NOTES.

Determination of Electrokinetic Charge and Potential by the Sedimentation Method. Part VII. Silica in Some Solutions containing Multivalent Anions.*

By C. I. Dulin and G. A. H. Elton.

[Reprint Order No. 4712.]

Electrokinetic charges and potentials have been determined by the sedimentation method for fused silica powder in dilute aqueous solutions of sulphuric acid, potassium sulphate, potassium ferricyanide, and potassium ferrocyanide. The procedure was similar to that previously described, but an improved method of smoothing the sedimentation results was used. Various workers (see, *e.g.*, Rutgers and de Smet, *Trans. Faraday Soc.*, 1945, **41**, 758; 1947, **43**, 102; Buchanan and Heymann, *J. Colloid Sci.*, 1949, **4**, 151) have found experimentally that the electrokinetic potential of many systems varies linearly with the logarithm of the electrolyte concentration, and Robinson (*J. Chem. Physics*, 1946, **14**, 721) has given a tentative theoretical explanation of this effect. A study of our previous results for silica (Parts I, III, and V, *J.*, 1952, 286; 1953, 1168, 2099) shows that this rule is obeyed by silica in solutions containing univalent cations, but not in those containing multivalent cations, where cation hydrolysis is possible. The expression relating the

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* Part VI, *J.*, 1953, 3690.

electrokinetic potential, ζ, with the charge, σ, is that given by Benton and Elton (*J.*, 1953, 2096), *viz.*,

$$\sigma = \left[\frac{\varepsilon \boldsymbol{k}T}{2\pi}\right]^{\frac{1}{2}}[\Sigma n_i(\mathrm{e}^{-z_i\boldsymbol{e}\zeta/\boldsymbol{k}T} - 1)]^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n_i is the number of ions of type i per unit volume of the bulk solution, z_i is the valency, ε is the dielectric constant in the diffuse layer, $\boldsymbol{k}$ is Boltzmann's contsant, $\boldsymbol{e}$ is the electronic charge, and T is the absolute temperature. For fairly large values of ζ (of the order of 100 mv, as obtained with univalent cations), the contribution of terms due to anions (from solvent, solute, or hydrolysis products) is negligible (see Part III, *loc. cit.*), and $\mathrm{e}^{\boldsymbol{e}\zeta/\boldsymbol{k}T} \gg 1$, so that equation (1) reduces to

$$\sigma^2 = Ac\mathrm{e}^{\boldsymbol{e}\zeta/\boldsymbol{k}T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where A is a constant, and c is the normality. Also

$$\zeta = M \log c + N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where M and N are constants. The charge is related to the sedimentation velocity, u, by the expression

$$\sigma^2 = B\kappa(1/u - 1/u_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where B is a constant, κ is the specific conductivity of the suspension used, and u_0 is the limiting velocity. In solutions of sufficient concentration to render negligible the contribution of the solvent to the conductivity of the suspension, we may assume that κ is proportional to c over moderate ranges of concentration, *i.e.*, that the equivalent conductivity does not vary greatly over the range. With this assumption, we obtain from (2), (3), and (4)

$$\log (1/u - 1/u_0) = P \log c + Q \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where P and Q are constants. The data for all solutions with univalent cations fit this equation well, and good straight lines are obtained when $\log (1/u - 1/u_0)$ is plotted against $\log c$, slight deviations occurring at the lowest concentrations, owing to the increasing relative contribution of the solvent to the conductivity of the suspension. The best straight line may be determined by the method of least squares, and this method is particularly useful for smoothing results obtained in the higher concentration ranges, where u is not very different from u_0. The results given in the Table for the electrolytes with multivalent anions were calculated from data smoothed in this way.

