The evidence obtained is held to support the hemiquinoid formula for the dye advanced by Gomberg and Tabern and an analogous formula for the monosodium salt.

It appears probable that the halogen derivatives of fluorescein, in general, are of analogous structure.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TUFTS COLLEGE]

THE ADDITION OF AMINO AND HYDRAZINO BASES TO NITROSTYRENE[1]

BY DAVID E. WORRALL

RECEIVED APRIL 14, 1927 PUBLISHED JUNE 7, 1927

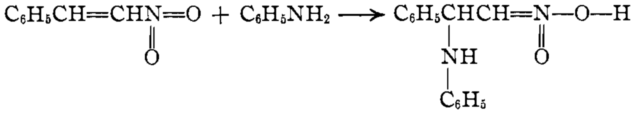
While the properties and reactions of such unsaturated substances as benzalacetophenone or ethyl cinnamate have been extensively investigated, much less is known concerning the chemistry of ethylene derivatives containing a nitro group; yet the latter are tractable solids easily prepared and purified, provided an aromatic group is present. Accordingly, nitrostyrene, $C_6H_5CH{=}CHNO_2$, a typical unsaturated nitro compound of this class, has been studied with regard to its chemical behavior toward some representative substances known to react with α, β unsaturated ketones and esters and which, therefore, by inference might be expected to combine with nitrostyrene. This paper contains the results obtained with ammonia and various organic bases derived from ammonia and hydrazine containing an amino group. Posner[2] in a systematic investigation of the action of hydroxylamine on α,β unsaturated acids and esters derived from cinnamic acid found that the same base reacts with nitrostyrene, forming a saturated nitro compound. With this exception, apparently no work has been done previously in this particular field.

It has been found in this Laboratory that such common reagents as aniline and phenylhydrazine react very readily indeed with nitrostyrene, forming colorless crystalline addition products. Nitrostyrene is an α,β unsaturated nitro compound containing a conjugated unsaturated system and accordingly is capable of 1,4 addition. There seems no reason to doubt that these amino derivatives react with nitrostyrene in this manner. The reaction starts through the mobile hydrogen of the amino group which, because of its chemical affinity for oxygen, becomes linked to that element. The rest of the molecule attaches itself to carbon (of the ethylene group), more remote from the nitro group.

---

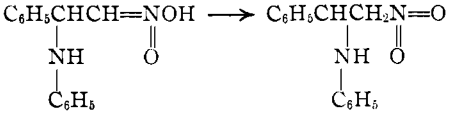
[1] This problem was suggested by Professor A. Michael, to whom the writer is greatly indebted, and much of the work was done in his Laboratory.

[2] Posner, *Ann.*, **389**, 114 (1912).



$$C_6H_5CH{=}CH\underset{\substack{\|\\ O}}{N}{=}O + C_6H_5NH_2 \longrightarrow C_6H_5\underset{\substack{|\\ NH\\ |\\ C_6H_5}}{CH}CH{=}\underset{\substack{\|\\ O}}{N}{-}O{-}H$$

The resulting unsaturated pseudo acid is of an unstable type; hence, it spontaneously rearranges into a saturated nitro derivative, the substance actually isolated.



$$C_6H_5\underset{\substack{|\\ NH\\ |\\ C_6H_5}}{CH}CH{=}\underset{\substack{\|\\ O}}{N}OH \longrightarrow C_6H_5\underset{\substack{|\\ NH\\ |\\ C_6H_5}}{CH}CH_2\underset{\substack{\|\\ O}}{N}{=}O$$

I

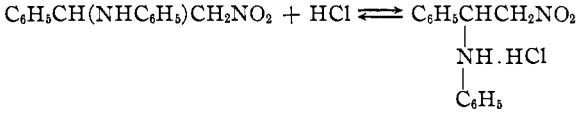
To prepare this substance it is merely necessary to mix the two components, using molecular equivalents, with or without a solvent, at room temperatures. Crystals appear in a few hours, although by seeding the mixture, which shows considerable tendency to remain in a fused condition, the formation of the solid phase can be greatly hastened. In favorable cases, with *p*-toluidine, for example, the addition product appears in a few minutes if seeded with a bit of the substance previously prepared.

