[COMMUNICATION NO. 1998, FROM THE KODAK RESEARCH LABORATORIES]

Structure of Certain Polyazaindenes. V. Syntheses.

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Received December 8, 1959

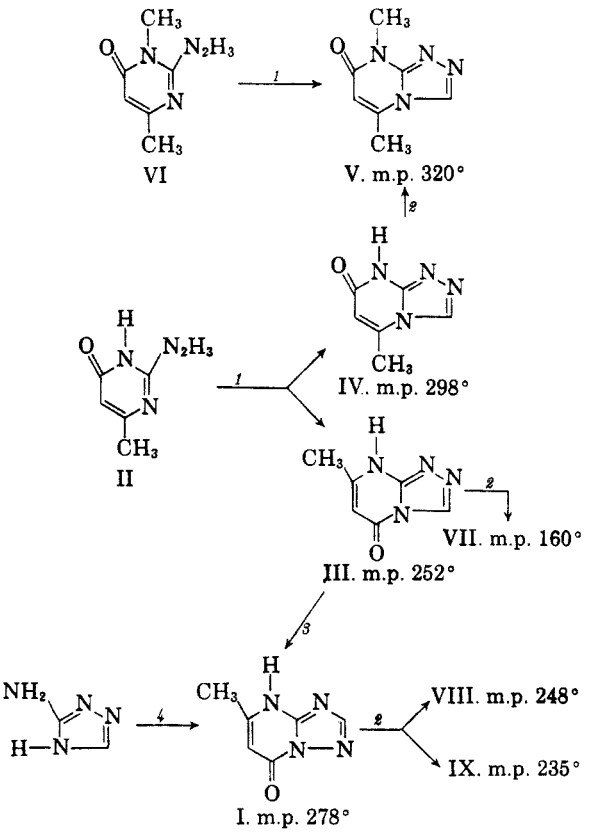
Syntheses of 6-methyl-4-oxo-1,3,3a,7-tetrazaindene, 4-methyl-6-oxo-1,2,3a,7-tetrazaindene, the methylation product of the latter, and a number of related substances are described. This chemical evidence furnishes independent corroboration of the structures deduced by other methods.

The reaction product of ethyl acetoacetate with 3-amino-1,2,4-triazole has previously been shown to be 6-methyl-4-oxo-1,3,3a,7-tetrazaindene[1b] on the basis of spectral evidence.[1b,2]

In view of the diversity of opinion which exists in this field,[3–7] it was deemed desirable to confirm this conclusion by a proof of structure of I based on chemical evidence. With this end in view, 2 - hydrazino - 4 - hydroxy - 6 - methylpyrimidine (II) was treated with ethyl orthoformate; both possible products, 6-methyl-4-oxo-1,2,3a,7-tetrazaindene (III) and 4-methyl-6-oxo-1,2,3a,7-tetrazaindene (IV), were formed. Methylation of IV gave 4,7 - dimethyl - 6 - oxo - 1,2,3a,7 - tetrazaindene (V), as proved by its identity with the substance obtained by the same cyclization of 1,4-dimethyl-2-hydrazino-6-pyrimidone (VI). The latter resulted from the action of hydrazine upon 1,4-dimethyl-2-methyl - 2 - methylmercapto - 6 - pyrimidone, a substance of known structure.[8] These reactions established the structures of IV and V. The second and only other product formed in the reaction must be III, which results from the alternate mode of cyclization. Methylation of III gives *x*,6-dimethyl-4-oxo-1,2,3a,7-tetrazaindene (VII), a substance quite different from the product obtained by ring closure of VI, indicating that III is not related to the 6-one series. It has been previously shown that III is rearranged to I by acid, a reaction which can readily be accounted for.[2]

Further evidence for these formulations was forthcoming from the synthesis and identification

CHART I



Reagents: *1*, ethyl orthoformate; *2*, methyl sulfate and alkali; *3*, hot formic acid; *4*, ethyl acetoacetate.

of three of the isomeric methylmercapto compounds. Treatment of the hydrazine II with carbon disulfide produced both possible products, 4-methyl-6-oxo-1,2,3a,7-tetrazaindene-3-thiol (X) and 6-methyl-4-oxo-1,2,3a,7-tetrazaindene-3-thiol (XI). The conversion of X to IV by oxidation with dilute nitric acid confirms the structure of X as a 6-one. Therefore, XI must be the 4-one, as indicated. Dethiolation of XI yields the expected 4-one III. Stepwise methylation of X gave the 4-methyl-3-methylmercapto-6-oxo-1,2,3a,7-tetrazaindene (XII) and 4,7-dimethyl-3-methylmercapto-6-oxo-1,2,3a,-7-tetrazaindene (XIII), respectively. This latter substance is also obtained by ring closure of VI with phenyl isothiocyanate to give 4,7-dimethyl-6-oxo-1,2,3a,7-tetrazaindene-3-thiol (XIV), followed by methylation. This sequence of reactions

(1a) At the Research Laboratories, Kodak Limited, Harrow, England.

