# THE STRUCTURE OF THE AROMATIC TRIAZENES

TOD W. CAMPBELL[1] AND BRUCE F. DAY[2]

*Department of Chemistry, University of California, Los Angeles, California*

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CONTENTS

## I. INTRODUCTION AND STATEMENT OF THE PROBLEM

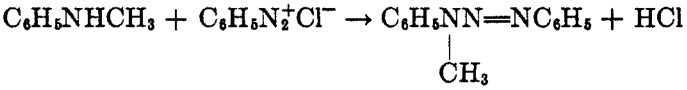
When a tertiary aromatic amine, such as dimethylaniline, is treated with a diazonium salt in neutral or basic solution, coupling occurs on the para position of the amine, and the product is a substituted azobenzene.

$$C_6H_5N(CH_3)_2 + C_6H_5N_2^+Cl^- \rightarrow C_6H_5N{=}NC_6H_4N(CH_3)_2\text{-}p + HCl$$

With a primary or secondary aromatic amine, however, *N*-coupling occurs to give substituted triazenes[3]:

$$C_6H_5NH_2 + C_6H_5N_2^+Cl^- \rightarrow C_6H_5N{=}NNHC_6H_5 + HCl$$

Diazoaminobenzene or
1,3-diphenyltriazene



$$C_6H_5NHCH_3 + C_6H_5N_2^+Cl^- \rightarrow C_6H_5\underset{\displaystyle CH_3}{\underset{|}{N}}N{=}NC_6H_5 + HCl$$

*N*-Methyldiazoaminobenzene or
3-methyl-1,3-diphenyltriazene

Griess (15) was the first to prepare diazoamino compounds. He found that both aromatic and aliphatic amines are capable of undergoing reaction with

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[1] Present address: Western Regional Research Laboratory, Albany, California.

[2] Present address: Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware.

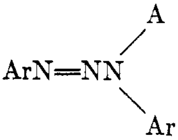
[3] *Chemical Abstracts* employs "diazoamino compounds" for a heading in its system (Chem. Abstracts **39**, 5921 (1945)) but indexes the individual compounds under triazenes:

$$R\text{—}\underset{1}{N}{=}\underset{2}{N}\text{—}\underset{3}{N}\text{—}R'$$

When N-3 carries a hydrogen atom the method of indexing simply defines a compound and should not be interpreted as being a correct representation of a structure.

diazonium compounds in basic or neutral solution. The following permutations of the triazene nucleus are known (28) (Ar = aromatic, A = aliphatic):

$\mathrm{ArN{=}NNHAr}$ $\mathrm{ArN{=}NN(Ar)_2}$
$\mathrm{ArN{=}NNHA}$
$\mathrm{AN{=}NNHA}$ $\mathrm{AN{=}NNA_2}$
$\mathrm{ArN{=}NNA_2}$



$\mathrm{ArN{=}NN(A)(Ar)}$ $\mathrm{(ArN{=}N)_2NAr}$
$\mathrm{(ArN{=}N)_2NH}$ $\mathrm{(ArN{=}N)_2NA}$
$\mathrm{ArN{=}NNH_2}$

The synthesis of most of these various classes is straightforward and consists in the addition of a diazonium salt to the appropriate amine; the latter component may be either aromatic, aliphatic, or mixed. For obvious reasons this method is not applicable to the preparation of triazenes which are formally derived from an aliphatic diazonium compound. They may be synthesized by the action of a Grignard reagent on an azide (3, 6):

$$\mathrm{CH_3MgBr + CH_3N_3 \rightarrow CH_3N{=}NNHCH_3}$$

The purely aliphatic triazenes are unstable and difficult to work with; hence very little is known about them.

The compounds of the class represented by the formula $\mathrm{ArN{=}NNH_2}$ can not be prepared from a diazonium compound and ammonia, since a bis-compound is invariably formed. One member of this class, phenyltriazene, $\mathrm{C_6H_5N{=}NNH_2}$, has been prepared by the action of anhydrous ethereal stannous chloride on phenyl azide (5); it is very unstable.

The aromatic triazenes with which this paper will deal are light yellow solids when pure but upon precipitation from a reaction mixture are often orange to deep red in color. The problem of purification is serious in many cases, and it has been only in the last decade that procedures were developed which furnish truly pure products. Dwyer (7) used cadmium hydroxide as a precipitating agent to remove the highly colored impurities in nitrodiphenyltriazenes, and more recently chromatographic adsorption on alumina has been shown to be an excellent method of purification (2). The colored impurities are usually difficult to remove by crystallization and the consequent inability to obtain pure material appears to have led in some cases to differences of opinion in interpretation of structure. For example, Mangini and Dejudicibus suggested a "malenoid-fumaroid" transformation as being responsible for the color changes of diazaminobenzenes in alkali (22). Dwyer later showed these color changes to be due to the presence of benzenediazoaminoazobenzene[4]

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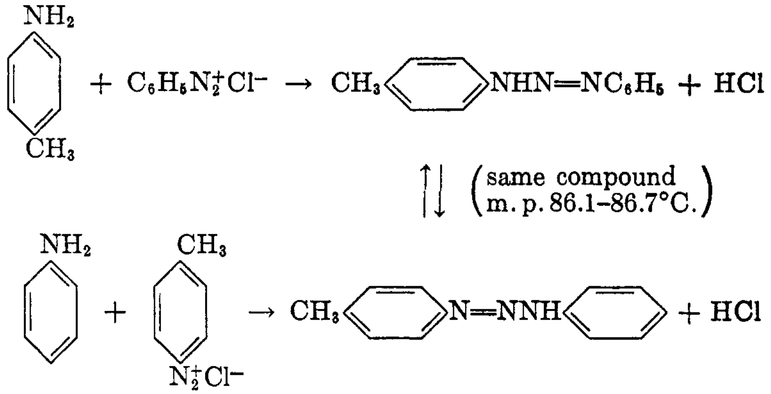
[4] Representation of a triazene by a structure such as this does not imply that this is necessarily the correct structure with regard to the position of the hydrogen.

and demonstrated that the alkali metal salts of many diazoaminobenzenes are yellow, like the parent compounds (8).

The most intriguing property of the triazenes is the tautomerism which they exhibit; consequently there arose from the very first an intense interest in the problem of determining the exact structure of these substances.

Griess (16) was the first to encounter the problem when he found that he obtained the same product from *p*-toluidine and benzenediazonium ion as he did from aniline and *p*-toluenediazonium ion.



