

81. *Free Organic Radicals in the Gaseous State. Part IV. Synthesis of Antimony Cacodyl and Related Substances by the Use of Free Methyl and Free Ethyl.*

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IN previous communications (Part I, *Ber.*, 1929, **62**, 1335; Part II, *ibid.*, 1931, **64**, 2702; Part III, *ibid.*, p. 2708; see also *Z. Elektrochem.*, 1931, **37**, 577) the investigation of the reactions of free methyl and ethyl with zinc, antimony, and a few other elements served the purpose of proving the existence of the two radicals in the free state and of studying the mechanism of their reactions. The present contribution describes an attempt to utilise their activity for the systematic preparation of methyl and ethyl compounds of arsenic, antimony, and bismuth. Some of the products so obtained are new, attempts to synthesise them by the usual methods having failed.

It has already been pointed out that the impact of free methyl on antimony does not result in the formation of a homogeneous product; besides the colourless trimethylstibine, there is produced a substance of a strikingly red colour (in the solid state) which has now been shown, in agreement with a previous supposition (Parts I, p. 1341, and II, p. 2707), to be *bisdimethylantimony* ("antimony cacodyl"). Analogous experiments with arsenic showed that a still greater variety of products is formed: both radicals afford mono-, di-, and tri-alkyl derivatives. On the other hand, with bismuth only trialkyls have been identified. In all cases we examined the influence of temperature on the reacting mirror; for the synthesis of the highly alkylated and therefore easily volatile products, room temperature sufficed, but the yield of the less volatile di- and mono-alkyls is distinctly improved by heating the mirror. This device made it possible to obtain *bisdiethylantimony*.

I. *Reaction of Free Methyl and Free Ethyl with Arsenic.*—If at room temperature a mirror of arsenic is attacked by free methyl, *bisdimethylarsenic* (cacodyl; Bunsen, *Annalen*, 1842, **42**, 14) and trimethylarsine are formed, the former being the main product; free ethyl yields analogous compounds. Small quantities of less volatile yellow oils were also formed. Contact with air decomposes these compounds into white substances containing arsenic and having a disagreeable garlic-like odour.

The yields of the yellow oils were markedly increased by heating the arsenic mirrors. In an atmosphere of hydrogen, the methyl product polymerised slowly to a dark red solid, but the ethyl product remained unchanged. The arsenic content of the methyl compound agreed with that required for monomethylarsine. Substances of similar nature and composition have been described by various authors; although the recorded boiling points (see Experimental) vary considerably, it seems likely that all of them were cyclic pentamethylpentarsines, and that our substance, with a similar boiling point, is identical with them.

II. *Reaction of Free Methyl and Free Ethyl with Antimony.*—Cold and hot mirrors of antimony, treated with free methyl, formed trimethylstibine, together with a smaller quantity of a brilliantly red substance, which was shown by analysis and molecular-weight determination to be *bisdimethylantimony*, the analogue of Bunsen's cacodyl. Free ethyl gave very similar results, but the antimony mirror had to be heated for the production of the *bisdiethylantimony*; cold mirrors yielded almost exclusively triethylstibine. The former substance resembles its methyl analogue in colour but has a much lower melting point.

In both the methyl and the ethyl reactions, small quantities of black products were formed, the methyl compound being the more sensitive to air, but insufficient was obtained for detailed examination. A similar product was assumed by Schmidt (*Annalen*, 1920, **421**, 222) to be cyclic pentamethylpentastibine.

Since the dialkyl products were obtainable in fair quantity, we studied them in some detail. So far, antimony compounds of a similar structure have been known only in the aromatic series. Schmidt (*loc. cit.*) and Blicke, Oakdale, and Smith (*J. Amer. Chem. Soc.*, 1931, **53**, 1025) described a *bisdiphenylantimony*, but the existence of the corresponding

amyl compound (Berlé, *Annalen*, 1856, **97**, 321) is doubted by Morgan and Davies (*Proc. Roy. Soc.*, 1926, *A*, **110**, 523). Moreover, the latter authors failed to isolate bisdimethylantimony from the reaction of zinc with dimethylbromostibine, and we have confirmed their results, the failure obviously being due to the fact that bisdimethylantimony, although stable in a pure state, is decomposed at about 50° in the presence of zinc bromide. Our method avoids this difficulty, and although the yield is comparatively low (20—30 mg. per hour) the apparatus needs little supervision.

