NOTES.

990. *The Preparation of* DL-α-*Methylhistidine Dihydrochloride.*

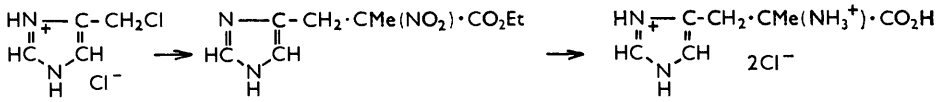
By B. ROBINSON and D. M. SHEPHERD.

THE three enzymes β-(3,4-dihydroxyphenyl)alanine decarboxylase, 5-hydroxytryptophan decarboxylase, and histidine decarboxylase are all inhibited by DL-β-(3,4-dihydroxyphenyl)-α-methylalanine (α-methyl-DOPA),[1] and 5-hydroxytryptophan decarboxylase is inhibited by 5-hydroxy-α-methyltryptophan (α-methyl-5HTP).[2] As the synthesis of the histidine analogue of the last compound, α-methylhistidine, has not been reported,

[1] Sourkes, *Arch. Biochem.*, 1954, **51**, 444; Smith, *Brit. J. Pharmacol.*, 1960, **15**, 319; Mackay and Shepherd, *ibid.*, p. 552; Udenfriend, Lovenberg, and Weissbach, *Fed. Proc.*, 1960, **19**, 7; Weissbach, Lovenberg, and Udenfriend, *Biochem. Biophys. Res. Comm.*, 1960, **3**, 225.

[2] Heinzelman, Anthony, Lyttle, and Szmuszkovicz, *J. Org. Chem.*, 1960, **25**, 1548.

we have prepared it, for study as a potential inhibitor of the above enzymes, by the route outlined in the formulæ.



The pharmacological studies on α-methylhistidine will be reported elsewhere.

Experimental.—*4-Chloromethylimidazole hydrochloride.* 4-Hydroxymethylimidazole hydrochloride [3] (30 g.) was added in portions of about 5 g. to redistilled thionyl chloride (125 c.c.) with shaking. After the initial exothermic reaction the solution was refluxed for 1 hr., during which time a light brown oil separated and solidified. The excess of thionyl chloride was then evaporated off, and the residual light brown solid recrystallized from ethanol–ether as off-white prisms, m. p. 139—141° (lit.,[4] 138—141°) (32·6 g., 96%).

Ethyl DL-β-*imidazol-4-yl-α-methyl-α-nitropropionate.* To a solution from sodium (4·2 g.) in dry ethanol (75 c.c.) at 0° was rapidly added with stirring a solution of ethyl α-nitropropionate [5] (17·4 g.) in dry ethanol (20 c.c.). An exothermic reaction ensued, and almost immediately the sodium salt of the nitro-ester crystallized. Stirring and cooling were continued, and 4-chloromethylimidazole hydrochloride (8·2 g.) in dry ethanol (100 c.c.) was added in about 30 min. Stirring was continued at room temperature for 36 hr. after which the ethanol was evaporated. The solid residue was dissolved in ice-cold 2N-hydrochloric acid, and extracted with ethyl acetate (3 × 60 c.c.). The aqueous solution was basified with an excess of saturated aqueous sodium carbonate and the base extracted with chloroform (4 × 75 c.c.), dried, and recovered as a light brown gum which crystallized on trituration with ethanol. Recrystallization from ethanol yielded white prisms, m. p. 116—118° (5·15 g., 32·5%). A further crop, m. p. 113—116° (1·6 g., 10%), was obtained by concentration of the mother-liquors. The pure *product* crystallized from ethanol as prisms, m. p. 119—121° (Found: C, 47·7; H, 5·95; N, 18·7. $C_9H_{13}N_3O_4$ requires C, 47·6; H, 5·7; N, 18·5%), $\lambda_{max.}$ 207—209 mμ (ε 7300 in EtOH), $\nu_{max.}$ (in Nujol) 1750s (C=O) and 1560s cm.$^{-1}$ (NO_2).

The ethyl acetate extracts, on drying and evaporation, gave a yellow oil (7·5 g.) that partially solidified under ether (m. p. 149—155°; 0·37 g.). Two recrystallizations from ethanol–ether gave *ethyl* DL-β-*imidazol-4-yl-α-methyl-α-nitropropionate hydrochloride* as needles, m. p. 164—165° (Found: C, 40·9; H, 5·4; N, 15·2, 15·9. $C_9H_{14}ClN_3O_4$ requires C, 41·05; H, 5·3; N, 15·95%), $\lambda_{max.}$ 207—210 mμ (ε 7500 in EtOH), $\nu_{max.}$ (in Nujol) 1760s (C=O), 1560s (NO_2), and 2700b cm.$^{-1}$ (NH^+). The product was readily soluble in water, giving a positive test for chloride. The ether-soluble material was unchanged ethyl α-nitropropionate (6·9 g.).

DL-α-*Amino*-β-*imidazol-4-yl-α-methylpropionic acid dihydrochloride* (DL-α-*Methylhistidine dihydrochloride*). A solution of ethyl DL-β-imidazol-4-yl-α-methyl-α-nitropropionate (4·0 g.) in ethanol (200 c.c.) was stirred at room temperature with hydrogen at 50 atm. for 14 hr. in the presence of platinum oxide (1 g.). Removal of the platinum and evaporation gave an oil (3·4 g., 96·5%) which did not crystallize and had $\lambda_{max.}$ 210—211 mμ (in EtOH), $\nu_{max.}$ (liquid film) 1740s (C=O), 3200bs cm.$^{-1}$ (NH) but no band at 1560 cm.$^{-1}$ (NO_2 absent).

The crude amine was heated in 11N-hydrochloric acid (25 c.c.) on a steam bath for 30 hr., and the solution was evaporated. The resulting brown gum (4·2 g.) crystallized from warm ethanol on addition of an equal volume of 11N-hydrochloric acid, to give white prisms, m. p. 183—185° (3·62 g., 87%). Recrystallization from ethanol–11N-hydrochloric acid gave pure DL-α-*methylhistidine dihydrochloride* as cubes, m. p. 184—185° (Found: C, 34·95; H, 5·65; N, 16·4. $C_7H_{13}Cl_2N_3O_2$ requires C, 34·85; H, 5·4; N, 17·4%), $\lambda_{max.}$ 211 mμ (ε 4820 in EtOH) [cf. histidine hydrochloride, $\lambda_{max.}$ 210—211 mμ (ε 4200 in EtOH)], $\nu_{max.}$ (in Nujol) 1725s (C=O) and 2500sb cm.$^{-1}$ (NH^+), pK_a 2·4 ± 0·1, 6·1 ± 0·1, and 9·9 ± 0·1 (cf. histidine dihydrochloride, pK_a 2·35 ± 0·1, 6·1 ± 0·1, and 9·6 ± 0·1).

One of us (B. R.) acknowledges the award of a Postdoctoral Research Fellowship by the Wellcome Foundation.

Department of Pharmacology and Therapeutics, University of St. Andrews, Queen's College, Dundee. [*Received, April 24th*, 1961.]

[3] Totter and Darby, *Org. Synth.*, 1944, **24**, 64.
[4] Turner, Huebner, and Scholz, *J. Amer. Chem. Soc.*, 1949, **71**, 2801.
[5] Kornblum and Blackwood, *Org. Synth.*, 1957, **37**, 44.

991. *Spectra of Ruthenates and Perruthenates.*

By J. L. Woodhead and J. M. Fletcher.

Ultraviolet Spectra.—A much used method [1] for determining ruthenium is based on its oxidation to ruthenate and measurement of the optical densities of the solution in the ultraviolet region. There are, however, conflicting values [1,2,3] for the molar extinction coefficients (ε_{Ru}) of ruthenate and perruthenate ions. We have redetermined these coefficients and at the same time have found the estimation of ruthenium in many of its complexes to be simpler and more reliable when the solution is converted with persulphate into a mixture, in any proportions over a wide range, of ruthenate and perruthenate and the value of ε_{Ru} at the isosbestic point is used.[3]

Primary standards used previously have been (*a*) the metal, (*b*) salts in which the ruthenium has been estimated by reduction to metal, and (*c*) ruthenium tetroxide. With (*a*) and (*b*) as standards, we find for various ruthenate–perruthenate mixtures in 2M-potassium hydroxide at 21°, an isosbestic point at 415 mμ with ε_{Ru} 1047, 1053, 1055 for solutions from the metal; with ε_{Ru} 1044, 1038 for those from commercial ruthenium trichloride; and with ε_{Ru} 1058, 1046 for those from $[RuNO{\cdot}OH(NH_3)_4]Cl_2$. There is a second isosbestic point at 273 mμ for which ε_{Ru} is 1005.

Determinations for ε_{Ru} at 460 mμ ($\lambda_{max.}$ for ruthenate) and at 385 mμ ($\lambda_{max.}$ for perruthenate) gave:

For ruthenate solutions	at 460 mμ	1714,	1720,	1700,	1715,	1716,	1692,	1720
	at 385 mμ	820,	830,	825,	826,	815,	865,	840
For perruthenate solutions ...	at 460 mμ	269,	290,	310,	256,	264		
	at 385 mμ	2170,	2176,	2183,	2162,	2175		

There was no significant difference between measurements at 15° and 30°. Averages of the figures are given in Table 1 along with previous determinations.

Table 1.

Values of ε_{Ru} in KOH solutions.

	Temp.	Ruthenate			Perruthenate			*X*
Wavelength (mμ)		317	385	460	317	385	460	
Marshall and Rickard [1] ...	25°	—		1742	—	—	—	—
Connick and Hurley [2]	25	~500	1030	1820	~2500	2275	283	1·23
Woodhead [3]	21	—	886	1692	—	2162	269	1·04
Larsen and Ross [3a]	—	—	—	1730	—	2150	—	—
This work	21	301	831	1710	2302	2173	278	1·06

A suitable criterion to apply to these and the earlier results is the value they give for the ratio *X*, defined as $(\varepsilon_{ruthenate} - \varepsilon_{perruthenate})_{460\ m\mu}/(\varepsilon_{perruthenate} - \varepsilon_{ruthenate})_{385\ m\mu}$. It can be shown that *X* is also equal to $\Delta D_{460\ m\mu}/\Delta D_{385\ m\mu}$ where ΔD is the change in optical density of a particular solution, identical except for a difference in the ratio of ruthenate to perruthenate. Alkaline solutions of potassium perruthenate are convenient for the determination of *X* because the conversion into ruthenate, $RuO_4^- + OH^- \longrightarrow >RuO_4^{2-}$, is slow at room temperature. Changes in the optical densities, measured in 1 cm. cells, of a solution of $3{\cdot}22 \times 10^{-4}$M-potassium perruthenate in M-potassium hydroxide at successive times after dissolution are given in Table 2.

The constancy of *D* at the isosbestic points 273 and 415 mμ showed that species other than ruthenate and perruthenate were not absorbing. The average of the values for *X*, 1·06, so found, when compared (Table 1) with those calculated from the reported values

[1] Marshall and Rickard, *Analyt. Chem.*, 1950, **22**, 745.
[2] Connick and Hurley, *J. Amer. Chem. Soc.*, 1952, **74**, 5012.
[3] Woodhead, U.K.A.E.A. Document, A.E.R.E.—R 3279, 1960.
[3a] Larsen and Ross, *Analyt. Chem.*, 1959, **31**, 176.

for ε_{Ru} at 385 and 460 mμ, supports the correctness of the figures now presented. For the same perruthenate solution, the optical densities at 317 mμ (where perruthenate shows a second peak) were also measured and the ratio $(\varepsilon_{ruthenate} - \varepsilon_{perruthenate})_{460\ m\mu}/(\varepsilon_{perruthenate} - \varepsilon_{ruthenate})_{317\ m\mu}$ was found to be 1·42. This ratio, in conjunction with a measured value of ε_{Ru} for ruthenate at 317 mμ, was used to obtain ε_{Ru} for perruthenate (Table 1) at this wavelength. This was necessary because the persulphate, added in the procedure to ensure freedom from ruthenate, absorbs strongly at 317 mμ.

TABLE 2.

Time (min.)	10	32	55	80
$\Delta D_{460\ m\mu}$	+0·42	+0·92	+1·68	+2·57
$\Delta D_{385\ m\mu}$	−0·39	−0·87	−1·61	−2·42
$\Delta D_{460\ m\mu}/D_{385\ m\mu}$ $(= X)$	1·07	1·06	1·04	1·06

The rather high values (Table 1) of Connick and Hurley may arise from their employing molar extinction coefficients for ruthenium tetroxide which are high; values lower by 5% have been given for these coefficients.[4]

Infrared Spectrum (with A. M. DEANE).—Apart from a weak band (overtone or combination) at 1656 cm.$^{-1}$, potassium perruthenate showed only a very strong broad band, partly resolved, at 827 and 846 cm.$^{-1}$. The occurrence of this metal–oxygen stretching band at a frequency lower than for $[MnO_4]^-$ (900 cm.$^{-1}$) and for $[ReO_4]^-$ (913 cm.$^{-1}$) implies that the range, 900—1100 cm.$^{-1}$, proposed [5] for the diagnosis of M=O bonds, should be extended to lower frequencies, since the bond length, 1·79 Å, for Ru=O in $[RuO_4]^-$ is consistent with some double-bond character.[6]

Experimental.—We had prepared cæsium tetrachlororuthenate for other studies. "Specpure" ruthenium metal and the other ruthenium compounds were from Johnson, Matthey & Co. Ltd. Commercial ruthenium trichloride and $[RuNO{\cdot}OH(NH_3)_4]Cl_2$ were analysed for ruthenium by reduction to metal,[7] the purity of which was established by spectrographic analyses. Commercial potassium perruthenate, dried at 110° (Found: K, 20·8; Ru, 45·6. (Calc. for $KRuO_4$: K, 19·1; Ru, 49·4%), had 3% of the ruthenium in a form other than ruthenate or perruthenate.