(A)

(B)

The resulting 4-methyldiphenyltriazene (1-phenyl-3-*p*-tolyltriazene) contains an "allylic" nitrogen system, and it is evident that the tautomeric shift of the imino hydrogen can take place easily, by one or more of a variety of possible mechanisms. The following questions regarding this tautomeric system should be considered:

(*1*) Does either A or B represent the structure of the product and, if so, which one is correct?

(*2*) If the product is neither A nor B above, is it a simple mixture of A and B? If so, what is the composition of the mixture?

(*3*) If the product is not a simple mixture of A and B, how can it be best represented structurally?

(*4*) Does the product have the same composition in solution as it has in the pure solid state?

The literature discussed below is concerned largely with these questions. It is reviewed in the following pages more or less in chronological order.

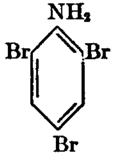
## II. ATTEMPTS TO ELUCIDATE THE STRUCTURE OF TRIAZENES BY CHEMICAL MEANS

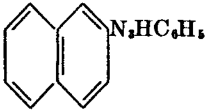
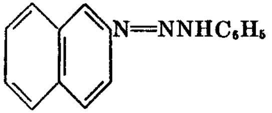
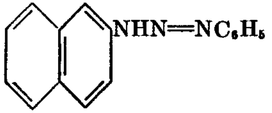
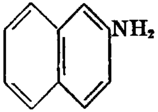
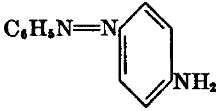
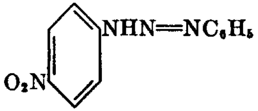
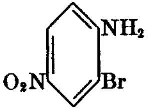
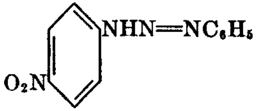
### *A. By cleavage of the molecule*

The first workers to concern themselves with the problem of the structure of triazenes were Nölting and Binder (25), who sought to trace the tautomerism by means of reactions such as cleavage by acid, reduction, acetylation, and alkylation. They found no pattern which could be used to determine structure and instead encountered a more or less random reactivity, which is summarized in table 1.

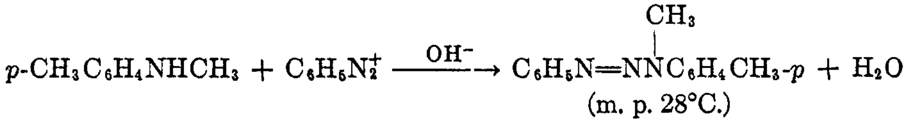
TABLE 1

*Cleavage products of Nölting and Binder*

| COMPOUND | REACTION | PRODUCTS | INDICATED STRUCTURE |
|---|---|---|---|
| $p$-$CH_3C_6H_4N_3HC_6H_5$ | Zn + HCl | $C_6H_5NH_2$, $C_6H_5NHNH_2$, $p$-$CH_3C_6H_4NH_2$, $p$-$CH_3C_6H_4NHNH_2$ | $p$-$CH_3C_6H_4N{=}NNHC_6H_5$ (A)<br>and<br>$p$-$CH_3C_6H_4NHN{=}NC_6H_5$ (B) |
|  | $Br_2$ | $p$-$CH_3C_6H_4N_2^+Br^-$,  | A |
|  | $C_6H_5NH_2$, 60°C. | $C_6H_5N{=}NC_6H_4NH_2$-$p$, $p$-$CH_3C_6H_4NH_2$ | B |
|  | $C_6H_5N(CH_3)_2$ | $p$-$CH_3C_6H_4N{=}NC_6H_4N(CH_3)_2$-$p$, $C_6H_5NH_2$ | A |
|  | $C_6H_5OH$ | $C_6H_5N{=}NC_6H_4OH$-$p$, $p$-$CH_3C_6H_4NH_2$ | B |
|  | $H_2SO_4$ (dilute) | $C_6H_5NH_2$, $C_6H_5OH$, $p$-$CH_3C_6H_4OH$, $p$-$CH_3C_6H_4NH_2$ | A + B |
|  | Ethylation; then dilute acid | $C_6H_5NHC_2H_5$, $p$-$CH_3C_6H_4NHC_2H_5$, $p$-$CH_3C_6H_4OH$, $C_6H_5OH$ | A + B |
| $p$-$BrC_6H_4N_3HC_6H_5$ | Dilute acid | $C_6H_5OH$, $p$-$BrC_6H_4NH_2$ | $C_6H_5N{=}NC_6H_4Br$-$p$ |

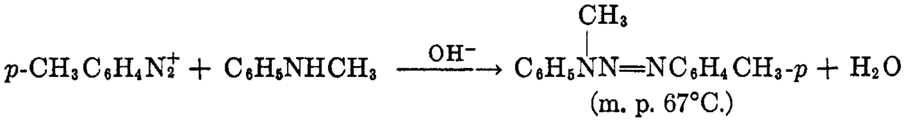
| | | | |
|---|---|---|---|
|  | $H_2SO_4$ (dilute) | $C_6H_5NH_2$, $C_6H_5OH$, 2-$C_{10}H_7OH$, 2-$C_{10}H_7NH_2$ |  (A)<br>and<br> (B) |
| | $C_6H_5NH_2$ |   | B |
| | $C_6H_5OH$ | $C_6H_5N{=}NC_6H_4OH$-p, 2-$C_{10}H_7NH_2$ | B |
| p-$O_2NC_6H_4N_3HC_6H_5$ | $H_2SO_4$ (dilute) | $C_6H_5OH$, p-$O_2NC_6H_4NH_2$ |  |
| | $Br_2$ | $C_6H_5\overset{+}{N_2}Br^-$,  |  |
| | $C_6H_5NH_2$ | p-$O_2NC_6H_4NH_2$, $C_6H_5NH_2$,<br>$C_6H_5N{=}NC_6H_4NH_2$-p,<br>p-$H_2NC_6H_4N{=}NC_6H_4NO_2$-p | p-$O_2NC_6H_4NHN{=}NC_6H_5$,<br>p-$O_2NC_6H_4N{=}NNHC_6H_5$ |

In the case where there is an alkyl group in place of the imino hydrogen no tautomerism is encountered and two distinct substances are produced from the reaction of *N*-methylaniline with *p*-toluenediazonium salt and of *N*-methyl-*p*-toluidine with benzenediazonium salt.



$$p\text{-}CH_3C_6H_4NHCH_3 + C_6H_5N_2^+ \xrightarrow{OH^-} C_6H_5N{=}N\overset{CH_3}{\overset{|}{N}}C_6H_4CH_3\text{-}p + H_2O$$

(m. p. 28°C.)



