(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).

ROCHESTER 4, N. Y.

(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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Received December 19, 1958

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]

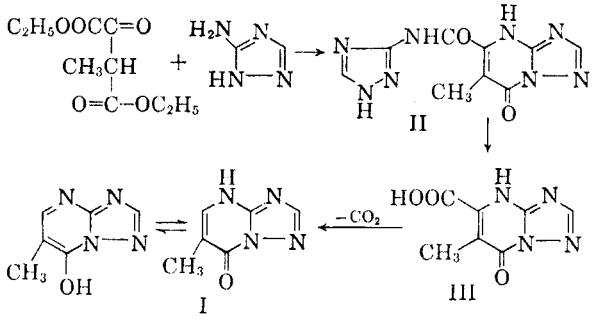
(1) C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. VanAllan, *J. Org. Chem.*, **24**, 779, 787 (1959).

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

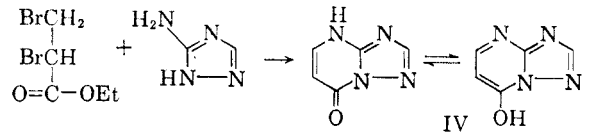
(3) E. Birr, *Z. wiss. Phot.*, **50**, 107 (1955).

Several preparative procedures have been employed. The most general is the interaction of ethyl acetoacetate and a 3-amino-1,2,4-triazole. Analogous reactions have been carried out using alkylated acetoacetic esters, diketene, ethyl ethoxalylpropionate, ethyl α,β-dibromopropionate, and ethyl ethoxymethylenemalonate. A second procedure employs an ortho-ester and 2-hydrazino-4-hydroxy-6-methylpyrimidine. The ester may be replaced by formic acid or dimethylformamide. Substances obtained by the same procedures were assumed to have the same bond arrangement; in several instances, this was confirmed by a comparison of the absorption spectra.[1]

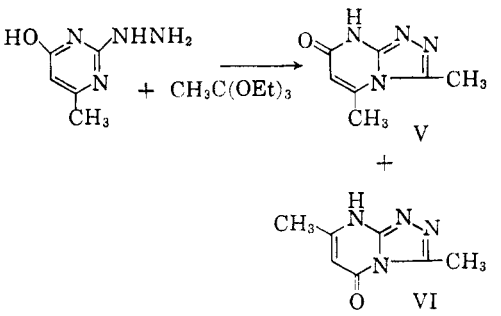
A few notes on the individual substances are in order. 5 - Methyl - 4 - oxo - 1,3,3a,7 - tetrazaindene (I) was obtained from 3-amino-1,2,4-triazole and ethyl ethoxalylpropionate. The first product that separated appeared to be a solvated 5-methyl-4-oxo-6-(3-triazolylcarbamyl)-1,3,3a,7-tetrazaindene (II), which, upon subsequent hydrolysis, gave 6-carboxy - 5 -methyl - 4 - oxo - 1,3,3a,7 - tetrazaindene (III). The latter underwent easy decarboxylation to the 5-methyl-4-oxo derivative (I).



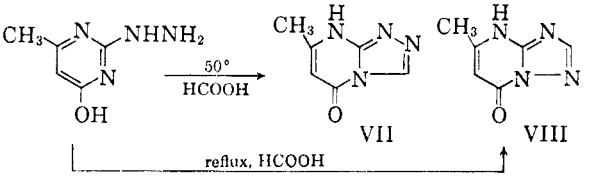
4-Oxo-1,3,3a,7-tetrazaindene (IV) resulted from the interaction of ethyl α,β-dibromopropionate and 3-amino-1,2,4-triazole.

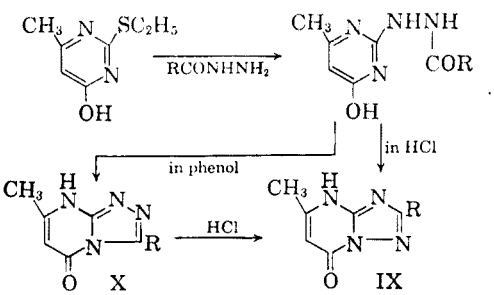


In a manner analogous to that discussed in the previous paper,[1] when 2-hydrazino-4-hydroxy-6-methylpyrimidine was treated with an ortho ester, a mixture of the two expected isomers (V and VI) in the 1,2,3a,7-series resulted; these were separated by fractional crystallization.