(1b) Part I, 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).

(2) Part II, 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) E. J. Birr, *Z. wiss. Phot.*, **47**, 2927 (1952).

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

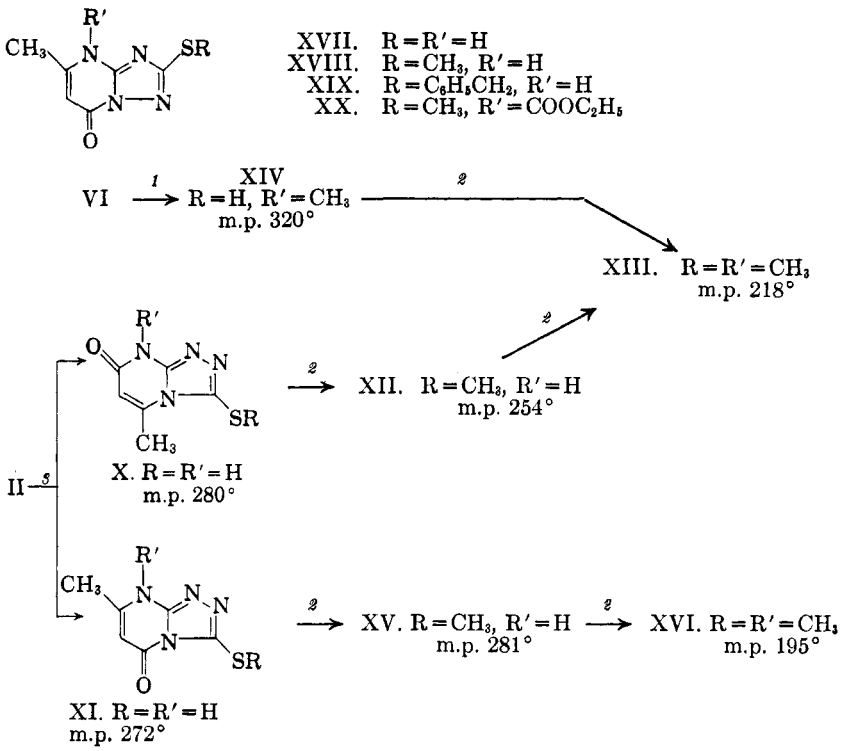
(5) J. D. Bower and F. P. Doyle, *J. Chem. Soc.*, 727 (1957).

(6) D. J. Fry and B. Whitear, Résumés des Communications. Tome II. Division de Chimie Organique. XVIe Congrès International de Chimie Pure and Appliquée, Paris, July 1957, p. 166.

(7) D. J. Fry, U. S. Patent 2,566,629 1951. [*Chem. Abstr.*, **46**, 1380 (1952)].

(8) H. L. Wheeler and D. F. McFarland, *Am. Chem. J.* **42**, 106 (1909).

CHART II



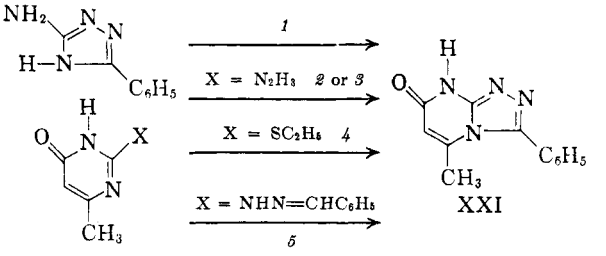
Reagents: *1*, phenyl isothiocyanate; *2*, methyl sulfate and alkali; *3*, carbon disulfide and pyridine.

establishes the structures of XI and XIII and confirms the structure of X. In a similar manner, methylation of XI gives 6-methyl-3-methylmercapto-4-oxo-1,2,3a,7-tetrazaindene (XV) and 6,7-dimethyl-3-methylmercapto-4-oxo-1,2,3a,7-tetrazaindene (XVI). The third isomer, 6-methyl-2-methylmercapto-4-oxo-1,3,3a,7-tetrazaindene (XVIII), is described in the literature.[7] Each of the derivatives, X, XI, and XVIII, has been dethiolated to the corresponding tetrazaindene. The preparation and dethiolation of the benzyl ether XIX is described in the experimental section. The dethiolation of XVIII proceeded more smoothly when the acidic hydrogen was acylated, yielding XX; the loss of the carbethoxyl group, owing to the alkali present in the catalyst preparation, was slower than the removal of the sulfur atom. The reported[7] preparation of XVII from amino mercaptotriazole could not be duplicated.

