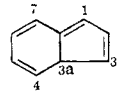
TABLE VIII

PROPERTIES OF POLYAZAINDENES




| No. | Substituents and Positions | Method of Prep. | M.P., °C. | Empirical Formula | Analysis Calcd. % C | % H | % N | Found % C | % H | % N |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 4-Oxo-1-thia-3a,7-diazaindenes | | | | | | |
| IV | 5-$COOC_2H_5$[a] | A | 186 | $C_9H_8N_2O_3S$ | 48.4 | 3.5 | | 48.3 | 3.5 | |
| IVa | 5-$COOC_2H_5$-3-$CH_3$[b] | A | 192 | $C_{10}H_{10}N_2O_3S$ | 50.5 | 4.1 | | 51.8 | 5.1 | |
| IVb | 5-COOH | C | 285 dec. | $C_7H_6N_2O_4S$ | 39.2 | 2.8 | | 39.0 | 2.6 | |
| XIV | None[c] | [d] | 116 | $C_6H_4N_2OS$ | 47.3 | 2.6 | | 47.3 | 2.9 | |
| XIVa | 6-$CH_3$[c] | B | 112 | $C_7H_6N_2OS$ | 50.6 | 3.6 | | 50.3 | 3.9 | |
| XIVb | 3,6-$(CH_3)_2$[e,f] | D | 133–135 | $C_8H_8NOS$ | | | | | | |
| XXIII | 6-$CH_3$-3-$C_6H_5$[g] | B | 238–240 | $C_{13}H_{10}N_2OS$ | 64.5 | 4.5 | | 63.4 | 4.3 | |
| XXIV | 5-$COOC_2H_5$-3-$C_6H_5$[a] | A | 174 | $C_{14}H_{12}N_2O_3S$ | 60.0 | 4.0 | | 60.1 | 4.1 | |
| XXV | 5-$COOC_2H_5$-2-Cl[b] | A | 149 | $C_9H_7ClN_2O_3S$ | 41.8 | 2.7 | | 42.0 | 2.7 | |
| | 5-$COOC_2H_5$-3-$C_6H_5C_6H_4$[b] | A | 169 | $C_{21}H_{16}N_2O_3S$ | 66.0 | 4.4 | | 66.8 | 4.3 | |
| | 5-$COOC_2H_5$-3-$NO_2$[h] | A | 225 | $C_9H_7N_3O_5S$ | 39.4 | 2.5 | | 39.4 | 2.9 | |
| | | | | 4-Oxo-1-thia-3,3a,7-triazaindenes | | | | | | |
| V | 5-$COOC_2H_5$-2-$C_2H_5$[g] | A | 96 | $C_{10}H_{11}N_3O_3S$ | 47.5 | 4.3 | | 47.6 | 4.6 | |
| Va | 5-$COOC_2H_5$-2-$CH_3$[a] | A | 140 | $C_9H_9N_3O_3S$ | 45.2 | 3.8 | | 45.2 | 3.6 | |
| XV | 2-$C_2H_5$-6-$CH_3$[c] | D | 40 | $C_8H_9N_3OS$ | 49.2 | 4.6 | | 49.0 | 4.7 | |
| | | | | 4-Oxo-1-thia-2,3a,7-triazaindene | | | | | | |
| VI | 5-$COOC_2H_5$-3-$CH_3$[c] | A | 110 | $C_9H_9N_3O_3S$ | 45.2 | 3.8 | 17.5 | 45.3 | 3.6 | 17.6 |
| | | | | 4-Oxo-1,3a,7-triazaindenes | | | | | | |
| VII | 5-$COOC_2H_5$[i] | B | 253 | $C_9H_9N_3O_2$ | 52.2 | 4.4 | 20.3 | 52.4 | 4.3 | 20.6 |
| XVI | 6-$CH_3$[i] | B | 239 | $C_7H_7N_3O$ | | | 28.2 | | | 27.8 |
| | | | | 7-Oxo-1,4,7a-triazaindenes | | | | | | |
| VIII | 2-$CH_3$-6-$COOC_2H_5$[j] | B | 294 | $C_{10}H_{11}N_3O_3$ | | | 19.0 | | | 18.7 |
| XVII | 2,5-$(CH_3)_2$[j] | B | 253 | $C_8H_9N_3O$ | 58.5 | 5.5 | 25.8 | 59.4 | 6.5 | 26.3 |
| | 2-$CH_3$-5-$C_6H_5$[j] | B | 286 | $C_{13}H_{11}N_3O$ | | | 18.6 | | | 19.3 |
| | 5-$CH_3$-2-$C_6H_5$[j] | B | >315 | $C_{13}H_{11}N_3O$ | 69.3 | 4.9 | 18.6 | 69.8 | 5.0 | 19.6 |
| | 5-$CH_3$[j] | B | 307 | $C_7H_7N_3O$ | 56.4 | 4.7 | 28.2 | 56.0 | 4.8 | 28.6 |
| | 2-$CH_3$-6-COOH | C | >285 dec. | $C_8H_7N_3O_3$ | 49.7 | 3.6 | | 49.4 | 4.0 | |

[a] Recrystallization from ethanol. [b] Butanol. [c] Ligroin. [d] Decarboxylation of IVb. [e] H. Antaki and V. Petrow, *J. Chem. Soc.*, 551 (1951). [f] Benzene-ligroin. [g] Toluene-ligroin. [h] Ethyl nitrate. [i] Water. [j] Dimethylformamide.

