[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

THE CRISSCROSS ADDITION ON CONJUGATE SYSTEMS. THE ACTION OF CYANIC ACID, THIOCYANIC ACID AND ISOCYANATES ON AZINES.

BY J. R. BAILEY AND A. T. McPHERSON.

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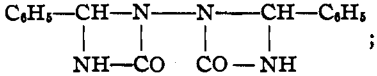
Introduction.

Thiele in his comprehensive study of the unsaturated compounds[1] concludes that, as a rule, with a conjugate system of double bonds, more especially C = C — C = C and C = C — C = O addition takes place on the 1,4 position rather than on the 1,2 or 3,4 position. Subsequently it developed that Thiele's conclusions were not justified, for, as shown by Straus,[2] *e. g.*, the addition of bromine on the system C = C — C = C takes place on both the 1,2 and 1,4 positions. Staudinger[3] has shown that ketenes also react with the system C = C — C = O with addition on both the 1,4 and 3,4 positions. However, in the addition of hydrogen and nitrogen peroxide[4] on conjugate systems only the 1,4 position is involved. Another class of reactions of conjugate systems is that of polymerization, such as takes place with butadienes to octodienes as exemplified in the synthesis of a caoutchouc from isoprene.

Bailey and Moore[5] discovered a new reaction of azines in their addition of 2 mols. of cyanic acid on 1 mol. of benzalazine, $C_6H_5CH = N — N = CHC_6H_5$, and in this paper it is shown that thiocyanic acid and phenyl isocyanate behave in a similar way toward azines. In the case of azines, addition, as far as our observation goes, never takes place on the 1,4 position. It may occur, as in the addition of HCN[6] on the 1,2 and 3,4 positions simultaneously, but as the HCN addition does not result here in ring formation, it should be observed that a 1,3–2,4 addition would have the same result as a 1,2–3,4 addition. For the $C_6H_5CH = N — N = CHC_6H_5.2HCNO$ compound the proof is conclusive that a carbonyl group is joined to each nitrogen and this fact eliminates all structural possibilities for the product except two.

(I).



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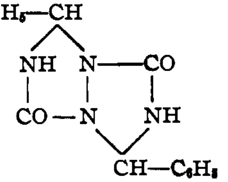
(II).



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[1] *Ann.*, **306**, 87 (1899).

[2] *Ber.*, **42**, 2866 (1909).

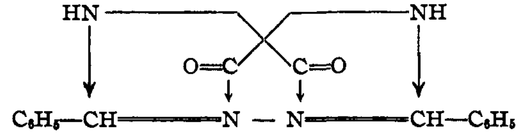
[3] "Die Ketene," p. 108 (1912).

[4] Wieland and Stenzl, *Ann.*, **360**, 299 (1908).

[5] THIS JOURNAL, **39**, 279 (1917).

[6] *Ann.*, **290**, 22 (1896); **303**, 87 (1898).

The formation of II implies a 1,3 and 2,4 addition *simultaneously* and, unlike the 1,2, 3,4 or 1,4 additions on conjugate systems, the 1,3 and 2,4 additions are interdependent; in other words, a reaction like that of cyanic acid on benzalazine to form product (II) represents an *intramolecular coupled reaction.* The reactions of the systems $C = C - C = C$ and $C = C - C = O$ usually lead to the complexes $C = C - C - C$ or $C - C = C - C$ and $C = C - C - O$, $C - C = C - O$, or $C - C - C = O$, respectively, *i. e.*, the conjugate system passes to a complex still unsaturated but containing only one double bond. In case the reaction between cyanic acid and benzalazine has found a correct interpretation in the assumption of a 1,3–2,4 coupled addition, it is of a new type for conjugate systems. For this form of reaction we propose the name, "crisscross" addition, a name suggested by the following graphic representation of the reaction between cyanic acid and benzalazine:



When an unsaturated molecule of the ethylene type, such as $NH = CO$, undergoes crisscross addition on a conjugate system, it is evident that a binuclear, five-atom ring complex must result, with the atoms of the conjugate system in the 2,3 positions serving as connecting links between the two nuclei.

Staudinger[1] emphasizes the analogy between isocyanates and ketenes; "the ketenes in their method of preparation as well as in their reactions have much in common with substances containing twin double bonds." The formulas $R_2C = C = O$ and $R - N = C = O$ he employs to indicate the analogy. As Staudinger considers ketones more reactive than isocyanates, it was to be expected that the former would readily condense with azines, especially in view of the fact that $C = N$ complex in Schiff bases shows an additive reaction toward ketones.[2] Repeated attempts by us under modified conditions to effect a crisscross addition of diphenylketene on benzalazine as well as ketazine were unsuccessful. Unfortunately, as far as our observation goes, there is no published work on the behavior of ketenes toward butadiene or substituted butadienes. Here, since a *symmetrical* binuclear ring complex might result, the probability of a crisscross addition would necessarily be greater than in the case of the conjugate system, $C = C - C = O$.

W. J. Hale, of the University of Michigan, has by letter taken issue with Bailey and Moore as to the constitution of their $C_6H_5CH = N - N =$

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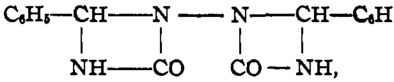
[1] "Die Ketene," p. 2 (1912).

[2] *Ann.*, **336,** 95 (1907).