It is quite surprising to find that the five reactions outlined in chart III all lead to 4-methyl-3-phenyl-6-oxo-1,2,3a,7-tetrazaindene (XXI), since different products have been claimed previously.[5] The identity of these products was established by comparison of their infrared and ultraviolet absorption spectra. The structure of XXI is based solely on the similarity of its ultraviolet absorption spectrum to that of other known 6-ones.[1]

Change of the aminotriazole substituent from hydrogen, methyl, or methylmercapto to phenyl has altered the course of the reaction so that the product changes from a 4-oxo-1,3,3a,7-tetrazaindene to a 6-oxo-1,2,3a,7-tetrazaindene. Evidently the phenyl substituent has reduced the basicity of the two nitrogen atoms conjugated with it (N^2 and N^a), so that amide formation is faster than aminocrotonate formation. The resulting amide lacks the charge distribution of the aminocrotonate, since the acylated N^a is not basic. Subsequent reaction is that of the most basic nitrogen, N^4, in Michael addition to the enolic form of the ketoamide (compare ref. 2). It is surprising that the four alternate reactions shown in Chart III failed to yield any trace of compounds representing ring closure into position 3 of the pyrimidine ring. Like other 6-ones, XXI is stable to acid, so that but one aryl compound is available.

CHART III

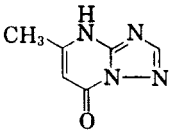


Reagents: *1*, ethyl acetoacetate; *2*, phenyl benzoate; *3*, ethyl orthobenzoate; *4*, benzhydrazide; *5*, lead tetraacetate.

The ultraviolet absorption data for the 6-methyl-4-oxo-1,3,3a,7-tetrazaindenes are collected in Table I. All show the same type of absorption. In particular, the ratio of absorption coefficients of band c

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF 6-METHYL-4-OXO-1,3,3A,7-TETRAZAINDENES

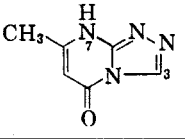


Substituent	M.P.	λ_a	λ_b	λ_c	λ_c/λ_b[f]
I None[a,b]	278	[e]	256 (6.4)[c]	278 (10.8)	1.7
VIII x-CH_3[d]	248	[e]	245 (4.8)	275 (11.5)	2.4
IX x-CH_3[d]	235	[e]	246 (7.9)	282 (18.4)	2.3
XVIII 2-SCH_3	284–286	229 (24.7)	267 (10.2)		0.41[g]
XX 7-$CO_2C_2H_5$	183	[e]	248 (4.5)	278 (9.3)	2.0
XXII 5-CH_3[b]	305	[e]	248 (4.3)	289 (10.5)	2.4
XXXII 2-CH_3[b]	310	210 (23.5)	238 (2.8)	272 (9.5)	3.4
XXXIII 2-SCH_3-7-CH_3	160–170	231 (22.0)	270 (9.8)		0.45[g]
XXXV 2-SCH_3-7-$CO_2C_2H_5$	191	228 (25.0)	259 (9.4)	273 (9.0)	

[a] In neutral solution this compound shows a single peak 272 (9.9); a trace of base yields the spectrum shown. [b] The syntheses of these substances have been reported in previous papers.[1,2,10] [c] All ϵ values are to be multiplied by 10^3; solvent is methanol; wave lengths in mμ. [d] VIII and IX are the products obtained by methylation of I. [e] Curves not run to shorter wave lengths. [f] Ratio of ϵ values. [g] Ratio ϵ of band b to band a.

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF 6-METHYL-4-OXO-1,2,3A,7-TETRAZAINDENES



Substituent	M.P.	λ_a	λ_b	λ_c	λ_c/λ_b[b]
III None	252	210 (17.7)	246 (4.8)	294 (6.8)	1.4
VII x-CH_3[a]	160		245 (5.0)	303 (12.7)	2.54
XI 3-SH	270–272	245 (12.0)	284 (8.3)	325 (7.5)	0.90
XV 3-SCH_3	281–282	231 (14.2)	260 (7.0)	309 (7.1)	1.0
XVI 3-SCH_3-7-CH_3	195	235 (8.0)	263 (9.0)	314 (10.4)	1.1

[a] Obtained by methylation of III. [b] Ratio of ϵ values.

to band b varies between 1.5 to 3.4, in line with previous observations of the spectra of related 4-one type compounds.[1] It is interesting to note that I gives two monomethylation products, VIII and IX, which differ greatly in solubility, and considerably in melting point and ultraviolet spectra; yet the absorption properties fall within the limits deduced as proper for this structure.[1] Negative Zeisel determinations indicated lack of *O*-methylation,[9] and the C-methyl product, 5,6-dimethyl-4-oxo-1,3,3a,7-tetrazaindene (XXII),[3] also differed from both VIII and IX.

Table II shows that the 4-oxo-1,2,3a,7-tetrazaindenes as a class absorb at longer wave lengths than the 4-oxo-1,3,3a,7-tetrazaindene series and have a somewhat lower $\lambda c/\lambda b$ ratio. The general shape of the curves, however, is similar to those in Table I.

A pronounced change occurs in the character of the ultraviolet absorption spectra of the 6-oxo-1,2,3a,7-tetrazaindenes, compared to those of the 4-oxo compounds, as is evidenced by the data in Table III. This series is characterized by a single, high-intensity band, with inflections occurring at about 250 and 300 mμ. Only in the case of IV and X are these inflections developed into real bands.