It is seen that the charge in sulphuric acid is 200—600 e.s.u. less than that in potassium sulphate solution, owing to the fact that in acid solution the contribution of ions from the solvent to the electrokinetic charge is largely suppressed (see Parts III and V, *locc. cit.*). The charges and potentials for sulphuric acid are similar to those previously reported for hydrochloric and nitric acids, while those for potassium sulphate, ferricyanide, and ferrocyanide are similar to those for potassium chloride and nitrate. These results indicate that, as is usually found, the valency of the anion has little effect on the magnitude of the charge and potential for a negatively charged surface, the important factor being the valency of the cation.

	σ, e.s.u./cm.^{2}				ζ, mv			
c, N	H_2SO_4	K_2SO_4	$K_3Fe(CN)_6$	$K_4Fe(CN)_6$	H_2SO_4	K_2SO_4	$K_3Fe(CN)_6$	$K_4Fe(CN)_6$
1×10^{-3}	3488	3792	3706	3489	95·4	98·8	98·6	95·7
5×10^{-4}	2916	3498	3218	3150	103·8	112·7	109·2	108·2
2×10^{-4}	2226	2721	2731	2578	113·3	123·4	122·6	120·9
1×10^{-4}	1805	2148	2223	2140	120·2	129·1	129·2	128·1
5×10^{-5}	1453	1765	1752	1750	126·9	136·8	135·4	135·4
2×10^{-5}	1093	1299	1328	1364	135·8	144·2	145·1	145·9
1×10^{-5}	878	1080	1190	1130	142·3	153·0	155·3	154·0

All values of charge and potential are negative.

BATTERSEA POLYTECHNIC, LONDON, S.W.11.

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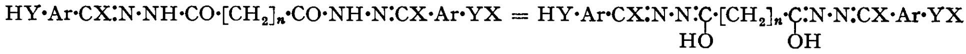
Chemical Reactions of Complexes. Part VI. Dinuclear Dihydrazide–Nickel Complexes.*

By LUIGI SACCONI.

[Reprint Order No. 4853.]

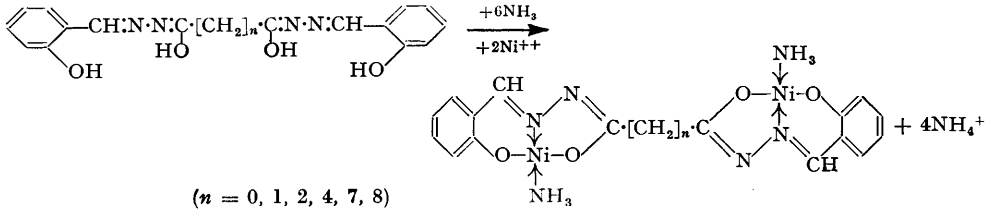
DIHYDRAZONES obtained by condensation of aliphatic dicarboxydihydrazides with salicylaldehyde, 2-hydroxy-1-naphthaldehyde, *o*-aminobenzaldehyde, or *o*-hydroxyacetophenone, have tautomeric formulæ :



$$\mathrm{HY{\cdot}Ar{\cdot}CX{:}N{\cdot}NH{\cdot}CO{\cdot}[CH_2]_{\mathit{n}}{\cdot}CO{\cdot}NH{\cdot}N{:}CX{\cdot}Ar{\cdot}YX} = \mathrm{HY{\cdot}Ar{\cdot}CX{:}N{\cdot}N{:}\underset{\mathrm{HO}}{C}{\cdot}[CH_2]_{\mathit{n}}{\cdot}\underset{\mathrm{OH}}{C}{:}N{\cdot}N{:}CX{\cdot}Ar{\cdot}YX}$$

(Ar = C_6H_4 or $C_{10}H_6$; X = H or Me; Y = O or NH; n = 0, 1, 2, 4, 6, 7, or 8)

They react in their enolic forms with nickel acetate in aqueous-alcoholic ammonia as bistridentate complexing agents, forming dinuclear dihydrazido-diammine–dinickel complexes, exemplified as follows for salicylaldehyde :

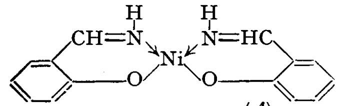


(n = 0, 1, 2, 4, 7, 8)

The formation of the complexes may be assisted by the conjugation in the imidic forms, $=\!\mathrm{N}{\cdot}\dot{\mathrm{C}}{\cdot}\mathrm{O}-$, necessarily involved in the complexing.