[COMMUNICATION NO. 1995 FROM THE KODAK RESEARCH LABORATORIES]

# The Structure of Certain Polyazaindenes. II. The Product from Ethyl Acetoacetate and 3-Amino-1,2,4-triazole

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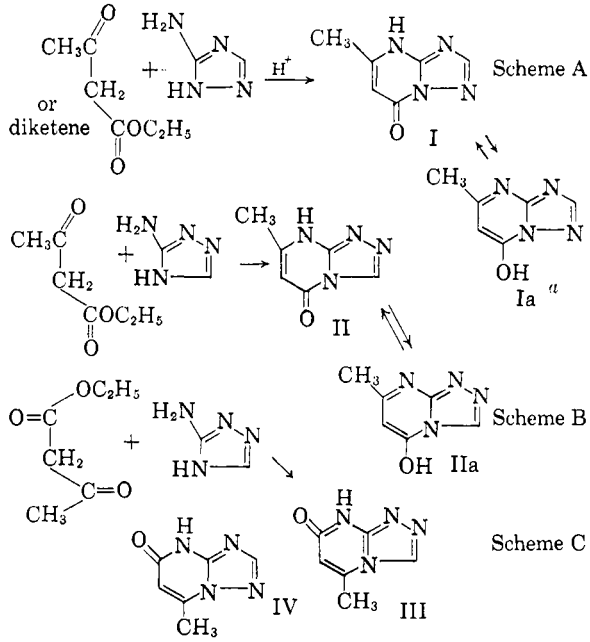
3-Amino-1,2,4-triazole and ethyl acetoacetate or diketene give only one of the four possible isomeric substances, which is 6-methyl-4-oxo-1,3,3a,7-tetrazaindene. Two of the other isomers are obtained from 2-hydrazino-4-methyl-6-hydroxypyrimidine and ethyl orthoformate. One of the latter is isomerized to the first substance by strong acid. A number of related compounds are described and their interrelationships are shown. The accumulated spectral and chemical evidence support the structure named; the latter is also in accord with theoretical considerations.

In a study of the reaction between aminotriazoles and 1,3-dicarbonyl compounds, Bülow[1,2] obtained a substance from 3-amino-1,2,4-triazole and ethyl acetoacetate to which he assigned the structure Ia, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene.[2,3] Since the structure was not determined by the method of synthesis, it was assumed that the

(1) C. Bülow, *Ber.*, **42**, 2599, 3555, 4429 (1909).
(2) C. Bülow and K. Haas, *Ber.*, **42**, 4638 (especially, p. 4642)(1909).

*ketonic* carbonyl group had reacted with the amino group of the triazole, with subsequent cyclization, as shown in Scheme A. However, ring closure could equally well have occurred as shown in Scheme B, leading to isomer II. Furthermore, the *ester* group could have reacted with the amino group, with subsequent cyclization either way, Scheme C, leading to isomers III and IV. Thus, the synthesis is ambiguous. The empirical formula and bicyclic nature of the product are clearly established; the position of the substituents and the nature of the tautomerism are not.

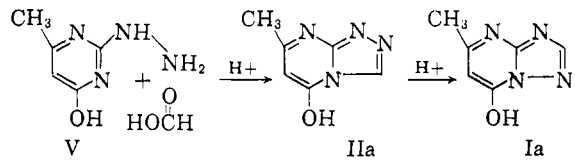



[a] The *a* designation represents the tautomeric form.

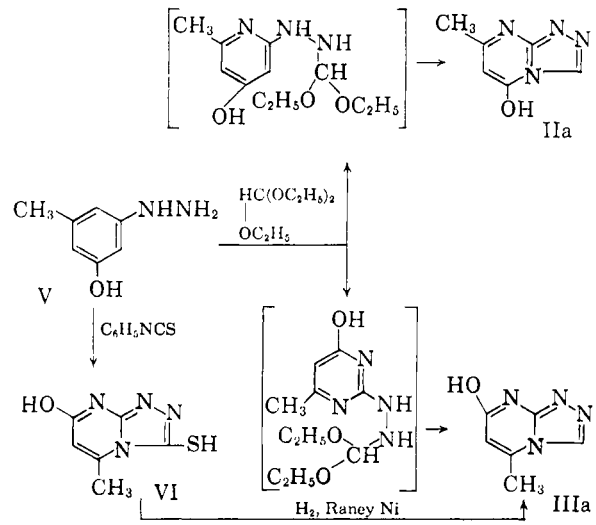
Birr and Walther[4] devised what appeared to them to be an unequivocal synthesis; by cyclizing 2-hydrazino-4-hydroxy-6-methylpyrimidine (V) with formic acid, the same substance was obtained as resulted from aminotriazole and ethyl acetoacetate. Hence, it was concluded that the nitrogen atoms had the 1,2,3a,7-arrangement, as shown in (IIa). Repetition of Birr and Walther's work in these Laboratories led to the discovery that the nature of the product depended on the acidity of the reacting solution. Under conditions milder than Birr and Walther's, an isomer was obtained, which, amazingly, in boiling formic acid, was isomerized to the long-known 1,3,3a,7-isomer! Thus, Birr and Walther's synthesis is not unambiguous. Homologs were obtained in a similar manner under slightly altered experimental conditions.

(3) The German authors used the name "6-methyl-1,3-triazo-7,*O*'-pyridazine-4-hydroxylic acid." Beilstein (main work, 4th ed., Vol. XXVI, p. 433) has renamed the oxo form I, "7-oxo-5-methyl-6,7-dihydro-1,3,4-triazaindolizine," dropping the "6,7-dihydro-" in the case of the tautomer shown in structure Ia. The authors of this paper have continued to use the "a" system, used in the preceding paper.

(4) E. Birr and W. Walther, *Ber.*, **86**, 1401 (1953).