Isosbestic point at 415 mμ. Solutions containing known amounts of ruthenium were prepared (*a*) by gently boiling the trichloride (0·02 g.) and $[RuNO{\cdot}OH(NH_3)_4]Cl_2$ (0·03 g.) with 2M-potassium hydroxide (50 ml.) and potassium persulphate (0·25 g.) until the orange-red colour of ruthenate just changed to the green of perruthenate; (*b*) by fusing ruthenium metal (0·005—0·033 g.) at 500° with potassium hydroxide (0·15 g.) and potassium nitrate (0·25 g.) and dissolving the melt in 2M-potassium hydroxide (about 50 ml.) containing potassium persulphate (0·25 g.). Aliquot parts (10 ml.) from these stock solutions were boiled for different periods (1—4 min.) with more potassium persulphate (0·1 g.) to give different proportions of ruthenate and perruthenate and then diluted to 50 ml. with 2M-potassium hydroxide. Their spectra were measured between 400 and 420 mμ. The average value (1047) of ε_{Ru} at 415 mμ was constant in concentrations of alkali from 0·2M to 2M and in the useful range from 10^{-4}M- to 2×10^{-3}M-ruthenium and has been adopted for ruthenium determinations in these laboratories. Ruthenium was lost from boiling <2M-potassium hydroxide; in 6 min. a 0·2M-solution with $2{\cdot}14 \times 10^{-3}$M-Ru lost 26% and one of M-potassium hydroxide only 4%.

Ruthenate solutions. (*a*) Ruthenium metal (0·010—0·033 g.) was fused at 500° with potassium hydroxide and nitrate, and the melt extracted into cold 2M-potassium hydroxide (100 ml.). The optical density at 415 mμ showed that all the ruthenium was oxidised to Ru^{VI} or Ru^{VII}. (*b*) Cæsium tetrachlororuthenate(VI) (0·069 and 0·040 g.) was dissolved in 200 ml. of cold 2M-potassium hydroxide. To each ruthenate solution, potassium persulphate (~0·05 g.) was added to prevent the slow disproportionation which gives ruthenium dioxide. Absence of perruthenate was established by there being no change in D at 385 mμ in the presence of 0·05M-potassium iodide.

[4] Wehner and Hindman, *J. Amer. Chem. Soc.*, 1950, **72**, 3911.
[5] Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.
[6] Silverman and Levy, *J. Amer. Chem. Soc.*, 1954, **76**, 3317.
[7] Gilchrist, Raleigh, and Wichers, *J. Amer. Chem. Soc.*, 1935, **57**, 2567.

Perruthenate solutions. Ruthenate solutions (50 ml.; ~2×10^{-3}M-Ru), prepared from $Cs_2[RuO_2Cl_4]$, were oxidised by boiling them for 3—6 min. with potassium persulphate (0·25 g.) in 0·1—1M-potassium hydroxide. The ruthenium concentrations of the cooled solutions were calculated from the optical density at 415 mμ to correct for loss of Ru^{VIII} by volatilisation. Contact with carbon tetrachloride showed the absence of Ru^{VIII} in the aqueous phase.

Spectra. Absorption spectra were measured in fused silica cells at 21°: with a Unicam S.P. 500 spectrophotometer, and the infrared spectrum for mulls in Nujol between rock-salt windows with a Hilger H.800 spectrophotometer fitted with a rock-salt prism.

We thank Professor R. E. Connick for discussions by correspondence and for suggesting the use of potassium iodide to test for the purity of ruthenate solutions.

CHEMISTRY DIVISION, ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, NEAR DIDCOT, BERKS. [*Received, April 28th,* 1961.]

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992. *The Cross-linking of Cellulose and its Derivatives. Part V.*[1] *The Stability of Some* N*-Substituted* β*-Aminobutyric Acids and their Esters.*

By W. M. CORBETT, J. E. MCKAY, and W. TAYLOR.

IN Part I of this series [2] the addition of amines to cellulose crotonate was shown to be a suitable means of controlled cross-linking of cellulose and its derivatives. This reaction leads to the formation of *N*-substituted β-aminobutyrates which in the presence of water at room temperature are known to undergo hydrolysis and, at higher temperatures, the resulting free acids revert to crotonic acid and the corresponding amine, thus:

$$NHR{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2R' \longrightarrow NHR{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H \longrightarrow CHMe{:}CH{\cdot}CO_2H + NH_2R$$

The elimination is not due to heat alone, for crotonic acid was not detected when the acids were heated alone at 100°, and it must be initiated by attack of water at the hydrogen atoms on the α-carbon atom. The stability of aqueous solutions of several *N*-substituted β-aminobutyric acids has been examined so that the effect of the nature of the *N*-substituent may be shown. The elimination was followed by addition of sulphuric acid to the β-amino-acid solutions, distillation of the crotonic acid at 50° under reduced pressure, and determination of the crotonic acid in the distillate by oxidation with potassium permanganate. This process causes a small amount of elimination (<0·5%).

An aqueous solution of *NN'*-ethylenedi-(β-aminobutyric acid) (I) at 50° undergoes degradation only very slowly (Table 1), but at 100° the reaction is more rapid, levelling off

TABLE 1.

Decomposition of aqueous *NN'*-ethylenedi-(β-aminobutyric acid).

Time (hr.) at 100°	0	1·5	3·7	6	8	13	19
Crotonic acid formed (equiv.)	0·034	0·224	0·292	0·311	0·332	0·340	0·338
Time (hr.) at 50°	2	4	6·3	8·5	12·5		
Crotonic acid formed (equiv.)	0·018	0·022	0·024	0·022	0·024		

after 12 hr. when 0·35 equiv. of crotonic acid per equiv. of acid (I) had been produced. After 19 hr. the dibasic acid was recovered in 40% yield, indicating that the main reaction was decomposition to the monobasic acid (II; R = $CH_2{\cdot}CH_2{\cdot}NH_2$) and crotonic acid. Paper chromatography of the residue gave spots corresponding to β-(2-aminoethylamino)-butyric acid (II; R = $CH_2{\cdot}CH_2{\cdot}NH_2$) and ethylenediamine, the latter in very small amounts. The decomposition of other *N*-substituted β-aminobutyric acids, prepared by

[1] Part IV, Corbett and Winters, *J.*, 1961, 4823.
[2] Corbett and McKay, *J. Soc. Dyers and Colourists*, in the press.

addition of ethanolamine, benzylamine, *N*-acetylethylenediamine, hexylamine, and 6-*O*-3′-aminopropyldi-*O*-isopropylidene-D-galactose [3] to crotonic acid are given in Fig. 1. Interference with the crotonic acid estimation, probably by the isopropylidene groups, was

$(\cdot CH_2 \cdot NH \cdot CHMe \cdot CO_2H)_2$ (I) $NHR \cdot CHMe \cdot CH_2 \cdot CO_2H$ (II) $NH(CHMe \cdot CH_2 \cdot CO_2H)_2$ (III)

observed for the carbohydrate derivative although crotonic acid could be determined satisfactorily in the presence of di-*O*-isopropylidene-D-glucose. In this case corrected values were obtained by deduction of the value given by extrapolation to zero time.

Fig. 1 shows that the stabilities of the acids vary considerably, but cannot be related directly to structure. Of interest is the carbohydrate acid which is relatively stable, decomposing at a rate similar to that of β-aminobutyric acid itself.

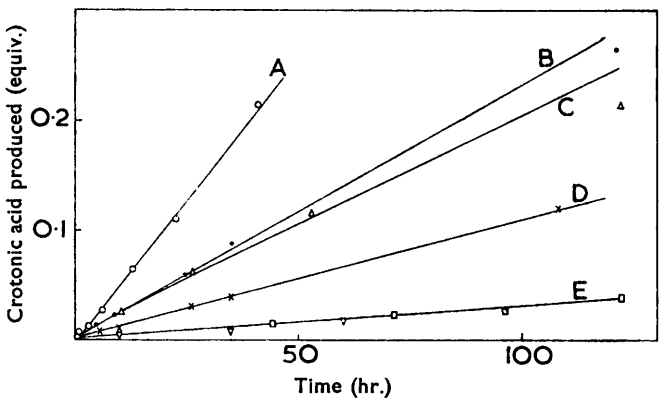
Hydrolysis of aqueous suspensions of ethyl β-benzylamino- and β-hexylamino-butyrate and of ββ′-iminodibutyrate [4] (III) has been followed by estimation of ethanol formed.

TABLE 2.

Hydrolysis of aqueous suspensions of esters.

	(II; R = CH_2Ph)			(II; R = n-C_6H_{13})			(III)		
Time (hr.)	5	24	100	7·25	24	77	5	27·5	74
EtOH formed (equiv.)	0·26	0·80	1·03	0·47	0·96	1·01	0·43	0·55	0·52

The first two react at a steady rate, being completely hydrolysed after 70 hr. (Table 2). In contrast, the ester of the dibasic acid undergoes rapid hydrolysis to about 50% completion



Decomposition of aqueous solutions of amino-acids (II) where R = (A) $HO \cdot CH_2 \cdot CH_2$, (B) CH_2Ph, (C) $NHAc \cdot CH_2 \cdot CH_2$, (D) n-hexyl, (E) □ H and ▽ 6-*O*-3′-aminopropyl-di-*O*-isopropylidene-D-galactose.

at which value it remains constant. This levelling off arises from neutralisation of the amino-group by acid liberated by hydrolysis of the first ester group with consequent disappearance of base catalysis.

Experimental.—Addition of n-hexylamine to ethyl crotonate. A solution of ethyl crotonate (30 g.) and n-hexylamine (30 g.) in absolute ethanol (100 ml.) was kept at room temperature for 6½ days and then evaporated. The resulting syrup was refluxed for 1 hr. with water (300 ml.) and then extracted with ether. Evaporation of the aqueous phase gave a residue which after several recrystallisations from ethanol–acetone–ether yielded ***β-n-hexylaminobutyric acid*** **(9 g.)**, m. p. 154—155° (Found: C, 64·1; H, 11·2; N, 7·8. $C_{10}H_{21}NO_2$ requires C, 64·2; H, 11·2; N,

[3] Corbett and McKay, *J*, 1961, 2930.
[4] Morsch, *Monatsh.*, 1932, **60**, 50.

7·5%). Distillation of the concentrated ether extract gave *ethyl* β-*n-hexylaminobutyrate* (32·0 g.), b. p. 89—90°/0·01 mm. (Found: C, 66·6; H, 11·7; N, 6·9. $C_{12}H_{25}NO_2$ requires C, 67·0; H, 11·7; N, 6·5%).

Addition of benzylamine to ethyl crotonate. A solution of ethyl crotonate (34·2 g.) and benzylamine (32·1 g.) in ethanol (100 ml.) was kept for 4½ days at room temperature, then concentrated to a syrup which partly crystallised. The syrup was mixed with ether and filtered, to give benzylamine crotonate (0·4 g.), m. p. 85—91°: after two recrystallisations from ethyl acetate–light petroleum (b. p. 40—60°) (Found: C, 67·9; H, 7·7; N, 7·2. Calc. for $C_{11}H_{13}NO_2$: C, 68·4; H, 7·8; N, 7·3%). Evaporation of the ether solution gave a syrup which was refluxed for 1 hr. with water (300 ml.), then extracted with ether. The aqueous phase, on evaporation, gave a solid which after recrystallisation from ethanol–acetone–ether gave β-*benzylaminobutyric acid* (14 g.), m. p. 178—179° (Found: C, 68·4; H, 7·9; N, 7·4. $C_{11}H_{15}NO_2$ requires C, 68·4; H, 7·8; N, 7·3%). Evaporation of the ether extract gave a syrup which distilled at b. p. 110—117°/0·05 mm. to give *ethyl* β-*benzylaminobutyrate* (22 g.) (Found: C, 70·9; H, 8·8; N, 6·3. $C_{13}H_{19}NO_2$ requires C, 70·7; H, 8·7; N, 6·3%).

Decomposition of N-*substituted* β-*aminobutyric acids.* Samples were withdrawn periodically from refluxed 0·1N-aqueous solutions of the acids, and, after addition of an equal volume of 0·1N-sulphuric acid, were distilled under reduced pressure at 50° with intermittent addition of water (100 ml.). The crotonic acid in the distillate was measured by oxidation with an excess of potassium permanganate. This methodg ave 95% recovery when applied to standard crotonic acid solutions.

Hydrolysis of N-*substituted ethyl* β-*aminobutyrates* (With Mr. B. SAGAR). Samples from agitated 0·1N-aqueous suspensions of the esters were chromatographed at 27° on a Pye argon chromatograph (column 4 ft.) comprising 120—150 mesh ballotini containing 0·7% of Flexol plasticiser 8N8 (Union Carbide Co.). The areas of the ethanol peaks were estimated by the triangulation method, and compared with that obtained for 0·1M-aqueous ethanol.

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993. *Oxaloacetic Acid. Part I. The Nature of Oxaloacetic Acid in the Solid State and in Neutral, Aqueous Solution.*

By BARBARA E. C. BANKS.