$CHC_6H_5.2HCNO$ compound. He contends that the chemical behavior of the substance argues for the constitution,



$$\begin{array}{llll} C_6H_5-CH & -N & -\,N- & CH-C_6H_5 \\ \quad\;\; | & \;\;| & \;\;| & \;| \\ \quad NH & -CO & CO- & NH, \end{array}$$

one of the formulas discussed in the Bailey-Moore article as a possible interpretation of the substance. By permission of Hale his arguments in support of this contention may be quoted:

> "A ring of the triazolotriazole type would be very stable toward acids. The N-rings are of course basic and acids only protect them further. Alkalies will attack such rings in the presence of oxidizing agents and even here the oxidation often proceeds very slowly. We may cite here the triazopyridazine of Bülow[1]
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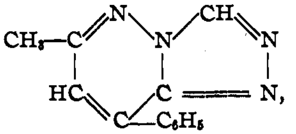
> 
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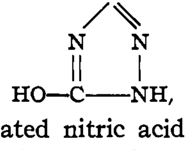
> a compound oxidized only with difficulty in the presence of alkaline permanganate. This same compound was found to be unaffected by boiling nitric acid or by sulfuric acid. Bülow found that nitric acid merely added its molecule to his new type of ring structure. The ring structure proposed in the Bailey-Moore article for the $C_6H_5CH = N - N = CHC_6H_5.2HCNO$ compound should have much in common with this new type discovered by Bülow, and in fact I know of no better example with which to draw comparisons. Certain it is that steam distillation carried out in alkaline solution could not effect the decomposition that was observed. The reaction products which have been obtained constitute an interesting study, but, from my point of view, must have come from a much more unstable substance than the triazole type."
>
> "The great ease with which benzaldehyde can be eliminated from the compound at once recalls the methylene-urea ring. The formula which is proposed as the third possibility in the Bailey-Moore article is the one which I believe to be correct."

The bis-benzylideneurea formula, championed by Hale, it will be granted, can explain in a very simple way the formation of three of the cleavage products obtained by Bailey and Moore from the $C_6H_5CH = N - N = CHC_6H_5.2HCNO$ compound, to wit,

$$C_6H_5CH = N - N = CHC_6H_5,\ C_6H_5CH = N - NH - CONH_2,$$
$$\text{and } NH_2CO - NH - NH - CONH_2.$$

However, the formation of Young and Witham's triazole,



by the action of "concentrated nitric acid at a temperature below 10° in excellent yield," from a substance of constitution (I) would, to say the least, be unexpected. Furthermore, in the alkali hydrolysis there is ob-

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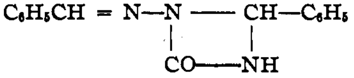
[1] *Ber.*, 42, 2208, 2594 (1909).

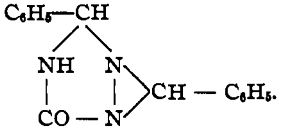
tained in poor yield a beautifully crystallizing substance, which differs from the original $C_6H_5CH = N — N = CHC_6H_5.2HCNO$ compound by one HCNO equivalent. The evidence is conclusive against the substance having the structure,



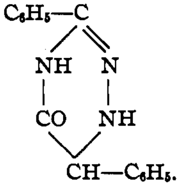
$$\begin{array}{lcl} C_6H_5CH = N—N & — & CH—C_6H_5 \\ \quad\quad\quad\quad\quad | & & | \\ \quad\quad\quad\quad\quad CO & — & NH \end{array}$$

as would be expected, were it obtained from a substance of structure (I).[1] The great stability of the compound rather argues for the constitution,

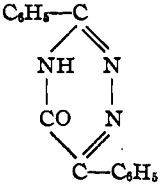
(III).



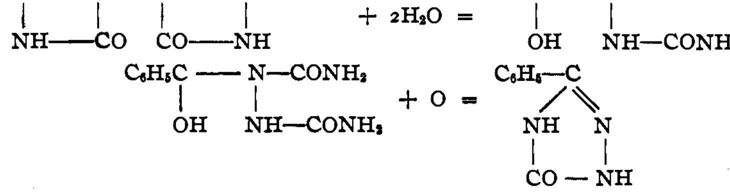
Another possibility is,



As shown in the experimental part of this paper, the compound $C_6H_5CH = N — N = CHC_6H_5,HCNO$ is nitrated but not oxidized by nitric acid. It would be expected of a triazine of this structure, that it would be readily oxidized to[2]



The formation of complex (III) from the bitriazole (II) can be very simply explained, whereas its formation from benzylideneurea (I) would necessitate a hydrolysis of both benzylideneurea rings with a subsequent regrouping to form two different rings as shown in structural Formula III. Hale's interpretation of the nitric acid reaction is as follows:



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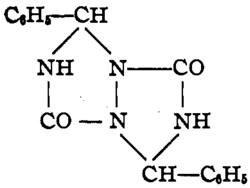
[1] THIS JOURNAL, 39, 288 (1917).

[2] Cf. *Ann.*, 303, 82 (1898).

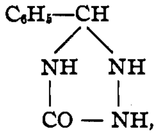
The weakness in Hale's argument lies in the fact that he ignores the effect that the *state of saturation* has on the stability of heterocyclic compounds. Wedekind[1] states this effect clearly:

> "The stability of the true heterocyclic rings has given rise to the assumption of so-called potential valencies, just as happens in the case of benzene as exemplified by the Armstrong-Baeyer formula. Through partial or complete saturation of the potential valencies rings of alicyclic character result, which in relation to cleavage closely resemble the labile, heterocyclic rings found in lactones, lactides, lactames, as well as in cyclic anhydrides, imides, alkylene esters, etc."

