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]

C. F. H. ALLEN, H. R. BEILFUSS, D. M. BURNESS, G. A. REYNOLDS, J. F. TINKER, AND J. A. VANALLAN

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.

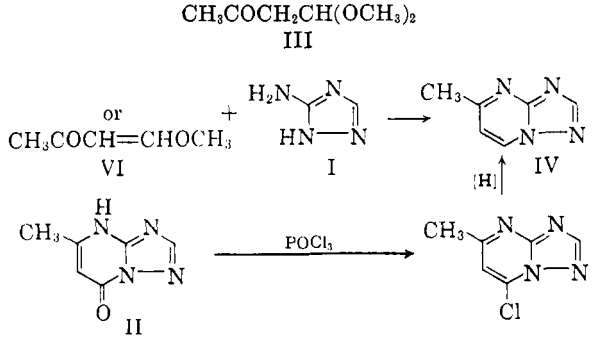
(2) C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. VanAllan, *J. Org. Chem.*, **24**, 787 (1959).

(3) D. M. Burness, *J. Org. Chem.*, **21**, 97 (1956).

(4) C. Bülow and K. Haas, *Ber.*, **42**, 4638 (1909); N. Heimbach, U. S. Patent **2,443,136** (1948); *Chem. Abstr.*, **42**, 6685 (1948).

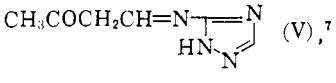
(5) N. Heimbach, U. S. Patent **2,450,397** (1948); *Chem. Abstr.*, **43**, 4165 (1949).

The reaction of 4,4-dimethoxy-2-butanone with I produced solely, and in good yield, a product which proved to be identical with the 6-methyl-1,3,3a,7-tetrazaindene (IV) obtained from II, as shown.



Thus, of the four possible products (methyl at 4 or 6, nitrogens at 1,2,3a,7 or 1,3,3a,7), only one was obtained. The relation demonstrated here between II and IV leads to the conclusion that each possesses the same C—N skeleton. This is not necessarily valid in the 1,2,3a,7-tetrazaindene series, since it has been shown[2] that acidic conditions (such as prevail during the phosphoryl chloride reaction) may cause rearrangement. That no rearrangement occurs in the present case was shown by the regeneration of II from the chloro compound by hydrolysis.

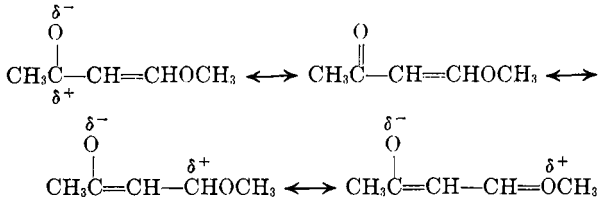
As with a β-keto ester, there are two possible sites for the initial reaction of the amino group (*i.e.*, the most basic center) of I with a β-keto acetal. By analogy to the corresponding reaction with aniline,[3] however, the acetal group of III would be expected to react first to give the intermediate,



which, when cyclized, would produce either 4-methyl-1,2,3a,7- or 4-methyl-1,3,3a,7-tetrazaindene. Obviously, this is at variance with the correct structure (II) of the oxo compound.

Efforts were made to isolate or determine in some fashion the nature of the intermediate, but to no avail. The reaction proceeded at the low temperature of boiling benzene, slowly but completely to the end-product. Determination of the composition of the initial distillate obtained at the start of the reaction showed a methanol–water ratio of 2.5 (theory for the complete reaction is 3.5), confirming the fact that the two steps occur simultaneously or in rapid succession.

Further evidence that the first step may well involve the intermediate, V, was obtained when the reaction was carried out with 4-methoxy-3-buten-2-one (VI). The latter reacts with aniline to yield, only under milder conditions, the same product ($C_6H_5N{=}CHCH_2COCH_3$) as is obtained with the β-keto acetal (III). The reaction of I with VI undoubtedly proceeds preferentially by a 1,4-addition mechanism[8] to produce the same intermediate (V) as before, and indeed the same methyltetrazaindene was isolated.