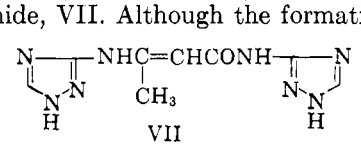



An independent synthesis of (II) (the 1,2,3a,7-isomer) was carried out here by the action of ethyl orthoformate on the same 2-hydrazinopyrimidine. This reaction can give two products (II and III), since ring closure can take place through either nitrogen atom of the pyrimidine, and *both* were obtained! The third isomer (IIIa)[5] was also formed from the hydrazine (V) and phenyl isothiocyanate, by way of the mercapto intermediate (VI). Thus,




*three* (I–III) *of the four isomers possible* are readily synthesized. Many attempts to obtain the fourth isomer (IV), and to accomplish an unequivocal synthesis of any *one*, were unsuccessful. For instance, 1-benzylthiourea and ethyl acetoacetate gave 1-benzylthiouracil, which was readily monomethylated by dimethyl sulfate and sodium hydroxide, but this product did not react with hydrazine. This suggested that *N*-methylation took place, rather than the desired attack at the sulfur atom.

Diketene and ethyl acetoacetate usually give the same products when employed in reactions of this type, and in this instance, both gave the same isomer, I. In addition, diketene gives a trimolecular product, which, it seems to us, is best represented as the amide, VII. Although the formation of this

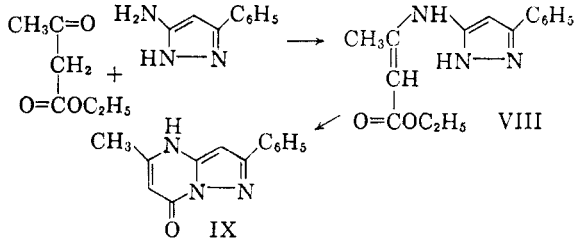



product indicates that the reaction proceeds stepwise, it cannot be used to show at which carbonyl

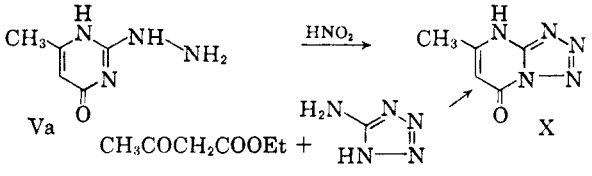
(5) Although these substances have the isomeric oxo structure (refer to 1st paper), for convenience in comparison the hydroxy form is often employed in this and succeeding papers.

group of ethyl acetoacetate the aminotriazole reacts first. This substance (VII) has been mentioned in the patent literature,[6,7] but given a different structure. The products are identical whatever procedure is followed.

Although it is generally known[8] that the ketonic carbonyl group of ethyl acetoacetate reacts preferentially with amines under acidic conditions, the only evidence applicable here is by analogy when a 3-aminopyrazole is substituted for the aminotriazole.[9] In this instance, the intermediate aminocrotonate (VIII) was actually isolated. It can cyclize in only one way, owing to the lack of the fourth nitrogen atom (*cf.* aminotriazole). The two reactions and the substances (I and IX) are entirely comparable. Corroborating evidence



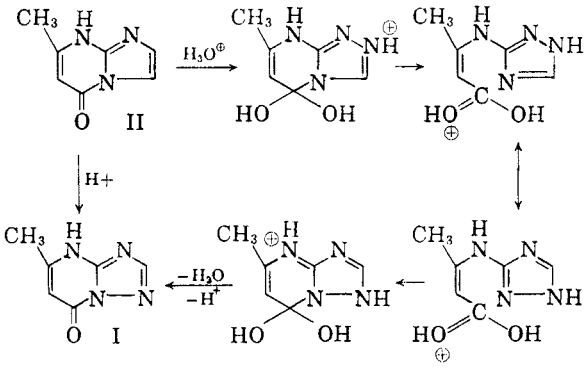
is also available from the corresponding compound in the pentazaindene series. Two independent reactions, (a) action of nitrous acid on the hydrazinopyrimidine (Va), and (b) interaction of ethyl acetoacetate and 5-aminotetrazole, gave products that were identical in all physical properties, including absorption spectra;[10] these are formulated as



Finally, a study was made of the residues from the preparation of the 1,3,3a,7-isomer (I) after removal of the latter. The residues, which amounted to 5% of the reaction mixture, were submitted to a countercurrent distribution in a Craig extractor.[11] Two products were definitely present; the major material (90+%) was the bisamide (VII); the remainder was 3-acetamido-1,2,4-triazole. A possible trace of the 1,2,3a,7-isomer (II) was suggested, but there was not the slightest evidence of anything that could be interpreted as the missing fourth isomer (IV). These products are consistent with the mechanisms that are suggested in this paper.

The rearrangement of the 1,2,3a,7-isomer (II) to the 1,3,3a,7-form (I) by strong acids is easily visualized as outlined in Chart I.

Chart I



Most of the physical and chemical properties of the tetrazaindene are best accounted for by the oxo structure (I);[5] among these may be mentioned absorption spectra, behavior at a dropping mercury electrode, and reactions outlined here. It behaves like similar heterocyclic nitrogen compounds, forming a 4-chloro derivative (XI) when treated with phosphoryl chloride. The chlorine atom is available for reactions of double decomposition. Thus, upon hydrolysis, the parent hydroxy compound (I) is regenerated. By suitable procedures, the 4-thiono (XII), 4-carboxymethylmercapto (XIII), 4-amino, 4-azido, and 4-triazolylamino derivatives (XIV) have been prepared. The chlorine atom can be replaced by hydrogen catalytically, giving 6-methyl-1,3,3a,7-tetrazaindene (XV); the latter has been prepared by two independent syntheses and a variety of conditions.[12]

Chlorination of I gives a 5-chloro derivative (XVI); the position of the chlorine atom was shown by an independent synthesis of the same substance from 3-aminotriazole and ethyl α-chloroacetoacetate. Persulfate gives a 5-hydroxy compound (XVII). The reactions are summarized in Chart II.

