[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

THE PREPARATION AND DECOMPOSITION OF UNSYMMETRICAL MERCURI-ORGANIC COMPOUNDS. A METHOD OF ESTABLISHING THE RELATIVE DEGREE OF NEGATIVITY OF ORGANIC RADICALS[1]

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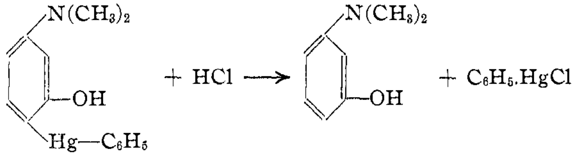
It has been pointed out by Kharasch and Chalkley[2] that the stability of organic mercurial compounds is a direct function of molecular constitution. They studied the effect of amino and hydroxyl groups in a molecule on the lability of the mercury in the *para* or *ortho* positions, bringing out the fact that the former group has the greater labilizing effect. In addition it was shown that the acetylation of the hydroxyl group or the formation of the quaternary salt decreased the lability of the mercury and other positive groups *ortho* and *para* to them. The difference in stabilities of the various mercurial compounds was ascertained by the addition of hydrogen sulfide water to a pyridine solution of the compounds, and noting the time of blackening, due to the formation of mercuric sulfide.

The high lability of the mercury *ortho* and *para* to two negative groups, as in *m*-dimethylaminophenol, indicates a much higher degree of reactivity of the mercury than in others in which the mercury is more stable, as in the case of phenyl- or methylmercuric chloride. Hence, if a molecule of the type of phenylmercuric-4-hydroxy-3-dimethylaniline were treated with hydrochloric acid, the following reaction would be expected, because the mercury in this *para* position is more highly ionized from the benzene carbon than from that of the phenyl group.



Consequently, the decomposition of unsymmetrical mercury compounds with an acid, like hydrochloric acid, may be used as an index of the degree of negativity of the radical attached to the mercury, because that radical which is more electronegative will break off more readily. The following represents the general reaction: $RHgR_1 + HCl \longrightarrow RHgCl + R_1H$. By varying the radicals R and R_1, it should be possible to establish the order of "negativity" of all types of organic radicals.

Only a few of these unsymmetrical mercuri-organic derivatives are

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[1] Read before the Organic Division of the American Chemical Society at the Milwaukee Meeting, September, 1923. Preliminary communication.

[2] Kharasch and Chalkley, THIS JOURNAL, **46**, 1211 (1924).

recorded in the literature and the Grignard reaction has been the only method of obtaining them.[3]

They have not been studied at all as far as their decomposition reactions with acids are concerned. There is one interesting fact, however, that has been noticed in regard to them and that is their ready decomposition, upon distillation, into two symmetrical molecules, $2RHgR_1 \longrightarrow RHgR + R_1HgR_1$.

This latter fact is what would be expected, if we consider the ionization of these unsymmetrical molecules. Of the two radicals R and R_1, one is more strongly electronegative than the other, and if we consider this to be R, the primary ionization of the molecule would be represented by the equation, $RHgR_1 \longrightarrow R^- + HgR_1^+$. At the same time, there would be a slight tendency for the molecule to ionize according to this second equation, $RHgR_1 \longrightarrow RHg^+ + R_1^-$. Consequently, if these four ions all exist at one time or another in the vapor phase, the R_1, which is the least electronegative of the two radicals, would tend to attach itself to that ion which would be apt to be the more stable, or least ionized, namely R_1Hg^+, thus forming a symmetrical molecule. The formation of the other symmetrical molecule, RHgR, follows as a natural consequence of this first reaction.

It is interesting to note here that Hilpert and Grüttner claim not only that these unsymmetrical molecules are extremely unstable upon distillation but also that they were unable to prepare an unsymmetrical molecule of the type of *p*-tolylmercuri-phenyl, because the product decomposed instantly to give two symmetrical molecules.[4]

$$2\ p\text{-}CH_3.C_6H_4HgC_6H_5 \longrightarrow (p\text{-}CH_3.C_6H_4)_2Hg + (C_6H_5)_2Hg$$

We have also obtained molecules which are much more unsymmetrical than that indicated above, namely, phenylmercuric-2,4,6-trinitrophenyl and *p*-tolylmercuric-2,4,6-trinitrophenyl, and found them to be stable even at temperatures above 200°.

