where a relates to the original disc, b to the same disc after compressing it to about 10 per cent (the discs were rotated about an axis parallel to the X-ray beam). The shift of the  $\alpha_1\alpha_2$ -lines amounts to about one sixth of their distance apart, corresponding to a decrease in spacing of about 0.04 per cent.

Wood observed that the rate of broadening of lines from different planes differed likewise<sup>3</sup>. A directional effect was also observed in our case in the sense that the degree of lattice distortion of a definite plane is dependent on the relative orientation of crystal lattice and direction of deformation; for this experiment, strips of the recrystallised band were stretched by about 2 per cent parallel (Fig. 1c) and at 45° (Fig. 1d) to the direction of rolling, that is, nearly parallel to a [100]- and a [110]-direction respectively. The severe distortion in the second case might perhaps be related to the fact, found for aluminium, that crystals stretched in that direction exhibit an extremely pronounced recrystallisation power4.

In conclusion, I wish to thank Mr. F. M. Jacobs for his help in taking the photographs.

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### Lattice Parameters of Solid Solutions in Silver

In continuation of work on valency effects in alloys, I have recently measured the lattice parameters of the primary solid solutions in silver formed by the elements cadmium, indium, tin and antimony, which follow immediately after silver in the Periodic Table. This work has led to the discovery that in dilute solid-solutions of these elements, the alloys of the same equivalent composition have identical lattice parameters. By the term equivalent composition is meant the atomic percentage of the solute element multiplied by its valency, and the above relation implies that if the lattice parameters of the alloys are plotted against the equivalent compositions, the points for all of the four alloy-systems lie on a single curve. Alternatively, it may be said that the initial expansion of the silver lattice produced by one atom of the above elements is proportional to the valency.

The relation is thus of the same type as that previously found for the depression of freezing point of silver by the same elements, and may perhaps indicate an effect proportional to the repulsion between a solute and a solvent ion.

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### Dipole Moments of Ethyl and Phenyl Isocyanates

The dipole moments1 and the Raman spectra2 indicate that the isothiocyanate group, -N = C = S, is linear. The isocyanates are now found to resemble the isothic eyanates. The Raman spectra indicate that the group  $-{\bf N}={\bf C}={\bf 0}$  in the isocyanic esters is linear3, and this conclusion agrees with inferences drawn from the dipole moments.

Ethyl and phenyl isocyanates we find to have moments of 2.81D and 2.28D respectively. other value for the ethyl compound is available, but the published results for phenyl isocyanate are 2.34~D at  $18^{\circ}$  in benzene and 2.23~D at  $25^{\circ}$  in carbon tetrachloride<sup>5</sup>, the mean being 2.28 D.

The difference between the moments of the corresponding isothiocyanate and isocyanate gives the value of the excess of the C=S over the C=O moment. This difference deduced from other compounds is given below.

Ethyl isothiocyanate 3.31 0.50 Ethyl isocyanate 2.81Phenyl isothiocyanate 3.00Phenyl isocyanate 2.28 0.72Thiobenzophenone Benzophenone  $3.37 \\ 2.95$  0.42 Dianisyl thioketone Dianisyl ketone  $\frac{4.44}{3.90}$ 0.54

Bergmann has published two values of the moment of phenyl isothiocyanate, namely<sup>6</sup>, 2.76~Dand 3.00 D, and it will be seen that the former value exceeds the moment of phenyl isocyanate by 0.48 D. The other figures are in satisfactory agreement with each other.

The solvent used in the present experiment was benzene, and measurements were at 20°. Ethyl isocyanate, prepared from potassium ethyl sulphate and potassium cyanate, was twice fractionated, dried by sodium sulphate and refractionated. The moment was measured immediately. The physical constants were: boiling point, 59.8°/759 mm.;  $d_4^{20}$  0.9031;  $n_D^{20}$  1.3808. Phenyl isocyanate from Kahlbaum was dried and fractionated: boiling point,  $161.7^{\circ}/752 \text{ mm.}$ ;  $d_A^{20} 1.0946$ ;  $n_D^{20} 1.5363$ .

> $P_E$ 2.81 D 2.28 D Ethyl isocyanate Phenyl isocyanate 185 c.c. 144 c.c. 18.3 c.c. 33.9 c.c.

The details of these results and those for analogous compounds will shortly be published.

> J. R. Partington. E. G. COWLEY.

Queen Mary College, University of London. May 17.

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## Interchange of Heavy Atoms in Organo-Metallic Compounds

The interchange of heavy atoms in organo-metallic compounds, reported by Mrs. Leigh-Smith and Dr. Richardson<sup>1</sup>, using the radioactive indicator method, is in line with work done by Hilpert and Grüttner<sup>2</sup>, who, however, found evidence of detachment of the organic radicals from the metal. They found that a reversible reaction took place between mercury diphenyl and metallic bismuth, with formation of a little diphenyl, at 250° in hydrogen.