It will be seen that the evidence in favor of structures I and Ia is cumulative; the most convincing is based on the absorption spectra (refer to Part I). Additional support, as well as an explanation of some of the reactions, is afforded by mechanistic considerations.

(6) N. Heimbach and W. Kelly, Jr., U. S. Patent 2,444,608 (1948); *Chem. Abstr.*, **42**, 7180 (1948).

(7) N. Heimbach and W. Kelly, Jr., U. S. Patent 2,475,136 (1949); *Chem. Abstr.*, **43**, 8294 (1949).

(8) C. R. Hauser and G. A. Reynolds, *J. Am. Chem. Soc.*, **70**, 2402 (1948).

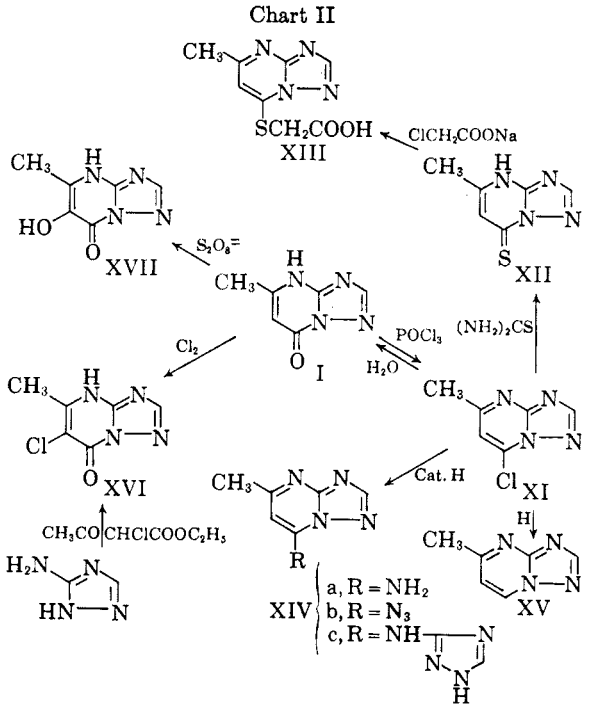
(9) S. Chechi, P. Papini, and M. Ridi, *Gazz. chim. ital.*, **85**, 1160 (1955); *Chem. Abstr.*, **50**, 10098 (1956).

(10) C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. VanAllan, *J. Org. Chem.*, **24**, 779 (1959).

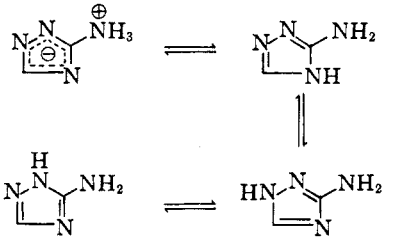
(11) L. C. Craig, W. Hausmann, E. H. Ahrens, Jr., and E. J. Harfenist, *Anal. Chem.*, **23**, 1236 (1951). We are indebted to Dr. M. Hill for this operation.

(12) C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. VanAllan, *J. Org. Chem.* **24**, 796 (1959).

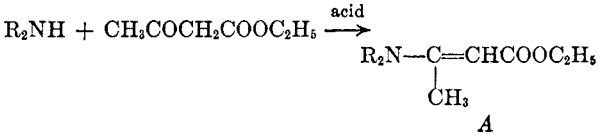
Chart II



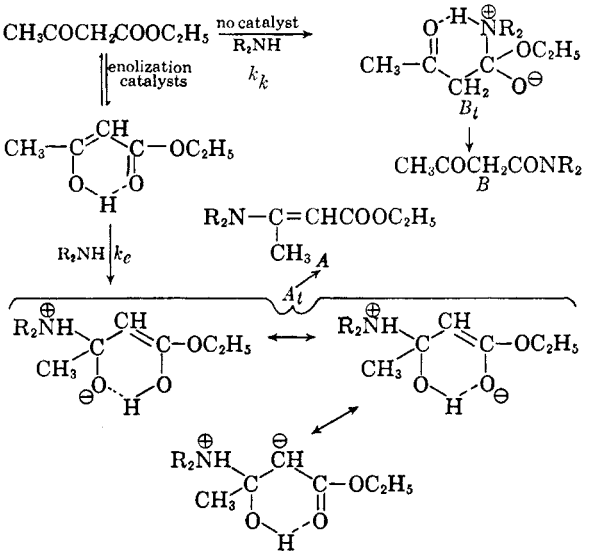
*Mechanistic discussion.* In ionizing solvents, the aminotriazole is best represented as:



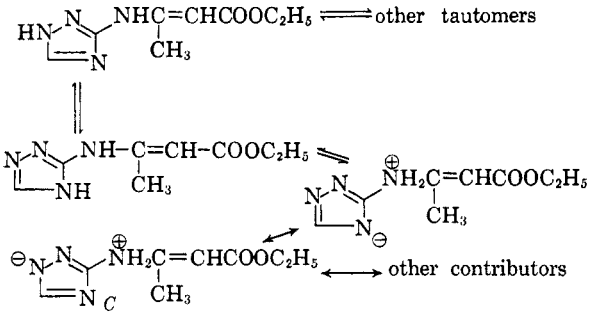
It is well known[8] that, under mild acedic catalysis, acetoacetic ester reacts with amines rapidly and exclusively at the ketonic carbonyl group, producing substituted aminocrotonates, *A*.[13]



Clearly, catalysts promoting enolization favor the path to *A*. The rate of addition to the enol, $k_e$, is faster than that to the ketone, $k_k$, partly as a consequence of better stabilization of the charge in the transition state, $A_t$, compared to $B_t$. It is possible to mobilize all the equilibria between *A* and *B* so that the ratio of products obtained is