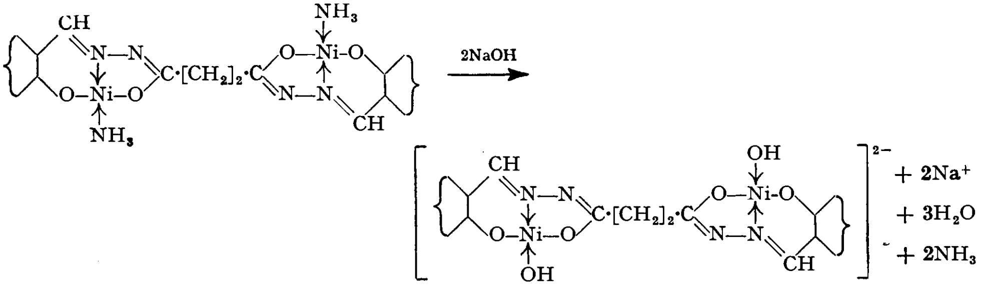
The complexes are very sparingly soluble in water and inert organic solvents. At >200° they give off ammonia. They are diamagnetic, indicating that the nickel central atoms are in the dsp^2 square-planar state (Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367).

If the nickel acetate in ammonia is brought in reaction with compounds R·CH:N·N:CH·R and the aldehydes or the ketone, then imino-derivatives of type (*A*) are formed.



(*A*)

If treated with aqueous-alcoholic sodium hydroxide, the dinuclear complexes lose ammonia, forming the alkaline salts of the hydroxo-complexes, exemplified below. This complex is very stable towards alkali and insoluble in water and organic solvents. It is diamagnetic and therefore planar with respect to the four dsp^2 covalent bonds.



Experimental.—Hydrazones. An aqueous or aqueous-alcoholic solution of the dihydrazide (1 mol.) was heated with the aldehyde or ketone (*ca.* 2—2·5 mols.), dissolved in alcohol, on the water-bath for ½—1 hr. The *dihydrazone* separated. By addition of water larger yields were

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* Part I, *J. Amer. Chem. Soc.*, 1952, **74**, 4503; Part II, *Z. anorg. Chem.*, 1953, **271**, 176; Parts III and IV, *Gazzetta*, 1953, **83**, 884, 894; Part V, *Z. anorg. Chem.*, in the press.

obtained. The products (Table 1) were yellow, except for the first three and the last, which were colourless, and were sparingly soluble in aqueous-alcoholic ammonia or sodium hydroxide in which they gave yellow solutions.

TABLE 1. *Dihydrazones*, $HY{\cdot}Z{\cdot}CX{:}N{\cdot}NH{\cdot}CO{\cdot}[CH_2]_n{\cdot}CO{\cdot}NH{\cdot}N{:}CX{\cdot}Z{\cdot}YH$.

X	Y	Z	*n*	M. p.	Found, N (%)	Formula	Reqd., N (%)
H	O	C_6H_4	0	310° *	17·6	$C_{16}H_{14}O_4N_4$	17·2
			7	190—191	12·9	$C_{23}H_{28}O_4N_4$	13·2
			8	213—214	12·75	$C_{24}H_{30}O_4N_4$	12·8
H	O	$C_{10}H_6$ †	1	226—228 *	12·5	$C_{25}H_{20}O_4N_4$	12·7
			2	277 *	12·1	$C_{26}H_{22}O_4N_4$	12·3
			4	313—314 *	11·0	$C_{28}H_{26}O_4N_4$	11·6
			6	294—295	10·65	$C_{30}H_{30}O_4N_4$	11·0
			7	244—245	11·0	$C_{31}H_{32}O_4N_4$	10·7
			8	227—229	10·4	$C_{32}H_{34}O_4N_4$	10·4
Me	O	C_6H_4	0	311—312 *	15·8	$C_{18}H_{18}O_4N_4$	15·8
			2	250—252 *	14·9	$C_{20}H_{22}O_4N_4$	14·7
			8	208—209	12·1	$C_{26}H_{34}O_4N_4$	12·0
H	NH	C_6H_4	1	225—229 *	24·35	$C_{17}H_{18}O_2N_6$	24·8
			6	216—217	20·5	$C_{22}H_{28}O_2N_6$	20·6
			8	191—192	19·3	$C_{24}H_{32}O_2N_6$	19·25

