recrystallized from acetone. A crystalline material melting at 232° was obtained (yield 12 g.).

Anal. Calcd. for $C_{42}H_{30}O_3$: C, 86.2; H, 5.5. Found: C, 86.5, 86.3; H, 5.6, 5.3.

When a sample of the anhydride was boiled with alcoholic sodium hydroxide and the solution acidified, the di-triphenylmethylsuccinic acid was formed. It was identified by conversion to the dimethyl ester whose melting point is more satisfactory.

Summary

Triphenylmethyl and benzylxanthyl have been found to add in the 1,4 position to certain 1,3-dienes and pyrrole. Two molecules of triphenylmethyl combine with the ethylenic linkage of maleic anhydride.

CAMBRIDGE, MASSACHUSETTS

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The Micro Estimation of Sulfur and Phosphorus in Organic Compounds

BY ADALBERT ELEK AND DOUGLAS W. HILL[1]

In a previous communication a micro-bomb was described for the quantitative micro determination of halogens in organic compounds.[2] The sample to be analyzed was oxidized in the bomb by means of sodium peroxide. From the success of the method in this instance it appeared probable that other estimations requiring a similar preliminary destruction of the organic material might be rapidly and successfully carried out in this apparatus. We therefore turned our attention to the estimation of organically bound sulfur and phosphorus.

Up to this time the majority of micro-estimations of sulfur in organic combination have been performed either by the combustion of the substance or by a micro modification of the Carius procedure. The use of the micro-bomb previously described[3] is much to be preferred to these methods in point of time, accuracy and ease of manipulation. The exact procedure for the determination is given in the experimental part.

The estimation of phosphorus has previously been accomplished by combustion of the substance or by heating it several times with a mixture of concentrated sulfuric and nitric acids with subsequent addition of perhydrol. A further method, which has been successfully employed in this Laboratory, was described by one of us[4] and involves the fusion of the sample under investigation with a mixture of potassium nitrate and po-

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(1) Commonwealth Fund Fellow.

(2) Elek and Hill, THIS JOURNAL, **55**, 2550 (1933).

(3) Supplied by The Parr Instrument Co., Moline, Ill. (Since our previous communication illium alloy has been found to have certain advantages over platinum plating and the present bombs are constructed of this metal.)

(4) Elek, THIS JOURNAL, **50**, 1213 (1928).

tassium hydroxide in an open dish. The present method has an advantage over this in that, since all the materials are enclosed in the bomb, there is no possibility of loss by spattering. It seems obvious from our previous communication that, in the case of liquid organic phospho compounds, the present method might have a decided advantage.

In all these methods the phosphorus is estimated as ammonium phosphomolybdate. The composition of this salt as precipitated is not exactly known, but Lorenz has shown[5] that if the same quantities of reagents are used and the same method followed, precipitates of the same composition are obtained, so that an empirical but accurate factor for the phosphorus may be used. We have used the factor 0.014524 consistently. Lieb[6] uses the factor 0.014525 and Kuhn,[7] who examined the method for the determination of very small amounts of phosphorus, uses 0.01456.

The object of this communication has been to show that the use of the micro-bomb can be extended to estimations other than of halogens. We see no reason why the method should not be equally applicable to the estimation of such elements as selenium, arsenic and antimony.

Experimental

Determination of Sulfur.—The fusion is made in exactly the same way as previously described for the estimation of the halogens.[2] It is important that the rubber washer between the lid and the cup be boiled with caustic soda before making any determinations. In the bottom of the bomb are placed 30 mg. of a mixture of potassium nitrate and sugar (3:1) and 3 to 10 mg. of the sample to be analyzed is added. This is covered with 1.5 g. of sodium peroxide and after clamping the lid in position, the whole is well shaken. As in the case of the halogen estimations the success of the analysis depends to a large extent on the successful admixture of the contents of the bomb. Fusion is made by holding the bomb in a good Bunsen flame, taking care not to heat too near the lid. It is then cooled under the tap and opened. The lid is rinsed with hot distilled water and the washings collected in a test-tube 200 mm. in length and 20 mm. in diameter. The bomb and its contents are placed in the test-tube and more hot water added to about 15 cc. When the fused mass is completely dissolved the bomb is lifted out by means of a stiff platinum wire and rinsed with a small amount of hot distilled water. The solution is cooled in ice and when cold 5 cc. of concentrated hydrochloric acid is added slowly. The acid solution is filtered with slight suction to remove any particles of carbon and the test-tube and filter are washed with water.

The filtrate is transferred to a 150-cc. beaker with the usual rinsing and evaporated on the water-bath to a small volume (5 to 10 cc.). This small volume is then transferred to a round-bottomed Pyrex glass dish with a lip and of 50 cc. capacity. The dish must be steamed several times before the first usage. It has been found beneficial to evaporate the majority of the water in a beaker since the operation can be carried out more quickly and with less fear of creeping than in a dish. To the liquor in the dish, after transferring from the beaker, is added 1 cc. of a 2.5% solution of barium chloride and the whole evaporated to dryness. The solid residue is moistened with 10% hydrochloric acid and the evaporation repeated. Once is sufficient for this operation.

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(5) Lorenz, *Z. anal. Chem.*, **51**, 161 (1912).

(6) Lieb, "Quantitative Organic Microanalysis," Pregl., 2d. ed., 1930, p. 153.

(7) Kuhn, *Hoppe-Seylers Z.*, **129**, 66 (1923).