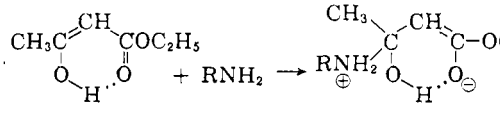
The reaction of 3-amino-1,2,4-triazole with VI was run under the mildest of conditions, at 25°, in *N*,*N*-dimethylformamide; again, it was impossible to isolate an intermediate compound. The methyltetrazaindene crystallized from the reaction mixture as a pure compound in 56% yield, practically identical with the yield of anil obtained with aniline.

In another experiment, this reaction was run at 25° in dimethyl sulfoxide as a solvent (which is essentially transparent in the region of 4.0–6.8 μ) and the reaction was followed by infrared examination of samples of the reaction mixture at various intervals. No definite conclusions could be drawn from the spectra, owing largely to overlapping absorptions.

It is possible that the course of the reaction of the aminotriazole with the β-keto acetal is identical with that of the methoxyvinyl ketone, after a preliminary step involving the loss of methanol, a reaction which proceeds readily under acid catalysis. The higher temperatures required for condensations with the acetal are similar to those necessary for this elimination reaction, which here

(6) 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).

(7) This may appear at first to be contradictory to the reaction with acetoacetic ester which is known to condense with amines under mild acidic catalysis at the ketonic carbonyl group. The difference lies in the far greater electronegativity of the carbethoxy group which facilitates addition of the amine to the enolic form of the β-keto ester.

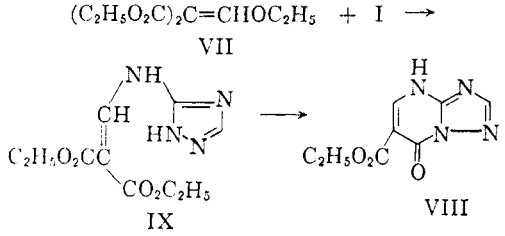


The acetal group, on the other hand, is not electronegative, so that the carbonyl of a β-keto acetal resembles more closely that of a simple ketone in reactivity; ketones ordinarily react with amines with considerable difficulty.

(8) The tendency for 1,4-addition to VI is actually somewhat greater than in the case of methyl vinyl ketone which also reacts in this manner [N. Murata, H. Arai, and Y. Tashima, *J. Chem. Soc. Japan*, **56**, 709 (1953); *Chem. Abstr.*, **49**, 7517 (1955)]. The additional resonance possibilities due to the methoxyl group make for a still more positive center at the number four carbon atom.

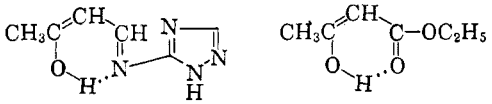
may well be catalyzed by the mildly acidic 3-amino-1,2,4-triazole.

Another possibility which must be considered is that the 1,4-addition might involve the 2-position of the triazole ring rather than the amino group; this could lead directly to IV. This is most improbable in view of the results in the analogous case involving ethyl ethoxymethylenemalonate (VII). Addition to this enol ether necessarily involves the amino group of I, for the ultraviolet absorption spectrum of the product conforms to that of a 4-oxo-1,3,3a,7-tetrazaindene (VIII) rather than the alternate 6-oxo isomer.[6]



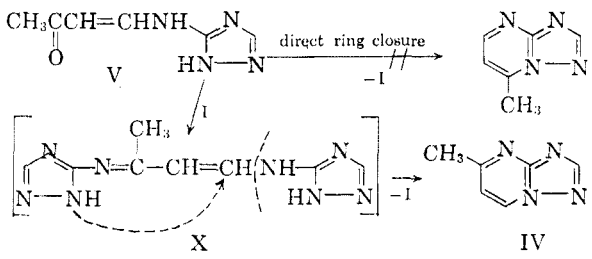
VII IX VIII

It is clear that some other intermediate must interpose between V and IV. Condensation of V with aminotriazole[9] leads to such an intermediate.