It may be well to emphasize again the need for obtaining *all* physical data in comparing and determining identity of these polyazaindenes. For instance, melting points and mixed melting points by themselves are inadequate and may even be misleading. The infrared *and* ultraviolet absorption spectra are of inestimable value. The numerous erroneous conclusions in the literature are undoubtedly drawn from insufficient data.

EXPERIMENTAL

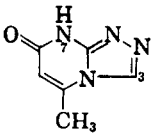
4-Methyl-6-oxo-1,2,3a,7-tetrazaindene (IV). *By oxidation of X.* Two g. of X was added to dilute nitric acid (10 ml. of nitric acid (d = 1.42) made up to 25 ml. with water). A vigorous reaction ensued, with the evolution of oxides of nitrogen. The clear, yellow solution was poured into water,

(9) The *O*-methyl compound could not be obtained from 4-chloro-6-methyl-1,3,3a,7-tetrazaindene[2] and sodium methoxide in carefully dried methanol, only I being obtained.

(10) Part III, C. F. H. Allen, H. R. Beilfuss, D. M. Burness, G. A. Reynolds, J. F. Tinker, and J. A. VanAllan, *J. Org. Chem.*, **24**, 793 (1959).

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA OF 4-METHYL-6-OXO-1,2,3A,7-TETRAZAINDENES



Substituent	M.P.	λ_a	λ_b	λ_c	λ_c/λ_b
IV None	298	210 (22.7)	248 (7.0)		
X 3-SH	280	229 (10.7)	258 (12.8)	315 (3.7)	0.29
XII 3-SCH_3	254	229 (22.4)		~300 (1.2)[a]	
XIII 3-SCH_3-7-CH_3	218	229 (19.4)		~300 (1.5)[a]	
XXI 3-C_6H_5	>330	242 (26.7)	~264 (18.4)[a]		
XXXIV x-CH_3-3-C_6H_5[b]	315–320	234 (14.5)		~282 (4.8)[a]	

[a] ~ denotes shoulder. [b] Obtained by methylation of XXI.

made alkaline with sodium bicarbonate, and the solid collected; this gave 1.2 g. of IV, m.p. 298°, after crystallization from butanol.

Anal. Calcd. for $C_6H_6N_4O$: C, 48.0; H, 4.0. Found: C, 48.0; H, 4.2.

Its identity with the product obtained by the ring closure of II with ethyl orthoformate was confirmed by infrared and ultraviolet spectral analysis.

4,7-Dimethyl-6-oxo-1,2,3a,7-tetrazaindene (V). (a) *By methylation of* IV. A mixture of 0.6 g. of IV, 10 ml. of water, 0.2 g. of sodium hydroxide, and 0.3 ml. of dimethyl sulfate was allowed to stand for 2 days. The product precipitated and was crystallized from water, giving 0.5 g. of V, m.p. 320°.

(b) *By ring closure of* VI. A solution of 0.6 g. of VI in 5 ml. of formic acid was refluxed for 2 hr. The formic acid was evaporated and the residue crystallized from water to give V, m.p. 320°.

Anal. Calcd. for $C_7H_8N_4O$: C, 51.2; H, 4.9; N, 34.0. Found: C, 51.2; H, 5.0; N, 34.1.

(c) A solution of 1.2 g. of VI in 10 ml. of ethyl orthoformate was refluxed for 3 hr., after which the solution was evaporated to dryness and the residue twice recrystallized from water to give colorless crystals, m.p. 320°.

Anal. Calcd. for $C_7H_8N_4O$: C, 51.2; H, 4.9; N, 34.0. Found: C, 51.4; H, 4.9; N, 33.5.

x,6-Dimethyl-4-oxo-1,2,3a,7-tetrazaindene (VII). A mixture of 4.0 g. of III, 35 ml. of water, and 1.75 g. of sodium hydroxide was treated with 3.4 g. (2.5 ml.) of dimethyl sulfate and allowed to stand 4 days in an open beaker. The precipitate was filtered off and crystallized from ligroin (b.p. 90–100°) to give VII, long needles, m.p. 160°. The yield was 2.1 g.

Anal. Calcd. for $C_7H_8N_4O$: C, 51.2; H, 4.9; N, 34.0. Found: C, 51.4; H, 5.0; N, 33.8.

2-Hydrazino-1,4-dimethyl-6-pyrimidone (VI).[11] A solution of 12 g. of 1,4-dimethyl-2-methylmercapto-6-pyrimidone[3] and an excess of 95% hydrazine (6 ml.) in 90 ml. of butanol was refluxed for 5 hr. The mixture was chilled overnight and filtered. The crude product (7.7 g.), m.p. 196–198.5°, after one crystallization from alcohol, gave pure VI, m.p. 198°.