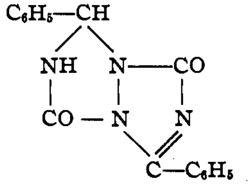
Hale regards



as a *tetrahydro*triazolotriazole, while Bailey and Moore consider it *hexahydro*. According to the latter interpretation it, written in its enolic form, becomes *dihydro*, a fact which emphasizes the *impossibility of potential valencies* in a bitriazole of this type. The unknown parent substance here,



is beyond question *tetrahydro*, with its enolic form *dihydro*. Were the two H's on the NH-NH complex substituted by the divalent group — CON = C — C_6H_5, there would result



which is certainly a *tetrahydro*triazolotriazole. If this reasoning be logical, the Bailey-Moore triazolotriazole must be *hexahydro*.

Hale, as quoted above, refers to the similarity in structure between Bülow's triazopyridazine and the supposed triazolotriazole of Bailey and Moore. The mere fact that the latter substance contains the complex NH — CO — N in each nucleus, while the Bülow compound is oxygen free, precludes any analogy in the chemical behavior of two substances with with such intrinsic differences in their constitution. A much more

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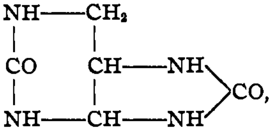
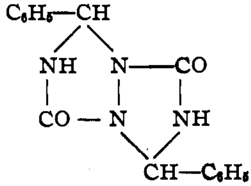
[1] "Heterocyklische Verbindungen," p. 6–7 (1901).

appropriate substance, from which to forecast the chemical behavior of a substance constituted like the triazolotriazole is purone,



reported by Tafel,[1] as this contains in each nucleus the same complex, N — CO — NH — CH, as is present in

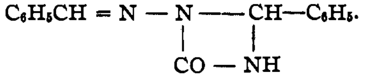


and, what is equally important, both substances represent *completely saturated* binuclear heterocyclic complexes. Purone exists in an enolic form, which Tafel terms isopurone, and the reactions of the purone molecule are frequently preceded by a change to this tautomeric form. Purone, like the supposed bitriazole, readily undergoes cleavage with alkalies, acids, and oxidizing agents, in other words purone in its chemical behavior is entirely different from the less saturated purine compounds. The following quotation from the paper of Tafel emphasizes the analogy between purone and the Bailey-Moore compound:

> "On warming with barium hydroxide, as well as with caustic alkalies, purone dissolves with a change to isopurone and on continued boiling barium carbonate is formed and ammonia evolved. On warming purone, dissolved in 50% H_2SO_4, the solution gradually turns yellow and this color next passes to a cherry red; at the same time a caramel odor is observed. If purone is warmed on the water bath with 50% HNO_3, the solution colors reddish brown, then yellow, and after a short time a violent gas evolution sets in. From the reaction products a crystallizable product could not be isolated."

The evidence in favor of the bitriazole formula as against the bis-benzylideneurea structure for the $C_6H_5CH = N — N = CHC_6H_5.2HCNO$ compound may be summarized as follows:

(1) If in its reaction with benzalazine cyanic acid adds onto the 1,2 and 3,4 positions simultaneously, it is theoretically possible for *one* mol. of cyanic acid to add on, giving the hydrazone



$$C_6H_5CH = N - \underset{\displaystyle CO}{N} - \underset{\displaystyle NH}{CH} - C_6H_5.$$

Repeated trials to arrest the reaction at this stage proved unavailing, both in case of cyanic acid and phenyl isocyanate.

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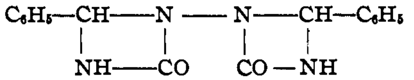
[1] *Ber.*, 34, 268 (1901).

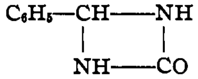
(2) Our attempts to bring about reactions between hydrazones, Schiff bases, and semicarbazones have been without result, an indication that there is no tendency here for the formation of four atom rings of the methylene-urea type. Staudinger[1] records the failure of similar experiments to bring about a reaction between Schiff bases and phenyl isocyanate.

(3) By steam distillation in potassium hydroxide solution it is possible to eliminate from the $C_6H_5CH = N - N = CHC_6H_5.2HCNO$ one HCNO equivalent.[2] Were the original cyanic acid compound bis-benzylidene urea, benzalaminobenzylideneurea, referred to under 1, would be the substance logically expected to result. The product obtained here does not possess the properties of a hydrazone, *nor does it revert to the parent substance by treatment with HCNO in glacial acetic acid.*

(4) Attempts to split the molecule by reduction with zinc dust and glacial acetic acid both in the case of the $C_6H_5CH = N - N = CHC_6H_5.2HCNO$ and $C_6H_5CH = N - N = CHC_6H_5.2C_6H_5NCO$ compounds were unavailing.[3] A substance like



represents a ditertiary hydrazine[4] and reduction here might lead to benzylidene urea,



(5) The supposed bitriazoles show strikingly similar properties to Tafel's saturated cyclic diureide, purone, and, as a matter of fact, the bitriazoles here concerned can also be regarded as saturated cyclic diureides,

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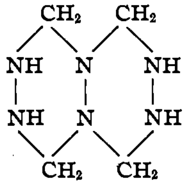
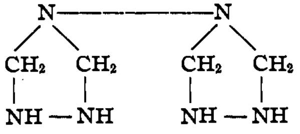
[1] "Die Ketene," p. 126.

