

NOTES.

The Oxidation of 2- and 4-Nitro-4'-methyldiphenyl with Chromyl Chloride. By WILLIAM S. M. GRIEVE and DONALD H. HEY.

AN alternative method for the preparation of 4-nitrodiphenyl-4'-aldehyde has been sought in view of the irregularity of the m. p. (initially at 135°; 127° after repeated crystallisation from alcohol or benzene) of the material obtained by the nitration of diphenyl-4-aldehyde (J., 1933, 971).

4-Nitrodiphenyl-4'-aldehyde.—A suspension of 4-nitro-4'-methyldiphenyl (10 g.), prepared by the nitration of 4-methyldiphenyl (J., 1932, 1891), in redistilled carbon tetrachloride (350 c.c.) was gradually added to a stirred solution of chromyl chloride (18 g.) in carbon tetrachloride (40 c.c.) at room temperature (compare Law and Perkin, J., 1907, 91, 258; 1908, 93, 1633). After 2 days, the solution was poured into water and saturated with sulphur dioxide and the yellow solid was separated, washed with hot aqueous sodium bicarbonate, and recrystallised from alcohol, giving 4-nitrodiphenyl-4'-aldehyde (4.5 g.) in pale yellow needles, m. p. 127—128° alone or in admixture with the product obtained from the nitration of diphenyl-4-aldehyde (Found: C, 68.85; H, 4.0; N, 6.2. Calc. for $C_{13}H_9O_3N$: C, 68.7; H, 4.0; N, 6.2%). Acidification of the bicarbonate washings precipitated 4-nitrodiphenyl-4'-carboxylic acid (0.25 g., m. p. 330—335°; ethyl ester m. p. and mixed m. p. 112°). Evaporation of the clear dried

carbon tetrachloride layer left a crystalline yellow solid (5.0 g., m. p. 90—100°), which on repeated crystallisation from light petroleum gave a further quantity of 4-nitrodiphenyl-4'-aldehyde and a small quantity of a second compound, m. p. 130—133°, which contained chlorine.

2-Nitrodiphenyl-4'-aldehyde.—A solution of 2-nitro-4'-methyldiphenyl (10 g.), prepared from sodium *p*-toluenediazoate and nitrobenzene (J., 1932, 1893), in carbon tetrachloride (50 c.c.), was similarly treated with chromyl chloride (15 g. in 50 c.c. of carbon tetrachloride). After the saturation with sulphur dioxide, evaporation of the dried carbon tetrachloride layer left a viscous residue, which was treated with saturated aqueous sodium bisulphite for 24 hours. The brown solid which separated was washed with ether and boiled with hydrochloric acid; the semi-solid residue, after several crystallisations from alcohol, yielded 2-nitrodiphenyl-4'-aldehyde (2 g.), m. p. 101° alone and in admixture with the product obtained from the nitration of diphenyl-4-aldehyde (Found: C, 69.1; H, 3.7; N, 6.6. Calc. for $C_{13}H_9O_3N$: C, 68.7; H, 4.0; N, 6.2%).—THE UNIVERSITY, MANCHESTER. [Received, November 23rd, 1934.]

Oxygen Addition Compounds of Acetylenes. By CHARLES A. YOUNG, R. R. VOGT, and J. A. NIEUWLAND.

IN order to explain the formation of the products of the reaction between acetylene and oxygen, Bodenstein (*Z. physikal. Chem.*, 1931, 12, B, 155) postulated the intermediate formation of a peroxide.

We have found that many acetylenes upon exposure to oxygen or air liberate iodine from potassium iodide, oxidise ferrous to ferric compounds, form a yellow coloration with titanium sulphate, and give other reactions indicating the presence of active oxygen, probably in the form of peroxides. These oxygen derivatives will accordingly be referred to as peroxides in this paper.

A study of a wide variety of acetylenes, chiefly of the types $RC\equiv CH$, $RC\equiv CR'$, and $RC\equiv CX$, where R and R' represent alkyl and aryl groups, and X denotes a halogen, has shown that aromatic acetylenes acquire oxidising properties to a much less extent than do the alkyl derivatives. Only those acetylenes which are normally liquids or which have been melted appear to form peroxides. No peroxides have been found in acetylene itself. The behaviour of halogeno-acetylenes is somewhat irregular. Iodine linked to acetylenic carbon appears to retard the formation of peroxides in the lower members of the alkyl series, and in the higher members it apparently has little influence.

In several cases an acetylene was prepared by two or more widely different methods: all the samples formed peroxides with equal degrees of readiness and to the same extent. Consequently, it is improbable that the peroxides are due to traces of olefins present as impurities, since the same quantity of olefins would certainly not be formed by the various methods of preparation. It is possible that the acetylenes first polymerise, yielding olefinic derivatives which form peroxides. However, mono- and di-alkylacetylenes form similar quantities of peroxides. It is probable, therefore, that the acetylenes themselves form peroxides.

The peroxide of butylacetylene is rapidly destroyed by manganese dioxide, vanadium pentoxide, sodium peroxide, sodium hydroxide, metallic sodium, concentrated sulphuric acid, concentrated hydrochloric acid, silica gel, and bone black. Quinol greatly retards but does not prevent the formation of peroxides in butylacetylene. Traces of benzoyl peroxide or water accelerate for a few days the rate of peroxide formation in freshly distilled butylacetylene. Increased pressures of oxygen have no apparent effect.

During the past few years a number of cases have arisen in this laboratory in which rather anomalous results were obtained in polymerisation and other addition reactions of acetylenes. It is possible that these discrepancies in results were due to the catalytic action of the oxidising impurities in the acetylenes, and it is intended to repeat a number of these experiments with careful control of the peroxide impurities.—NOTRE DAME, INDIANA, U.S.A. [Received, August 10th, 1934.]