The method which we have used to prepare these unsymmetrical mercurial compounds is very simple and allowed us to prepare a series of unsymmetrical derivatives without the trouble of preparing Grignard's reagent. It depends upon the elimination of carbon dioxide from the mercury salt of certain carboxylic acids, which readily decompose into carbon dioxide and the corresponding hydrocarbon. This particular method has

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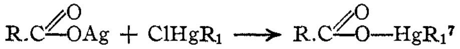
[3] Hilpert and Grüttner, *Ber.*, **48**, 908 (1915).

[4] Since that time one of us and Russell Marker, in an extensive study to determine the relative degree of negativity of common organic radicals, have prepared this unsymmetrical molecule and thirty others by means of the Grignard reagent and the method described in this article, and studied their decomposition with mercuric chloride and also with hydrogen chloride. The work will appear very shortly and we should like to reserve for further study the decomposition of these unsymmetrical molecules with various reagents as reported at the Milwaukee meeting.

been used before by Kharasch[5] and also by Kharasch and Staveley[6] in the preparation of a number of mercuri-organic compounds which have not been prepared by any other means.

In this way the unsymmetrical molecules described in this paper and a large number of other unsymmetrical molecules were readily obtained. The acids chosen were the ones that had been shown in our previous research[5,6] to decompose readily into carbon dioxide and the hydrocarbon.

The method employed to obtain these unsymmetrical derivatives consisted first in preparing the compound $\mathrm{R.C}\overset{\mathrm{O}}{/\!\!/}\!\!\mathrm{—OHg—R_1}$ by treating the silver salt of the acid with $\mathrm{R_1HgCl}$.



$$\mathrm{R.C}\overset{\mathrm{O}}{/\!\!/}\!\!\mathrm{—OAg} + \mathrm{ClHgR_1} \longrightarrow \mathrm{R.C}\overset{\mathrm{O}}{/\!\!/}\!\!\mathrm{—O—HgR_1}^{7}$$

The salt, contained in a Pyrex test-tube, was immersed in a concd. sulfuric acid bath. The tube was connected with a high-vacuum pump, and then the bath heated slowly to a temperature at which there was evidence of evolution of carbon dioxide. This temperature was maintained for about ten minutes; the tube was then removed from the bath, allowed to cool somewhat, and the pump was disconnected. The treatment of the products obtained differs slightly after this stage and is described under each compound, in the experimental part of this paper.

In a recent paper, Koten and Adams[8] have apparently overlooked our communication[9] and record two compounds prepared by the method outlined above. One of these compounds had already been reported by us at the time of the Milwaukee meeting.[9] However, we feel justified in including it in this paper, for the above-mentioned authors do not offer any proof of the constitution of the molecules, and also because we believe our method, recorded in the experimental part, allowed us to prepare the products in a purer condition. Thus, for the *p*-tolylmercuric-2,4,6-trinitrobenzoate Koten and Adams record a melting point of 227° while our product melted at 234–237°. Our procedure for obtaining the unsymmetrical molecules is different from the one used by Koten and Adams. The carbon dioxide is eliminated from the molecule in a vacuum as suggested in a former paper.[5]

The structure of these unsymmetrical molecules is ascertained by decomposition with mercuric chloride, and the identification of the end products. It is of considerable interest to note here that the methylmercuric-

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[5] Kharasch, THIS JOURNAL, **43**, 2238 (1921).

[6] Kharasch and Staveley, *ibid.*, **45**, 2961 (1923).

[7] The acids thus far studied are 2,4,6-trinitrobenzoic, dimethyl and diethyl aceto-acetic, malonic, phthalic and benzoylacetic. The radicals $\mathrm{R_1}$ so far studied are methyl, ethyl, propyl, butyl, phenyl, tolyl, naphthyl and various substituted benzene radicals.

[8] Koten and Adams, THIS JOURNAL, **46**, 2768 (1924).

[9] Ref. 1. Kharasch and Grafflin, *Science*, **58**, 1510 (1923).

