NOTES.

Preparation of 2-Phenylquinoline from o-*Nitrostyryl Phenyl Ketone.* By R. J. W. LE FÈVRE and J. PEARSON.

THE following modification of Friedländer's method (*Ber.*, 1882, **15**, 2574) is better than that of Döbner and Giesecke (*Annalen*, 1887, **242**, 291) for the preparation of 2-phenylquinoline (cf. J., 1930, 2238).

A mixture of *o*-nitrobenzaldehyde (2 g.) and acetophenone (1·6 g.), cooled in H_2O, was saturated with dry HCl and left over-night. The brown cryst. product was kept molten until free from HCl, then allowed to solidify, pressed on porous tile, and crystallised from aq. EtOH; cream-coloured platelets (2·8 g.) of *o*-nitrostyryl phenyl ketone were obtained, m. p. 122—123°, in agreement with Sorge (*Ber.*, 1902, **35**, 1065).

A solution of this ketone (10 g.) in EtOH (300 c.c.) and conc. HCl (10 c.c.) was treated with Fe filings (8 g.) during 15 min., refluxed for 2 hr., filtered, and saturated with HCl; the bulk of the EtOH was then evaporated. The 2-phenylquinoline hydrochloride (10 g.) deposited on cooling crystallised from EtOH–conc. HCl in yellow needles, m. p. 163—165°. The crude moist hydrochloride was stirred with dil. NH_3 aq., the residue dissolved in EtOH and NH_3 aq. (5 c.c.), the solution boiled for ½ hr. (norit), filtered, partly evaporated, and, after addition of warm H_2O, allowed to cool; the 2-phenylquinoline deposited (65% yield; m. p. 78—80°) formed white needles, m. p. 85—86°, after three crystns. from aq. EtOH (Knorr, *Annalen*, 1888, **245**, 379, gives 86°). The picrate had m. p. 191—192°, dichromate, m. p. 145—148°, and ferrichloride, m. p. 169—170°.

Interaction of o-*Nitrobenzaldehyde and Acetophenone.*—The method by which Sorge (*loc. cit.*) prepared *o*-nitrostyryl phenyl ketone usually gave in our hands mainly indigotin. For instance, a solution of *o*-nitrobenzaldehyde (20 g.) and acetophenone (16 g.) in EtOH (200 c.c.) on treatment with 10% NaOH aq. (100 c.c.) quickly turned brown with evolution of heat. After filtration and several boilings with EtOH a blue powder with a coppery lustre (*ca.* 4 g.) was obtained which had the characteristic properties of indigotin (sublimation; colour of solutions in $PhNH_2$, $PhNO_2$, and conc. H_2SO_4; reduction by glucose and NaOH; dyeing; microcryst. appearance) (Found: N, 9·4, 9·4. Calc.: N, 10·7%). The alc. extracts gave small yields (0—1 g.) of *o*-nitrostyryl phenyl ketone, m. p. 118—120°. The filtrate from the indigotin–nitrochalkone ppt. gave benzoic acid (3·6 g.), m. p. 111—112°, mixed m. p. 114—116°.

m- and *p*-Nitrobenzaldehyde readily condensed with acetophenone under both the alkaline and the acid conditions described above, giving the corresponding nitrochalkones, m. p. 145—146° and 164° respectively.—UNIVERSITY COLLEGE, LONDON, W.C.1. [*Received, September 16th*, 1932.]

The Action of some Metallic Oxides on Benzotrichloride and Benzal Chloride.

By WILLIAM DAVIES and JOHN H. DICK.

A VIGOROUS action occurs when pure ZnO (1 g.-mol.) is gradually added to benzotrichloride (1 g.-mol.) at 100°. When the reaction has subsided, the product is heated at 100° for 1 hr. and extracted with C_6H_6, giving a 58% yield of benzoyl chloride (b. p. 196—199°).

Under similar conditions, with the exception that the initial temp. is 120°, commercial fused $ZnCl_2$ (1 g.-mol.) and benzotrichloride (1 g.-mol.) produce a 40% yield of benzoyl chloride. This reaction is due to the actual or potential presence of ZnO (owing to the $ZnCl_2$ having absorbed H_2O), because pure dry $ZnCl_2$ (prepared from dry HCl and Zn spangles in dry Et_2O and then strongly heated) does not convert benzotrichloride into benzoyl chloride. When to the inactive mixture of this $ZnCl_2$ (1 g.-mol.) and benzotrichloride (1 g.-mol.) at 120°, H_2O (1 g.-mol.) is gradually added, a 16% yield of benzoyl chloride is obtained and no benzotrichloride is left.

This type of replacement of two Cl atoms by the O of oxides has not been described in the scientific literature, but is included in D.R.-P. 13127 (1883), and related reactions are referred to in U.S.P. 1,557,154 (1926), E.P. 308,231 (1929), and D.R.-P. 331,696 (1914).