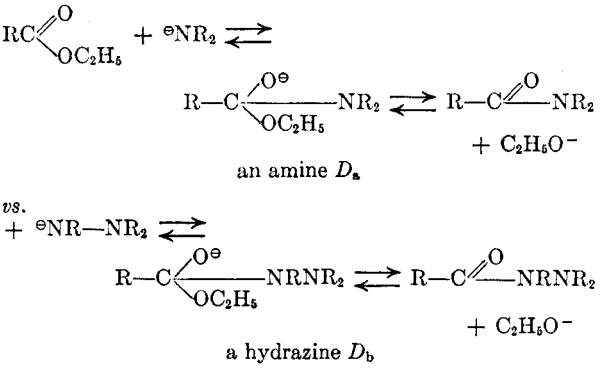


equal to the ratio of rates. Under these circumstances[8] the anil, *A*, is formed, showing experimentally that $k_e$ is much larger than $k_k$. Furthermore, the reaction forming *A* must occur with a basic nitrogen possessing an attached hydrogen. The NH of the triazole ring is not basic; the structure of the only possible intermediate is thus *C*. (If the two steps of the reaction were simultaneous, no true intermediate would be formed;



yet the influences would be the same, so that the argument as to the structure does not require the existence of the intermediate.) Birr's synthesis[4] from β-chlorocrotonic ester with aminotriazole should also, *via* a Michael addition, lead to *C*.

The subsequent step of the condensation is an addition to the ester carbonyl: Here, the reaction



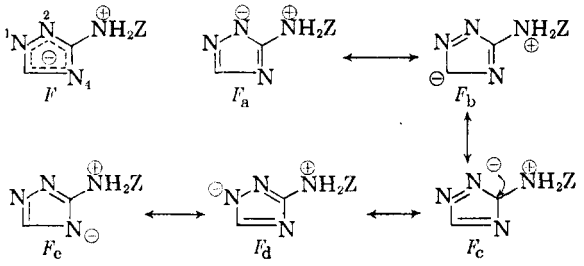
(13) The structure of vinylamines and of compounds like *A* has recently been discussed [B. Witkop, *J. Am. Chem. Soc.*, **78**, 2873 (1956)]. Aroyl (and acyl) acetic esters and aromatic amines form aroylacetanilides in the absence of an acidic catalyst; water must be excluded to get the best yields. Conversely, traces of acid and water favor reaction at the ketonic carbonyl group (*Org. Syntheses*, **Coll. Vol. III**, 108).

should be most rapid with that tautomer of *C* carrying a negative charge on the appropriate nitrogen atom. Of the two remaining paths, $D_a$ and $D_b$, the fastest will correspond to the reaction with the more nucleophilic site. Usually, the order of nucleophilicity follows the order of basicity, but hydrazine (a weaker base) is more nucleophilic than ammonia; trimethylhydrazine is a much weaker base than dimethylamine. (Comparing $E_a$ and $E_b$, we find that replacing $R_3C$— by $R_2N$—,

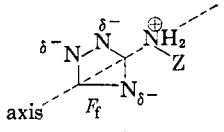
that is, substituting a more electronegative group, has decreased the electron contribution about $N^\alpha$ furnished by this bond. The $N^\alpha$ makes up for this decrease by becoming more electronegative, so that it is a stronger acid.[14,15]

Furthermore, groups in which the negative charge is diffuse are more highly nucleophilic; thiocyanate and azide, bases of medium strength, are among the most powerful nucleophilic agents. It follows that insight to the configuration of the transition state cannot be obtained from consideration of the separate parts.

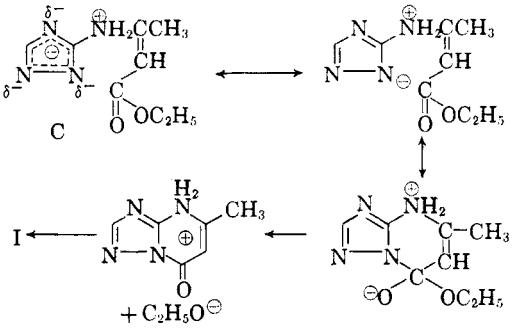
The whole is best represented as *F*, or, more explicitly, by the several contributors $F_a$ . . . $F_e$



($Z$ = $\beta$-crotonate residue). Of these, the forms with a negative charge on carbon $F_b$ and $F_e$ will contribute very little, and are ignored in the summary, $F_f$. The greater electronegativity of the hydrazine



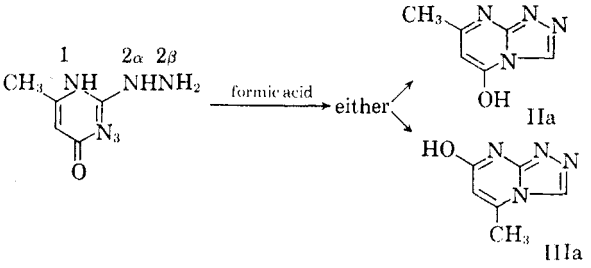
system may also increase its share of the charge at the expense of the nitrogen at position 4. The resulting effect, as shown in $F_f$, is a greater negative charge on the side of the axis toward position 2 than that toward position 4. This charge guides the carboxyl group toward the vicinity of position 2 (of the triazole ring) so that the reaction takes the path shown in Scheme G.



Scheme G

The acidity of the ring NH of aminotriazole and of the intermediate allows the ready tautomerization to the zwitterionic form, so that the further reaction, once the proper geometry has been achieved, can proceed through resonance contributors and loss of fragments. Consequently, we should expect this step to go rapidly: this has been confirmed experimentally.[16]

The cyclization of the 2-hydrazinopyrimidine by formic acid or its equivalent is equally well explained.



