

We early suggested<sup>1</sup> the determination of active hydrogen by dissolving the unknown in deuterium oxide followed by a determination of the changed density of the water distilled off. Others<sup>2,3</sup> have independently made use of the principle.

An experimentally simple embodiment of the same principle has now occurred to us which consists merely in dissolving the substance to be analyzed in deuterium oxide, evaporating to dryness and determining the increase in weight due to the replacement of active hydrogen by deuterium. This method has been applied to two known substances and the results are given in the following table. Other experimental work along similar lines which need not be detailed here has convinced us of the applicability of the method. The substances in small weighing bottles were simply dissolved in 0.25 ml. of 99.5% deuterium oxide and then carefully evaporated and dried to constant weight in vacuum desiccators, and weighed again.

Substance analyzed	Hydroxyproline			Urea		
	2H	3H	4H	3H	4H	5H
Sample, mg.						
After treatment, mg.						
Incr. after subtr. 5 $\gamma$ blank						
Calcd. increases	0.128	0.192	0.256	0.297	0.383	0.479

The theoretical increases were calculated on the basis of complete replacement by deuterium. This assumption would introduce practically no error in the first determination and a very slight error in the second. A small increase in weight, about 5  $\gamma$ , is noted when a glass weighing bottle itself is treated with heavy water.

The method need not be limited to water soluble substances since interchange should occur in ether or pyridine solution. In case of compounds which do not dry readily, appropriate means will have to be taken to bring the material to the same degree of dryness before and after treatment with deuterium oxide. Since the principle is so simple and the manipulation involves nothing beyond drying and weighing, it appears that no serious difficulty should be involved in applying the method. We hope other investigators to whom this type of work is less incidental, will perfect and extend the

(1) Roger J. Williams, "Introduction to Organic Chemistry," third edition, D. Van Nostrand Co., New York, 1935, p. 576.

(2) Bonhoeffer and Brown, *Z. physik. Chem.*, **223**, 172 (1933).

(3) Hamill and Freudenberg, *THIS JOURNAL*, **57**, 1427 (1935).

method which has been experimented with in our laboratory only in a preliminary way.

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## Some Bismuth Derivatives of Diphenyl

BY DAVID E. WORRALL

Since the number of known organic compounds of bismuth is meager, previous work on diphenyl derivatives of the arsenic group has been extended to include this element.<sup>1</sup> Arylation was accomplished through the organo magnesium compound, for the Wurtz-Fittig method employing sodium, used so successfully with other members of the group, failed with bismuth.

### Experimental

**Tri-biphenylbismuth.**—One hundred grams of *p*-bromodiphenyl was changed into the magnesium compound according to the directions of Bent.<sup>2</sup> After dilution with several volumes of ether, 36 g. of powdered bismuth chloride was added directly (in small lots) with shaking and the mixture allowed to stand overnight. The ether was removed by decantation, after which the residue was decomposed as usual. A small amount of dilute acid was added to remove basic salts. The black precipitate was then filtered, dried and extracted successively with hot alcohol and chloroform. A small amount of dibiphenyl separated from the chloroform extract on cooling, after which the filtrate was concentrated to a small volume. On the addition of an equal volume of alcohol a crystalline product formed; yield approximately 43 g.

*Anal.* Calcd. for  $C_{36}H_{27}Bi$ : C, 64.7; H, 4.0. Found: C, 65.0; H, 4.3.

It is insoluble in alcohol, but dissolves readily in chloroform, separating in the form of tiny flat needles that melt at 182–183°.

**Tri-biphenylbismuth Dichloride.**—To the above substance dissolved in carbon tetrachloride was added chlorine dissolved in the same solvent; yield nearly quantitative. The product was recrystallized from chloroform-alcohol mixture, from which it separated as small plates melting with decomposition at 198–200°, if heated slowly.

*Anal.* Calcd. for  $C_{36}H_{27}BiCl_2$ : Cl, 9.6. Found: Cl, 9.5.

The dibromide prepared in a similar manner formed pale yellow plates that melted indefinitely with decomposition when heated.

*Anal.* Calcd. for  $C_{36}H_{27}BrBr_2$ : Br, 19.3. Found: Br, 19.1.

Both halides dissolved in fuming nitric acid, forming nitro derivatives that deflagrated if heated quickly.

