NOTES.

The Latent Heats of Evaporation of Nitromethane and Benzonitrile.

By JAMES CHARLES PHILIP and SIDNEY CHARLES WATERTON.

IN the literature there are notable discrepancies between the experimental and the theoretical values of the boiling point elevation constants K of nitromethane and benzonitrile. This is clear from the following figures (Landolt and Börnstein):

	$K_{exp.}$	$K_{theor.}$
Nitromethane	1·95°	2·44°
Benzonitrile	3·65	4·88

Using carefully purified material, we have made a quantitative study of the effect of *p*-nitrophenetole and benzil on the boiling point of nitromethane, and of diphenylamine on the boiling point of benzonitrile, and have obtained for the constant the respective values 1·86° and 3·87°, in moderately good agreement with the above figures for $K_{exp.}$.

It seemed probable, therefore, that the values 114·75 cal./g.

(Berthelot) and 87·7 cal./g. (Luginin, Kahlenberg) for the latent heats of nitromethane and benzonitrile respectively—values on which the foregoing figures for $K_{\text{theor.}}$ were based—are in error. A redetermination of the latent heat of evaporation was accordingly made for each liquid by Campbell Brown's method (J., 1903, **83**, 987), with one or two minor modifications. The accuracy of the procedure followed was checked by determining the latent heat of evaporation of benzene, for which the value 94·4 cal./g. was obtained, in close agreement with the best recorded figures.

The results for the latent heat of evaporation of nitromethane and benzonitrile were 135·4 cal./g. and 106·5 cal./g. With these figures the van 't Hoff formula gives for $K_{\text{theor.}}$ the values 2·05° and 4·01° respectively, only slightly higher than the figures for $K_{\text{exp.}}$. After these measurements had been completed it was found that Mathews, Ramsdell, and Thompson (*J. Amer. Chem. Soc.*, 1926, **48**, 562) had redetermined the latent heat of evaporation of nitromethane, obtaining the value 134·9 cal./g., with which our result for that liquid is in excellent agreement.—IMPERIAL COLLEGE, LONDON, S.W.7. [*Received, September 29th*, 1930.]

The Decomposition of Benzenediazonium Sulphate by Aliphatic Alcohols. By HERBERT HENRY HODGSON and ARNOLD KERSHAW.

BENZENEDIAZONIUM sulphate is decomposed by the aliphatic alcohols named in the table, giving either an ether or benzene and an aldehyde, ether formation greatly preponderating. Since every molecule of benzene produced is accompanied by one of aldehyde, the estimation of the former was made by means of the *p*-nitrophenylhydrazone of the latter. The data in the table show decreasing formation of benzene from benzyl alcohol to *n*-butyl, methyl alcohol being an exception.

Determination of Aldehyde Formation.—Dry benzenediazonium sulphate (10 g.) was warmed with 100 c.c. of the alcohol (excess of which has no appreciable effect on the result) and distillation was maintained until only 20 c.c. remained. The vapours passed through a fractionating column (rod and 10 discs) and a double-surface condenser into two absorption flasks in series containing a solution of *p*-nitrophenylhydrazine hydrochloride (3 g.) in ethyl alcohol (30 c.c.). The *p*-nitrophenylhydrazone formed was weighed. With the higher alcohols there was a tendency towards violent decomposition of the benzenediazonium sulphate, which necessitated very gradual heating of the reaction mixture. Owing to the sparing solubility of benzenediazonium sulphate in the higher alcohols, the effect of adding water (30 c.c.) was examined in the case of *iso*propyl alcohol: a lower yield of *p*-nitrophenylhydrazone (3·6% instead of 5%) was obtained. The decomposition with benzyl alcohol was carried out under reflux and the benzaldehyde formed was removed by steam distillation.

Results, expressed as mol. % aldehyde on mol. amount of benzenediazonium sulphate taken.

Alcohol.	Experiment 1.	Experiment 2.
Benzyl alcohol	19·7	19·3
Methyl alcohol	Unweighable	Unweighable
Ethyl alcohol	9·5	9·3
n-Propyl alcohol	4·7	4·7
*iso*Propyl alcohol	4·8	5·1
*iso*Propyl alcohol and water	3·6	3·7
n-Butyl alcohol	1·3	1·2

—TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, August 2nd*, 1930.]

A New Complex Hydrocarbon of the Probable Formula $C_{16}H_{14}$.

By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON.

DURING experiments on the synthesis of heterocyclic organic arsenical compounds from ββ′-dichlorodivinylchloroarsine, $(CHCl{:}CH)_2AsCl$, a complex hydrocarbon was isolated in the following manner.