* With decomp. † From 2 : $1\text{-}HO{\cdot}C_{10}H_6{\cdot}CHO$.

TABLE 2. *Ammino-complexes* (*see formula in text*).

						Found, %			Required, %		
No.	Ar	X	Y	*n*	Formula	N	NH_3	Ni	N	NH_3	Ni
1	C_6H_4	H	O	0	$(C_{16}H_{10}O_4N_4)(NH_3)_2Ni_2$	17·25	—	24·7	17·7	—	24·8
2	,,	,,	,,	1	$(C_{17}H_{12}O_4N_4)(NH_3)_2Ni_2$	—	7·2	24·0	—	7·0	24·1
3	,,	,,	,,	2	$(C_{18}H_{14}O_4N_4)(NH_3)_2Ni_2$	16·7	—	23·4	16·75	—	23·4
4	,,	,,	,,	4	$(C_{20}H_{18}O_4N_4)(NH_3)_2Ni_2$	—	6·4	22·2	—	6·4	22·15
5	,,	,,	,,	7	$(C_{23}H_{24}O_4N_4)(NH_3)_2Ni_2$	14·5	—	20·45	14·7	—	20·5
6	,,	,,	,,	8	$(C_{24}H_{26}O_4N_4)(NH_3)_2Ni_2$	—	5·9	19·85	—	5·8	20·0
7	$C_{10}H_6$ *	,,	,,	1	$(C_{25}H_{16}O_4N_4)(NH_3)_2Ni_2$	13·9	—	20·1	14·3	—	20·0
8	,,	,,	,,	2	$(C_{26}H_{18}O_4N_4)(NH_3)_2Ni_2$	—	5·6	19·3	—	5·7	19·5
9	,,	,,	,,	4	$(C_{28}H_{22}O_4N_4)(NH_3)_2Ni_2$	12·8	—	18·2	13·35	—	18·6
10	,,	,,	,,	6	$(C_{30}H_{26}O_4N_4)(NH_3)_2Ni_2$	12·5	—	17·9	12·8	—	17·8
11	,,	,,	,,	7	$(C_{31}H_{28}O_4N_4)(NH_3)_2Ni_2$	—	5·0	17·3	—	5·1	17·5
12	,,	,,	,,	8	$(C_{32}H_{30}O_4N_4)(NH_3)_2Ni_2$	12·3	—	17·05	12·25	—	17·1
13	C_6H_4	,,	NH	1	$(C_{17}H_{14}O_2N_6)(NH_3)_2Ni_2$	—	7·0	24·1	—	7·0	24·2
14	,,	,,	,,	2	$(C_{18}H_{16}O_2N_6)(NH_3)_2Ni_2$	—	6·6	23·3	—	6·8	23·5
15	,,	,,	,,	6	$(C_{22}H_{24}O_2N_6)(NH_3)_2Ni_2$	19·7	—	20·9	20·1	—	21·1
16	,,	,,	,,	8	$(C_{24}H_{28}O_2N_6)(NH_3)_2Ni_2$	—	5·6	20·2	—	5·8	20·1
17	,,	CH_3	O	0	$(C_{18}H_{14}O_4N_4)(NH_3)_2Ni_2$	16·55	—	23·35	16·7	—	23·4
18	,,	,,	,,	2	$(C_{20}H_{18}O_4N_4)(NH_3)_2Ni_2$	14·9	—	20·7	14·85	—	20·75
19	,,	,,	,,	8	$(C_{26}H_{30}O_4N_4)(NH_3)_2Ni_2$	13·6	—	19·1	13·7	—	19·1

* From 2 : $1\text{-}HO{\cdot}C_{10}H_6{\cdot}CHO$.