[2] *Loc. cit.*

[3] Hoffman and Storm (*Ber.*, 45, 1729 (1912)) obtained in the interaction of formaldehyde and hydrazine "tetraformaltriazine," which represents two condensed triazine nuclei with two nitrogens common to each ring,



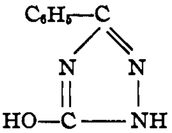


This structure is given preference over a second possibility, a bis-triazole of the structure. Hoffman and Storm state that "it would be expected that in the reduction of a substance of the bistriazole type a cleavage would occur between the nitrogens occupying the one position in the two triazole rings. However, tetraformaltriazine is not attacked by sodium amalgam in aqueous solution." Obviously the problem of structure presented in tetraformaltriazine is strictly analogous to the one at hand in our paper.

[4] Cf. Wieland, "Die Hydrazine," p. 62 (1913).

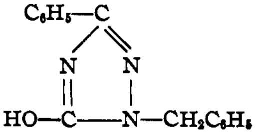
since they contain a urea rest in each nucleus. The fact should be emphasized that purone, although containing a smaller per cent. of oxygen than the more unsaturated uric acid, in contrast to the latter, is readily hydrolyzed both by acids and alkalies, a behavior parallel with that of the bitriazoles. As far as our observation goes, completely saturated mononuclear triazoles of the 1,2,4 type are unknown, and the above contrast in the chemical behavior between purone and uric acid warrants the statement that there is nothing unexpected in the ready cleavage of the saturated bitriazole (II), as contrasted with the great stability of the ring complex in the closely related hydroxyphenyltriazole of Young and Witham.

(6) If it be assumed that any other than the bitriazole structure can explain the formation of phenylhydroxytriazole,

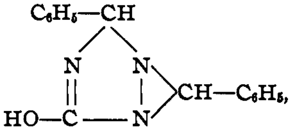


from the $C_6H_5CH = N - N = CHC_6H_5.2HCNO$ compound by the action of nitric acid, the fact that this reagent, as shown in the experimental part of this paper, does not produce the above triazole from any of the following substances:

$NH_2CONHN = CHC_6H_5$

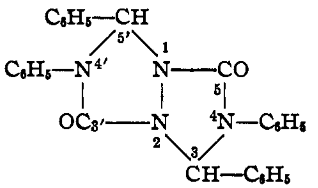


and the Bailey-Moore compound of the probable structure,

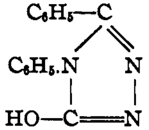


excludes all of these as possible intermediary products in the action of nitric acid on the $C_6H_5CH = N - N = CHC_6H_5.2HCNO$ compound.

In the new work discussed in this paper on the crisscross addition it is shown that phenyl isocyanate, similarly to cyanic acid, condenses with benzalazine, *m*-nitrobenzalazine, cinnamalazine, and furalazine. The structure assigned these substances can be exemplified by the phenyl isocyanate-benzalazine compound,



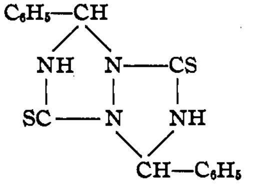
from which, in conformity with the nomenclature adopted for the cyanic acid compounds, the name 5,3′-diketo-3,4,4′,5′-tetraphenylhexahydro-1,2-triazolotriazole is evolved. In contrast to the diphenylbitriazoles, these substances are very resistant to cleavage. However, a corresponding behavior of the two classes of substances is shown in the alkali hydrolysis. From the tetraphenyl bitriazole there is obtained by the action of potassium hydroxide benzalphenylcarbamylhydrazone, $C_6H_5NHCO.NHN = CH\text{-}C_6H_5$. The constitution of this hydrazone was established (1) by synthesis from phenyl isocyanate and benzalhydrazine, $C_6H_5CH = NNH_2$; (2) by its oxidation with ferric chloride to diphenylhydroxytriazole,



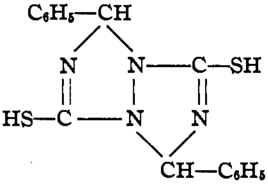
(3) by its reduction to α-benzyl-β-phenylcarbamylhydrazine, $C_6H_5NH\text{-}CONHNHCH_2C_6H_5$; and (4) by its hydrolysis to phenylcarbamylhydrazine, $C_6H_5NHCO - NHNH_2$. At elevated temperatures the tetraphenylbitriazole dissociates into phenyl isocyanate and benzalazine, while the diphenylbitriazole dissociates into cyanic acid and benzalazine.

Cyanic acid addition products of cinnamalazine and furalazine have been prepared, but, since they are difficult to obtain in a state of purity, they were not further investigated.

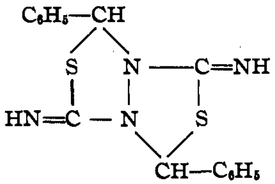
Like cyanic acid, thiocyanic acid, where it reacts with azines, adds on in the proportion of two mols. of HCNS to one mol. of the azine. The $C_6H_5CH = N - N = CHC_6H_5.2HCNS$ compound, which can be obtained in excellent yield and perfectly pure, probably has the structure



or



This structure is given preference over the possibility,



because of the alkali solubility and acid insolubility of the compound. However, desulfurization under different conditions by the very efficient method of Johnson, Pfau, and Hodge[1] by the use of chloroacetic acid did not succeed, in all probability because of the instability of the bitriazole complex at the temperature necessary to effect the reaction.