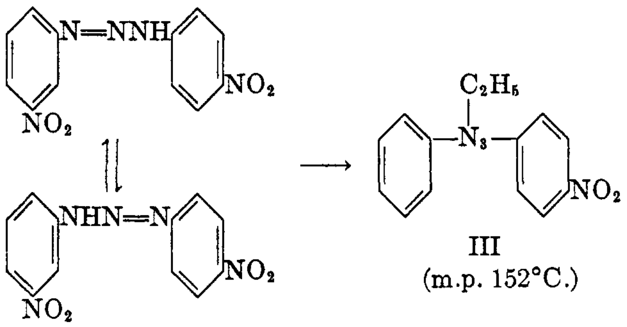
$$p\text{-}CH_3C_6H_4N_2^+ + C_6H_5NHCH_3 \xrightarrow{OH^-} C_6H_5\overset{CH_3}{\overset{|}{N}}N{=}NC_6H_4CH_3\text{-}p + H_2O$$

(m. p. 67°C.)

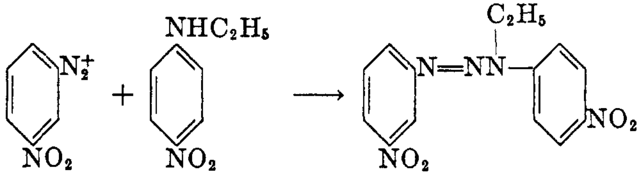
The action of phenol, dilute sulfuric acid, and hydrogen produces the expected cleavage products and in no instance have the products ever indicated the migration of the *N*-alkyl group.

*B. By alkylation of the imino nitrogen*

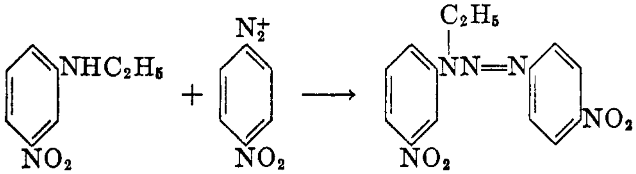
The next attack on the problem was by Meldola and Streatfeild (24), who attempted to settle the question by alkylation of the diazoamino compounds in



III
(m.p. 152°C.)



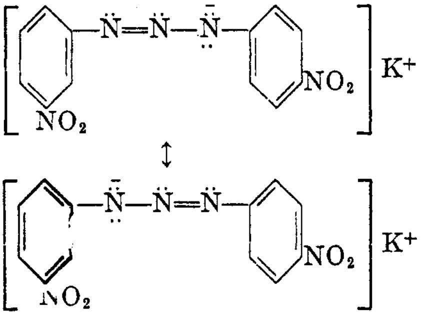
I
(m.p. 174–175°C.)



II
(m.p. 187°C.)

basic solution. They found that the imino hydrogen was acidic in character and readily formed a salt in basic solution. This salt in turn was easily alkylated. The alkylation of 1-(*p*-nitrophenyl)-3-(*m*-nitrophenyl)triazene gave what appeared to be a new ethyl derivative (III), m.p. 152°C., which was different from either of those previously prepared and raised the question of the possible occurrence of *three* *N*-ethyl compounds.

On acid cleavage, however, I and II gave only the two products which would be expected in each case, while III gave all four possible products. This unexpected result caused a surprisingly large amount of speculation before it was found that if an equal amount of I and II were heated together in benzene solution the crystals which were deposited on cooling were identical with III. This fact was confirmed by Smith and Watts (29), who found III to be a 50:50 solid solution of I and II, a conclusion borne out by absorption spectra data. Cryoscopic measurements of III showed that complete dissociation occurred in solution. It is interesting that an approximately equimolar mixture of the two alkyl derivatives was produced on alkylation. Superficially, it would appear to indicate that there is no stabilization of one form of the anion over the other form in the alkylation process.



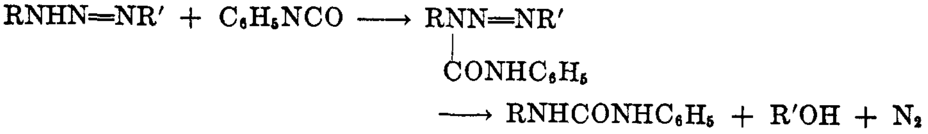
However, application of the experimental work described above to the subject of the structure of triazenes is subject to serious criticisms. These will be discussed at length in a later section.

### *C. By "fixation" of the tautomeric imino hydrogen atom*

The work of Goldschmidt, Holm, and Molinari (13, 14) and of Sarauw (27) constituted the next advance in the determination of structure. These workers used phenyl isocyanate and phosgene, respectively, in benzene solution in order to fix the position of the imino hydrogen. Sarauw's work is analogous to Goldschmidt's but it is less complete, although the same conclusions were reached; for this reason Goldschmidt's work will be used for discussion.

Goldschmidt found that treatment of an aromatic triazene with phenyl isocyanate gave a single compound, which could be hydrolyzed to a diarylurea, a phenol, and nitrogen. Extensive application of this reaction convinced Goldschmidt that the initial product of the reaction was a single diazourea. Furthermore, hydrolysis of the diazourea always yielded a diarylurea in which the more negative aryl group in the diazoamino compound is part of the urea molecule.

The less negative aryl group of the diazoamino system is found as a phenol. The reaction is illustrated below:

