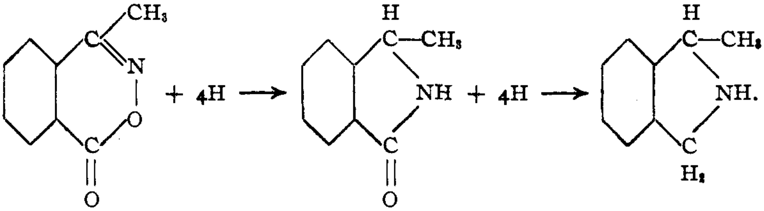
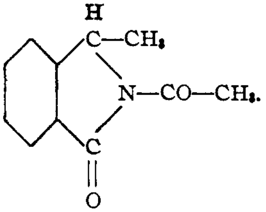
and acetic acid results in the formation of phthalimidine and dihydroisoindole, some phthalimide being produced at the same time by internal rearrangement of the anhydroxime.

(2) The reduction of *o*-acetyl benzoic anhydroxime under like conditions gives 1-methyl phthalimidine and 1-methyl dihydroisoindole.



It does not yield any 1-methyl isoindole even when the action is moderated.

(3) An acetyl derivative of 1-methyl phthalimidine is described.



(4) β-Ketobutyric anhydroxime (methyl isoxazolone) yields ammonia and butyric acid upon reduction in acid media. There is no evidence of the production of a tetratomic ring.

SEATTLE, WASH.

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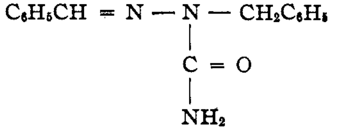
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

# THE USE OF CYANIC ACID IN GLACIAL ACETIC ACID. II. THE ADDITION OF CYANIC ACID ON BENZALAZINE.

BY J. R. BAILEY AND N. H. MOORE.

Received September 12, 1916.

Bailey and his co-workers have shown that, in the case of a number of weak nitrogen bases, difficultly soluble in water, carbamide derivatives are readily formed in glacial acetic acid solution by stirring in finely ground potassium cyanate.[1] In this article it is further shown that this modified form of the Woehler synthesis is serviceable in the preparation of benzylideneaminobenzylurea



$$C_6H_5CH = N - \underset{\underset{NH_2}{|}}{\underset{C = O}{\underset{|}{N}}} - CH_2C_6H_5$$

HCNO adds onto benzalbenzylhydrazine, $C_6H_5CH_2NHN = CHC_6H_5$,

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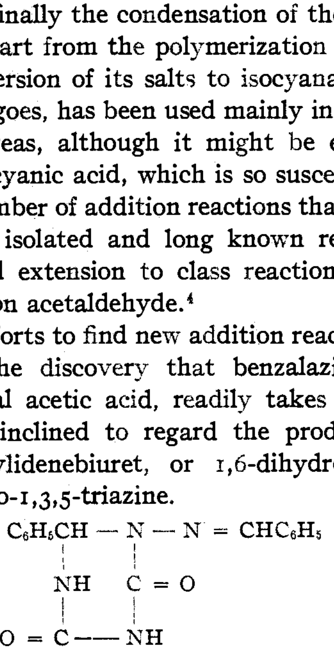
[1] THIS JOURNAL, 37, 940, 1884 (1915); 38, 1784 (1916).

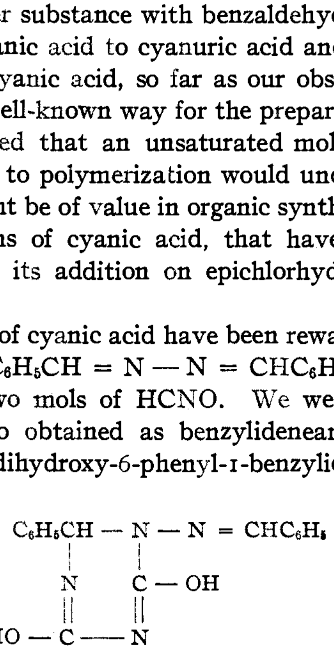
the latter substance being readily soluble in the cold in glacial acetic acid. Owing here to solubility relations and the weak basic nature of the hydrazone, no result can be obtained in water solution. The above benzylideneaminobenzylurea was prepared originally by Busch, Opferman and Walther[1] by a process which involved the conversion of benzylidenebenzylhydrazine to benzylhydrazine and the benzylhydrazine to aminobenzylurea,[2] and finally the condensation of the latter substance with benzaldehyde.