ββ′-Dichlorodivinylchloroarsine (23·3 g.; 1 mol.), benzene (50 c.c.), and anhydrous aluminium chloride (14·7 g.; 1·1 mols.) were heated together under reflux on the water-bath. A vigorous reaction ensued, hydrogen chloride was freely evolved, and a deep brown liquid remained. After 1½ hours, the product was cooled and ice was added, followed by hydrochloric acid and benzene. After thorough agitation, the liquid was filtered and the benzene layer was separated, dried with calcium chloride, and evaporated on the water-bath. The residue, distilled under reduced pressure, gave no unchanged ββ′-dichlorodivinylchloroarsine. The fraction boiling between 145° and 230°/9 mm. was reddish-brown and readily solidified. It was readily soluble in alcohol when crude, but became sparingly soluble when pure. After two crystallisations the *compound* was obtained in pale yellow plates (about 1 g.), m. p. 179—180°, unchanged by further crystallisation. Its dilute alcoholic solution was pale yellow and exhibited a strong blue-violet fluorescence (Found: C, 92·8, 92·8; H, 7·0, 6·75; *M*, in benzene, 193, 198. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%; *M*, 206. $C_{15}H_{14}$ requires C, 92·75; H, 7·25%; *M*, 194). Only oils could be obtained from the alcoholic mother-liquors.

The hydrocarbon is stable to boiling alkaline permanganate; it is moderately easily soluble in benzene and carbon tetrachloride when hot but is sparingly soluble in the cold solvents.

On bromination of the hydrocarbon in carbon tetrachloride solution, hydrogen bromide was evolved and a microcrystalline yellowish-brown solid was precipitated. This was recrystallised from glacial acetic acid, in which it was sparingly soluble, and obtained in golden-yellow needles, darkening at 210° but remaining unmelted at 310°. The compound is almost insoluble in alcohol, acetone and carbon tetrachloride. It is a *dibromo*-derivative of the hydrocarbon, the bromine content pointing strongly to the formula $C_{16}H_{14}$ for the hydrocarbon itself (Found: Br, 44·45. $C_{16}H_{12}Br_2$ requires Br, 43·9%. $C_{15}H_{12}Br_2$ requires Br, 45·4%).

The $C_{16}H_{14}$ formula for the hydrocarbon is much more probable than the $C_{15}H_{14}$ formula, since the molecule of each of the initial organic materials contains an even number of carbon atoms. It is difficult to see how a substance containing an odd number of carbon atoms in its molecule could appear as the final product.

No attempt has been made to determine the constitution of the hydrocarbon, the amount available being very small.

Attempts to prepare heterocyclic organic arsenicals by the action of ethyl sodiomalonate on ββ'-dichlorodivinylchloroarsine without and with prior treatment with sodium ethoxide were not successful, acetylene being liberated in all the reactions.—GUY'S HOSPITAL MEDICAL SCHOOL (UNIVERSITY OF LONDON), LONDON, S.E.1. [*Received, October* 13*th*, 1930.]

Preparation of Anhydrous Stannous Chloride. By HENRY STEPHEN.

A SIMPLER method than that previously described (J., 1925, **127**, 1874) for the preparation of anhydrous stannous chloride is the treatment of stannous chloride ($SnCl_2,2H_2O$; 1 mol.) with acetic anhydride (2 mols.). The dehydration is almost instantaneous, much heat is evolved, and the anhydrous salt separates. After being washed free from acetic acid with dry ether, it can be preserved indefinitely in a desiccator. It crystallises in long needles from acetic acid containing a little acetic anhydride (Found: Sn, 61·9; Cl, 36·9. Calc. for $SnCl_2$: Sn, 62·6; Cl, 37·4%). The anhydrous compound does not appear to be hygroscopic, and it is readily soluble in acetone and amyl alcohol, insoluble in benzene, toluene, xylene, and chloroform. It dissolves readily in absolute methyl and ethyl alcohols, but a trace of water causes immediate hydrolysis with the formation of an opalescent precipitate, which is presumably stannous oxychloride. On one occasion a sample of the anhydrous salt which had not been entirely freed from acetic acid was kept bottled for about 6 weeks. A pronounced odour of ethyl acetate had then developed, indicating reduction by the stannous chloride of a portion of the acetic acid to alcohol, followed by esterification.—THE UNIVERSITY OF THE WITWATERSRAND, JOHANNESBURG, SOUTH AFRICA. [*Received, November* 17*th*, 1930.]

A Labile Compound of Benzeneazo-β-naphthol and β-Naphthol. By HERBERT HENRY HODGSON and WOLF ROSENBERG.

