[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO, AND THE OTHO S. A. SPRAGUE MEMORIAL INSTITUTE.]

AROMATIC MERCURI-ORGANIC DERIVATIVES.

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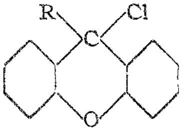
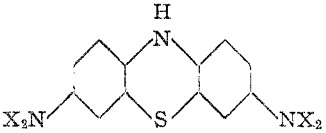
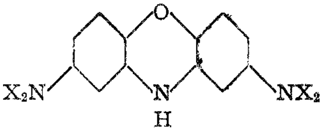
Introduction.

During the course of investigation of mercuri-organic derivatives undertaken for the Sprague Memorial Institute, the amount of data has accumulated to such an extent that it has been deemed advisable to publish some of the results thus far obtained. This paper contains some preliminary work on the preparation of a 6-membered atomic heterocyclic compound which contains a metal in place of a non-metal. In this case mercury was the metal experimented with. It was put in place of nitrogen in a ring of the azine type. Work is now being carried on to substitute mercury for oxygen, sulfur, and nitrogen, in the type of rings illustrated below.







A detailed study of the influence of different groups on the position taken by mercury when introduced into a substituted benzene nucleus is also under investigation.

The theory of mercurization will be published at a later date.

Experimental.

The Preparation of *m*-Bromo-dimethyl-aniline, *m*-$BrC_6H_4N(CH_3)_2$.—This compound was first prepared by Wurster,[2] by treating *m*-bromo-aniline with methyl iodide in a sealed tube. The method has the disadvantage that large quantities of *m*-bromo-dimethyl-aniline cannot be made in a single operation. Since we were not interested in obtaining pure *m*-bromo-dimethyl-aniline as such, but a pure *p*-nitroso-*m*-bromo-dimethyl-aniline, the following method was adopted. A quantity of *m*-bromo-aniline (75 g.) was suspended in water (900 cc.) and heated to about 80°. Sodium carbonate (300 g.) and dimethyl sulfate (300 g.) were then added in small portions, care being taken that the solution was always alkaline. The addition should take about 1.5 hours. After all of the dimethyl sulfate had been added, the solution was agitated for an hour and then subjected to steam distillation. The oil which came over was separated

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[1] The material presented here is used by Morris S. Kharasch in his dissertation presented in part fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

[2] Wurster, *Ber.*, 12, 1818 (1879).

from the distillate, the latter extracted twice with ether, and the portions combined. The ether solution was dried with sodium sulfate, the ether distilled off, and the oil distilled *in vacuo*. A colorless oil came over which, however, turned yellow on standing. Yield, 75 g.

The product thus obtained contains unchanged *m*-bromo-aniline, *m*-bromo-monomethyl-aniline and *m*-bromo-dimethyl-aniline. To separate these 3 substances, the usual method was employed. The oil was dissolved in 2.5 mols. of 20% hydrochloric acid, the solution cooled to 0°, and the calculated amount of sodium nitrite[1] dissolved in a little water was added in small amounts. The hydrochloride of the *p*-nitroso-*m*-bromo-dimethyl-aniline separated. The solution was then extracted repeatedly with ether until a sample test showed the absence of *m*-bromophenyl-methyl-nitrosamine in the latter.[2] The precipitate—the hydrochloride of the *p*-nitroso-*m*-bromo-dimethyl-aniline—was then filtered off and dried in a vacuum desiccator.

_p_-Nitroso-_m_-bromo-dimethyl-aniline, $(CH_3)_2NC_6H_3BrNO$.—This compound was also prepared by Wurster, who gave its melting-point but no analytical data, owing to the fact that the compound decomposed when he tried to bring it to constant weight by drying it on the water-bath. The compound is also not recorded in Richter's Lexikon. It was thought, therefore, advisable to analyze it.