Two isomeric forms of crystalline, enolic oxaloacetic acid are reported to have m. p. 152° (*cis*) and 182° (*trans*).[1-3] The keto-acid has not been obtained crystalline. Meyer[4] showed, by bromine titration, that oxaloacetic acid is largely ketonic in aqueous solution. His estimate of the proportion (16—20%) of the enolic form present at equilibrium is, however, at variance with the value obtained by Hantzsch[5] (3%) from ultraviolet-absorption measurements. Gruber *et al.*[6] recently found that the two allegedly isomeric forms had identical infrared spectra and suggested, on this basis, that the difference in melting point was due only to the presence of traces of solid keto-acid as impurity.

[1] Wohl and Oesterlin, *Ber.*, 1901, **34**, 1139.
[2] Wohl, *Ber.*, 1907, **40**, 2282.
[3] Michael and Bucher, *Ber.*, 1896, **29**, 1792; *Ber.*, 1895, **28**, 2511.
[4] Meyer, *Ber.*, 1912, **45**, 2860.
[5] Hantzsch, *Ber.*, 1915, **48**, 1407.
[6] Gruber, Pfleiderer, and Wieland, *Biochem. Z.*, 1956, **328**, 245.

Wohl and Oesterlin's method of preparation [1] of the two crystalline forms of oxaloacetic acid is by decomposition of the pyridine salt of hydroxymaleic anhydride by 12% or 30% sulphuric acid giving, respectively, solids melting at 152° and 180°. In our hands, consistently with the report by Gruber *et al.*, no true melting points can be observed. Materials having a continuous range of decomposition points (144—172°) are obtained by varying the sulphuric acid concentration. Further, the decomposition point of the supposed low-melting modification can be raised by recrystallisation from solvents containing traces of sulphuric acid (Table 4). Decomposition points were measured in a conventional melting point aparatus and were unaffected by exhaustive drying of the samples (*in vacuo*, over P_2O_5) or by treatment of the glass melting-point tubes with acid. Recrystallisation of oxaloacetic acid from solvents containing traces of hydrochloric acid, acetic acid, pyridine, or triethylamine was without effect on the decomposition point. Traces of methanesulphonic acid and dimethyl sulphate produced effects qualitatively similar to, though smaller than, those of sulphuric acid.

All crystalline samples of oxaloacetic acid (decomp. point 144—172°) had identical infrared spectra. Two samples (decomp. 144° and 172°) were found to have identical crystal powder diagrams. It is, therefore, concluded that the variation in decomposition point is of complex origin and does not indicate the existence of two distinct, solid, isomeric forms.

When solid oxaloacetic acid is dissolved in an aqueous buffer solution, a rapid decrease in ultraviolet absorption is observed, due to formation of the keto-acid. Gruber *et al.* determined the rate of ketonisation by reducing the keto-acid, as it was formed, by the coenzyme DPNH under the influence of an excess of the enzyme malic dehydrogenase.* The rate of the enzymic reduction is then equal to the rate of ketonisation of the substrate. In the present work, a less cumbersome, direct spectrophotometric technique has been used. The following points have been established. (*a*) The molar extinction coefficient, $\varepsilon_{280\ m\mu}$ (enol), of the enolic form of oxaloacetic acid, obtained by extrapolation of the optical data, does not vary with decomposition point. The view [6] that the variation of the decomposition point is due to the presence of traces of the keto-acid is, therefore, unfounded. (*b*) The extrapolated value of $\varepsilon_{280\ m\mu}$ (enol) is in fair agreement with the molar extinction coefficient of oxaloacetic acid in ether, in which solvent the acid is known to be enolic.[4,5] (*c*) The rate of ketonisation is, as would be expected, buffer-catalysed and pH-dependent. A detailed study of the kinetics of this process will be reported later.

The equilibrium molar extinction coefficient of oxaloacetic acid has been determined in a number of buffer solutions in the pH range 5·0—10·0 and in solutions of sodium hydroxide (Table 3). The higher values obtained in borate buffer are, presumably, due to complex formation between the enolic acid and borate.[7] Formation of a Schiff's base between the keto-acid and the unsubstituted amino-group of 2-amino-2-hydroxymethylpropane-1,3-diol (Tris) may account for the rather higher values of $\varepsilon_{280\ m\mu}$ in this buffer than in phosphate buffer at the same pH. The large increase in absorption in 0·1N-sodium hydroxide is presumably due to ionisation of the enolic hydroxyl group.

If the extinction coefficient of the keto-acid is assumed to be of the same order as that of the next higher homologue, α-oxoglutaric acid, values of the tautomeric equilibrium constant, $K = c_{enol}/c_{keto}$, can be computed from the optical data. In buffers other than borate or Tris, K is constant (corresponding to 15·5—16% of enol) in the pH range 5·0—10·0.

The amount of enol present at equilibrium has also been determined by bromine titration, by the method described. The value obtained in this way (15·5—15·8%) is in excellent agreement with that computed from the optical data.

* It is known that the keto-form of oxaloacetic acid is the biologically active substrate for this enzyme.

[7] Greenwood and Greenbaum, *Biochem. Biophys. Acta*, 1953, **10**, 623.

The isomeric form of the solid oxaloacetic acid has not been certainly identified but the absence of a peak, in the infrared spectrum, in the region of the normal OH stretching frequency (2·8 μ) suggests that the enolic hydroxyl group is strongly hydrogen-bonded. This would be the case for the *trans*-enolic isomer.

TABLE 1.

t (sec.)	Optical density (280 mμ)	$10^3(k_1 + k_{-1})$ (sec.$^{-1}$)	t (sec.)	Optical density (280 mμ)	$10^3(k_1 + k_{-1})$ (sec.$^{-1}$)
0	1·202	—	207	0·534	5·39
25	1·083	5·10	235	0·487	5·37
52	0·962	5·30	280	0·427	5·39
85	0·843	5·26	340	0·366	5·38
115	0·743	5·38	430	0·303	5·38
146	0·662	5·35	499	0·277	5·42
175	0·594	5·39	∞	0·206	

TABLE 2.

Temp.	1·5°	1·5°	1·5°	1·5°	12·0°	25·0°
Phosphate (M)	0·100	0·075	0·050	0·025	0·100	0·100
$10^3(k_1 + k_{-1})$ (sec.$^{-1}$)	5·34	3·66	2·36	1·27	~15	~56
$\varepsilon_{280\ m\mu}$ (enol)	3430	3320	3430	3360	—	—

Experimental and Results.—Oxaloacetic acid was prepared from tartaric acid by Wohl and Oesterlin's method.[1] The product was recrystallised from hot acetone by the addition of hot benzene (Found: C, 37·0; H, 3·3; equiv., 131. Calc. for $C_4H_4O_5$: C, 36·4; H, 3·8%; equiv., 132). Buffer solutions were prepared from " AnalaR " reagents, except commercial 2-amino-2-(hydroxymethyl)propane-1,3-diol.

Ultraviolet absorption techniques. Measurements were made on a Unicam S.P. 500 spectrophotometer fitted with a temperature-controlled cell holder. The absorption changes occurring on dissolving oxaloacetic acid in aqueous buffer at neutral pH's were followed by a modification of the method of Gruber *et al.*[6] A small amount of the solid (*ca.* 0·025 g.) was dissolved in ethanol (5 c.c.) at −10°. An aliquot part (0·025 c.c.) of the ethanol solution was added to the buffer (3 c.c.) in a 1 cm. stoppered silica cell in the cell holder. The optical density (at 280 mμ) was determined at suitable time intervals. Below room temperature, dry nitrogen was blown through the cell holder to prevent misting on the optical surfaces. The sum of the first-order rate coefficients for ketonisation (k_1) and enolisation (k_{-1}) was calculated from the equation

$$k_1 + k_{-1} = \frac{2{\cdot}303}{t} \log \frac{D_0 - D_{eq}}{D_t - D_{eq}},$$

where t is the time (sec.) and D_0, D_{eq}, and D_t are the optical densities (280 mμ) at zero time, equilibrium, and t seconds respectively. Table 1 shows the results of a typical kinetic run, in 0·1M-phosphate buffer (pH 7·38) at 1·5°.

Table 2 gives the values of $(k_1 + k_{-1})$ at different concentrations of phosphate buffer (pH 7·38) and different temperatures in 0·1M-phosphate buffer together with values of $\varepsilon_{280\ m\mu}$ (enol) obtained by extrapolation of the optical data at the lowest temperature.

The equilibrium molar extinction coefficients of oxaloacetic acid in a number of buffer solutions and in solutions of sodium hydroxide are given in Table 3.

Bromination method. Oxaloacetic acid (0·16—0·25 g.) was dissolved in 0·1M-phosphate buffer (5 c.c.; pH 7·38) and allowed to reach tautomeric equilibrium (30 min., 25°). An aliquot part (4 c.c.) of the equilibrated solution was added to a slight excess (6 c.c.) of methanolic ~0·1N-bromine (containing M-lithium bromide) precooled to −20°. After varying times (30—120 sec.) the excess of bromine was removed by addition of di-isobutylene (4 c.c.). An excess of 10% aqueous potassium iodide (20 c.c.) was added and the solution left at 25° for

TABLE 3.

Buffer	pH	$\varepsilon_{280\ m\mu}$	Buffer	pH	$\varepsilon_{280\ m\mu}$	Buffer	pH	$\varepsilon_{280\ m\mu}$
Acetate	5·00	540	Phosphate ...	8·00	542	CO_3^{2-}–HCO_3^-	9·89	535
Phosphate ...	5·90	535	Tris	7·50	625	Borate	9·20	1,447
Phosphate ...	6·43	533	Tris	8·29	635	Borate	9·81	929
Phosphate ...	6·92	543	Tris	9·08	594	0·01N-NaOH...		659
Phosphate ...	7·38	550	CO_3^{2-}–HCO_3^-	9·28	548	0·1N-NaOH ...		1,950

$\varepsilon_{280\ m\mu}$ of oxaloacetic acid in ether is 3320. $\varepsilon_{280\ m\mu}$ of α-oxoglutaric acid in phosphate buffer (0·1M; pH 7·38) is 24.

TABLE 4.

Vol. H_2SO_4/100 c.c. of acetone	0·05	0·08	0·10	0·12	0·14	0·20	0·30
Decomp. pt. (corr.)	163°	165°	167°	162°	159°	151°	147°

30 min. The liberated iodine was titrated with 0·1N-sodium thiosulphate (soluble sodium–starch glycollate indicator).

Bromination was complete in 90 sec. at −20°. The percentage of enol estimated by this method was 15·5—15·8%.

Decomposition points. Table 4 shows the change in decomposition point on recrystallisation of a sample of oxaloacetic acid originally decomposing at 151°, from acetone–benzene containing traces of sulphuric acid.

Infrared spectra. These were measured for Nujol mulls on the Perkin-Elmer Infracord and on the Grubb-Parsons infrared spectrometers. The main absorption peaks occur at 1723, 1697, 1638, 1429, 1266, and 1235 cm.$^{-1}$.

Powder diffraction photographs. These were taken on a Phillips powder camera with Cu-$K\alpha$ radiation.

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994. *Solvent extraction of Septivalent Rhenium. Part III.*[1] *Heterogeneous Equilibria in the System, Aqueous Nitric Acid–Potassium Perrhenate–Dibutyl Phosphate.*

By AVIEZER STEVAN KERTES and ANNA BECK.

THIS paper extends our earlier work [1] on extraction of rhenium(VII) by tributyl phosphate and tri-iso-octylamine to cover, in all, three types of extractants: those extracting inorganic species by molecular association (Bu_3PO_4); those involving anion-exchange mechanism (R_3N); and those involving a cation-exchange mechanism (Bu_2HPO_4).

The two previous papers suggest that the rhenium-bearing species is exclusively the undissociated, or ion-paired, perrhenic acid, $HReO_4$, which is probably a general phenomenon for the metal oxy-acids.[2] In dealing with the extraction of perrhenic acid from aqueous nitric acid solutions, not only the rhenium(VII) species has to be considered, but also the extraction of nitric acid. Consequently, the system discussed in this series of papers is similar to those dealing with the extraction of strong complex acids of the type $HM^{III}X_4$ from strong mineral acids HX, where co-extraction of two strong acids has to be considered. Now, the extraction ratio of either of these acids from the aqueous phase containing a mixture of the two into dibutyl hydrogen phosphates will depend mainly on two factors: (i) the relative free-energy change favourable for the transfer of the ion-pairs into the solvent phase, and (ii) the mass-action effect in the aqueous phase. It seems to be of interest, therefore, to study, first, the simpler two-phase system of only three components, namely, water, nitric acid, and dibutyl hydrogen phosphate. The results, recently summarised,[3] on the solute–solvent interaction in the above system, showed that the molecular species existing in the organic phase when in equilibrium with aqueous nitric acid up to about 9M, are only the dimer dihydrate $(Bu_2HPO_4,H_2O)_2$ and a molecular adduct of the composition $(Bu_2HPO_4,H_2O)_2,HNO_3$ to the virtual exclusion of other species. The above nitric acid solvate is formed by the following reaction (water of hydration being omitted for simplicity):

$$(Bu_2HPO_4)_{2,o} + HNO_{3,a} \longrightarrow (Bu_2HPO_4)_2,\ HNO_{3,o} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1] Parts I and II, *J.*, 1961, 1921, 1926.
[2] Knapp, Smutz, and Spedding, ISC–766, 1957; Gerlit, Proc. Internat. Conf. Peaceful Uses of Atomic Energy, Geneva, 1955, United Nations, Vol. VII, p. 145.
[3] Kertes, Beck, and Habousha, *J. Inorg. Nuclear Chem.*, in the press.

and for the corresponding equilibrium quotient the value $K_{HNO_3} = 2{\cdot}1$ has been calculated. (The subscripts o and a refer to the organic and the aqueous phase, respectively. $HNO_{3,a}$ refers to undissociated acid.)