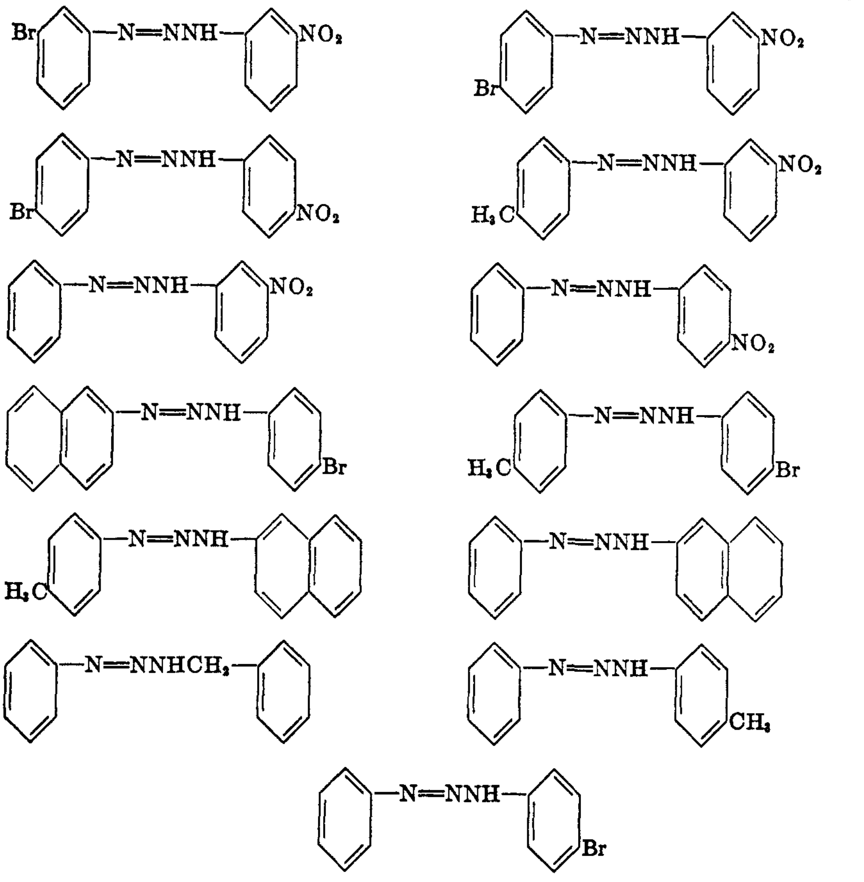


$$\mathrm{RNHN{=}NR' + C_6H_5NCO \longrightarrow \underset{\mathrm{CONHC_6H_5}}{RN}{=}NR'}$$

$$\longrightarrow \mathrm{RNHCONHC_6H_5 + R'OH + N_2}$$

TABLE 2

*Goldschmidt's triazene structures*

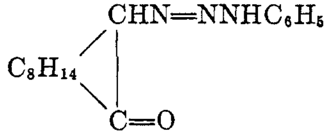


Goldschmidt carefully investigated his products; upon the evidence secured he laid down the rule that the imino hydrogen is always next to the most negative aromatic ring. In this manner he assigned the structures in table 2.

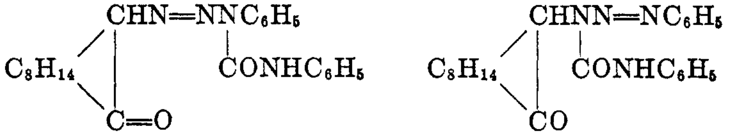
Some workers disagreed with Goldschmidt's conclusions. For instance, Heumann and Oeconomides (18) found that treatment of 1-(4-chlorophenyl)-3-(4-methylphenyl)triazene with aniline gave products which indicated a structure opposite to that of the bromo derivative in Goldschmidt's work. There is also the conflicting evidence of Nölting and Binder.

Goldschmidt felt that only one diazourea was isolated because the imide hydrogen was immobile in nonpolar solvents such as benzene. However, the most important evidence against the determination of structure by means of phenyl isocyanate is that advanced by Forster and Garland in connection with aliphatic-aromatic triazenes (12).

Dimroth (3, 4, 5, 6) had prepared 1-methyl-3-phenyltriazene, 1-ethyl-3-phenyltriazene, and 1-benzyl-3-phenyltriazene. Treatment with dilute hydrochloric acid gave aniline, nitrogen, and an alkyl chloride and indicated that the —NH— group was next to the phenyl ring. However, phenyl isocyanate gave the opposite answer. Forster and Garland (12) used camphoramine to prepare 1-camphoryl-3-phenyltriazene; for the first time they found that both acid cleavage and phenyl isocyanate indicated the same structure, that is:



Even more significant, though, was the isomerization of the camphoryltriazene derivative on standing.



Forster and Garland felt that this transfer[5] of the —CONHC$_6$H$_5$ group was

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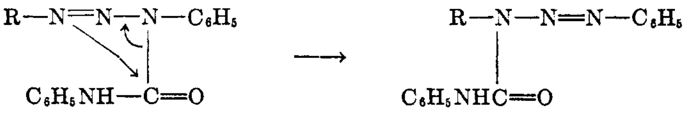
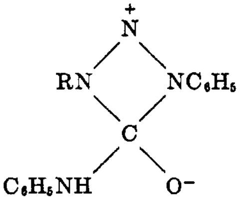
[5] This interesting rearrangement may involve a cyclic process similar to that which has been postulated for the rearrangement of allyl groups in three-carbon systems (A. C. Cope *et al.*: J. Am. Chem. Soc. **69**, 1893 (1947) and previous papers) and for the Claisen rearrangement (D. S. Tarbell: Chem. Revs. **27**, 495 (1940)). When the substituents on the triazene are similar an equilibrium mixture would be predicted, just as in the original triazene.



An intermediate such as



could be involved.

found in this case only because of the bulky camphor ring, that in the case of Dimroth's triazenes the change occurred too rapidly to be observed, and that their structures should be written as:

$$C_6H_5NHN{=}NCH_3, \quad C_6H_5NHN{=}NC_2H_5, \quad \text{and} \quad C_6H_5NHN{=}NCH_2C_6H_5$$

thus reconciling the results of acid cleavage and of treatment with pheny isocyanate.

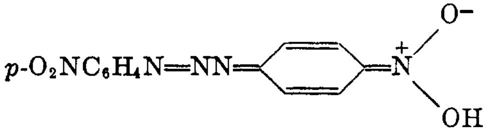
It is entirely possible that the aromatic triazenes are mixtures before treatment with phenyl isocyanate and that one of the resulting ureas is then converted at a finite rate completely into the other, or to an equilibrium mixture. It is also possible that there is a selective attack of the reagent on one form and that the equilibrium is continually shifted until only one product is obtained. With these facts in mind Goldschmidt's conclusions become less positive in character and their exact value and significance are hard to assess.

