over a 30-min. period. The mixture was diluted with hexane and the organic layer separated. Fractional distillation yielded 8.5 g. (18%) of pentamethylchlorodisilane, 25.3 g. (45%) of unchanged octamethyltrisilane, and 26.2 g. (26%) of a clear liquid, b.p. 103-106° (36 mm.). The titratable halogen in this latter fraction indicated it to be hexamethyldichlorotrisilane (% chlorine 28.9; found 27.8). None of the expected heptamethylchlorotrisilane was isolated.

DEARBORN, MICH.

[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

Mercuration of Some Derivatives of 1,2,3,6-Tetrahydropyridazine

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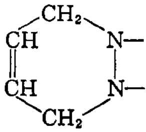
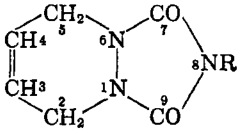
The preparation of some mercurated 1,6,8-triazabicyclo[4.3.0]nonanes (III), 1,6-diazabicyclo[4.4.0]decanes (VIII), and a mercurated hexahydropyridazine is described. The structure of III (X = OH, R = H, R′ = CH_3) is discussed.

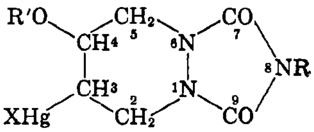
The formation of 1,2-dicarbamyl-1,2,3,6-tetrahydropyridazine (I) and its pyrolytic conversion to 1,6,8-triazabicyclo[4.3.0]-3-nonene-7,9-dione (II, R = H) have been reported.[1] Also, the preparation of a series of highly active diuretic agents of general formula III from II has been described, but without comment.[2] Some of the phenomena noted in the production of these mercurated compounds appear worth reporting.



I



II



III

The conditions for alkoxymercuration of II were standard—*i.e.*, mixing a hot alcoholic solution of II with a hot alcoholic solution of mercuric acetate followed by addition of a few drops of concentrated nitric acid as a catalyst. In the mercuration reaction involving II where R was H, if the reaction mixture were allowed to cool before addition of the nitric acid catalyst, an intermediate separated which contained loosely bound mercury[3] and gave analytical values corresponding to the simple salt II where R was $HgOCOCH_3$. Addition of nitric acid to a methanolic suspension of this salt resulted in its rapid dissolution and formation of the 3-mercurated derivative discussed below.

Compound II with R other than H regularly furnished compound III with X = $OCOCH_3$.[2] These products showed no tendency toward hydrolysis in the presence of water to give a hydroxymercuri derivative. In the reaction above involving II where R was H (the solvent was methanol), the product invariably had the composition $C_7H_{11}HgN_3O_4$,[2] which corresponded to III with X = OH, R = H, and R′ = CH_3 or to a hydrated inner salt form, either monomeric or polymeric.

This product was amorphous, extremely insoluble in water, soluble in dilute sodium hydroxide solution, and recoverable unchanged by addition of carbon dioxide to this alkaline solution. In spite of its amorphous character the product invariably held one molecule of loosely bound water.[4]

Occasionally, when an alkaline solution of this mercury compound had stood for fifteen to thirty minutes, the development of cloudiness and subsequent precipitation of a crystalline solid was observed. The formation of this crystalline product was more rapid and complete in dilute ammonium hydroxide. The infrared spectra of the amorphous and crystalline materials were quite similar and the analytical values on the crystalline material (including water determination) indicated no change in chemical composition. Indeed, when the amorphous material was triturated in warm water with seeds of the crystalline material, it slowly crystallized and its infrared spectrum was then identical with that of material which had crystallized from alkaline solution.

This mercurated product showed $\epsilon_{223\ m\mu(sh)}^{C_2H_5OH}$ 6700 which suggested an enolized form of the imide group. The unmercurated starting material II (R = H) showed $\epsilon_{219\ m\mu(sh)}^{C_2H_5OH}$ 5600. Addition of sodium hydroxide to these samples produced shifts to ϵ_{227} mμ (sh) 6200 and ϵ_{223} mμ (sh) 5000 respectively. The general enolized character of the urazole ring system seems probable, *cf.*, structure IV.

