Studies on Organic Reagents for the Colorimetric Analysis of Germanium. II. Synthesis of a New Reagent and its Reaction with Germanium

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In the previous report[1] it was observed that the absorption band of the solution of heterocyclic compounds such as fluorone and cumarine derivatives shows red shift in the presence of germanium. The authors examined many organic reagents for germanium which have been reported so far by other workers[2,3,4,5]. The results of the experiments showed that among these reagents phenylfluorone is the best because it has high sensitivity for germanium. In addition, the analytical procedure using this reagent is simple, and the reaction is obstructed by few ions. On the other hand, it forms slightly soluble compound with germanium. This makes colorimetric determination very difficult. Moreover, the absorbancy of the colored solution varies with the time elapsed since the solution was prepared. In this study, therefore, the present authors tried

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[1] K. Kimura, K. Saito and M. Asada, This Bulletin **29**, 635 (1956).

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[3] H. J. Cluley, *Analyst*, **76**, 523 (1951).

[4] C. K. N. Nair and J. Gupta, *J. Sci. Ind. Research*, **10 B**, 300 (1951); ibid., **11 B**, 274 (1952).

[5] Y. Oka and S. Matsuo, *J. Chem. Soc. Japan*, **74**, 931 (1953).

to synthesize a new reagent which is similar to phenylflurone but has none of such defects as described above.

Since it is very difficult to find out a specific reagent for germanium, germanium has to be separated from other elements before it is subjected to quantitative determination. The best procedure for the separation of a trace of germanium seems to be the distillation of germanium tetrachloride from a fairly concentrated hydrochloric acid solution. If we could determine germanium in the distillate with or without simple pretreatment, the procedure would be very convenient for analysis. For this reason it is desirable to find out a new reagent which reacts specifically with germanium, forming a soluble complex in a strongly hydrochloric acid solution. The authors considered that one of the phenylfluorone derivatives, 2, 6, 7-trihydroxy-9-(4′-dimethylaminophenyl)-fluorone, is a reagent suitable for such purpose. Hereafter we call this reagent dimethylaminophenyl-fluorone. Since such a compound has never been described in the literature of the subject, the authors tried to synthesize this reagent by similar procedure which was widely used for the synthesis of phenylfluorone and its analogous compounds⁶⁾.

Experiment

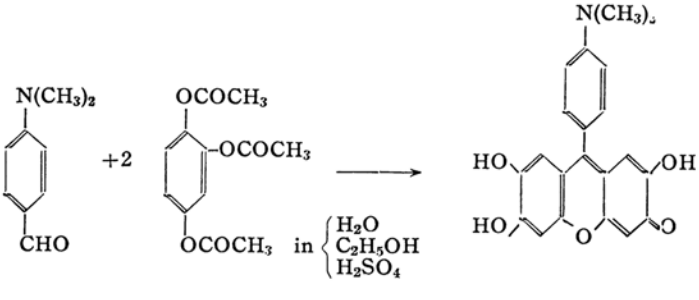
The Synthesis of the New Compound

Reagents Used.—*p-Dimethylaminobenzaldehyde*: First-grade reagent prepared by Tokyo Kasei Ind., Co. Japan, was used without any purification.

Hydroxyhydroquinone triacetate: The reagent was synthesized⁷⁾ from commercial *p*-benzoquinone, anhydrous acetic acid and concentrated sulfuric acid. Recrystallized twice from 95% ethanol solution.

Ethanol: Commercial 95% ethanol.

The Procedure for Synthesis.—To a mixture of 160 ml. of ethanol, 160 ml. of water and 16 ml. of concentrated sulfuric acid in a round-bottomed flask was added 37 g. of hydroxyhydroquinone triacetate and 11 g. of dimethylaminobenzaldehyde*. Under a reflux condenser the solution was heated in a water bath for twenty hours. Then the solution was allowed to cool until the precipitation of orange crystalline substance was completed. The precipitate was filtered and washed with water until the red color of the washing solution almost disappeared. The crystals seemed to be hydrolyzed easily and the colour of crystals was changed after washing. The precipitate on the filter paper was mixed with a larger amount of water and the system was heated until the hydrolysis was complete. The hydrolyzed precipitate was filtered under suction, washed thoroughly with water and dried in a vacuum desiccator. To 1 to 2 g. of the product was added a mixture of 50 ml. of ethanol, 50 ml. of water and 5 ml. of concentrated sulfuric acid. The resulting system was heated on a water bath to dissolve the precipitate. The small amount of active charcoal was added to the resulting solution. The charcoal adsorbed a dark-reddish brown substance which was supposed to be a polimerized product. The suprenatant solution was filtered through a hot funnel. The cooling of filtrate resulted in the formation of yellowish orange crystalline precipitate. The precipitate was filtered, washed thoroughly with a small amount of the mixture of ethanol and water. And then it was mixed with a large amount of water. The hydrolysis of the precipitate was performed by heating. The filtration, washing and drying up of the precipitate was repeated several times for the purpose of recrystallization. The authors are of the opinion that the followtng reactions occurred in this procedure.