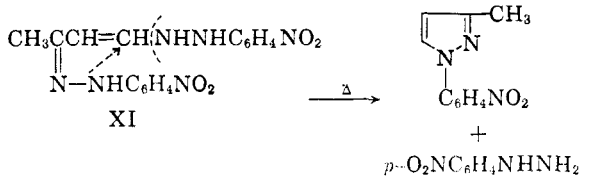
V

This bis compound, X, then spontaneously loses a mole of aminotriazole to form 6-methyl-1,3,3a,7-tetrazaindene (IV). The aminoanil (X) could not, however, be isolated.



V X IV

Support for such a mechanism was gained from a study of the reaction of *p*-nitrophenylhydrazine with VI. An attempt to condense *a single mole* of the hydrazine with the methoxyvinyl ketone, under the same mild conditions employed with I, produced the bishydrazone, XI. This, when heated, cyclized to the known 3-methyl-1-*p*-nitrophenylpyrazole with loss of one mole of *p*-nitrophenylhydrazine. This is the same behavior as is postulated for X.



XI

A similar process occurs in the related case where 5-aminotetrazole replaces I. Of the two isomers possible in this case, only one has been obtained in each of five syntheses; this is formulated by analogy as 6-methyl-1,2,3,3a,7-pentazaindene (XII). These methods involved (1) reaction of III with 5-aminotetrazole in xylene-DMF at 140°, (2) reaction of III with 5-aminotetrazole in glacial acetic acid, (3) reaction of VI with 5-aminotetrazole at 25°, (4) dehydroxylation of 6-methyl-4-oxo-1,2,3,-3a,7-pentazaindene, and (5) the action of nitrous acid on 2-hydrazino-4-methylpyrimidine.

Numerous other azoles were found to react with III, and III, in turn, could be replaced by other β-keto acetals; thus, the reaction is quite general for the synthesis of polyazaindenes containing only hydrocarbon substituents in the 6-membered ring. The actual structures of the products formed in most of these reactions are not known and the names assigned are based on analogy. The compounds prepared are listed in Tables I and II.

The reaction of 4,4-dimethoxy-3-methyl-2-butanone (XIII) with I in boiling xylene produced two isomers; one of these was found to be identical with the compound obtained by reduction of 5,6-dimethyl-4-oxo-1,3,3a,7-tetrazaindene (formed by interaction of ethyl α-methylacetoacetate with 3-amino-1,2,4-triazole) and is, therefore, 5,6-dimethyl-1,3,3a,7-tetrazaindene (XIV). The fact that the second isomer, although analytically pure, was low-melting and melted over a range (91–99°) might be due to inseparable isomers, although the infrared spectrum indicates the presence of very little, if any, of the higher-melting isomer.

It seems unlikely that the amino group of I would react first with the carbonyl; instead, this acetal loses methanol (much more readily than III) to form an unsaturated ketone,[10] the reactive species. Accordingly, the structure assigned to the second isomer is 4,5-dimethyl-1,3,3a,7-tetrazaindene (XV).

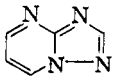
In two other instances, it was possible to isolate two separate, isomeric tetrazaindenes. These were from the reactions of 3,5-diamino-1,2,4-triazole with 2-methoxymethylenecyclohexanone (XVI), and with β,β-dimethoxypropiophenone (XVII). In these

(9) The carbonyl group of V should be more active than that of its precursors, III or VI; there is now a close resemblance between its enolic form and that of acetoacetic ester which, as stated earlier, has been found to condense with amines at the ketonic carbonyl.