Apart from the polymerization of cyanic acid to cyanuric acid and the conversion of its salts to isocyanates, cyanic acid, so far as our observation goes, has been used mainly in the well-known way for the preparation of ureas, although it might be expected that an unsaturated molecule like cyanic acid, which is so susceptible to polymerization would undergo a number of addition reactions that might be of value in organic syntheses. Two isolated and long known reactions of cyanic acid, that have not found extension to class reactions, are its addition on epichlorhydrine[3] and on acetaldehyde.[4]

Efforts to find new addition reactions of cyanic acid have been rewarded by the discovery that benzalazine, $C_6H_5CH = N - N = CHC_6H_5$, in glacial acetic acid, readily takes up two mols of HCNO. We were at first inclined to regard the product so obtained as benzylideneaminobenzylidenebiuret, or 1,6-dihydro-2,4-dihydroxy-6-phenyl-1-benzylideneamino-1,3,5-triazine.

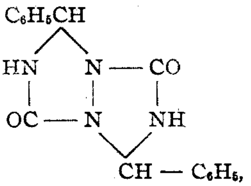


or



because its formation here would be strictly analogous to the polymerization of cyanic acid to cyanuric acid. However, this interpretation of the reaction product was soon discarded, because acid hydrolysis (HCl) yields hydrazodicarbonamide, $H_2NCONH - NHCONH_2$, a conclusive proof that in the new substance there is attached to each nitrogen of the benzalazine rest a carbonyl group.

The formula that now appeared the most probable is one with a "twin" triazole nucleus,



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[1] *Ber.*, 37, 2327 (1904).

[2] *J. prakt. Chem.*, [2] 62, 83 (1900).

[3] *Ber.*, 11, 2136 (1878).

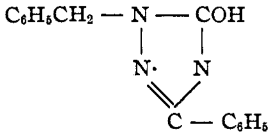
[4] *Ann.*, 59, 296 (1845).

which is in agreement with the acid hydrolysis. However, a study of the hydrolysis products obtained by the action of potassium hydroxide on the original HCNO addition product seemed at first to eliminate this formula also as untenable. Two products are obtained in this reaction, one alkali soluble and the other alkali insoluble. The former was identified as benzalsemicarbazone, $NH_2CONHN = CHC_6H_5$, and analysis showed the latter to have the empirical formula $C_{15}H_{13}ON_3$. The facts indicate that the $C_{15}H_{13}ON_3$ compound is not an intermediary product in the formation of benzalsemicarbazone, the latter resulting, as it were, as follows:

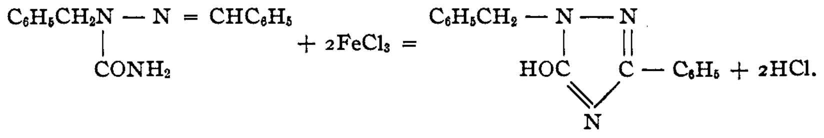
$$C_{15}H_{13}ON_3 + H_2O = C_6H_5CH = NNH - CONH_2 + C_6H_5CHO$$

The benzalsemicarbazone is rather formed directly from the bitriazole, at least there is no evidence of an intermediary product; the reaction involved in the formation of the benzalsemicarbazone takes place very rapidly in the boiling alkaline solution, as can be judged from the rate the benzaldehyde distills over, whereas, if the $C_{15}H_{13}ON_3$ compound, after purification, be submitted to steam distillation in alkaline solution, no benzalsemicarbazone results. In alkaline solutions of varying concentration, it was found that both reactions take place simultaneously and, therefore, attempts to establish conditions under which the $C_{15}H_{13}ON_3$ compound would be formed to the exclusion of the benzalsemicarbazone were fruitless.

If the HCNO addition product on benzalazine be a binuclear triazole and in its hydrolysis product one triazole nucleus be retained, the substance having the formula $C_{15}H_{13}ON_3$ might logically be regarded as 5-hydroxy-3-phenyl-1-benzyl-1,2,4-triazole.



The work of Young and Witham[1] suggested a synthesis of the above triazole that would establish its constitution beyond question, to wit, the oxidation with ferric chloride of benzylideneaminobenzylurea.