Anal. Calcd. for $C_6H_{10}N_4O$: N, 36.3. Found: N, 36.5.

Isomeric x,6-dimethyl-4-oxo-1,3,3a,7-tetrazaindenes (VIII) and (IX). To 15 g. of the sodium salt of I in 25 ml. of water was added 12.9 g. (10 ml.) of dimethyl sulfate; the solution became quite hot. After the latter had stood for 1 week, about 4.0 g. was collected by filtration, m.p. 237–240°; it was recrystallized from dimethylformamide and gave VIII, plates, m.p. 246–248°. The original filtrate was treated with sodium carbonate and evaporated to dryness. The residue was extracted with hot dimethylformamide and filtered. On cooling, the white crystals which separated were collected and crystallized from butanol to give IX (1.5 g.), m.p. 234–235°. This isomer is very soluble in water and soluble in alcohol.

Anal. Calcd. for $C_7H_8N_4O$: C, 51.2; H, 4.9; N, 34.0. Found: (VIII), C, 51.2; H, 4.9; N, 34 1; (IX), C, 51.2; H, 5.2; N, 34.2.

6-Methyl-2-methylmercapto-4-oxo-1,3,3a,7-tetrazaindene (XVIII). A mixture of 100 g. (0.67 mole) of 2-amino-5-methylmercapto-1,2,4-triazole, 160 g. (1.2 moles) of ethyl acetoacetate, and 500 ml. of acetic acid was refluxed for 5 hr. and allowed to stand overnight. The solid was collected and recrystallized from water to yield 104 g. of product, melting at 285–286°.

4-Methyl-6-oxo-1,2,3a,7-tetrazaindene-3-thiol (X) and *6-methyl-4-oxo-1,2,3a,7-tetrazaindene-3-thiol* (XI) from II. The reaction was carried out using sodium hydroxide, or trimethylamine, or sodium hydroxide and pyridine with essentially the same results.

To a solution of 28 g. of II in 80 ml. of water and 8 g. of sodium hydroxide was added 140 ml. of pyridine, followed by 15.2 g. (12 ml.) of carbon bisulfide. The mixture was stirred for 15 min. and then heated on the steam bath for 1.5 hr. The solution was evaporated to dryness *in vacuo*, the residue dissolved in water, the solution acidified with hydrochloric acid, and the solid collected. The solid was extracted with 2 l. of water, filtered hot, and the filtrate cooled. The insoluble material (11.5 g.) was X, m.p. 277–279°, which can be recrystallized from a very large amount of water (m.p. 280°). The solid that separated from the filtrate on cooling was XI, which, after another recrystallization from water, melted at 270–272°. The filtrates were concentrated and cooled to yield more XI (total yield, 7.8 g.).

Anal. Calcd. for $C_6H_6N_4OS$: C, 39.5; H, 3.3; N, 30.8. Found: (XI) C, 39.4; H, 3.6; N, 30.8; (X) C, 39.2; H, 3.4; N, 31.0.

6-Methyl-3-methylmercapto-4-oxo-1,2,3a,7-tetrazaindene (XV). To a solution of 7.8 g. of XI in 200 ml. of water and 2.8 g. of sodium hydroxide, was added 5.4 g. of dimethyl sulfate, with stirring. After it had been stirred 0.5 hr., the solution was acidified with concentrated hydrochloric acid, cooled in the refrigerator, and the solid collected and recrystallized from water to yield 7.5 g. of XV, m.p. 280–281°.

Anal. Calcd. for $C_7H_8N_4OS$ C, 42.8; H, 4.1; N, 28.6. Found C, 43.1; H, 4.0; N, 28.5.

4-Methyl-3-methylmercapto-6-oxo-1,2,3a,7-tetrazaindene (XII). To a solution of 7 g. of X in 50 ml. of water and 1.6 g. of sodium hydroxide was added 3.6 ml. of dimethyl sulfate. After it had been stirred 15 min., the solution was acidified with concentrated hydrochloric acid and the solid collected (m.p. 233–265°). The solid was extracted with 200 ml. of boiling water. The insoluble material and the material that separated from the filtrate were the starting material. The filtrates from the reaction mixture and the recrystalli-

(11) We are indebted to Miss J. Fournier, for the preparation of the substances VI and VIII.

zation were combined, concentrated to a small volume, and cooled. The solid that separated was recrystallized from a little water and then ethanol to yield 2 g. of XII, m.p. 254°.

Anal. Calcd. for $C_7H_8N_4OS$: C, 42.8; H, 4.1; N, 28.6. Found: C, 42.8; H, 4.1; N, 28.7.

4,7-Dimethyl-6-oxo-1,2,3a,7-tetrazaindene-3-thiol (XIV). A mixture of 3.1 g. (0.033 mole) of VI and 3.0 g. (1.82 ml.) of phenyl isothiocyanate in 50 ml. of methanol was refluxed for 1 hr. The precipitated product was collected by filtration to give 3.0 g. of XIV, m.p. 318–320°, which was cystallized from ethoxyethanol to give pure XIV, m.p. 320°.