(10) This behavior is parallel to that observed in the synthesis of XIII itself, in which a considerable quantity of unsaturated ketone is formed; very little is formed in the case of III. [E. Royals and K. Brannock, *J. Am. Chem. Soc.*, 75, 2050 (1953) and unpublished observations of these Laboratories.]

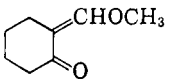
TABLE I

1,3,3a,7-TETRAZAINDENES

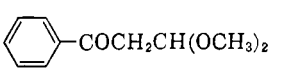


Number	Substituents	Precursors Acetal	Precursors Azole	Reaction Solvent	Yield, %	M.P., °C.	Analyses Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
XXI	Unsubstituted	[a]	I	Acetic acid[b]	22 (crude)	140–142[c]	50.0	3.3	46.8	50.4	3.3	46.7
IV	6-CH_3	III	I	Xylene	63	182.5–183[c]	53.7	4.5	41.8	53.7	4.5	42.0
IV	6-CH_3	III	I	Benzene	57 (crude)[d]	173–180						
IV	6-CH_3	III	I	Acetic acid	53 (crude)	179–183[c]						
IV	6-CH_3	III	I	None; heat only	66 (crude)	173–178[c]						
IV	6-CH_3	VI	I	DMF[b]	57	181.5–183						
XIV[b]	5,6-Di-CH_3	XIII	I	Xylene	69[e]	178–178.5[c]	56.8	5.4	37.8	56.9	5.3	38.1
XV[b]	4,5-Di-CH_3					91–99[f]	56.8	5.4	37.8	57.1	5.5	37.7
XXII	2-SCH_3-6-CH_3	III	[g]	Xylene	65	125–126[j]	46.7	4.5	31.1	46.6	4.3	31.3
XXIII	2-NH_2-6-CH_3	III	[h]	Xylene	58	210–211.5[k]	48.3	4.7	47.0	47.9	5.1	47.3
XIX[i]	2-NH_2-4-C_6H_5	XVII	[h]	Xylene	95[e]	268.5–269[j]	62.6	4.3	33.1	62.6	4.3	33.1
XVIII[i]	2-NH_2-6-C_6H_5	XVII	[h]	Acetic acid	85[e]	236.5[l]	62.6	4.3	33.1	62.4	4.3	33.6

[a] 1,1,3,3-Tetraethoxypropane, Eastman Chemical No. 7118. [b] See Experimental. [c] Recrystallized from benzene. [d] After a 4-day period at reflux. The yield based on unrecovered triazole was 79%. [e] Crude mixed isomers. [f] Unchanged after repeated recrystallization from methylcyclohexane or ligroin (65–75°). [g] 3-Amino-5-methylmercapto-1,2,4-triazole [F. Arndt and E. Milde, *Ber.*, **54**, 2089 (1921)]. [h] 3,5-Diamino-1,2,4-triazole; courtesy of American Cyanamid Co. [i] Both reactions produced small amounts of the other isomer and a by-product (XX). See Experimental. [j] Recrystallized from xylene. [k] Recrystallized from *N,N*-dimethylformamide. [l] Recrystallized from *n*-butanol.



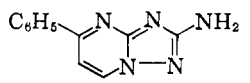
XVI



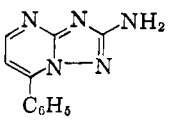
XVII

cases, steric effects might operate to change the course of reaction from that characteristic of III.

In the case of β,β-dimethoxypropiophenone, the two isomers obtained had vastly different ultraviolet spectra. The reaction run in xylene produced predominantly the higher-melting isomer of λ_{max} 339. The lower-melting isomer, which was detected (*via* infrared) but not isolated from the xylene reaction, predominated when glacial acetic acid was used as solvent;[11] this had a λ_{max} of 311. This difference could be attributed to a change in ring structure from a 1,3,3a,7- to a 1,2,3a,7-tetrazaindene,[12] but more likely is due to a difference in location of the phenyl substituent. Thus, the cross-conjugated type of structure such as exists in XVIII absorbs at a shorter wave length than the linear conjugated system of XIX.