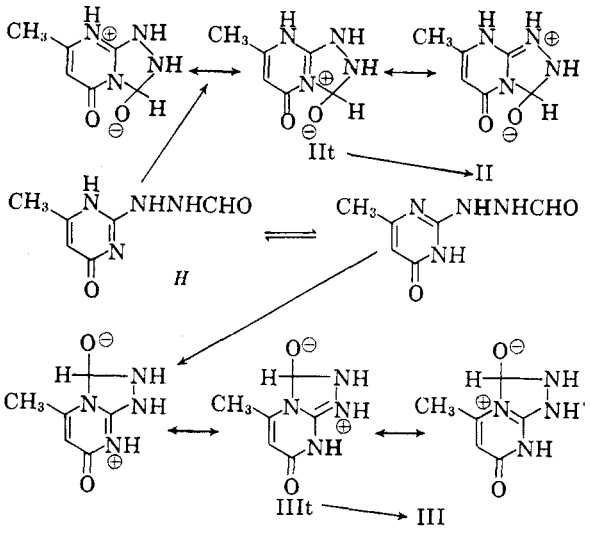
The first reaction of the hydrazine is formylation at $2\beta$, since amines are easily converted to amides in warm formic acid. The reaction is reversible and proceeds most rapidly at the most basic $2\beta$ nitrogen. Thus, attention must be focused on the formyl derivative, *H*. (The formylhydrazine cannot be isolated, but the acetylhydrazine has been obtained.)

Since the nitrogen atoms of the pyrimidine ring in *H* are vinylogously related, any electrical character of either one of the atoms is conducted to the other. That is, a reaction can take place with equal facility at either nitrogen atom; the two possibilities of reaction correspond to $S_{N2}$ and $S_{N2'}$ types. The tautomerism between the two forms of *H* cannot control the course of the reaction (since it is, in all probability, a very fast interconversion). The stabilization of the charge is identical in both transition states; in both, the resonance of the pyrimidine nitrogens is lost. Ring closure to either

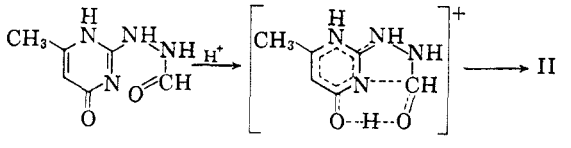
(14) The basic ionization constant of trimethylhydrazine [J. B. Class, J. G. Aston, and T. S. Oakwood, *J. Am. Chem. Soc.*, **75**, 2937 (1953)] is $6 \times 10^{-8}$, while that of dimethylamine is $5.2 \times 10^{-4}$.

(15) Quaternization of 1,2,4-triazole, a reaction that should proceed most rapidly at the most basic nitrogen, results in alkylation at position 4 [G. F. Duffin, J. D. Kendall, and H. R. J. Waddington, *Chem. & Ind. (London)*, 1458 (1954)] in agreement with the argument.

(16) That is, no matter how gentle the conditions, no intermediate can be isolated.



position might occur. Indeed, under neutral conditions, both isomers are formed. In an acidic solution, however, hydrogen-bonding between the two oxygen atoms in the transition state so favors the path leading to the 4-oxo isomer, II, that none of the other isomer can be found, despite its lower solubility.



## EXPERIMENTAL

*6-Methyl-4-oxo-1,3,3a,7-tetrazaindene* (I). 1. *Bülow's method:*[1] If very pure 3-amino-1,2,4-triazole is employed, the crude yield may be as high as 95%.

2. *The diketene reaction:* 3-Amino-1,2,4-triazole (32 g.; 0.38 m.) was dissolved in 700 ml. of hot, dry dioxane, the solution cooled to 50°, and diketene (34 g.; 0.387 m.) in 100 ml. of dry dioxane slowly added, with stirring. The solution was stirred 1 hr. and refluxed an additional hr., when a solid began to separate. The mixture was chilled and the solid collected. Evaporation of the filtrate to dryness and recrystallization from ethanol gave 5 g. of 3-amino-1,2,4-triazole. The solid obtained from the reaction was recrystallized from 400 ml. of 95% ethanol to give 15 g. of a solid which was a mixture of long rods and short crystals. No separation could be effected on repeated recrystallizations from ethanol but extraction of the mixture with cold water dissolved the short crystals. The long rods were recrystallized from ethanol to give 4 g. of 6-methyl-4-oxo-1,3,3a,7-tetrazaindene (I), m.p. 278°. The aqueous extract was evaporated to dryness and the residue recrystallized from alcohol to give 11 g. of *N,N'*-di-1,2,4-triazol-3-yl-*β*-aminocrotonamide (VII), m.p. 221–222°.

*Anal.* Calcd. for $C_8H_{10}N_8O$: C, 41.0; H, 4.3; N, 47.8. Found: C, 41.3; H, 4.6; N, 48.0.

Another run made as just described, using dry tetrahydrofuran as the solvent, gave the same azaindene, m.p. 278°, and an isomeric material which melted at 229–230°. It was not determined whether this was a single isomer or a mixture of isomers. When the experiment was repeated on a larger scale, only the compound melting at 278° and 3-acetamido-1,2,4-triazole were obtained.

*4-Chloro-6-methyl-1,3,3a,7-tetrazaindene* (XI). A mixture of 120 g. of 6-methyl-4-oxo-1,3,3a,7-tetrazaindene (I) and 600 ml. of phosphoryl chloride was refluxed for 2 hr., the excess chloride removed under vacuum, ice and chloroform were added to the residue, and the mixture was made basic with a saturated sodium carbonate solution. The chloroform layer was dried, and passed through a column packed with activated alumina to remove its orange color. Removal of the solvent from the effluent left 55 g. (37%) of the desired product, m.p. 151–152°. The yield was considerably higher without the alumina treatment, but the product was then highly colored. The yield was also higher if a very dilute solution was used and the alumina washed with much chloroform. It is quite soluble in chloroform and recrystallizes well from benzene.