On the other hand, when conditions are not favorable, whether because of the chemical nature of the substance or for some other reason, the reaction simply does not go. It cannot be forced by heating, for nitrostyrene is very sensitive to outside influences in the presence of bases and is easily destroyed by hydrolysis or polymerization. Many negative results were obtained. Out of something like forty substances examined, thirteen were found to form addition compounds with nitrostyrene. Aniline and *p*-toluidine were the only common aromatic amines (containing one amino group) examined which react by addition with nitrostyrene. None of the substituted anilines, unless *p*-toluidine is considered as coming in this category, was observed to form an addition compound with nitrostyrene. While it is not difficult to explain the non-reactivity of aniline derivatives containing negative substituents in the ring, *p*-chloro-aniline or *p*-nitro-aniline, for instance, the results obtained with the naphthylamines, biphenylamine and toluidine (*o*- and *p*-) are less understandable. Both α- and β-naphthylamines form oils when mixed with the molecular equivalent of nitrostyrene dissolved in alcohol. These oils partially solidify on cooling in a freezing mixture, but on warming to room temperatures again become fused. Unchanged nitrostyrene is present even after standing for several months. Heating results in tar formation from which nitrostyrene can be extracted. Similar results take place with biphenylamine, $C_6H_5C_6H_4NH_2$. Obviously, the naphthyl and biphenyl groups have sufficiently diminished the activity of mobile hydrogen in the amino group so that it is incapable of reacting with nitrostyrene. This decrease in mobility of hydrogen may come about from the chemical nature of the negative naphthyl group, just as the introduction of bromine into aniline decreases its basicity and, therefore, its reactivity toward nitrostyrene. It is also probable, however, that non-chemical forces due to spacial relations may have something to do with the decrease in activity of naphthylamine and biphenylamine, and that nitrostyrene is a particularly sensitive reagent for a study of these effects.

Certainly there seems no escape from the conclusion that the position of the substituent and not the chemical nature of it is responsible for the chemical behavior of the toluidines toward nitrostyrene. *p*-Toluidine adds so easily at room temperature that the crystalline product is observable in a few minutes. However, both *o*- and *m*-toluidine, under the experimental conditions used, failed to react with nitrostyrene, even on heating, and while they may form addition products under certain conditions which were not attained experimentally, it is certain that the addition goes far less readily than with *p*-toluidine. Hence *m*-toluidine furnishes an interesting example of steric hindrance brought about by a substituent in the *meta* position, a much less common phenomenon than hindrance to addition reactions by *ortho* substituents.

Another sort of disturbance was found with substances of the nature of ammonia, hydrazine, aminoguanidine, and *p*-dimethylphenylenediamine, all of which contain hydrogen sufficiently mobile to react with nitrostyrene and which do not present non-chemical obstacles. This disturbance is the considerable tendency for nitrostyrene to react with itself or polymerize to an inert substance of unknown structure and molecular weight known as nitrometastyrene, a reaction aided by alkaline reagents such as sodium methylate. Nitrometastyrene is formed quantitatively from nitrostyrene in the presence of these organic bases dissolved in alcohol with no evidence of the formation of addition products. The tendency for nitrostyrene to polymerize is catalyzed by moisture, so that in the complete absence of water, a condition not easily attained with hydrazine or aminoguanidine, it is probable that the unsaturated nitro compound would react by addition with the amino derivatives. This was successfully demonstrated with ammonia, for dry ammonia is easily prepared in benzene solution and in this environment no difficulty was experienced in forming an addition product with nitrostyrene. Piperidine reacts by addition with nitrostyrene, the only secondary amine examined that gave positive results. The primary aliphatic amines are apparently different in their behavior toward nitrostyrene. The reactions now under observation do not form solid products.