This reaction yields smoothly a beautifully crystallizing $C_{15}H_{13}ON_3$ compound, which is undoubtedly the desired hydroxyphenylbenzyltriazole, but it proved to be isomeric with the substance obtained in the alkali hydrolysis.

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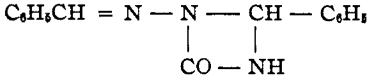
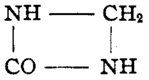
[1] *J. Chem. Soc.*, 77, 224 (1900).

Consideration was also given the formula

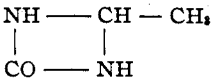
as a possible interpretation of the structure of the reaction product of cyanic acid on benzalazine. This $C_{16}H_{14}O_2N_4$ compound would then be bis-benzylideneurea and the probable structure of its $C_{15}H_{13}ON_3$ derivative,



The prototype of the cylic complex in this benzylideneaminobenzylideneurea, methyleneurea,[1]



and its methyl derivative, ethylidene urea,[2]



are recorded in the literature. However, attention might be directed to the fact that no conclusive proofs have been advanced to show that these substances are in fact *cyclic* ureides. Their physical properties indicate quite conclusively that they represent polymerized molecules and this fact would rather suggest that they have the general formulas $(CH_2 = N - CONH_2)_x$ and $(CH_3CH = N - CONH_2)_y$, respectively. This view is strengthened by the consideration that a number of substances containing the complex $C = N$ are known only in polymerized forms. Working with Schiff's ethylideneurea, on the assumption that it is in reality polymerized $CH_3CH = N - CONH_2$, we attempted to add prussic acid on to the molecule and also attempted its reduction with sodium amalgam in alkaline alcoholic solution. These experiments did not lead to the desired $CH_3CH(CN)NH - CONH_2$ and $CH_3CH_2NH - CONH_2$, respectively. Although depolymerization under such conditions sometimes takes place with the formation of monomolecular derivatives,[3] this is not always the case, and the negative results obtained cannot serve as an argument in favor of the cyclic structure of methyleneurea and ethylideneurea.

That the original cyanic acid addition-product is not bis-benzylideneurea is proved conclusively from the following considerations: Its $C_{15}H_{13}ON_3$ derivative differs from it by the elements HCNO and it might be

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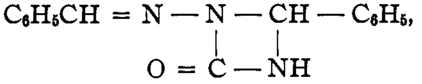
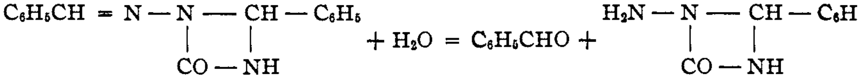
[1] *Monatsh.*, 12, 94; *Ber.*, 29, 2751 (1896).

[2] *Ann.*, 151, 206 (1869).

[3] This Journal, 37, 935 (1915).

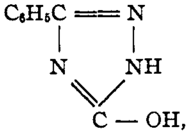
expected that benzalazine, treated with one mol of KCNO in glacial acetic acid, would yield this as an intermediate product. It would also be expected that the $C_{15}H_{13}ON_3$ compound would prove to be benzylideneaminobenzylideneurea,  $\begin{array}{l} C_6H_5CH = N - N - CH - C_6H_5, \\ \qquad\qquad\qquad\quad | \qquad | \\ \qquad\qquad\quad O = C - NH \end{array}$ and that on treatment with KCNO in glacial acetic acid, it would revert to the parent substance. Repeated trials brought conviction that neither of these reactions can be effected. Furthermore, were benzylideneaminobenzylideneurea the substance in hand, hydrolysis to aminobenzylideneurea with the splitting off of benzaldehyde should be readily effected.



$$\begin{array}{l} C_6H_5CH = N - N - CH - C_6H_5 \\ \qquad\qquad\quad | \qquad\; | \\ \qquad\qquad CO - NH \end{array} + H_2O = C_6H_5CHO + \begin{array}{l} H_2N - N - CH - C_6H \\ \qquad\quad | \qquad\; | \\ \qquad CO - NH \end{array}$$

As a matter of fact, the substance can be recrystallized from dilute sulfuric acid unchanged.