Cadmium and lead oxides produce some tar and only small amounts of benzoyl chloride. Fe_2O_3 reacts vigorously (even at the ordinary temp. when the reaction has once started), but the formation of large amounts of HCl and tar indicates that probably a Friedel–Crafts reaction takes place with the benzoyl chloride initially formed. Al_2O_3 reacts slightly, producing a small amount of tar, and P_2O_5 does not react at all.

When benzal chloride is used and the reaction is carried out in the usual way with ZnO (at 100°), large quantities of tar and HCl are produced. If, however, C_6H_6 is used as a diluent and the ZnO is added at such a rate that some oxide is always present, little tar and HCl are formed and when the product is decomposed by H_2O a 30% yield of benzaldehyde is obtained after distillation.

A vigorous reaction ensues when ordinary ZnF_2 (50 g., 1·5 mols.) is added to benzotrichloride (64·6 g., 1 mol.) in a Cu flask at 100°, and after 6 hr.'s heating at 120° a 65% (27 g.) yield of benzoyl fluoride, b. p. 155—156°, is obtained. This reaction is explained by the fact that "ordinary" ZnF_2, whether made by double decomposition from $ZnCl_2$ and sol. fluorides and dried for 3 hr. at 180°, or bought from different European firms and similarly dried, always contains a large quantity of ZnO. This is shown by the compound being yellow when hot and white when cold. Probably the ZnO converts the benzotrichloride into benzoyl chloride, which then reacts with ZnF_2.—THE UNIVERSITY OF MELBOURNE. [*Received, April 25th,* 1932.]

Rhatany Catechin. By M. NIERENSTEIN.

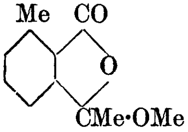
NUMEROUS investigations of rhatany tannin, present in the bark of various kinds of "rhatany root" (Wehmer, "Die Pflanzenstoffe," 1911, p. 322), since its discovery by Vogel (*Taschenbuch für Chemiker*, 1820, **1**, 73) indicate that it is probably a catechu tannin derived from some catechin-like substance. This is now confirmed by the identification of *d*- and *dl*-gambir-catechin in the "rhatany root" from Bolivia (*Krameria argentia*, Mart.). Rhatany tannin is thus probably identical with the catechu tannin present in the cutches from the leaves of *Uncaria gambir*, Roxb., and *U. acida*, Roxb., which have been shown to contain these two catechins (Nierenstein and co-workers, *J. Amer. Chem. Soc.*, 1931, **53**, 1505).

The finely powdered bark of about 800 g. of "rhatany root," kindly supplied by Dr. F. E. Thomas of La Paz, Bolivia, was mixed with white sand and extracted with $CHCl_3$, followed by EtOH-free Et_2O, and the residue obtained on evaporation of the Et_2O was fractionated from H_2O acidified with AcOH, 3·1 g. of crude *dl*-gambir-catechin and 1·8 g. of crude *d*-gambir-catechin being obtained. Both fractions were acetylated and gave after several crystns. from EtOH and a little acetone the following data : (i) penta-acetyl *dl*-gambir-catechin, m. p. and mixed m. p. 156° (Found : C, 59·7; H, 5·0%); (ii) penta-acetyl *d*-gambir-catechin, m. p. and mixed m. p. 137°; $[\alpha]_D^{16^\circ}$ + 37·6° in $C_2H_2Cl_4$ [Found : C, 60·0; H, 5·0. Calc. for $C_{15}H_9O_6(CO\cdot CH_3)_5$: C, 60·0; H, 4·8%].—THE UNIVERSITY, BRISTOL. [*Received, September 3rd,* 1932.]

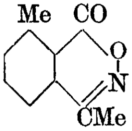
The Oxidation Products of 1 : 2 : 5-*Trimethylnaphthalene.* By I. M. HEILBRON and D. G. WILKINSON.

WE have shown (J., 1930, 2546) that on oxidation of 1 : 2 : 5-trimethylnaphthalene with chromic acid both neutral and acid products are formed, the bulk of the latter being 3-methylacetophenone-2-carboxylic acid, m. p. 126°, the methyl ester of which, prepared *via* the silver salt, has m. p. 47—48°. Westenberg and Wibaut (*Rec. trav. chim.*, 1931, **50**, 108) independently studied the oxidation of this hydrocarbon with chromic acid. They also isolated 3-methylacetophenone-2-carboxylic acid (somewhat impure, m. p. 116°), but in place of the methyl ester, m. p. 47—48°, obtained by esterification with methyl alcohol and hydrogen chloride an ester, m. p. 67—68°. The discrepancy in m. p. of the two esters has led us to re-examine the properties of the above-mentioned acid. Both esters have been prepared, but whereas the lower-melting isomeride acts as a ketone and readily forms a semicarbazone (Heilbron and Wilkinson, *loc. cit.*), the higher-melting form fails to react with semicarbazide acetate and is undoubtedly the ψ-ester (I) (cf. Auwers and Heinze, *Ber.*, 1919, **52**, 584). Treatment of either 3-methylacetophenone-2-carboxylic acid or the normal methyl ester with hydroxylamine gives the *oxime anhydride*, m. p. 174° (II) (cf. Daube, *Ber.*, 1905, **38**, 206), and not the free oxime as suggested by Westenberg and Wibaut (*loc. cit.*).