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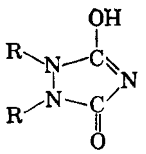
(1) W. T. Hunter, U. S. Pat. 2,813,867, Nov. 19, 1957; R. L. Clarke, U. S. Pat. 2,813,866, Nov. 19, 1957.

(2) R. L. Clarke and F. W. Gubitz, U. S. Pat. 2,813,865, Nov. 19, 1957.

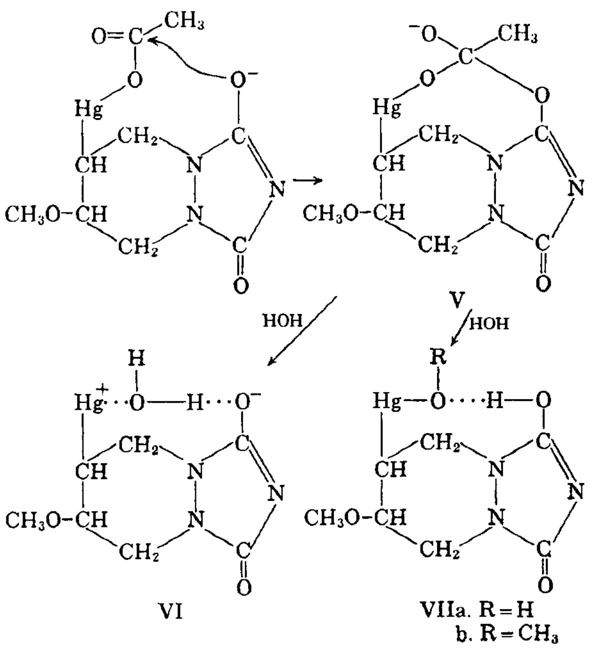
(3) Addition of dilute sodium hydroxide to an aqueous suspension of this material produced a precipitate of mercuric oxide whereas compounds of type III did not.

(4) The normal Karl-Fischer procedure for determination of water in this material gave anomalous results, but when the sample was shaken with methanol for 3 hr., the insoluble material removed by filtration, and the water which had been absorbed by the methanol was titrated, the presence of one equivalent of water could be demonstrated.



IV

The structure of this product resulting from methoxymercuration of II (R = H) is not firmly established. There is certainly a clear implication that failure to isolate the 4-acetoxymercuri product is attributable to involvement of an enolate anion from the heterocyclic ring. In sodium hydroxide solution, acetoxymercuri compounds are generally converted to the corresponding hydroxymercuri compounds—*i.e.*, from anionic attack by hydroxyl with replacement of the acetoxyl groups. In the present case, if the anion produced through enolization, acting as a nucleophile, reacted as shown in the following equation, the intermediate form, V, could evolve acetate ion and form a zwitterion, VI, which might well be hydrated as shown.



Concerning the marked insolubility of this amorphous product in water, the water-insolubility of mercuri inner salts has been widely reported,[5] and Rowland, Perry, Foreman, and Friedman[6] have described a somewhat analogous case of presumed zwitterion formation (monomeric or polymeric) with 3-hydroxymercuri-2-methoxypropylurea. The small change in ultraviolet absorption observed upon addition of alkali to the mercurial or its precursor, II, furnishes no information for or against the presence of a charged species as found in VI.

The charged atoms of the zwitterion VI can approach each other relatively closely if the mercury atom assumes the axial conformation[7] and the six-membered ring assumes a boat conformation. A discussion of the presence of a zwitterion form in anhydro mercurated carboxylic acids is given by Whitehead.[8]

A second possible structure is that which would result from simple hydrolysis of V and is shown in formula VIIa. Recovery of an equivalent of water from this structure by methanol treatment could be explained by conversion of VIIa to a methoxymercuri compound, VIIb. The infrared spectrum of the solid which had been treated with methanol to remove water was very diffuse and indicated that the solid was a complex mixture. This fact was substantiated by inconsistent analytical values for carbon, hydrogen, mercury, and nitrogen. A methoxyl analysis was of questionable value, as it gave low results for this series of compounds. The value found for VIIa was 6.5% (calcd. 7.7%). The methoxyl value found for the dehydrated material was 14.7% (calcd. for VIIb, 15.1%). Thus there was apparently an increased methoxyl content in the product from dehydration by methanol. This methoxyl content could also be explained by solvation of the structure VI with methanol instead of water.

