204. *The Action of Bases on Nitrophenylhydrazines. Part II.*

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MACBETH and PRICE (J., 1934, 1637) showed that the action of bases on 2 : 4-dinitrophenylhydrazine gave rise mainly to dinitrobenzene, *mm'*-dinitroazoxybenzene, and 6-nitro-1-hydroxy-1 : 2 : 3-benztriazole, the proportions of the products depending on the concentration of the base. The data available did not warrant the assumption that the amount of triazole formed was independent of the cation present, but this is now shown to be true in a series of experiments carried out at 20° and 60°. The results (Table I) confirm the previous observation that a minimum yield of triazole is obtained at a certain concentration of alkali, and that simultaneously maxima are recorded in the yields of dinitrobenzene and dinitroazoxybenzene.

Müller and Weisbrod (*J. pr. Chem.*, 1925, **111**, 307) found that the action of hydrazine on 1-chloro-2 : 4-dinitronaphthalene gave rise to dinitronaphthol, dinitronaphthalene, dinitroazonaphthalene, and a nitronaphthatriazole, but did not isolate any of the corresponding 2 : 4-dinitronaphthylhydrazine. We have confirmed their results except that, in agreement with our work on dinitrophenylhydrazine, the supposed dinitroazonaphthalene appears actually to be 4 : *4′-dinitro-*2 : *2′-azoxynaphthalene.* The failure to isolate any dinitronaphthylhydrazine and the marked occurrence of dinitronaphthol seemed to us to be connected with the reactivity of the chlorine atom or other group in the 1-position. This suggestion is confirmed, for examination shows that 1-chloro-2 : 4-dinitronaphthalene is some ten times more susceptible to hydrolysis than the corresponding chlorodinitrobenzene (Table II).

EXPERIMENTAL.

Action of Bases on 2 : 4-*Dinitrophenylhydrazine.* The conditions of experiment and the isolation of the products were as previously described (*loc. cit.*), except that the triazole was separated from inorganic salts by extraction with alcohol. The weights of products obtained from 4 g. of 2 : 4-dinitrophenylhydrazine are recorded below, the figures under the heading "Mols." being obtained from these by calculating the number of mols. of product (to the nearest half mol.) per 100 mols. of dinitrophenylhydrazine.

TABLE I.

Reagent.		Triazole.		Dinitrobenzene.		Dinitroazoxybenzene.	
		Wt.	Mols.	Wt.	Mols.	Wt.	Mols.
NaOH	0·24*N* at 20°	0·72	20	0·81	24	1·34	46
,,	0·48*N* ,,	0·45	12·5	0·81	24	1·47	50
,,	0·95*N* ,,	0·38	10·5	0·87	25·5	1·54	53
,,	1·9 *N* ,,	0·36	10	0·85	25	1·54	53
,,	2·6 *N* ,,	0·46	12·5	0·77	22·5	1·49	51
,,	3·6 *N* ,,	0·65	18	0·67	19·5	1·35	46
,,	4·8 *N* ,,	0·88	24	0·64	19	1·16	40
,,	5·7 *N* ,,	1·20	33	0·49	14·5	1·02	35
,,	0·24*N* at 60°	1·0	27·5	0·78	23	1·14	39
,,	0·12*N* ,,	1·5	41	0·70	20·5	0·84	29
,,	0·06*N* ,,	2·34	64·5	0·42	12·5	0·38	26
,,	0·03*N* ,,	2·78	76·5	0·30	9	0·02	0·5
KOH	0·24*N* at 20°	0·69	19	0·85	25	1·38	47·5
,,	0·48*N* ,,	0·49	13·5	0·87	25·5	1·52	52·5
,,	0·95*N* ,,	0·38	10·5	0·85	25	1·56	53·5
,,	1·9 *N* ,,	0·33	9	0·81	24	1·60	55
,,	2·6 *N* ,,	0·45	12·5	0·73	21·5	1·52	52·5
,,	3·6 *N* ,,	0·62	17·5	0·62	18·5	1·41	48·5
,,	4·8 *N* ,,	0·88	24	0·49	14·5	1·22	42
,,	5·8 *N* ,,	1·21	33·5	0·34	10	1·09	37·5
,,	0·24*N* at 60°	0·94	25·5	0·76	22·5	1·18	40·5
,,	0·12*N* ,,	1·46	40	0·68	20	0·86	29·5
,,	0·06*N* ,,	2·36	65	0·44	13	0·40	13·5
,,	0·03*N* ,,	2·76	76	0·24	14	0·04	1·5
Baryta	0·38*N* at 60°	0·76	20·5	0·78	23	1·30	44·5
,,	0·19*N* ,,	1·02	28	0·74	22	1·10	38
,,	0·09*N* ,,	1·74	48	0·62	18·5	0·74	25·5
,,	0·05*N* ,,	2·40	66	0·40	12	0·34	11·5