Schiff states that his supposed ethylideneurea in cold nitric acid hydrolyzes, yielding urea. In studying the action of nitric acid on the $C_{16}H_{14}O_2N_4$ compound, there was obtained a product of the formula $C_8H_7ON_3$, which proved to be 5-hydroxy-3-phenyltriazole,



a substance, which Young and Witham obtained in oxidizing benzalsemicarbazone with ferric chloride.[1]

The bi-nuclear triazole formula appears as the only one among the possibilities considered capable of interpreting the chemical changes that the $C_{16}H_{14}O_2N_4$ molecule undergoes. The facts at hand indicate that the addition of two molecules of HCNO on benzalazine is interdependent and that the reaction involved is an "intramolecular coupled reaction." The bitriazole formula gives expression to two important points that do not find interpretation in the other possible structural formulas: (1) An intermediary product, $C_6H_5CH = N - N = CHC_6H_5.HCNO$, between benzalazine and $C_6H_5CH = N - N = CHC_6H_5.2HCNO$ is theoretically impossible; (2) the loss of one HCNO equivalent from the molecule necessitates an intramolecular regrouping with the formation of a substance so constituted that it cannot revert to the bitriazole by the addition of HCNO. The fact that nitric acid converts the substance to Young and Witham's triazole and that caustic alkali eliminates an HCNO equivalent suggests for consideration the formula:

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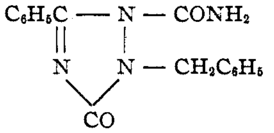
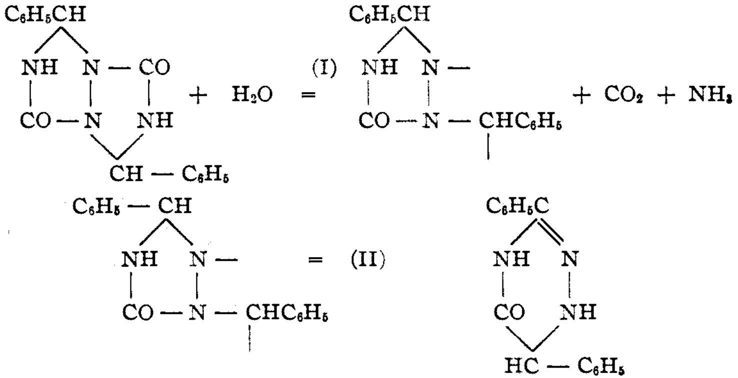
[1] *J. Chem. Soc.*, 77, 226 (1900).

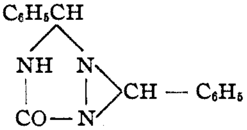


However, this possibility, if for no other reason, is definitely excluded by the fact that a diacetyl derivative has been prepared. There remain for consideration for the $C_{15}H_{13}ON_3$ derivative only two structural formulas: (1) It may be that through an intramolecular rearrangement a triazine results in the alkali hydrolysis of the $C_{16}H_{14}O_2N_4$ compound, which reaction the following equations may serve to explain:



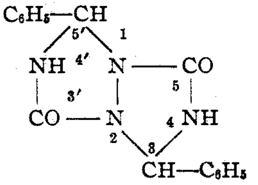
(2) The methine carbon in the benzylidene group, attached to the N in the 1 position, can join in ring formation directly to the N in the 2 position, producing from complex (I) 5-hydroxy-3-phenyl-1,2-benzylidenetriazole,

(III)

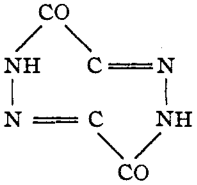


Although considerable work has been done in our attempts to reach a decision between these two formulas, as yet we have not succeeded in effecting a chemical change in the substance that might throw light on its structure.

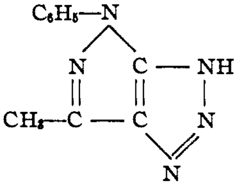
A binuclear triazole with two nitrogens common to each ring constitutes a new type in organic chemistry, and we are indebted to Prof. W. J. Hale for suggesting the very appropriate name here of triazolotriazole. With the atoms in the two rings numbered as follows



the name 5,3′-diketo-3,5′-diphenyl-hexahydro-1,2-triazolotriazole is evolved. For the tautomeric, enolic structure the name becomes 5,3′-dihydroxy-3,5′-diphenyl-dihydro-1,2-triazolotriazole. As Prof. Hale pointed out, the substance can also be designated as diphenyltriazolonotriazolone. This is in conformity with R. v. Rothenburg's name for



pyrazolonopyrazolone.[1] Another system of naming polynuclear heterocyclic complexes, very extensively employed, may be exemplified with



which Michaelis and Klopfstock[2] report as 1-phenyl-3-methyl-4,5-azimidopyrazol. Our substance might in conformity with this name be called 3-keto-5-phenyl-1,2-carbonyl-aminobenzyl-tetrahydro-1,2,4-triazole. For the sake of brevity the substance is referred to in the text as bitriazole, which is in conformity with the usage in Richter, *e. g.*, bithiophene may be cited.