The possibility that the amorphous material under discussion is a polymer is not precluded. Further, a polymer could conceivably have formed by chain-reaction mercuration involving the mercuriacetate salt of II described above.

The crystalline mercurated product which separated upon dissolution of the amorphous material in dilute sodium hydroxide or ammonium hydroxide could well have formed by partial hydrolysis of the salt form present in alkaline solution with an accompanying shift in equilibrium promoted by the great insolubility of the crystalline material. Thus, there was considerably more complete precipitation (80%) from ammonium hydroxide solution (weak base) than from sodium hydroxide solution (17%). There is the possibility that the crystalline precipitate could also be a dimer or polymer.

Attempts to prepare the acetoxymercuri compound (III, R = H, R′ = CH_3, X = $OCOCH_3$) by other means involved (1) dissolving VI in glacial acetic acid and precipitation of the mercurial with ether and (2) treatment of the chloromercuri derivative described below (III, R = H, R′ = CH_3, X = Cl) with silver acetate. Only compound VI (or structure VIIa) was isolated. Apparently under all conditions reported here the enolate anion was able to displace acetoxyl and regenerate VI (or VIIa). However, as is described below, a halo-

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(5) *Cf.*, *Organic Compounds of Mercury*, F. C. Whitmore, Chemical Catalog Co., Inc., New York, N. Y., 1921, pp. 49, 74, 311, 313.

(6) R. L. Rowland, W. L. Perry, E. L. Foreman, and H. L. Friedman, *J. Am. Chem. Soc.*, **72,** 3595 (1950).

(7) This conformation is not unfavorable. *Cf.*, F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.*, **81,** 6337 (1959).

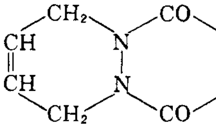
(8) C. W. Whitehead, *J. Am. Chem. Soc.*, **80,** 2178 (1958).

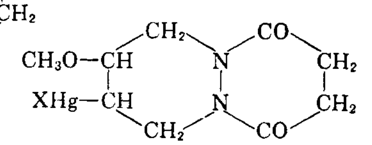
gen on the mercury (III, X = Cl or Br with R = H, and R′ = CH_3) was not displaced.

Treatment of the amorphous mercurated product (hereafter referred to for convenience as VI) with sodium chloride gave 3-chloromercuri-4-methoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione monohydrate (III, X = Cl, R = H, R′ = CH_3) which proved to have an oral diuretic potency twice that of Chlormerodrin (in dogs) while possessing only one-fourth the emetic activity.[9]

Further compounds prepared in the series under discussion and previously unreported are 3-bromomercuri-4-methoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (III, X = Br, R = H, R′ = CH_3), 3-chloromercuri-4-methoxy-8-methyl-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (III, X = Cl, R = R′ = CH_3), 3-acetoxymercuri-8-*n*-dodecyl-4-methoxy-1,6,8-triazabicyclo[4.3.0]-nonane-7,9-dione (III, X = $OCOCH_3$, R = *n*-$C_{12}H_{25}$, R′ = CH_3) and 3-chloromercuri-4-*n*-propoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (III, X = Cl, R = H, R′ = *n*-C_3H_7).

As a part of this general investigation, compound I was mercurated to furnish 4-chloromercuri-5-methoxy-1,2-dicarbamylhexahydropyridazine. In addition, 1,6-diazabicyclo[4.4.0]-8-decene-2,5-dione VIII, prepared by the reaction of succinic anhydride with 1,2,3,6-tetrahydropyridazine,[10] was mercurated to give 8-acetoxymercuri-9-methoxy-1,6-diazabicyclo[4.4.0]decane-2,5-dione, IXa. Treatment of IXa with sodium chloride afforded 8-chloromercuri-9-methoxy-1,6-diazabicyclo[4.4.0]-decane-2,5-dione, IXb.