The addition products of nitrostyrene with the aromatic amines are crystalline with well-defined melting points and are soluble in the ordinary organic solvents. They exhibit slight basic properties and, although insoluble in the mineral acids, form salts with the latter which are instantly hydrolyzed by water.



$$C_6H_5CH(NHC_6H_5)CH_2NO_2 + HCl \rightleftharpoons C_6H_5\underset{\substack{|\\ NH.HCl\\ |\\ C_6H_5}}{C}HCH_2NO_2$$

II

With hot water the decomposition goes further, for a tar is formed containing among other things benzaldehyde and nitrostyrene. The compounds formed from semicarbazide and thiosemicarbazide exhibit similar properties. The piperidino derivative is much more sensitive to water, changing quickly on contact with moisture into the free base and nitrometastyrene. Naturally, the presence of a nitro group in these addition compounds has a loosening effect on adjacent hydrogen and they are soluble in alkali through the formation of metal derivatives. The anilino derivative changes as follows.

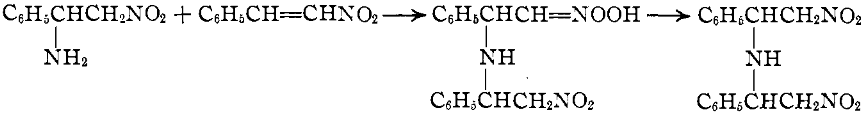
$$C_6H_5CH(NHC_6H_5)CH_2NO_2 \rightleftharpoons C_6H_5CH(NHC_6H_5)CH{=}NOOH \xrightarrow{NaOH} H_2O + C_6H_5CH(NHC_6H_5)CH{=}NOONa$$

III

This sodium salt is quite inert at 0°, hence it is easily isolated. It quickly picks up moisture at room temperatures, changing into a tar from which nitrometastyrene can be isolated.

Phenylhydrazine is even more reactive than aniline toward nitrostyrene. This also holds true for other corresponding derivatives of hydrazine and ammonia. While the increase in activity is not sufficient to bring about a reaction with *p*-bromophenylhydrazine, β-naphthylhydrazine does react. β-Naphthylamine was not observed to form an addition product with nitrostyrene. The non-reactivity of α-naphthylhydrazine in marked contrast to the decided activity of β-naphthylamine, which forms a crystalline derivative with the unsaturated nitro compound in a few minutes, is noteworthy. Here again forces non-chemical in nature appear to come into play, although aromatic derivatives containing an active group in the side chain and non-adjacent to the ring, which is true of naphthylhydrazine, are usually considered as immune to such influences. β-Naphthylhydrazine may be regarded as an *ortho*-substituted phenylhydrazine. Accordingly, the amino group is related to the substituent with regard to Position 1, 3 as it is in *m*-toluidine, a substance non-reactive toward nitrostyrene. Asymmetrical diphenylhydrazine, as well as *p*-tolylhydrazine, form addition compounds with nitrostyrene. The hydrazino derivatives are more basic than the corresponding amino, for they are soluble in dil. hydrochloric acid, from which salts separate out subsequently. On the other hand, while soluble in alkali, metal salts were not isolated. The hydrazino derivatives are easily decomposed into tar-like mixtures.

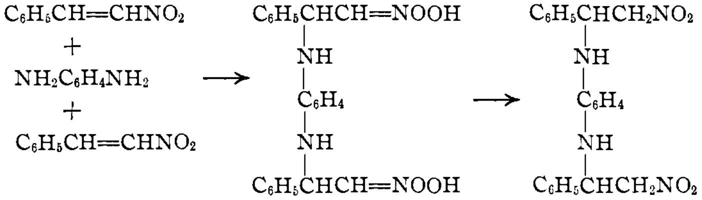
Ammonia itself reacts with two molecular equivalents of nitrostyrene, and attempts to confine the reaction to one equivalent were unsuccessful. Evidently the primary addition product contains hydrogen sufficiently mobile to react with more nitrostyrene as follows.