Our experiments indicate that the azines of acetaldehyde, acetone, benzophenone, and acetophenone will not condense with either cyanic acid or phenyl isocyanate under conditions employed by us in the case of other azines. Furthermore, all attempts to extend the reaction to mustard oils led to smears, from which crystallizable products were not obtained.

Molecular weight determinations reported in this paper, establish beyond question the molecular formulas, $C_6H_5CH = N — N = CHC_6H_5.2HCNO$ and $C_6H_5CH = N — N = CHC_6H_5.2C_6H_5NCO$ for the products obtained in the interaction of benzalazine with cyanic acid and phenyl isocyanate, respectively.

Experimental Part.

5,3′-Diketo-3,4,4′,5′-tetraphenylhexahydro-1,2-triazolotriazole. — On heating 2 mols. of phenyl isocyanate and 1 mol. of benzalazine in a sealed tube at 160–170°, a white, crystalline solid results. This triazolotriazole, which is difficultly soluble in most organic solvents, may be purified by washing with ether and crystallizing from glacial acetic acid. It is soluble to about 1 part in 30 in boiling glacial acetic acid, and crystallizes on cooling in small, rhombohedral plates which melt with decomposition at 263°. Having no imino hydrogens the tetraphenyl bitriazole, in contrast to the corresponding diphenyl bitriazole referred to elsewhere in this paper, is insoluble in alkalies, and cleavage of the molecule by the action of concentrated potassium hydroxide solution is effected only at elevated temperatures. Concentrated hydrochloric acid as well as 20% sodium hydroxide does not react with the substance at 150°. Nitrous acid gas has no effect on it in acetic acid solution, even at boiling temperature. Alkaline permanganate is reduced in boiling solution but the products of the reaction were not isolated. Attempts to reduce the bitriazole were unsuccessful. One g. of the substance, after being boiled 4 hours with a solution of 3 g. of stannous chloride in 50 cc. concentrated hydrochloric acid and 50 cc. glacial acetic acid, was recovered, unchanged. In a second experiment 1 g. of the bitriazole was boiled 4 hours with 3 g. zinc powder, 10 g. glacial acetic acid, and 100 g. alcohol without change.

Calc. for $C_{28}H_{22}O_2N_4$: C, 75.33; H, 4.96; N, 12.55. Found: C, 75.05; H, 4.95; N, 12.67.

Molecular Weight Determinations of the Bailey-Moore dihydroxydiphenyltriazolotriazole and of the diketotetraphenyltriazolotriazole by the elevation of the boiling point were made. With the first substance in six determinations, 0.4205, 0.6352, 0.8596, 1.0908, 1.2962, 1.5182 g. in

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[1] THIS JOURNAL, 34, 1041 (1912).

28.00 g. alcohol gave the respective elevations of 0.067°, 0.100°, 0.127°, 0.157°, 0.170° and 0.211°, from which the mean value 288 was calculated in comparison with the theoretical value 294. With the second substance, 0.2480, 0.6970 and 0.8326 g. in 27.9 g. of glacial acetic acid gave the elevations, 0.052°, 0.144° and 0.174°, respectively, from which was calculated the average value 435 as against the theoretical 446.

Attempts to add 1 mol. of phenyl isocyanate on 1 mol. of benzalazine under the conditions employed above with the exception that equimolecular amounts of the two substances were used, always yielded the bitriazole and a brown, ether soluble product which was probably an $N_2(CHC_6H_5)_3$ compound of unknown constitution described by Curtius and Jay as an intermediary product in the decomposition of benzalazine at elevated temperatures into nitrogen and stilbene.[1] This experiment indicates that the reaction of phenyl isocyanate on benzalazine is a crisscross addition, *i. e.*, the addition of the 2 mols. of isocyanate on 1 mol. of the azine is interdependent and that an intermediary product, $C_6H_5CH = N — N = CHC_6H_5.1C_6H_5NCO$ is impossible.

α-Benzal-β-phenylcarbamylhydrazone, $C_6H_5NHCONHN = CHC_6H_5$.—This substance is produced, together with benzaldehyde and benzoic acid, by heating at 130° the tetraphenyl bitriazole for 15–30 minutes with 4 or 5 parts of 1 : 1 potassium hydroxide solution in a nickel crucible, and floats on the surface of the alkali melt as a yellow solid. On washing with water and crystallizing from alcohol a beautiful, white mass of interlacing needles is obtained. The hydrazone crystallizes readily from benzene, alcohol, and dilute acetic acid, and is difficultly soluble in ether, petrolic ether, and water. It melts at 180° apparently undecomposed. The same substance is readily synthesized from benzalhydrazine, $C_6H_5CH = NNH_2$, and phenyl isocyanate which react violently at ordinary temperatures with the production of a solid mass; or the reaction is better conducted in a benzene, ether, or petrolic ether solution from which the product separates as a white crystalline mass.

Calc. for $C_{14}H_{13}ON_3$: C, 70.26; H, 5.47; N, 17.58. Found: C, 70.22; H, 5.58; N, 17.75.

α-Benzyl-β-phenylcarbamylhydrazine, $C_6H_5NHCONHNHCH_2C_6H_5$.—When the reduction of benzalphenylcarbamylhydrazone is effected with sodium amalgam in boiling alcoholic solution by the method of Kessler and Rupe,[2] benzylphenylcarbamylhydrazine separates in small, uniform prisms, which after recrystallization from alcohol and from benzene, melt at 138° without apparent decomposition.