### *D. Investigations of metal salts*

After a gap of thirty years, during which no significant contributions were made to the question of the structure of triazenes, Dwyer (8) took up the problem and studied the metallic salts which triazenes form. He found that treatment of the orange and red triazenes with cadmium hydroxide gave rise to light yellow substances which had melting points higher than those previously reported and were purer. In addition, the reaction of these light yellow compounds with base gave salts of the same yellow color rather than the red color previously believed to be due to the triazene salts. The nitro-substituted triazenes were also adsorbed very strongly in solution on cadmium and magnesium hydroxides and the colors of the ortho and para compounds in alkali were much more brilliant than those of the *m*-nitro isomers. Investigation showed that the colored lakes of the *o*- and *p*-nitro compounds with magnesium hydroxide in alkali could best be explained by the existence of an isonitro acid form. Two forms of certain extremely pure *o*- and *p*-dinitrodiphenyltriazenes were actually isolated. By crystallization from alcoholic ammonia solutions of different concentration there could be obtained a yellow modification and a red modification, to which the following structures were assigned:

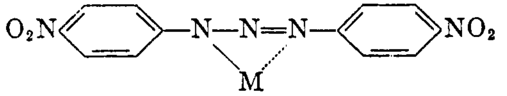
$$p\text{-}O_2NC_6H_4N{=}NNHC_6H_4NO_2\text{-}p$$

and

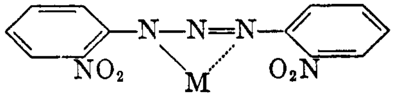


The evidence for such structures is good, and the fact that *m*-nitro compounds do not exist in any but the yellow form lends added support.

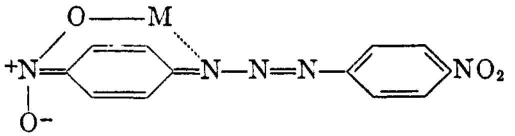
Further work also showed that the potassium and mercuric salts of diazoaminobenzene, the silver salt of the 3-nitro compound, and the silver and mercuric salts of the 4-nitro compound exist in only the yellow form. The 3,3'-dinitrodiazoaminobenzene also gave only one form. The 2,2'- and 4,4'-dinitro compounds, however, with strongly electropositive metals gave two stable salts: a stable yellow salt of the triazene and a dark red salt of the aci-form. The following structures were proposed:



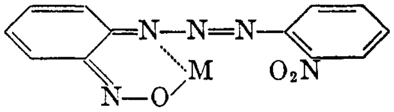
(yellow)



(yellow)

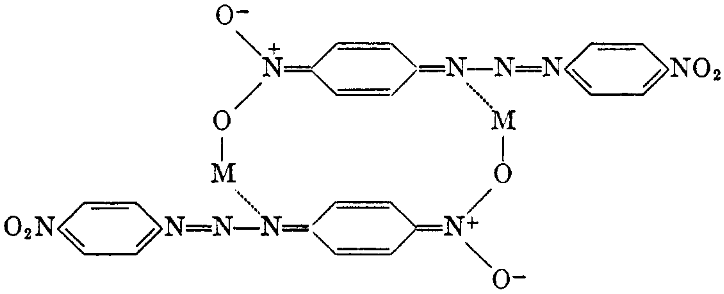


(red)



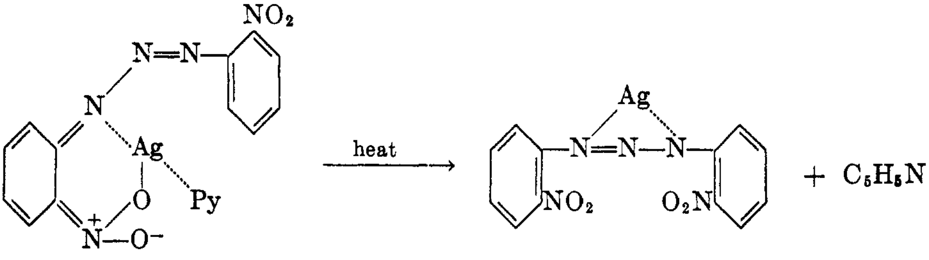
(red)

The structure for the *o*-nitro isomer appears reasonable, but that of the *p*-nitro form is open to serious objections. First, it would not appear that the *O*-metal-*N* bond would be long enough to extend over the required distance. Second, and most important, the planar quinoid-type resonance form cannot be buckled in order to bring the oxygen and nitrogen atoms closer together. It would seem a better formulation in the case of the *p*-nitrotriazene to write the red form as bimolecular:

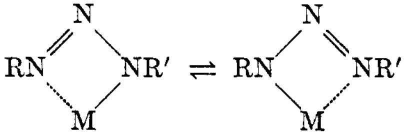


In the case of weakly electropositive metals such as silver, additional stabilization is provided by a coördinated pyridine molecule (see page 310).

Dwyer reasoned that in the red salt there was little chance for the silver to be coördinated anywhere except to the nitrogen nearest the nitro group, a debatable point in itself. When the pyridine is removed by heating, the silver should then remain attached to the same nitrogen if there is no "dynamic equilibrium" in the triazene salt. Ethyl iodide on the yellow salt obtained from the purple pyridine-coördinated 3,4′-dinitrodiazoaminobenzene gave the same product that Meldola and Streatfeild found. Dwyer thus concluded that the silver atom in the yellow form is bound to both the 1- and the 3-nitrogens in the triazene system. Later studies (10, 11), including coördination and molecular weight experiments, indicated that the metallic salts of diazoamino compounds should be formulated as internal complexes in which the chelating group is the triazene system.



(red) (yellow)



Additional evidence of the covalency is found in the ready solubility of the metal salts in organic media and in magnetic susceptibility measurements in which it is demonstrated that resonance is a contributing factor in stabilizing the chelated system (11). This fact, coupled with Dwyer's inability to prepare the isonitro acid form from any monosubstituted triazene except in the presence of a stabilizing molecule such as pyridine, suggests that it is impossible for more than one metal chelate to exist in the case of the simple monosubstituted triazenes.

It should be pointed out, however, that Dwyer's attempts at imine hydrogen fixation *via* the isonitro acid salts conceivably failed because his fundamental assignments of salt structures were in error.

Mangini (22, 23) disagrees completely with Dwyer as regards the structure of the triazene salts and insists that the observable color changes are due simply to *cis–trans* isomerism. He assigns to the *trans* salts a light color and to the dark salts a *cis* configuration,

$$\begin{array}{l}\mathrm{RN}\\ \|\\ \mathrm{NNR'}\\ \quad\mathrm{M}\end{array}$$

(light-colored)

$$\begin{array}{l}\mathrm{NR}\\ \|\\ \mathrm{NNR'}\\ \quad\mathrm{M}\end{array}$$

(dark-colored)

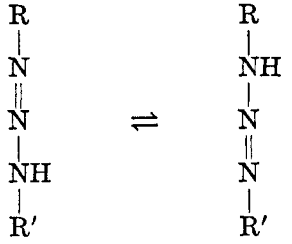
where R and R′ are aryl, both substituted and unsubstituted.