VIII


IXa. X = $OCOCH_3$
b. X = Cl

EXPERIMENTAL[11]

8-Acetoxymercuri-1,6,8-triazabicyclo[4.3.0]-3-nonene-7,9-dione (II, R = $HgOCOCH_3$). To a boiling solution of 1.83 g. (0.012 mole) of 1,6,8-triazabicyclo[4.3.0]-3-nonene-7,9-dione (II, R = H) in 45 ml. of methanol was added a solution of 3.82 g. (0.012 mole) of mercuric acetate in 25 ml. of warm methanol. The warm mixture was filtered to remove suspended impurities, refluxed for 2 hr., and cooled to room temperature. White needles precipitated which were collected, washed with methanol and absolute ether, and dried at 65° *in vacuo*. This product (3.1 g., 70% yield) melted at 192–194° dec. (uncorr.) and could be recrystallized from methyl, ethyl, or isopropyl alcohol. It gave the analytical values reported below, however, in its originally precipitated condition.

Anal. Calcd. for $C_8H_9HgN_3O_4$: Hg, 48.72; N, 10.20. Found: Hg, 48.4; N, 10.2.

Treatment of 8-acetoxymercuri-1,6,8-triazabicyclo[4.3.0]-3-nonene-7,9-dione (II, R = $HgOCOCH_3$) *with nitric acid in methanol.* When a boiling solution of 2.1 g. (0.005 mole) of the title compound in 50 ml. of boiling methanol was treated with 1 drop of concd. nitric acid, precipitation of a finely divided white amorphous powder began within 30 sec. The mixture was boiled briefly, cooled, and filtered. The powder thus separated was washed with methanol and dried at 76° for 6 hr. Its infrared spectrum was superimposable on that of an authentic sample of amorphous *anhydro 3-hydroxymercuri-4-methoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione monohydrate* (VI) (see below).

Amorphous anhydro 3-hydroxymercuri-4-methoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione monohydrate (VI). To a solution of 12.25 g. (0.08 mole) of 1,6,8-triazabicyclo[4.3.0]-3-nonene-7,9-dione[1] (II, R = H) in 325 ml. of boiling methanol was added a filtered solution of mercuric acetate (25.5 g., 0.08 mole) in 115 ml. of boiling methanol. Six drops of concd. nitric acid were added whereupon a white solid precipitated almost immediately. The mixture was stirred at reflux for 2 hr., cooled, and filtered, and the collected solid was washed with water, methanol, and ether to give 26.3 g. (74% yield) of white, amorphous powder (dried at 65°/10 mm. for 16 hr.). This product gave an infrared spectral curve identical with that of the material described below as precipitated from alkaline solution.

Anal. Calcd. for $C_7H_{11}HgN_3O_4$: Hg, 49.93; N, 10.46. Found: Hg, 50.0; N, 10.6.

A solution of 89 g. (0.22 mole) of the amorphous powder in 1 l. of 0.2*N* aqueous sodium hydroxide solution was filtered to remove a small amount of insoluble material and then treated with carbon dioxide gas until precipitation of the product was complete. The product was collected by filtration, washed with water, alcohol, and ether and dried at 60° *in vacuo* for 4 hr. to give 46 g. (38% yield from II, R = H) of the title compound (VI), m.p. 295–300° dec., $\epsilon_{223\ m\mu(sh)}^{C_2H_5OH}$ 6700.

Anal. Calcd. for $C_7H_{11}HgN_3O_4$: Hg, 49.93; N, 10.46; O, 15.93; H_2O,[4] 4.5. Found: Hg, 49.9; N, 10.8; O, 15.9; H_2O, 4.6.