Calc. for $C_{14}H_{15}ON_3$: C, 69.68; H, 6.27. Found: C, 69.83; H, 6.18.

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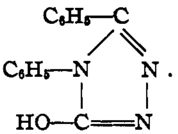
[1] *J. prakt. Chem.*, [2] **39**, 45 (1889).

[2] *Ber.*, **45**, 26 (1912).

5-Hydroxy-3,4-diphenyltriazole,



—Benzalphenylcarbamylhydrazone may be oxidized to hydroxydiphenyltriazole by the method of Young and Witham[1] by heating in a sealed tube to 130° with alcoholic ferric chloride. The triazole separates from the alcohol as a mass of long, fine, interlacing needles, and melts after recrystallization from alcohol at 260° without decomposition. Attempts to obtain this substance by oxidation of the tetraphenylbitriazole with nitric acid as well as alkaline permanganate were unsuccessful. Characteristic for the triazole is a difficultly soluble potassium salt which separates as a matted mass of long, slender needles on dissolving the substance in hot 1 : 2 potassium hydroxide solution and cooling.

Calc. for $C_{14}H_{11}ON_3$: C, 70.84; H, 4.68; N, 17.73. Found: C, 70.98; H, 4.69; N, 17.86.

Phenylsemicarbazine, $C_6H_5NHCONHNH_2$. — On heating benzalphenylcarbamylhydrazone with 1 : 1 or 1 : 2 sulfuric acid in a current of steam, benzaldehyde is split off quantitatively and phenylsemicarbazine separates as the sulfate. The free hydrazine is obtained by making alkaline with ammonia and extracting with chloroform. Evaporation of the chloroform yields a slightly yellow product, which, after further purification by repeated crystallization from alcohol and from benzene, melts at 128° undecomposed. The phenylsemicarbazine is readily reconverted to benzalphenylcarbamylhydrazone by shaking with benzaldehyde in water.

Calc. for $C_7H_9ON_3$: C, 55.60; H, 6.00; N, 27.81. Found: C, 55.86; H, 6.01; N, 27.94.

The Decomposition of Bitriazoles on Heating.—When the above bitriazole is heated it melts with decomposition; phenyl isocyanate distils off, leaving benzalazine as a yellow liquid, which on subsequent heating passes over as stilbene, with the evolution of nitrogen.[2] Phenyl isocyanate was identified by its odor and by conversion to diphenyl urea. The stilbene, after redistillation and recrystallization from alcohol, melted at 125° as given in Beilstein.

It was also found that the corresponding Bailey-Moore dihydroxydiphenyltriazolotriazole dissociates similarly at elevated temperatures into stilbene, nitrogen, and cyanic acid, the latter, of course, polymerizing to

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[1] *J. Chem. Soc.*, **77**, 226 (1900).

[2] Cf. Curtius and Jay, *J. prakt. Chem.*, [2] **39**, 45 (1889).

cyanuric acid, which was identified by its property of sublimation and by the characteristic, difficultly soluble copperammonium salt.[1]

5,3′-Diketo-4,4′-diphenyl-3,5′-dimetanitrophenylhexahydro-1,2-triazolotriazole.—When 2 mols. of phenyl isocyanate and 1 mol. of metanitrobenzalazine are heated in a sealed tube for an hour at 150° they react to give a brownish white, crystalline mass, which is readily purified by washing with ether and crystallizing from benzene and then from glacial acetic acid. The solubilities are similar to those of the corresponding tetraphenyl bitriazole. The substance melts with decomposition at 260°.

Calc. for $C_{28}H_{20}O_6N_6$: C, 62.67; H, 3.76; N, 15.67. Found: C, 62.87; H, 3.82; N, 15.93.

5,3′-Diketo-4,4′-diphenyl-3,5′-distyrylhexahydro-1,2-triazolotriazole.—On heating 1 mol. of cinnamalazine and 2 mols. of phenyl isocyanate in a sealed tube at 140–150° for 2 hours, a brownish white, crystalline reaction product is obtained. On purification by washing with ether and crystallizing from glacial acetic acid, the substance is obtained as a mass of interlacing needles, melting at 243° with decomposition. This bitriazole is very soluble in boiling chloroform, moderately so in glacial acetic acid and benzene, and practically insoluble in other common solvents.

Calc. for $C_{32}H_{26}O_2N_4$: C, 77.08; H, 5.27; N, 11.24. Found: C, 76.81; H, 5.23; N, 11.33.

5,3′-Diketo-4,4′-diphenyl-3,5′-difurylhexahydro-1,2-triazolotriazole.—This bitriazole is prepared from furalazine and phenyl isocyanate similarly to the preceding substance. After washing the crude product with ether, it can be recrystallized from glacial acetic acid and then from amyl alcohol be obtained pure in the form of minute prisms, which melt at 257° with decomposition. It is only sparingly soluble in the common organic solvents.

Calc. for $C_{24}H_{18}O_4N_4$: C, 67.57; H, 4.26; N, 13.15. Found: C, 67.34; H, 4.34; N, 13.38.