$$C_6H_5\underset{\substack{|\\ NH_2}}{CH}CH_2NO_2 + C_6H_5CH{=}CHNO_2 \longrightarrow C_6H_5\underset{\substack{|\\ NH\\ |\\ C_6H_5CHCH_2NO_2}}{CH}CH{=}NOOH \longrightarrow C_6H_5\underset{\substack{|\\ NH\\ |\\ C_6H_5CHCH_2NO_2}}{CH}CH_2NO_2$$

This compound is better neutralized than the addition products previously considered and does not form salts with the strong acids. It recrystallizes unchanged from hot concd. hydrochloric acid, but is quickly decomposed by alkali at room temperatures.

Compounds of a somewhat similar type are obtained from the action of *p*-phenylenediamine and benzidine, as each of these bases contains two amino groups and therefore reacts with two molecular equivalents of the unsaturated nitro compound. With phenylenediamine the following reactions ensue, assuming that the two amino groups add simultaneously.



$$\begin{array}{c} C_6H_5CH{=}CHNO_2\\ +\\ NH_2C_6H_4NH_2\\ +\\ C_6H_5CH{=}CHNO_2 \end{array} \longrightarrow \begin{array}{c} C_6H_5CHCH{=}NOOH\\ |\\ NH\\ |\\ C_6H_4\\ |\\ NH\\ |\\ C_6H_5CHCH{=}NOOH \end{array} \longrightarrow \begin{array}{c} C_6H_5CHCH_2NO_2\\ |\\ NH\\ |\\ C_6H_4\\ |\\ NH\\ |\\ C_6H_5CHCH_2NO_2 \end{array}$$

V

A similar reaction takes place with benzidine. These addition products, as would be predicted, form salts with both acids and bases. They have high melting points and are not easily purified because they are only sparingly soluble in most organic solvents. *m*-Phenylenediamine and *p*-phenylenediamine were not observed to form addition products with nitrostyrene.

Experimental Part

α-Nitro-β-anilino-β-phenylethane (I).—To 5 g. of nitrostyrene was added 3.2 g. of aniline. The mixture liquefied on stirring, with a slight evolution of heat and the development of a deep red color. Crystals appeared in a few hours, then the whole mass rapidly solidified. It was purified by recrystallization from alcohol, separating from the solvent in white, prismatic crystals; yield, 6.5 g.; m. p., 86–87°.

Anal. Calcd. for $C_{14}H_{14}O_2N_2$: N, 11.6. Found: 11.9.

Hydrochloric Acid Salt (II).—To 1 g. of nitro-anilinophenylethane dissolved in alcohol was added an equal volume of concd. hydrochloric acid. The salt separated out, on standing, in long, needle-like crystals. It was filtered and washed with absolute alcohol; m. p., 126–127°.

Anal. Calcd. for $C_{14}H_{14}O_2N_2.HCl$: HCl, 13.1. Found: 13.0.

The hydrobromic acid salt (rodlets, m. p. 113–114°) and the nitric acid salt (needles, m. p. 113–114°) were prepared by similar methods. It was necessary first to dilute nitric acid with an equal volume of water. Attempts to obtain a salt with sulfuric acid failed.

Sodium Salt (III).—A portion of nitro-anilinophenylethane was dissolved in the least volume of alcoholic sodium hydroxide, diluted with three to four volumes of water, and filtered. On cooling in a freezing mixture, a voluminous precipitate of colorless needles separated. The mixture was filtered through a funnel cooled with ice, washed with cold alcohol diluted with water and finally pressed on a porous plate. This residue was used directly for analysis, after standing for a few minutes. It decomposed into a tar, upon standing even in the absence of moisture, and had no definite melting point.

Anal. Calcd. for $C_{14}H_{13}O_2N_2Na$: Na, 8.7. Found: 7.9.