The final solid residue is taken up in 25 cc. of distilled water and allowed to stand overnight. The barium sulfate is filtered off in the manner described by Pregl[8] by first decanting the supernatant liquid into a micro Neubauer crucible without disturbing the precipitate in the bottom of the dish. Warm distilled water acidified with about 1% hydrochloric acid is then added and the precipitate stirred up. This is a more effective way of removing occluded soluble material in the precipitate than washing on the filter. The remainder of the operation is carried out exactly as described by Pregl, using water and alcohol alternately to remove the precipitate completely.

Table I gives the results obtained with some sulfur compounds analyzed by this method. The reagents must be completely free from sulfur and all the compounds on which data are given in this communication were purified before analysis.

TABLE I

Substance	Sample, mg.	$BaSO_4$, mg.	Sulfur found, %	Sulfur calcd., %
6-*p*-Tolylsulfo-1,2-monacetone-3,5-benzylidene glucose	8.210	4.234	7.08	6.93
5-Acetyl-*p*-tolylsulfo monacetone xylose	7.685	4.700	8.40	8.30
	9.360	5.685	8.34	8.30
p-Toluenesulfonyl chloride	6.390	7.835	16.84	16.83
	6.612	8.150	16.93	16.83
Thiourea	3.630	11.160	42.24	42.20
	4.639	14.230	42.13	42.20

Determination of Phosphorus.—The sample to be analyzed (3 to 10 mg.) is fused with sodium peroxide and the fusion mixture dissolved in a small volume of water as described above. The solution, including the rinsing water, is cooled in ice and acidified with 10 cc. of nitric acid containing sulfuric acid as described by Lorenz.[5] The acid solution is filtered with slight suction and the volume of the solution and rinsing water measured. It is then transferred to a thick-walled test-tube 200 mm. in length and 45 mm. in diameter (capacity 175 cc.). After heating the solution for ten minutes in the water-bath there is added an equal volume of sulfate–molybdate solution, prepared according to the directions of Lorenz.[5] The yellow precipitate is allowed to settle overnight and filtered in the manner described by Lieb[6] using 2% ammonium nitrate solution and alcohol alternately to wash the test-tube and precipitate.

The following table gives the results obtained with phosphorus-containing compounds analyzed by this method.

TABLE II

Substance	Sample, mg.	Ammonium phosphomolybdate, mg.	Phosphorus found, %	Phosphorus calcd., %
Sodium glycerophosphate	4.990	42.220	12.29	12.30
	5.320	45.100	12.31	12.30
Strychnine hexosediphosphate	3.836	16.089	6.09	6.15
	4.033	16.860	6.07	6.15
Tyrosinephosphoric acid	4.315	35.481	11.94	11.90

Summary

The use of the micro-bomb designed for the estimation of halogens in organic compounds has been extended to other elements.

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[8] Pregl, "Quantitative Organic Microanalysis," 2d ed., 1930, p. 143.

Results for the analysis of organically combined sulfur and phosphorus are given.

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Saponification of Diarylnitrosamines and Attempts to Prepare a Salt of Aquo-ammononitrous Acid

BY W. CONARD FERNELIUS AND GEORGE W. WATT

In accordance with Franklin's ammonia system of compounds, the substance represented by the formula H_2NNO may be regarded as an aquo-ammononitrous acid.[1] The nitrosamines, then, are esters of this acid and should yield salts upon saponification: $R_2NNO + 2KNH_2 \longrightarrow R_2NK + KHNNO + NH_3$.

The present study has shown that potassium amide in liquid ammonia solution reacts readily and completely with the aromatic nitrosamines to form not a salt of aquo-ammononitrous acid, but rather nitrogen gas and potassium hydroxide, possible decomposition products of an extremely unstable salt, KHNNO: $R_2NNO + 2KNH_2 \longrightarrow R_2NK + KOH + N_2 + NH_3$. This reaction has been found to take place quantitatively in liquid ammonia solution with both diphenylnitrosamine and di-*p*-tolylnitrosamine and with a number of basic amides. No direct evidence was found for the formation of the salt KHNNO as an intermediate product. Attempts to saponify diphenylnitrosamine dissolved in toluene with solid sodium amide gave low yields of nitrogen and tarry products. Although fused hydroxides effect a saponification of the nitrosamines,[2] it was found that diphenylnitrosamine is not saponified by alcoholic potassium hydroxide.

A brief study of the reactions of methylphenylnitrosamine and dibenzylnitrosamine with potassium amide in liquid ammonia solution has shown that these nitrosamines do not react in a manner similar to diphenylnitrosamine and di-*p*-tolylnitrosamine, since no nitrogen is liberated and there is no evidence of the formation of the metal salts of the parent amines.

Experimental

In carrying out the liquid ammonia reactions described in this paper, the familiar technique of Franklin and his co-workers[3] was employed. Gases evolved during a reaction were collected in the manner described by Bergstrom.[4]

Preparation of Materials.—The diphenylnitrosamine used in these experiments, an

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[1] Franklin, "Liquid Ammonia as a Solvent and the Ammonia System of Compounds," A. C. S. Monograph, in press. *Cf.* Fernelius and Johnson, *J. Chem. Ed.*, **7**, 1854 (1930).

[2] Bamberger, *Ber.*, **27**, 1179 (1894); *cf.* **33**, 1957 (1900).

[3] For references see Schurman and Fernelius, THIS JOURNAL, **52**, 2427 (1930).

[4] Bergstrom, *ibid.*, **47**, 2320 (1925); *cf.* Johnson and Fernelius, *J. Chem. Ed.*, **6**, 449 (1929).