Crystalline compound VI. When 2.0 g. of amorphous compound VI was wet with 2 ml. of water and treated with 25 ml. of 2*N* ammonium hydroxide, all the solid dissolved and after about 10 min. a crystalline solid began to precipitate. After 2 hr. the solid was collected, washed three times with water, twice with acetone, and once with ether, and dried for 2 hr. at 65° (10 mm.) to give 1.6 g. (80% yield) of crystalline compound VI, m.p. 295–296° dec. The infrared spectrum of this compound was similar to, but not identical with, that of amorphous compound VI (potassium bromide pellet).

Anal. Calcd. for $C_7H_{11}HgN_3O_4$: Hg, 49.93; N, 10.46; H_2O,[4] 4.5. Found: Hg, 50.4; N, 10.5; H_2O, 4.4.

When 2.05 g. of amorphous compound VI was wet with 5 ml. of water and treated with 5 ml. of 1*N* sodium hydroxide with stirring, all the solid dissolved. A faint cloudiness was removed by filtration. Within 10 min. the solution had started to deposit a crystalline solid. After an hour the solid was collected and washed with water, alcohol, and ether to give 0.35 g. (17% yield) of crystalline compound VI, m.p. 290–291° dec. Its infrared spectrum (potassium bromide pellet) was identical with that of the compound precipitated from ammonium hydroxide solution.

Anal. Calcd. for $C_7H_{11}HgN_3O_4$: Hg, 49.93. Found: Hg, 50.2.

Attempted preparation of 3-acetoxymercuri-4-methoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione. (A) Absolute ether was

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[9] W. B. McKeon, Jr., and F. P. Luduena, to be published.

[10] P. Baranger, J. Levisalles, and M. Vuidart, *Compt. rend.*, **236**, 1365 (1953).

[11] All melting points are corrected unless otherwise noted. Appreciation is extended to the Physical and Analytical Sections of this institute for the spectral and analytical data.

added to a solution of 16.08 g. of anhydro 3-hydroxymercuri-4-methoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione monohydrate (VI) in 50 ml. of glacial acetic acid until precipitation was essentially complete. The precipitated white powder was collected, washed with ether and dried at 70° (10 mm.) for 8 hr. to give 15.45 g. of solid, m.p. 275° dec. The infrared spectrum of this solid was identical with that of the starting material.

(B) A solution of 0.44 g. of 3-chloromercuri-4-methoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione monohydrate in 25 ml. of hot water was treated with 0.17 g. of silver acetate in 25 ml. of hot water. The precipitate of silver chloride which formed immediately was filtered off and the filtrate was cooled to room temperature. A further small precipitate which formed was separated. The filtrate was concentrated to dryness *in vacuo* to give an amorphous solid which smelled strongly of acetic acid. The solid was washed with methanol and dried at 80° (10 mm.) for 8 hr. to give a white powder having an infrared spectrum identical with that of the anhydro compound VI.

3-Chloromercuri-4-methoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione monohydrate (III, X = Cl, R = H, R′ = CH_3). A solution of 16.1 g. (0.04 mole) of anhydro 3-hydroxymercuri-4-methoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione monohydrate (VI) in 50 ml. of acetic acid at 40° was diluted with 350 ml. of water, filtered, and treated with a solution of 11.7 g. (0.2 mole) of sodium chloride in 50 ml. of water. Upon standing, the solution deposited diamond shaped prisms which were collected, washed with water, methanol, and ether and dried (14.3 g.). The solid was dissolved in 1.1 l. of water heated to 88° only,[12] the solution was cooled, and the precipitated solid was collected, washed with methanol and ether, and dried to give 10.0 g. (57% yield) of the title compound, m.p. 144–147° dec. This material gave the analytical values shown below. Exposure of the crystals to a drying atmosphere with or without heat caused the crystals to effloresce and the resulting powder contained only a fraction of a molecular equivalent of water.

Anal. Calcd. for $C_7H_{12}ClHgN_3O_4$: C, 19.19; H, 2.76; Hg, 45.77; N, 9.59. Found: C, 19.3; H, 2.7; Hg, 45.0; N, 9.7.