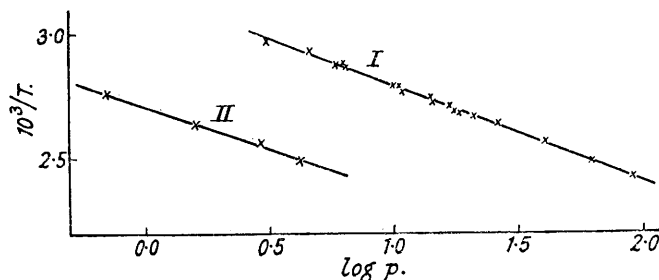
The most surprising property of bisdimethylantimony is its change of colour at the melting point: at 17.5° the bright red, needle-shaped crystals melt to a faintly yellow oil. At liquid-air temperature the colour is lighter than at room temperature, rather more orange; during slow warming, its colour deepens gradually and reaches its most intense tint immediately before melting. Its solutions in benzene, alcohol, ether, naphthalene, and camphor have a lighter colour than the oil. In water it sinks without dissolving or reacting; it dissolves in concentrated sulphuric acid with evolution of sulphur dioxide but without blackening.

Bisdimethylantimony reacts readily with mercury, so its vapour pressure was determined in a mercury-free manometer with the help of Bodenstein's silica spiral. The results are given in the following table, p being the pressure (in mm. of mercury) and t the temperature:

Vapour pressure of bisdimethylantimony.

t .	p .	t .	p .	t .	p .	t .	p .	t .	p .	t .	p .
64°	3.1	75.5°	5.9	86.5°	10.5	94.5°	14.5	100.5°	18.3	118°	40.5
69	4.6	76	6.4	89	10.9	97	16.9	102.5	21.1	130	62.7
75	6.3	86	10.1	92.5	14.2	99.5	17.6	107	26.1	140.5	91.2

Curve I in the fig. shows that, on plotting $\log p$ against the reciprocal of the absolute temperature, a straight line is obtained, whence we calculate the molecular heat of evaporation to be approximately 12 kg.-cals.



Determinations of the molecular weight in solutions in both benzene and camphor confirmed the bis-constitution, and showed that the compound is not appreciably dissociated; it seems, therefore, unlikely that the astonishingly strong colour of the solid is due to the formation of free radicals of dimethylantimony: special investigation will be necessary to explain the colour.* Spectroscopic examination shows two absorption bands in the green.

Bisdimethylantimony is very sensitive to oxygen: a quantity of about 100 mg., exposed to air, catches fire, and a smaller quantity fumes; in both cases a disagreeable garlic-like odour is perceptible. Benzene solutions also are oxidised in air, with formation of a white precipitate of dimethylantimonic acid (Morgan and Davies, *loc. cit.*); they also decolorise iodine and bromine solutions, and attempts to prepare definite products, by adding an equivalent quantity of one of the halogens and evaporating the solvent,

* We know of only one other instance of a strongly coloured organic substance which temporarily loses its colour when heated: the deep red base of diethylrhodamine gives a colourless solution in hot toluene, just as the red bisdimethylantimony becomes almost colourless in alcohol or benzene; but the explanation of the former colour change (Kuhn, *Naturwiss.*, 1932, **20**, 622) cannot be applied to the case of the antimony compound.

afforded yellow oils with an antimony content corresponding to the formula $(\text{CH}_3)_2\text{SbHal}$. These partly solidified, and were quickly oxidised by air, developing white fumes. They were probably identical with the substances described by Morgan and Davies (*loc. cit.*), but their quantity was too small for their homogeneity to be ensured.

Bisdiethylantimony shows similar properties. At room temperature it is a yellow oil. When cooled to liquid-air temperature, it solidifies as an amorphous glassy mass, which, however, crystallises on slow heating; the colour is at first orange and becomes bright yellow near the melting point (-61°). At higher temperatures the compound is somewhat less stable than the methyl analogue, decomposition beginning at 155° . In spite of its lower m. p., it is much less volatile than the methyl compound; the vapour pressures are so small at the low temperatures to which the measurements necessarily have to be confined that the readings of the quartz spiral manometer cannot have a high degree of accuracy. From the results (see below, and Curve II), we deduce a molecular heat of vaporisation of approximately 14 kg.-cals.

Vapour pressure of bisdiethylantimony.