The cyclizations of hydrazinopyrimidines give different products under different conditions. For instance, 2-hydrazino-4-hydroxy-6-methylpyrimidine, on warming (50°) in formic acid, gives 4-oxo-6-methyl-1,2,3a,7-tetrazaindene (VII); in boiling formic acid, the hydrazine is converted to the 1,3,3a,7-isomer (VIII). In boiling phenyl acetate, the hydrazine is converted to the rearranged dimethyl isomer, (IX, R = CH_3). When the free hydrazine in acetic acid or its acetyl derivative in formic acid is employed, only a trace of IX (R = CH_3) is produced, but hydrogen chloride in acetic acid brings about the rearrangement of X (R = CH_3) satisfactorily. 2-Ethylmercapto-6-methyl-4-hydroxypyrimidine can also be used as a starting material, provided it is given a prior treatment with acethydrazide. The analogous β-hydroxyethyltetrazaindenes (IX, X. R = CH_2CH_2OH) are obtainable by slight modifications of the same procedures. The 1,2,3a,7-form results from ring closure in phenol, whereas the rearranged 1,3,3a,7-isomer is obtained if hydrogen chloride in acetic acid is employed.



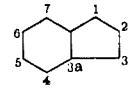


Birr has listed a series of 6-alkylated-4-oxo-1,3,3a,7-tetrazaindenes (erroneously named as "1,2-3a,7"). Some of these, and the 6-benzyl derivative were also prepared in these Laboratories. The 2-hydroxymethyl (IX. R = CH_2OH) compound was obtained by the standard synthesis from a substituted aminotriazole.

(4) C. Bülow, *Ber.*, **42**, 2208, 2599, 3555, 4429 (1909).
(5) C. Bülow and K. Haas, *Ber.*, **42**, 3648 (1909).
(6) N. Heimbach and W. Kelly, Jr., U. S. Patent **2,444,605** (1948).

TABLE I

PROPERTIES OF TETRAZAINDENES



No.	Position of Subs. 1,3,3a,7-series 2	4	5	6	M.P., °C.	Empirical Formula	Analyses, % Calcd. C	H	N	Found C	H	N
IV		OH			204–205[a]	$C_7H_{10}N_4O_2$	46.4	5.5	30.9	45.9	5.2	30.6
		OH	CH_3	CH_3	304–305[b]	$C_7H_8N_4O$	51.2	4.9	34.2	50.9	5.0	34.7
XI		OH		C_2H_5	212–214	$C_7H_8N_4O$	51.2	4.9	34.2	51.4	5.0	34.3
		OH		C_7H_{15}	128–130	$C_{12}H_{18}N_4O$	61.4	7.7	23.9	61.3	8.1	24.2
		OH		$C_{11}H_{23}$	128–131[c]	$C_{16}H_{26}N_4O$	66.2	9.0	19.3	65.9	8.9	19.8
		OH		$C_6H_5CH_2$	240	$C_{12}H_{10}N_4O$	63.8	4.4	24.8	63.8	4.5	24.9
	CH_3	Cl		CH_3	149–150[d]	$C_7H_7ClN_4$	46.0	3.8	30.7	46.1	4.6	31.0
IX	CH_2OH	OH		CH_3	227–229	$C_7H_8N_4O_2 \cdot {}^1/_2H_2O$	44.5	4.8	29.7	44.5	4.7	29.8
IX	CH_2OH	OH		CH_3	275–277	$C_7H_8N_4O_2$	46.6	4.5	31.1	45.8	4.8	31.1
IX	CH_2Cl	OH		CH_3	211–260[d]	$C_7H_7ClN_4O$	42.4	3.5		42.4	3.7	
IX	C_7H_{15}	OH		CH_3	172	$C_{13}H_{20}N_4O$	62.9	8.1	22.6	62.9	8.0	22.2
IX	$C_{11}H_{23}$	OH		CH_3	163	$C_{17}H_{28}N_4O$	67.1	9.2	18.4	66.9	9.4	18.6
I		OH	CH_3		>300	$C_6H_6N_4O$			37.4			37.4
III		OH	CH_3	COOH	>325	$C_7H_6N_4O_3$	43.3	3.1	29.4	43.2	3.4	28.9
IX	C_2H_4OH	OH		CH_3	262–263	$C_8H_{10}N_4O_2$	49.5	5.2	28.8	49.7	4.9	28.4
V	CH_3[e]	CH_3		OH	309–310	$C_7H_8N_4O$	51.2	4.9	34.2	50.9	5.0	34.5
VI	CH_3[e]	OH		CH_3	310–311	$C_7H_8N_4O$	51.2	4.9	34.2	51.4	5.1	34.7
X	C_2H_4OH[e]	OH		CH_3	237–240	$C_8H_{10}N_4O_2$	49.5	5.2	28.8	50.0	6.3	28.9