Products from salicylaldehyde and adipohydrazide and from *o*-aminobenzaldehyde and succinohydrazide, were not pure. Those from salicylaldehyde and malono- and succinohydrazide were prepared by Blanksma and Bakels (*Rec. Trav. chim.*, 1939, **58**, 497).

Preparation of the complexes. A suspension of the hydrazone in alcohol was added to a solution of nickel acetate (*ca.* 2·5 mols.) in concentrated aqueous ammonia (1 g. in 10—15 ml.). Heating on the water-bath gave a red-brown solution from which the *complex* was precipitated. After cooling, this was filtered off, washed with alcohol and ether, and dried (P_2O_5). Yields were good. The dried samples were usually pure. Nickel was determined as nickel–dimethylglyoxime, ammonia by the micro-Kjeldahl method. Colours and forms of the complexes were : nos. 1, 7, 11, 18, orange needles; 2, 4, red plates; 3, 16, reddish-orange plates; 6, 9, 10, orange-yellow needles; 13, brown plates; 14, reddish-brown plates; 15, red prisms; 8, 12, 17, 19, orange; 5, orange-yellow.

Sodium dihydroxo-N′N‴-*di*-(2-*hydroxy*-1-*naphthylmethylene*)*succinylhydrazinodinickelate.* The corresponding ammino-complex (0·4 g.), suspended in aqueous-alcoholic 4% sodium hydroxide (4 ml.), was mixed with alcohol (30 ml.) and boiled on the water-bath for a few minutes. Water (10 ml.) was added, precipitating the *hydroxo*-complex (0·3 g.) (Found, in air-dried sample : N, 8·1; Ni, 16·7; Na, 6·6. $C_{26}H_{20}O_6N_4Ni_2Na_2,3H_2O$ requires N, 8·0; Ni, 16·7; Na, 6·7%).

Susceptibility measurements. These were made by means of the modified Bhatnagar balance (Sacconi, *Atti Accad. Lincei*, 1949, **6**, 639; Bhatnagar and Mathur, *Phil. Mag.*, 1929, **8**, 1041). The diamagnetism of the complexes was beyond doubt, but individual results are not reported because of the difficulty of removing paramagnetic impurities.

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Some Derivatives of Pyridinecarboxyhydrazides.

By D. D. LIBMAN, D. L. PAIN, and R. SLACK.

[Reprint Order No. 4879.]

THE derivatives of pyridine-3- and -4-carboxyhydrazide listed in the Table have been prepared for antitubercular tests. The following methods have been used: (I) Reaction of quaternary salts of ethyl nicotinate and *iso*nicotinate with hydrazine hydrate in ethanol (cf. Yale, Losee,

