CCXXXIV.—2 : 4 : 6-*Trichlorophenylhydrazine.*

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Although several derivatives of 2 : 4 : 6-trichlorophenylhydrazine have been prepared (J., 1915, **107**, 1508; 1923, **123**, 3053; 1925, **127**, 1690, 2408; 1928, 2758; etc.), the compound itself and its more characteristic derivatives have never been described.

It is most easily prepared by reducing 2 : 4 : 6-trichlorobenzenediazonium chloride with stannous chloride, reduction by sulphite not giving a good yield.

2 : 4 : 6-Trichlorophenylhydrazine forms a very stable *hydrochloride*, and colourless β-*acetyl*-, β-*benzoyl*-, and β-*benzoyl*-α-*acetylhydrazides*. With aldehydes, ketones, and ketonic acids, it forms a

series of well-crystallised *hydrazones*, which frequently have lower melting points than the corresponding phenylhydrazones.

EXPERIMENTAL.

2 : 4 : 6-*Trichlorophenylhydrazine Hydrochloride.*—30 G. of 2 : 4 : 6-trichloroaniline (1 mol.), dissolved in 80 c.c. of boiling acetic acid, were added with vigorous stirring to 220 c.c. of concentrated hydrochloric acid. The trichloroaniline hydrochloride which separated as a thin paste was diazotised slowly at 0° to −5° (mechanical stirrer) with 10·5 g. of sodium nitrite (1 mol.) dissolved in 40 c.c. of water (1—1½ hours). The diazonium solution was filtered to remove any unchanged trichloroaniline and added slowly to a mechanically stirred solution of 70 g. of stannous chloride in 220 c.c. of concentrated hydrochloric acid maintained below 5° (1 hour). Trichlorophenylhydrazine hydrochloride, which separated gradually as a colourless solid, was collected and recrystallised from boiling 10% hydrochloric acid (1100 c.c.). Yield, 27—30 g. (70—80%). 2 : 4 : 6-*Trichlorophenylhydrazine hydrochloride* crystallises from boiling water, in which it is rather sparingly soluble, in colourless, six-sided leaflets. When strongly heated, it volatilises completely without previously melting. Heated in a sealed capillary tube, it does not darken or melt even at 350° (Found : Cl, 57·15. $C_6H_5N_2Cl_3$,HCl requires Cl, 57·1%).

2 : 4 : 6-Trichlorophenylhydrazine separates at once as a colourless solid when a concentrated solution of sodium acetate is added to a solution of the hydrazine hydrochloride in boiling water. It crystallises from boiling light petroleum (b. p. 80—100°), in which it is rather sparingly soluble, in slender colourless prisms, m. p. 143—144° (decomp.). It can be preserved unchanged in a sealed tube, but oxidises and turns brown if kept in the air. It is rapidly oxidised by alkaline permanganate, or Fehling's solution, yielding nitrogen and 1 : 3 : 5-trichlorobenzene.

β-*Acetyl*-2 : 4 : 6-*trichlorophenylhydrazide* is formed with evolution of heat when the hydrazine reacts with an equivalent amount of acetic anhydride. It crystallises from boiling acetic acid, or alcohol, in which it is easily soluble, in colourless short prisms, m. p. 157° (Found : Cl, 40·1. $C_8H_7ON_2Cl_3$ requires Cl, 40·2%).

β-*Benzoyl*-2 : 4 : 6-*trichlorophenylhydrazide*, prepared by the Schotten–Baumann method, crystallises from boiling alcohol, in which it is moderately easily soluble, in slender colourless prisms, m. p. 163·5° (Found : Cl, 33·7. $C_{13}H_9ON_2Cl_3$ requires Cl, 33·7%).

β-*Benzoyl*-α-*acetyl*-2 : 4 : 6-*trichlorophenylhydrazide* is formed when the above is boiled with acetyl chloride for several minutes. It

separates from boiling alcohol, in which it is very soluble, in small colourless compact prisms, m. p. 156° (Found : Cl, 29·5. $C_{15}H_{11}O_2N_2Cl_3$ requires Cl, 29·8%).

Citraconyl-2 : 4 : 6-*trichlorophenylhydrazide* separates from boiling alcohol, in which it is moderately easily soluble, in colourless six-sided prisms with domed ends, m. p. 166—167° (decomp.) (Found : Cl, 34·6. $C_{11}H_7O_2N_2Cl_3$ requires Cl, 34·85%). This hydrazide dissolves in dilute alkali solution and is precipitated unchanged by acids. It reduces ammoniacal silver nitrate in the cold.

Cinnamaldehyde-2 : 4 : 6-*trichlorophenylhydrazone* separates from boiling alcohol, in which it is somewhat sparingly soluble, in very pale yellow, almost colourless, long, slender prisms, m. p. 104—105° (Found : Cl, 32·65. $C_{15}H_{11}N_2Cl_3$ requires Cl, 32·7%).

Benzaldehyde-2 : 4 : 6-*trichlorophenylhydrazone* crystallises from boiling acetic acid, in which it is moderately easily soluble, in fine long colourless prisms, m. p. 91—92° (Found : Cl, 35·5. $C_{13}H_9N_2Cl_3$ requires Cl, 35·6%). Although this hydrazone is less sensitive to light than benzaldehydephenylhydrazone, a specimen which had been kept exposed to the light of a laboratory for several months developed a deep red colour and partly decomposed.

Salicylaldehyde-2 : 4 : 6-*trichlorophenylhydrazone* separates from boiling alcohol, or acetic acid, in which it is easily soluble, as a felt of colourless hair-like needles, m. p. 98·5—99·5° (Found : Cl, 33·4. $C_{13}H_9ON_2Cl_3$ requires Cl, 33·7%).

2 : 4-*Dinitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone* crystallises from boiling acetic acid, in which it is sparingly soluble, in scarlet flattened prisms, m. p. 109—110° (Found : Cl, 27·4. $C_{13}H_7O_4N_4Cl_3$ requires Cl, 27·3%).

2 : 4 : 6-*Trinitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone* crystallises from boiling alcohol, in which it is moderately easily soluble, in brick-red flattened prisms, m. p. 145—146° (Found : Cl, 24·65. $C_{13}H_6O_6N_5Cl_3$ requires Cl, 24·5%).

Acetone-2 : 4 : 6-*trichlorophenylhydrazone* separates from alcohol, in which it is very easily soluble, in colourless hair-like prisms, m. p. 58—59° (Found : Cl, 42·2. $C_9H_9N_2Cl_3$ requires Cl, 42·3%).

Benzophenone-2 : 4 : 6-*trichlorophenylhydrazone* crystallises from boiling alcohol, in which it is moderately easily soluble, in long slender colourless prisms, m. p. 106—107° (Found : Cl, 28·5. $C_{19}H_{13}N_2Cl_3$ requires Cl, 28·3%).

Mesoxalic acid 2 : 4 : 6-*trichlorophenylhydrazone* is readily soluble in boiling alcohol and separates in pale yellow, slender prisms of rather indefinite melting point. Placed in a bath at 175° and heated rapidly, it melts at 183° (decomp.) (Found : Cl, 34·0. $C_9H_5O_4N_2Cl_3$ requires Cl, 34·2%).

Pyruvic acid 2 : 4 : 6-*trichlorophenylhydrazone* crystallises from boiling alcohol, in which it is readily soluble, in short six-sided prisms with domed ends, m. p. 126—127° (Found : Cl, 37·5. $C_9H_7O_2N_2Cl_3$ requires Cl, 37·8%).

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