NOTES.

The Reducing Action of Bornylmagnesium Chloride. By IAN RUSSELL SHERWOOD and WALLACE FRANK SHORT.

IN an attempt to synthesise substances belonging to the terpene group from bornylmagnesium chloride it was found that this Grignard reagent possesses powerful reducing properties. The reagent, prepared by Houben's method (*Ber.*, 1906, **39**, 1701) from bornyl chloride (m. p. 129°), was carefully freed from the unattacked metal (8%) before use. *iso*Valeraldehyde (1 mol.) and bornylmagnesium chloride (2 mols.) in ether (4 mols.) below 0° produced *iso*amyl alcohol (3 : 5-dinitrobenzoate, m. p. 62°; α-naphthylamino-compound, m. p. 104°) in almost theoretical yield. Under the same conditions, citral furnished geraniol (b. p. 112—115°/12 mm., $n_D^{13°}$ 1·4800, $d_{4°}^{13°}$ 0·894; diphenylurethane, m. p. 81°). Piperitone (1 mol.) and bornylmagnesium chloride (2 mols.) when boiled for 6 hours in toluene (4 mols.) yielded phellandrene (b. p. 173—176°, $n_D^{13°}$ 1·4744, $d_{4°}^{13°}$ 0·853), identified by the preparation of the nitrosite (m. p. 107°). No piperitol could be detected when the reaction was conducted in ethereal solution. Owing to the absorption of oxygen by the Grignard reagent, a small quantity of borneol (3 : 5-*dinitrobenzoate*, m. p. 154·5°. Found : N, 8·2. $C_{17}H_{20}O_6N_2$ requires N, 8·1%) was produced in each of the above reactions.

Our thanks are due to the Chemical Society for a grant for the purchase of materials. One of us (I. R. S.) is indebted to the New Zealand Department of Scientific and Industrial Research for the award of a National Research Scholarship.—AUCKLAND UNIVERSITY COLLEGE, UNIVERSITY OF NEW ZEALAND. [*Received, October 6th,* 1931.]

The Action of Grignard Solutions on the 10-*Methoxyanthrones.* By EDWARD DE BARRY BARNETT.

K. H. MEYER (*Annalen*, 1911, **379**, 68) obtained 10-methoxyanthrone in amounts of 0·2 g. by the action of methyl alcohol on 10-bromoanthrone, but it is readily obtained in 90% yield when 11 g. of 10-bromoanthrone, 5 g. of calcium carbonate, and 150 c.c. of methyl alcohol are boiled for 4 minutes. When it was treated with benzylmagnesium chloride (3 mols.) in a freezing mixture, and the product worked up in the usual way after being kept over-night at the ordinary temperature, a mixture of anthraquinone, 10 : 10′-dimethoxy-10 : 10′-dianthrone, and 10-*methoxy*-9-*benzyl*-9 : 10-*dihydroanthranol* was obtained. The last-named compound was isolated by its easy solubility in cold acetone and after recrystallisation from *cyclo*hexane formed colourless prisms, m. p. 129° (Found: C, 83·5; H, 6·4. $C_{22}H_{10}O_2$ requires C, 83·5; H, 6·3%). When warmed on the water-bath with glacial acetic acid to which a little concentrated hydrochloric acid had been added, it yielded 10-chloro-9-benzylanthracene, m. p. 128° alone or mixed with an authentic sample (Cook, J., 1926, 2168) (Found: C, 83·3; H, 5·0. Calc.: C, 83·3; H, 5·0%).

10-Methoxy-1 : 4-dimethylanthrone on treatment with methylmagnesium iodide (3 mols.) yielded 10-*methoxy*-1 : 4 : 9-*trimethyl*-9 : 10-*dihydroanthranol*, which separated from *cyclo*hexane in crystals, m. p. 148° (Found: C, 80·6; H, 7·5. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%), but treatment of this with hydrochloric and acetic acids yielded no definite product.

By the action of phenylmagnesium bromide on 10-methoxy-1 : 4-dimethylanthrone and treatment of the product with hydrochloric acid, 10-phenyl-1 : 4-dimethylanthrone was obtained, but the yield was poor and the product difficult to purify. The use of benzylmagnesium chloride and of *o*-tolylmagnesium bromide resulted only in resinous products. It is concluded from the above that the action of Grignard solutions on the 10-methoxyanthrones does not form a convenient synthesis of the *meso*-alkyl and *meso*-aryl anthrones.—SIR JOHN CASS TECHNICAL INSTITUTE, JEWRY STR., LONDON, E.C.3. [*Received, November 5th*, 1931.]

The Calculation of Degrees of Dissociation of Weak Electrolytes.

By WILLIAM H. BANKS.

THE equation connecting the change in the sum of the ionic mobilities of electrolytic ions with change in concentration in dilute solution, at any temperature, is

$$\Lambda_x = \Lambda_0 - b\sqrt{\alpha C} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Λ_x and Λ_0 are the sum of the mobilities at concentration C and at infinite dilution, respectively, b is the "Onsager slope," and α, the degree of dissociation, is equal to Λ/Λ_x.

Now in determining degrees of dissociation it is necessary to know the value of Λ_x, and the usual method of calculating this quantity is by a series of approximations (see Davies, "Conductivity of Solutions," p. 87) involving the initial use of Λ_x for Λ_0 in the right-hand side of equation (1). This method is laborious, and a procedure is now described whereby Λ_x may be calculated directly.

Since Λ_x differs from Λ_0 by only a few units at low concentrations, we may write $\Lambda_0 - \delta\Lambda_0 = \Lambda_x$.