Action of Substituted Anilines on Nitrostyrene.—The following substances were not observed to form addition products: acetanilide, mono- and dimethylaniline, the nitroanilines, *p*-chloro-aniline, aminobiphenyl, *p*-aminophenol, phenetidine, *p*-amino-ethyl benzoate, *p*-amino-acetophenone and its oxime. Rosaniline polymerized nitrostyrene.

TABLE I

SUBSTITUTED β-AMINO DERIVATIVES OF α-NITRO-β-PHENYLETHANE

Subs.	Formula	Cryst. form	M. p., °C.	Analysis N_2 Calcd., %	Analysis N_2 Found, %	Remarks
p-Toluidino	$C_{15}H_{16}O_2N_2$	Prisms	82–84	10.9	11.0	Easily forms supersatd. solns. HCl salt, needles, m. p. 132°, prepared. Na and K salts made
p-Aminodiphenylamino	$C_{20}H_{19}O_2N_3$	Needles	113 with decomp.	12.6	12.7	Base prepared from tropaolin. Sol. in acetone
Phenylhydrazino	$C_{14}H_{15}O_2N_3$	Long needles	75	16.3	16.6	HCl salt, needles, m. p. 135–136°. HNO_3 salt, m. p. 77°. Subs. changes to an oil on standing a few days
Diphenylhydrazino	$C_{20}H_{19}O_2N_3$	Rods	81–82	12.6	12.7	Forms in a few minutes on mixing components
β-Naphthylhydrazino	$C_{18}H_{17}O_2N_3$	Needles	117–118	13.7	13.9	Recryst. from acetone-alcohol mixture
p-Tolylhydrazino	$C_{15}H_{17}N_2O_3$	Lustrous yellow plates	86–87	15.5	15.9	Decomposes in a few days, on standing

Table I (*Concluded*)

Subs.	Formula	Cryst. form	M. p., °C.	Analysis N_2 Calcd., %	Found, %	Remarks
Semicarbazido	$C_9H_{12}O_3N_4$	Prisms	131–132	25.0	25.2	Sol. in concd. HCl, separating out as salt
Thiosemicarbazido	$C_9H_{12}O_2SN_4$	Prisms	128–129	23.3	23.6	Large volume of alcohol used to dis. components sparingly sol. in alcohol
Piperidino	$C_{13}H_{18}O_2N_2$	Small needles	71–72	12.0	12.3	Components mixed in dry ether and evapd. in a vacuum. Very sensitive to moisture, forming original base and nitrometastyrene

No reaction was observed between nitrostyrene and the following substances: *o*-toluidine, *m*-toluidine, α-naphthylamine, β-naphthylamine, amino-azobenzene, *p*-methylamino-azobenzene, *p*-amino-acetanilide, *p*-bromophenylhydrazine, *p*-nitrophenylhydrazine, α-naphthylhydrazine, urea and thio-urea. Nitrostyrene was changed into nitrometastyrene by benzylamine, *p*-dimethylphenylenediamine, asymmetrical methylphenylhydrazine, guanidine, aminoguanidine and hydrazine.

α,α′-Diphenyl-β,β′-dinitro-diethylamine (IV).—Ordinary alcohol containing ammonia quickly polymerized nitrostyrene, even when attempts were made to exclude moisture. Accordingly, experiments were made with other solvents and it was found that in benzene solution the formation of nitrometastyrene could be suppressed. Dry ammonia gas was slowly bubbled for an hour through 5 g. of nitrostyrene dissolved in 50 cc. of benzene. The filtered solution was then evaporated to dryness in a vacuum. The residue now crystallized from alcohol, separating in clusters of silky, white needles; m. p., 122–123°; yield, 3.4 g. It does not form salts with the mineral acids.

Anal. Calcd. for $C_{16}H_{17}O_4N_3$: N, 13.3. Found: 13.4.