The Ferrohalides of Pyridine and Quinoline. By F. SHERWOOD TAYLOR.

THE elements manganese, cobalt, nickel, and copper form salts, $R_2MHal_4(aq.)$ or $2RHal, MHal_2(aq.)$, where M is one of the above four metals, R is pyridinium or quinolinium, and Hal is chlorine or bromine. The colours of these salts, both in the solid state and in saturated aqueous solution, in general resemble those of solutions of the simple chloride, $MHal_2$, in the concentrated halogen acid. The colours of three of the four pyridinium and quinolinium ferrohalides now described follow the above rule.

Pyridinium Ferrochloride.—(1) Alcoholic solutions of pyridinium chloride and hydrated ferrous chloride were mixed: the yellow needles that separated were washed with acetone and dried in a current of dry carbon dioxide. (2) Hydrated ferrous chloride (20 g.) was mixed with concentrated hydrochloric acid (30 c.c.) and pyridine (16 g.). The solution was saturated with hydrogen sulphide, filtered, and reduced to half its bulk by distillation in a current of carbon dioxide. The yellow needles that separated were washed and dried as before; m. p. 127—128° after softening at about 110° [Found: (1) Fe, 15.6; Cl, 39.4; (2) Fe, 15.8; Cl, 39.8. $(C_5H_5NH)_2FeCl_4$ requires Fe, 15.6; Cl, 39.7%]. The salt was not deliquescent, but gradually darkened in air from pale yellow to orange. Concentrated aqueous solutions were yellow, but on dilution assumed the pale green colour associated with ferrous salts.

Quinolinium ferrochloride dihydrate, prepared by method (2) above, recrystallised from alcohol, washed with acetone, and dried in a current of carbon dioxide, formed small yellow leaflets [Found: Fe, 11.4; Cl, 28.7. $(C_9H_7NH)_2FeCl_4 \cdot 2H_2O$ requires Fe, 11.6; Cl, 28.9%]. It softened at 86° and melted at 97° with some separation of solid. At higher temperatures water and quinolinium chloride were evolved.

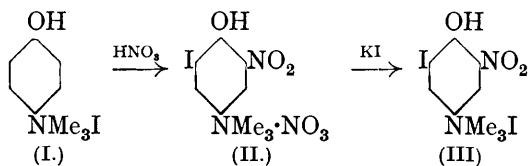
Attempts to prepare the anhydrous material by mixing alcoholic solutions of the anhydrous constituents gave products which were apparently mixtures.

Pyridinium Ferrobromide.—A solution of "iron bromide" (25 g.) in hydrobromic acid (75 c.c., *d* 1.5) and water (30 c.c.) was saturated with hydrogen sulphide until the brown colour had disappeared. It was then sucked through a pad of asbestos fibre (to remove sulphur), pyridine (20 g.) added, and the solution distilled in a vacuum until crystals appeared on cooling. These were filtered off in an atmosphere of carbon dioxide and washed with acetone on the filter. The crystals were clear green when first washed, but on exposure to air darkened and deliquesced very rapidly and could not be dried without discoloration [Found: Fe, 10.4; Br, 58.9. $(C_5H_5NH)_2FeBr_4$ requires Fe, 10.4; Br, 59.7%]. The deliquescence, rapid oxidation, and green colour of this salt are in marked contrast to the properties of the other salts here described.

Quinolinium ferrobromide dihydrate was prepared by essentially the same method as was used for pyridinium ferrobromide. The mixed solutions, however, after concentration in a vacuum, set solid, and this solid was recrystallised from hot acetone. The crystals were filtered off, washed with cold acetone, and dried in a current of dry carbon dioxide. They were bright yellow with a tinge of orange [Found: Fe, 8.4; Br, 47.5. $(C_9H_7NH)FeBr_4 \cdot 2H_2O$ requires Fe, 8.3; Br, 47.6%]. When heated, they darkened, softened at 81°, and melted at 89° with some separation of solid.—EAST LONDON COLLEGE, UNIVERSITY OF LONDON. [Received, October 22nd, 1934.]

Action of Nitric Acid upon p-Hydroxyphenyltrimethylammonium Iodide. By KENNETH C. ROBERTS.

In an attempt to synthesise 2-amino-4-dimethylaminophenol it was observed that dilute nitric acid reacts with *p*-hydroxyphenyltrimethylammonium iodide (I) in the manner indicated (I→II), 3-nitration being accompanied by replacement of I' by NO₃' and nuclear iodination. Both the *iodonitro-nitrate* (II) and the corresponding *iodide* (III) resisted decomposition to the tertiary base.



5(?)-Iodo-3-nitro-4-hydroxyphenyltrimethylammonium Nitrate (II).—Treatment of (I) with 2*N*-nitric acid at the boiling point gave a red solution which decomposed violently with evolution of iodine. The mixture was boiled until no free iodine remained; the solid obtained crystallised from water in yellow needles, decomp. above 210° (Found: C, 27.8; H, 4.0. $C_9H_{12}O_6N_3I$ requires C, 28.0; H, 3.1%).

5(?)-Iodo-3-nitro-4-hydroxyphenyltrimethylammonium Iodide (III).—An aqueous solution of (II) with potassium iodide (cf. *Ber.*, 1919, 52, 295) gave a dark yellow, crystalline precipitate. After recrystallisation from water this decomposed above 225° (Found: N, 6.4, 6.5. $C_9H_{12}O_3N_2I_2$ requires N, 6.2%).—KING'S COLLEGE, LONDON. [Received, November 22nd, 1934.]