

NOTES.

Acetyl-o-phenylenediamine and Acetyl-1:2:3-benztriazole. By
FRANK BELL and JOSEPH KENYON.

THE cumbersome procedure for the preparation of acetyl-*o*-phenylenediamine described by Leuchs (*Ber.*, 1907, **40**, 1085) can with advantage be replaced by the following simplified method. Aluminium amalgam is added to a solution of *o*-nitroacetanilide in moist ether until the yellow colour of the solution is discharged. Owing to its limited solubility in ether, acetyl-*o*-phenylenediamine separates from the solution along with aluminium hydroxide, from which it is extracted by means of boiling benzene. It separates from benzene in small, lustrous plates, m. p. 132°.

On addition of the calculated amount of sodium nitrite to a solution of this compound in hydrochloric acid, there is produced an immediate precipitate of acetyl-1:2:3-benztriazole, which crystallises from alcohol in compact needles, m. p. 51° (Found: $\text{CH}_3\cdot\text{CO}$, 26.7. $\text{C}_8\text{H}_7\text{ON}_3$ requires $\text{CH}_3\cdot\text{CO}$, 26.7%). Acetyl-1:2:3-benztriazole is hydrolysed with extreme ease to give 1:2:3-benztriazole (m. p. 98°), which on acetylation reforms the acetyl derivative of m. p. 51°.—BATTERSEA POLYTECHNIC, LONDON, S.W. 11. [*Received, February 23rd, 1926.*]

Density of Boric Oxide from a Fractional Crystallisation of Boric Acid. By HENRY VINCENT AIRD BRISCOE, PERCY LUCOCK ROBINSON, and GEORGE EDWARD STEPHENSON.

A PREVIOUS communication (Briscoe, Robinson, and Stephenson, *J.*, 1925, **127**, 155) described a systematic fractional crystallisation of boric acid, involving about 1150 crystallisations. As the analytical method then applied proved useless to detect any differences in the atomic weight of boron resulting from this treatment, two end-fractions of boric acid which were still available were converted into boric oxide glass and the densities of these samples were compared by the flotation method recently described (*idem*, this vol., p. 70). The flotation liquid was the mixture of pentachloroethane and trimethylene bromide previously used having $d_4^{17.00}$ 1.79773 and $d_4^{19.45}$ 1.79372.

The data and results are as follows :

Origin of Sample.	Flotation Temp.	Density.	Relative Atomic weight.
Head Fraction Series B	18.18°	1.79415	10.790
Tail Fraction Series B	19.00	1.79445	10.796

In these determinations, the beads of each sample showed rather greater variations in density among themselves than did those derived from the various mineral sources (except sample No. 6) described in the previous communication. Therefore the authors attach little value to the third decimal figure in the present results and consider that these simply serve to indicate, in consonance with the results of a previous investigation on bromine (Robinson and Briscoe, J., 1925, **127**, 138), that fractional crystallisation of boric acid has produced no change as great as 0.01 in the atomic weight of boron.

The authors desire to acknowledge a grant from the Department of Scientific and Industrial Research enabling one of them (G. E. S.) to take part in this work.—UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE, NEWCASTLE-UPON-TYNE. [*Received, March 12th, 1926.*]

A Synthesis of 1 : 2-Dihydroquinaldine. A Correction. By
FREDERICK ALFRED MASON.