The experimental results for the distribution of perrhenate between aqueous nitric acid and undiluted dibutyl hydrogen phosphate (4·85M) or mixtures of this with carbon tetrachloride are shown in Fig. 1 as a function of the concentration of nitric acid in the initial aqueous solution. The total concentration of rhenium originally in the aqueous solution was $1{\cdot}8 \times 10^{-2}$M in all the experiments shown. The experiments were extended

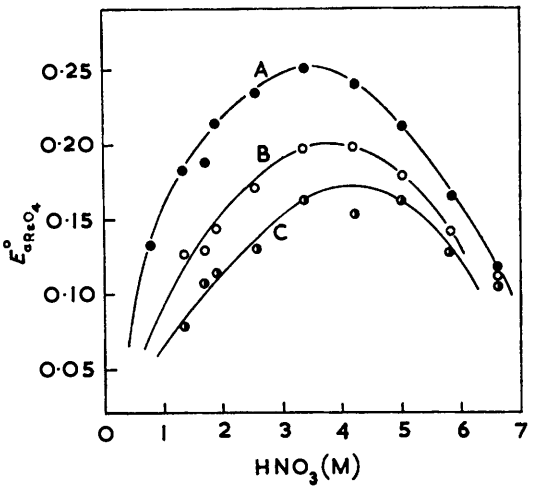

FIG. 1. Extraction ratio of perrhenate with changing nitric acid concentration in the initial aqueous solution : dibutyl hydrogen phosphate concentration = (A) 4·85M, (B) 4·36M, and (C) 3·88M.

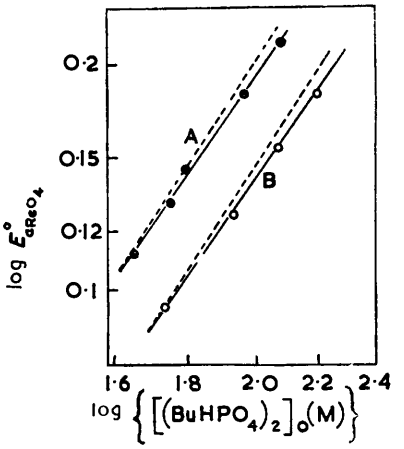

FIG. 2. Log–log plot of the perrhenate extraction ratio against $[Bu_2HPO_4)_2]_0$ for (A) 1·88M- and (B) 1·34M-nitric acid. The broken lines are drawn with a slope of 3.

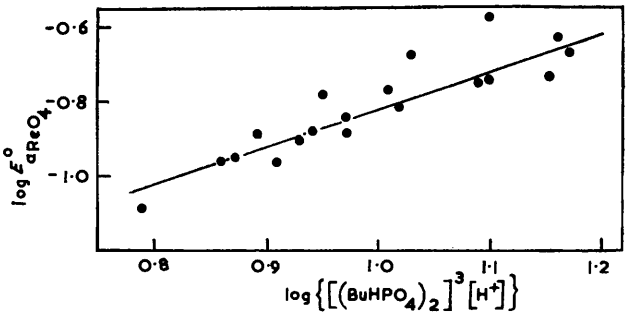

FIG. 3. Log–log plot of the perrhenate extraction ratio against $[(Bu_2HPO_4)_2]_o^3[H^+]_a$ for 4·85M-, 4·36M-, and 3·88M-dibutyl hydrogen phosphate and nitric acid concentrations up to 3·34M in the initial aqueous solution. The three most divergent points are those for the highest nitric acid concentrations.

to higher and lower nitric acid concentrations than those shown in the Figure, and also to dibutyl hydrogen phosphate concentrations lower than 3·88M, but the difficulties involved in the analytical determinations of rhenium in very low concentration in the organic phase render the measurements of very low E_a° values unreliable. The curves are similar in shape to the graph with tributyl phosphate instead of dibutyl hydrogen phosphate, but the maximum occurs at a different concentration of acid. The solvation number of rhenium(VII) in the ester phase was found by the slope of a log–log plot of E_a° against the concentration of free dibutyl hydrogen phosphate, *i.e.*, the portion of the ester not engaged in the nitric acid adduct, as calculated by assuming [3] complete formation of

$(Bu_2HPO_4)_2,HNO_3$ in the equilibrium organic phase at constant nitric acid concentration. The straight lines in Fig. 2, representing this graph, show a slope of nearly 3, suggesting that a trisolvate of rhenium extractable species exists in the ester phase. The above results suggest that the reaction

$$3(Bu_2HPO_4)_{2,o} + HReO_{4,a} \longrightarrow \{(Bu_2HPO_4)_2\}_3,HReO_{4,o} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

represents the extraction mechanism of rhenium by dibutyl hydrogen phosphate. The amounts of undissociated perrhenic acid in the presence of various high concentrations of nitric acid could not be calculated from the results presented in this paper, nor are they available from elsewhere (they must be very different from those in perchloric acid [4]); therefore, in order to evaluate the formation constant of the compound $\{(Bu_2HPO_4)_2\}_3,HReO_4$, equation (2) was rewritten as

$$3(Bu_2HPO_4)_{2,o} + H^+_a + ReO^+_{4,a} \longrightarrow \{Bu_2HPO_4)_2\}_3,HReO_{4,o} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The equilibrium quotient of equation (3) differs from that of equation (2) in that it includes the dissociation constant of perrhenic acid. As the ratio $\{(Bu_2HPO_4)_2\}_3,HReO_4 : ReO_4^-$ can be expressed in terms of the measured extraction ratio of rhenium(VII), the equilibrium quotient of equation (3) can finally be written as

$$K_{HReO_4} = E_a^\circ/[(Bu_2HPO_4)_2]_o^3[H^+]_a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Equation (4) requires that a graph of log E_a° against log $[(Bu_2HPO_4)_2]_o^3[H^+]_a$ should yield a straight line with a slope of unity and an intercept on the ordinate axis representing pK. Such a graph is shown in Fig. 3, with p$K = 1{\cdot}796$, *i.e.*, $K_{HReO_4} = 0{\cdot}016$. In calculating the equilibrium quotient, no significant trend was observed up to about 3M-nitric acid in the aqueous phase, but it has become increasingly apparent that serious limitations are imposed at higher acid content by a lack of determined activity coefficients for the organic solutes.

In conclusion, it may be said that dibutyl hydrogen phosphate and presumably other dialkyl hydrogen phosphates, have a low affinity for perrhenic acid, which seems to be a fairly general phenomenon for metal oxy-acids.[5] Further, it seems reasonable to suggest that dialkyl hydrogen phosphates act as trialkyl phosphates in the extraction of mineral acids [6] by forming molecular species in the organic phase without involving an ion-exchange mechanism.

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[4] Bailey, Carrington, Lott, and Symons, *J.*, 1960, 290.
[5] Boyd and Larson, *J. Phys. Chem.*, 1960, **64**, 988.
[6] Dyrssen and Krašovec, *Acta Chem. Scand.*, 1959, **13**, 561.

995. *A Novel Cyclisation Procedure for the Preparation of Chloro- and Other Purines.*

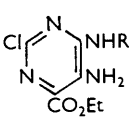
By JIM CLARK and J. H. LISTER.

BRIEF mention has already been made of the use of a mixture of dimethylformamide and phosphoryl chloride for conversion of 4,5-diaminopyrimidines into purines.[1] Other purines have now been synthesised in the same way and the procedure has been shown to be particularly useful for the direct preparation of purines with a chlorine atom in the pyrimidine ring. Such compounds have previously been made by heating 4,5-diamino-chloropyrimidines, under reflux, with diethoxymethyl acetate [2] or a mixture of ethyl orthoformate and acetic anhydride.[3]

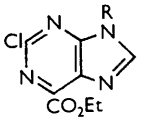
A feature of the new method is the ease with which very weakly basic diamines are converted into purines under mild conditions. This is illustrated by cyclisation of the

[1] Clark and Ramage, *J.*, 1958, 2821.
[2] Montgomery and Temple, *J. Amer. Chem. Soc.*, 1957, **79**, 5238; Montgomery and Holum, *ibid.*, 1958, **80**, 404.
[3] Montgomery, *J. Amer. Chem. Soc.*, 1956, **78**, 1928.

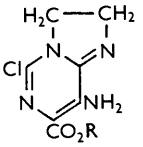
2-chloropyrimidines (I—III) to the corresponding purines (IV—VI). Ethyl 4,5-diamino-2-chloropyrimidine-6-carboxylate * (I) in particular is very unreactive and does not condense with 1,2-dicarbonyl compounds although reactions of this type form the basis of the very widely used Isay synthesis of pteridines.[4] For example, the compound was recovered after being heated for several hours with polyglyoxal in boiling 2-ethoxyethanol. In spite of this the diamine (pK_a 2·6), which is about 2500 times less basic than 4,5-diaminopyrimidine (pK_a 6·0),[5] was readily cyclised to the purine by dimethylformamide and phosphoryl chloride. Another diamine (II) which is about 1000 times less basic still (pK_a <0) was equally readily cyclised by the same method, in excellent yield. In the case of the 5-amino-4-2′-chloroethylaminopyrimidine (III) the purine synthesis succeeded in spite of competition from an alternative cyclisation which would have yielded the imidazolopyrimidine (VII).[1]



(I)



(IV)

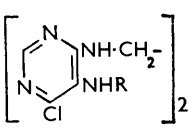


(VII)

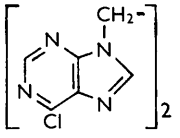
(II) R = $CH_2 \cdot CO_2Et$ (V)

(III) R = $CH_2 \cdot CH_2Cl$ (VI)

In certain cases the new method has proved successful with 4,5-diaminopyrimidines which did not give purines with the more usual cyclising agents. For example, although acetic anhydride–ethyl orthoformate and the 1,2-dipyrimidinylaminoethane (VIII; R = H) gave only the diacetamido-derivative (VIII; R = Ac),[6] the phosphoryl chloride–dimethylformamide mixture gave the required purine (IX) in very good yield.



(VIII)



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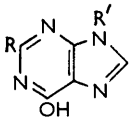
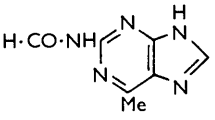


(X)



(XI)

The method appears to be generally applicable, provided no group liable to attack by the reagents is present. The conditions are so mild as to leave nuclear hydroxyl groups unchanged, thus both xanthine (X; R = OH, R′ = H) and a derivative of hypoxanthine (X; R = H, R′ = cyclohexyl) have been prepared from suitable hydroxypyrimidines. The 2-formamidopurine (XI) was obtained from 2,4,5-triamino-6-methylpyrimidine.

Although generally the heat of reaction produced by adding the phosphoryl chloride to the diaminopyrimidine–dimethylformamide mixture appears to be sufficient, in some cases heating on the water bath may be necessary to complete the reaction. Working up is very simple and usually consists of reducing the volume of the mixture, adding ice or water, and adjusting the pH as required.

This method of supplying the 8-carbon atom of a purine is an extension of the Vilsmeier–Haack formylation [7] which is an established procedure for the introduction of aldehyde groups into reactive heterocyclic nuclei. Another variant of this reaction, in which *o*-formamido-thioamides were cyclised to 4-mercaptopyrimidines by treatment with dimethylformamide and hydrogen chloride, was recently reported to give better yields than existing methods.[8]

Experimental.—Ethyl 2-chloropurine-6-carboxylate (IV). A mixture of ethyl 4,5-diamino-2-chloropyrimidine-6-carboxylate (0·2 g.), freshly distilled *NN*-dimethylformamide (10

* The synthesis of this compound and some physical data will be published shortly.

[4] Isay, *Ber.*, 1906, **39**, 250; Albert, *Quart. Rev.*, 1952, **6**, 225.
[5] Albert, *J.*, 1955, 2690.
[6] Lister, unpublished work.
[7] Vilsmeier and Haack, *Ber.*, 1927, **60**, 119; Minkin and Dorofeenko, *Uspekhi Khim.*, 1960, **29**, 1301.
[8] Taylor and Zoltewicz, *J. Amer. Chem. Soc.*, 1961, **83**, 248.

ml.), and phosphoryl chloride (1 ml.) was set aside for 1 hr., then heated on the water bath for 0·25 hr. Volatile matter was removed, under reduced pressure, on the water bath and the residue was treated with cold water (10 ml.) and a little dilute aqueous ammonia. *Ethyl 2-chloropurine-6-carboxylate* (0·16 g.) was filtered off and crystallised from 2-ethoxyethanol (charcoal) as plates, m. p. 254° (decomp.) (Found: C, 42·4; H, 2·9; N, 24·0. $C_8H_7ClN_4O_2$ requires C, 42·4; H, 3·1; N, 24·7%), exhibiting a slight blue fluorescence in ultraviolet (Wood's) light.