Dwyer and Earl (21) have pointed out that Mangini has offered no evidence that his triazenes were pure and that his observed color changes are probably due in large measure to contaminating benzenediazoaminobenzenes.[6]

## III. GENERAL CRITICISMS OF CHEMICAL METHODS OF PROOF OF STRUCTURE FOR MOBILE SYSTEMS

In general, one must be extremely cautious about assigning, on the basis of chemical evidence alone, a definite structure to a chemical substance which is capable of tautomerism, especially when the tautomerism is as facile as it is in the triazene system.

All of the reactions of the triazenes described above presumably go at finite rates; hence they should be governed by accepted rules of chemical behavior. For example, let us assume that a triazene in solution produces a system such as



B A

which in a certain solvent is in equilibrium at two concentrations, $C_A$ and $C_B$. Add to this system a substance X, which is to react with the species present in

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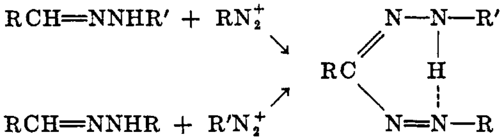
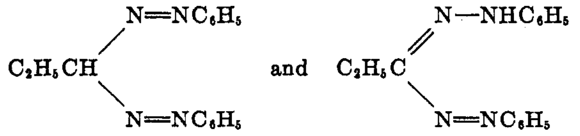
[6] The reaction of a hydrazone and a diazonium salt gives rise to a compound called a formazan. These compounds exhibit tautomerism similar to that in the triazene system (1, 17, 20, 26).



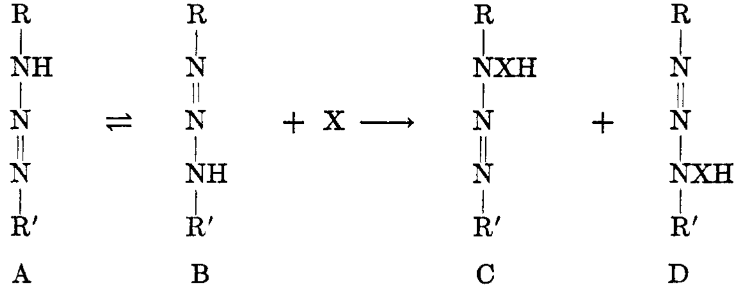
The compound 2,3-diphenyl-5-ethylformazan has been obtained in two forms—one as orange needles, m.p. 102–103°C., the other as red needles, m.p. 73–75°C.—which have been assumed to be *cis-trans* isomers (17), although other interpretations may be possible. For example, the possibility that the red and yellow forms are represented by structures such as



(yellow) (red)

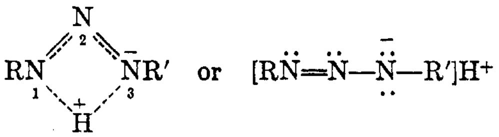
has not been eliminated. Formazans readily form chelated complexes with bivalent metals (20).

some manner designed to "fix" the position of the tautomeric hydrogen (or of the double bond):



After this "fixation" is complete, C and D are measured by suitable means and the experimental ratio of $C_A/C_B$ is calculated. If this is to be the correct answer, then the following points must be clarified:

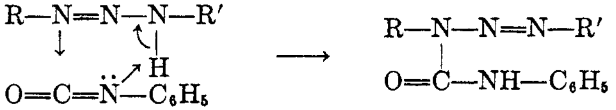
(*1*) It must be established that reaction of X is actually with the species A and B and not with some intermediate, such as



which, in truth, might constitute a large percentage of the total species.

(*2*) It must be established that the products C and D are not interconvertible under the conditions of isolation or formation.

(*3*) It must be established that the reaction of X is actually with the nitrogen atom bearing the mobile hydrogen. For example, it is not inconceivable that a triazene could react with phenyl isocyanate by a cyclic mechanism which would be geometrically quite favorable:



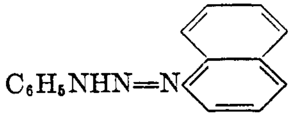
(*4*) It must be established that the reactions of A with X and of B with X occur at the same rate, or it must be established at what relative rates these reactions occur, since A and B are presumed to be in equilibrium.

(*5*) An essentially quantitative recovery of the starting material (A + B) as C and D must be made.

It is in the light of the above conditions that the various methods employed to prove the structure of triazenes by chemical means should be considered.

Cleavage of the triazene molecule by reagents such as acid, phenols, etc., as listed in table 1, has not been shown to fit rigorously any of the above stipulations, so it can be dismissed as a method of proof of structure.

A disturbing factor in this series of experiments is that various reagents under somewhat similar conditions sometimes give all four possible products when acting on a diazoamino compound, and in other cases give only two products with a similar reagent. For example, phenyl-α-naphthyltriazene when treated with alcoholic hydrogen chloride at 0°C. gives aniline and α-naphthyldiazonium chloride, a result which suggests the following formula as correct.



Phenyl-β-naphthyltriazene, which should have the same structure, when treated with dilute sulfuric acid at room temperature gives all four products, a result which suggests that both forms are present. Alkylation of a triazene in the presence of sodium hydroxide or other strong alkali, while interesting, is essentially useless in determining the structure of a triazene. In strong alkali the triazene exists not as such, but as a resonating anion,

$$R{-}N{=}N{-}\ddot{N}{-}R \leftrightarrow R{-}\ddot{N}{-}N{=}N{-}R$$

which by its very nature must be a single species, regardless of the structure of the starting triazene. Further, there is no reason for assuming that the alkylation of this anion will give a mixture of products which in any way reflects the structure of the original compound. Also, it is open to question as to whether the 50:50 mixture obtained on alkylating the triazene anion is merely a eutectic mixture which is easily isolated. Such a process could easily leave an excess of one product unisolated.

Proofs of structure which involve fixation of the hydrogen atom are perhaps the most reasonable, though not at the present stage. Thus, if the five criteria above can be established, significant results might be obtained.

Any attempts to assign a structure on the basis of studies of metal salts and chelates are open to objections similar to those raised against the proof of structure by alkylation.

## IV. PHYSICAL METHODS OF DETERMINATION OF STRUCTURE

Attempts to prove structure by physical measurements are few. Only two papers have been published in which the authors make an effort to elucidate the structure of triazenes by physical means.