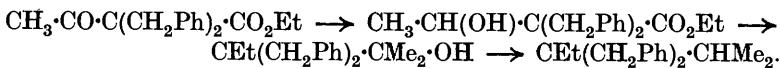
In a previous communication (J., 1925, **127**, 1032), a description was given of a synthesis of "1 : 2-dihydroquinaldine," having the properties of the substance recorded by R ath (*Ber.*, 1924, **57**, 555). As subsequent work (*e.g.*, Meisenheimer and Stolz, *Ber.*, 1925, **58**, 2330; K onig and Buchheim, *ibid.*, p. 2868) has cast doubts upon the validity of some of R ath's results, a re-examination of the present author's product has been made. The melting points of the recrystallised picrates of the "1 : 2-dihydroquinaldine" and of quinaldine were carefully compared and no depression was observed on admixture, so that the product obtained by the author and described as 1 : 2-dihydroquinaldine was in fact a mixture consisting largely of quinaldine itself, and the prefix "1 : 2-dihydro" should accordingly be deleted from the title. From the results of the previous analysis, which agreed almost exactly with the theoretical figures for dihydroquinaldine (0.0882 g. gave 0.2674 g. CO₂ and 0.0605 g. H₂O : C, 82.7; H, 7.6%. 0.1451 g. gave 12.4 c.c. N₂ at 18° and 754 mm. N, 9.7%) it now seems certain that the product obtained was a mixture of quinaldine and a hydrogenated substance, possibly tetrahydroquinaldine or *isobutylaniline*. This would agree with the work of Jones and Evans (J., 1911, **99**, 334), who showed that the so-called "aldol base" from *p*-toluidine gave, on treatment with acids, a mixture of 2 : 6-dimethylquinoline and 2 : 6-dimethyl-tetrahydroquinoline; similar results were obtained with the "aldol base" from *m*-xylylidine (compare also Mills, Harris, and Lambourne, J., 1921, **119**, 1924).

Owing to the small amount dealt with, attempts to separate the

mixture were unsuccessful; its exact composition can be settled only by further investigation with larger quantities of material.—DYSON PERRINS LABORATORY, OXFORD. [Received, March 8th, 1926.]

The Reduction of Ethyl Dibenzylacetoacetate. By ELLEN
SUSAN HILL.

DIALKYL- and diaryl-substitution products of ethyl acetoacetate should, theoretically, be convertible into quaternary hydrocarbons by well-known general reactions; ethyl dibenzylacetoacetate, for example, might be transformed into ethylisopropylidibenzylmethane :



Many attempts to carry out the first of these stages have been made; an alcoholic solution of the ester was treated with sodium, sodium amalgam, zinc and acids, hydrogen and colloidal platinum, amalgamated zinc and acids; and the ester was treated with sodium and amyl alcohol, but the only products isolated were the unchanged substance and an acid, m. p. 89° (see below). The ester was also unattacked by phosphorus pentachloride and therefore could not be reduced indirectly through the dichloro-derivative. Its stability under the conditions noted suggests steric hindrance.

By the action of sodium (twenty times the theoretical) on an ethereal solution of the ester floating on sodium hydroxide solution, two additional products were isolated. One of these was a neutral oil distilling at about 290° and probably dibenzylacetone (C, 84.6; H, 7.2; *M*, 212. C₁₇H₁₈O requires C, 85.7; H, 7.4%; *M*, 238), and the other an acid, crystallising from light petroleum, melting at 152—153° and probably hydroxyethyldibenzylacetic acid (Found : Ag, 27.6. C₁₈H₁₉O₃Ag requires Ag, 27.6%). The yields were so small that the compounds were not fully identified.

In attempting to prepare ethyl dibenzylacetoacetate (m. p. 57°) by the action of benzyl chloride on a methyl-alcoholic solution of sodium methoxide an ester melting at 41° was obtained. This was proved to be *methyl dibenzylacetate* by preparing it from dibenzylacetic acid (m. p. 89°) and methyl alcohol. The acid (m. p. 89°) obtained by the hydrolysis of ethyl dibenzylacetoacetate was proved to be dibenzylacetic acid; it would seem, therefore, that the compound described by Fittig and Christ as dibenzylacetoacetic acid (*Annalen*, 1892, **268**, 123) is really dibenzylacetic acid.—UNIVERSITY COLLEGE, NOTTINGHAM. [Received, January 21st, 1926.]

Synthesis of Naphthathioxins. By REGINALD CHILD and SAMUEL SMILES.