2,4,6-trinitrophenyl derivative presumably decomposes into two symmetrical molecules, for the product of the reaction is a symmetrical hexanitro-mercuridiphenyl molecule, and probably mercuridimethyl, which has not as yet been isolated. The former product was confirmed by analysis and by mixed melting points with hexanitro-mercuridiphenyl, prepared by another method.[10]

The decomposition of phenylmercuric-2,4,6-trinitrophenyl and *p*-tolylmercuric-2,4,6-trinitrophenyl with hydrogen chloride has also been carried out. The decomposition of these molecules with hydrogen chloride led to the formation of benzene and toluene, respectively, and 2,4,6-trinitrophenylmercuric chloride. This indicates that both tolyl and phenyl groups are more negative than 2,4,6-trinitrophenyl and the introduction of nitro groups into the benzene ring weakens the electronegativity of the radical. This last phase of the work, in connection with the decomposition of a large number of unsymmetrical derivatives with hydrochloric acid and the significance of the results from the standpoint of the electronic interpretation of valence,[4] will be reported in a later paper.

Experimental Part

The Preparation of Methylmercuric-2,4,6-trinitrobenzoate, $(NO_2)_3.C_6H_2.COOHg-CH_3$.—To 3.6 g. of silver trinitrobenzoate, suspended in 120 cc. of benzene, was added 2.4 g. of methylmercuric chloride, and the whole mixture was shaken for 25 minutes. At the end of that time a heavy, white, flocculent precipitate suddenly formed. The mixture was then heated on the hot-plate, filtered hot, and the residue washed with hot benzene. The benzene filtrate was evaporated first in air and then in a vacuum over sulfuric acid; yield, 4.3 g.

Anal. Subs., 0.3717: 28.75 cc. of dry N_2 (24°, 746 mm.). Calcd. for $C_8H_5N_3O_8Hg$: N, 8.92. Found: 8.83.

The fluffy, white salt is highly electrified and has a bitter taste. It melts and decomposes at 165°, since a gas is evolved at that temperature. It is soluble in hot benzene, very soluble in acetone, slightly soluble in cold toluene, alcohol and ether.

The Behavior of Methylmercuric-2,4,6-trinitrobenzoate when Heated in a Vacuum at a High Temperature.—The methylmercuric-2,4,6-trinitrobenzoate was first treated with a small amount of ether to cut down its electrification. Two g. was then transferred to a Pyrex test-tube and heated in a vacuum up to 160–162°. At this temperature there was evidence of a gas being given off and the reaction became more violent as it progressed. The bath was kept at this temperature for ten minutes and the product changed from white to tan during the process. After cooling, the product was washed with ether, and then crystallized from hot benzene. The product obtained from hot benzene was a fine white flocculent precipitate, and upon washing with ether it became a fine, white powder. It was dried in a vacuum over sulfuric acid. The product obtained is soluble in hot benzene and acetone, but practically insoluble in alcohol or ether. In the melting-point determination, the substance started to shrink at 200°,

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[10] Since the completion of Miss Grafflin's paper the senior author has succeeded in isolating the unsymmetrical compound, methylmercuric-2,4,6-trinitrophenyl. It will be described with the report on the decomposition of other unsymmetrical molecules of 2,4,6-trinitrophenyl, with hydrogen chloride (Kh.).

became a semi-fluid between the temperatures of 210° and 217°, and a liquid at 245°. When a small amount of hexanitro-mercuridiphenyl was mixed with it the melting-point range was not affected. Combustions were made on some of this purified sample.

Anal. Subs., 0.1074; 12.6 cc. of dry N_2 (24°, 747 mm.). Calcd. for $C_{12}H_4N_6O_{12}Hg$: N, 13.46. Found: 13.26.

It is evident from these results that the unsymmetrical molecule has decomposed into two symmetrical molecules, namely, hexanitro-mercuridiphenyl and mercuridimethyl, which latter product, however, has not been definitely identified.[10]

The Preparation of Phenylmercuric-2,4,6-trinitrobenzoate, $(NO_2)_3.C_6H_2.COOHg\text{-}C_6H_5$.—To 3 g. of silver trinitrobenzoate, suspended in 30 cc. of benzene, was added 2.4 g. of phenylmercuric chloride, and the mixture was shaken until reaction had taken place. This was shown by the fact that the mixture became white and thick, resembling an emulsion. After the mixture had been shaken for 30 minutes it was transferred to a Wiley extractor, 20 cc. more of benzene added, and the product was extracted for several hours. After a time the substance, which is very soluble in hot benzene, showed in the filtrate. After extraction, the salt, a light, fluffy precipitate, was collected on a filter and dried in a vacuum over sulfuric acid; yield, 3.1 g.; m. p., 228°.