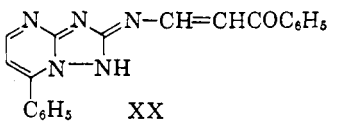


XVIII (λ_{max} 311 mμ)



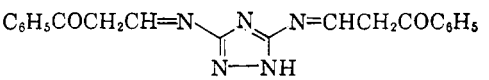
XIX (λ_{max} 339 mμ)

The reaction in either solvent produced a by-product derived from two moles of the acetal (XVII) and one of 3,5-diamino-1,2,4-triazole. In view of the elemental composition and the ultraviolet spectra (λ_{max} = 373; ϵ = 58,800), this by-product is tentatively considered to have the highly conjugated structure XX. Acid hydrolysis of XX produced the high-melting isomer, XIX.



XX

This series of transformations is most reasonable in terms of a 1,3,3a,7-tetraza structure (rather than a 1,2,3a,7- one) provided XX is formed only from the dianil, XXI. Both steric hindrance and statistical influence favor the rate leading to the 1,3,-3a,7- isomer.



XXI

The formation of a product such as XX, in which it is evident that condensation with the second mole of β-keto acetal has occurred *via* the acetal group and not the carbonyl, lends additional support to the argument regarding the first step in the reaction of β-keto acetals with amino-substituted azoles.

EXPERIMENTAL[13]

Conditions for the reactions of the various amino azoles with β-keto acetals and properties of the resulting products are shown in Tables I and II. Except as noted, the reac-

(11) The higher-melting isomer was also isolated from the reaction in acetic acid.

(12) The 1,3,3a,7-tetrazaindenes have a λ_{max} in the longer-wave-length region of 16 to 26 mμ lower than the corpresonding compounds of 1,2,3a,7-structure.[6]

(13) All melting points are corrected.

TABLE II

MISCELLANEOUS POLYAZAINDENES

Number	Product	Precursors: Acetal	Precursors: Azole	Reaction Solvent	Yield, %	M.P., °C.	Analyses: Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
XII[a]	6-Methyl-1,2,3,3a,7-pentazaindene	III	5-Aminotetrazole	Xylene-DMF	50	133.5–134[e]	44.4	3.7	51.8	44.5	3.4	51.5
XII[a]	6-Methyl-1,2,3,3a,7-pentazaindene	III	5-Aminotetrazole	Acetic acid	91 (crude)	130–132.5[f]						
XII[a]	6-Methyl-1,2,3,3a,7-pentazaindene	VI	5-Aminotetrazole	DMF	72	132.5–134						
XXIV	5-Methyl-1,2,3a,4-tetrazaindene	III	4-Amino-1,2,4-triazole	Xylene	16	168–169[f]	53.7	4.5	41.8	54.0	4.7	42.0
XXV	2-Methyl-1,4a,9-triazafluorene	III	2-Aminobenzimidazole	Xylene	59	233.5–234[g]	72.2	4.9	22.9	71.7	4.8	23.1
XXVI	2-Amino-5,6,7,8-tetrahydro-1,3,3a,9-tetrazabenz(f)indene	XVI[b]	2,5-Diamino-1,2,4-triazole	Xylene	52[c]	317.5–318.5[g]	57.1	5.8	37.1	57.3	5.9	36.9
XXVII	(Isomeric structure)					256–264[d]	57.1	5.8	37.1	57.3	6.4	37.4

[a] See Experimental. [b] 2-Methoxymethylenecyclohexanone (XVI), see ref. 10. [c] Crude mixed isomers. [d] Undoubtedly unresolved mixture (from *n*-butanol); however, infrared analysis indicates absence of XXVI. [e] Recrystallized from ethanol. [f] Recrystallized from benzene. [g] Recrystallized from xylene.

tions were carried out in the refluxing solvent (no catalyst required) with a packed column and a water separator, until formation of the water–methanol phase was essentially complete. The product crystallized from the reaction mixture and was purified by recrystallization from the designated solvent with Pittsburgh Carbon Type RB. Reactions run in acetic acid were refluxed for 4 to 6 hr. Supplementary details are given in Tables I and II and in the following examples.