The above discussion, concerning the formation of a bitriazole with two nitrogens in common to the rings of the binuclear system, suggests the possibility of other additive reactions in the case of substances with *conjugate* systems of double bonds[3] in the molecule, that will lead to the discovery of new types of condensed two-ring systems of the naphthalene type, containing two nitrogens, as in the present case, two carbons, or a nitrogen and a carbon in common. It is self evident that such complexes may in accordance with structural theory be produced, where there exists in the molecule any of the following conjugate systems of double bonds: $C=N-N=C$, $N=C-C=N$, $N=C-N=C$, $N=C-C=C$, $C=N-C=C$, and $C=C-C=C$.

Work on the extension of the cyanic acid addition reaction to include other azines will be reported in a later article, as well as the behavior

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[1] *J. prakt. Chem.*, 51, 63 (1895).

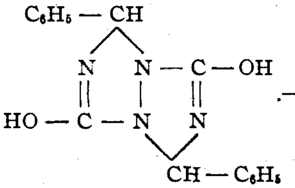
[2] *Ann.*, 354, 112 (1907).

[3] J. Thiele, *Ibid.*, 306, 90 (1899).

of azines toward isocyanates and mustard oils.[1] To insure our priority in the study of the reaction of thiocyanic acid with azines, it may be stated that potassium thiocyanate, stirred into a glacial acetic acid solution of benzalazine, produces in excellent yield a reaction product which, purified by recrystallization from benzene, melts at 193° with decomposition. An investigation of this substance is now in progress by the authors.

## Experimental Part.

### 5,3′-Dihydroxy-3,5′-diphenyldihydro-1,2-triazolotriazole,



.—To 45 g. of benzalazine in 225 cc. of glacial acetic acid are added with stirring 52.5 g. (3 mols) of finely pulverized potassium cyanate in 3 g. portions at intervals of 5 minutes. The solution, which is kept cool with ice water, shows only a slight gas evolution, becoming viscous as the reaction proceeds, and finally the bitriazole, colored a light yellow by a small amount of unchanged benzalazine, crystallizes out. The addition of 450 cc. of water precipitates a further amount of the substance. For purification the product is washed with water, any benzalazine removed by ether extraction, and the substance then recrystallized from alcohol. The above experiment yields 38 g. of the bitriazole, or 73% of the theoretical, if the regained benzalazine be taken into consideration. No appreciable increase in the yield was obtained by employing the cyanate in greater excess than that used above. The new substance, which is practically insoluble in water, can be recrystallized from glacial acetic acid, alcohol or acetic ether, while in the other common organic solvents it is only sparingly soluble. It separates from alcohol in thin plates with dome-shaped end faces, which at 207–208° begin to soften, turning yellow, and at 234° melt with gas evolution to a yellow liquid, which immediately solidifies, and does not remelt, even when heated as high as 280°. When allowed to crystallize slowly from alcohol, the substance can be obtained in the form of slender prisms, often more than a centimeter in length. The phenolic nature of the bitriazole is shown by its ready solubility in caustic alkalies and its insolubility in cold hydrochloric acid. It does not decompose alkali carbonates, but on the other hand is precipitated from its KOH solution by carbon dioxide. In ammonium hydroxide it is difficultly soluble but much more soluble than in water.

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[1] Since this article was submitted for publication an investigation of the action of phenylisocyanate on benzalazine has shown that the reaction proceeds quantitatively producing the expected N-N-bistriazole.—Bailey and McPherson.

