Nitroso 2,4,6-Trimethylbenzyl-2,4,6-trimethylbenzal Hydrazone, $(CH_3)_3C_6H_2CH_2N(NO)N : CHC_6H_2(CH_3)_3$.

To a strong alcoholic solution of 2,4,6-trimethylbenzyl-2,4,6-trimethylbenzal hydrazone, cooled by ice water, was added a few drops of concentrated hydrochloric acid. To this cold solution, which was shaken after each addition, was added gradually a concentrated solution of sodium nitrite. Long, satin-like needles separated at once and increased in number upon the addition of water. The successful carrying-out of this experiment requires the use of freshly prepared hydrazone.

The nitroso derivative was filtered off, washed well with water to remove the excess of sodium nitrite, and recrystallized from alcohol. The long, yellow, satin-like crystals melted at 117°.

The analysis gave 13.09 per cent. N. Calculated, 13.00 per cent.

The nitroso derivative is very soluble in chloroform, ether, benzene, and toluene. It is less soluble in acetone and glacial acetic acid. It is soluble in warm ethyl, methyl, and amyl alcohols, and insoluble in water. It is a stable compound.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

ARSENIC PENTACHLORIDE.

BY CHARLES BASKERVILLE AND H. H. BENNETT.

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THE non-existence of arsenic pentachloride has for a long time been regarded as remarkable, especially so when the analogues of that element having atomic weights below and above it, phosphorus and antimony, show pentavalence toward the halogens.

Hurtzig and Geuther[1] endeavored to prepare it by treating arsenious acid with phosphorus pentachloride. Mayerhofer[2] passed chlorine into arsenic trichloride at —10° C., removing the excess of chlorine by a stream of carbon dioxide, and failed to obtain the body. Janovsky[3] treated phosphorus pentachloride with arsenic trihydride at 0° C. with negative results. Dumas[4]

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[1] *Ann. Chem. Pharm.*, 111, 171.

[2] *Ibid.*, **158**, 326.

[3] *Ber. d. chem. Ges.*, **8**, 1636 (1875).

[4] *Ann. Chem.* (Liebig), **33**, 337.

thought he had arsenic pentachloride, but Capitaine[1] proved it to be a mixture of As_4O_6 and $AsCl_3$. Weber having prepared $SbCl_5PCl_5$, Cronander[2] sought its analogue $AsCl_5PCl_5$, but only obtained $AsCl_3PCl_5$. Marignac[3] obtained AsF_5 as a double fluoride of potassium. Sloane[4] prepared AsI_5 and endeavored to secure the pentachloride by saturating arsenic trichloride with chlorine at —23° C. at ordinary pressure and obtained the ratio $As:Cl::1:4.447$. There was a gradual decrease in the ratio up to 24° C. when it became 1 :4.08, then there was an abrupt change rapidly approaching 1 :3. Such observations made the existence of As_2Cl_8 quite conceivable.

Baeyer's pentahalogen compounds of arsenic in which one to four chlorine atoms have been replaced by alkyl radicals and Michaelis'[5] work with phenyl residues are well known. Recently the pentavalent organic arsenic compounds have become much augmented by the extensive work of Michaelis.[6]

The procedure of Sloane[7] offered encouragement, provided the reaction should be carried out at a lower temperature. Chemically pure arsenic trichloride was prepared and redistilled from concentrated sulphuric acid and its purity determined by analysis. About 5 cc. of the liquid were placed in a dry test-tube buried in solid carbon dioxide loosely packed in a Dewar bulb and dry chlorine led in. The crystalline trichloride (m. p. —18° C.) assumed a greenish yellow color and became liquid, which grew in bulk. Besson[8] showed that arsenic trichloride saturated with chlorine at zero does not solidify at —30° C. Davy also showed that it does not freeze at —29° C. when well saturated with chlorine. After a few minutes, the time varying with different experiments, the stream of gas was cut off and the excess of liquid chlorine removed by fractional distillation. Chlorine boils at —33.6° C. We verified this by completely boiling away several cubic centimeters of chlorine at —33° C. in other experiments. As a safeguard we allowed the temperature to rise to —31° C.

[1] *Jour. Pharm.*, **25**, 524.

[2] *Rer. d. chem. Ges.*, **3**, 1466 (1873).

[3] *Ann. Chem.* (Liebig), **145**, 249.

[4] *Chem. News*, **46**, 194 (1881).

[5] *Ber. d. chem. Ges.*, **8**, 1316 and **9**, 1566.

[6] *Ann. Chem.* (Liebig), **320**, 271 (1902).

[7] *Loc. cit.*

[8] *Compt. rend.*, **109**, 940.

The liquid was cooled again to —35° C. and samples were removed as the temperature rose by means of a small pipette chilled to the temperature of the refrigerating agent. These samples in one experiment were placed directly in water; in another it was deemed better to place them in a dilute sodium hydroxide solution. In the former case immediate solution occurred with those portions removed at temperatures below —25° C., while at those higher a white precipitate, evidently of arsenious oxide, formed, increasing in amount with elevation of temperature. The orthoarsenic acid was determined as magnesium pyroarsenate and chlorine as silver chloride. The filtrate from the magnesium ammonium arsenate in the former was tested for the presence of arsenious compounds. None were found up to —25° C., when arsenious acid was found in traces increasing in amount with rise of temperature. The ratio between arsenic as arsenic acid, and chlorine, was 1 : 5 or $AsCl_5$. At —25° C. the ratio rose to 1 : 6. The loss of chlorine and consequent return to the trivalent condition became more and more marked, the higher the temperature.

The following analytical results were obtained for two temperatures in one experiment:

Temperature. °C.	Amount taken.	Chlorine found. Per cent.	Theoretical.	Ratio obtained. As : Cl.
—35	0.1796	69.93	70.26	1 : 4.93
—25	0.26675	73.21	....	1 : 5.78

Arsenic pentachloride is readily soluble in carbon disulphide and absolute ether cooled to —30° C. From the latter, when chilled several degrees, it crystallizes in yellow prisms. It loses chlorine when heated above —28° C. On exposure to the air it fumes, evolving hydrochloric acid vapor and as the temperature rises forms crystals, most likely of the trichloride, which melt soon to the liquid state. A special preparation was made and sealed in a tube. The greenish-yellow liquid when cooled to —38° or —40° C. (we had no thermometer for determining this accurately) formed beautiful yellow crystals.

It is not regarded necessary to give our several unsuccessful preliminary experiments to secure the body for analysis. Suffice it to say that placing the body in a pipette or weighing-bottle at the temperature of the air brought about its immediate decomposition to the original trichloride, chlorine being evolved.

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