Anal. Calcd. for $C_7H_8N_4OS$: C, 42.8; H, 4.1; N, 28.6. Found: C, 42.7; H, 4.0; N, 28.8.

4,7-Dimethyl-3-methylmercapto-6-oxo-1,2,3a,7-tetrazaindene (XIII). (a) *From* XIV. A mixture of 1.7 g. of XIV, 15 ml. of water, and 2 ml. of 50% sodium hydroxide solution was treated, dropwise, with 1.5 ml. of dimethyl sulfate. The reaction mixture solidified on shaking, and after it had stood for 2 hr., the product was filtered off and crystallized from ethanol to give 1.1 g. of fine, hairlike crystals, m.p. 218°.

Anal. Calcd. for $C_8H_{10}N_4OS$: C, 45.7; H, 4.8. Found: C, 45.6; H, 4.7.

(b) *From* XII. To a solution of 5.5 g. of XII and 1.5 g. of sodium hydroxide in 50 ml. of water was added 3 ml. of dimethyl sulfate, in portions, along with sufficient sodium hydroxide to keep the solution strongly basic. After the solution has been stirred for 0.5 hr., it was acidified, cooled in the refrigerator, and the solid collected and recrystallized from ethanol to yield 2.2 g. of XIII, m.p. 218–218.5°.

Anal. Calcd. for $C_8H_{10}N_4OS$: C, 45.7; H. 4.8; N, 26.6. Found: C, 45.8; H, 4.9; N, 26.6.

6,7-Dimethyl-3-methylmercapto-4-oxo-1,2,3a,7-tetrazaindene (XVI). To a solution of 4 g. of XV and 1 g. of sodium hydroxide in 100 ml. of water was added 2 ml. of dimethyl sulfate. After it had been stirred for 1 hr., the solid was collected and washed with water. Recrystallization from ethanol gave 2 g. of XVI, m.p. 195–196°.

Anal. Calcd. for $C_8H_{10}N_4OS$: C, 45.7; H, 4.8; N, 26.6. Found: C, 45.6; H, 5.1; N, 26.8.

4-Methyl-3-phenyl-6-oxo-1,2,3a,7-tetrazaindene (XXI). This substance was obtained by five different procedures. The identity of the products was shown by comparison of absorption curves. All but one were analyzed; the product from Method D gave the following results:

Anal. Calcd. for $C_{12}H_{10}N_4O$: C, 63.6; H, 4.4; N, 24.8. Found: C, 63.7; H, 4.4; N, 24.9.

Method A. A mixture of 5 g. of 2-hydrazino-4-hydroxy-6-methylpyrimidine and 25 g. of phenyl benzoate was refluxed for 3 hr. The mixture was steam distilled, the solid residue collected, washed with ethanol, and recrystallized from aqueous dimethylformamide three times, to yield 2.6 g. of XXI, m.p. >330°.

Method B. A mixture of 2.2 g. of 3-amino-5-phenyl-1,2,4-triazole, 2 ml. of ethyl acetoacetate, and 10 ml. of acetic acid was refluxed 3 hr., cooled, and the solid collected. Recrystallization from ethoxyethanol gave 2.5 g. of XXI, m.p. >325°.

Method C. A mixture of 7 g. of 2-hydrazino-4-hydroxy-6-methylpyrimidine and 100 ml. of ethyl orthobenzoate was heated at 190–200° for 12 hr., during which time 8.5 ml. of ethanol was collected (theoretical = 8 ml.). The dark solution was cooled and the solid collected and recrystallized from ethoxyethanol to yield XXI. Attempts to work up the reaction mixture in order to obtain another isomer were unsuccessful.

Method D. A mixture of 4.6 g. of 2-benzalhydrazino-6-methyl-4-pyrimidone and 9 g. of lead tetraacetate in 150 ml. of acetic acid was refluxed for 1 hr., and the solution concentrated and diluted with water. The solid was collected and recrystallized from methanol to yield 3.5 g. of XXI, m.p. >325°.

Method E. (a) *2-β-Benzhydrazido-4-hydroxy-6-methylpyrimidine.* A mixture of 34 g. of 2-ethylmercapto-4-hydroxypyrimidine, 27 g. of benzhydrazide, and 500 ml. of ethanol was refluxed 24 hr., concentrated to about 100 ml., cooled, and filtered. The white solid, sintered at about 122°, resolidified and remelted at 270–271°.

(b) *4-Methyl-3-phenyl-6-oxo-1,2,3a,7-tetrazaindene* (XXI). Ten g. of the hydrazide and 25 g. of phenol were heated on a steam cone for 1.5 hr., then refluxed for 4 hr. The phenol was steam distilled; the solid residue was digested with 800 ml. of water and recrystallized from dimethylformamide. One and seven-tenths g. of XXI was obtained.

