359. *The Action of Bases on Nitrophenylhydrazines: 2:4-Dinitrophenylhydrazine.*

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CURTIUS and DEDICHEN (*J. pr. Chem.*, 1894, **50**, 241) first called attention to the formation of nitrophenylhydrazines by the action of hydrazine hydrate on chlorodinitrobenzene and other chloronitro-compounds. Later Curtius and Mayer (*ibid.*, 1907, **76**, 369) showed the formation of 6-nitro-1-hydroxy-1 : 2 : 3-benztriazole as a secondary product due to the subsequent action of the excess of the base. Spiegel (*Ber.*, 1908, **41**, 886) showed that the alkaline action of hydrazine hydrate is effective in converting 2 : 4-dinitro-1-piperidinobenzene into the same triazole, and a further study of similar reactions with nitrophenylhydrazines was made by Müller and his co-workers (*J. pr. Chem.*, 1925, **111**, 273, 277, 293, 307).

The amount of triazole formed is now shown to depend on the concentration of the base, but sufficient evidence is not yet available to warrant the assumption that it is independent of the cation present. Other products are dinitrobenzene and *mm'*-dinitroazoxybenzene; and a brown flocculent acid is also produced in increasing amount as the p_H increases, possibly owing to the action of the alkali on the dinitrobenzene (Lobry de Bruyn, *Rec. trav. chim.*, 1894, **13**, 119).

The molecular quantities of products formed per 100 g.-mols. of dinitrophenylhydrazine are plotted against the normality of the base in Figs. 1 and 2. From these it is seen that the amount of triazole formed decreases with increase in the normality of the baryta employed; and further decreases in the case of sodium hydroxide solutions until a minimum is reached with approximately 2·4*N*-alkali, after which increased yields are obtained. Side by side with this the reverse is noted in the case of dinitrobenzene and dinitroazoxybenzene, with each of which a maximum is recorded. The points marked by asterisks on the baryta curves represent the corresponding yields obtained with sodium hydroxide solution of the same normality, and give an indication that the catalysis of the reactions is independent of the cation present.

FIG. 1.

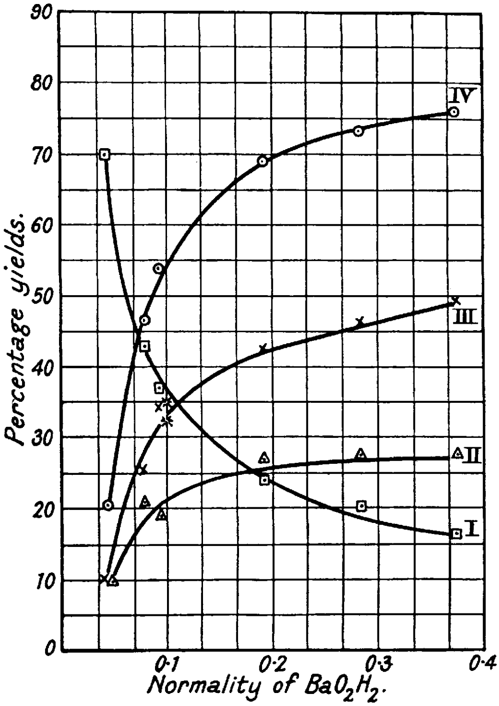
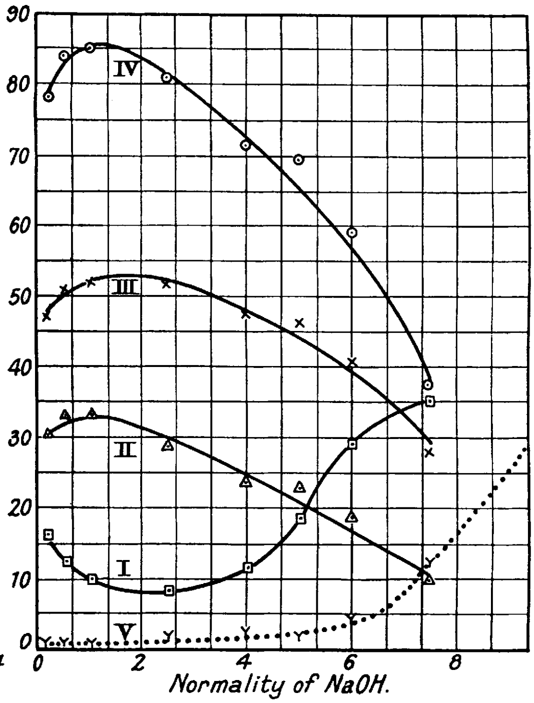


FIG. 2.



I. 6-*Nitro*-1-*hydroxy*-1 : 2 : 3-*benztriazole*.
II. m-*Dinitrobenzene*.
III. mm′-*Dinitroazoxybenzene*.
IV. m-*Dinitrobenzene and* mm′-*dinitroazoxybenzene*.
V. *Amorphous, unidentified acid*.

EXPERIMENTAL.