5,3′-Dihydroxy-3,5′-distyryldihydro-1,2-triazolotriazole. — On adding an excess of pulverized potassium cyanate to cinnamalazine, suspended in about 10 parts of glacial acetic acid, complete solution is soon effected with a discharge of the yellow color, and then on dilution with water the reaction product separates out as a crystalline powder. This bitriazole, after being purified by dissolving in 10% potassium hydroxide solution and precipitating with acetic acid, crystallizing from alcohol, and precipitating from acetone solution with petrolic ether, melts at 192° with decomposition. Since it decomposes somewhat on heating in solution, as indicated

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[1] *Ann.*, **62**, 250 (1847).

by the analytical results, the substance is difficult to obtain pure and is colored a light yellow.

Calc. for $C_{20}H_{18}O_2N_4$: C, 69.34; H, 5.24; N, 16.18. Found: C, 68.81; H, 5.27; N, 15.96.

5,3′-Dihydroxy-3,5′-difuryldihydro-1,2-triazolotriazole. — Furalazine dissolves readily in glacial acetic acid, giving a deep red-colored solution. When potassium cyanate is added, small portions at a time, to the cold solution of the azine the color changes to a light yellow, and there is only a slight gas evolution. After standing about an hour, the glacial acetic acid solution is diluted with water, whereupon the bitrazole admixed with a considerable quantity of the unchanged azine precipitates. On treating the crude product with ammonia, filtering off the unchanged azine, and neutralizing with acetic acid, about 25% of the calculated amount of the bitriazole is obtained. The substance was never obtained pure, because it decomposes slightly on heating in solution. The sample used in the analysis melted at 191° and had a light yellow color after crystallization from dilute alcohol.

Calc. for $C_{12}H_{10}O_4N_4$: C, 52.55; H, 3.65; N, 20.44. Found: C, 53.10; H, 4.05; N, 19.48.

5,3′-Dimercapto-3,5′-difuryldihydro-1,2-triazolotriazole. — When an excess of potassium thiocyanate is added to a solution of furalazine in glacial acetic acid, the color becomes perceptibly lighter and, on standing several hours, a slightly yellow precipitate begins to separate out. As in the case of the addition of cyanic acid on benzalazine the reaction does not go to completion, but a small amount of the azine remains unchanged, even when the thiocyanate is present in excess. After standing a day the bitriazole is filtered off and washed with water, while a further small amount may be obtained by diluting the acetic acid solution. Although the substance can be recrystallized from either dilute acetic acid or alcohol, partial decomposition accompanies this method of purification. A product of light buff color, decomposing at 154–156° is obtained by dissolving the product in cold potassium hydroxide solution, precipitating with dilute acetic acid, and washing with water and dilute alcohol. The substance has solubilities similar to those of the corresponding dimercaptodiphenyltriazolotriazole described later.

Calc. for $C_{12}H_{10}O_2N_4S_2$: N, 18.30; S, 20.94. Found: N, 18.25; S, 21.07.

5,3′-Dimercapto-3,5′-diphenyldihydro-1,2-triazolotriazole.[1] — To 20.8 g. of benzalazine in 125 cc. of glacial acetic acid are added with stirring 45 g. of potassium thiocyanate in small portions. From the solution, which is kept cool during the reaction, there separates after short standing about 48 g. of the above bitriazole, colored light yellow by some unchanged

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[1] The investigation of the action of thiocyanic acid on benzalazine was carried out by J. R. Bailey and N. H. Moore.

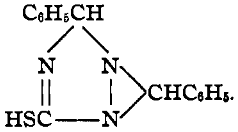
benzalazine. On dilution of the acid solution with water there is obtained a further small amount of the reaction product. To separate the bitriazole from admixed benzalazine, it is dissolved in potassium hydroxide solution and precipitated by making the solution acid with hydrochloric acid. Further purified by recrystallization from glacial acetic acid and then from dilute alcohol, the substance is obtained in thin, rhombic plates, which begin to soften at about 181° and melt with decomposition to a red liquid at 187°. It is readily soluble in ether, acetic ether, and acetone, and only slightly soluble in chloroform, benzene, and water. Nitric acid reacts violently with the substance with a copious evolution of nitrous fumes, but from the reaction mixture on dilution with water there was obtained a resinous substance, which showed no tendency to crystallize. If the bitriazole be dissolved in cold, concentrated sulfuric acid and the solution then be diluted with water, a layer of benzaldehyde is formed in addition to a smear which was not further investigated. The insolubility of the bitriazole in concentrated hydrochloric acid shows that it does not possess basic properties. In acetone solution it readily reduces permanganate, while on the other hand it is not reduced by boiling in glacial acetic acid with zinc dust. In contrast to the corresponding oxygen compound the mercapto bitriazole is very stable toward alkalies: 1.5 g. of the substance in 200 cc. of 10% potassium hydroxide solution, submitted to steam distillation for 1.5 hrs., gave a distillate with only a slight odor of benzaldehyde, while from the original alkaline solution there was regained on acidifying more than 1 g. of unchanged substance. However, when heated at an elevated temperature in a sealed tube, as indicated below, it decomposes with the formation of a product differing from the original substance by an HCNS equivalent. Attempts to desulfurize the $C_6H_5CH = N - N = CHC_6H_5.2HCNS$ compound by the use of chloroacetic acid were without result and we were not successful in the preparation of an acetyl derivative by the use of acetic anhydride.

Calc. for $C_{16}H_{14}N_4S_2$: C, 58.89; H, 4.29; N, 17.18; S, 19.63. Found: C, 58.82; H, 4.39; N, 17.34; S, 19.73.

