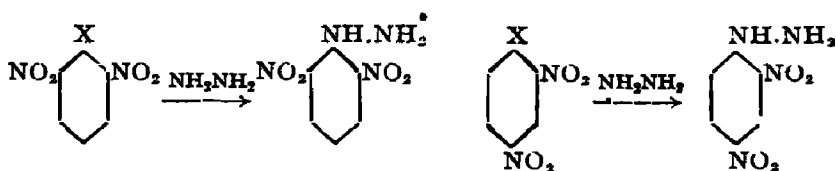


BEHAVIOUR OF CHLORONITROBENZENES WITH HYDRAZINE AND
HYDRAZINE DERIVATIVES. PART I. PREPARATION OF 2-CHLORO-
-4: 6-DINITRO- AND 2-BROMO-4:6-DINITRO-PHENYLHYDRAZINES
AND THEIR HYDRAZONES

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A few polynitrophenylhydrazine derivatives have been prepared by the action of hydrazine on such compounds in which either a chlorine or a nitro group is labile due to presence of at least two NO₂ either in *o: o* or in *o: p* positions. 2-Chloro- and 2-bromo-4:6-dinitrophenylhydrazines have been reacted with a number of carbonyl compounds to yield phenylhydrazones.

Hydrazine and substituted hydrazines are useful for a variety of purposes. They find use in the synthesis of many types of cyclic compounds, such as the pyrazoles, the triazoles, the diazines, etc. and also as reagents for carbonyl compounds. Some of them such as phenylhydrazine, phenylmethylhydrazine, *p*-nitrophenylhydrazine etc. were obtained by the reduction of diazonium and other suitable compounds (Fischer, *Annalen*, 1878, 190, 152; Bischler, *Ber.*, 1889, 22, 2801; Purgotti, *R. Acad. Lincei*, 1893, *w*, 7, 267). A few polynitrophenylhydrazines were prepared by the action of hydrazine on such compounds in which either a chlorine atom or a nitro group was labile due to the presence of at least two nitro groups, either in both of the *ortho* positions or in the *ortho* and in the *para* positions:



[where X = a halogen atom or a nitro group]

Thus by the substitution of the halogen atom by a hydrazino group (-NH.NH₂) 1-chloro-2:4:6-trinitrobenzene, 1-chloro-2:4-dinitrobenzene, 1-chloro-2:6-dinitrobenzene, 1-chloro-3-methyl-2:4-dinitrobenzene, 1,3-dichloro-4:6-dinitrobenzene gave respectively 2:4:6-trinitrophenylhydrazine (Purgotti, *Gazzetta*, 1894, 24, 113), 2:4-dinitrophenylhydrazine (Purgotti, *ibid.*, 555), 2: 6-dinitrophenylhydrazine (Borsche and Rantscheff, *Annalen*, 1911, 379, 171), 3-methyl-2:4-dinitrophenylhydrazine (Borsche and Fiedler, *Ber.*, 1913, 46, 2129), 3-chloro-4:6-dinitrophenylhydrazine (Borsche, *Ber.*, 1921, 54, 669) and by replacement of a nitro group by a hydrazino group 2:4:5-trinitrotoluene,

2:3:5-trinitrotoluene, 3:4:5-trinitrotoluene, 2:3:4-trinitrotoluene yielded respectively 3-methyl-4:6-dinitrophenylhydrazine (Giua, *Gazzetta*, 1919, 49, 171; *R. Acad. Lincei*, 1919, v, 28, 365), 2-methyl-4:6-dinitrophenylhydrazine (Brady and Bowman, *J. Chem. Soc.*, 1921, 119, 894), 4-methyl-2:6-dinitrophenylhydrazine (Brady and Bowman (*loc. cit.*)), 3-methyl-2:6-dinitrophenylhydrazine (Giua, *Gazzetta*, 1918, 48, 14; *R. Acad. Lincei*, 1918, v, 27, 251).