No.	Compound	Method	M. p.	Appearance	Solvent
Pyridine-4-carboxyhydrazide.					
1	Dodecyliodide	I	109—111°	Orange needles	EtOH
2	*N''*-Acetyl methiodide	III	208—209	Orange prisms	MeOH
3	*N''N''*-Diacetyl methiodide [a]	III	172	Yellow plates	EtOH
4	*N''*-Acetyl dodecyliodide	III	175	Pale yellow plates	,,
5	*N''N''*-Diacetyl dodecyliodide [a]	III [b]	287 [c]	Yellow plates	,,
6	*N''*-Acetyl benzylchloride	III	245 [c]	Colourless needles	MeOH
7	*N''*-*iso*Propylidene methiodide	IV	198—200	Yellow prisms	90% EtOH
8	*N''*-*iso*Propylidene dodecyliodide	IV	107—110	Yellow needles	EtOAc
9	*N''*-Furfurylidene methiodide	IV	250	Yellow needles	MeOH
10	*N''*-*p*-Methylbenzylidene	II	190	Colourless plates	EtOH
11	*N''*-(5-Hydroxypentylidene)	II	131	Colourless plates	,,
12	*N''*-(2-Ethylbutylidene)	II	119—120	Colourless needles	EtOAc
13	*N''*-*cyclo*Pentylidene	II	170	Colourless needles	EtOH
14	[Hexamethylenebis-1-(pyridinium-4-carboxyhydrazide bromide)]	I	213—215	Orange needles	MeOH
Pyridine-3-carboxyhydrazide.					
15	Dodecyliodide	I	117—118	Pale yellow plates	EtOH
16	Methiodide	I	186	Dark red needles	Aq. MeOH
17	*N''*-*iso*Propylidene dodecyliodide	IV	76—77	Yellow plates	EtOAc
18	*N''*-*iso*Propylidene methiodide	IV	195	Pale yellow plates	EtOH

	Found (%)			Required (%)	
No.	N	Hal	Formula	N	Hal.
1	9·75	29·1	$C_{18}H_{32}ON_3I$	9·7	29·4
2	13·05	39·1	$C_9H_{12}O_2N_3I$	13·1	39·3
3	11·3	34·2	$C_{11}H_{14}O_3N_3I,\frac{1}{2}H_2O$	11·3	34·2
4	9·05	26·8	$C_{20}H_{34}O_2N_3I$	8·85	26·7
5	8·0	24·65	$C_{22}H_{36}O_3N_3I$	8·1	24·6
6	13·7	11·55	$C_{15}H_{16}O_2N_3Cl$	13·7	11·6
7	13·1	40·9	$C_{10}H_{14}ON_3I$	13·2	39·8
8	8·75	27·25	$C_{21}H_{36}ON_3I$	8·9	26·9
9	11·7	35·7	$C_{12}H_{12}O_2N_3I$	11·75	35·6
10	17·9	—	$C_{14}H_{13}ON_3$	17·6	—
11	18·65	—	$C_{11}H_{15}O_2N_3$	19·0	—
12	19·6	—	$C_{12}H_{17}ON_3$ [d]	19·2	—
13	20·5	—	$C_{11}H_{13}ON_3$ [e]	20·7	—
14	15·2	29·1	$C_{18}H_{26}O_2N_6Br_2,2H_2O$	15·1	29·1
15	9·7	29·9	$C_{18}H_{32}ON_3I$	9·7	29·4
16	14·9	45·3	$C_7H_{10}ON_3I$	15·05	45·5
17	8·8	27·0	$C_{21}H_{36}ON_3I$	8·9	26·9
18	12·8	39·7	$C_{10}H_{14}ON_3I$	13·2	39·8

[a] This structure of diacetylhydrazides is assumed (cf. Heller, Köhler, Gottfried, Arnold, and Herrmann, *J. pr. Chem.*, 1928, **120**, 49; Fox and Gibas, *J. Org. Chem.*, 1953, **18**, 1375). [b] With addition of K_2CO_3. [c] With decomp. [d] Found: C, 65·8; H, 7·5. Reqd.: C, 65·8; H, 7·8%. [e] Found: C, 65·2; H, 5·8. Reqd.: C, 65·0; H, 6·4%.

Martins, Holsing, Perry, and Bernstein, *J. Amer. Chem. Soc.*, 1953, **75**, 1933). (II) Condensation of pyridine-3- and -4-carboxyhydrazide with a carbonyl compound (*idem, loc. cit.*) or acetic anhydride. (III) Quaternation of the products from method (II) with an alkyl halide. (IV) Condensation of quaternary salts of pyridine-4-carboxyhydrazide with a carbonyl compound.