Anal. Subs., 0.2162: 15.4 cc. of dry N_2 (24°, 742 mm.). Calcd. for $C_{13}H_7N_3O_8Hg$: N, 7.88. Found: 7.99.

The product is a soft, white, crystalline substance, resembling matted, fine fibrous threads. It is very soluble in hot benzene, also in acetone, giving a yellow solution, and rather insoluble in cold alcohol or ether.

The Preparation of Phenylmercuric-2,4,6-trinitrophenyl, $(NO_2)_3.C_6H_2.Hg.C_6H_5$.—Two g. of phenylmercuric-2,4,6-trinitrobenzoate was placed in a Pyrex test-tube which was connected to a high-vacuum pump and heated to 222°. At this temperature, which was maintained for five minutes, the product turned slightly darker and began to shrink. At 226° melting on the edges was just apparent and the product turned darker. After five minutes, the bath was heated to 228° and as soon as the compound began to melt on the bottom, the tube was removed and the pump disconnected. The grayish product obtained was washed with 15–20 cc. of ether and the solid collected on a filter. The melting point of the ether-soluble fraction was 208°. The residue after the ether washing was a light grayish-tan product; yield, 1.73 g.; m. p., 227°, over a range of 10°. This precipitate was then dissolved in hot benzene, the solution filtered and the filtrate allowed to cool. A solid separated which was collected on a filter and washed well with ether. The solid was then dried in a vacuum over sulfuric acid. The product thus obtained was a cream-colored, fine powder and melted sharply at 227.5°. A considerable depression of the melting point was observed when the substance was mixed with hexanitro-mercuridiphenyl.

Anal. Subs., 0.2245, 0.2280, 0.1753; 17.4, 17.8, 13.4 cc. of dry N_2 (at 23°, 27°, 27°, and 744, 740, 748 mm., respectively). Calcd. for $C_{12}H_7N_3O_6Hg$: N, 8.59. Found: 8.75, 8.65, 8.56.

The cream-colored powder obtained was found to be soluble in hot benzene, crystallizing from cold benzene; it is only slightly soluble in alcohol and ether, and is soluble in acetone.

The Behavior of Phenylmercuric-2,4,6-trinitrophenyl with Mercuric Chloride.—To 0.9 g. of phenylmercuric-2,4,6-trinitrophenyl, suspended in 60 cc. of alcohol, was added 0.6 g. of mercuric chloride. The mixture was refluxed on the hot-plate for three hours until wholly dissolved and until the solution gave no test for free mercury with stannous chloride in hydrochloric acid. It was then filtered hot and cooled in an ice-bath. A solid separated and was collected on a filter; weight, 0.6 g.; m. p., 251°. When mixed with known phenylmercuric chloride, the melting point was 247°. The filtrate was concentrated to about one-half its volume and more substance separated, which proved to be more phenylmercuric chloride. The filtrate was then evaporated to dryness. The solid thus obtained (0.6 g.) was identified as trinitrophenylmercuric chloride; m. p., 200°. The melting point showed no depression when mixed with some trinitrophenylmercuric chloride prepared by another method. Consequently, the two end products obtained prove without a doubt that the original compound must have been an unsymmetrical molecule of the formula given under its preparation. $C_6H_5Hg.C_6H_2(NO_3)_3 + HgCl_2 \longrightarrow C_6H_5HgCl + (NO_2)_3.C_6H_2.HgCl$.

The Preparation of *p*-Tolylmercuric-2,4,6-trinitrobenzoate, $(NO_2)_3.C_6H_2COOHg.C_6H_4.CH_3$.—To 5.8 g. of silver trinitrobenzoate suspended in 150 cc. of benzene, was added 3.3 g. of tolylmercuric chloride. The mixture was refluxed for 1.5 hours, and at the end of this time the filtrate gave a negative test for halogen. The precipitate was extracted in a Wiley extractor, first with benzene and then with acetone. The benzene extract was evaporated almost to dryness over a water-bath, then transferred to a porous plate and dried in a vacuum over sulfuric acid. The product obtained was a grayish-white substance, resembling finely matted asbestos; yield from the benzene extract, 3.8 g.; m. p. 234–237°, a gas being given off at this temperature. The acetone extract yielded a red liquid which when evaporated to dryness gave a brown, sticky residue. The yield was about 0.1 g. but the product was rejected. It is very soluble in hot benzene (from which it crystallizes upon cooling), is soluble in acetone and practically insoluble in cold alcohol, ether or toluene.