Raney nickel dethiolation of the methylmercapto derivative. A mixture of 2 g. of the methylmercapto tetrazaindene (XVIII), 2 g. of potassium carbonate, 2 teaspoons of commercial Raney nickel, and 500 ml. of water was refluxed 2 hr., with stirring. The mixture was filtered hot, the Raney nickel washed thoroughly with hot water, the filtrate acidified with nitric acid, and the tetrazaindene precipitated by the addition of silver nitrate. The precipitated silver salt was washed with water until neutral, suspended in 200 ml. of boiling water, and hydrogen sulfide was passed through the suspension until no more silver sulfide separated. The hot mixture was filtered, the filtrate concentrated to 25 ml., treated with Norit, filtered, and cooled to yield 0.9 g. of material melting at 278–279° that proved to be identical with 6-methyl-4-oxo-1,3,3a,7-tetrazaindene (I).

Raney nickel dethiolation of the 3-thiol. In a similar manner, 0.7 g. of 6-methyl-4-oxo-1,3,3a,7-tetrazaindene (I) was obtained from 2 g. of 6-methyl-4-oxo-1,3,3a,7-tetrazindene-2-thiol (XVII).

Oxidative dethiolation of 3-mercapto-6-methyl-4-oxo-1,2,3a,7-tetrazaindene (XI). To a solution of 10 ml. of concentrated nitric acid and 15 ml. of water was added 2 g. of the mercapto compound XI. After the oxides of nitrogen were no longer evolved and the solid was completely dissolved, the solution was diluted with 275 ml. of water and silver nitrate added. The silver salt was collected, washed free of acid with water, suspended in 250 ml. of boiling water, and hydrogen sulfide was passed through the suspension until no more silver sulfide separated. The mixture was filtered and the filtrate treated with Norit, filtered, concentrated to 25 ml., and chilled, yielding 0.2 g. of solid, m.p. 248–250°, which proved to be identical with a sample of 6-methyl-4-oxo-1,2,3a,7-tetrazaindene (III).

Attempted oxidative dethiolation of 6-methyl-4-oxo-1,3,3a,7-tetrazaindene-2-thiol. Two g. of the mercapto compound XVII was added to 10 ml. of concentrated nitric acid and 15 ml. of water. The mixture was stirred at room temperature until no more brown fumes were evolved, and the solid was collected and washed with water. The solid was digested with 250 ml. of boiling water and dried to yield 1.3 g. of material, m.p. above 330°, which was considered to be the disulfide.

Anal. Calcd. for $C_{12}H_{10}N_8O_2S_2$: C, 38.9; H, 2.2; N, 31.0. Found: C, 39.3; H, 2.5; N, 31.1.

Dithiobiurea dibenzyl ether. Seventy-five g. (0.5 mole) of dithiobiurea was dissolved in a solution of 48 g. of sodium hydroxide in 800 ml. of water and 185 g. (1.1 moles) of benzyl bromide was slowly added, with stirring, the temperature being kept at about 15° by external cooling. The mixture was stirred at room temperature overnight and the solid was collected on a Büchner funnel and then recrystallized from a mixture of benzene and ligroin (b.p. 90–100°). Yield, 74 g. of the product as white plates, m.p. 88–89°.

Anal. Calcd. for $C_{16}H_{18}N_4S_2$: C, 58.2; H, 5.5; N, 17.0. Found: C, 58.5; H, 5.6; N, 17.1.

3-Amino-5-benzylmercapto-1,2,4-triazole. A mixture of 72 g. (0.22 mole) of the dibenzyl compound and 400 ml. of 1*N* sodium hydroxide solution was heated on the steam bath with stirring for 8 hr. The mixture was filtered and the cooled filtrate was neutralized with hydrochloric acid. An oil separated which solidified on chilling. The solid was collected, washed with water, and recrystallized from a mixture of benzene and alcohol. Yield, 20 g. of product, m.p. 105–106°.

Anal. Calcd. for $C_9H_{10}N_4S$: C, 52.4; H, 4.9; N, 27.2. Found: C, 52.6; H, 5.0; N, 26.9.

2-Benzylmercapto-6-methyl-4-oxo-1,3,3a,7-tetrazaindene (XIX). A mixture of 20 g. of the triazole and 15 ml. of acetoacetic ester in 150 ml. of acetic acid was refluxed 5 hr. and then cooled. The solid was collected and recrystallized from ethanol. Yield, 15 g. of product, m.p. 252°.

Anal. Calcd. for $C_{13}H_{12}N_4OS$: C, 57.3; H, 4.4; N, 20.6. Found: C, 57.4; H, 4.5; N, 19.9.

6-Methyl-4-oxo-1,3,3a,7-tetrazaindene-2-thiol (XVII). To a solution of 6.5 g. of XIX in 200 ml. of liquid ammonia was added small pieces of sodium until the blue color persisted. The ammonia was allowed to evaporate at room temperature and the residue was dissolved in water, filtered, and the filtrate acidified with hydrochloric acid and chilled. The solid was collected and recrystallized from water. Yield, 4.3 g. of product, m.p. 287–288°.