*Anal.* Calcd. for $C_6H_5N_4Cl$: C, 42.7; H, 3.0; N, 33.2. Found: C, 42.8; H, 3.2; N, 33.7.

The substance is very easily hydrolyzed to I, even by the moisture in the air.

*6-Methyl-4-thiono-1,3,3a,7-tetrazaindene* (XII). A mixture of 5 g. (0.03 mole) of the chloro compound (XI) and 3.8 g. (0.03 mole) of thiourea in 50 ml. of ethanol was refluxed 3 hr. and then most of the alcohol was distilled off under vacuum. To the residue was added 75 ml. of 0.53*N* NaOH, the mixture was refluxed 0.5 hr., filtered hot, the filtrate was acidified with acetic acid and cooled, and the solid collected and recrystallized from aqueous dimethylformamide. Yield, 4 g. (72%) of product, m.p. 310° dec.

*Anal.* Calcd. for $C_6H_6N_4S$: C, 43.4; H, 3.6; N, 33.7. Found: C, 43.6; H, 3.8; N, 34.0

*4-Carboxymethylmercapto-6-methyl-1,3,3a,7-tetrazaindene* (XIII) A mixture of 3.2 g. of the thiono compound and 3 g. of sodium chloroacetate in 40 ml. of water was heated on the steam-bath, sodium carbonate was added until solution was nearly complete, and the heating was continued for 15 min. After filtering off a small amount of insoluble material (disulfide from the mercaptan), the filtrate was acidified with hydrochloric acid and cooled. Yield, 1.5 g. (44%) of product, m.p. 246–247° (recrystallized from water).

*Anal.* Calcd. for $C_8H_8N_4O_2S$: C, 42.8; H, 3.6; N, 25. Found: C, 42.4; H, 3.5; N, 24.4.

*4-(1,2,4-Triazolyl-3-amino)-6-methyl-1,3,3a,7-tetrazaindene* (XIVc). A mixture of 1.8 g. of sodium carbonate, 3.4 g. of 4-chloro-6-methyl-1,3,3a,7-tetrazaindene, 1.8 g. of 3-amino-1,2,4-triazole, and 25 ml. of nitrobenzene was refluxed for 2 hr. It was then cooled, the solid was collected, washed with water and ether, and recrystallized from dimethylformamide. Yield, 2 g. of white product, m.p. >315°.

*Anal* Calcd for $C_8H_8N_8$: N, 51 8 Found: N, 51.5

*4-Azido-6-methyl-1,3,3a,7-tetrazaindene* (XIVb). A mixture of 4 g. of the chloro compound, 3 g. of sodium azide in 10 ml. of water and 10 ml. of methanol was refluxed for 1.5 hr., then 20 ml. of water was added and the mixture chilled. The product that separated was removed and recrystallized from water; m.p., 120° dec. Yield, 3.4 g. (84%).

*Anal.* Calcd. for $C_6H_6N_7$: N, 56.1. Found: N, 56.4.

*4-Amino-6-methyl-1,3,3a,7-tetrazaindene* (XIVa).[17] A solution of 10 g. of the azide in 125 ml. of methanol was reduced at 25–30° and 50 p.s.i. of hydrogen in the presence of 1–2 g. of Raney nickel. The pressure rose as nitrogen was evolved.[18] The residue, after removal of the catalyst and solvent, was recrystallized from water, decolorizing with Norit. Yield, 7 g. (81%); m.p. 244°.

*Anal.* Calcd. for $C_6H_7N_5$: C, 48.3; H, 4.7. Found: C, 48.4; H, 4.7.

*5-Chloro-6-methyl-4-oxo-1,3,3a,7-tetrazaindene* (XVI). 1. *From 6-methyl-4-oxo-1,3,3a,7-tetrazaindene:* Into a stirred solution of 15 g. of 6-methyl-4-oxo-1,3,3a,7-tetrazaindene

(17) This amine has been mentioned in the literature several times. In our hands, none of the procedures were successful. N. Heimbach and W. Kelly, Jr., U. S. Patent **2,449,225** [*Chem. Abstr.*, **43**, 52 (1949)]. D. J. Fry, U. S. Patent **2,566,658** [*Chem. Abstr.*, **46**, 1379 (1952)].

(18) We are indebted to Mr. J. F. Stenberg for this reduction.

(I) in 750 ml. of water at 60° there was passed a current of chlorine for 45 min. After cooling to 35°, the solid (3.4 g.) was collected on a filter. It was recrystallized from dimethylformamide (with a Norit decolorization) on addition of one-third its volume of water. Yield, 2.7 g. (15%). It begins to char at about 300° but melts >350°.

*Anal.* Calcd. for $C_6H_5N_4OCl$: C, 39.0; H, 2.7; N, 30.4. Found: C, 39.3; H, 2.9; N, 30.4.

3. *From ethyl α-chloroacetoacetate and 3-amino-1,2,4-triazole:* To 28 ml. (0.15 mole) of ethyl acetoacetate there was added 24 ml. of sulfuryl chloride and the solution was heated on the steam-bath 2 hr. To this crude ethyl α-chloroacetoacetate there was added 100 ml. of acetic acid and 12.6 g. (0.15 mole) of 3-amino-1,2,4-triazole; the mixture was refluxed for 4 hr., cooled, and the solid collected and recrystallized from dimethylformamide. Yield, 25 g. The product was identical with that obtained by chlorination of I, as shown by the infrared absorption curve.