[a] The alcoholate. Birr[3] gives 287–288° for the unsolvated substances. [b] Birr[3] gives 291–292°. [c] Birr[3] gives 100–101°, doubtless a hydrate. [d] Cl: Calcd., 19.5. Found, 19.4. [e] In 3-position of the 1,2,3a,7- compound.

EXPERIMENTAL

Most of the procedures employed for the preparation of the various substances have been described in the previous papers of this series. The properties of the new tetrazaindenes are collected in Table I.

The various tetrazaindenes that contain oxo groups resemble those described in the preceding paper.[1] The most conspicuous property is the tendency to retain solvent of crystallization. One solvent may partially or entirely replace another on recrystallization.

5-Methyl-4-oxo-1,3,3a,7-tetrazaindene (I). A mixture of 3-amino-1,2,4-triazole (8.4 g., 0.1 mole), ethyl ethoxalylpropionate (21 g., 0.1 mole), and 54 ml. of acetic acid was refluxed for 3 hr. After standing at room temperature overnight, the solid was collected and recrystallized from dimethylformamide to give 5–8 g. of 5-methyl-4-oxo-6-(3-triazolylcarbamyl)-1,3,3a,7-tetrazaindene (II) as the monohydrate,[7] m.p. 275°, and sometimes as the monoalcoholate,[7] m.p. 257°. Hydrolysis of 8 g. of this material by boiling for 5 hr. with 85 ml. of 4% hydrochloric acid gave 5 g. of 6-carboxy-5-methyl-4-oxo-1,3,3a,7-tetrazaindene (III). The latter compound was decarboxylated by heating for 10 min. in boiling Dowtherm to give 5-methyl-4-oxo-1,3,3a,7-tetrazaindene.

4-Oxo-1,3,3a,7-tetrazaindene (IV). A solution of 17 g. (0.2 mole) of 3-amino-1,2,4-triazole and 52 g. (0.2 mole) of ethyl α,β-dibromopropionate in 100 ml. of pyridine was refluxed for 3 hr., cooled, and diluted with an equal volume of water. The cream-colored solid was collected and recrystallized from alcohol to give 7 g. of product as the alcoholate.

2-Hydroxymethyl-6-methyl-4-oxo-1,3,3a,7-tetrazaindene (IX, $R = CH_2OH$). The necessary 3-amino-5-hydroxymethyltriazole glycolate was prepared as follows: To 1.24 kg. of aminoguanidine bicarbonate in a 12-l. flask was added 2 kg. of 70% aqueous glycolic acid, octyl alcohol being added to control foaming. When foaming had ceased, 10 ml. of concentrated nitric acid was added so that it wet the sides of the flask above the liquid. The whole was refluxed for 24 hr. The liquid was poured into an enameled pan, cooled to 5° for 15 min., the solid was collected on a filter, sucked dry, and recrystallized from 2 l. of ethanol. This solution was cooled to 5° for 15 min. and filtered. Yield of triazole, m.p 113–115°, 78–95 g. (45–55%).

Anal. Calcd. for $C_5H_{10}N_4O_4$: C, 31.5; H, 5.3; H, 29.5. Found: C, 32.0; H, 5.2; N, 31.4.

