, 2.4. Found: C, 38.1; H, 2.7.

Repeated crystallization from alcohol of the residue left in the original mother liquor produced eventually a substance that separated from ligroin as tiny yellow needles, m. p. 82–83°. This isomer, the 2-nitro derivative, on analysis gave data identical with those reported for the 3-nitro compound and in the one experiment tried did not form an addition compound. Only negative results were obtained in attempts to form addition compounds of the new 3-nitro derivative with aromatic amines, or to obtain a polymer. The odor of bromonitromethane was evidence that some hydrolysis occurred, but even with phenylenediamine no Schiff base was isolated from the black tar that formed.

α-Nitro-β-chloro-β-[3-nitro-4-methylphenyl]-ethylene.—Nitration of the chlorine derivative of I resulted in small pale yellow needles (from alcohol), m. p. 107–108°.

Anal. Calcd. for $C_9H_7ClN_2O_4$: C, 44.5; H, 3.3. Found: C, 44.9; H, 3.1.

No search was made for the isomer probably present. All attempts to form addition compounds with the chloro derivative were fruitless.

α-Nitro-α-methyl-β-[4-methylphenyl]-ethylene, V.—This substance obtained from nitroethane and toluic aldehyde using amylamine separated from petroleum ether as yellow prismatic needles, m. p. 55°; yield approximately 50%.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.8; H, 6.2. Found: C, 67.4; H, 6.1.

All attempts to form addition compounds using ammonia, *p*-toluidine and *p*-phenylenediamine failed, also attempts to prepare a polymer. A small amount of V was brominated in the customary manner and the oil-like product heated under a reflux condenser with potassium acetate for four to five hours. The mixture was worked up yielding a pale yellow oil. With this impure sample only negative results followed attempts to form an addition compound with toluidine.

α-Nitro-α-methyl-β-(3-nitro-4-methylphenyl)-ethylene, VI.—Nitration of V gave a substance separating from ligroin as narrow yellow plates, m. p. 72–73°.

Anal. Calcd. for $C_{10}H_{10}N_2O_4$: C, 54.1; H, 4.5. Found: C, 54.0; H, 4.7.

α-Nitro-α-methyl-β-(*p*-toluidino)-β-[3-nitro-4-methylphenyl]-ethane.—*p*-Toluidine formed an addition compound with VI after several hours. It separated from alcohol in clusters of bright golden platelets, m. p. 109–110°, dec.

Anal. Calcd. for $C_{17}H_{19}N_3O_4$: C, 62.0; H, 5.8. Found: C, 62.1; H, 5.8.

On mixing VI with a warm alcohol solution of *p*-phenylenediamine a black tar quickly formed from which, by digestion with warm alcohol, a crystalline product was obtained. It crystallized from acetone in tiny hair-like pale yellow crystals, m. p. 254–255°. As it was stable toward alkali and therefore not an addition compound, the substance was not examined further.

3,5-Diphenyl-4-(4-methylphenyl) Isoxazolone Oxide.—A suspension of 10 g. of 4-methylnitrostilbene in 50 cc. of alcohol was saturated with ammonia. The melting point of the product, removed at the end of an hour, indicated a mixture. It was heated with hydrochloric acid to destroy the condensation product of aldehyde, phenylnitromethane and ammonia otherwise difficult to remove.[6] The residue separated from a large volume of alcohol in long slender needles, m. p. 171–172°.[8]

Anal. Calcd. for $C_{22}H_{19}O_2N$: C, 80.2; H, 5.8. Found: C, 80.2; H, 5.9.

Dibenzoyl-4-methylphenylmethane Monoxime.—The filtrate from VII after steam distillation and crystallization from ligroin yielded a small amount of needle-like crystals, easily soluble in alcohol, m. p. 160–161°.

Anal. Calcd. for $C_{22}H_{19}NO_2$: C, 80.2; H, 5.8. Found: C, 79.8; H, 5.9.

It is quickly changed by hot hydrochloric acid into the corresponding isoxazole.

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[8] Meisenheimer and Matarbeiter, *Ann.*, **468**, 254 (1929), obtained, as a by-product in the preparation of 4-methylnitrostilbene, a small amount of white needle-like crystals melting at 168° and sparingly soluble in methyl alcohol. Based on an analysis the formula $C_{21}H_{13}NO_2$ was deduced for the unknown substance, which was probably VII.

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.

MEDFORD, MASS. RECEIVED SEPTEMBER 21, 1938

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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).