Cold concentrated sulfuric acid produces a violent decomposition of the substance with the elimination of benzaldehyde, while with concentrated nitric acid it is possible to break up one of the triazole nuclei, leaving the other intact in the form of hydroxyphenyltriazole. While the bitriazole is very sensitive toward oxidizing agents, all attempts to obtain reduction products of the substance failed. The bitriazole dissolves in 40% formaldehyde on warming, producing in all probability an addition product,[1] which can be purified by evaporation *in vacuo* to dryness and then precipitation of an alcoholic solution of the residue with petrolic ether. It is thus obtained as a gelatinous mass. However, as the product on drying gives off formaldehyde and passes back to the original substance, no satisfactory analytical results were obtained. The bitriazole in alcoholic solution shows no color reaction with ferric chloride and gives no precipitation with platinic chloride or picric acid. The alkali salts are soluble in alcohol, as no separation of these is obtained when sodium or potassium alcoholate or alcoholic caustic alkalies are added to an alcoholic solution of the bitriazole. An attempt to determine the molecular weight of the bitriazole by the boiling-point method with alcohol as the solvent was unsuccessful, because of the slight temperature elevation obtained. A determination of the solubility of the bis-triazole in alcohol then showed it to be about 1 to 22.

Calc. for $C_{16}H_{14}O_2N_4$: C, 65.31; H, 4.76; N, 19.05. Found: C, 65.12; H, 4.96; N, 19.08.

**Diacetyl Derivative of the Bitriazole.**—A solution of the bitriazole in an excess of acetic anhydride, to which has been added a small amount of fused sodium acetate, is boiled for one-half hour, the reaction mixture is then allowed to cool, and finally, after dilution of the solution to three times its volume with water, the excess of anhydride is decomposed by warming. The acetyl derivative separates in excellent yield and a further small amount can be obtained by benzene extraction of the acetic acid solution. It is readily soluble in benzene, ether, and alcohol, and only slightly soluble in water and petrolic ether. It was purified for analysis by precipitation from a benzene solution with petrolic ether and finally by recrystallization from alcohol. From the latter solvent it is obtained in fan-shaped clusters of fine needles, which begin to soften at about 147° and melt with decomposition at 167°.

Calc. for $C_{20}H_{18}O_4N_4$: C, 63.49; H, 4.76; N, 14.82. Found: C, 63.40; H, 4.70; N, 14.96.

**The Action of Potassium Hydroxide on the Bitriazole.**—If the bitriazole be dissolved in about ten times its weight of 10% KOH and then subjected to steam distillation, there appears in the distillate, as soon as the solution boils, benzaldehyde, and from the alkaline

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[1] Cf. Einhorn, *Ann.*, 343, 207 (1905).

solution there separates a crystalline solid, colored slightly yellow by a small amount of benzalazine. As a rule the decomposition of the bitriazole is completed after the steam distillation has been carried on for one-half hour. The above alkali insoluble product was identified as benzalsemicarbazone by comparison with a stock sample of this preparation and by analysis. The reaction involved in its formation from the bitriazole may be expressed by the equation

$$C_{16}H_{14}O_2N_4 + 2H_2O = C_6H_5CH = NNH - CONH_2 + CO_2 + NH_3.$$

Calc. for $C_8H_9ON_3$: C, 58.90; H, 5.52; N, 25.76. Found: C, 58.76; H, 5.50; N, 25.76.

There remains in the filtrate above from the benzalsemicarbazone an alkali soluble product, which is precipitated on acidification with hydrochloric acid. The product so obtained on treatment with concentrated ammonium hydroxide dissolves for the most part, but there is always left in small amount a residue. This latter substance, which is soluble in caustic alkalies and can be recrystallized from alcohol in short prismatic plates melting at about 195°, was not further investigated. The ammonia soluble compound, purified by recrystallization from acetic ether and then from alcohol, was obtained in microscopic prisms with pyramidal end faces, melting undecomposed at 208°. It is difficultly soluble in water and only slightly soluble in benzene and ether. It dissolves readily in glacial acetic acid and from the solution on dilution with water separates in characteristic stellate aggregates of short needles. The constitution of the substance as $C_{15}H_{13}ON_3$ was conclusively established by analyses of the preparation obtained at different times, and its formation may be explained by the following equation:

$$C_{16}H_{14}O_2N_4 + H_2O = C_{15}H_{13}ON_3 + NH_3 + CO_2$$

Calc. for $C_{15}H_{13}ON_3$: C, 71.71; H, 5.18; N, 16.73.

Found: C, 71.49, 71.61, 71.62; H, 5.18, 5.09, 5.09; N, 16.87, 16.89.

