NOTES.

Note on the Co-ordination Number of Bivalent Lead. By R. Colin Haworth and Frederick G. Mann.

Thiourea is known to co-ordinate very readily with many metallic salts, giving derivatives of comparatively high stability; it is of value, therefore, in that a metallic atom may show a higher co-ordination valency when linked to thiourea than when linked to many other organic molecules. Rosenheim and Meyer (*Z. anorg. Chem.*, 1906, **49**, 18) described a thiourea–lead nitrate compound to which they ascribed the unlikely composition $11CS(NH_2)_2,2Pb(NO_3)_2$. We have had occasion to repeat this preparation: the *compound* crystallises from water in colourless needles, m. p. 160° (decomp.), and has the composition $6CS(NH_2)_2,Pb(NO_3)_2$. Molecular-weight determinations show that the salt undergoes considerable dissociation in boiling dilute aqueous solution, from which, however, it crystallises unchanged again on cooling. If the six thiourea molecules are co-ordinated normally to the lead atom, giving a salt, $[\{CS(NH_2)_2\}_6Pb](NO_3)_2$, the lead has now the electronic state of uranium. It is possible that the thiourea molecules are not, however, co-ordinated to the lead, and that the substance is a " molecular addition compound : " this could be decided only by *X*-ray crystal analysis.

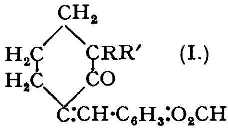
Preparation.—Solutions of lead nitrate (3 g.) and thiourea (4·5 g., 6·5 mols.) in hot water (10 c.c. and 15 c.c.) are mixed and cooled. The white crystals which separate are collected, and recrystallised from water; m. p. 160° (decomp.) (Found : C, 9·3; H, 3·0; N, 24·9; S, 24·0; Pb, 26·5; *M*, micro-ebullioscopic in 0·81% aqueous solution, 79; in 1·45% solution, 79; in 2·004% solution, 82; in 4·962% solution, 96. $C_6H_{24}O_6N_{14}S_6Pb$ requires C, 9·1; H, 3·0; N, 24·9; S, 24·4; Pb, 26·3%; *M*, 787). The above composition was confirmed by analysis of several preparations.

It is the possible formation of similar compounds that renders necessary the use of excess of litharge in the preparation of dicyandiamide from thiourea (Haworth and Mann, this vol., p. 606).—University Chemical Laboratory, Cambridge. [*Received, September 29th*, 1943.]

Preparation of Derivatives of 2 : 2-*Dialkyl*cyclo*hexanone.* By Arthur J. Birch.

In view of Johnson's publication (*J. Amer. Chem. Soc.*, 1943, **65**, 1317) on the direct introduction of angular methyl groups, it seems advisable to place on record some preliminary experiments along the same lines carried out in 1940, and included in Birch, D.Phil. Thesis, Oxford, 1940.

The method consists in the protection of the methylene group in the 6-position of a 2-alkyl*cyclo*hexanone by condensation with piperonal, and alkylation of the product by means of sodamide and an alkyl halide, thus forcing the formation of a quaternary carbon atom. 6-*Piperonylidene*-2-*methyl*cyclo*hexanone* (I; R = Me, R′ = H) was methylated to 2 : 2-*dimethyl*-, and ethylated to 2-*methyl*-2-*ethyl*-6-*piperonylidene*cyclo*hexanone* (I; R = Me, R′ = Me and Et respectively). The constitution of the former was proved by its formation from 2 : 2-dimethyl*cyclo*hexanone and piperonal. Although a similar type of methylation was carried out by Koebner and Robinson (J., 1941, 566), the structure of the product was not rigidly proved. By analogy with the above alkylations it is evident that the products obtained by these authors are correctly formulated, so, in conjunction with Johnson's method (*loc. cit.*) for removing the arylidene group, the method should prove of great value in the synthesis of steroids.


(I.)

6-*Piperonylidene*-2-*methyl*cyclo*hexanone*.—Piperonal (32 g.), 2-methyl*cyclo*hexanone (27 g.), and a solution of sodium (0·5 g.) in alcohol (100 c.c.) were mixed, left for 4 days, and poured into water. The product was extracted with ether and recovered as a pale yellow resin, b. p. 230—245°/13 mm., which crystallised in contact with alcohol. Recrystallised from a small volume of the same solvent, it formed pale yellow prisms (17 g.), m. p. 74—75° (Found: C, 73·6; H, 6·5. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·6%).

6-*Piperonylidene*-2 : 2-*dimethyl*cyclo*hexanone*.—(I) The above product (10 g.) in toluene (50 c.c.) was refluxed with finely powdered sodamide (1·7 g.) for 90 minutes, and methyl iodide (8 g.) added, heating being continued for a further hour. The mixture was cooled and poured into water, the product collected in a little ether, and the solvent removed. The residue crystallised from a little alcohol in pale yellow, flat needles (8 g.), m. p. 67°, which considerably depressed the m. p. of the starting material (Found: C, 74·4; H, 7·0. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0).

(II) 2 : 2-Dimethyl*cyclo*hexanone (25 g.) (Adamson, Marlow, and Simonsen, J., 1938, 774) and powdered sodamide (5 g.) were refluxed in benzene (50 c.c.) until the evolution of ammonia ceased, and piperonal (30 g.) was added to the ice-cooled solution. After washing with water, the product was worked up in the usual manner, being obtained as a yellow resin, b. p. 230—245°/10 mm., which crystallised from alcohol in pale yellow, flat prisms, m. p. 67°, undepressed by the sample obtained by method (I).

6-*Piperonylidene*-2-*methyl*-2-*ethyl*cyclo*hexanone*.—6-Piperonylidene-2-methyl*cyclo*hexanone (7 g.) in benzene (20 c.c.) was treated as above with sodamide (1·1 g.) and ethyl iodide (5 g.). The product boiled at 245°/10 mm., and crystallised from an equal volume of alcohol in cream-coloured plates (4·5 g.), m. p. 60—61° (Found: C, 74·9; H, 7·4. $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·3%).

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