Cyclization. A mixture of 1 kg. of 3-amino-5-hydroxymethyltriazole glycolate, 4.5 l. of practical ethyl acetoacetate, and 80 ml. of glacial acetic acid was heated on the steam-cone for 24 hr., cooled to 25°, filtered, and washed with ethanol. The damp cake was dissolved in 3 l. of boiling water, decolorized and filtered, and 3 l. of concentrated hydrochloric acid was added to the hot solution. After cooling at 5° for 1 hr., the product was filtered and dried. A quantitative yield of the pure white anhydrous material resulted (crystallization from water yielded a hemihydrate).

2-Chloromethyl-6-methyl-4-oxo-1,3,3a,7-tetrazaindene (IX, $R = CH_2Cl$). A mixture of 900 g. of 2-hydroxymethyl-6-methyl-4-oxo-1,3,3a,7-tetrazaindene and 2 or 3 l. of recently distilled phosphoryl chloride was heated gently until dissolved, and then 20–40 min. longer and cooled. It was poured upon ice and filtered promptly (the filtrate will heat up in a few minutes if not drowned out). The solid was washed with cold water and recrystallized in portions from water (100 ml. per g.) using Darco, and allowing the hot solution to boil briskly for at least 10 min. Yield was 400 g.

3,4-Dimethyl-6-oxo- and 3,6-dimethyl-4-oxo-1,2,3a,7-tetrazaindenes (V *and* VI). 1. *From a pyrimidinehydrazine and an ortho ester.* A mixture of 5 g. of 2-hydrazino-4-hydroxy-6-methylpyrimidine[2] and 200 ml. of ethyl orthoacetate was refluxed for 24 hr., cooled, and the solid collected. The crude material was recrystallized from 3 l. of water to give 3,6-dimethyl-4-oxo-1,2,3a,7-tetrazaindene (VI), m.p. 310°. The filtrate was concentrated to half its volume to give more of the same material (3.5 g. combined yield). The filtrate was concentrated to about 25 ml. and cooled, and the solid that was obtained was recrystallized twice from water and once from ethanol to give 0.8 g. of 3,4-dimethyl-6-oxo-1,2,3a,7-

(7) Indicated by the analytical results; the solvent-free form is obtainable, but only by stringent drying.

tetrazaindene (V), m.p. 308–310°. The absorption spectra were given previously.[1]

2. *From 2-acethydrazido-4-hydroxy-6-methylpyrimidine.* A mixture of 10 g. of 2-hydrazino-4-hydroxy-6-methylpyrimidine[2] and 50 ml. of pyridine was treated with 5 ml. of acetyl chloride. The temperature rose to about 50°, and a solid separated. After 0.5 hr., the mixture was filtered. The white solid, m.p. 213–216°, was crystallized from 125 ml. of water. Yield was 1.7 g., m.p. 251–253° dec.

Anal. Calcd. for $C_7H_{10}N_4O_2$: C, 46.1; H, 5.5; N, 30.8. Found: C, 46.1; H, 5.8; N, 30.8.

It may be noted that the hydrazides melt with foaming, suggesting a loss of water on heating. Treatment of this material with formic acid at 70 ± 5° for 1 hr. leaves it unchanged. In boiling formic acid (4 hr.), substantially pure 3,6-dimethyl-4-oxo-1,2,3a,7-tetrazaindene (VI) is formed, contaminated with a detectable amount of the rearranged isomer, 2,6-dimethyl-4-oxo-1,3,3a,7-tetrazaindene (IX. R = CH_3).