A quantity of the hydrochloride of *p*-nitroso-*m*-bromo-dimethyl-aniline (5 g.) was suspended in 75 cc. of water, cooled to 0°, 40 cc. of ether added, and enough carbonate to render the solution decidedly alkaline. The ether extract was then separated from the solution, and the latter extracted 3 more times with ether, 50 cc. being used each time. The ether extracts were combined, dried with sodium sulfate, and $^3/_4$ of the ether distilled off. The solution was then transferred to an evaporating dish and allowed to evaporate spontaneously. Beautiful long green needles were obtained which melted with decomposition at 148°.[3] For analysis the base was recrystallized twice from very small amounts of ether.

Subs., 0.1082: AgBr, 0.0886.

Calc. for $C_8H_{11}ON_2Br$: Br, 34.87. Found: 34.84.

_m_ - Bromo - dimethyl - _p_ - phenylene - diamine Dihydrochloride, $BrNH_2C_6H_3N(CH_3)_2.2HCl$.—The hydrochloride of *p*-nitroso-*m*-bromo-dimethyl-aniline was reduced in the following manner. Twice the calculated amount of stannous chloride necessary for the reduction was dissolved in conc. hydrochloric acid, the solution diluted somewhat, warmed to 40°, and the *p*-nitroso-*m*-bromo-dimethyl-aniline hydrochloride, mixed

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[1] To avoid an excess of sodium nitrite, the oil was assumed to be pure *m*-bromo-dimethyl-aniline.

[2] Lieberman's nitrosamine test.

[3] Wurster also gave 148° as the melting-point of the compound.

with hydrochloric acid to the consistency of a thick paste, added to it in small portions. The reduction was practically instantaneous. The complex tin salt of the dihydrochloride of the *m*-bromo-dimethyl-*p*-phenylene-diamine separated. Enough water was then added to bring it back into solution, and the tin precipitated as stannic sulfide from the hot solution with hydrogen sulfide. Before being filtered the solution was diluted with an equal amount of water, warmed to 80°, and hydrogen sulfide passed through it for a half an hour longer. This procedure has been found very satisfactory, requiring very little time and precipitating the tin quantitatively in one operation. The water in the filtrate was distilled off *in vacuo*. The dihydrochloride of *m*-bromo-dimethyl-*p*-phenylene-diamine remained behind. It was purified by preparation of the free base and distillation of the latter *in vacuo*. The base was then dissolved in ether and dry hydrogen chloride passed into the solution. The dihydrochloride was precipitated. It was dried in a vacuum desiccator.

Subs., 0.1941: 16.80 cc. dry N_2 at 20° and 726.3 mm.
Calc. for $C_8H_{10}N_2Br.2HCl$: N, 9.81. Found: 9.64.

***m*-Bromo-dimethyl-*p*-phenylene-diamine,** $BrNH_2C_6H_3N(CH_3)_2$.—The free base was obtained by the method previously outlined. The oily distillate solidified on cooling in white, almost colorless, needles; m. p. 47.5°. The free base turned dark on exposure to light and air. When it was dissolved in dil. hydrochloric acid and the solution was saturated with hydrogen sulfide and treated with ferric chloride, an intensely blue coloration was produced.

Subs., 0.2749: AgBr, 0.2406.
Calc. for $C_8H_{11}N_2Br$: Br, 37.18. Found: 37.25.

***o*-Dibromo-Bindschedler's Green.**—The same method was employed as was used originally by Bindschedler for the preparation of Bindschedler's Green.[1] To a mixture of 2.15 g. of *m*-bromo-dimethyl-*p*-phenylene-diamine and 2 g. of *m*-bromo-dimethyl-aniline,[2] 2 g. of conc. hydrochloric acid in 50 cc. of water was added. The solution was cooled to —2° and oxidized by a solution of 2 g. of potassium dichromate and 0.6 g. of glacial acetic acid in 20 cc. of water. The oxidizing agent was added drop by drop. The flask was shaken continuously during the addition of the oxidizing agent. The dyestuff partly precipitated out. Sufficient water was then added to redissolve it, the solution heated to 40–50° and 5 g. of zinc chloride added to it. It was allowed to stand in ice-water for 2 hours longer and the precipitate collected on a filter, washed with a small quantity of cold water, then with alcohol, and finally with ether. It was dried in a vacuum desiccator. A dark amorphous powder was

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[1] Bindschedler, *Ber.*, **16**, 864 (1883).