Ethyl 2-chloro-6-ethoxycarbonyl-9-purinylacetate (V). A mixture of ethyl 5-amino-2-chloro-6-ethoxycarbonyl-4-pyrimidinylaminoacetate [9] (II) (0·5 g.), *NN*-dimethylformamide (10 ml.), and phosphoryl chloride (1 ml.) was treated as described above except that no ammonia was required. Almost pure *ethyl 2-chloro-6-ethoxycarbonyl-9-purinylacetate* (0·43 g.), m. p. 134°, was obtained; this crystallised from ethanol as plates, m. p. 135° (Found: C, 45·9; H, 4·2. $C_{12}H_{13}ClN_4O_4$ requires C, 46·1; H, 4·2%), giving a slight blue fluorescence in ultraviolet (Wood's) light.

1,2-*Di*-(6-*chloro*-9-*purinyl*)*ethane* (IX). 1,2-Di-(5-amino-4-chloro-6-pyrimidinylamino)-ethane [6] (4·7 g.) in *NN*-dimethylformamide (40 ml.) was treated slowly with phosphoryl chloride (10 ml.), with some cooling, and left for 2 hr. The mixture was taken to dryness and the residue treated with ice (25 g.). The clear solution quickly deposited a yellow crystalline product (4·7 g., 82%) which on recrystallisation from propan-1-ol gave 1,2-*di*-(6-*chloro*-9-*purinyl*)*ethane* as colourless needles, m. p. 284—286° (Found: C, 43·5; H, 2·6; N, 33·6. $C_{12}H_8Cl_2N_8$ requires C, 43·0; H, 2·4; N, 33·5%).

9-*Cyclohexylhypoxanthine* [10] (X; R = H, R′ = cyclohexyl). Phosphoryl chloride (0·5 ml.) was added to a solution of 5-amino-4-cyclohexylamino-6-hydroxypyrimidine (0·5 g.) in dimethylformamide (5 ml.), and the mixture was treated as above. The resulting aqueous solution was brought to pH 6 and refrigerated overnight. The crude product was filtered off (0·4 g., 76%) and recrystallised from water, giving 9-*cyclohexylhypoxanthine* as prisms, m. p. 274—276° (Found: C, 60·2; H, 6·4; N, 25·6. $C_{11}H_{14}N_4O$ requires C, 60·5; H, 6·5; N, 25·7%).

2-*Formamido*-6-*methylpurine* (XI). A mixture of 2,4,5-triamino-6-methylpyrimidine (1 g.), dimethylformamide (12 ml.), and phosphoryl chloride (2 ml.) was treated as above. The *product* crystallised from water as colourless prisms (0·15 g.), m. p. >300° (Found: C, 47·75; H, 4·2; N, 39·2. $C_7H_7N_5O$ requires C, 47·3; H, 4·0; N, 39·5%).

Xanthine (X; R = OH, R′ = H). Obtained from 4,5-diamino-2,6-dihydroxypyrimidine as above, the product crystallised from water (charcoal) and agreed in analysis and ascending chromatography (in ammonium hydrogen carbonate solution [11]) with an authentic sample of xanthine (R_F 0·45) (Found: C, 39·3; H, 2·5. Calc. for $C_5H_4N_4O_2$: C, 39·5; H, 2·65%).

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The Royal College of Advanced Technology, Salford.
Chester Beatty Research Institute,
Institute of Cancer Research: Royal Cancer Hospital,
Fulham Road, London, S.W.3. [*Received, May 23rd,* 1961.]

[9] Clark and Layton, *J.*, 1959, 3411.
[10] Montgomery and Temple, *J. Amer. Chem. Soc.*, 1958, **80**, 409.
[11] Hems, *Arch. Biochem. Biophys.*, 1959, **82**, 485.

996. *The Preparation of Ammonium Alkyl Hydrogen Phosphites.*

By T. D. Smith.

The general method for the preparation of ammonium salts of organic phosphorous acids consists of the ammonolysis of organic phosphites in a suitable solvent or the treatment of the barium salt with ammonium sulphate. Diammonium iso-octyl phosphate [1] has been prepared by passing ammonia into a mixture of phosphorus pentoxide and iso-octyl alcohol, whilst the ammonolysis of pentaethyl tripolyphosphate in chloroform gives ammonium diethyl phosphate, ethyl hydrogen phosphoramidate, and diethylphosphoramide.[2,3]

[1] Rudel and Gargisa, U.S.P. 2,791,495.
[2] Simon and Stölzer, *Chem. Ber.*, 1956, **89**, 2253.
[3] Rätz and Thilo, *Z. anorg. Chem.*, 1953, **272**, 333.

In a study of the structure of organic acid phosphates the reaction of dialkyl hydrogen phosphites with ammonium thiocyanate was investigated:

$$PHO(OR)_2 + NH_4{\cdot}SCN \longrightarrow PHO(OR)(ONH_4) + RSCN$$

Previous studies [4] involving alkylation by dialkyl phosphites indicated that trialkyl phosphates react similarly; trialkyl phosphates reacted with ammonium thiocyanate to yield ammonium dialkyl phosphates.

Experimental.—Ammonium thiocyanate (0·04 mole) was heated at 125° with the dialkyl hydrogen phosphite (0·04 mole) for 4 hr. With dimethyl hydrogen phosphite the upper phase was separated, washed with 10% aqueous potassium carbonate, and water; it was distilled, and identified as methyl thiocyanate (1·9 g.), b. p. 130°.

The lower phase was treated with acetone (200 ml.), and the ammonium alkyl hydrogen phosphite separated. After filtration, the residue was washed with dry ether, recrystallised from acetone–ethanol, pumped until free of solvent, and stored over phosphorus pentoxide. The salient features of the various syntheses are detailed in the Table.

Product	Yield (%)	M. p.	Found (%) C	Found (%) P	Found (%) N	Reqd. (%) C	Reqd. (%) P	Reqd. (%) N
$(NH_4)MeHPO_3$ ...	92	108	10·6	27·4	12·4	10·7	27·3	12·3
$(NH_4)EtHPO_3$ ...	80	94	18·9	24·4	11·0	18·6	24·2	10·8
$(NH_4)Pr^iHPO_3$ ...	53	37	25·5	22·0	9·9	25·7	21·8	9·7
$(NH_4)Bu^nHPO_3$ ...	28	87	31·0	20·0	9·0	31·2	19·6	8·9
$(NH_4)Me_2PO_4$	74	103	16·8	21·7	9·8	16·7	21·5	9·8
$(NH_4)Et_2PO_4$	59	102	28·7	18·1	8·2	28·4	17·9	8·1

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UNIVERSITY COLLEGE OF NORTH WALES, BANGOR. [*Received, May 30th*, 1961.]

[4] Smith and Parker, *J.*, 1961, 442.

997. *The Disproportionation of Carbodi-imides.*

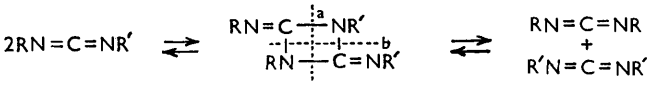
By I. G. HINTON and R. F. WEBB.

IN a study of potential cross-linking agents for polymer systems we have examined the preparation and properties of a series of biscarbodi-imides, the nitrogen analogues of the technically important di-isocyanates. The carbodi-imides were prepared by condensation of diamines such as ethylene-, hexamethylene-, and *m*-phenylene-diamine with alkyl isothiocyanates and dehydrosulphurisation of the resulting thioureas by mercuric oxide. The crude biscarbodi-imides were obtained as oils and characterised by conversion in high yield into the crystalline bisureas by treatment with glacial acetic acid.

Attempted distillation of the crude biscarbodi-imides gave only symmetrical carbodi-imides and involatile polymeric residues; thus hexamethylenebis(cyclohexylcarbodi-imide) gave dicyclohexylcarbodi-imide and an involatile polymer, presumably poly-(hexamethylenecarbodi-imide). At lower temperature and pressure certain biscarbodi-imides, *e.g.*, tetramethylenebis-(t-butylcarbodi-imide) can be distilled unchanged.[1]

The thermal disproportionation has been confirmed for the unsymmetrical carbodi-imide, isopropylphenylcarbodi-imide, which distilled unchanged at 110°/14 mm. but when distilled at atmospheric pressure gave di-isopropylcarbodi-imide and diphenylcarbodi-imide.

The disproportionation probably proceeds through the formation of cyclic dimers (or trimers) [2] which depolymerise with bond fission at a or b: as shown for the dimer:



the reaction being essentially similar to the reversible formation of keten and allene dimers.

[1] G.P. 924,751/1955.
[2] Khorana, *Chem. Rev.*, 1953, **53**, 145.

Continuous removal of a lower-boiling symmetrical carbodi-imide from the equilibrium mixture will drive the disproportionation to completion.

Experimental.—Hexamethylenebis(cyclohexylthiourea). Cyclohexyl isothiocyanate (40 g.) and 70% aqueous hexamethylenediamine (23·8 g.) in acetone (200 ml.) were left at room temperature for 15 hr. The solvent was evaporated *in vacuo*, and the residue washed with light petroleum (b. p. 40—60°) and recrystallised from methanol to give the *bisthiourea* (55 g.), m. p. 143—145° (Found: C, 60·4; H, 9·6; N, 13·7; S, 16·1. $C_{20}H_{38}N_4S_2$ requires C, 60·2; H, 9·6; N, 14·1; S, 16·1%).

Hexamethylenebis(cyclohexylcarbodi-imide). The bisthiourea (40 g.) and yellow mercuric oxide (250 g.) were suspended in boiling carbon disulphide (500 ml.) and stirred under reflux for 20 hr. Powdered calcium chloride (40 g.) and Hyflo Supercel (50 g.) were added; the mixture was filtered and evaporated. The residual oil (24 g.) was taken up in light petroleum (b. p. 40—60°), shaken with Hyflo Supercel, filtered to remove unchanged thiourea, and evaporated, leaving the crude biscarbodi-imide as a yellow oil (19 g.), $\nu_{max.}$ 2150 cm.$^{-1}$.

When the crude carbodi-imide (4 g.) was dissolved in glacial acetic acid (20 ml.) the solution became hot and deposited colourless crystals; the mixture was poured into cold water (100 ml.), and the solid (3·8 g.) collected, washed with boiling acetone, recrystallised from glacial acetic acid, washed with acetone, and dried to give *hexamethylenedi(cyclohexylurea)*, m. p. 230—232° (Found: C, 65·3; H, 10·3. $C_{20}H_{38}N_4O_2$ requires C, 65·5; H, 10·4%).

Disproportionation of the biscarbodi-imide. The crude biscarbodi-imide was distilled, first at 14 mm. through a 20″ Vigreux column, to give materials (*a*) (2·9 g.), b. p. 100°/14 mm., cyclohexyl isothiocyanate produced in a side reaction, and (*b*) (2·4 g.), b. p. 150—154°/14 mm., dicyclohexylcarbodi-imide. The residue was further distilled at 0·35 mm. without the column to give materials (*c*) (1·6 g.), b. p. 91—92°/0·35 mm., dicyclohexylcarbodi-imide, (*d*) (3·9 g.), b. p. 92—200°/0·35 mm., mainly hexamethylenebis(cyclohexylcarbodi-imide), and (*e*) (2·5 g.), a black residue. On treatment with acetic acid, fractions (*b*) and (*c*) both gave dicyclohexylurea, m. p. and mixed m. p. 232°; fraction (*d*) gave hexamethylenedi(cyclohexylurea), m. p. and mixed m. p. 230—232°.

Isopropylphenylcarbodi-imide. Phenyl isothiocyanate (54 g.) and isopropylamine (50 g.) were mixed in light petroleum (700 ml.). After an exothermic reaction had subsided, the mixture was heated under reflux for ½ hr. and then cooled. Colourless plates (73 g.) of isopropylphenylthiourea were collected and washed with light petroleum. The thiourea (73 g.) was added to a stirred suspension of yellow mercuric oxide (180 g.) in carbon disulphide (500 ml.). After the exothermic reaction had subsided, the mixture was heated for ½ hr., powdered calcium chloride (50 g.) and Hyflo Supercel (50 g.) were added, and the mixture was filtered and evaporated, giving the *carbodi-imide* (25 g.), b. p. 111—112°/14 mm. (Found: C, 74·5; H, 7·6; N, 17·8. $C_{10}H_{12}N_2$ requires C, 75·0; H, 7·6; N, 17·5%). Treatment with acetic acid gave isopropylphenylurea, m. p. 154—155° (lit.,[3] 156°) after recrystallisation from aqueous ethanol (Found: C, 67·7; H, 8·0; N, 15·5. Calc. for $C_{10}H_{14}N_2O$: C, 67·4; H, 7·9; N, 15·7%).

Disproportionation of isopropylphenylcarbodi-imide. The carbodi-imide (23·5 g.) was allowed to boil gently at atmospheric pressure under a 20″ Vigreux column. The liquid temperature rose steadily from 220° to 280° while the still-head temperature fell from 160° to 100°. The distillate (12·3 g.) was redistilled at 14 mm., to give di-isopropylcarbodi-imide (6·6 g.), b. p. 43—44°/14 mm. (Found: N, 22·0. Calc. for $C_7H_{14}N_2$: N, 22·2%), which with acetic acid gave di-isopropylurea, m. p. 190° (sublimes) (lit.,[4] 192°). The combined distillation residues were distilled at 14 mm. to give isopropylphenylcarbodi-imide (5·3 g.), b. p. 112—115°/14 mm., an intermediate fraction (2·0 g.), and diphenylcarbodi-imide (10·4 g.), b. p. 175—176°/14 mm. (Found: N, 14·4. Calc. for $C_{13}H_{10}N_2$: N, 14·4%), which with acetic acid gave diphenylurea, m. p. 237° (lit.,[5] 235°) (from acetone).