The $C_{15}H_{13}ON_3$ compound, on standing several days with absolute prussic acid, underwent no change, and attempts to add hydrogen onto the molecule failed, which facts, along with our failures to effect hydrolysis, argue against the substance being a hydrazone. Dissolved in glacial acetic acid, the $C_{15}H_{13}ON_3$ compound does not add on HCNO to revert to the original bitriazole. The substance, after being treated with dilute sulfuric acid solution in a sealed tube at 150° for one hour, was regained unchanged, and a similar treatment with dilute potassium hydroxide solution at 125° had no effect. Sodium nitrite added to a glacial acetic acid solution of the compound does not give a nitroso derivative. It reduces alkaline permanganate slowly, but the oxidation product has not been isolated. As yet only a few grams of the $C_{15}H_{13}ON_3$ compound have been available for the study of its reactions, since the yield of this substance in the alkali hydrolysis of the bitriazole is poor. In working with small amounts of the bitriazole, better results are obtained than when large amounts are employed.

**The Hydrolysis of the Bitriazole to Hydrazodicarbonamide and Hydrazine.**—The bis-triazole, on boiling with concentrated hydrochloric acid, slowly dissolves, giving off benzaldehyde. If the greater part of the acid is boiled off, and the solution neutralized with ammonia, a white, crystalline solid separates, which is insoluble in alcohol and ether, and can be recrystallized from water. The product, thus purified, proved on comparison identical with a stock sample of hydrazodicarbonamide, and its constitution was further confirmed by a nitrogen determination.

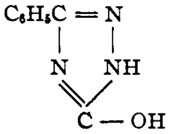
Calc. for $C_2H_6O_2N_4$: N, 47.54. Found: N, 47.41.

The filtrate from the hydrazodicarbonamide, on treatment with benzaldehyde, yielded benzalazine, showing the hydrolysis with HCl as resulting in the formation of both hydrazodicarbonamide and hydrazine hydrochloride.

$$C_{16}H_{14}O_2N_4 + 2H_2O = NH_2CO - NHNH - CONH_2 + 2C_6H_5CHO$$

$$NH_2CO - NHNH - CONH_2 + 2H_2O + 4HCl = NH_2NH_2.2HCl + 2NH_4Cl + 2CO_2.$$

**The Oxidation of the Bitriazole to 5-Hydroxy-3-phenyltriazole,**



.—If 2 g. of the bitriazole be added gradually to 10 cc. of concentrated nitric acid at a temperature below10°, it passes into solution on stirring with the evolution of a colorless gas and after a short time the reaction product, colored a light yellow, crystallizes out in excellent yield. As soon as no more gas is given off, the acid solution is diluted to three times its volume with water and filtered. When heated, it begins to shrink and char at about 300°, melting with decomposition to a dark brown liquid at 321–322°. After analysis had revealed the formula of this compound as $C_8H_7ON_3$, it was carefully compared with a sample of 5-hydroxy-3-phenyl-1,2,4-triazole, prepared by oxidizing benzalsemicarbazone with alcoholic ferric chloride,[1] and the two preparations proved in every respect identical. The hydroxyphenyltriazole can also be prepared from the bitriazole by oxidation of the latter with alkaline permanganate. In the oxidation of the bitriazole with nitric acid, which process is accompanied by an evolution of $CO_2$, the imino nitrogen of the $C_6H_5CH$-NHCO group, removed from the bitriazole molecule in the oxidation, is converted to ammonia, since the acid solution on making strongly alkaline with potassium hydroxide gives a test for this. It was further

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

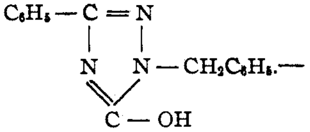
noticed that to the nitric acid filtrate from the hydroxyphenyltriazole there was imparted a strong odor of a nitro aromatic compound.

Calc. for $C_8H_7ON_3$: C, 59.63; H, 4.35; N, 26.09. Found: C, 59.50; H, 4.43; N, 26.24.