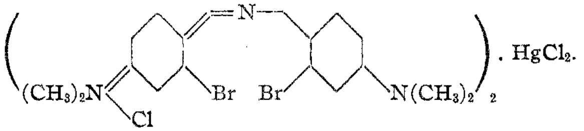
[2] Prepared by the method of Wurster, *ibid.*, **16**, 864 (1883).

thus obtained which was slightly soluble in water, imparting to the latter an intensely green color. The yield was very good.

Subs., 0.3618: 27.40 cc. dry N_2 at 24.5° and 731 mm.
Subs., 0.4860: ZnO, 0.0382.
Calc. for $C_{32}H_{36}N_6Br_4Cl_2.ZnCl_2$: N, 8.25; Zn, 6.37. Found: N, 8.36; Zn, 6.31.

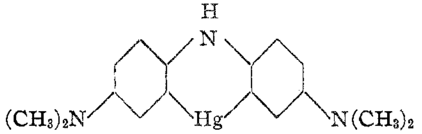
The analysis readily shows that in this case also 2 molecules of the dye combine with one of zinc chloride.

The mercuric chloride double salt was obtained by solution of the zinc chloride double salt in water at 40–50°, and addition of mercuric chloride. The structure of the compound thus obtained is expressed by the following formula,



Subs., 0.1373: HgS, 0.0278.
Calc. for $C_{32}H_{36}Br_4Cl_2.HgCl_2$: Hg, 17.17. Found: 17.47.

Work is also under way on the isolation of the leuco-dibromo-Bindschedler's Green, and the replacing in the latter of the 2 bromine atoms by mercury to give a compound of the following type,



which, when oxidized, would give a representative of a new class of organic mercury derivatives.

m - **Bromo - phenylmethyl - nitrosamine,** *m*-$BrC_6H_4N(CH_3NO)$.—As previously stated, the methylation of *m*-bromo-aniline by the use of dimethyl sulfate gave rise to 2 derivatives, the mono-methyl and the dimethyl *m*-bromo-anilines. These 2 were separated by the use of sodium nitrite as given in detail in the preparation of *p*-nitroso-*m*-bromo-dimethylaniline. The ether extract of the acid solution contained the *m*-bromomethylphenyl-nitrosamine. The ether was distilled off and the oil subjected to steam distillation. The distillate was then extracted with ether, the solution dried with sodium sulfate, and the ether distilled off. When the sides of the crystallizing dish were cooled and scratched the oil solidified in feathery clusters of fine yellowish needles; m. p., 49°. Yield, 10 g.

Subs., 0.2049: AgBr, 0.1782.
Calc. for $C_7H_7ON_2Br$: Br, 37.17. Found: Br, 37.01.

The compound gives the characteristic Lieberman's nitroso-amine reaction and in the pure condition is very stable.

p-Nitroso-m-bromo-monomethylaniline, $BrNOC_6H_3NHCH_3$. — The m-bromo-methylphenyl-nitrosamine was rearranged according to the method of Fisher and Hepp.[1] The nitrosamine (4 g.) was dissolved in ether (8 g.) and alcohol (16 g.), saturated with hydrogen chloride at 10°, added. A red coloration was produced after the addition of the alcohol. It took fully 2 days for the reaction to go to completion. A beautiful pink compound was obtained. This compound, the hydrochloride of p-nitroso-m-bromo-monomethyl-aniline, is very stable, much more so than the hydrochloride of the dimethyl-aniline derivative. It was kept 3 weeks in an open dish without changing color. Its melting-point was not sharp. At 140° it turned yellow, and at 168° melted with apparent decomposition. It hydrolyzed immediately to give the free base on suspension in water. The free base was isolated and purified by the same method as that given for p-nitroso-m-bromo-dimethyl-aniline.

Subs., 0.1055: 12.11 cc. dry N_2 at 20 and 736 mm.
Calc. for $C_7H_7ON_2Br$: N, 13.06. Found: 12.95.