CIBA (A. R. L.) LIMITED,
DUXFORD, CAMBS.

[*Received, June 7th*, 1961.]

[3] Manguin, *Ann. Chim.* (*France*), 1911, **22**, 321.
[4] Hofmann, *Ber.*, 1882, **15**, 756.
[5] Weith, *Ber.*, 1876, **9**, 821.

998. *Phosphino-arylboranes.*

By G. E. Coates and J. G. Livingstone.

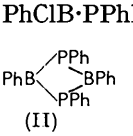
Phosphinodiarylboranes derived from monofunctional phosphines and boranes, *e.g.*, $Ph_2B{\cdot}PPh_2$ from Ph_2BCl and Ph_2PH, are monomeric and relatively resistant to hydrolysis and oxidation.[1] We now describe a few products derived from bifunctional phosphines or boranes.

Phenylphosphinidenebis(diphenylborane), $(Ph_2B)_2PPh$, from chlorodiphenylborane and phenylphosphine, and the analogous compound phenylbis(diphenylphosphino)borane, $(Ph_2P)_2BPh$, from dichlorophenylborane and diphenylphosphine, are both sensitive to atmospheric oxidation and are readily converted into the corresponding phenyl-substituted oxy-acids of boron and phosphorus by the action of aqueous alkaline hydrogen peroxide, *e.g.*:

$$(Ph_2P)_2BPh \longrightarrow 2Ph_2PO_2H + Ph{\cdot}B(OH)_2$$

Both these P–B compounds are colourless and are monomeric in benzene, but a yellow polymer is gradually deposited when a benzene solution of $(Ph_2P)_2BPh$ is heated under an inert atmosphere.

Dichlorophenylborane and phenylphosphine form a 1 : 1 complex, which slowly evolves hydrogen chloride when its solution in xylene is boiled. When hydrogen chloride evolution ceases, three products can be isolated: chloro(phenylphosphino)phenylborane, $PhClB{\cdot}PPhH$ (I), b. p. 98—100°/*ca.* 10^{-3} mm.; a colourless compound $(PhB{\cdot}PPh)_2$ (II), m. p. 89—91°, which is quantitatively oxidized to phenylboronic and phenylphosphonic acid; and a yellow involatile compound (III) containing just over 1% of chlorine. The most reasonable structure for compound (II) is cyclic. On the basis of our dipole-moment study of phosphinoboranes of the type $Ar_2B{\cdot}PAr'_2$, which indicated that phosphorus is a very weak π-donor to boron, we regard compound (II) as co-ordinatively unsaturated except for interaction with the phenyl groups.



(II)

The yellow product (III), which is insoluble in benzene, and yields phenylboronic and phenylphosphonic acids in the molar ratio 0·96 : 1 on oxidation, is probably a polymer containing B–Cl and P–H end groups: $PhBCl{-}[{-}PPh{\cdot}BPh{-}]_n{-}PPhH$. Its chlorine content indicates that n is about 13. A small P–H content was indicated by a weak infrared absorption at 4·33 μ. The amounts of products (I), (II), and (III) were in the approximate ratios 3 : 1 : 3.

Attempts to condense dichlorophenylborane and phenylphosphine in the presence of two mols. of triethylamine were not successful; only one mol. of amine hydrochloride separated but no crystalline product could be isolated from the two-phase benzene solution which probably contained the triethylammonium salt of a phosphinophenylborane anion.

In our earlier paper [1] on phosphinodiarylboranes, in which their dipole moments were shown to be in the direction $Ar_2B{\cdot}\overrightarrow{PAr_2}$, the polarity was ascribed mainly to electron flow from the aryl groups to the boron 2*p*-orbital, and similarly from the phosphorus atom to the aryl groups bound to it. As a check on this interpretation we hoped to measure the dipole moments of dimesityl- and di-(4-biphenylyl)-(di-*m*-tolylphosphino)borane. In the first compound we expected the steric requirements of the mesityl groups to prevent conjugation with the boron 2*p*-orbital, leading to a reduction of moment, while in the second compound the electron flow over a greater distance should result in a larger moment [than that of $Ph_2B{\cdot}P(C_6H_4Me\text{-}m)_2$]. The preparation of both compounds is described below, but they were too sparingly soluble to allow their dipole moments to be measured.

Experimental.—Preparations were carried out in a nitrogen atomosphere.

Phenylphosphinidenebis(diphenylborane), $(Ph_2B)_2PPh$. Chlorodiphenylborane (10 g., 0·05 mole) in dry xylene (50 c.c.) was slowly added to a mixture of triethylamine (6·5 c.c., 0·05 mole) and phenylphosphine (2·6 c.c., 0·025 mole) in xylene (50 c.c.). After the mixture had been

[1] Coates and Livingstone, *J.*, 1961, 1000.

refluxed for 24 hr., cooled, and filtered from triethylammonium chloride, evaporation yielded the *phosphine*, which was crystallized from benzene–hexane and had m. p. 148—150° (Found: C, 81·8; H, 5·6. Found, by hydrogen peroxide oxidation: PhP, 24·2; Ph_2B, 75·1. $C_{30}H_{25}B_2P$ requires C, 82·2; H, 5·7; PhP, 24·7; Ph_2B, 75·3%). The degree of association, measured cryoscopically at 0·125, 0·151, 0·249, and 0·317 weight % in benzene solution, was 0·99, 1·01, 1·04, and 1·19.

Bis(diphenylphosphino)phenylborane, $PhB(PPh_2)_2$. Dichlorophenylborane, m. p. 5·1—5·5° (4·0 g., 0·025 mole), in benzene (30 c.c.) was added to a solution of diphenylphosphine (9·3 g., 0·05 mole) and triethylamine (5·1 g., 0·05 mole) in benzene (50 c.c.) at room temperature. The mixture was refluxed for 24 hr., cooled, and filtered under nitrogen from triethylammonium chloride. The filtrate was evaporated and the yellow residue extracted with benzene, leaving a small amount of yellow insoluble polymer. The colourless *product* (9·2 g., 78%) crystallized from benzene–hexane and had m. p. 143—144° (Found, by oxidation: PhB, 17·5; Ph_2P, 79·8. $C_{30}H_{25}BP_2$ requires PhB, 18·0; Ph_2P, 80·9%). The degree of association, measured cryoscopically at 0·733, 1·101 and 1·124 weight % in benzene solution, was 0·92, 1·01, and 1·03.

Prolonged heating of the colourless monomer in benzene yielded more of the insoluble yellow polymer, m. p. 120—132° (Found, by oxidation: PhB, 16·0; Ph_2P, 79·9%). No halogen could be detected in the yellow product, which was insoluble in all common organic solvents. Both monomer and polymer were unaffected by boiling dilute aqueous acid or alkali.

Reaction between phenylphosphine and dichlorophenylborane. Dichlorophenylborane (4·0 g., 0·025 mole) in dry hexane (20 c.c.) was slowly added to an equimolar amount of phenylphosphine (2·8 g.) in the same solvent (20 c.c.) contained in a double Schlenk tube equipped with a sintered filter disc.[2] The colourless crystalline and extremely hygroscopic *adduct* was collected by filtration under nitrogen, washed with solvent, and dried by pumping [6·4 g., 75%; m. p. 62—64° (sealed tube)] (Found: Cl, 26·5, 26·8. $C_{12}H_{12}BCl_2P$ requires Cl, 26·4%).

A mixture of phenylphosphine (11·0 g., 0·1 mole) and dichlorophenylborane (15·9 g., 0·1 mole) in xylene was refluxed until evolution of hydrogen chloride had apparently ceased (16 hr.). The solvent was evaporated, and then vacuum distillation yielded *chlorophenyl(phenylphosphino)borane* [PhPH·BClPh] (I) (10·5 g.), b. p. 98—100°/*ca.* 10^{-3} mm., as a colourless fuming liquid (Found: Cl, 15·7, 16·1; PhB, by hydrolysis, 38·2. $C_{12}H_{11}BClP$ requires Cl, 15·4; PhB, 38·1%).

The orange glassy residue from the distillation was extracted with hot benzene. Evaporation of the extract yielded the colourless *tetraphenyl-1,3-diphospha-2,4-diboretan* (II) (3·6 g.), m. p. 89—91° (Found, by oxidation: PhB, 44·7; PhP, 55·6. $C_{24}H_{20}B_2P_2$ requires PhB, 44·8; PhP, 55·2%). The molecular weight, cryoscopically at 0·515, 0·874, 1·164, and 1·593 weight % in benzene, was 340, 344, 356, and 375 ($C_{24}H_{20}B_2P_2$ requires *M*, 344). The orange-yellow residue (III) from the benzene extraction (11·5 g.) had m. p. 168—175° (Found: Cl, 1·3; by oxidation, PhB, 42·8; PhP, 50·5%).

*Dimesityl(di-*m*-tolylphosphino)borane.* The sodium derivative of di-*m*-tolylphosphine (0·025 mole) in tetrahydrofuran (50 c.c.) was slowly added to fluorodimesitylborane[3] (6·7 g., 0·025 mole) in the same volume of solvent at −30°. The mixture was then allowed to come to room temperature, boiled for 1 hr. under reflux, and filtered. Evaporation of the filtrate yielded 1·2 g. of *product*, but the main bulk was an insoluble residue left when sodium fluoride had been dissolved out of the white precipitate by washing it with water. The total amount of product recovered was 5·4 g. (47%), and the m. p. 264—265° (Found: C, 81·5; H, 8·2. Found, by oxidation: $mesityl_2B$, 55·3; *m*-$tolyl_2P$, 45·2. $C_{32}H_{36}BP$ requires C, 82·6; H, 7·9; $mesityl_2B$, 55·3; *m*-$tolyl_2P$, 45·7%).

We were unable to prepare this compound from fluorodimesitylborane, di-*m*-tolylphosphine, and triethylamine in boiling benzene or xylene.

*Di-(4-biphenylyl)(di-*m*-tolylphosphino)borane*, $[(m\text{-}CH_3\cdot C_6H_4)_2P\cdot B(p\text{-}C_6H_5\cdot C_6H_4)_2]$, m. p. 77—78°, was obtained in 46% yield from the phosphine, chlorodi-4-biphenylylborane, and triethylamine in boiling benzene [Found: C, 85·8; H, 5·9. Found, by oxidation: $(p\text{-}C_6H_5\cdot C_6H_4)_2B$, 58·6; *m*-$tolyl_2P$, 39·9. $C_{38}H_{32}BP$ requires C, 86·0; H, 6·0: $(p\text{-}C_6H_5\cdot C_6H_4)_2B$, 59·9; *m*-$tolyl_2P$. 40·1%]. Both this and the preceding compound were insoluble in ether, hydrocarbons, acetone, ethyl methyl ketone, chloroform, and carbon tetrachloride.

Infrared spectra.—The mesityl and the 4-biphenylyl compound had very strong absorption

[2] Fischer, Hafner, and Stahl, *Z. anorg. Chem.*, 1955, **282**, 47.
[3] Brown and Dodson, *J. Amer. Chem. Soc.*, 1957, **79**, 2305.

bands at 1435 and 1497 cm.$^{-1}$, respectively (pressed in potassium iodide discs), which we assign to a B–P stretching vibration. Both bands showed the isotopic splitting commonly found in the spectra of boron compounds. It is significant that the B–P frequency of the mesityl compound is less than that of any other diarylphosphinodiarylborane we have studied, and that of the 4-biphenylyl compound is greater.

The infrared spectra of the other phosphinoarylboranes described in this Note were generally too complex for assignments to be made.

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999. *Thiophthalimides.*

By R. J. W. CREMLYN.

THE only members of this group of compounds recorded in the literature are mono- and di-thiophthalimide,[1] *N*-phenylthiophthalimide,[2] and *N*-butylthiophthalimide.[3]

The *N*-substituted monothiophthalimides described in this paper were prepared from the corresponding *N*-aryl- [4] or *N*-alkyl-phthalimide [5] by reaction with phosphorus pentasulphide (1 mole) in boiling xylene for 5—6 hours. For the dithiophthalimides 2 moles of phosphorus pentasulphide were used and heating was continued for 8—12 hours. The purification of the products was often difficult, especially that of the lower *N*-alkyl derivatives, which were usually low in sulphur content. There was sometimes extensive decomposition and "mixed crystal" formation between the corresponding mono- and di-thiophthalimides.

The thiophthalimides are, apparently, more stable than thiosuccinimides, because they could not be converted into the corresponding thiophthalamic acids by treatment with aqueous ethanolic sodium hydroxide (cf. ref. 6). The thiophthalimides were synthesised as potential fungicides, and to assist in their identification in plant tissue their ultraviolet absorption spectra were determined. The *N*-alkylthiophthalimides (in ethanol) exhibit three characteristic maxima, at 220—225, 295—300, and 330—335 mμ (ε 22,000—24,000, 8000—9000, and 7000—8000, respectively). The same three absorption bands are also shown by the *N*-arylthiophthalimides, except that these have shifted slightly (~5 mμ) in the direction of longer wavelength. The maximum at 295—300 mμ is absent from dithiophthalimides, but the two other characteristic bands are again present, though they have moved 5—10 mμ in the direction of longer wavelength. Also the intensity of the band at 340—360 mμ has approximately doubled; this peak is due to the presence of the thiocarbonyl group, which is known to give an absorption maximum at ~330 mμ.[7] The additional band at 235—245 mμ is also probably due to this group,[8] as phthalimides exhibited bands at 221 and 290 mμ only. These last maxima are almost certainly functions of the absorption of the carbonyl group in conjugation with the benzene nucleus (cf. succinimides, which do not show peaks in this region [9]).