2,6-Dimethyl-4-oxo-1,3,3a,7-tetrazaindene (IX. $R = CH_3$). A solution of 5 g. of 2-hydrazino-4-hydroxy-6-methylpyrimidine[2] in 50 ml. of phenyl acetate was refluxed for 4 hr., cooled, and filtered. The white solid was crystallized from water; it melted at 311–313°. The infrared absorption was identical with that of material prepared from ethyl acetoacetate and 3-amino-5-methyl-1,2,4-triazole.[8]

4-Chloro-2,6-dimethyl-1,3,3a,7-tetrazaindene. A mixture of 30 g. of 2,6-dimethyl-4-oxo-1,3,3a,7-tetrazaindene (prepared from 3-amino-5-methyl-1,2,4-triazole and ethyl acetoacetate[8]) and 100 ml. of freshly distilled phosphoryl chloride was refluxed for 1 hr., evaporated to dryness, the residue washed with chloroform, and then shaken with ice water and chloroform. The second chloroform solution was dried over sodium sulfate, passed through a 1½-in. by 36-in. column of alumina (Alcoa F-20, 200-mesh), and evaporated to dryness. The pure white chloride was obtained in a yield of 18 g. (54%).

4-Hydroxy-2-β-hydroxypropionhydrazido-6-methylpyrimidine. This was formed by refluxing equimolecular proportions of β-hydroxypropionhydrazide[9] and 2-ethylmercapto-4-hydroxy-6-methylpyrimidine in aqueous alcohol for 20 hr., cooling to 25°, and filtering. The crude solid (60–75% yield), m.p. 223–226°, with evolution of gas, was usually used directly, but could be recrystallized from water, after which it melted at 223–234°, with foaming.

2-β-Hydroxyethyl-6-methyl-4-oxo-1,3,3a,7-tetrazaindene (IX. $R = C_2H_4OH$). A mixture of 6.3 g. of the hydrazide, 500 ml. of glacial acetic acid, and 50 ml. of concentrated hydrochloric acid was refluxed for 20 hr., filtered hot from small impurities, and cooled. A white solid separated (12 g., m.p. 257–260°). Recrystallized from water, it yielded 6.5 g., m.p. 262–263°.

3-β-Hydroxyethyl-6-methyl-4-oxo-1,2,3a,7-tetrazaindene (X. $R = C_2H_4OH$). Eight g. of the hydrazide in about 100 g. of phenol was refluxed for 1 hr., cooled, and the phenol steam-distilled. A white solid crystallized from the water. Yield was 3.3 g., m.p. 237–240°.

ROCHESTER 4, N. Y.

(8) J. Thiele and K. Heidenreich, *Ber.*, **26**, 2599 (1893).

(9) T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert, and F. T. Fredorek, *J. Am. Chem. Soc.*, **73**, 3168 (1951).

[COMMUNICATION NO. 1997 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK COMPANY]

The Structure of Certain Polyazaindenes. IV. Compounds from β-Keto Acetals and β-Methoxyvinyl Ketones[1]

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Received December 19, 1958

The reaction of 4,4-dimethoxy-2-butanone or 4-methoxy-3-buten-2-one with 3-amino-1,2,4-triazole leads to 6-methyl-1,3,3a,7-tetrazaindene. The mode of formation and relation to the product from ethyl acetoacetate are discussed. This reaction of β-keto acetals with amino-substituted azoles appears to be general for the synthesis of polyazaindenes.

The reaction between 3-amino-1,2,4 triazole (I) and ethyl acetoacetate is now known[2] to produce 6-methyl-4-oxo-1,3,3a,7-tetrazaindene (II); however, at the time the following work was undertaken there existed neither spectral evidence nor convincing chemical proof in that regard. Numerous attempts had been made to isolate an intermediate compound from this reaction, or related reactions, but to no avail.

In earlier work involving reactions of β-keto acetals with aromatic amines and hydrazines,[3] it was possible to isolate intermediate condensation products, which could be characterized so that the structure of the product of a subsequent cyclization was clearly evident. It seemed reasonable to expect a similar degree of success in the reaction of 3-amino-1,2,4-triazole with 4,4-dimethoxy-2-butanone (III).

β-Biketones are known to react with 3-amino-1,2-4-triazole to give dialkyltetrazaindenes,[4] while diethyl ethoxymethylenemalonate produces a product with an ethoxycarbonyl substituent.[5,6]

(1) This paper is Part III of another series from these Laboratories "Beta-Keto Acetals," Parts I and II of which appeared in *J. Org. Chem.*, **21**, 97, 102 (1956). A portion of the subject matter of this paper appears in U. S. Patent **2,837,521**, dated June 3, 1958.

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