The free base is green. It has no definite melting-point. It turns dark at 100° and explodes at 124°. An ether solution of the base is yellowish-green in thin layers and green in thick.

p-Nitroso-phenol-o-mercuric-chloride, $HOC_6H_3(4)NO(2)HgCl$.— Three g. of o-phenol-mercuric chloride was gradually added to a solution of 0.42 g. of sodium hydroxide and 0.86 g. of sodium nitrite in 23 cc. of water. The solution was warmed to 30–40° and a few drops of 2 molar sodium hydroxide solution added to it until all of the o-phenol-mercuric-chloride had gone into solution. When finely powdered, it goes into solution rapidly in the given amount of sodium hydroxide.[2] It was cooled to —4° or —5° and 2.3 g. of conc. sulfuric acid in 6 cc. of water added very slowly. The flask was constantly shaken during the operation. The addition of the acid should take about 45 minutes. The solution first turned pink, due to the formation of the sodium salt of the p-nitroso-phenol-o-mercuric chloride, but it grew darker and darker in color as more of the acid was added. A dark-colored precipitate was also formed. After all the acid had been added, the solution was shaken for 15 minutes longer, and allowed to stand in a freezing mixture for 2 hours to complete the precipitation. The solution was then filtered and the residue, after being washed a few times with small amounts of cold water, dried in a vacuum desiccator over solid sodium hydroxide and soda lime. A beautiful bordeaux-colored compound was thus obtained which can be kept indefinitely over soda lime without decomposition. It can be recrystallized

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[1] Fisher and Hepp, *Ber.*, **19**, 2991 (1886).

[2] It has also been found very advantageous to moisten the o-phenol-mercuric-chloride with a few drops of alcohol. It then dissolves in the alkali very readily—for very obvious reasons.

from xylene in which it is slightly soluble and also from anisol from which it separates in very small needles of a light brown color.

Subs., 0.1930: 6.72 cc. dry N_2 at 22° and 732.3 mm.

Subs., 0.1352: AgCl, 0.0547.

Calc. for $C_6H_4O_2NClHg$: N, 3.92; Cl, 9.92. Found: N, 3.90; Cl, 10.07.

The compound, like *p*-nitroso-phenol, gives the Lieberman's nitrosamine test. It is partly soluble in ether, imparting to the latter an intensely green color. It behaves in all respects except solubility, like *p*-nitroso-phenol, of which it is a substituted derivative as noticed from the method of preparation. The mercury in *ortho* position to the hydroxyl group in phenol is known not to decrease the activity of the *para* hydrogen atom, as illustrated by the fact that it is possible to couple *o*-phenol-mercuric-chloride with diazo compounds.[1]

***p*-Nitroso-aniline-*o*-mercuric-chloride,** $NH_2C_6H_3(4)NO(2)HgCl$.—To 2 g. of *p*-nitroso-phenol-*o*-mercuric-chloride, 2.4 g. of ammonium chloride, 6.6 g. of dry ammonium acetate, and 0.2 g. of ammonium carbonate were added and the mixture warmed on the water-bath for 1/2 hour with vigorous stirring.[2] It was then poured into 75 cc. of cold water, and allowed to stand 1/2 hour. A slightly brown amorphous precipitate was obtained. It was filtered off, washed well with cold water until the washings gave no test for ammonia to Nessler's reagent and dried in a vacuum desiccator over sodium hydroxide. For purification, it was recrystallized from anisol.

Subs., 0.1431, 0.1311: (1) 9.80 cc. dry N_2 at 23° and 729.5 mm., (2) 8.90 cc. dry N_2 at 19° and 739.5 mm.

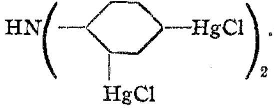
Subs., 0.1248: AgCl, 0.0530.

Subs., 0.1252: HgS, 0.0823.

Calc. for $C_6H_5ON_2ClHg$: N, 7.89; Cl, 9.98; Hg, 56.31. Found: N, 7.53; Cl, 10.18; Hg, 56.57.

The compound is slightly soluble in benzene and ether, coloring both green. An alcohol solution is reddish-yellow.