Experimental.—N-*Substituted phthalimides.* The arylphthalimides were generally prepared by boiling phthalic anhydride and the appropriate arylamine in glacial acetic acid, as described by Vanags.[4] The higher *N*-alkylphthalimides were best obtained by heating a mixture of

[1] Drew and Kelly, *J.*, 1941, 627, 630.
[2] Reissert and Holle, *Ber.*, 1911, **44**, 3033.
[3] Baguley and Elvidge, *J.*, 1957, 709.
[4] Vanags, *Acta Univ. Latviensis, Kim. Fakultat*, 1939, Ser. 4, No. 8, 405; *Ber.*, 1942, **75**, 719.
[5] Rice, Reid, and Grogan, *J. Org. Chem.*, 1954, **19**, 884.
[6] Reissert and Moré, *Ber.*, 1906, **39**, 3298.
[7] Braude, *Ann. Reports*, 1945, **42**, 112.
[8] Gillam and Stern, "An Introduction to Electronic Absorption Spectra," Arnold, London, 1954, p. 49.
[9] Turner, *J.*, 1957, 4555.

phthalic anhydride and the alkylamine at 160—170°, following the procedure used for the preparation of *N*-alkylsuccinimides.[5] The lower members were obtained by heating a mixture of phthalimide, anhydrous potassium carbonate, and the appropriate alkyl halide in anhydrous dimethylformamide.[10]

Thiophthalimides. The general preparative procedure was as follows: The *N*-substituted phthalimide (10—20 g.) was dissolved in xylene (200—400 c.c.) and heated at ~100°. Then finely divided phosphorus pentasulphide (1 mole) was added with mechanical stirring, and the mixture gently boiled under reflux. After 1 hr. the liquid generally darkened, and heating was continued until slight further darkening occurred (4—5 hr.). The mixture was filtered hot, allowed to cool, and refiltered. The xylene was removed under reduced pressure, and the dark brown oil dissolved in hot ethanol (charcoal), filtered through " Hyflo-supercel," and evaporated under reduced pressure to the point of crystallisation, the crude solid being purified by recrystallisation from this solvent. If the product was a liquid, it was purified by high-vacuum distillation. For the preparation of dithiophthalimides the general procedure was similar, except that 2 moles of phosphorus pentasulphide were used, and the heating period was increased to 8—12 hr.

Attempted preparation of N-*methoxyphenylthiophthalamic acid.* *N*-(*o*-Methoxyphenyl)-thiophthalimide (4 g.) was treated with 10% sodium hydroxide solution (35 c.c., 5 moles) and

N-Alkylthiophthalimides.

N-Subst.	M. p./b. p.	Yield (%)	Formula	Found (%) C	H	N	S	Reqd. (%) C	H	N	S
Me	94—96°	34	C_9H_7NOS	61·9	3·9	8·0	18·7	62·3	3·9	7·9	18·2
Cl·CH_2	85—88	60	C_9H_6ClNOS	46·6	2·9	6·8	15·6	46·3	2·8	6·6	15·2
$EtO_2C·CH_2$	46—50	48	$C_{12}H_{11}NO_3S$	57·4	4·4	5·7	12·0	57·8	4·4	5·6	12·2
n-C_6H_{13}	125—130/0·1 mm.	54	$C_{14}H_{17}NOS$	68·4	6·7	5·9	12·2	68·0	6·9	5·7	12·8
n-C_8H_{17}	150—154/0·3	65	$C_{16}H_{21}NOS$	69·6	7·4	5·1	10·9	69·8	7·6	5·1	11·5
n-C_9H_{19}	180—185/0·2	63	$C_{17}H_{23}NOS$	70·7	7·7	4·5	10·8	70·6	7·9	4·8	11·0
n-$C_{16}H_{33}$	54—56	72	$C_{24}H_{37}NOS$	75·0	9·3	3·6	7·9	74·4	9·6	3·6	8·3
N-Arylthiophthalimides.											
4-Cl·C_6H_4	158—160°	40	$C_{14}H_8ClNOS$	61·8	3·1	4·9	12·0	61·5	2·9	5·1	11·7
2-Cl·C_6H_4	108—110	48	$C_{14}H_8ClNOS$	62·0	2·8	5·1	11·8	61·5	2·9	5·1	11·7
3-Cl·C_6H_4	144—146	30	$C_{14}H_8ClNOS$	61·3	2·9	4·8	11·2	61·5	2·9	5·1	11·7
4-MeO·C_6H_4	134—136	41	$C_{15}H_{11}NO_2S$	67·3	4·1	5·1	11·5	66·9	4·1	5·2	11·9
2-MeO·C_6H_4	108—110	65	$C_{15}H_{11}NO_2S$	67·0	4·3	5·0	12·0	66·9	4·1	5·2	11·9
3-Me·C_6H_4	156—160	28	$C_{15}H_{11}NOS$	72·1	4·3	5·5	12·2	72·5	4·4	5·9	12·1
2,4-$Me_2C_6H_3$	126—128	58	$C_{16}H_{13}NOS$	72·2	4·8	5·2	11·5	71·9	4·9	5·2	12·0
2,5-$Me_2C_6H_3$	104—106	70	$C_{16}H_{13}NOS$	72·4	4·9	5·0	11·6	71·9	4·9	5·2	12·0
Dithiophthalimides.											
Ph	150—153	22	$C_{14}H_9NS_2$	65·4	4·0	6·0	25·2	65·9	3·5	5·5	25·1
2-Me·C_6H_4	128—130	50	$C_{15}H_{11}NS_2$	67·2	3·9	5·2	23·4	66·9	4·1	5·2	23·8
4-Me·C_6H_4	148—150	17	$C_{15}H_{11}NS_2$	67·3	4·1	4·9	23·5	66·9	4·1	5·2	23·8
4-MeO·C_6H_4	122—124	10	$C_{15}H_{11}NOS_2$	63·1	3·6	5·0	21·9	63·2	3·7	4·9	22·5
α-$C_{10}H_7$	148—149	37	$C_{18}H_{11}NS_2$	71·0	3·6	4·6	21·7	70·8	3·6	4·6	22·0
Cl·CH_2	115—117	20	$C_9H_6ClNS_2$	47·2	2·7	6·0	28·2	47·4	2·6	6·1	28·1

the suspension warmed (together with 5 c.c. of ethanol) for 3 hr. at 80—90°. Most of the solid dissolved; the mixture was filtered, acidified with dilute hydrochloric acid, and extracted with ether (250 c.c.). The extract was washed three times with water, dried (Na_2SO_4), filtered, and evaporated. The residue was unchanged *o*-methoxyphenylthiophthalimide, m. p. and mixed m. p. 108—110°. Similar unsuccessful attempts were made to hydrolyse nine other thiophthalimides, and in each case the starting material was recovered unchanged.

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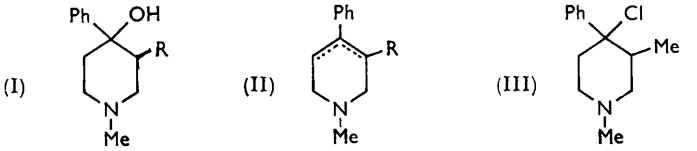
[10] Billman and Cash, *Proc. Indiana Acad. Sci.*, 1952, **62**, 158.

1000. *Action of Thionyl Chloride upon Alcohols derived from Alpha- and Beta-prodine.**

By A. F. Casy.

Evidence for the configurations of epimeric alicyclic alcohols can be obtained from results of their reactions with thionyl chloride. Thus Maurit and Preobrazhenskii [1] assigned *cis*- and *trans*-configurations to isomers of methyl 4-hydroxy-1-methylpiperidine-3-carboxylate that gave arecoline and the chloro-compound, respectively, after such treatment.

Reaction between 1,3-dimethyl-4-phenylpiperidin-4-ol (I; R = Me), derived from alphaprodine by alkaline hydrolysis, and thionyl chloride gave a mixture in which the tetrahydropyridine (II; R = Me) hydrochloride predominated.



Evidence that the minor components were the chloro-compound (III) and the alcohol (I; R = Me) hydrochlorides is provided by the results of chlorine analysis and by infrared absorption studies. The mixture could not be satisfactorily separated by crystallization. The chloro-compound was unstable since solution of the mixture in water, liberation of basic material with ammonia, and reconversion of base into salt, gave the pure tetrahydropyridine (II; R = Me) hydrochloride. McElvain and Safranski [2] obtained similar results with 1-methyl-4-phenylpiperidin-4-ol (I; R = H). In contrast, reaction between thionyl chloride and the epimeric alcohol (from betaprodine) gave a high yield of the chloro-compound (III) hydrochloride that could be recovered after treatment with aqueous ammonia.

Evidence for the same conformation of the hydroxyl group in 1,3-dimethyl-4-phenylpiperidin-4-ol from alphaprodine and in 1-methyl-4-phenylpiperidin-4-ol is provided by their identical reactions with thionyl chloride, axially-placed hydroxy-groups, expected in the more stable (chair) conformation of the alcohol (I; R = H), and chloro-groups providing the required stereochemical conditions for ionic eliminations. Isolation of a stable chloro-compound from the alcohol from betaprodine shows the last to differ from the above alcohols in respect of hydroxyl conformation which is, therefore, equatorial in the alcohol from betaprodine. This interpretation is consistent with assigned configurations [3] (3-Me, 4-Ph *trans* and *cis* for alpha- and beta-prodine, respectively).

Experimental.—A stirred solution of 1,3-dimethyl-4-phenylpiperidin-4-ol (5·0 g.), m. p. 100—101°, derived from alphaprodine,[4] in dry chloroform (25 ml.) was cooled to −20° and treated with freshly distilled thionyl chloride (6·5 g.) in dry chloroform (25 ml.), added dropwise. The addition was complete after 20 min., and the mixture was then heated under reflux for 4 hr., cooled, and diluted with ether. Crystals separated on storage at 5°. Recrystallization from ethanol–ether gave material, m. p. 191—192°, depressed to 189° on mixing with pure tetrahydro-1,3-dimethyl-4-phenylpyridinium chloride, m. p. 187°; [5] it had $\lambda_{max.}$ 236 mμ (ε 9650) in water and a small absorption peak at 3450 cm.$^{-1}$ [cf. pure pyridine derivative, $\lambda_{max.}$ 236 mμ (ε 11,230)] (Found: Cl, 16·85%; equiv., 231. Calc. for $C_{13}H_{18}NCl$: Cl, 15·9%; equiv., 224). The mixture in water was made alkaline with aqueous ammonia and the base extracted with ether. After being dried (Na_2SO_4), the solvent was removed; the residue, after treatment with ethanolic hydrogen chloride, gave tetrahydro-1,3-dimethyl-4-phenylpyridinium chloride, m. p. and mixed m. p. 187—188°.

* These are General Medical Council's approved names for α- and β-1,3-dimethyl-4-phenyl-4-propionyloxypiperidine.

[1] Maurit and Preobrazhenskii, *Zhur. obshchei Khim.*, 1958, **28**, 968.
[2] McElvain and Safranski, *J. Amer. Chem. Soc.*, 1950, **72**, 3134.
[3] Beckett, Casy and Kirk, *J. Medicin. Pharmaceut. Chem.*, 1959, **1**, 37.
[4] Beckett, Casy, Kirk, and Walker, *J. Pharm. Pharmacol.*, 1957, **9**, 939.
[5] Casy, Beckett, and Armstrong, *Tetrahedron*, in the press.

Treatment of 1,3-dimethyl-4-phenylpiperidin-4-ol (2·0 g.), m. p. 118°, derived from betaprodine,[4] with thionyl chloride (2·9 g.) as above gave *4-chloro-1,3-dimethyl-4-phenylpiperidinium chloride* (1·4 g.), m. p. 154° after recrystallization from ethanol–ether (Found: C, 59·9; H, 7·3; N, 5·45; Cl, 27·05%; equiv., 263. Calc. for $C_{13}H_{19}Cl_2N$: C, 60·0; H, 7·3; N, 5·4; Cl, 27·3%; equiv., 260). This hydrochloride was recovered after treatment with aqueous ammonia as above.

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1001. 1,2-*Dihydro*-1,4-*dihydroxy*-2-*oxoquinolines Preparation by Reductive Cyclisation with Hydrazine Hydrate and Palladium–Charcoal.*

By R. T. COUTTS, M. HOOPER, and D. G. WIBBERLEY.

HYDROXAMIC ACIDS related to quinoline have been prepared by oxidation of 2-ethoxyquinolines with subsequent hydrolysis,[1] cyclisation of *o*-hydroxyaminophenylpropiolic acid with hydrochloric acid,[2] or reductive cyclisation of a suitable *o*-nitro-acid or -ester.[3] These methods either involve the use of relatively inaccessible starting materials or yield the hydroxamic acid as the minor product of reaction. Dewar and Mole [4] have shown that certain aromatic nitro-compounds are readily reduced to the corresponding amines by the action of hydrazine hydrate in the presence of palladium–charcoal. We have shown that the reduction of methyl or ethyl *o*-nitrobenzoylacetate under these conditions gives a very good yield of 1,2-dihydro-1,4-dihydroxy-2-oxoquinoline. Attempts to extend the method to the synthesis of a series of 3-substituted analogues were only partly successful. In the attempted reductive cyclisation of methyl α-bromo-α-*o*-nitrobenzoylacetate concurrent reduction of the bromo-group took place, and in the reduction of methyl or ethyl *o*-nitrobenzoylacetoacetate the acetyl group was removed by hydrolysis. Both reactions yielded 1,2-dihydro-1,4-dihydroxy-2-oxoquinoline as sole product. Side reactions also preponderated in the attempted reductive cyclisation of ethyl α-cyano-α-*o*-nitrobenzoylacetate where the products were anthranilic acid and a compound presumed to be 4-amino-1,2,4-triazole-3,5-diacethydrazide, and in the case of diethyl *o*-nitrobenzoylmalonate where the only identifiable product was malonhydrazide. Reductive cyclisation of methyl or ethyl α-*o*-nitrobenzoylpropionate by the same method gave an excellent yield of 1,2-dihydro-1,4-dihydroxy-3-methyl-2-oxoquinoline and, in an analogous manner, methyl α-(*o*-nitrobenzoyl)butyrate yielded the 3-ethylquinolone.