An alcoholic solution of mercuric chloride added to an alcoholic solution of the mercaptobitriazole gives immediately an orange-yellow salt in practically quantitative yield, difficultly soluble in all common organic solvents.

Calc. for $C_{16}H_{16}N_4S_2.HgCl_2$: N, 9.38. Found: N, 9.33.

Action of Potassium Hydroxide on 5,3′-Dimercapto-3,5′-diphenyl-dihydro-1,2-triazolotriazole.—2 g. of the mercapto-bitriazole, heated in a sealed tube with 15 cc. conc. KOH for two hours at a temperature of 140–150°, react with a formation of a small amount of benzalazine, and the liberation of part of the nitrogen as ammonia but none as hydrazine. On acidification with hydrochloric acid there separates from the solution about 0.7 g. of a white solid, and a vigorous evolution of hydrogen sulfide occurs. The substance crystallizes from glacial acetic acid in the form of slender prisms which melt without decomposition at 166°. It is readily soluble in ether, fairly soluble in glacial acetic acid and alcohol, difficultly soluble in benzene, chloroform, and acetic ether, and insoluble in water. It is readily soluble in alkalies but insoluble in mineral acids. Attempts to desulfurize by boiling with chloroacetic acid were unsuccessful. The substance was found to differ from the original substance by one HCNS equivalent, and is probably 5-mercapto-3-phenyl-1,2-benzylidenetriazole,



Calc. for $C_{15}H_{13}N_3S$: C, 67.41; H, 4.87; N, 15.81; S, 11.98. Found: C, 67.34; H, 5.02; N, 15.60; S, 12.09.

Action of Nitric Acid on Benzalsemicarbazone, $C_6H_5CH = N—NH — CO — NH_2$.—Were Hale's contention for the bisbenzylideneurea formula for the reaction product of cyanic acid on benzalazine correct, the formation of Young and Witham's triazole[1] by the action of concentrated nitric acid would necessarily be preceded by the cleavage of each ring complex in the molecule. As Bailey and Moore in the alkali hydrolysis of the cyanic acid compound obtained benzalsemicarbazone, it appeared of interest to test the behavior of the latter substance toward nitric acid. It was found that at a temperature of 20° there was very little action and most of the semicarbazone could be regained unchanged, while at 80° the semicarbazone was decomposed. In neither case was there triazole formation. As 5-hydroxy-3-phenyl-1-benzyl-1,2,4-triazole and the supposed 5-hydroxy-3-phenyl-1,2-benzaltriazole, two compounds reported in the Bailey-Moore paper, differ in their empirical formulas from the $C_6H_5CH = N — N = CHC_6H_5.2HCNO$ compound by an HCNO equivalent, their behavior toward nitric acid was studied under similar conditions to those above in the action of nitric acid on benzalsemicarbazone. Here the nitric acid acts as a nitrating agent but in neither case was Young and Witham's triazole or a nitro derivative of this formed. Whatever be the constitution of the $C_6H_5CH = N — N = CHC_6H_5.$-$2HCNO$ compound, it is evident from these experiments that all three of the above substances are excluded as intermediary products in its conversion to Young and Witham's triazole by the nitric acid treatment.

Our work on the crisscross addition with azines suggested the possibility of triazole formation from diazoacetic ester, *e. g.*, HCNO might be expected to give with

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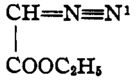
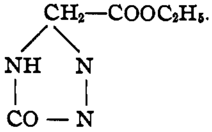
[1] *Loc. cit.*



$$\begin{array}{l}CH{=}N{\equiv}N^{1}\\ |\\ COOC_2H_5\end{array}$$

the substance,



However, we were unable to bring about a reaction here with either cyanic acid or phenyl isocyanate. Furthermore, unsuccessful attempts were made to effect a crisscross addition of phenyl isocyanate on oxalic ester, as the latter substance contains the conjugate system, $O = C — C = O$. At 220–230° the phenyl isocyanate was changed to triphenyl isocyanuric acid. The product, purified by recrystallization from glacial acetic acid, which we find preferable to alcohol, melted at 281°, whereas Wislicenus found the melting point to be 275°.[2]

Calc. for $C_{21}H_{15}O_3N_3$: N, 11.77. Found: N, 11.89.

Finally cyanogen, which contains the conjugate system, $N{\equiv}C — C{\equiv}N$, was passed into boiling phenyl isocyanate without the substances reacting.

AUSTIN, TEXAS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

THE MASS ACTION OF WATER ON DYES.

BY WILLIAN M. DEHN.

Received February 27, 1917.

If solutions of the common indicators and other dyes, contained in beakers, are treated with running tap-water, the colors of some of these are changed at certain dilutions. If the original solution was acidic and its color was changed by dilution, more acid will restore the first color. If the original solution was alkaline and its color was changed by dilution, more alkali will restore the first color. Some dyes tolerate only a trace of acids or alkalies in order that they may yield colored solutions which are transformed by dilution; other dyes require much acid or much alkali to yield colored solutions which are transformed by dilution.

Chromoisomerism Produced by Water.

In Weakly Acidic Solution.—If methyl orange, reddened by a trace of acid, is treated with running tap-water, the color gradually changes to a pure yellow; if acid is now added to this dilute yellow solution, some tint of red is restored. However, if methyl orange solutions originally

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[1] Cf. Thiele, *Ber.*, 44, 2522, 3336 (1911).

[2] *Ann.*, 308, 236 (1899).