Conditions of Experiment.—The ammonia and hydrazine hydrate solutions were refluxed with 2 : 4-dinitrophenylhydrazine (Brady, J., 1931, 757) until reaction was complete (aqueous solution, 2 hours; alcoholic solutions, 2½ hours approx.). Baryta solutions were heated at 60° under reflux for times varying from 10 minutes (0·3*N*) to 5 hours (0·03*N*). Reactions with sodium hydroxide proceeded at room temperature (15° ± 2°) for from 15 minutes (7·5*N*) to 24 hours (0·5*N*), but the exothermic nature of the reaction necessitated cooling of the more concentrated solutions.

Isolation of Products.—A gaseous product, mainly nitrogen, was given off, but no great reliance could be placed on quantitative determinations of the amounts liberated. Traces of ammonia were formed in the reactions with baryta and sodium hydroxide, and a series of estimations showed that, if it were formed by the direct breakdown of the dinitrophenylhydrazine molecule, this occurred only to the extent of about 2%. We were unable to detect any resultant dinitroaniline.

To effect separation of the other constituents, the reaction mixture was acidified with hydrochloric acid and steam-distilled until all the dinitrobenzene had passed over, the distillate was warmed to 40° and allowed to cool, and the dinitrobenzene was filtered off, washed, dried in a vacuum desiccator, and weighed; the amount of dissolved dinitrobenzene in the filtrate (0·525 g. per l.) was added to the yield.

The solid residue obtained from the distilling flask was twice extracted with boiling water. The combined filtrates on evaporation gave 6-nitro-1-hydroxy-1 : 2 : 3-benztriazole and sodium or barium chloride; the latter was washed out with ice-cold water, and the triazole dried at 100°.

The residue after the triazole extraction was boiled with dilute sodium hydroxide solution; filtration then left *mm'*-dinitroazoxybenzene, and a brown flocculent acid was thrown out on acidification of the alkaline extract.

Identification of the Products.—(a) *m*-Dinitrobenzene was identified by mixed m. p. 90°. The naphthalene compound, m. p. 51—52°, was prepared by combination in boiling benzene. (b) 6-Nitro-1-hydroxy-1 : 2 : 3-benztriazole was characterised by its detonation point (206° after crystallisation from alcohol). The aniline salt, m. p. 159—160° (Curtius and Mayer, *loc. cit.*), and the acetate, m. p. 152—154° after crystallisation from benzene containing a little acetic anhydride (Brady, J., **1923**, **123**, 2258), were also prepared. (c) *mm'*-Dinitroazoxybenzene, recrystallised from alcohol, had m. p. and mixed m. p. 146—147° (Werner and Stiasny, *Ber.*, 1899, **32**, 3256). It was converted, by heating at 140° with concentrated sulphuric acid, into *mm'*-dinitro-*p*-hydroxyazobenzene, m. p. 171·5—172° after recrystallisation from aqueous alcohol (Klinger and Pitschke, *Ber.*, 1885, **18**, 2552).

Experimental Yields.—The weights of product obtained from 5 g. of dinitrophenylhydrazine are recorded below; and from these the number of mols. of product per 100 mols. of the dinitrophenylhydrazine have been calculated and plotted in the graphs as "percentage yields." Only the weight % of the unidentified amorphous acid is given, as no conversion factor is available. The weights are given to the nearest centigram.

Reagent.	Triazole.		Dinitrobenzene.		Dinitroazoxy-benzene.		Acid.	
	Wt.	Mols.	Wt.	Mols.	Wt.	Mols.	Wt.	%.
Ammonia (*d* 0·945)		70		17	trace			5
Hydrazine hydrate, 10% aqueous		82·5		1	—			1
Hydrazine hydrate, 10% in 80% EtOH		90	—		—		—	
Baryta 0·37*N*	0·73	16	1·15	27	1·78	49	—	—
,, 0·28*N*	0·91	20	1·15	27	1·67	46	—	—
,, 0·19*N*	1·09	24	1·12	26·5	1·54	42·5	—	—
,, 0·09*N*	1·68	37	0·83	19·5	1·25	34·5	—	—
,, 0·07*N*	1·95	43	0·89	21	0·93	25·5	—	—
,, 0·04*N*	3·18	70	0·42	10	0·38	10·5	—	—
NaOH 0·2*N*..................................	0·75	16·5	1·29	30·5	1·73	47·5	0·05	1
,, 0·5*N*..................................	0·57	12·5	1·40	33	1·85	51	0·05	1
,, 1·0*N*..................................	0·45	10	1·40	33	1·89	52	0·05	1
,, 2·5*N*..................................	0·39	8·5	1·23	29	1·89	52	0·1	2
,, 4·0*N*..................................	0·52	11·5	1·02	24	1·73	47·5	0·13	2·5
,, 5·0*N*..................................	0·84	18·5	0·98	23	1·69	46·5	0·1	2
,, 6·0*N*..................................	1·32	29	0·78	18·5	1·47	40·5	0·2	4
,, 7·5*N*..................................	1·59	35	0·41	9·5	1·00	27·5	0·6	12
* ,, 0·1*N*..................................	1·48	32·5	—	—	1·27	35	—	—

* Experiment at 60° for comparison with baryta yields.

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