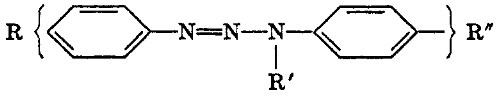
### *A. Apparent molecular weight*

Hunter (19) measured the molecular weight of a series of substituted triazenes and found that in solution there was a definite association of molecules which appears to increase rapidly with concentration. His results are tabulated in table 3. The data indicate a very definite trend with concentration for the triazenes which are capable of tautomerism, while the *N*-methyl (or *N*-alkyl) derivatives appear to show normal molecular weights, within the limits of experimental error.

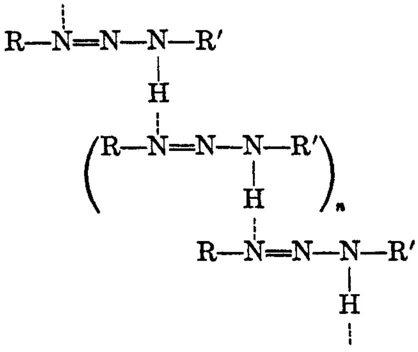
On this basis, Hunter has suggested that the tautomeric triazenes are associated to a greater or less extent in solution, and perhaps completely in the solid state. He has postulated two possible modes of association, one linear and one cyclic. The linear form would be:

TABLE 3

*Association of triazenes*

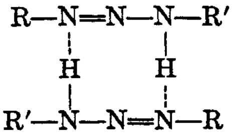


| SUBSTITUENTS | | | RANGE OF CONCENTRATIONS | RANGE OF $\alpha = \frac{\text{EXPERIMENTAL MOLECULAR WEIGHT}}{\text{CALCULATED MOLECULAR WEIGHT}}$ |
|---|---|---|---|---|
| R | R′ | R″ | | |
| | | | *grams/100 g. benzene* | |
| H | H | H | 1.07– 9.88 | 0.95–1.17 |
| 2-$CH_3$ | H | 4-$CH_3$ | 0.77– 5.55 | 0.97–1.12 |
| 4-$CH_3$ | H | 4-$CH_3$ | 0.78– 4.75 | 1.00–1.10 |
| 2-$CH_3O$ | H | 2-$CH_3O$ | 0.76– 8.72 | 0.94–1.12 |
| 4-$CH_3$ | H | H | 0.93– 9.31 | 1.00–1.16 |
| 3-$CH_3$ | H | 4-$CH_3$ | 0.70– 7.97 | 0.96–1.16 |
| 4-$CH_3O$ | H | 4-$CH_3O$ | 1.17– 7.14 | 1.01–1.24 |
| 4-$C_2H_5O$ | H | 4-$C_2H_5O$ | 0.67– 2.56 | 0.83–1.05 |
| 4-Br | $CH_2C_6H_5$ | H | 3.51– 9.8 | 0.96–0.97 |
| 2-$CH_3O$ | $CH_3$ | H | 1.32– 7.77 | 0.95–0.96 |
| 3-$CH_3$ | $CH_3$ | H | 1.27–10.73 | 0.96–1.01 |
| 4-Br | $CH_3$ | H | 2.98–10.62 | 0.96–1.02 |
| 4-$CH_3O$ | $CH_3$ | H | 1.88–10.66 | 0.95–1.02 |



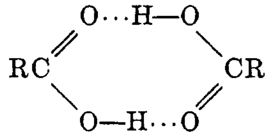
$$\begin{array}{l} \text{R—}\overset{\vdots}{\text{N}}\text{=N—}\underset{\text{H}}{\underset{|}{\text{N}}}\text{—R}' \\ \quad\left(\text{R—}\overset{\vdots}{\text{N}}\text{=N—}\underset{\text{H}}{\underset{|}{\text{N}}}\text{—R}'\right)_n \\ \qquad\quad \text{R—}\overset{\vdots}{\text{N}}\text{=N—}\underset{\underset{\vdots}{\text{H}}}{\underset{|}{\text{N}}}\text{—R}' \end{array}$$

The cyclic form is represented as:



$$\begin{array}{c} \text{R—N=N—N—R}' \\ \vdots \qquad | \\ \text{H} \qquad \text{H} \\ | \qquad \vdots \\ \text{R}'\text{—N—N=N—R} \end{array}$$

The cyclic structure is more likely, since evidence points to the possession of a *trans* configuration by the triazenes. This in turn makes possible a strainless eight-membered ring analogous to that formed by the dimeric carboxylic acids.



### *B. Dipole moments*

Le Fevre and Vine (21) have studied the dielectric constants, densities, and refractive indices of a series of triazenes in benzene. From the data, they calculated the polarizations of the solutions and the dipole moments. The latter are shown in table 4.

The polarization of solutions of triazenes in benzene decreases significantly with concentration, a result which, in agreement with the work of Hunter, implies an association of molecules to a less polar dimer (or polymer).

TABLE 4

*Dipole moments (in Debyes) of some triazenes (21)*

| TRIAZENE | DIPOLE MOMENT | TRIAZENE | DIPOLE MOMENT |
|---|---|---|---|
| $C_6H_5N{=}NNHC_6H_5$ | 0.90 | $C_6H_5N{=}NNHC_6H_4Br$-$p$ | 2.00 |
| $p$-$ClC_6H_4N{=}NNHC_6H_4Cl$-$p$ | 1.90 | $C_6H_5N{=}NN(CH_3)C_6H_5$ | 1.49 |
| $p$-$BrC_6H_4N{=}NNHC_6H_4Br$-$p$ | 1.80 | $C_6H_5N{=}NNHC_6H_4NO_2$-$p$ | 4.79 |
| $p$-$CH_3C_6H_4N{=}NNHC_6H_4CH_3$-$p$ | 0.93 | $p$-$BrC_6H_4N{=}N\underset{\substack{\vert \\ CH_3}}{N}C_6H_4Br$-$p$ | 2.52 |

Since the moment (table 4) of diphenyltriazene (in an infinitely dilute solution, it should be noted) is changed markedly by the symmetrical substitution of groups in the para positions of the benzene rings, the axes of the benzene rings cannot be parallel.

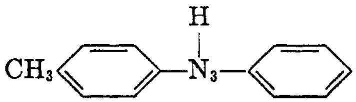
From the known bond moments for C—Cl, C—$CH_3$, etc. it is possible to calculate (21) that the axes of the benzene rings appear to be inclined at an angle of about 141°.

It is difficult to assess the significance of these measurements, since the interpretation of dipole moments of a system as complex as this is difficult, to say the least. However, one qualitative fact should be commented upon. It was found possible to calculate the apparent angle between the benzene rings, 141°, from a variety of symmetrically substituted triazenes; however, attempts to calculate this angle from data for monosubstituted triazenes gave completely inconsistent values.