*5-Hydroxy-6-methyl-4-oxo-1,3,3a,7-tetrazaindene* (XVII). Ammonium persulfate (34 g.; 0.15 mole) in 70 ml. of water was added dropwise over a period of 1 hr. to a stirred, cold solution of 15 g. (0.1 mole) of 6-methyl-4-oxo-1,3,3a,7-tetrazaindene (I), dissolved in 220 ml. of 3*N* sodium hydroxide. The 6-methyl-4-oxo-1,3,3a,7-tetrazainden-5-yl sulfate was collected (15 g.) and recrystallized from water.

A mixture of 7 g. of the sulfate and 28 ml. of 5*N* hydrochloric acid was refluxed 0.5 hr., cooled, and the solid collected. The crude product was recrystallized from dimethylformamide to give 3.5 g. of XVII, m.p. above 330°, with progressive darkening above 300°.

*Anal.* Calcd. for $C_6H_6N_4O_2$: C, 43.4; H, 3.6. Found: C, 44.0; H, 4.0.

*4-Methyl-6-oxo-1,2,3a,7-tetrazaindene* (III); *synthesis via 3-mercapto-4-methyl-6-oxo-1,2,3a,7-tetrazaindene.* To a solution of 7 g. (0.05 mole) of 2-hydrazino-6-methyl-4-oxopyrimidine (V) in 2 l. of hot absolute alcohol there was added 7 g. of phenyl isothiocyanate, the mixture was refluxed for 15 min., was allowed to stand overnight, and the solid product was collected. After recrystallization from water, 5 g. of 3-mercapto-4-methyl-6-oxo-1,2,3a,7-tetrazaindene (VI), m.p. 280°, was obtained.

*Anal.* Calcd. for $C_6H_6N_4OS$: C, 40.0; H, 3.3; N, 30.1; S, 17.7. Found: C, 39.6; H, 3.7; N, 31.1; S, 18.5.

For desulfurization, 5 g. of VI in 250 ml. of water and 3 tablespoons of commercial Raney nickel was refluxed for 3 hr., with stirring. The mixture was filtered and the filtrate evaporated to 50 ml., cooled, and the solid collected and recrystallized from water to give 0.6 g. of product, m.p. 295–298°.

*Anal.* Calcd. for $C_6H_6N_4O$: C, 48.0; H, 4.0. Found: C, 47.7; H, 5.4. Although the analysis of this material was not considered to be satisfactory, it was shown to be identical with a pure sample, prepared as described below, both by mixed melting point and absorption curves.

*Synthesis and separation of mixture of 6-methyl-4-oxo- and 4-methyl-6-oxo-1,2,3a,7-tetrazaindenes.* A mixture of 2-hydrazino-6-methyl-4-oxopyrimidine (V) (5 g.) and ethyl orthoformate (200 ml.) was refluxed for 72 hr., cooled, and the orange solid collected.[19,20] The crude reaction product was recrystallized from water and the material that was obtained was recrystallized twice more from water and once from ethanol to give 1.7 g. (32%) of 4-methyl-6-oxo-1,2,3a,7-tetrazaindene (III), m.p. 296–298°.

*Anal.* Calcd. for $C_6H_6N_4O$: C, 48.0; H, 4.0; N, 37.3. Found: C, 47.9; H, 3.9; N, 37.3.

The filtrates from the recrystallizations were evaporated to a small volume, filtered hot, and the filtrate cooled in the refrigerator. The solid that was obtained was recrystallized three times from water to give 2.5 g. (48%) of 6-methyl-4-oxo-1,2,3a,7-tetrazaindene (II), m.p. 252–254°.

*Anal.* Calcd. for $C_6H_6N_4O$: C, 48.0; H, 4.0; N, 37.3. Found: C, 48.1; H, 4.0; N, 37.1.

In an alternate procedure, 100 ml. of dimethylformamide was used in place of the ortho ester, yielding 1 g. of III and 3 g. of II. A mixture of dimethylformamide and ethyl orthoformate gave about the same mixture.

*6-Methyl-4-oxo-1,2,3a,7-tetrazaindene.* A solution of 10 g. of 2-hydrazino-6-methyl-4-oxopyrimidine (V) in 15 ml. of 98% formic acid was kept at 50–60° for 1 hr. and evaporated to dryness below 60°. The solid was crystallized from water, yielding 7.7 g. (72%) of II, m.p. 251–253°, identical in all respects to that prepared as described in the preceding section. This material, when refluxed in formic acid, was transformed into 6-methyl-4-oxo-1,3,3a,7-tetrazaindene (I), identical in melting point, mixed melting point, and ultraviolet and infrared spectra with that prepared according to ref. (1).

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(19) It is believed that the orange color is due to a formazan formed by the reaction of 2 moles of hydrazine with 1 mole of ethyl orthoformate followed by oxidation, but a pure material has not been isolated.

(20) This reaction has also been studied by Mr. L. A. Williams, of the Kodak Limited Research Laboratories, Harrow, England.

[COMMUNICATION NO. 1996 FROM THE KODAK RESEARCH LABORATORIES]

# The Structure of Certain Polyazaindenes. III. 1,2,3a,7- and 1,3,3a,7-Tetrazaindenes

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This paper contains a description of the preparation and properties of 1,2,3a,7- and 1,3,3a,7-tetrazaindenes not specifically pertinent to topics discussed in the first two papers.

A considerable variety of tetrazaindenes is now known. Some examples having the nitrogen atom in the 1,2,3a, and 7- or the 1,3,3a, and 7-positions are described in this and the preceding papers of the series,[1] as well as in the earlier literature.[2–6]

(1) C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. VanAllan, *J. Org. Chem.*, **24**, 779, 787 (1959).

(2) E. Birr and W. Walther, *Ber.*, **86**, 1401 (1953).

(3) E. Birr, *Z. wiss. Phot.*, **50**, 107 (1955).