Temp.	89°	107°	118°	129°
<i>p</i> (mm. Hg)	0·7	1·6	2·9	4·2

Determination of the molecular weight in benzene showed no sign of dissociation. The obvious conclusion that the colour is not due to a partial splitting into free radicals seems all the more probable, for in such a case we should expect the ethyl compound to have a greater tendency to dissociate than the methyl compound and therefore to show a deeper colour, whereas the contrary is the case.

The ethyl compound is less readily oxidised by air than the methyl compound: it fumes but does not catch fire; the odour of the fume is also garlic-like.

Atmospheric oxidation of the benzene solution affords white *diethylantimonic acid*, $(\text{C}_2\text{H}_5)_2\text{SbO}\cdot\text{OH}$, which is odourless, soluble in water, insoluble in ether, and only slightly soluble in alcohol. Its reaction is neutral towards methyl-orange, acid towards phenolphthalein; it is reduced by stannous chloride, the characteristic odour of the trivalent antimony alkyls being produced.

The reactions of bisdiethylantimony with iodine and bromine are similar to those of the methyl compound, equivalent quantities of the halogens producing respectively (i) an orange solid and a yellow oil and (ii) a white solid and a pale yellow oil. The antimony content of the last corresponds to the formula $(\text{C}_2\text{H}_5)_2\text{SbBr}$.

In order to elucidate the reason for the colour of the bisdialkylantimony compounds, we attempted to apply our procedure to the synthesis of the *n*-propyl and the *isobutyl* compound, but although we took every precaution to shorten the track of the expected free radicals, *n*-propyl and *isobutyl*, we found no trace of their compounds with antimony. In agreement with a previous result (Part II, p. 2707), the main product was bisdimethylantimony.

III. *Reaction of Free Methyl and Free Ethyl with Bismuth.*—Since the action of free radicals on antimony had yielded substances which could not be prepared by the usual methods, it seemed probable that bismuth would yield corresponding compounds. As with arsenic and antimony, the behaviour of bismuth towards the free radicals depended on the temperature. Cold mirrors afforded only trialkyls, but with heated mirrors, there were formed, in addition, a difficultly volatile violet-red substance from free methyl and a black substance from free ethyl. The former melted below room temperature to a yellow oil and at once became transformed into a black solid; from its low volatility, as compared with trimethylbismuthine, and the similarity in colour to bisdimethylantimony, we conclude that this compound was bisdimethylbismuth. The black substance from free ethyl was apparently produced by spontaneous decomposition of initially-formed bisdiethylbismuth. These substances were not obtained in quantity sufficient for analysis, but they merit further investigation, for the bismuth analogues of cacodyl are not known (*cf. Blicke, loc. cit.*).

Summarising, it may be said that by the action of free methyl and ethyl on arsenic,

antimony, and bismuth, only such compounds were produced as were volatile under the conditions of experiment. In agreement with this is the fact that the molecular complexity of the products diminishes in passing from arsenic, through antimony, to bismuth. While the most volatile, arsenic, can form pentameric monoalkyls, such substances are formed with antimony only to a minor extent, and not at all with bismuth.

IV. *Reaction of Free Methyl and Free Ethyl with Beryllium.*—In disagreement with the foregoing regularity was the fact that free radicals had not hitherto been found to react with beryllium (Hahnfeld, Diss., Königsberg i. Pr., 1932, p. 15), although its alkyls do not possess a particularly low volatility: dimethylberyllium (Gilman and Schulze, J., 1927, 2665) sublimes at 200°, and diethylberyllium boils at 110°/15 mm. Since beryllium could not be distilled in a high vacuum, its mirrors were produced by the thermal decomposition in a quartz tube of diethylberyllium,* freed from halogen by treatment with silver and silver oxide. In agreement with previous results, no reaction could be observed with either methyl or ethyl. This inertness did not arise from leakage in the apparatus, since lead mirrors placed before or after the beryllium mirror were readily removed, but must be attributed to impurity of the mirror—a conclusion strengthened by its dirty brown-black appearance. This could only originate from an attack of the beryllium on the quartz, although, according to Borchers (*Metallwirt.*, 1931, 10, 863), such attack should only occur above 1400°. To eliminate the effect of the silica wall, a well-cleaned piece of gold foil, which had been ignited in hydrogen, was placed in the tube and tested for its inertness towards free radicals, and beryllium was deposited thereon in quantity sufficient to form a brilliant metallic layer. A current of hydrogen was then passed through the apparatus until no more diethylberyllium was given up by the tap grease. If free methyl, from the thermal decomposition of ethyl-lead at 950° (cf. below), or free ethyl was then led over the mirror at 150°, in both cases white substances condensed in the liquid-air-cooled U-tube following the quartz tube. The methyl product was solid at room temperature, but the ethyl compound melted below room temperature to a colourless liquid, according to the properties of dimethyl- and diethyl-beryllium respectively. Both substances in contact with the air formed white oxidation products in which beryllium was identified. Beryllium, therefore, is attacked by free radicals, and the generality of the above rule is established.