3-Bromomercuri-4-methoxy-1,6,8-triazabicyclo[4.3.0.]-nonane-7,9-dione (III, X = Br, R = H, R′ = CH_3). A solution of 16.1 g. (0.04 mole) of anhydro 3-hydroxymercuri-4-methoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione monohydrate (VI) in 50 ml. of acetic acid was diluted with 350 ml. of water and treated with a solution of 20.6 g. (0.2 mole) of sodium bromide in 50 ml. of water. The solid which separated was collected (14.2 g.) and dissolved in 2.2 l. of a hot (92°) 9% aqueous dimethylformamide solution. Cooling this solution afforded massive prisms which were collected, washed with methanol and ether, and dried at 60° for 8 hr. to give 8.4 g. (45% yield) of the title compound, m.p. 177–178° dec.

Anal. Calcd. for $C_7H_{10}BrHgN_3O_3$: C, 18.09; H, 2.17; Hg, 43.17. Found: C, 18.1; H, 2.1; Hg, 43.0.

3-Chloromercuri-4-methoxy-8-methyl-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (III, X = Cl, R = R′ = CH_3). To a hot solution of 9.1 g. (0.029 mole) of mercuric acetate in 50 ml. of methanol was added 4.77 g. (0.029 mole) of 8-methyl-1,6,8-triazabicyclo[4.3.0]-3-nonene-7,9-dione[2] and 2 drops of concd. nitric acid. The mixture was heated under reflux for 15 min. and then chilled. The 10.7 g. of white solid which precipitated was collected and dissolved in 50 ml. of warm water. When this solution was treated with 8 ml. of saturated salt solution, a gum separated which solidified on cooling. The 9.6 g. of material so obtained was recrystallized from 500 ml. of boiling water using Darco G-60 to remove a haziness. The massive white prisms which separated melted at 238.5–240° dec., 7.5 g. (60% yield).

Anal. Calcd. for $C_8H_{12}ClHgN_3O_3$: C, 22.12; H, 2.79; Hg, 46.19. Found: C, 22.5; H, 3.0; Hg, 45.1.

3-Acetoxymercuri-8-n-dodecyl-4-methoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione (III, X = $OCOCH_3$, R = n-$C_{12}H_{25}$, R′ = CH_3). A hot solution of 7.7 g. (0.024 mole) of 8-*n*-dodecyl-1,6,8-triazabicyclo[4.3.0]-3-nonene-7,9-dione[2] and 7.65 g. (0.024 mole) of mercuric acetate in 75 ml. of methanol was treated with 2 drops of concd. nitric acid and then heated under reflux for 30 min. Removal of the methanol and most of the acetic acid (produced in the reaction) by warming *in vacuo* gave a colorless oil which solidified. The solid was recrystallized twice from a minimum of methanol with filtration to remove a haziness from the solution. An additional recrystallization of the 7.6 g. at hand by dissolving the solid in 50 ml. of benzene at 45°, cooling the solution to room temperature, filtering it to remove a cloudiness, and adding 12 ml. of pentane to effect precipitation gave a somewhat waxy solid which, after drying for 5 hr. at 78° (10 mm.), melted at 118.5–121° (3.6 g., 25% yield).

Anal. Calcd. for $C_{21}H_{37}HgN_3O_5$: Hg, 32.77; N, 6.87. Found: Hg, 32.9; N, 6.8.