In the preparation of the above compound, smaller or larger quantities of the *p*-nitroso-phenol-*o*-mercuric-chloride sometimes remain unchanged. So it is always advisable to test the *p*-nitroso-aniline-*o*-mercuric-chloride by the Lieberman's nitrosoamine reaction for its presence. If the test is positive, the precipitate must be washed by decantation with a 2 molar solution of sodium hydroxide until the washings are colorless—the phenol derivative being soluble. It is then washed free from alkali with cold water and dried in a vacuum desiccator over sodium hydroxide.

Diphenylamino - tetramercuric - chloride, 
$HN\left(-C_6H_3(HgCl)-HgCl\right)_2$.—Di-

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[1] Dimroth, *Centr.*, **1901**, I, 450.

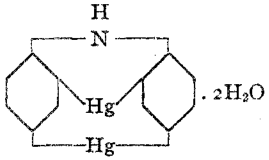
[2] Fisher and Hepp, *Ber.*, **20**, 2475 (1887).

phenylamine (6.5 g.) was heated with mercuric chloride (2.7 g.) until the latter seemed to go into solution. A crackling noise was heard and the reaction went on of its own accord with the evolution of heat. The solution was first yellow, then brown, and finally dark brown. It was then poured into glacial acetic acid and boiled. The acid was decanted. The washing with glacial acetic acid was continued until the decanted liquid poured into water gave no precipitate, indicating that the product was free from diphenylamine. The filtrate was tested for mercuric chloride until the precipitate was washed free from it. A light yellow amorphous compound was thus obtained as a residue which, after being boiled with alcohol, was dried in a vacuum desiccator.

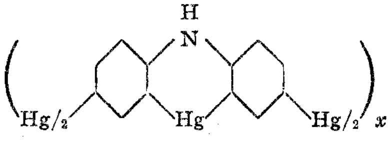
Subs., 0.8889: 10.20 cc. of N_2 at 21° and 734.2 mm.
Subs., 0.1940: AgCl, 0.1012.
Subs., 0.1699: HgS, 0.1426.
Calc. for $C_{12}H_7NCl_4Hg_4$: N, 1.26; Cl, 12.81; Hg. 72.26. Found: N, 1.28; Cl, 12.98; Hg, 72.10.

The compound is insoluble in all organic solvents. It does not melt when heated to 260°. When boiled with pyridine, it seems to undergo decomposition. This is probably a ring formation as large quantities of mercuric chloride are found in the pyridine. It is being investigated. From consideration of analogous cases the positions taken by the mercury are most likely *para* and *ortho* to the nitrogen. Thus, *p*-toluidine yields a mono-substitued derivative when treated with mercuric acetate or chloride, *o*-toluidine a di-substituted derivative, and *m*-toluidine a tri-substituted derivative. In these compounds mercury occupies the positions, relative to the nitrogen, *p*, *p-o*, *p-o-o*, respectively. Furthermore, the literature is abundant with instances of similar substitutions. In no case, however, has a mercury compound been prepared in which mercury would occupy a position *meta* to an amino nitrogen. We feel, therefore, in some way justified in assigning the above structure to the diphenylamine derivative.

3,3′-Mercuri-mercazine,



or

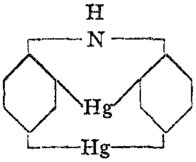


To 5 g. of diphenylamine-tetramercuric-chloride in 60 cc. of alcohol was added 10 g. of sodium thiosulfate in a little water. The precipitate turned dark immediately. The solution was warmed to 70° and kept at that temperature for 15 minutes, the whole being shaken during the operation. Sufficient water was then added to get a homogeneous solution, the solution boiled a few minutes and then filtered. The precipitate was washed with alcohol and then with ether, dried and then analyzed.