Anal. Found: C, 68.10; H, 4.75; N, 4.07. Calcd.: C, 69.30; H, 4.69; N, 3.83%.

Properties of the Product.—M. p. >250°C. Colour: Red, Green fluorecence. Form: While the sulfate forms plate-like crystals, its hydrolyzed product is powder. Solubility: Insoluble in water. Slightly soluble in ethanol, giving an orange solution.

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6) C. Lieberman and S. Lindenbarum, *Ber.*, **37**, 1171 (1904); ibid., 2728; F. Kehrmann and M. Gunther, *Ber.*, **45**, 2884 (1923); W.R. Orndorff and C. Wang, *J. Am. Chem. Soc.*, **47**, 290 (1925); ibid., **49**, 1284 (1927); Rajendra Nath Sen and Nripendra Nath Sarkar, ibid., **45**, 2984 (1923); ibid., **47**, 1079 (1925).

7) "Organic Syntheses, Collective Volume I", John Wiley & Sons Inc., New York (1948), p. 317.

* Two mol. of hydroxyhydroquinone triacetate and one mol. of dimethylaminobenzaldehyde are used to prepare the reagent. A mixture of ethanol, water and concentrated sulfuric acid in the proportion of 10:10:1 was used as a solvent to dissolve the above compounds. The proportion of each compound in the solvent and the amount of the solvent are fixed at such values that the compounds were completely dissolved and the yield of the resulting product was maximum.

The addition of acid to the ethanol solution of the compound increased its solubility and the colour of solution became deep red. When the addition of acid was continued further, the red colour of solution was diminished and changed from orange to yellow. At the same time, the solubility was decreased. The concentration of acid which was necessary to change the colour of the solution was dependent on the amount of the reagent in the solution.

Absorption Curves of the Reagent Solution.—The following samples were used to measure absorption curves. The original solution was prepared by dissolving 1 mg. of new compound in 50 ml. of ethanol.

Sample 1: 5 ml. of the original solution was diluted with ethanol to 25 ml.

Sample 2: The original solution was mixed with 2 ml. of 0.2 N -HCl and diluted with ethanol to 25 ml. The concentration of acid in the resultant solution was 0.016 N.

Sample 3: The original solution was mixed with 2 ml. of 2 N-HCl and diluted with ethanol to 25 ml. The final acid concentration was 0.16 N.

Sample 4: The original solution was mixed with 2 ml. of 6 N HCl and diluted with ethanol to 25 ml. The final acid concentration was 0.48 N.

Sample 5: The original solution was mixed with 5 ml. of 6 N-HCl and diluted with ethanol to 25 ml. The final acid concentration was 1.2 N. The results are shown in Fig. 1.

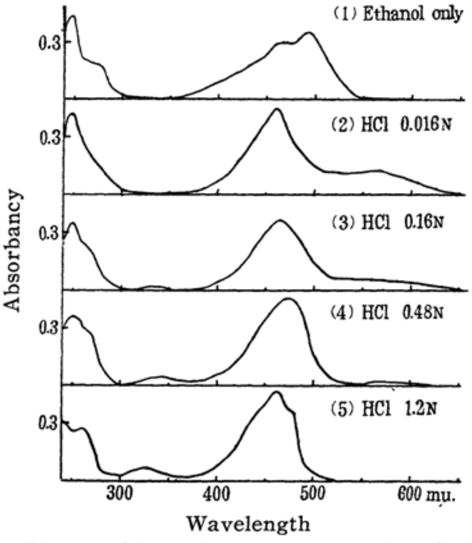


Fig. 1. Absorption curves of dimethylaminophenylfluorone.