LESSER and GAD have recently described (*Ber.*, 1925, **58**, 2557) experiments on the synthesis of $\alpha\beta'$ -naphthathioxin; the present note gives the results of experiments made previously with a similar object. Di- β -naphthyl ether when heated with sulphur and a trace of iodine at 280° for 3 hours, or when treated with sulphur chloride and aluminium chloride, gave small quantities of $\alpha\alpha'$ -naphthathioxin (m. p. 165°), which was isolated by means of the picrate. On the other hand, in accordance with the experience of Lesser and Gad, attempts to obtain $\alpha\beta'$ -naphthathioxin by similar treatment of α -naphthyl β -naphthyl ether were unsuccessful. Lesser and Gad obtained 4-chloro- α -naphthyl β -naphthyl 2:1'-sulphide by treating a mixture of β -naphthol and 4-chloro- α -naphthol with sulphur chloride; but the substance is readily obtained in quantity from the reaction of β -naphthol with 4-chloro- α -naphthyl 2-sulphur bromide, the latter substance being formed from bromine and the corresponding disulphide in carbon tetrachloride. The corresponding sulphur chloride could not be obtained, owing to the ease with which chlorine displaces sulphur from the disulphide. Treatment of the foregoing $\alpha\beta'$ -sulphide with dehydrating agents gave a small yield of a substance (m. p. 157°) which from its properties appears to be a naphthathioxin.—KING'S COLLEGE, LONDON. [Received, February 3rd, 1926.]

Critical Temperature of Mercury. By LEONARD ALFRED SAYCE and HENRY VINCENT AIRD BRISCOE.

APPLYING the law of Guldberg and Guye (*Z. physikal. Chem.*, 1890, **5**, 374, etc.), that the critical temperature of a non-associated liquid is one and a half times its normal boiling point when both constants are expressed on the absolute scale, to the case of mercury, we should conclude that its critical temperature is 675°. From a brief note in a paper by Traube and Teichner (*Ann. Physik*, 1904, **13**, 620) it would appear, however, that this temperature is above 1000°. Further, calculation from surface tension data indicates that it is about 1550° (Journeau, *Bull. Soc. chim.*, 1924, **35**, 1293). This figure is so widely different from that given by the Guldberg and Guye law that it seemed advisable to make a further attempt to measure the critical temperature experimentally.

For this purpose, pure redistilled mercury was enclosed in a capillary tube of transparent silica having a bore of 2 mm. and walls 3 mm. in thickness. One end of the tube was sealed off, and

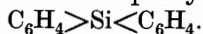
the other was attached to "Hyvac" and mercury diffusion pumps while the mercury was boiled and recondensed several times to free it from dissolved gases. Finally, a portion of the tube 4 cm. long was sealed off, containing a column of mercury 1 cm. long. This silica "bomb" was supported vertically in the middle of a horizontal iron pipe 30 cm. long and 5 cm. in internal diameter, which was heated electrically by a winding of "nichrome" wire. The ends of the pipe were shielded by plate-glass and the bomb was closely observed by means of a telescope. At a temperature above 1000° , the bomb burst. Immediately before this occurred, the mercury, although at a bright red heat, was still liquid, the contrast being quite distinct between the opaque liquid and the perfectly transparent vapour.

In view of the above, the experimental determination of the critical temperature of mercury would seem to be a matter of great difficulty. It is suggested, however, that mercury might be enclosed in a very stout-walled silica vessel of considerable size and heated inductively to its critical temperature by high-frequency oscillatory currents circulating in its vicinity. It might thus be possible to heat the mercury to the critical temperature while the silica vessel was so far cooled by radiation and conduction that its strength would be maintained.

We desire to acknowledge a grant from the Department of Scientific and Industrial Research enabling one of us (L. A. S.) to take part in this work.—ARMSTRONG COLLEGE, NEWCASTLE-UPON-TYNE. [*Received, February 4th, 1926.*]

Some Organo-silicon Compounds. By RONALD RUMSEY
WIDDOWSON.

