from all other meteorites in chemical composition (they contain carbon, organic compounds, water-soluble compounds, and much combined water) and in mineralogical composition (the silicate material is largely chlorite, a hydrated magnesium–iron silicate). Chlorite decomposes on heating above about 600° C. to give olivine and orthopyroxene; if carbon is present, a natural smelting will take place, reducing some of the combined iron to metallic iron, and thereby increasing the magnesium content of the silicates. The reactions can be represented as follows:

$$\underset{\text{chlorite}}{Mg_4Fe_2Si_4O_{10}(OH)_8} \rightarrow \underset{\text{olivine}}{2(Mg,Fe)_2SiO_4} + \underset{\text{orthopyroxene}}{2(Mg,Fe)SiO_3} + 4H_2O$$

$$\downarrow +2C$$

$$4MgSiO_3 + 2Fe + 2CO_2$$

These reactions will produce the mineralogical composition of the usual chondritic meteorites, an aggregate of olivine and/or orthopyroxene, with some metallic iron. This relationship between carbonaceous chondrites and the other chondritic meteorites was pointed out by Wiik[2], who stated: "This is intended only to give a picture of the chemical relations between the subgroups, and not intended to suggest the genesis". I believe this is not only a chemical relationship but also a genetic one.

The texture and structure of the chondritic meteorites is quite remarkable if they have originated in any body with a considerable gravitational field. Many of them are very porous and friable, so much so that they can be crumbled in the hand, indicating they were not consolidated under pressure. They generally contain nickel–iron in amounts ranging from 5 to 25 per cent, this metal being intimately mixed with the low-density silicate minerals and showing no sign of gravitational segregation. Both these features are readily explicable if these meteorites are the product of chemical reconstitution of carbonaceous chondrites triggered off by heating to 600° C. or higher. A possible explanation is that carbonaceous chondrites represent aggregates of primitive cosmic dust, and that most of them have, during the course of geological time, approached sufficiently close to the Sun to be heated enough to set off the reactions converting them to olivine–pyroxene chondrites.

Suggestive evidence in favour of such an explanation is provided by the age data on chondrites. Gerling and Rik[3] have measured the ages of several chondrites by the potassium–argon method, and found them to differ one from another, ranging from 720×10^6 years up to $3,000 \times 10^6$ years. Different ages for different chondrites are to be expected on the hypothesis outlined here, since the potassium–argon age will give the time since recrystallization.

The hypothesis outlined here can be tested if we can devise methods for determining the temperature of crystallization of the minerals making up the chondrites. A few clues are already available. The St. Marks stone contains quartz, and hence its temperature of crystallization (at zero pressure) cannot have exceeded 867° C. The Indarch stone contains tridymite, which, if it crystallized within the field of stability of this mineral, implies a temperature of crystallization between 867° and 1,470° C. Other geochemical thermometers which should be investigated are: (*a*) composition relationships between olivine and co-existing pyroxene; (*b*) the nature of the plagioclase feldspar (present in small amount in most stone meteorites), whether low-temperature or high-temperature; (*c*) the nature of the nickel–iron phases—both kamacite and tænite are present in many stony meteorites, but usually as individual grains, not in Widmanstätten intergrowths. Investigations along these lines are proceeding in this Museum.

If the origin of the chondritic meteorites is that outlined above, the other meteorite types—achondrites, pallasites, and siderites—can be explained as the products of gravitational differentiation of a planetary or asteroidal body formed by the aggregation of chondrites. Such a body would probably pass through a molten stage as a result of the heat produced by aggregation, chemical reactions, and nuclear disintegrations. Given a moderate gravitational field, this would produce a silicate mantle overlying a metallic core. Subsequent disintegration would give rise to the essentially metal-free achondrites, and the silicate-free siderites, the few pallasites coming from a transition zone. In this connexion it should be noted that diamonds have been found only in siderites and achondrites, indicating that only these meteorites crystallized under sufficiently high pressures.

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CHEMISTRY

Pentafluoropyridine

In two recent communications[1,2], a general method for the preparation of perfluoro-aromatic compounds was described. It involved the defluorination of saturated[2] and unsaturated[1] cyclic fluorocarbons over a metal surface at 400–600°, when the corresponding aromatic fluorocarbons were produced. For example, hexafluorobenzene was obtained[1] from octafluoro*cyclo*hexa-1 : 3- or -1 : 4-diene, and octafluoronaphthalene[2] from perfluorodecalin; several other examples were also described[2].