Then from (1) $\delta\Lambda_0 = b\sqrt{\Lambda C/(\Lambda_0 - \delta\Lambda_0)}$

$$= b(\Lambda C)^{\frac{1}{2}}/\Lambda_0^{\frac{1}{2}}\,(1 - \delta\Lambda_0/\Lambda_0)^{\frac{1}{2}}$$

and by expansion $= b(\Lambda C)^{\frac{1}{2}}/\Lambda_0^{\frac{1}{2}}\left(1 - \frac{1}{2}\,\frac{\delta\Lambda_0}{\Lambda_0} + \frac{1}{8}\,\frac{\delta\Lambda_0{}^2}{\Lambda_0{}^2}\quad .\quad .\quad .\right)$

The third term in the expansion may be neglected, the error so introduced in the value of Λ_x being almost equal to this term. A consideration of its magnitude indicates that it does not exceed the limit of experimental accuracy (0·01—0·02%) attainable in modern conductivity measurements. This will be understood the better from the figures below.

Elimination of this term leads to a quadratic equation in $\delta\Lambda_0$, *viz.*,

$$\delta\Lambda_0{}^2 - 2\Lambda_0 \,.\, \delta\Lambda_0 + 2b(\Lambda_0 \,.\, \Lambda C)^{\frac{1}{2}} = 0$$

the solution of which is

$$\delta\Lambda_0 = \Lambda_0 \pm \sqrt{\Lambda_0{}^2 - 2b(\Lambda_0 \,.\, \Lambda C)^{\frac{1}{2}}}$$

$$i.e.,\quad \Lambda_0 - \Lambda_x = \Lambda_0 \pm \sqrt{\Lambda_0{}^2 - 2b(\Lambda_0 \,.\, \Lambda C)^{\frac{1}{2}}}.$$

The only root applicable to the case in question leads to

$$\Lambda_x = \sqrt{\Lambda_0{}^2 - 2b(\Lambda_0 \,.\, \Lambda C)^{\frac{1}{2}}}$$

from which Λ_x may be calculated directly.

The following illustrative figures are from data on *o*-chlorobenzoic acid at 25° (Davies, *op. cit.*, p. 87) :

$C = 0{\cdot}00166$; $\Lambda = 218{\cdot}0$; $b = 147{\cdot}0$; $\Lambda_0 = 384{\cdot}1$
Λ_x as calculated by three approximation steps is 379·5,
Λ_x ,, ,, ,, the above relationship is $379{\cdot}5_4$.

The magnitude of the neglected term is $(4{\cdot}6/384{\cdot}1)^2/8 = 18 \times 10^{-6}$, and if it is taken into consideration, Λ_x becomes $379{\cdot}5_5$.

The author wishes to express his appreciation of the interest Dr. C. W. Davies has shown in this work, and of his kind permission to use the example contained in his book.—BATTERSEA POLYTECHNIC, S.W.11. [*Received, October 14th*, 1931.]

The Dehydration of Selenious Acid. By NORMAN RAE.

SELENIOUS acid when recrystallised from water readily yields crystals of the formula H_2SeO_3. This is stated to be a deliquescent substance. When placed in a desiccator, the crystals developed white spots at some points. Freshly prepared crystals (5·386 g.) were therefore placed in a desiccator over phosphoric oxide and weighed from time to time. White spots were observed on the second day (wt., 5·3565 g.) and continued to develop. The loss of weight continued for 50 days and then ceased (final wt., 4·616 g.). If loss of combined water is assumed to begin with the appearance of the white spots, then 5·3565 g. lost 0·7405 g., *i.e.*, 13·83% (Calc. for H_2SeO_3 : H_2O, 13·95%). The final product was selenium dioxide, and when dissolved in water, it checked correctly with caustic soda. No reference to this dehydration at room temperature can be found in the literature.—UNIVERSITY COLLEGE, COLOMBO, CEYLON. [*Received, May 4th*, 1931.]

The Double Compound of Aluminium Chloride with Hydrogen Cyanide.

By LEONARD ERIC HINKEL and RICHARD TREVOR DUNN.

ACCORDING to Perrier (*Compt. rend.*, 1895, **120**, 1423) aluminium chloride forms two additive compounds with hydrogen cyanide, $AlCl_3$,HCN and $AlCl_3$,2HCN. The former is stated to be formed when aluminium chloride is added to a solution of hydrogen cyanide in carbon disulphide at 14°. This claim has not been substantiated, since the two liquids are practically immiscible. When finely powdered aluminium chloride is rapidly added in small quantities to hydrogen cyanide at room temperature, a vigorous reaction occurs, the aluminium chloride going into solution. The action gradually lessens with continued addition of aluminium chloride and finally a stage is reached where the liquid suddenly begins to deposit crystals of $AlCl_3$,2HCN. Decantation of the supernatant liquid and rapid drying of the residual mass on a warm porous plate yields a white solid, which, unless immediately powdered, undergoes considerable browning due to polymerisation of small quantities of retained hydrogen cyanide (Found : Al, 14·7. Calc. : Al, 14·45%). The compound, which is also formed when hydrogen cyanide is added to aluminium chloride suspended in benzene, is unstable in moist air and gradually evolves hydrogen cyanide in a vacuum desiccator. Hydrogen cyanide is removed completely at 100°. The compound is soluble in dry ether, in which it is dissociated into its components, evaporation of the ether removing all the hydrogen cyanide.—UNIVERSITY COLLEGE, SWANSEA. [*Received, November 3rd*, 1931.]