OF certain organo-silicon compounds described by Hart (*Rep. Brit. Assoc.*, 1887, 661), one, obtained by the action of sodium on a mixture of ethylene dibromide and silicon tetrachloride, is called dichlorosilicoethylene dibromide, $(\text{CH}_2\text{Br}-\text{CH}_2)_2\text{SiCl}_2$; another, produced from trimethylene dibromide in a similar manner, is described as trimethylenesilicon dichloride, $\text{CH}_2\langle\text{CH}_2\rangle\text{SiCl}_2$, and its product of hydrolysis as trimethylenesilicon oxide. A dark brown solid, obtained from a mixture of silicon tetrachloride and *o*-dichlorobenzene, is named di-*o*-diphenylenesilicium,



Although the evidence offered in the paper is by no means convincing, the "compounds" there described are recorded in Beilstein's "Handbuch."

At Professor Kipping's suggestion and under his supervision, the author has repeated very carefully some of Hart's experiments under the same conditions. From ethylene dibromide and from *o*-dichlorobenzene no silicon compounds were formed in appreciable quantities; experiments with trimethylene dibromide were not made. These facts, a study of Hart's paper, and the general results of recent work seem to show that the organo-silicon compounds mentioned above may with advantage be deleted from the literature (compare Bygdén, *Ber.*, 1915, **48**, 1236).—UNIVERSITY COLLEGE, NOTTINGHAM. [Received, January 29th, 1926.]

Deposition of Metallic Zinc on the Positive Pole of a Simple Voltaic Cell. By SPENCER ROBERT HUMBY and MICHAEL WILLCOX PERRIN.

SOME observations first made in 1924 seemed to indicate that in simple voltaic cells which were left in action for some time metallic zinc was deposited on the copper plates. A large number of experiments have shown that this is the case.

Zinc and copper dipping into dilute sulphuric acid or zinc sulphate solution were connected together externally as in a simple voltaic cell; after some time the copper became covered with a layer of metallic zinc.

The following pairs of metals were treated in exactly the same way: zinc and platinum, zinc and silver, zinc and lead, zinc and iron, iron and silver, and it was found that zinc was deposited upon platinum, silver, lead, or iron, and iron upon silver. In each case, the more electropositive metal was thus deposited on the more electronegative one.

In Daniell cells, also, after short-circuiting for some days, a deposit was obtained on the copper consisting of both copper (from the copper sulphate solution) and zinc.

In the case of the simple $\text{Zn}|\text{H}_2\text{SO}_4|\text{Cu}$ cell, zinc was deposited while the liquid in the cell was still acid. In another experiment, the liquid was stirred by bubbling hydrogen through it, but this made no difference to the results. The zinc was deposited slowly and continuously, as was shown by weighing a platinum plate at intervals during the course of the experiment. When the two poles of the cell were disconnected, the zinc was dissolved off the copper provided the solution still remained acid.

The current with a $\text{Zn}|\text{ZnSO}_4|\text{Cu}$ cell fell to 0.006 amp. almost immediately and then more slowly to 0.0001 amp. in 30 minutes.

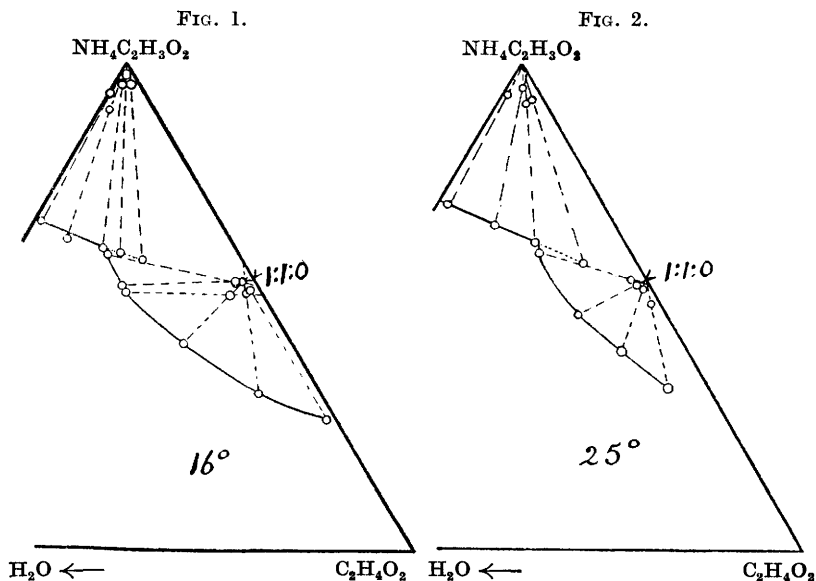
Various papers were found bearing on the subject. Odling (*Quart. J. Chem. Soc.*, 1857, **9**, 289) states that in several instances