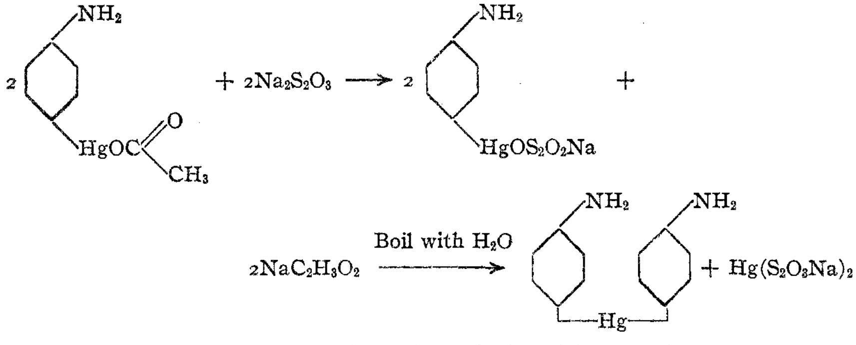
Subs., 0.1949: 4.60 cc. of dry N_2 at 21° and 730.2 mm.
Subs., 0.1478: HgS, 0.1142.
Subs., 0.3082: CO_2, 0.2739; H_2O, 2.09.
Subs., 0.2133: AgCl, 0.0008.
Calc. for $C_{12}H_{11}ONHg_2$: N, 2.33; C, 23.97; H, 1.83; Hg, 66.50. Found: N, 2.53; C, 24.22; H, 2.09; Hg, 66.60.

The compound is of a gray color, resembling finely precipitated metallic mercury. It is insoluble in all organic solvents. When heated to 100° in a vacuum, mercury distils over. The substance is unstable when treated with nitric acid. The product of nitration is soluble in sodium hydroxide with a red coloration.

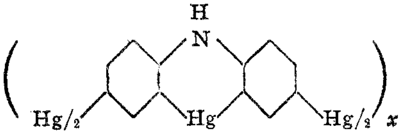
The structural formula of this compound is of great interest. The structure which suggests itself from the method of preparation is,



since from the work of Pesci[1] on aniline mercuri-acetate and similar compounds it is quite evident that the sodium thiosulfate acts in the following way



The intermediate compounds have been isolated by Pesci. On the other hand, the *para* mercury bridge would give rise to a 10-atom ring with respect to the nitrogen which would probably be extraordinarily unstable and, therefore, not likely to form. Then again, there is the possibility of the formation of a complex molecule of the type



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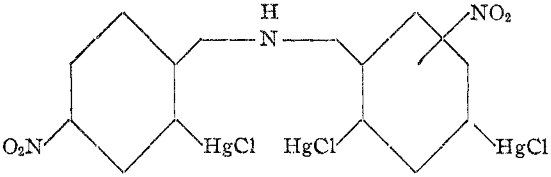
[1] Pesci, *Gazz. chim. ital.*, **29**, I, 394 (1899).

We have not been able so far, however, to confirm either assumption, owing to the insolubility of the compound in all solvents.

***p,o,o'*-3-Mercuric-chloride-di-nitro(??)diphenylamine,**



To 5 g. of diphenylamine-tetramercuric-chloride 20 g. of a mixture of conc. nitric acid (2 parts sp. gr. 1.4), sulfuric acid (1 part), and water (one part) were added. It was warmed carefully for 2 minutes. The nitration took place with vigor. When the reaction had completed itself, the contents were poured into water, boiled, and the solution filtered. The residue was washed with alcohol and ether and dried in a vacuum desiccator.

Subs., 0.2491, 0.1732: (1) 10.00 cc. of dry N_2 at 20° and 728 mm.; (2) 6.60 cc. of dry N_2 at 21° and 740 mm.

Subs., 0.2518: CO_2, 0.1532; H_2O, 0.0159.

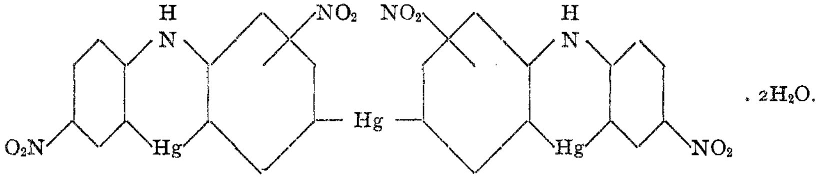
Subs., 0.2000: AgCl, 0.0900.

Subs., 0.1320, 0.1831: (1) HgS, 0.0954; (2) 0.1328.

