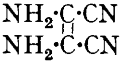
NOTES.

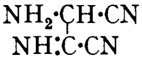
A Reply to Hinkel, Richards, and Thomas: "Studies on Hydrogen Cyanide. Part X. The Tetrapolymer." By E. GRYSZKIEWICZ-TROCHIMOWSKI.

INVESTIGATING the chemical behaviour of the tetrapolymer of hydrogen cyanide, the author believed it to be diaminomaleinitrile (I) (*Rocz. Chem.*, 1922, **1**, 471; 1928, **8**, 165; *J. Soc. Phys. Chim. Russ. Univ. Leningrad*, 1924, **55**, 551), but Hinkel, Richards, and Thomas (J., 1937, 1432) criticised this view, preferring the structure (II), aminoiminosuccinonitrile, and overlooking the fact that the two formulæ are tautomeric.



$$\begin{array}{l} NH_2\cdot C\cdot CN \\ \quad\ \| \\ NH_2\cdot C\cdot CN \end{array}$$

(I.)



$$\begin{array}{l} NH_2\cdot CH\cdot CN \\ \quad\ | \\ \ NH{:}C\cdot CN \end{array}$$

(II.)

The reactions of the tetrapolymer with nitrous acid and with glyoxal, to form a dicyanotriazole and a dicyanopyrazine, respectively, are easily explained only by assuming the formula (I), for (II) would necessitate, not only the migration of the hydrogen atom, but also the formation of intermediate products, for which there is no evidence. (Hinkel, Richards, and Thomas overlooked the fact that the author had investigated these products.)

The two chief arguments upon which Hinkel, Richards, and Thomas base their formula are: (i) that the tetrapolymer behaves as a mono-acid base, and (ii) that it reacts with only one molecule of benzaldehyde; but they ignore the facts that the two cyano-groups would diminish the basic properties of the two amino-groups, and that many other diamines (*e.g.*, *o*-phenylenediamine) react with only one molecule of an aldehyde, forming iminazole derivatives. Their production of 2-phenyliminazole by successive oxidation, saponification, and decarboxylation of the benzylidene derivative of the tetrapolymer is more readily explained by formula (I) than (II). In any case, the tautomeric relationship of the two structures renders all such evidence inconclusive.—WARSAW. [*Received, June 30th*, 1938.]

The Thermal Decomposition of Di-n-butyl-lead Dichloride. By DAVID P. EVANS.

IN 1935 Burawoy, Gibson, and Holt (J., 1935, 1024) obtained pure butane and pure hexane respectively by the thermal decomposition of diethyl- and di-*n*-propyl-monocyanogold below 100°, and suggested that alkyl radicals (free ethyl and *n*-propyl) were the primary products of the decomposition. Earlier in the same year, Jones, Evans, Gulwell, and Griffiths (*ibid.*, p. 39) described a number of dialkyl-lead dichlorides containing the alkyl groups *n*-butyl, *n*-amyl, and *dl*-amyl, and in each case it was noted that decomposition occurred readily (*e.g.*, in contact with hot alcohol) with formation of lead chloride. It was thought that this decomposition might take place according to the equation $PbR_2Cl_2 = PbCl_2 + R_2$ (1), with possible formation of free alkyl radicals prior to the evolution of hydrocarbon.

When 20 g. of pure, dry, powdered di-*n*-butyl-lead dichloride were heated in a small distillation flask under ordinary pressure at 130° (oil-bath) for 30 minutes, a clear, colourless liquid distilled at constant temperature (77°), which proved to be *n*-butyl chloride (2·4 g.) and not octane. Further, the solid residue in the distillation flask contained a substance which was very soluble in alcohol, ether, and benzene; when this was extracted with hot alcohol, and the extract poured into water, 9 g. of a white solid were deposited, which, on recrystallisation from glacial acetic acid, yielded small needles (melting to a clear liquid at 109—110°) (Found: Pb, 50·5; *M*, in benzene 406. Calc. for $C_{12}H_{27}ClPb$: Pb, 50·1%; *M*, 413·5), identical with the tri-*n*-butyl-lead chloride, m. p. 109—110°, described by Pfeiffer, Truskier, and Disselkamp (*Ber.*, 1916, **49**, 2445). The solid residue remaining after extraction of this compound consisted almost entirely of lead chloride, which dissolved in boiling water; on addition of hydrochloric acid, and cooling, the aqueous solution gave 7 g. of inorganic lead salt. The weights of the several products indicate that di-*n*-butyl-lead dichloride probably decomposes according to the equation $2PbBu_2Cl_2 = BuCl + PbCl_2 + Bu_3PbCl$ rather than according to equation (1).—TECHNICAL COLLEGE, CARDIFF. [*Received, August 3rd*, 1938.]