When working on alkyl bismuth compounds under the direction of Prof. W. J. Jones at Cardiff, I attempted to prepare mixed alkyl-bismuthines, and obtained results indicating some looseness of binding between the bismuth atom and the alkyl residues. On treating amyl bismuth dichloride with ethyl magnesium bromide, triethylbismuthine and trin-amyl-bismuthine were obtained in addition to *n*-amyl-diethyl-bismuthine. Challenger<sup>3</sup> obtained similar results with ethyl magnesium bromide and

diphenyl-bromobismuthine, suggesting that organic radicals are readily liberated from their compounds with bismuth.

Exchange of metal atoms will probably occur with many typical organo-metallic compounds, where the link between carbon and metal is weaker than that between carbon and a non-metal of the same group of the Periodic Table; also, the strength of binding decreases with increasing atomic weight of the central atom

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l Station Hill, Maesteg, Glam. May 27.

<sup>1</sup> NATURE, **135**, 828, May 18, 1935. <sup>2</sup> Ber., **46**, 1685; 1913. <sup>3</sup> J. Chem. Soc., 105, 2210; 1914.

# Synthesis of Dehydroandrosterone by the Decomposition of γ-Sitosterol from Soya Beans

Two substances have been isolated from the urine of men which resemble the male hormone in their ability to stimulate the growth of the capon's comb1. One of these, androsterone, described in detail by Butenandt and Tscherning<sup>2</sup>, has been produced artificially by Ruzicka and his collaborators<sup>3</sup> by means of the oxidative decomposition of epi-dihydrocholesterol acetate, and has thereby been recognised 3-epi-oxy-allo-ætio-cholanone-(17). A second oxyketone containing two hydrogen atoms less has been obtained by Butenandt and Dannenbaum<sup>4</sup> from an unsaturated chloroketone, C19H27OCl, occurring in extracts of urine, by replacement of the chlorine atom by a hydroxyl group. On carrying out the analogous replacement reaction using the saturated chloroketone, androsterone was obtained. reactions leave the question unanswered as to the position of the double bond and the steric position of the hydroxyl group.

I have elucidated this by carrying out the synthesis of the hormone by means of the decomposition of one of the known sterols. Acetylated sitosterol obtained from soya beans was chlorinated in the 5,6-position in order to protect the double bond, and the side chain was afterwards removed by vigorous oxidation with chromic acid, more or less according to the classical method of Ruzicka by which the identity of the ring system of sitosterol and cholesterol has From the dechlorinated and been determined<sup>5</sup>. saponified reaction mixture, a sparingly soluble semicarbazone was obtained; this, after hydrolysis, gave beautiful crystals of an oxyketone which proved to be chemically and physiologically identical with dehydroandrosterone obtained from urine in this laboratory. This oxyketone has a melting point at 147°-148° C. (corr.), the mixed melting point with dehydroandrosterone showing no depression; oxime, leaflets or needles, melting point and mixed m.p. 190° C. (corr.); benzoate, melting point 252°-253° C. (corr.); specific rotation,  $+13.5^{\circ}$  in absolute alcohol. The capon unit is about 210γ, which is the same as the dose required of natural dehydroandrosterone (androsterone =  $70\gamma$ ). Dehydroandrosterone is therefore 3-oxy- $\triangle$ -5-6-ætiocholenone-(17).

This configuration of the ring system is similar to that of sitosterol and cholesterol, which is interesting in as much as it has been found possible, by a modification of the existing process (K. David<sup>6</sup>) to

prepare, in this laboratory, dehydroandrosterone from urine in almost the same quantity as androsterone.

The details of this work will be published elsewhere.

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### Selective Accumulation of Lipochrome

It is well known that different animals deal with carotenoids derived from vegetable sources in various ways. The adipose tissue of the horse and the cow contain considerable amounts of polyene-hydrocarbons (carotenes), but it does not accumulate polyene-alcohols (xanthophylls). A precisely opposite selection would appear to take place in the fat of the hen.

We tried to locate the organ in which this selection takes place and chose the horse for the following experiment. The blood serum of the horse is free from xanthophyll, and therefore the elimination of this carotenoid takes place before it enters the general circulation. So the question arises, whether the polyene-alcohols are not absorbed at all by the gut. or whether they reach the liver and are transformed or eliminated there. To choose between these alternatives, we took blood samples, therefore, while absorption of large amounts of green food was going on, from the portal vein of a narcotised horse. xanthophyll was found in the serum, the lipochrome of which was identical with that taken from the jugular vein; but the carotene content was found to be increased.

This observation makes it quite probable that xanthophylls do not cross the wall of the gut and that selection already takes place in the digestive organs of the horse.

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# Keratin Digestion in the Larvæ of the Clothes Moth

The digestion of keratin in the larvæ of the ordinary clothes moth, Tineola biselliella, was investigated by means of the micro-methods developed by Linderstrøm-Lang and Holter. In the secretion of the middle intestine a powerful proteinase was found having a pH optimum about 9.3 (40°, splitting up casein) and, contrary to animal trypsin-kinase, being but little sensitive to addition of thiol compounds (sodium sulphide, sodium thioglycolate). The pH of the secretion of animals fed with wool was about 10 (measured with the glass electrode in a carbon dioxide free chamber) and gave a strong nitroprusside reaction which was most clearly visible in the half-digested hairs present as contamination in the secretion. The reaction disappeared soon after the secretion had been exposed to the air; only a very small further visible change of the hairs was