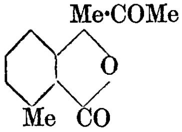
We reported previously that, by esterification by means of methyl alcohol and sulphuric acid of the oily acid residues left after removal of 3-methylacetophenone-2-carboxylic acid, two further methyl esters, m. p.'s 71—72° and 78—79° respectively, were obtained in small amount. From the formula of the former we concluded that it was methyl 4-methylacetophenone-2-carboxylate, but this is erroneous, as we now find it is identical with the ψ-ester (I). The higher-melting substance proved to be the ester of 3 : 4-dimethylacetophenone-2-carboxylic acid; it is now obvious from its mode of formation that it also must be the ψ-ester, which formulation is supported by its inability to form a semicarbazone.



(I.)



(II.)



(III.)

Among the neutral products isolated, mention was previously made of a colourless substance, m. p. 70—71°, giving analytical data agreeing with the empirical formula $(C_4H_4O)_n$. Owing to the minute amount of material in our hands, we were unable to examine the substance in detail, but suggested that it might be 5 : 8-diacetoxy-1 : 6-dimethylnaphthalene, $C_{16}H_{16}O_4$. Westenberg and Wibaut (*loc. cit.*) have also isolated this compound, the identity of which with our own has been confirmed by mixed m. p. determinations, and have proved that it is actually the lactone methyl ketone, $C_{12}H_{12}O_3$ (III).

ψ-Ester of 3-*Methylacetophenone*-2-*carboxylic Acid.*—The acid was prepared from the hydrocarbon as previously described (Heilbron and Wilkinson, *loc. cit.*) and converted into the ψ-ester by saturating a solution in MeOH with dry HCl and leaving the mixture at room temp. for 15 hr. The crude ψ-ester was precipitated with H_2O and crystallised from light petroleum, forming colourless prisms, m. p. 71—72°.

Oxime Anhydride.—A solution of 3-methylacetophenone-2-carboxylic acid in EtOH aq. was treated with the requisite amount of free NH_2OH and left at room temp. for 7 days. The product, which then separated, crystallised from EtOH in needles, m. p. 174°. The *oxime anhydride* can also be prepared directly from the normal methyl ester in the same manner (Found : C, 68·6; H, 5·3. $C_{10}H_9O_2N$ requires C, 68·6; H, 5·1%).

We thank Dr. L. Westenberg for establishing by means of mixed m. p.'s the identity of his products and ours.—THE UNIVERSITY, LIVERPOOL.

[*Received, September* 10*th*, 1932.]

Dipole Moments of Quinoline and iso*Quinoline.* By R. J. W. LE FÈVRE and J. W. SMITH.

Materials.—The C_6H_6 was that used previously (this vol., p. 2239). "Pure" quinoline (200 c.c.) was fractionated through a column and not more than 20 c.c. of the middle fraction were used. *iso*Quinoline, available in a solid colourless condition, was twice melted and frozen out.

Measurements.—The dielectric consts. of dil. C_6H_6 solutions of quinoline and *iso*quinoline were measured at 25° by the method described previously (*loc. cit.*). The densities of the same solutions were determined at the same temp. From these results, the total mol. polarisations of the solutes were calculated in the usual manner. The electronic polarisation, P_E, of the solute was assumed not to differ appreciably from the molecular polarisation calc. for the Na D line from the data of Bruhl (*Z. physikal. Chem.*, 1895, **16**, 193).

The significant data are tabulated below, where f represents the mol.-fraction, M the mol. wt., ε the dielectric const., ρ the density, and P the mol. polarisation. The subscripts 1 and 2 refer to the solute and solvent, respectively.