Anal. Subs., 0.1288: 8.6 cc. of dry N_2 (21°, 744 mm.). Calcd. for $C_{14}H_9O_8N_3Hg$: N, 7.67. Found: 7.59.

The Preparation of *p*-Tolylmercuric-2,4,6-trinitrophenyl, $(NO_2)_3.C_6H_2Hg.C_6H_4.CH_3$.—The elimination of carbon dioxide from this molecule was carried out as described for the phenyl derivative. A 2g. sample was used. At 200° the product began to darken. The sulfuric acid bath was heated slowly to 225° and kept there for five minutes, during which time the product shrank somewhat and turned slightly darker. At 232° it turned a very dark gray and there was evidence of melting on the edges and of evolution of a gas. After five minutes the tube was removed and cooled. The grayish-black product obtained was first washed with ether. The ether washings were evaporated leaving a solid that melted at 188°. The product remaining after the ether washing (1.7 g.) was extracted in a Wiley extractor, using toluene as the solvent. An orange-colored solution was obtained which was concentrated on a water-bath to a volume of 10 cc. and then filtered hot. The filtrate was evaporated to dryness on the water-bath, and yielded a fine orange-tan colored powder; m. p., 203° sharp. A considerable depression of the melting point was observed when the product was mixed with hexanitro-mercuridiphenyl.

Anal. Subs., 0.2715, 0.1589; 20.3, 12.12 cc. of dry N_2 (20°, 24.5° and 740 mm.). Calcd. for $C_{13}H_9N_3O_6Hg$: N, 8.33. Found: 8.48, 8.52.

This product was treated with mercuric chloride in alcoholic solution, in a manner similar to that described for the phenyl compound, and the end products were identified by melting points to be tolylmercuric chloride and 2,4,6-trinitrophenylmercuric chloride.

Summary

1. An extension of the method of Kharasch for the preparation of unsymmetrical mercuri-organic compounds is described.

2. The decomposition of these unsymmetrical molecules with mercuric chloride and hydrogen chloride is recorded.

3. It has been shown that both tolyl and phenyl are more strongly electronegative radical than is 2,4,6-trinitrophenyl.
4. The preparation of a number of new compounds is described.

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[Contribution from the Carnegie Institution of Washington]

STUDIES IN SWELLING. I. THE SWELLING OF AGAR-AGAR GELS AS A FUNCTION OF WATER CONTENT BEFORE SWELLING[1]

By Beverly L. Clarke

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The purpose of this paper is to present experimental results which indicate the general form of the curve obtained when the percentage swelling of agar-agar gels in distilled water is plotted against the water content of the gel immediately before swelling.

This work was suggested when thin agar plates, originally prepared in this Laboratory by the method described by MacDougal,[2] were found to have undergone some change incident upon standing in air for three years, which reduced the swelling in distilled water, more than 3000% when freshly prepared, to less than 1000%. The swelling capacity in various solutions had decreased proportionately.

In attempting to explain this "aging" effect, the author found that agar plates could be artificially "aged," that is, their swelling could be greatly reduced, by simply placing them in an oven at 70° for two days. The same result was obtained by placing the plates in a desiccator over sulfuric acid for a somewhat longer time.

The inference that "aging" in the case of agar is at least accompanied by desiccation was thus firmly established. It was possible to reduce the swelling of the three-year-old plates still further by placing them over sulfuric acid for some days.

In the light of the modern theories of gel structure, it is probable that some structural alteration accompanies the drying out. This change is probably in the direction of agglomeration of particles to reduce the specific absorbent surface. Since the decrease in swelling, which develops slowly at ordinary temperatures and under normal pressures of aqueous vapor ("natural aging"), may be enormously accelerated at higher temperatures and under low vapor pressures ("artificial aging"), it seems necessary to assume that the structural change follows and is a consequence of the loss of water.

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[1] Presented before the Southern Arizona Section of the American Chemical Society, April 9, 1925, at Tucson, Arizona.

[2] MacDougal, *Botan. Gaz.*, **70,** 2 (1920).