3-Chloromercuri-4-n-propoxy-1,6,8-triazabicyclo[4.3.0]-nonane-7,9-dione (III, X = Cl, R = H, R′ = n-C_3H_7). To a solution of 5.1 g. (0.03 mole) of 1,6,8-triazabicyclo[4.3.0]-3-nonene-7,9-dione[2] in 150 ml. of hot *n*-propyl alcohol was added a solution of 9.6 g. of mercuric acetate in 150 ml. of *n*-propyl alcohol followed by 6 drops of concd. nitric acid. The mixture was heated on the steam bath for 2.75 hr., left at room temperature overnight, chilled in an ice bath, and filtered. The amorphous solid collected was washed with ether and this 11.7 g. of presumably *anhydro 3-hydroxymercuri-4-n-propoxy-1,6,8-triazabicyclo[4.3.0]nonane-7,9-dione* was dissolved in 2*N* sodium hydroxide. The solution was clarified by filtration and then treated with gaseous carbon dioxide to reprecipitate the amorphous mercurated product. Without further purification, the product (8.7 g.) was dissolved in 25 ml. of warm acetic acid, the solution was diluted with 8 ml. of water, and 5 ml. of saturated salt solution was added. The desired chloromercuri compound precipitated as a crystalline solid. It was collected and washed with ethanol and ether. This solid was recrystallized from a mixture of water and dimethylformamide to give 6.25 (47% yield from the nonene-7,9-dione) of prism clusters which melted at 198° dec.

Anal. Calcd. for $C_9H_{14}ClHgN_3O_3$: C, 24.11; H, 3.15; Hg, 44.75; N, 9.37. Found: C, 24.2; H, 2.9; Hg, 44.0; N, 9.1.

4-Chloromercuri-5-methoxy-1,2-dicarbamylhexahydropyridazine. To a solution of 8.5 g. (0.05 mole) of 1,2-dicarbamyl-1,2,3,6-tetrahydropyridazine (I) dissolved in 1 l. of boiling methanol was added a hot solution of 15.9 g. (0.05 mole) of mercuric acetate in 125 ml. of methanol containing 0.5 ml. of concd. nitric acid. The chalky-white precipitate which separated was redissolved by warming and adding 12.5 ml. of glacial acetic acid. The reaction mixture was allowed to stand at room temperature for 18 hr. and the solid product which had separated was collected to give 18 g. of crude 4-acetoxymercuri-5-methoxy-1,2-dicarbamylhexahydropyridazine (78% yield).

The crude acetoxymercuri compound (0.039 mole) was suspended in a solution containing 1.6 g. (0.04 mole) of sodium hydroxide in 150 ml. of water. The mixture was warmed on a steam bath to 35–40° to dissolve the solid, and the solution was filtered through diatomaceous earth to remove insoluble black mercurous salts. The filtrate was saturated with carbon dioxide and to this solution of 4-hydroxymercuri-5-methoxy-1,2-dicarbamylhexahydropyridazine was added a solution containing 2.4 g. (0.04 mole) of sodium chloride in 10 ml. of water. The resulting solution was cooled and again saturated with carbon dioxide. The product crystallized and was collected to give 11.6 g. (0.022 mole) of 4-chloromercuri-5-methoxy-1,2-dicarbamylhexahydropyridazine (44% yield, based on I), m.p. 224–229° dec. (uncorr.). The crude product was purified by dissolving it in a solution of 0.9 g. (0.022 mole) of sodium hydroxide in 100 ml. of water warmed to 3°. The 5–40 solu-

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(12) Boiling water appeared to cause decomposition.

tion was filtered and the filtrate cooled and saturated with carbon dioxide. The solid material which separated was collected, washed with absolute alcohol and ether, and dried *in vacuo* to give 8.3 g. (40% yield from I) of pure title compound, m.p. 232–233°.

Anal. Calcd. for $C_7H_{13}ClHgN_4O_3$: C, 19.23; H, 3.00; Hg, 45.88; N, 12.81. Found: C, 19.0; H, 3.3; Hg, 45.1; N, 13.0.

1,6-Diazabicyclo[4.4.0]-8-decene-2,5-dione (VIII). Succinic anhydride (10 g., 0.1 mole) was added to 8.4 g. (0.1 mole) of 1,2,3,6-tetrahydropyridazine[10] with external cooling to control the reaction. The mixture was then heated at 250–260° until gas evolution ceased and cooled to give a crystalline solid. This solid was recrystallized from 95% ethanol to give 10 g. (60% yield) of massive prisms, m.p. 190–200°. Two further recrystallizations from ethanol, one from water, and one from ethanol gave 6.1 g. of material with melting point 196–200° (37% yield).