		Quinoline.			iso*Quinoline.*		
f_1	0	0·01543	0·02321	0·04678	0·01174	0·02655	0·04335
$M_1f_1 + M_2f_2$	78	78·787	79·184	80·386	78·599	79·354	80·211
ε	2·2725	2·384	2·438	2·603	2·383	2·525	2·681
ρ	0·8738	0·8782	0·8804	0·8870	0·8774	0·8820	0·8871
$P_1f_1+P_2f_2$ (c.c.)	26·585	28·32	29·17	31·55	28·27	30·32	32·47
P_2f_2 (c.c.) ...	26·585	26·18	25·97	25·34	26·27	25·88	25·43
P_1f_1 (c.c.) ...	—	2·14	3·20	6·21	2·00	4·44	7·04
P_1 (c.c.) ...	—	138·7	136·6	132·7	170·4	167·2	162·4

Quinoline. Extrapolated value of P_1 for inf. diln. = 141 c.c.; $P_E = 41·87$ c.c. (Bruhl, *loc. cit.*); hence $P_A + P_0 = 99$ c.c., and $\mu = 2·184 \times 10^{-18}$ e.s.u.

iso*Quinoline.* Extrapolated value of P_1 for inf. diln. = 173·7; $P_E = 41·45$ c.c. (Bruhl, *loc. cit.*); hence $P_A + P_0 = 132·2$ c.c., and $\mu = 2·524 \times 10^{-18}$ e.s.u.

Published values (e.s.u. × 10^{-18}) are: pyridine, 2·11 (Lange, *Z. Physik*, 1925, **33**, 169); quinoline, 2·25 (Rolinski, *Physikal. Z.*, 1928, **29**, 658). Bergmann, Engel, and Meyer (*Ber.*, 1932, **65**, 446) record the following values: pyridine, 2·21; quinoline, 2·14; *iso*quinoline, 2·53.

The slight but definite increase in the moment in passing from quinoline to *iso*quinoline recalls the phenomenon observed among naphthalene derivatives and suggests that substitution in *iso*quinoline should be, as with quinoline, independent of the N atom and governed mainly by the 5 : 8-naphthalene type of reactivity.

The fact that the dipole moment of quinoline is a little higher than that of pyridine also illustrates the analogy of these heterocyclic compounds with the benzene–naphthalene series.—UNIVERSITY COLLEGE, UNIVERSITY OF LONDON. [*Received, August 22nd*, 1932.]

The Thioper-rhenates. By H. V. A. BRISCOE, P. L. ROBINSON, and E. M. STODDART.

PREVIOUSLY (J., 1931, 1439) we stated that thioper-rhenates probably exist in the red solution produced when H_2S is passed into alk. per-rhenate solution, but that no compound could be isolated. Feit (*Z. angew. Chem.*, 1931, **44**, 65), by precipitating such solutions with $TlNO_3$, obtained yellow, cryst. $TlReO_3S$. Following as nearly as possible his instructions, however, we were unable to obtain any sign of this product (J., 1931, 2976). Dr. Feit then kindly sent us a specimen of his product and supplied us with more detailed instructions, as follows: " A cold saturated solution of $KReO_4$ is gassed with H_2S for 2 days; after standing over-night it is again treated with H_2S for a further 2 days, the precipitated rhenium sulphide is filtered off, and 0·1—0·05*N*-$TlNO_3$ added; the yellow substance is filtered off, and recrystallised from water."

From a preparation carried out precisely according to these instructions, we obtained a very small quantity of Feit's compound. It yielded no S when shaken with acetone, but on heating was converted into black rhenium sulphide. It is thus clear that Feit has obtained definite evidence of the existence of thioper-rhenates and we are glad to publish this correction of our former statement. A solution of $KReO_4$ after treatment with H_2S for 2 days gave no evidence of the formation of the thio-salt, so that standing and resaturation would appear to be an essential part of the process.—UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE, NEWCASTLE-UPON-TYNE. [*Received, October 4th,* 1932.]

Thermionic Potentiometer for the Measurement of p_H. By A. E. J. VICKERS, J. A. SUGDEN, and R. A. BELL.

IN a footnote to a recent paper (this vol., p. 2471) Morton criticises an apparatus described by us for the continuous recording of p_H (*J. Soc. Chem. Ind.*, 1932, **51**, 545, 570) on the ground that it does not give constancy of zero or maintain constancy of calibration, and the position of the footnote leads the reader to infer incorrectly that our apparatus operates on the principle of the ballistic apparatus described by Fox and Groves (*ibid.*, p. 7T).

We have had a number of apparatus of our pattern in operation for long periods of time (several months) and have found no alteration either in zero or in calibration. Our apparatus operates on well-known principles, worked out by Winch (*J. Inst. Elec. Engineers*, 1930, **68**, 533), Willey and Foord (*Proc. Roy. Soc.*, 1932, *A*, **135**, 166), Wynn-Williams (*Proc. Camb. Phil. Soc.*, 1927, **23**, 810), Brentano (*Phil. Mag.*, 1929, **7**, 685), Meyer, Rosenberg, and Tank (*Arch. Sci. Phys. Nat.*, 1920, **5**, 260), and Rosenberg (*Z. Physik*, 1921, **7**, 18). The sensitivity is 0·5 millivolt, a sensitivity superior to that claimed by Morton.—[*Received, October 8th,* 1932.]