Calc. for $C_{12}H_6O_4N_3Cl_3Hg_3$: N, 4.39; C, 14.93; H, 0.63; Cl, 11.03; Hg, 62.24. Found: N, 4.29; C, 14.72; H, 0.70; Cl, 11.13; Hg, 62.52.

The compound is of a light brown color. It is insoluble in all organic solvents. It is partly soluble in sodium hydroxide, giving the solution a red coloration.

Mercury-bis-3-di-nitro(?)-mercazine,



Starting with the above nitro compound, this compound was prepared by the same method as used for 3,3'-mercuri-mercazine.

Subs., 0.2248: 14.20 cc. of dry N_2 at 20° and 738.7 mm.

Subs., 0.1384: CO_2, 0.1218; H.

Subs., 0.1101: HgS, 0.0642.

Calc. for $C_{24}H_{10}O_{10}N_6Hg_3$: N, 7.09; C, 24.24; H, 1.52; Hg, 50.54. Found: N, 7.16; C, 24.01; H, 1.98; Hg, 50.26.

The compound is of a light brown color. It is insoluble in all organic solvents. When treated with sodium hydroxide, it gives to the latter a light red coloration. It resembles the other mercazine derivative in many respects. When heated in a vacuum to 100°, it loses mercury. Heated to 54° in a vacuum for fifteen minutes, it loses 5.22% of water.

Conclusions.

1. A few methods have been outlined for the preparation of a 6-atom heterocyclic ring containing mercury in place of a non-metal.

2. The preparations of a number of new derivatives of *m*-bromo-dimethyl-aniline, *m*-bromo-monomethyl-aniline Bindshedler's green, mercury derivatives of nitroso-phenol, nitroso-aniline, phenylamine and nitro-diphenylamine have been described. These compounds were obtained as a result of carrying out the above procedures.

Work on the problem is being continued.

Chicago, Ill.

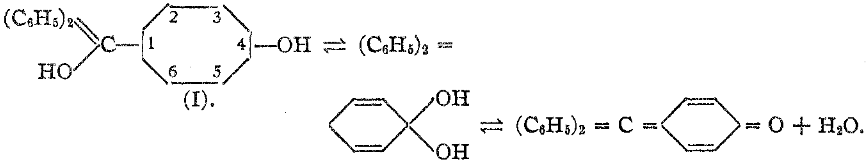
[Contribution from the Chemical Laboratory of the University of Michigan.]

TAUTOMERISM IN THE TRIARYL CARBINOL SERIES; DI-PHENYL-4-HYDROXY-1-NAPHTHYL CARBINOL AND DI-PHENYL-2-HYDROXY-1-NAPHTHYL CARBINOL.

By M. Gomberg and F. W. Sullivan, Jr.

Received June 15, 1920.

It has been shown in previous papers[1] from this laboratory that *p*-hydroxy-triphenyl carbinol exists in 2 tautomeric forms mutually convertible into each other, the benzenoid (I) and the quinonoid (II). The former, colorless, is converted into the latter, colored, by the agency of proper solvents, by heat, and by ultra-violet light. The quinonoid tautomer loses water on heating, to yield fuchsone (III). It is obvious that the benzenoid carbinol, on heating, should also yield the identical fuchsone, through the phase of temporary existence as the quinonoid carbinol. Such is really the case. Moreover, the benzenoid carbinol loses water much more slowly than the quinonoid tautomer does, a difference in behavior fully consistant with the constitutions assigned to the 2 carbinols, respectively.



(I). (II). (III).

Little is known as to how extensively this tendency to tautomerization is shared by substituted hydroxy-triaryl carbinols. Three possible variations of the occurrence of this phenomenon suggest themselves: first, as in the case of *p*-hydroxy-triphenyl carbinol itself, when the benzenoid and the quinonoid carbinol, as well as the fuchsone, all possess sufficient individual stability to permit the isolation of each in the solid state; second, when the equilibrium between the 2 carbinols is preëminently in favor

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[1] This Journal, **35**, 1035 (1913); **37**, 2575 (1915).