The compounds identified in this work are collected in the following table for convenience.

Compounds resulting from the action of free methyl and free ethyl on arsenic, antimony, and bismuth.

(The compounds surrounded by a frame are formed only when the mirrors are heated.)

Compounds.	Arsenic.		Antimony.		Bismuth.	
	Methyl.	Ethyl.	Methyl.	Ethyl.	Methyl.	Ethyl.
Trialkyls	AsMe ₃	AsEt ₃	SbMe ₃	SbEt ₃	BiMe ₃	BiEt ₃
Dialkyls	[AsMe ₂] ₂	[AsEt ₂] ₂	[SbMe ₂] ₂	[SbEt ₂] ₂	[BiMe ₂] ₂	
Monoalkyls	[AsMe] ₅	[AsEt] ₅				

EXPERIMENTAL.

The apparatus was essentially the same as that described in Part I. In order to increase the concentration of radicals, an alteration was made in that the vessel of tetramethyl-lead was maintained not at -70° but at -40°, and that of tetraethyl-lead at 0° instead of -25°.

Care must be exercised that in the decomposition of tetraethyl-lead the temperature is not raised above 600°, otherwise the ethyl undergoes decomposition, forming methyl: at 800° this decomposition was quite appreciable, and at 950° it was total. This radical was identified by the action of the decomposition products on antimony and beryllium; bisdimethylantimony was formed (identified by m. p.), and from beryllium a white solid was obtained which oxidised in the air, and in which beryllium was identified (for method, see below): this could only have been dimethylberyllium, for the diethyl compound is liquid at room temperature.

For the identification of the substances obtained, the U-tube in which the products were

* For this compound we are indebted to the kindness of Prof. H. Gilman, State College, Ames, Iowa. (See also Gilman and Wright, *J. Amer. Chem. Soc.*, 1933, 55, 2893.)

condensed was connected to a fractionation apparatus consisting of three U-tubes, separated by taps. Each was furnished with a capillary for determination of the m. p. and b. p. by Emich's method (*Monatsh.*, 1917, **38**, 219), and also, by means of a ground joint, with a tube which served for the removal of the substance. Since, owing to their ready oxidisability, the substances here investigated had to be kept out of contact with the air, we distilled them into this tube, which was constricted in its lower portion to facilitate sealing off. From the difference in weight between the empty tube and the two parts of the tube after sealing off, the weight of the substance could be determined, due allowance being made for the air-free volume in the sealed-off portion.

The analyses for arsenic and antimony were made by titration with potassium bromate (Norton and Koch, *J. Amer. Chem. Soc.*, 1905, **27**, 1247).

IA. *Action of Free Methyl on Arsenic.*—(a) *With cold mirrors.* The chief products were colourless compounds which oxidised in the air and condensed in the liquid-air-cooled condensation tube. These were separated by fractional distillation, the three U-tubes of the apparatus being kept at -26° , -58° , and -78° , and a very slow current of hydrogen being led through. At -26° cacodyl condensed (m. p. -6° , b. p. 165°) [Bunsen (*loc. cit.*) gives b. p. ca. 170° , m. p. -6° ; and Valeur and Gaillot (*Compt. rend.*, 1927, **185**, 779) give b. p. 163° , m. p. -5°]. Trimethylarsine solidified at -78° and had b. p. $74^\circ/760$ mm. [Cahours (*Annalen*, 1862, **122**, 338) gives b. p. ca. 70° ; Renshaw and Holm (*J. Amer. Chem. Soc.*, 1920, **42**, 1468) $50.7-51.7^\circ/747.5$ mm.; Valeur and Gaillot (*loc. cit.*) $50-52^\circ$; Natta (*Chem. Zentr.*, 1927, I, 416) $68-73^\circ$; Dyke and Jones (*J.*, 1930, 2429) $51-53^\circ$]. Since this substance was always formed in our experiments in only very small amounts (2-3 mg.), it was not possible to effect a further fractionation.

