

The arylamino-ethanols have been found to unite with the aryl-isothiocyanates and isocyanates and from the ureas thus obtained have been synthesized thiazolidines and oxazolidines of known structure.

In like manner the aryl-amino-propanols gave thio-ureas, which under the influence of acids, condensed to a 6-membered thiazane ring.

The  $\alpha$ -arylamino- $\beta$ -hydroxy- $\gamma$ -chloropropanes combined with mustard oils and formed the 5-hydroxy-thiazanes.

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[CONTRIBUTION FROM THE BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

## THE ESTIMATION OF ALIPHATIC NITRATE ESTERS IN THE PRESENCE OF CERTAIN NITRO-AROMATIC COMPOUNDS<sup>1</sup>

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Storm,<sup>4</sup> in a paper from this Laboratory, has shown that glycerine trinitrate in the presence of mononitro compounds cannot be estimated by means of the nitrometer, since the mononitro aromatic substance is converted into the dinitro compound, and the reading is correspondingly low.

To overcome this difficulty, Hyde,<sup>5</sup> in another paper from this Laboratory, proposed the separation of the glycerine trinitrate from the nitro derivative by treatment with immiscible solvents, one phase of which was carbon disulfide, while the second phase was a mixture of 75 parts of acetic acid and 25 parts of water. The technique involved in this method is so exacting, however, that it has apparently never been widely used and in this Laboratory is at present practically abandoned.

We have made preliminary experiments which appear to promise a convenient solution for this problem. Since it now appears that neither of us will have an opportunity to complete the study in the near future, we are reporting the results as they stand, with suggestions for further experiments.

Essentially, the method is that developed at the Kent Chemical Laboratory of Yale University by I. K. Phelps<sup>6</sup> for the estimation of inorganic nitrates.

The apparatus employed consisted of a 250 cc. Kjeldahl flask carrying a tight 2-holed rubber stopper in which was inserted a long-stemmed separatory funnel whose tip was drawn to a capillary so that it always stood full of liquid. An 8 mm. tube carrying a bulb to prevent splashing was also inserted in this stopper. This tube was bent twice at right angles and

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<sup>4</sup> Storm, *Eighth Inter. Cong. Appl. Chem.*, **4**, 117 (1912).

<sup>5</sup> Hyde, *THIS JOURNAL*, **35**, 1173 (1913).

<sup>6</sup> Phelps, *Am. J. Sci.*, [4] **14**, 440 (1902). Gooch, "Methods of Chemical Analysis," John Wiley and Sons Co., 1912, p. 259.

dipped below the surface of a shallow layer of mercury in a 250cc. Erlenmeyer flask. To prevent fouling of the mercury surface, a quantity of sodium carbonate and about 50 cc. of water were placed upon it.

At the beginning of each analysis, about 25 cc. of distilled water was placed in the Kjeldahl flask. This was then boiled vigorously, thus sweeping the air out of the system. The weighed nitrate ester, or its mixture with the nitro compounds, was meanwhile dissolved in glacial acetic acid and placed in the bulb of the separatory funnel. When the system was quite free from air, the flame was cautiously withdrawn, and the acetic acid solution of the sample run into the flask and rinsed down, first with a small quantity of glacial acetic acid and then with an excess but a known volume of standard ferrous sulfate solution, containing in addition sufficient sulfuric acid to prevent separation of the basic salt. This in turn was followed by conc. hydrochloric acid in volume approximately equal to the total volume of liquid in the flask previous to its introduction. The solutions were admitted only slowly, and the flame applied and withdrawn as needed. With care, the introduction of the solutions was easily accomplished without admitting air or mercury from the trap. The reaction mixture was then evaporated to a volume of some 10 or 15 cc. The residual acid was then nearly neutralized by a solution of sodium carbonate, the evolution of the carbon dioxide assisting in preventing the admission of mercury during the cooling process. When cool, the solution was diluted to a volume of about 600 cc. and transferred to a porcelain casserole; 2 or 3 g. of crystallized manganous sulfate was added, and the residual ferrous salt determined by titration with standardized potassium permanganate solution. From this value and the titer of the ferrous solution initially added, the quantity of nitrate ester is calculated.

Following are results obtained by the methods.

TABLE I  
RESULTS

Nitro aromatic substance taken	Wt. G.	Nitrate ester taken	Wt. of ni- trate ester				
			Wt. G.	KMnO <sub>4</sub> Cc.	found G.	Error G.	Error %
<i>p</i> -Nitrotoluene..	0.2186	None	....	0.10	Error 0.10 cc. of KMnO <sub>4</sub> solution		
None.....	none	Glycerine tri- nitrate	0.2162	42.18	0.2117	0.0045	-2.06
<i>p</i> -Nitrotoluene..	0.3070	Glycerine tri- nitrate	0.1992	39.08	0.1961	0.0031	-1.56
None.....	none	Mannite hexa- nitrate	0.0816	16.33	0.0816	0.0000	0.00
None.....	none	Mannite hexa- nitrate	0.1784	35.68	0.1783	0.0001	-0.06
Dinitrotoluene...	0.2036	Mannite hexa- nitrate	0.1722	34.20	0.1709	0.0013	-0.75
1 cc. of KMnO <sub>4</sub> solution = 0.005018 g. of glycerine trinitrate = 0.004996 g. of mannite hexanitrate.							

These results show conclusively that no important interference with the nitric-acid-ferrous-iron reaction is interposed by the organic matter present, and the method appears sufficiently promising to permit its use in the general estimation of aliphatic nitrate esters by those laboratories which do not have a nitrometer conveniently at hand.

It will be noted that the method gave low results with glycerine trinitrate, while with the mannite hexanitrate the results correspond closely with the calculated results. Glycerine trinitrate has an appreciable vapor tension<sup>7</sup> at 100° and part of this loss, at least, may have been due to the vaporization of the ester in steam before it was completely hydrolyzed. If so, this error could probably be eliminated by introducing the sample into a cold reaction mixture, followed by the gradual elevation of the reaction temperature. To insure absence of oxidation it would of course be necessary to replace the air by an inert gas.

Titration of the residual ferrous iron with potassium permanganate is impossible when the mixture contains nitro compounds which develop interfering colors, notably trinitrotoluene. Though not investigated, this difficulty may apparently be diminished or possibly completely overcome by estimating the ferric iron through reduction by hydrogen iodide in acid solution, since the color change, from starch blue to the acid ferrous iron, should not be seriously affected by the yellow-to-red shades imparted by the interfering nitro compound.

### Summary

Aliphatic nitrate esters may be estimated in the presence of certain nitro aromatic compounds by reduction with ferrous sulfate in excess, followed by titration of the unoxidized ferrous salt. A procedure sufficiently promising to permit its general use is described, together with suggestions for further experiments.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## THE PREPARATION OF 1,4-DIHALOGEN DERIVATIVES OF BUTANE

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The 1,4-dihalogen derivatives of butane are reagents that would be used more frequently in the organic laboratory if they were available. Several methods for their preparation have appeared in the literature but all are difficult to carry out. Probably the best method heretofore developed is that of J. von Braun for the preparation of tetramethylene bromide by splitting benzoyl pyrrolidine with phosphorus pentabromide.<sup>1</sup> This

<sup>7</sup> Marshall, "Explosives," P. Blakiston's Sons and Co., 1917, p. 735.

<sup>1</sup> von Braun, *Ber.*, **39**, 4119-25 (1906).