In strongly acidic solution in which the effect of amino group is almost negligible, the absorption curve of this compound is very similar to that of phenylfluorone. Considering the above-mentioned properties as well as the procedure for synthesis, there is little doubt that the compound is a reagent suitable for our purpose. For the measurement of absorption spectra, the commerical 95% ethanol was purified until the substance such as aldehyde showing the absorption bands at the near ultraviolet region was completely eliminated.

Reaction of the New Compound with Germanium

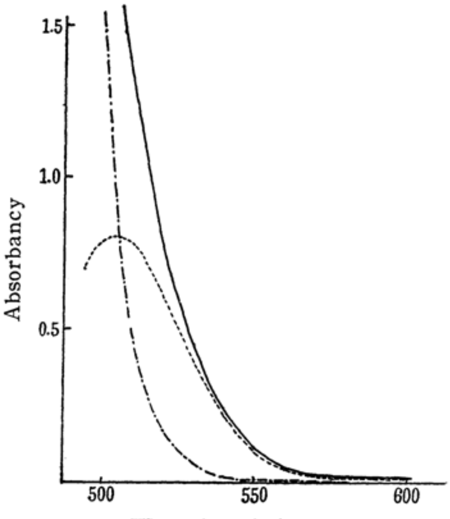
Reagents Used.—Germanium standard solution: The germanium dioxide used in this experiment was prepared by Tokyo Gas Co.. The standard solution was made by dissolving 1.00 g. of water-soluble powder (99.9% GeO_2) in hot water. Then the volume of the resulting solution was adjusted to 1 liter.

Two ml. of this solution was taken in 200 ml. volumetric flask and diluted up to 200 ml. The final solution contained 10.0 μg. of GeO_2 [6.94 μg. of Ge) per ml. The solution could not be preserved for a long time without the change of concentration.

0.05% solution of dimethylaminophenylfluorone: 0.050 g. of dimethylaminophenylfluorone was dissolved by heating in a mixture of approximately 80 ml. of ethanol and 5 ml. of 6 N-hydrochloric acid. After cooling, the solution was diluted with ethanol until the volume of solution became 100 ml. The final solution was deep red and contained 0.05 per cent of dimethylaminophenylfluorone by weight.

Hydrochloric acid: Commercial first-grade reagent (sp. gr. 1.2) was diluted with water.

Procedure.—Two ml. aliquots of standard GeO_2 solution were taken in four 25 ml. volumetric flasks. Then 1.3 ml., 6.3 ml. and 12.5 ml. of 2 N-HCl were added to the first three volumetric



—·—·— 0.01% Dimethylaminophylfluorone soln. only (reference soln.: distilled water)

———— Germanium added (〃)

------ Complex between Ge and dimethylaminophenylfluorone (reference soln.: 0.01% dimethylaminophenylfluorone soln)

Fig. 2. Absorption curves of the complex between germanium and dimethylaminophenylfluorone.

flasks respectively and 8.3 ml. of 6 N-HCl was added to the last volumetric flask. The volume of each solution was made up to approximately 15 ml. To the resulting solutions were added 5 ml. aliquots of 0.05% dimethylaminophenylfluorone solution and the final volume of the solutions were adjusted to 25 ml. The final concentration of hydrochloric acid in the solutions obtained are 0.1 N, 0.5 N, 1 N and 2 N, respectively. Four reference solutions were prepared without adding germanium. These solutions were compared with those containing germaium. The results are summarized in Table I.

TABLE I

Concentration of HCl	Reaction with Germanium
0.1 N	Red orange colour appeared immediately after the addition of reagent.
0.5 N	Same as above.
1 N	Orange colour appeared 5 minutes after the addition of reagent.
2 N	No change was observed.

After the addition of reagent, the solution contained 0.01% dimethylaminophenylfluorone by weight and 0.56 μg. of germanium per ml. Even when these solutions were kept standing for about fifty hours, no precipitate appeared. The absorption spectrum of the obtained complex is shown in Fig. 2. The figure shows the absorption spectrum of the complex in 0.5 N-HCl.

Conclusion

An attempt was made to synthesize a new colorimetric reagent for germanium which has no such defects as was observed in the other reagents. Using a comparatively simple procedure, a crystalline substance was obtained, which was found to be suitable for our purpose. The authors call this reagent dimethylaminophenylfluorone. The compound reacts with germanium in an acid solution and forms a soluble complex. The present experiments led us to the conclusion that this compound is an excellent reagent for the colorimetric analysis of germanium.

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