**Preparation of α-Benzylideneamino-β-benzylurea,** $C_6H_5CH_2N(CONH_2)N = CHC_6H_5$.—24 g. of benzylidenebenzylhydrazone, $C_6H_5CH_2NHN = CHC_6H_5$, prepared by the reduction of benzalazine with sodium amalgam according to the method of Curtius,[1] are dissolved in 50 cc. of glacial acetic acid and 13 g., or a slight excess over 2 mols, of finely pulverized KCNO gradually stirred in. As a rule, when about all the cyanate has dissolved, the addition product begins to separate, and after a short time the entire solution becomes solid. The yield of the semicarbazone by this process is about 85% of the theoretical. The substance is readily soluble in alcohol, ether, benzene, acetic ether, and glacial acetic acid, and insoluble in water, acids and alkalies. From ether it separates in prismatic plates, melting without decomposition at 156°. Strangely enough, attempts to steam off benzaldehyde in the presence of sulfuric acid, and thus pass to benzylsemicarbazide, $C_6H_5CH_2 — N(CONH_2)NH_2$, were not successful. This method of preparation of benzylidenebenzylsemicarbazone is a much simpler process than the one employed by Busch, Opfermann and Walther.[2]

Calc. for $C_{15}H_{15}ON_3$: C, 71.15; H, 5.93; N, 16.60. Found: C, 71.09; H, 5.89; N, 16.67.

**5-Hydroxy-3-phenyl-1-benzyl-1,2,4-triazole,**



5 g. of the above semicarbazone and 5 g. (4 mols) of ferric chloride in 20 cc. of alcohol are heated in a sealed tube in an oil bath four hours at 125–135°. On cooling the contents of the tube, the triazole crystallizes out in a matted mass of long, slender needles, while a certain amount of unoxidized semicarbazone remains dissolved in the alcohol. The new substance is very difficultly soluble in water and ether and fairly soluble in alcohol, benzene, and acetic ether. From its solution in alcohol or acetic ether it separates in fine needles, which begin to soften at about 214° and melt undecomposed at 228°. The triazole dissolves in ammonia and caustic alkalies and is reprecipitated with acids. An attempt to prepare an acetyl derivative failed: 2 g. of the triazole, 4 g. of acetic anhydride, and 3 g. of fused sodium acetate were heated in a sealed tube at 150° four hours. The contents of the tube were lixiviated with water

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[1] *J. prakt. Chem.*, 62, 90 (1900).

[2] *Loc. cit.*

and the undissolved substance filtered off. The product thus obtained proved to be unchanged triazole.

Calc. for $C_{15}H_{13}ON_3$: C, 71.71; H, 5.18; N, 16.73. Found: C, 71.79; H, 5.14; N, 16.89.

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# DIPHENYL BUTADIENE.

BY J. M. JOHLIN.

Received December 15, 1916.

Dimethyl butadiene is most readily prepared by the dehydration of pinakon. Diphenyl butadiene should be similarly obtained by the dehydration of acetophenon-pinakon. The object of this paper is to define more definitely a compound, $C_{16}H_{14}$, melting at 49°, obtained by Thoerner[1] and Zinke when they dehydrated acetophenon-pinakon by heating it with acetic anhydride, and to describe several new methods by which acetophenon-pinakon can be obtained.

Acetophenon-pinakon has been prepared by the reduction of acetophenon with metallic sodium.[2] The process is a slow one and the yield small. Three new methods were tried. Acetophenon was reduced with magnesium ribbon, in the presence of mercuric chloride, according to the method used by Holleman to prepare pinakon from acetone. Small amounts of acetophenon-pinakon could be isolated from the product obtained by this process. Somewhat better yields were obtained by converting diacetyl into its diphenyl pinakon by means of magnesium methyl iodide by Grignard's reaction. It is very conveniently obtained by converting benzil into its dimethyl pinakon by means of magnesium phenyl bromide by Grignard's reaction.

Acetophenon-pinakon by dehydration yields a hydrocarbon, $C_{16}H_{14}$, and although the compound has not been defined beyond being a hydrocarbon of the above composition, it is undoubtedly diphenylbutadiene. Characteristic derivatives of this compound could not be formed. A bromine derivative by the addition of bromine cannot be prepared, a fact no doubt to be laid to the proximity of the phenyl group to the unsaturated carbon atom. Attempts to brominate acetophenon-pinakon likewise were without satisfactory results. The dehydration of the pinakon when carried out in a sealed glass tube by heating with acetic anhydride at 180° yields varying results. There is generally formed a brown liquid from which, after neutralization, the hydrocarbon can be obtained by steam distillation. In one instance a viscous somewhat elastic ribbon was formed in the glass tube. This material, insoluble in acetic anhy-

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[1] *Ber.*, 13, 641 (1880).

[2] Beilstein, "Organische Chemie."