1,3,3a,7-Tetrazaindene (XXI). A solution of 8.4 g. of 3-amino-1,2,4-triazole (I) and 33 g. of 1,1,3,3-tetraethoxypropane was heated at reflux for 2 hr. in 50 ml. of glacial acetic acid containing 5 drops of concentrated hydrochloric acid. The solvent was removed under reduced pressure and the residue extracted with boiling benzene from which was obtained 2.9 g. (22% yield) of crude product, melting at 138–141°. Purification by passage of a benzene solution through a column of activated alumina, followed by elution with benzene-chloroform (3:1), produced the pure material of m.p. 140–142°.

6-Methyl-1,3,3a,7-tetrazaindene (IV). (a) *From 4,4-dimethoxy-2-butanone* (III) (see Table I).

(b) *From 4-methoxy-3-buten-2-one* (VI). A solution of 5 g. of VI and 4.2 g. of I in 25 ml. of *N,N*-dimethylformamide, held at 25° for 18 days, deposited 2.4 g. of peach-colored prisms, m.p. 181–182.5°. An additional 1.4 g. of slightly less pure material was obtained from the mother liquor after heating for 2 hr. and concentration to a small volume. Total yield, 3.8 g. (57%). Dimethyl sulfoxide can also be used advantageously in this reaction. Identity of the compound with that prepared from III was established by mixture melting points and the infrared spectra.

(c) *From 4-chloro-6-methyl-1,3,3a,7-tetrazaindene.* A mixture of 16.9 g. of the chloro compound,[2] 16.9 g. of magnesium oxide, 6 g. of 5% Pd-C, and 200 ml. of water was shaken under 37 p.s.i. of hydrogen in a Parr hydrogenation apparatus until the theoretical amount of hydrogen had been consumed (40 min.). Filtration and evaporation of the filtrate produced a solid which was dissolved in methanol and passed through a column of methanol-washed activated alumina. Evaporation of the effluent and recrystallization of the residue from benzene yielded 2.7 g. of pure IV, m.p. 180–182°. This was shown to be identical with the products in Parts *a* and *b* by mixture melting points and the infrared spectrum.

Dimethyltetrazaindenes (XIV and XV). The xylene reaction mixture, from 12 g. of 4,4-dimethoxy-3-methyl-2-butanone (XIII)[3] and 6.3 g. of I, deposited 5.3 g. of crystals, m.p. 119–148°, on cooling. These were recrystallized twice from benzene to give 1.2 g. of pure XIV, m.p. 178–178.5°, which was indistinguishable from the 5,6-dimethyl-1,3,3a,7-tetrazaindene (infrared spectrum and mixture melting point) prepared by the method which follows. Concentration of the xylene mother liquor produced 2.4 g. of the crude second isomer (XV), m.p. 90–105°. Repeated recrystallization from ligroin (65–75°) or methylcyclohexane failed to change the 91–99° melting point of the analytically pure material. Infrared analysis indicated the virtual absence of XIV.

5,6-Dimethyl-1,3,3a,7-tetrazaindene (XIV).[14] 4-Chloro-5,6-dimethyl-1,3,3a,7-tetrazaindene was prepared from the corresponding 4-hydroxy compound[4,15] by essentially the same procedure used for 4-chloro-6-methyl-1,3,3a,7-tetrazaindene.[2] Five grams of the chloro compound, 4.65 g. of magnesium oxide, 1.65 g. of 6% Pd-C, and 55 ml. of water were shaken for 1.5 hr. at 50 p.s.i. in a Parr hydrogenation apparatus (pressure drop, 7 lb.). The solution, after filtration, was taken to dryness and the residue recrystallized from benzene (Norit) to yield 2.3 g. (59%) of pure XIV, m.p. 177–178°.