Note on a Coloured By-product in the Preparation of 1 : 3 : 5-*Triphenylbenzene from Acetophenone.*

By R. J. W. Le Fèvre.

1 : 3 : 5-Triphenylbenzene can be conveniently prepared from acetophenone by auto-condensation under the action of potassium pyrosulphate–sulphuric acid mixtures for 30 hours at 45° (Odell and Hines, *J. Amer. Chem. Soc.*, 1913, **35**, 82). The yield of pure product, after crystallisation from acetic acid, is generally of the order 70% (present work), but if the reaction is carried out at *ca.* 150°, the product on cooling solidifies to a dark mass, from which, by extraction with hot water, etc., the hydrocarbon can be eventually obtained, but in lower yields.

It was noticed that these coloured acidic aqueous extracts lost their colour when neutralised, and regained it when reacidified with mineral acids. This suggested the presence of a pyrylium salt or salts. Accordingly, several litres of extracts from a number of preparations were clarified by charcoal, filtered, and treated with a concentrated solution of ferric chloride in hydrochloric acid. A yellow precipitate was produced, m. p. *ca.* 270°, raised to 273—275° by crystallisation from much acetic acid (Found: C, 54·6; H, 3·42. Calc. for $C_{23}H_{17}OCl_4Fe$: C, 54·5; H, 3·35%). The m. p. of a sample of 2 : 4 : 6-triphenylpyrylium ferrichloride, obtained from acetophenone, benzaldehyde, ferric chloride, and acetic anhydride (Dilthey, *J. pr. Chem.*, 1916, **94**, 53), was not affected by admixture with the above product. This identification was verified by preparing, *via* the pyranol, the corresponding perchlorate (Le Fèvre and Le Fèvre, J., 1932, 2894), m. p. 288°, and comparison with an authentic specimen.

The yields of ferrichloride were small (less than 5% of the weight of acetophenone used) and variable, being slightly greater when higher temperatures were employed for the condensation.

The Mechanism of the Reaction.—In Dilthey's preparation carbon atom 4 of the pyrylium ring is provided by the aldehyde group of benzaldehyde. It does not seem likely that in the present reaction this is also the case, for all the recorded transformations of acetophenone by concentrated sulphuric acid give benzoic acid, and not benzoylformic acid—which by decarboxylation could produce benzaldehyde. Krekeler (*Ber.*, 1886, **19**, 674), for example, showed that, although fatty acids were formed when thiophen ketones were treated with warm sulphuric acid ($C_4H_3S{\cdot}CO{\cdot}R \rightarrow C_4H_3S{\cdot}SO_2{\cdot}OH + R{\cdot}CO_2H$), yet acetophenone gave only benzoic acid, *i.e.*, the acetyl group was oxidised; in a later paper (*ibid.*, p. 2623) he showed that with hot pyrosulphuric acid only benzoic and benzenesulphonic acids were isolable.

Further, it does not seem probable that the carbon atom 4 is supplied by benzoic acid itself, but it is notable that benzoic anhydride *could* be effective. This is mentioned because benzoic acid is relatively easily dehydrated (*e.g.*, even by acetic anhydride; cf. " Organic Syntheses," Coll. Vol. I, 1932, 85), and the formation of 2 : 4 : 6-triphenylpyrylium salts from benzoic anhydride has previously been demonstrated (Le Fèvre, J., 1933, 1197).—The Sir William Ramsay and Ralph Forster Laboratories, University College, London. [*Received, August 24th,* 1938.]