α,α′-Diphenyl-β,β′-dinitro-diethyl-*p*-phenylenediamine (V).—To 10 g. of nitrostyrene partially dissolved in a few cc. of alcohol was added 3.7 g. of *p*-phenylenediamine, one-half the molecular equivalent. The two substances quickly went into solution and in a few minutes a voluminous precipitate consisting of rosets of brilliant red crystals formed. It was recrystallized from acetone, the only good solvent for this substance, to which alcohol had been added. The product thus obtained consisted of microscopic, yellow needles; m. p., 146–149°; yield, approximately 10 g.

Anal. Calcd. for $C_{22}H_{22}O_4N_4$: N, 13.8. Found: 14.0.

HYDROCHLORIC ACID SALT.—The phenylene derivative dissolved in hot concd. hydrochloric acid, separating out on cooling as the corresponding salt, colorless needles with no definite melting point. Salts were also made with hydrofluoric and hydrobromic acids.

SODIUM SALT.—Alcoholic sodium hydroxide solution was used to dissolve the substance. On cooling in a freezing mixture a bulky precipitate separated, consisting of tufts of colorless needles. The original addition product reformed on careful addition of dil. acetic acid.

The Action of *o*- and *m*-Phenylenediamine.—Molecular proportions of these bases were sealed in tubes with alcoholic nitrostyrene and heated as high as 150° for six hours. The tubes opened without pressure, on cooling, and in each case the heavy oil contained therein was found to consist of a mixture of the two original substances.

α,α-Diphenyl-β,β'-dinitro-diethylbenzidine, $CH_2NO_2CHC_6H_5NHC_6H_4C_6H_4NHCH$-$C_6H_5CH_2NO_2$.—To 10 g. of nitrostyrene dissolved in warm alcohol was added 6.1 g. of benzidine, one-half the molar equivalent. A heavy, dark red oil separated in a few minutes. On standing, it solidified into a hard mass which was recrystallized from acetone mixed with alcohol. From it was obtained 14 g. of small, yellow plates; m. p., 162°. With the exception of acetone and nitrobenzene, the benzidine derivative is nearly insoluble in the ordinary organic solvents. It is only slowly attacked by the mineral acids, but is quickly destroyed by warm potassium hydroxide solutions.

Anal. Calcd. for $C_{28}H_{26}O_4N_4$: N, 11.6. Found: 11.8.

Summary

1. Aniline, *p*-toluidine, *p*-aminodiphenylamine, phenylhydrazine, diphenylhydrazine, β-naphthylhydrazine, tolylhydrazine, piperidine, semicarbazide and thiosemicarbazide form β-substituted derivatives of phenylnitro-ethane with nitrostyrene.
2. Ammonia, *p*-phenylenediamine and benzidine react with two equivalents of nitrostyrene to form saturated nitro derivatives.
3. The resulting substances are basic enough to form salts with the halogen acids. Salt formation also takes place with alkali.
4. This addition reaction is limited to a comparatively few organic bases because of the tendency of nitrostyrene to form a polymer, and because substituents in the ring of aromatic derivatives have a hindering effect.

TUFTS COLLEGE, MASSACHUSETTS

NEW BOOKS

General Chemistry. By HAMILTON P. CADY, Professor of Chemistry in the University of Kansas. Second edition. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York City, 1926. xvii + 540 pp. 73 figs. 21 × 14.5 cm. Price $3.25.

This book is the second edition of Cady's "General Chemistry," published in 1916, and reviewed in THIS JOURNAL, **39**, 258 (1917) by W. S Hendrixson. Both editions constitute an abridgment and simplification of the author's earlier textbook entitled "Inorganic Chemistry," reviewed by Wm. Lloyd Evans [THIS JOURNAL, **35**, 495 (1913)].

"In working over this book for its present edition, special effort has been made to clarify all obscure points, and to make the definitions and laws stand out in relief by the use of different type. Considerable new matter has been added, especially in the sections dealing with atomic structure," and yet the book has been kept within the bounds of the usual college course.