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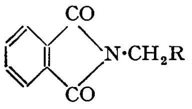
Some Reactions of Phthalimide.

By R. O. Atkinson.

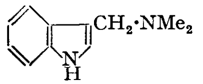
[Reprint Order No. 4942.]

Phthalimide has been found to react with formaldehyde and dimethylamine to form the base (I; R = NMe_2), which takes part in carbon alkylations in a similar manner to Mannich bases (Brewster and Eliel, " Organic Reactions," 1953, Vol. VII, p. 99), and may provide a useful method for the preparation of primary amines difficultly accessible by other means.

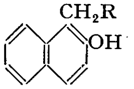
Initial attempts to form the base (I; R = NMe_2) by heating phthalimide, 40% formaldehyde solution, 30% dimethylamine solution, and acetic acid at 80° for a few minutes, or at 30° for several hours were unsuccessful, the product being *N*-hydroxymethylphthalimide (I; R = OH). The base was finally prepared by stirring the reaction mixture rapidly for 15 min. at room temperature, removing the unchanged phthalimide, and treating the filtrate with 25% sodium hydroxide solution at −10°. The yield was 76%, allowing for the recovered phthalimide.



(I)



(II)



(III)

The base (I; R = NMe_2) and the quaternary iodide (I; R = NMe_3}I) reacted with warm water to form the hydroxymethyl derivative (I; R = OH), whilst the hydrochloride in boiling alcohol gave phthalimide, thus precluding the use of these solvents as media for alkylation. The quaternary iodide with sodium cyanide in dimethylformamide gave phthalimidoacetonitrile in 81% yield.

Surprisingly, the unquaternised base, when heated with indole and a catalytic amount of sodium hydroxide at 180° for 2 hr., gave 3-phthalimidomethylindole (I; R = 3-indolyl) in 66% yield. Except for the few instances listed by Eliel (*J. Amer. Chem. Soc.*, 1953, **75**, 3589), bases which cannot undergo amine elimination and formation of an ethylenic intermediate take part in alkylation reactions only when quaternised (Snyder and Brewster, *ibid.*, 1949, **71**, 1058).

The recorded instances of nitrogen-alkylations by Mannich bases have all been amine-exchange reactions (*e.g.*, Snyder and Brewster, *ibid.*, 1948, **70**, 4230; Snyder and Eliel, *ibid.*, p. 4233; Bauer and Cymerman, *J.*, 1951, 3311). Phthalimide, which takes part readily in Michael-type additions (*e.g.*, Galat, *J. Amer. Chem. Soc.*, 1945, **67**, 1414; Atkinson and Poppelsdorf, *J.*, 1952, 2448), might be expected to react with Mannich bases and thus provide another route to certain primary amines.

Phthalimide and catalytic quantities of sodium hydroxide, heated with gramine (II) or 1-dimethylaminomethyl-2-naphthol (III; R = NMe_2) *in vacuo* at 180°, gave 3-phthalimidomethylindole (I; R = 3-indolyl) and 1-phthalimidomethyl-2-naphthol (III; R = phthalimido) in 82% and 69% yield respectively.

Potassium phthalimide with the methiodide (I ; $R = NMe_3$}I) in dimethylformamide solution gave diphthalimidomethane in 75% yield.

Since this work was completed the author learned (Hellmann, *Angew. Chem.*, 1953, **65**, 473) that kynuramine has been prepared recently by treating the Mannich base of *o*-aminoacetophenone with phthalimide and hydrolysing the product (U. Renner, Thesis, Tubingen, 1953).

Experimental.—N-*Dimethylaminomethylphthalimide.* Phthalimide (147 g.), 30% dimethylamine solution (150 c.c.), acetic acid (150 c.c.), and 40% formaldehyde solution (85 c.c.) were stirred together rapidly for 15 min. at room temperature. The unchanged phthalimide (99 g.) was removed, and the filtrate, cooled to −10°, was neutralised with 20% sodium hydroxide solution. The crystalline *base* was filtered off, washed with water, and recrystallised from alcohol, to give 50 g. (77%), m. p. 74—75° (Found : C, 64·4; H, 6·1; N, 13·5. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9; N, 13·7%).