(14) The authors are indebted to Mrs. M. K. Massad, of these Laboratories, for the preparation of this compound.

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

2-Amino-4-phenyl-1,3,3a,7-tetrazaindene (XIX). The crude product (11.7 g.) from the reaction run in xylene was extracted with 400 ml. of hot chlorobenzene. The extract, on cooling, yielded 3.8 g. of a mixture of XVIII, XIX, and XX, which, when extracted with *n*-butanol, left 0.2 g. of the highly insoluble, pale yellow 2-(2-benzoylethylideneamino)-4-phenyl-1,3,3a,7-tetrazaindene (XX), m.p. 282–283°; λ_{max} = 373 mμ, ε = 58,800 (solvent chloroform).

Anal. Calcd. for $C_{20}H_{15}N_5O$: C, 70.3; H, 4.4; N, 20.5. Found: C, 70.5; H, 4.4; N, 20.4.

A small amount (0.25 g.) of XIX was also isolated from the butanol extract, but the bulk of the material consisting essentially of a mixture of XVIII and XIX resisted separation. A second crop from the chlorobenzene extract consisted of 1.4 g. of nearly pure XIX which, after recrystallization from xylene, melted at 268.5–269° as slightly yellow platelets; λ_{max} = 339 mμ, ε = 15,700 (solvent chloroform).

2-Amino-6-phenyl-1,3,3a,7-tetrazaindene (XVIII). The crude product (12.2 g.) from the reaction run in glacial acetic acid was fractionally crystallized from *n*-butanol to give 0.6 g. of XX, 1 g. of XIX, and 3.1 g. of XVIII. The latter had m.p. 236.5°; λ_{max} = 311 mμ, ε = 10,500 (solvent chloroform).

Acid cleavage of 2-(2-benzoylethylideneamino)-4-phenyl-1,3,3a,7-tetrazaindene (XX). A small sample (0.1 g.) of XX in 50 ml. of 0.1*N* hydrochloric acid was heated under reflux for 48 hr. and the solution filtered. The filtrate was neutralized with dilute carbonate solution and cooled. Recrystallization of the resulting solid from xylene gave faintly yellow platelets, identical in melting point and ultraviolet spectra with XIX; the mixture melting point was not depressed.

6-Methyl-1,2,3,3a,7-pentazaindene (XII). (a.) *From 4,4-dimethoxy-2-butanone.* (1) The reaction in xylene required the addition of 0.15 volume of *N,N*-dimethylformamide to help solubilize the 5-aminotetrazole and allow the reaction to proceed. The bulk of the product separated on cooling the reaction mixture; the remainder was obtained by evaporation of the solvent and recrystallization from ethanol. (2) The reaction in acetic acid gave a good yield directly, which was enhanced by evaporation of the solvent and recrystallization from benzene.

(b.) *From 4-methoxy-3-buten-2-one.* In a manner similar to that described for the corresponding reaction in the tetraza series, a 72% yield of analytically pure material (m.p. 132.5–134°) was obtained after 3 days.

(c.) *From 2-hydrazino-4-methylpyrimidine.* A solution of 4.0 g. of the hydrazine[16] in 120 ml. of water was treated with 2.0 g. of sodium nitrite in 4 ml. of water, followed by 4 ml. of glacial acetic acid. After heating for 1.5 hr. at 90°, the solution was evaporated to dryness and extracted with benzene, from which 2.9 g. (68%) of slightly impure XII crystallized. Recrystallization produced material of m.p. 133–133.5°.