In the course of the present investigations a number of dinitrophenylhydrazines have been prepared. Two of them, 2-chloro- and 2-bromo-4:6-dinitrophenylhydrazine are described in this paper. Both of them have been obtained by the interaction of hydrazine and the corresponding reactive chloro compounds, viz., 1:2-dichloro-4:6-dinitrobenzene (Ullmann and Sane, *Ber.*, 1911, 44, 3734) and 1-chloro-2-bromo-4:6-dinitrobenzene (Sane and Joshi, *J. Chem. Soc.*, 1924, 125, 2482). These hydrazines are quite reactive and easily combine with aldehydic and ketonic compounds, sometimes by mixing the alcoholic solutions even in cold, to form the corresponding phenylhydrazones. Presence of concentrated sulphuric acid, in small amounts, accelerates the condensation, particularly in the case of aliphatic carbonyl compounds. They also do not yield osazones with sugars just like 2:4-dinitrophenylhydrazine (Allen, *J. Amer. Chem. Soc.*, 1932, 52, 2955).

EXPERIMENTAL.

2-Chloro-4:6-dinitrophenylhydrazine.—Hydrazine solution [obtained by mixing a solution of hydrazine sulphate (5.6 g.) in hot water (20 ml.) with potassium acetate (14 g.), boiling for 5 minutes, then mixing with alcohol (10 ml.) and finally filtering and washing with hot alcohol (10 ml.)] and 1:2-dichloro-4:6-dinitrobenzene (9.5 g.) were boiled together. Soon after a solid began to separate. After about 30 minutes the mass was cooled and filtered (7.5 g.). Chlorodinitrophenylhydrazine is slightly soluble in alcohol and crystallises from an excess of it in yellow crystals, m.p. 175°. (Found: Cl, 15.41. $C_6H_3O_4N_4Cl$ requires Cl, 15.25 per cent) (cf. Allen, *loc. cit.*).

2-Chloro-4:6-dinitrophenylhydrazine (1.8 g) was also obtained when a solution of 1:2-dichloro-4:6-dinitrobenzene (2.4 g.) in alcohol (10 ml.) and 50% hydrazine hydrate solution (2.5 ml.) were boiled together for 2 to 3 minutes.

2-Bromo-4:6-dinitrophenylhydrazine was obtained by the methods described above by taking proportionate quantity of 1-chloro-2-bromo-4:6-dinitrobenzene in place of 1:2-dichloro-4:6-dinitrobenzene. Bromodinitrophenylhydrazine is also slightly soluble in alcohol and crystallises from an excess of it in yellow crystals, m.p. 172°. (Found: Br, 29.23. $C_6H_3O_4N_4Br$ requires Br, 28.88 per cent.)

Preparation of Hydrazones from 2-Chloro- and 2-Bromo-4:6 dinitrophenylhydrazines.—Hydrazones are obtained in nearly quantitative yields by refluxing for 4-5 minutes a mixture of the phenylhydrazine (0.5 g.) in alcohol (5 ml.) and equimolecular proportions of the carbonyl compound, in presence of 1 to 2 drops of concentrated sulphuric acid. They are purified by crystallising from an excess of alcohol.

Carbonyl compounds.	Hydrazones from chloro-dinitrophenyl hydrazine.		Hydrazones from bromo-dinitrophenylhydrazine.	
	M.p.	Colour.	M.p.	Colour.
Acetone	138°	Dull yellow	125°	Yellow
Methylethyl ketone	104°	Orange-red needles	101°	"
Benzaldehyde	198°	Orange-yellow silky needles	190°	Orange
<i>p</i> -Hydroxybenzaldehyde	234°	Orange	248°	Orange-red
<i>m</i> -Hydroxybenzaldehyde	257°	"	266°	Orange-yellow
Salicylaldehyde	227°	"	220°	Orange-red
Anisaldehyde	214°	"	214°	"
Cinnamic aldehyde	187°	Orange-red	188°	"
Vanillin	234°	Orange-red	240°	Orange
Protocatechuic aldehyde	234°	Scarlet	245°	Deep red
<i>o</i> -Chlorobenzaldehyde	238°	Deep yellow silky needles	240°	Yellow
Acetophenone	165°	Orange silky needles	162°	Red
<i>p</i> -Methylacetophenone	194°	Orange-red	174°	Orange-red
Benzophenone	186°	Orange needles	188°	Orange-yellow

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