Anal. Calcd. for $C_6H_6N_4OS$: C, 39.5; H, 3.3; N, 30.8. Found: C, 39.6; H, 3.3; N, 30.7.

A run in which acetic acid was used in place of hydrochloric acid for the neutralization yielded 3.5 g. of the sodium salt of the mercaptotetrazaindene, m.p. 310°, with decomposition.

Anal. Calcd. for $C_6H_5N_4OSNa$: C, 35.1; H, 2.9; N, 27.3. Found: C, 34.8; H, 2.7; N, 27.1.

7-Carbethoxy-6-methyl-2-methylmercapto-4-oxo-1,3,3a,7-tetrazaindene (XX). A solution of 5 g. of 6-methyl-2-methylmercapto-4-oxo-1,3,3a,7-tetrazaindene (XVIII) in 1 g. of sodium hydroxide and 50 ml. of water was evaporated to dryness *in vacuo* and to the residue was added 5 g. of ethyl chloroformate and 100 ml. of benzene. The mixture was stirred at room temperature for 24 hr., heated to boiling, filtered, and the filtrate chilled. The solid was collected and recrystallized from benzene. Yield, 2.5 g. of product, m.p. 190–191°.

Anal. Calcd. for $C_{10}H_{12}N_4O_3S$: C, 44.8; H, 4.5; N, 20.9. Found: C, 44.6; H, 4.4; N, 21.2.

7-Carbethoxy-6-methyl-4-oxo-1,3,3a,7-tetrazaindene (XXXV) A mixture of 5 g. of the sodium salt of 6-methyl-4-oxo-1,3,3a,-7-tetrazaindene (I), 10 ml. of ethyl chloroformate and 250 ml. of benzene was stirred 24 hr. at room temperature. The mixture was worked up as above to yield 2 g. of product, m.p. 182–183°, with decomposition.

Anal. Calcd. for $C_9H_{10}N_4O_3$: C, 48.6; H, 4.5; N, 25.2. Found: C, 48.5; H, 4.5; N, 24.8.

Dethiolation of 7-carbethoxy-6-methyl-2-methylmercapto-1,3,3a,7-tetrazaindene. A mixture of 2 g. of the tetrazindene XX, 2 teaspoons of Raney nickel, and 500 ml. of absolute ethanol was refluxed 4 hr. The mixture was filtered hot and the Raney nickel extracted with 500 ml. of hot alcohol. The combined alcohol solutions were evaporated to 25 ml. and chilled. Yield, 0.4 g. of 6-methyl-4-oxo-1,3,3a,7-tetrazaindene, (I).

Acknowledgment. We are indebted to Dr. D. W. Stewart and Miss T. J. Davis, Rochester, and Mr. B. S. Goode, Harrow, of these Laboratories, for the absorption spectra.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

Pyridine Analogs of *p*-Terphenyl and *p*-Quaterphenyl

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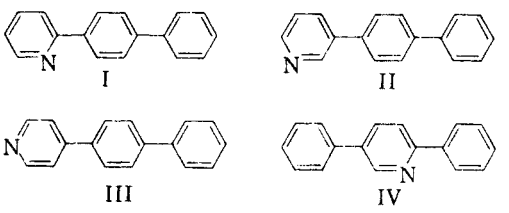
Received September 29, 1959

Four pyridine analogs of *p*-terphenyl and two of *p*-quaterphenyl have been synthesized for evaluation as scintillation solutes.

p-Terphenyl and its derivatives have been extensively studied as scintillation solutes.[1] A limitation on the usefulness of polyphenyls themselves for this purpose is their low solubility in toluene, the commonly used solvent. Although pyridine analogs of the polyphenyls offer a class of possible alternatives for use as scintillators, only a few such compounds are known. Of the twenty-five possible pyridine analogs of *p*-terphenyl, only four are reported in the literature. 4-(2-Pyridyl)biphenyl (I), 4-(3-pyridyl)biphenyl (II), and 4-(4-pyridyl)-biphenyl (III) have been synthesized by the reaction of the (*N*-nitrosoacetamidophenyl)pyridines with benzene.[2] The 2- and 4-isomers have also been prepared by the reaction of *p*-phenylbenzenediazonium chloride with pyridine.[2] An unseparated mixture of the six *p*-dipyridylbenzenes has been prepared[3] by the reaction of a mixture of diazotized



p-aminophenylpyridines with pyridine. None of the 2,5-diphenylpyridylpyridines or 2,5-dipyridylpyridines is known and no pyridine analogs of *p*-quaterphenyl are recorded. We wish to report at this time the results of a study of the synthesis and scintillation properties of some compounds of this type.

We have recently reported[4] the synthesis of 2,5-diphenylpyridine (IV), m.p. 174°, by the reaction of phenyllithium with 3-phenylpyridine. The structure of the product was proved by an alterna-

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