THE product obtained by coupling diazotised aniline with β-naphthol in an aqueous solution of sodium hydroxide (1 equiv.) and sodium carbonate (excess), on crystallisation from benzene, frequently yields a substance, m. p. 62—64°, containing benzene of crystallisation. This effloresces, leaving a crystalline residue, m. p. 79—80°, which crystallises unchanged from chloroform in brick-red feathery needles but again with benzene of crystallisation from benzene. Crystallisation of the benzene-free product from glacial acetic acid, pyridine, or alcohol gives benzeneazo-β-naphthol, which separates from benzene in stout, dark red, hexagonal prisms of almost metallic lustre, m. p. 133—134° (Rowe and Levin, *J. Soc. Dyers and Col.*, 1924, **40**, 2220, give m. p. 131°). When the coupling is carried out in aqueous sodium hydroxide, bicarbonate, acetate, or borate, only benzeneazo-β-naphthol results. The new *product* gives analytical data corresponding to an equimolecular proportion of benzeneazo-β-naphthol and β-naphthol (Found : N, 7·3. $C_{16}H_{12}ON_2,C_{10}H_8O$ requires N, 7·15%. Aqueous sodium hydroxide removes 36·8% of β-naphthol; calc., 36·7%).

When benzenediazonium sulphate reacts with aqueous sodium β-naphthoxide in equimolecular proportion, the double compound is formed exclusively, leaving an equivalent amount of unchanged diazonium salt in the solution, whereas excess of sodium β-naphthoxide affords a quantitative yield. When the reaction with equimolecular quantities is carried out in wet benzene suspension, the unchanged diazonium salt can be removed by means of water. Two specimens of the double compound containing benzene of crystallisation, m. p. 62—64°, gave a loss in a vacuum of 13·4% and 14·8% respectively (calc. for 1 mol. of benzene, 16·6%).

It is noteworthy that neither β-naphthol (Kuriloff, *Z. physikal. Chem.*, 1897, **23**, 673) nor benzeneazo-β-naphthol forms a compound with benzene.—TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, October* 3*rd*, 1930.]

The Preparation of Benzamide. By C. H. KAO and SHAO-YUAN MA.

NOYES and GOEBEL (*J. Amer. Chem. Soc.*, 1922, **44**, 2286) have shown that in the preparation of acetamide by the distillation of ammonium acetate the presence of an excess of acetic acid greatly accelerates the dehydration. It seemed probable that the same device might be useful for the dehydration of ammonium benzoate. Distillation of mixtures of ammonium benzoate and 95% acetic acid, however, gave no benzamide, and if the mixtures were heated under reflux for several hours before distillation the yields of benzamide obtained were small.

After many experiments with various quantities of the reagents the following method was found to give the best result. A mixture of 200 g. of benzoic acid, 180 g. of ammonium carbonate, and 300 c.c. of 95% acetic acid (the two solids do not mix well with glacial acetic acid even when hot) was placed in a 2-litre flask fitted with a glass tube, 160 cm. long and 2 cm. wide, which served as a fractionating column and was connected with a water-condenser. The mixture was heated gradually to boiling and was then distilled, so that not more than 100 c.c. passed over in one hour, until the temperature at the head of the column was 150°. Almost the whole of the acetic acid was thus removed. The residue in the flask was poured into twice its volume of cold water, neutralised with ammonium hydroxide, boiled with a little animal charcoal, and filtered. Benzamide separated in colourless plates on cooling. It was twice recrystallised from twice its weight of water, and dried at 110° (yield 96—98 g.). About half the benzoic acid was recovered from the combined filtrates.—NATIONAL TSING HUA UNIVERSITY, PEIPING, CHINA. [*Received, September 11th*, 1930.]

3-*Chloro*-o-*toluic Acid and its Conversion into* 3-*Chloro*-α-*hydroxyphthalide.* By LEOPOLD FERDINAND LEVY and HENRY STEPHEN.

THE only remaining unknown chloro-*o*-toluic acid, 3-*chloro*-o-*toluic acid*, has now been obtained from 3-amino-*o*-toluic acid (Gabriel and Thieme, *Ber.*, 1919, **52**, 1080) by the Sandmeyer reaction. It crystallises from hot water in colourless needles, m. p. 91·5° (Found : Cl, 20·7; equiv., 169·8. $C_8H_7O_2Cl$ requires Cl, 20·8%; equiv., 170·5). When the molten acid is treated with bromine, hydrogen bromide is evolved: the product, on being warmed with dilute sodium hydroxide solution, yields 3-*chloro*-α-*hydroxyphthalide* (compare Racine, *Annalen*, 1887, **239**, 76). This forms colourless plates, m. p. 138°, from dilute alcohol (Found : Cl, 18·9. $C_8H_5O_3Cl$ requires Cl, 19·2%).—THE UNIVERSITY OF THE WITWATERSRAND, JOHANNESBURG, SOUTH AFRICA. [*Received, November 17th*, 1930.]