The *methiodide*, obtained by refluxing the base in ether with an excess of methyl iodide, formed yellow crystals (70%), m. p. 239—240° (decomp.) (Found: N, 8·0; I^-, 34·7. $C_{12}H_{15}O_2N_2I$ requires N, 8·1; I^-, 33·5%). The *hydrochloride*, obtained in ether (yield 100%), had m. p. 154—155° (Found : N, 11·4; Cl^-, 14·6. $C_{11}H_{13}O_2N_2Cl$ requires N, 11·2; Cl^-, 14·8%).

Reaction of the base with water and alcohol. The base, heated with one mol. of acetic acid and water for 12 hr. at 30°, gave an almost quantitative yield of *N*-hydroxymethylphthalimide, m. p. 141—142° (Found : C, 67·1; H, 4·4; N, 8·6. Calc. for $C_9H_7O_2N$: C, 67·0; H, 4·3; N, 8·7%). Similar treatment of the hydrochloride in alcohol gave phthalimide, m. p. and mixed m. p. 242°.

Phthalimidoacetonitrile. A solution of the methiodide (6·9 g.) and sodium cyanide (1 g.) in dimethylformamide was heated under reflux for 1 hr., after which evolution of dimethylamine ceased. Dilution with water (60 c.c.) precipitated the crude nitrile, m. p. 118—120°. Recrystallisation from boiling water gave silky needles (3·1 g., 81%), m. p. 123—124° (Found : N, 14·9. Calc. for $C_{10}H_6O_2N_2$: N, 15·0%). Hydrolysis in acetic acid–hydrochloric acid (3 : 1) gave phthaloylglycine, m. p. 190—191° (Found : N, 6·8. Calc. for $C_{10}H_7O_4N$: N, 6·8%).

3-*Phthalimidomethylindole.* (*a*) The base (I; $R = CH_2 \cdot NMe_2$) (10·2 g.) was heated with indole (5·9 g.) and a few mg. of sodium hydroxide *in vacuo* at 180° for 2 hr. The resulting glass was triturated with alcohol, to give the *compound* (8 g., 65%). A portion recrystallised from alcohol had m. p. 182—183° (Found : C, 73·9; H, 4·4; N, 10·2. $C_{17}H_{12}O_2N_2$ requires C, 73·9; H, 4·3; N, 10·2%).

(*b*) Gramine (3·5 g.), phthalimide (2·9 g.), and a little sodium hydroxide similarly gave the same product (4·5 g., 82%), m. p. and mixed m. p. 182—183°.

1-*Phthalimidomethyl-2-naphthol.* 1-Dimethylaminomethyl-2-naphthol (10 g.), phthalimide (7·5 g.), and a few mg. of sodium hydroxide were ground together and heated *in vacuo* at 180° for 1 hr., whereafter evolution of gas ceased. The mixture was cooled and triturated with alcohol, to give the crude *compound*, which recrystallised from alcohol as pale yellow prisms (10·5 g., 69%), m. p. 202—203° (Found : C, 74·0; H, 4·3; N, 4·6. $C_{19}H_{13}O_3N$ requires C, 75·2; H, 4·3; N, 4·6%).

Diphthalimidomethane. Phthalimidotetramethylammonium iodide (6·5 g.), potassium phthalimide (3·7 g.), and dimethylformamide (20 c.c.) were heated under reflux for 6 hr., after which evolution of dimethylamine ceased. Dilution with water (20 c.c.) afforded the crude product, which was recrystallised from chloroform–alcohol (yield, 4 g., 65%) and had m. p. 226° (Found : N, 9·2. Calc. for $C_{17}H_{10}O_4N_2$: N, 9·15 %).

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