If dilute solutions of triazenes contain two discrete tautomeric forms

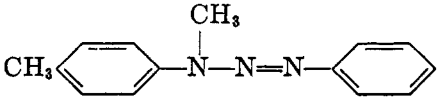
$$RN{=}NNHR' \quad \text{and} \quad RNHN{=}NR'$$

then it is probable that the two forms, when R and R′ are different, will have distinctly different dipole moments, depending on the nature of R and R′; hence the inconsistent angles calculated for monosubstituted triazenes become evidence of a sort for the occurrence of discrete tautomeric forms in solution. A more recent paper (1a) has described the determination of the dipole moments of the following compounds:



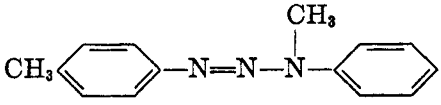
$\mu$ = 1.05 D

A



$\mu$ = 1.76 D

B



$\mu$ = 1.03 D

C

Because of the similarity of the electric moments of A and C the author assigned the structure $p\text{-}CH_3C_6H_4N{=}NNHC_6H_5$ to compound A. This arbitrary assignment of structure is not justified, since in compound C there is a N—$CH_3$ dipole, which is most certainly different from the N—H dipole in A. From the data of Le Fevre and Vine (table 4) *N*-methylation of symmetrical triazene increases its moment by 0.6–0.7 D. On this basis B would appear to be a more suitable model for the structure of A. However, on the basis of other considerations advanced above, it appears wiser not to advance a single structure for any triazene which is capable of tautomerism in solution.

## V. CONCLUSION

Examination of the evidence quoted above allows no definite conclusion to be made regarding the structure of triazenes. The best guess which can be made at the present time is that in solution an unsymmetrical triazene exists as two distinct easily interconvertible tautomers, which are capable of association. In the solid state, it may be dimeric in nature, with a cyclic structure such as the one suggested by Hunter (19)[7] and discussed above.

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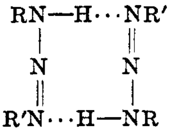
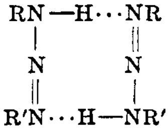
[7] A cyclic structure of this type is open to question, of course, since one would expect two discrete dimers:



$$\begin{array}{ccc} RN\text{—}H\cdots & NR' \\ | & \| \\ N & N \\ \| & | \\ R'N\cdots H\text{—} & NR \end{array}$$

and



$$\begin{array}{ccc} RN\text{—}H\cdots & NR \\ | & \| \\ N & N \\ \| & | \\ R'N\cdots H\text{—} & NR' \end{array}$$

the absence of which may be as hard to rationalize as the original identity of RN=N—NHR′ and R′N=N—NHR.

Any further work which is done on the problem of the structure of the triazenes should, in the opinion of the authors, be of the nature of physical measurements rather than with chemical diagnostic reagents, for the reasons cited above.

One of the most promising methods of attacking the problem would be to examine the solid compounds by x-ray methods, in order to determine the geometry of the molecule, i.e., to ascertain whether a structure such as that suggested by Hunter is possible. Further information could be deduced from bond lengths in the molecule, that is, whether the two nitrogen–nitrogen bonds are equivalent or not.

Other physical measurements which might be expected to contribute measurably to the problem are absorption spectra and polarographic reduction, although recently completed measurements of this type (2) on an extensive series of variously substituted triazenes have not contributed a clear-cut solution to the problem of the nature of triazenes in solution.

## VI. REFERENCES

(1) Bamberger, E., and Billiter, O.: Helv. Chim. Acta **14**, 231 (1931).

(1a) Davidson, A. R.: J. Chem. Education **27**, 598 (1950).

(2) Day, B. F., and Campbell, T. W.: Unpublished data.

(3) Dimroth, O.: Ber. **36**, 909 (1903); **38**, 670 (1905).

(4) Dimroth, O.: Ann. **335**, 1 (1904).

(5) Dimroth, O.: Ber. **40**, 2376 (1907).

(6) Dimroth, O., Eble, M. and Gruhl, W.: Ber. **40**, 2390 (1907).

(7) Dwyer, F. P.: Australian Chem. Inst. J. &. Proc. **5**, 67 (1938).

(8) Dwyer, F. P.: Australian Chem. Inst. J. &. Proc. **6**, 348, 362 (1939).

(9) Dwyer, F. P., and Ray, E.: Chemistry and Industry **59**, 136 (1940).

(10) Dwyer, F. P.: J. Am. Chem. Soc. **63**, 78 (1941).

(11) Dwyer, F. P., and Mellor, D. P.: J. Am. Chem. Soc. **63**, 81 (1941).

(12) Forster, M. O., and Garland, C. S.: J. Chem. Soc. **95**, 2051 (1909).

(13) Goldschmidt, H., and Holm, J.: Ber. **21**, 1016 (1888).

(14) Goldschmidt, H., and Molinari, E.: Ber. **21**, 2557 (1888).

(15) Griess, P.: Ann. **121**, 258 (1862).

(16) Griess, P.: Ber. **7**, 1618 (1874).

(17) Hausser, I., Jerchel, D., and Kuhn, R.: Ber. **82**, 515 (1949).

(18) Heumann, K., and Oeconomides, L.: Ber. **20**, 372, 904 (1887).

(19) Hunter, L.: J. Chem. Soc. **1937**, 320.

(20) Jerchel, D., and Fischer, H.: Ann. **563**, 301 (1949).

(21) Le Fevre, R. J. W., and Vine, H.: J. Chem. Soc. **1937**, 1805.

(22) Mangini, A., and Dejudicibus, I.: Gazz. chim. ital. **63**, 601 (1933).

(23) Mangini, A.: Gazz. chim. ital. **65**, 298 (1935); **67**, 384 (1937); J. Soc. Chem. Ind. **58**, 327 (1939).

(24) Meldola, R., and Streatfeild, F. W.: J. Chem. Soc. **49**, 624 (1886); **51**, 102, 434 (1887); **53**, 664 (1888); **55**, 412 (1889); **57**, 785 (1890).

(25) Nölting, E., and Binder, F.: Ber. **20**, 3004, 3014 (1887).

(26) von Pechmann, H.: Ber. **27**, 320 (1894).

(27) Sarauw, A.: Ber. **14**, 2442 (1881); **15**, 42 (1882).

(28) Saunders, K. H.: *The Aromatic Diazo Compounds*, second edition. Arnold and Company, London (1949).

(29) Smith, C., and Watts, C.: J. Chem. Soc. **97**, 562 (1910).