Reactivity of Halogens.—To an alcoholic solution of the chloro-compound (100 ml. of 0·01*M*-solution) brought to 25° in a thermostat, alcoholic potash (2 ml., *N*) was added and mixed by shaking. After a definite time interval the mixture was poured into hydrochloric acid (5 ml., 0·2*N*), rinsed, and titrated with 0·2*N*-hydrochloric acid. In the case of chlorodinitronaphthalene the salt of dinitronaphthol produced by hydrolysis served as the indicator, the colour changing sharply from deep red to yellow at the end-point. In the case of chlorodinitrobenzene, chloroform was added during the titration; on shaking, it dissolved the free dinitrophenol. A satisfactorily sharp end-point was thus reached when the aqueous layer became colourless.

TABLE II.

1-Chloro-2 : 4-dinitrobenzene.				1-Chloro-2 : 4-dinitronaphthalene.			
Time (mins.).	Ml. 0·2N-HCl reqd. for titration.	$\log_{10}\frac{b(a-x)}{a(b-x)}$.	k.	Time (mins.).	Ml. 0·2N-HCl reqd. for titration.	$\log_{10}\frac{b(a-x)}{a(b-x)}$.	$k \times 10^{-1}$.
1	9·4	0·0287	(6·74)	1	7·25	0·2071	(4·87)
2	9·1	0·0453	(5·32)	2	6·3	0·3844	(4·52)
4	8·6	0·0771	4·53	3·5	5·8	0·5594	3·75
5	8·25	0·1036	4·87	4	5·7	0·6097	3·58
8	7·7	0·1541	4·53	5	5·6	0·6690	3·14
10	7·35	0·1942	4·56	6	5·4	0·8293	3·25
15	6·8	0·2762	4·32	6·5	5·4	0·8293	3·0
20	6·45	0·3472	4·08	7	5·3	0·9461	3·17
25	6·1	0·4429	4·16	8	5·25	1·0212	3·0
30	5·8	0·5594	4·38	10	5·1	1·4065	3·3
40	5·5	0·7404	4·35				
Mean k (excluding values in parentheses)			4·42				3·27 × 10^{-1}
Mean k (from slope of the curve)			4·36				3·25 × 10^{-1}

a = Initial concentration of potassium hydroxide; b = initial concentration of the chloro-compound; x = change in concentration of the reactants.

Action of Hydrazine Hydrate on 1-*Chloro*-2 : 4-*dinitronaphthalene.*—Following the method of Müller and Weisbrod (*loc. cit.*) chlorodinitronaphthalene (25 g.) was refluxed in alcohol (180 ml.) with excess of hydrazine hydrate (20 ml. of 50%) for 6 hours. After separation from dinitronaphthalene, dinitronaphthol, and 5-nitro-3-hydroxy-αβ-naphtha-1 : 2 : 3-triazole (det. pt. 235°), the residue was dissolved in aqueous sodium hydroxide, and on acidification a reddish-brown solid was precipitated. This on crystallisation from nitrobenzene gave dark red, microscopic, twinned crystals of 4 : 4′-*dinitro*-2 : 2′-*azoxynaphthalene*, m. p. 305—306°, which were no longer soluble in alkali (Found : C, 61·4, 61·6; H, 3·2, 3·5. $C_{20}H_{12}O_5N_4$ requires C, 61·85; H, 3·1%).

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