At -55° we obtained a substance, m. p. -13° , which was apparently a mixture of both the foregoing compounds.

(b) *With heated mirrors.* The arsenic mirror was heated only at the end adjacent to the decomposition spiral, the temperature being such that the arsenic just did not distil away. The mirrors were then attacked a little beyond the spiral, where the temperature was no longer so high as to hinder reaction with the free radicals. When the arsenic was removed from this spot, the mirror was renewed. The cyclic pentamethylpentarsine separated in the quartz tube behind the mirror as a bright yellow oil, b. p. $193-200^\circ/15$ mm. Minute amounts of this oil were formed also from the cold mirror. The data in the literature for the b. p. of this substance are very discordant. Auger (*Compt. rend.*, 1904, **138**, 1706) found $190^\circ/15$ mm.; Steinkopf and Dudek (*Ber.*, 1928, **61**, 1908; see also Steinkopf, Schmidt, and Smie, *Ber.*, 1926, **59**, 1463), who termed the compound arsenomethane, found $190^\circ/13$ mm., and Palmer and Scott (*J. Amer. Chem. Soc.*, 1928, **50**, 536) found $178^\circ/15$ mm.; but Valeur and Gaillot (*loc. cit.*) give $190^\circ/5$ mm. The molecular complexity was determined by Steinkopf and his co-workers in various solvents as $(\text{CH}_3\cdot\text{As})_5$, and this was confirmed by Palmer and Scott (*loc. cit.*).

The oil smelt garlic-like, oxidised in the air, and when brought into contact with hydrochloric acid, changed into a red solid. It was deposited in the condensation tube also, along with the arsine, and here was transformed almost instantaneously into a dark red solid. It was difficult to obtain this substance entirely free from arsenic. After several experiments, 21.7 mg. of the compound had collected in the U-tube (Found: As, 82.3. Calc. for $\text{CH}_3\cdot\text{As}$: As, 83.3%). In spite of the small quantity, therefore, it seems probable that in this case also pentamethylpentarsine was present.

In addition to these high-molecular substances, readily volatile colourless products resulted, which were separated by fractional condensation as described above, and identified as trimethylarsine and bisdimethylarsenic.

IB. *Action of Free Ethyl on Arsenic.*—(a) *With cold mirrors.* The least volatile substance formed was again a very small amount of yellow oil, which showed, however, no tendency to polymerise. The more volatile products were fractionated, the U-tubes being cooled to -21° , -36° , and -55° . At -36° , bisdiethylarsenic (b. p. $185-187^\circ$) condensed (Landolt, *Annalen*, 1854, **89**, 319, gives b. p. $185-190^\circ$). The material condensing at -55° was again fractionated. It was kept at -42° while the trap was cooled in liquid air, and the fractionation interrupted as soon as a portion had distilled over. The distillate was triethylarsine (b. p. $140.5^\circ/736$ mm.) (Landolt, *loc. cit.*, gives $140^\circ/736$ mm.; Dyke and Jones, *loc. cit.*, give $138-139^\circ$).

(b) *With heated mirrors.* A yellow oil, which showed but little tendency to polymerise in presence of hydrochloric acid, condensed behind the mirror and in the condensation tube. From its analogy with the methyl compound, it may be regarded as the cyclic pentaethylpentarsine. As it was obtained only in very small amount, no further identification was attempted,

especially since there is no record of its b. p. Besides this compound, triethylarsine and bisdiethylarsenic again resulted; these were separated and identified as described above.

IIA. *Action of Free Methyl on Antimony.*—In this reaction, irrespective of the temperature of the mirror, a mixture of trimethylstibine and bisdimethylantimony resulted. This was fractionated, the first two U-tubes being kept at -15° and -50° , while the last was cooled in liquid air. To accelerate the fractionation, a little hydrogen (*ca.* 0.35 mm.) was passed through the apparatus. Trimethylstibine, b. p. 82° , condensed in the last U-tube (Landolt, *J. pr. Chem.*, 1861, **84**, 329, gives b. p. 80.6°). In the tube at -15° , bisdimethylantimony condensed as brilliant red needles, m. p. 17.5° [Found: Sb, 80.0, 79.8; C, 15.9; H, 4.2. $\text{Sb}(\text{CH}_3)_2$ requires Sb, 80.2; C, 15.8; H, 4.0%]; on oxidation in benzene solution, it gave dimethylantimonic acid (Found: Sb, 65.9, 65.9. Calc.: Sb, 65.9%).