Anal. Calcd. for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.8; H, 6.1; N, 16.8.

8-Acetoxymercuri-9-methoxy-1,6-diazabicyclo[4.4.0]decane-2,5-dione (IXa). To a solution of 10.6 g. (0.033 mole) of mercuric acetate in 100 ml. of hot methanol were added 4 drops of concd. nitric acid and a solution of 5.5 g. (0.033 mole) of 1,6-diazabicyclo[4.4.0]-8-decene-2,5-dione (VIII) in 110 ml. of hot methanol. The resulting solution was heated under reflux for 3 hr. and allowed to stand overnight. Crystalline solid precipitated. The mixture was chilled and filtered to give 11.1 g. A single recrystallization of this product afforded 9.2 g. (61% yield) of material which melted at 198° dec.

Anal. Calcd. for $C_{11}H_{16}HgN_2O_5$: Hg, 43.91; N, 6.13. Found: Hg, 43.4; N, 6.2.

8-Chloromercuri-9-methoxy-1,6-diazabicyclo[4.4.0]decane-2,5-dione (IXb). A mixture of 6.65 g. (0.04 mole) of 1,6-diazabicyclo[4.4.0]-8-decene-2,5-dione (VIII), 12.75 g. (0.04 mole) of mercuric acetate, 250 ml. of methanol and 4 drops of nitric acid was heated under reflux for 5 hr. The reaction mixture was filtered to remove suspended impurities and the filtrate was treated with 15 ml. of 25% aqueous sodium chloride solution. Chilling the mixture in an ice bath caused precipitation of 14.5 g. of the chloromercuri compound. Recrystallization of the product by warming it to 97° with a mixture of 200 ml. of water and 175 ml. of dimethylformamide and cooling afforded 13.77 g. (80% yield) of white prisms which softened at 240° and decomposed at 251°.

Anal. Calcd. for $C_9H_{13}ClHgN_2O_3$: C, 24.94; H, 3.02; Hg, 46.30. Found: C, 25.3; H, 3.2; Hg, 45.8.

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[CONTRIBUTION FROM THE ETHYL CORPORATION]

Synthesis and Isolation of Vinyllithium. Preparation from Lithium and Heavy Metal Vinyl Compounds

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Vinyllithium was prepared by the metathetical exchange reaction between phenyllithium and tetravinyllead in ether. Vinyllithium was also prepared and isolated from the metal exchange reactions between lithium and tetravinyllead or tetravinyltin in ether solvent. Vinylation with the isolated vinyllithium from the lithium-tetravinyllead reaction was demonstrated by conversion of tributyltin chloride to tributylvinyltin.

Lithium alkyls have been isolated and the properties of these materials have long been well known,[3] but the isolation and characterization of vinyllithium has not previously been described. Isobutenyllithium has been prepared by reaction of the alkenyl halide with lithium in diethyl ether or petroleum ether[4] but analogous attempts to prepare vinyllithium were unsuccessful. Although a reaction has been reported to occur between lithium and vinyl chloride in tetrahydrofuran,[5] vinyllithium was not claimed as a product. Vinylpotassium was prepared from potassium-sodium alloy and vinyl chloride in tetrahydrofuran[5] as well as from the exchange between amylsodium with ethylene in the presence of sodium isopropoxide.[6] Vinyllithium was first prepared as an ether solution by the reaction between tetravinyltin and phenyllithium in ether.[7] The vinyllithium, however, was not isolated from this solution, which was contaminated with lithium bromide originating from the preparation of the starting material, phenyllithium.

Another approach which can be taken for the preparation of vinyllithium is that of the cleavage of a heavy metal vinyl compound with lithium. It was reported that reaction between tetraethyllead and sodium in liquid ammonia results in the cleavage of just one group from the lead alkyl, yielding triethyllead sodium.[8] An attempt was made to obtain cleavage of all the alkyl groups from tetraalkyllead compounds by reaction with sodium in gasoline to yield lead and sodium alkyls.[3] Although lead deposited in these reactions, no sodium alkyls were isolated.

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