**Di-biphenylbismuth Chloride.**—This was prepared by the method of Challenger<sup>3</sup> using bismuth chloride with the

(1) Worrall, *THIS JOURNAL*, **52**, 664 and 2046 (1930).

(2) Bent, *THIS JOURNAL*, **54**, 1398 (1932).

(3) Challenger, *J. Chem. Soc.*, **107**, 19 (1915).

triarylbi-muth derivative in dry ether. A bright yellow powder rapidly separated out. It melted indefinitely when heated and probably contained some dichloride.

*Anal.* Calcd. for  $C_{24}H_{18}BiCl$ : Cl, 6.5. Found: Cl, 7.0.

**Tri-biphenylbi-muth Dinitrate.**—Alcoholic silver nitrate solution was added to an equivalent amount of tri-biphenylbi-muth dichloride suspended in a large volume of acetone. On concentrating the filtrate after removal of insoluble material, small plates were obtained that decomposed at approximately  $162^{\circ}$ , but deflagrated if heated quickly.

*Anal.* Calcd. for  $C_{36}H_{27}BiO_2N_2$ : Bi, 26.4. Found: Bi, 26.6.

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### Chile Seed

By W. A. BUSH

The seeds of the Chile pepper (sometimes called pimento) obtained from the pods of the Southern Pacific Coast cultural variety of *Capsicum Annuum* have received little mention in the literature from the point of view of their composition.

A representative sample of a quantity of sixteen tons of dried seeds accumulated during a year from pods mostly of Californian origin gave re-

sults differing somewhat from those obtained by Ebert and Bailey<sup>1</sup> from Southeastern seed.

Yields from the seed by drying and extraction were: oil, 26.10%; moisture, 6.25%; dried extracted meal, 67.65%. Analysis of the meal, free from oil and moisture, shows: protein ( $N \times 6.25$ ), 28.92%; fiber, 29.10%; ash, 5.61%; N-free extract (carbohydrates), 36.37%. The constants of the oil, obtained by hot pressing ( $100^{\circ}$ ) and then filtering are

Specific gravity, $24.5^{\circ}/25^{\circ}$	0.918
Refractive index at $25^{\circ}$	1.4738
Color (2.54 cm. column, Lovibond)	100 yellow—46 red
Acid number	2.18
Iodine number, Hanus	133.5
Acetyl number	7.0
Saponification number	192.0
Unsaponifiable matter	1.7%
Melting pt. of separated fatty acids	$21.2^{\circ}$

The resemblance to tomato seed oil is striking.<sup>2</sup> However, the presence of colored veins on the outer edges of the seeds imparts to the oil the deep color noted above and a characteristic burning taste and paprika-like aroma.

LOS ANGELES, CALIF.

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- (1) H. C. Ebert and H. S. Bailey, *Cotton Oil Press*, **7**, 35 (1924).  
(2) Felice Sorgès, *Chim. Ind. Agr. Biol.*, **8**, 232 (1929); N. Barskii, *Masloboino-Zhirovoe Delo*, No. 6, 56 (1932).

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## COMMUNICATIONS TO THE EDITOR

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### MUREXIDE AND LEUCOMUREXIDE

Sir:

The recent publication of Kuhn and Lyman [*Ber.*, **69**, 1547 (1936)] concerning the oxidation-reduction potential of murexide prompts this report of results obtained in this field.

**Preparation of Murexide.**—The uncertainty in the preparation of murexide emphasized by previous writers including Kuhn and Lyman (who obtained only a 2% yield) has been removed by employing glacial acetic acid as the reaction medium. Furthermore, recrystallization has been effected without heating, by salting out at room temperature. Thus, 16.1 g. of finely

powdered alloxantine suspended in 1600 cc. of boiling glacial acetic acid and treated with 80 g. of ammonium acetate with continued boiling for 1–2 minutes gave, on cooling, filtering, washing with acetic acid, alcohol and ether, and drying at  $100^{\circ}$ , 14.0 g. (calcd. 14.2 g.) of crude murexide. One gram of this dissolved in 900 cc. of water at  $30^{\circ}$  gave, on salting out the filtered solution with 60 g. of ammonium chloride, filtering, washing with 60% methanol and then with absolute methanol, and drying at  $110^{\circ}$ , about 75% of beautiful, reddish-brown crystals possessing a green reflex, which, on titration with sodium hydrosulfite, were found to be pure murexide.