By the addition of an equivalent amount of bromine, a bright yellow oil resulted which partly solidified; it was distilled off [Found: Sb, 53.1. Calc. for $(\text{CH}_3)_2\text{SbBr}$: Sb, 52.6%]. Addition of iodine gave a yellow oil (dimethyliodostibine), which also partly solidified.

We attempted to determine the molecular weight of bisdimethylantimony cryoscopically. As an indifferent atmosphere we used nitrogen, which was freed from oxygen by a simplification of Kautsky and Thiele's method (*Z. anorg. Chem.*, 1927, **152**, 342) {0.2405 g. of substance in 23.84 g. of benzene, gave Δt 0.161° ; M , 319.6. 0.2977 g. in 24.05 g. of benzene, Δt 0.205° ; M , 308. Calc. for $[\text{Sb}(\text{CH}_3)_2]_2$: M , 303.6}. Since it might be expected that any dissociation would be more pronounced at higher temperatures, we carried out a molecular-weight determination by Rast's micro-method (Found: M , 314.2, 313.1), and, although these determinations, on account of the smaller weights involved, were less accurate than those in benzene, they show that even at high temperatures dissociation does not occur.

IIB. *Action of Free Ethyl on Antimony.*—We confirmed Paneth and Lautsch's finding (Part II, p. 2707) that pure triethylstibine results from the action of free ethyl on a cold antimony mirror. At higher temperatures, however, several products occur in this case also, a mixture of a colourless oil and a yellow, less volatile compound being obtained. This was separated by fractional condensation, the U-tubes being cooled to -13° , -55° , and in liquid air. As in the separation of the methyl homologues, the fractionation was carried out in a slow stream of hydrogen (*ca.* 0.35 mm. Hg). White triethylstibine first distilled and condensed at -55° , b. p. $159^{\circ}/730$ mm. (Löwig and Schweizer, *Annalen*, 1850, **75**, 327, give b. p. $158.5^{\circ}/730$ mm.). The fractionation was continued until the yellow substance condensing at -13° showed a constant m. p. of -61° . This was bisdiethylantimony. Since it was very difficultly volatile, it was not distilled over, but allowed to flow directly into a weighing tube and sealed off {Found: Sb, 68.0, 68.0; C, 26.5; H, 5.5; M , cryoscopic in benzene, 376.6, 376.6. $[\text{Sb}(\text{C}_2\text{H}_5)_2]_2$ requires Sb, 67.7; C, 26.7; H, 5.6%; M , 359.7}.

By the oxidation of bisdiethylantimony in benzene solution, diethylantimonic acid, $(\text{C}_2\text{H}_5)_2\text{SbO}\cdot\text{OH}$, was formed as a colourless, odourless, amorphous substance (Found: Sb, 60.0. $\text{C}_4\text{H}_{11}\text{O}_2\text{Sb}$ requires Sb, 59.6%).

Addition of equivalent amounts of iodine and bromine to bisdiethylantimony gave the corresponding diethylhalogenostibines. The iodo-compound was obtained, together with a yellowish-red solid, as a yellow oil, and the bromo-compound as a bright yellow oil from which a white solid separated (Found: Sb, 47.4. Calc. for $\text{C}_4\text{H}_{10}\text{BrSb}$: Sb, 46.9%).

III. *Action of Free Methyl and Free Ethyl on Bismuth.*—By using cold mirrors, we obtained trimethylbismuthine, b. p. 110 — 111° (Marquardt, *Ber.*, 1887, **20**, 1518, gives 110° ; Schäfer and Hein, *Z. anorg. Chem.*, 1907, **100**, 298, give 106 — 107°), and triethylbismuthine, b. p. $112^{\circ}/79$ mm. (Marquardt, *loc. cit.*, gives $107^{\circ}/79$ mm.).

IV. *Action of Free Methyl and Free Ethyl on Beryllium.*—The detection of beryllium in the white products formed by atmospheric oxidation (see p. 369) was carried out by evaporating the substance to dryness with nitric acid and dissolving the residue in hydrochloric acid; on addition of quinalizarin and making the solution weakly alkaline, a cornflower-blue coloration at once resulted, and after some time a precipitate of the same colour was deposited. In the absence of beryllium the colour is violet-red.