(d.) *From 6-methyl-4-oxo-1,2,3,3a,7-pentazaindene.* (1) *6-Methyl-4-oxo-1,2,3,3a,7-pentazaindene.* Ten grams of 2-hydrazino-4-hydroxy-6-methylpyrimidine[17] and 5 g. of sodium nitrite were dissolved in 500 ml. of hot water, and acidified with excess acetic acid. The mixture was allowed to cool slowly, and finally chilled. The solid, recrystallized from water, yielded pure white needles; 5.5 g. (51%); m.p. 258–260° dec.

Anal. Calcd. for $C_5H_5N_5O$: C, 39.7; H, 3.3; N, 46.4. Found: C, 39.8, 40.0; H, 3.6, 3.4; N, 46.9.

(2) *4-Chloro-6-methyl-1,2,3,3a,7-pentazaindene.* A mixture of the hydroxy compound (50 g.) and phosphoryl chloride (250 ml.) was heated under reflux for 1.2 hr. and evaporated to dryness at reduced pressure on the steam-bath. The partially crystallized residue was stirred briefly with ice water and extracted with several portions (900 ml. total) of chloroform. The chloroform solution was dried over anhydrous magnesium sulfate, evaporated to dryness, and the residue recrystallized from benzene, yielding 24.8 g. of pale yellow crystals; m.p. 106.5–107.5°. The aqueous slurry from the chloroform extraction was filtered, and the crystalline solid dried over calcium chloride in a vacuum desiccator to yield an additional 19 g. of crude product. Recrystallization from benzene resulted in a total yield of 39.3 g. (70%); m.p. 106.5–107.5°.

Anal. Calcd for $C_5H_4ClN_5$: C, 35.4; H, 2.4; N, 41.3. Found: C, 35.7; H, 2.5; N, 41.4.

(3) *6-Methyl-1,2,3,3a,7-pentazaindene.* By a procedure similar to that described for the tetraza analog, the chloro compound was reduced in very poor yield (apparently due largely to the sensitivity of the product to basic conditions) to XII, m.p. 132.5–133°.

The identity of the products of all five methods of synthesis was shown by mixture melting points and by comparisons of the infrared and ultraviolet spectra.

Reaction of 4-methoxy-3-buten-2-one (VI) *with p-nitrophenylhydrazine.* A solution of 2.2 g. of VI (10% excess) and 3.0 g. of *p*-nitrophenylhydrazine in 5 ml. of *N,N*-dimethylformamide was allowed to stand for 22 hr. and then filtered, yielding 1.45 g. of orange crystals of m.p. 155–180° (dec.). Recrystallization from 500 ml. of acetonitrile gave 0.7 g. of m.p. 151–187° (dec.), which was unchanged on further recrystallization.

Anal Calcd. for $C_{16}H_{16}N_6O_4$ (dihydrazone): C, 53.9; H, 4.5; N, 23.6. Found: C, 54.3; H, 4.6; N, 24.1.

Heating the DMF filtrate produced 0.4 g. of 3-methyl-1-*p*-nitrophenylpyrazole,[3] m.p. 165.5°. When 0.6 g. of the pure bis(*p*-nitrophenylhydrazone) was heated at 180–200° for 5 minutes and the resulting solid recrystallized from ethanol, two fractions were obtained: (1) 0.25 g. of pure 3-methyl-1-*p*-nitrophenylpyrazole, and (2) 0.22 g. of a mixture of the latter with *p*-nitrophenylhydrazine (shown by the infrared spectrum).

Acknowledgment. The authors are indebted to Dr. D. W. Stewart and Miss T. J. Davis for infrared and ultraviolet spectra, and to Mr. D. Heseltine for his interest and efforts to help elucidate the structures of some of the products.

ROCHESTER 4, N. Y.

(16) T. Matsukawa, S. Ban, K. Shirakawa, and M. Yoneda, *J. Pharm. Soc. Japan*, **73**, 159 (1953); *Chem. Abstr.*, **47**, 11185 (1953).

(17) F. Birr and W. Walther, *Ber.*, **86**, 1402 (1953).