if a metal is immersed in a strong, boiling and rather acid solution of a salt of a more electropositive metal, that metal is deposited out of solution on the first, or more electronegative, metal. Raoult (*Compt. rend.*, 1873, **76**, 156) states that if pieces of gold and cadmium connected together are immersed in a boiling solution of cadmium sulphate or chloride, metallic cadmium is deposited on the gold. The gold may be replaced by copper and the cadmium by zinc or tin with the same results. Smith (*J. Amer. Chem. Soc.*, 1905, **27**, 540) states that sodium and potassium, potassium and barium, and sodium and barium are reciprocally replaceable in their amalgams.

The results so far obtained leave no doubt as to the reality of the phenomenon, but it is hoped that additional data will shortly be ready for publication.—WINCHESTER COLLEGE and NEW COLLEGE, OXFORD. [*Received, January 28th, 1926.*]

The System Ammonium Acetate-Acetic Acid-Water. By RUTH SUGDEN.

IN addition to the acid acetate $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2, \text{C}_2\text{H}_4\text{O}_2$, a hydrated complex of the composition $2\text{NH}_4\text{C}_2\text{H}_3\text{O}_2, 3\text{C}_2\text{H}_4\text{O}_2, \text{H}_2\text{O}$ has been



described by Berthelot (*Bull. Soc. chim.*, 1864, **22**, 440). At the suggestion of Professor Rivett, isotherms of the ternary system

have been determined at 16° and 25° and a few additional measurements made at 0°. Commercial chemicals (B.D.H., A.R.) were used. Analyses of saturated solutions and wet solids were carried out by the usual ammonia distillation method, a known excess of caustic soda being used from which, by back titration, the total acetate and hence the acetic acid present could be determined. Compositions in the following table are expressed in percentages of components by weight. Water (not quoted) may be obtained by difference.

% Composition of sat. soln.		% Composition of wet solid.		% Composition of sat. soln.		% Composition of wet solid.	
NH ₄ C ₂ H ₃ O ₂ .	C ₂ H ₄ O ₂ .	NH ₄ C ₂ H ₃ O ₂ .	C ₂ H ₄ O ₂ .	NH ₄ C ₂ H ₃ O ₂ .	C ₂ H ₄ O ₂ .	NH ₄ C ₂ H ₃ O ₂ .	C ₂ H ₄ O ₂ .
Temperature 16°.							
67.8	0.91	94.4		55.6	21.7	55.3	41.3
64.4	7.73	90.9	1.46	54.3	22.7	53.0	41.6
62.6	16.0	96.6	0.96	42.5	38.1	54.6	42.8
*61.1	19.7	96.6	2.27	32.6	57.3	53.2	44.2
*59.6	23.9	96.5	2.20	27.3	72.3	53.7	44.3
61.1	17.1	55.0	41.5				
Temperature 25°.							
70.6	2.15	94.2	1.17	60.7	23.2	55.5	42.6
67.0	12.0	95.7	2.77	48.5	36.2	54.6	43.4
63.3	21.1	92.3	5.1	41.0	47.6	54.3	45.0
*58.9	31.3	92.6	5.96	33.2	59.9	51.1	47.2
Temperature 0°.							
63.8	3.7	94.5	2.38	48.9	19.6	53.6	45.7
*61.1	15.8	93.6	3.74	28.1	61.6	52.6	46.1

* Signifies metastable.

These figures are plotted in the diagrams, from which it is seen that the existence of the complex 1 : 1 : 0 is confirmed, but that there is no evidence whatever for the existence of Berthelot's compound 2 : 3 : 1 at the temperatures examined.—UNIVERSITY OF MELBOURNE. [Received, February 8th, 1926.]