Dewar and Mole [4] found that reduction to the amino-group occurred almost instantaneously with very reactive nitro-derivatives of hydrocarbons, and with *p*-nitroanisole, but that nitrobenzene itself was reduced only slowly. The very good yields of hydroxamic acids obtained in this preliminary study, however, suggest that at least the partial reduction of the nitro-group is enhanced by an electron-attracting substituent in the *ortho*-position.

Experimental.—Methyl o-*nitrobenzoylacetoacetate.* The sodium derivative of methyl acetoacetate (122 g.) was treated with a solution of *o*-nitrobenzoyl chloride (185 g.) in benzene as described by Gabriel and Gerhard [5] for the ethyl ester. The *acetoacetate* (128 g.) separated from ethanol in prisms, m. p. 91—92° (Found: C, 53·8; H, 4·2; N, 5·2. $C_{12}H_{11}NO_6$ requires C, 54·3; H, 4·2; N, 5·3%).

Methyl o-*nitrobenzoylacetate.* The potassium derivative of the above acetoacetate (32 g.) in water (100 ml.) was stirred at 80—90° for 10 min. with ammonium chloride (10 g.). The oil which separated was removed. The operations were repeated a further 3 times with fresh additions of ammonium chloride. The combined red oil was converted into the potassium

[1] Newbold and Spring, *J.*, 1948, 1864; Cunningham, Newbold, Spring, and Stark, *J.*, 1949, 2091.
[2] Arndt, Ergener, and Kutlu, *Chem. Ber.*, 1953, **86**, 957.
[3] Friedlander and Ostermaier, *Ber.*, 1881, **14**, 1916; 1882, **15**, 332; Friedlander, *Ber.*, 1914, **47**, 3369; Heller and Wunderlich, *Ber.*, 1914, **47**, 2889.
[4] Dewar and Mole, *J.*, 1956, 2556.
[5] Gabriel and Gerhard, *Ber.*, 1921, **54**, 1069.

derivative (22 g.) by treatment with potassium hydroxide in ethanol, and the *acetate* (15·2 g.) liberated from a solution of this derivative in water by the passage of carbon dioxide. Crystallisation from ether–light petroleum gave prisms, m. p. 41—42° (Found: C, 54·0; H, 4·05; N, 6·3. $C_{10}H_9NO_5$ requires C, 53·8; H, 4·07; N, 6·3%).

Methyl α-bromo-α-o-nitrobenzoylacetate. Bromination of methyl *o*-nitrobenzoylacetate (1·5 g.) in carbon tetrachloride at room temp. gave the *bromo-acetate* (1·6 g.), crystallising from ethanol in pale yellow needles, m. p. 83—84° (Found: N, 4·6. $C_{10}H_8BrNO_5$ requires N, 4·6%).

Methyl α-o-nitrobenzoylbutyrate. The potassium derivative of methyl *o*-nitrobenzoylacetate (3·4 g.), ethyl iodide (3·0 ml.), and acetone (25 ml.) were refluxed for 5 hr. The mixture was diluted with water and the liberated oil extracted into ether and distilled, to yield a pale yellow *product* (2·1 g.), b. p. 140—142°/3·0 mm. (Found: C, 57·8; H, 5·9; N, 5·9. $C_{12}H_{13}NO_5$ requires C, 57·4; H, 5·2; N, 5·6%).

Methyl α-o-nitrobenzoylpropionate. This compound was obtained as an orange oil in the same manner from methyl iodide and methyl *o*-nitrobenzoylacetate but was not distilled before further reaction (Found: N, 5·8. Calc. for $C_{11}H_{11}NO_5$: N, 5·9%).

1,2-*Dihydro*-1,4-*dihydroxy*-2-*oxoquinoline.* (*a*) Methyl *o*-nitrobenzoylacetate (1·0 g.), 10% palladium–charcoal (0·1 g.), hydrazine hydrate (1·0 ml.), and ethanol (12 ml.) were refluxed for 30 min., a further 1·0 ml. of hydrazine hydrate was then added and refluxing continued for a further 30 min. The mixture was cooled, and the product and catalyst were collected and suspended in 2·0% sodium hydroxide (20 ml.). The suspension was filtered and the filtrate acidified with hydrochloric acid, to yield the quinolone (0·56 g.), m. p. 275—276° (decomp.), not raised on crystallisation from acetic acid (Found: C, 60·7; H, 3·8; N, 7·7. Calc. for $C_9H_7NO_3$: C, 61·0; H, 4·0; N, 7·9%). A similar reaction with more hydrazine hydrate (5·0 ml.) but reduced time (5 min.) gave a lower yield (0·48 g.) of the same quinolone. The quinolone was soluble in sodium hydrogen carbonate solution with evolution of carbon dioxide and gave a blue-green colour with ferric chloride. The dimethyl ether melted at 119—120° (Found: N, 6·8. Calc. for $C_{11}H_{11}NO_3$: N, 6·8%). Arndt *et al.*[2] give m. p. 276° (decomp.) for the quinolone and 124° for the dimethyl ether. The following compounds gave, in the yields stated, the same quinolone, identified in each case by its reactions with sodium hydrogen carbonate and ferric chloride, and its m. p. and mixed m. p.: ethyl *o*-nitrobenzoylacetate (88%), methyl (48%) and ethyl *o*-nitrobenzoylacetoacetate (51%), and methyl α-bromo-α-*o*-nitrobenzoylacetate (18%).

1,2-*Dihydro*-1,4-*dihydroxy*-3-*methyl*-2-*oxoquinoline.* Ethyl α-*o*-nitrobenzoylpropionate[5] (2·2 g.) was treated with hydrazine hydrate and palladium–charcoal under the above conditions. The mixture was filtered and evaporated to dryness. Trituration with dilute hydrochloric acid yielded the 3-*methylquinolone* (1·63 g.) which separated from acetic acid in prisms, m. p. 254—256° (decomp.) (Found: C, 63·0; H, 5·0; N, 7·1. $C_{10}H_9NO_3$ requires C, 62·9; H, 4·75; N, 7·3%). Reductive cyclisation of methyl α-*o*-nitrobenzoylpropionate gave the same product which was soluble in sodium hydrogen carbonate and gave a blue colour with ferric chloride.

3-*Ethyl*-1,2-*dihydro*-1,4-*dihydroxy*-2-*oxoquinoline.* In the manner described above for the 3-methylquinolone, methyl α-*o*-nitrobenzoylbutyrate (1·1 g.) was converted into this 3-*ethylquinolone* (0·87 g.) which separated from acetic acid in prisms, m. p. 223—224° (decomp.) (Found: C, 63·8; H, 5·4; N, 7·0. $C_{11}H_{11}NO_3$ requires C, 64·4; H, 5·4; N, 6·8%). The product was soluble in sodium hydrogen carbonate and gave a blue colour with ferric chloride.

Attempted reductive cyclisation of ethyl α-cyano-α-o-nitrobenzoylacetate. From an attempted reductive cyclisation of ethyl α-cyano-α-*o*-nitrobenzoylacetate (1·0 g.) the filtrate deposited a solid (0·14 g.), m. p. 182° (from ethanol). This product was presumed to be 4-amino-1,2,4-triazole-3,5-diacethydrazide (Found: C, 31·3; H, 5·7; N, 49·9. Calc. for $C_6H_{12}N_8O_2$: C, 31·6; H, 5·3; N, 49·2%), since nitriles are known to form similar 4-aminotriazoles on treatment with aqueous hydrazine.[6] The filtrate from the product was evaporated to dryness and the residual solid triturated with dilute hydrochloric acid, to yield anthranilic acid (0·28 g.), m. p. and mixed m. p. 144—145°.

Attempted reductive cyclisation of diethyl o-nitrobenzoylmalonate. From an attempted reductive cyclisation of diethyl *o*-nitrobenzoylmalonate (1·9 g.) the filtrate deposited plates of malonhydrazide (0·32 g.), m. p. 153—154° (Found: N, 42·4. Calc. for $C_3H_8N_4O_2$: N, 42·4%).

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[6] Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publ. Corp., New York, 1947, p. 74.

1002. *π-Molecular Complex of Hexamethylborazole with Tetracyanoethylene.*

By N. G. S. Champion, R. Foster, and R. K. Mackie.

The aromatic structure of borazole and substituted borazoles suggests that these molecules might form π-bonded intermolecular charge-transfer complexes [1] with other suitable molecules. In particular, the stability of such a complex of an electron acceptor with hexamethylborazole should be favoured because of the expected low ionisation potential of hexamethylborazole relative to borazole. Charge-transfer complexes usually have a broad featureless absorption band. In solution these complexes are in equilibrium with the component molecules, and cooled solutions, in which complex formation is increased, consequently show an intensification of this absorption.

Mixtures of hexamethylborazole (*b*) and tetracyanoethylene (*a*) in chloroform solution have such a band, not possessed by either component alone. The intensity of the band slowly decreases with time at room temperature which suggests that there is further reaction. From measurements of optical density of solutions of mixtures of the two components at various concentrations soon after mixing, the absorption may be attributed to a very weak complex (*c*) with a ratio of $a : b$ of 1 : 1, for which, at 21°, the association constant $K = 0{\cdot}7 \pm 0{\cdot}3$ l. mole^{-1} (where $K = [c]/[a][b]$, all concentrations in mole l.$^{-1}$): $\varepsilon_{max.} = 2000 \pm 500$, $\lambda_{max.} = 461$ mμ. The corresponding values for the hexamethylbenzene–tetracyanoethylene complex in chloroform at 21° are:

$$K = 27{\cdot}6 \pm 0{\cdot}5 \text{ l. mole}^{-1};\ \varepsilon_{max.} = 5080 \pm 90;\ \lambda_{max.} = 540 \text{ mμ}.$$

McConnell, Ham, and Platt [2] demonstrated the empirical relation between the ionisation potentials (I_p) of the donor molecules and the frequencies of the charge-transfer bands of complexes of the respective donor molecules with a given acceptor. Although there is no theoretical basis for this observation,[3] it appears to hold for a wide variety of molecular complexes.[4] Comparison of the frequency of the charge-transfer band of the hexamethylborazole–tetracyanoethylene complex with the frequencies of complexes of other donor molecules of known ionisation potential with tetracyanoethylene suggests that hexamethylborazole has $I_p \approx 8{\cdot}5$ ev, if this linear relationship is valid. Solutions of hexamethylborazole with chloranil in chloroform also show absorption additional to that of the components. This appears as a band ($\lambda_{max.} = 380$ mμ) which is close to a transition of chloranil but intensifies on cooling. By an application of the above empirical relation, the transition of the chloranil complex would correspond to $I_p \approx 8{\cdot}7$ ev for hexamethylborazole.

Experimental.—Materials. Hexamethylborazole was prepared *via* *NN'N''*-trimethylborazole [5] by Smalley and Stafiej's method,[6] and recrystallised from acetonitrile; it had m. p. 99° (Wiberg and Hertwig [7] give 99°). Tetracyanoethylene was prepared by the method of Cairns and his co-workers,[8] recrystallised from chlorobenzene, and thrice sublimed, having m. p. 198°. Chloroform and hexamethylbenzene were purified as described in an earlier paper.[9]

Analytical. Solutions were made up gravimetrically, and their optical densities were measured with an Optical CF4 spectrophotometer and a silica 10 mm. cuvette in a thermostatically controlled water-jacketed holder. The equilibrium constant for the hexamethylborazole complex was evaluated by Rose and Drago's method,[10] and for the hexamethylbenzene complex by Foster, Hammick, and Wardley's method.[11]

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[3] Reid and Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 3869; Mulliken, Proc. Internat. Conf. on Co-ordination Compounds, Amsterdam, 1955, p. 371.
[4] Briegleb and Czekalla, *Z. Electrochem.*, 1955, **59**, 184; Bier, *Rec. Trav. chim.*, 1956, **75**, 866; Foster, *Tetrahedron*, 1960, **10**, 96.
[5] Haworth and Hohnstedt, *Chem. and Ind.*, 1960, 559.
[6] Smalley and Stafiej, *J. Amer. Chem. Soc.*, 1959, **81**, 582.
[7] Wiberg and Hertwig, *Z. anorg. Chem.*, 1947, **255**, 141.
[8] Cairns, Carboni, Coffman, Engelhardt, Heckert, Little, McGeer, McKusick, Middleton, Scribner, Theobald, and Winberg, *J. Amer. Chem. Soc.*, 1958, **80**, 2775.
[9] Foster, *J.*, 1960, 1075.
[10] Rose and Drago, *J. Amer. Chem. Soc.*, 1959, **81**, 6138.
[11] Foster, Hammick, and Wardley, *J.*, 1953, 3817.