We now report the first synthesis of an unsaturated perfluoro-heterocyclic compound by a similar process. The starting material was undecafluoropiperidine, which was prepared by known routes—the electrochemical fluorination of either piperidine[3] or pyridine[3,4]. When passed through a heated nickel tube (2 ft. 6 in. long × 1 in. diameter) packed with nickel gauze, this gave pentafluoropyridine in moderate but significant yields. In a typical experiment, undecafluoropiperidine (3·4 gm.) was passed through the tube at 560° with a nitrogen flow-rate of 4·0 litres/hr. Gas-liquid chromatographic analysis (dinonyl phthalate/kieselguhr : nitrogen carrier gas) of the pyrolysate (2·1 gm.) showed that at least four components were present in addition to some unchanged starting material. The component with the highest retention time was separated from several combined pyrolysates (5·0 gm.) by preparative-scale gas-liquid chromatography[5] and was distilled *in vacuo* from phosphorus pentoxide to give pentafluoropyridine

(0·55 gm.), boiling point 84°, n_D^{20} 1·3834 (found: C, 35·6; C_5F_5N requires C, 35·5 per cent): mass-spectrometry, principal mass peaks: 169, C_5F_5N; 150, C_5F_4N; 138, C_4F_4N; 124, C_4F_4. The compound had $\lambda_{max.}$ at 254 mμ (ε, 2,700 in ethanol). The presence of strong bands in the infra-red spectrum at 1,650, 1,537, and 1,505 cm.$^{-1}$ was also consistent[6] with a pyridine structure, and the absence of strong bands at frequencies higher than 1,650 cm.$^{-1}$ showed that no olefinic bonds were present.

The other three components from the pyrolysis have not yet been identified, but are believed to be unsaturated.

Pentafluoropyridine is a colourless and almost odourless liquid. It is immiscible with water but miscible with organic solvents. We have been unable to detect any basic properties of the compound. A potentiometric titration in aqueous ethanol against *N*/20 acid showed no end-point. Hydrogen chloride in dry ether gave no hydrochloride, and no picrate was formed in ethanol solution. This behaviour is different from that of the primary amine pentafluoroaniline[7], which was weakly basic and formed an easily hydrolysable hydrochloride in ethereal solution. It is noteworthy that pyridine is a stronger base than aniline.

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A Modification for washing the Benzidine Sulphate Precipitate in the Determination of Sulphate

Among the numerous procedures that have been developed for determining sulphate with benzidine, that reported by Kent and Whitehouse[1] is most commonly employed as a micromethod. The reliability of the method has also been confirmed by me.

In this, as in all the other procedures, difficulty is experienced in removing the excess of benzidine from the benzidine sulphate precipitate without losing any of the latter. The difficulty was previously overcome by collecting the benzidine sulphate precipitate in a porous glass filter crucible and washing the unreacted soluble benzidine thoroughly. The method yields accurate and reproducible results provided that the filter is of standard porosity and the filtering time is held constant. Owing to the difficulties associated with the use of the filter crucible, the method is, however, time-consuming.

I have developed the following procedure for washing the benzidine sulphate after its precipitation by the method of Kent and Whitehouse. The contents of the precipitation tube are transferred to a centrifuge tube of about 10-ml. capacity which tapers to a sharp point. One drop of an aqueous suspension of barium sulphate which has been carefully rinsed free of excess barium or sulphate ions is then added and it is centrifuged for 5 min. at 3,000 r.p.m. Two more drops of the barium sulphate suspension are added, and the tube centrifuged for a further 15–20 min. The upper clear layer is then removed and the mouth of the tube dried with cellulose tissue. About 9 ml. of an alcohol–acetone (1 : 1) mixture is added to the tube, and the precipitate is broken up with a stiff steel wire. The tube is centrifuged about 5 min., two drops of the barium sulphate suspension are added, and the centrifugation continued for about 10 min. It should be noted that the total amount of barium sulphate added forms a cone 1–1·5 mm. high at the bottom of the tube when tightly packed. The upper clear layer is decanted, about 9 ml. of the alcohol–acetone mixture is added and the tube is centrifuged for about 10 min. After the supernatant has again been removed, 3 ml. of *N* hydrochloric acid is added to dissolve benzidine sulphate precipitate, which is broken up with a steel wire. After ½ hr., 2 ml. of water is added to the tube, and the latter is centrifuged for 5 min. The solution containing the benzidine is transferred to another tube for diazotization by the method of Kent and Whitehouse.

The microprecipitate of benzidine sulphate is always enclosed between two tightly packed layers of barium sulphate during the decantations. After the first centrifuged precipitate has been broken up, the benzidine adsorbed on the barium sulphate is removed by washing with the alcohol–acetone mixture. After the centrifuged precipitate has been broken up a second time, the pure benzidine sulphate is dissolved in the hydrochloric acid. The solubility of barium sulphate is so slight that it cannot cause any significant error.

In spite of its apparent complexity, the method can be readily employed in routine analyses. One hundred analyses can be performed daily with a centrifuge that takes 50 tubes and a larger throughput can be achieved by using a larger centrifuge. The accuracy of the method is about the same as reported by Kent and Whitehouse. The absorbance reading for the blank is 0·020 when a Beckman *DU* spectrophotometer is employed.

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Freezing-Point Depressions of Hoagland's 'Carbowax' Systems

Solutions of various osmotic pressures have been widely used in biology. Sugars and their derivatives, commonly used to maintain osmotic pressures, have the drawback that many, if not all, of these compounds can be metabolized by the test tissue or organism. McClenden and Blinks[1] described the use of 'Carbowax 4000' (polyethylene glycol) in maintaining various osmotic concentrations in a study of the Hill reaction. Excellent results were reported. This