CCCCXXXIV.—*Researches on Residual Affinity and Co-ordination. Part XXXI. Molybdyl Bis-β-diketones.*

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CHEMICAL literature contains references to two molybdenum derivatives of acetylacetone (Beilstein, 1918, Vol. I, p. 783): molybdous acetylacetone, formulated as $Mo(C_5H_7O_2)_2$ by Gach (*Monatsh.*, 1900, **21**, 112), and molybdyl bisacetylacetone, $MoO_2(C_5H_7O_2)_2$, first prepared by Rosenheim and Bertheim (*Z. anorg. Chem.*, 1903, **34**, 439). The composition indicated by Gach for his compound is extremely improbable, as his method of production is very similar to that employed by Rosenheim and Bertheim and in both experiments the starting material is some form of molybdenum trioxide. These two preparations have now been repeated and both products have been completely analysed and found to be identical.

In spite of the reducing action of acetylacetone on molybdenum trioxide and its hydrates, this reduction is subsidiary to the condensation occurring between unreduced trioxide and the diketone.

We have not been able to confirm the existence of molybdous acetylacetone, Gach's compound being undoubtedly molybdyl bisacetylacetone. The condensation has been shown to be a general reaction by the preparation of other molybdyl bis-β-diketones. Interaction occurs between molybdenum trioxide and such aliphatic diketones as propionylacetone, dipropionylmethane, and 3-ethylacetylacetone, and also with benzoylacetone and dibenzoylmethane containing aromatic radicals. Determinations of valency by Wardlaw's method (J., 1923, **123**, 969) show in all cases the presence of sexavalent molybdenum.

The discovery of a new hydrated molybdenyl monochloride by

Wardlaw and Wormell (J., 1924, **125**, 2370) afforded an opportunity of obtaining an acetylacetone derivative containing molybdenum in a lower state of oxidation, and by this means a hydrated *molybdenyl acetylacetone*, $MoO(C_5H_7O_2),2\frac{1}{2}H_2O$, has been realised.

Experiments made with molybdenum pentachloride and molybdenum oxysulphate, $Mo_2O_3(SO_4)_2$, showed that the tendency for quinquevalent molybdenum to yield acetylacetone derivatives is comparatively slight, although a green compound having the composition $MoO_2(C_5H_7O_2)$ was obtained by the aërial oxidation of molybdenyl acetylacetone.

EXPERIMENTAL.

Molybdyl Bisacetylacetone, $MoO_2(Me{\cdot}CO{\cdot}CH{\cdot}COMe)_2$.—On analysing the yellow substance prepared by the interaction of molybdenum trioxide and acetylacetone, Gach obtained Mo, 32·90%, corresponding with $Mo(C_5H_7O_2)_2$, which requires Mo, 32·65%; the proportions of carbon and hydrogen were not determined by him. The preparation was repeated by leaving molybdenum trioxide and acetylacetone in a closed vessel for 4 days; yellow crystals had then appeared among the trioxide, which meanwhile had undergone slight reduction to the oxide. These crystals were dissolved out by alcohol and crystallised repeatedly from this solvent. The compound, which was also soluble in chloroform, benzene, toluene, or acetone to yellow solutions, was insoluble in water, ether, or light petroleum; it melted at 175° and decomposed above 230° (Found: C, 36·8; H, 4·0; Mo, 29·1. Calc. for $C_{10}H_{14}O_6Mo$: C, 36·8; H, 4·3; Mo, 29·5%). A valency determination by Wardlaw's method showed that the molybdenum present was sexavalent and not bivalent.

The preparation was modified by heating together under reflux, in a stream of carbon dioxide, 7 g. of molybdenum trioxide, 10 g. of acetylacetone, and 20 c.c. of alcohol. The trioxide gradually became blue by reduction and the liquid assumed a dark green colour. On cooling, golden-yellow crystals separated which were picked out from co-precipitated blue oxide and recrystallised from alcohol. The green mother-liquor yielded further crops of crystals (Found: Mo, 29·3%).

Rosenheim and Bertheim (*loc. cit.*) condensed acetylacetone in alcoholic solution with either powdered molybdic oxide dihydrate, dimethyl molybdate, or oxalomolybdic acid; on boiling for a short time, yellow microscopic crystals separated. Complete analysis of this preparation gave data corresponding with $MoO_2(C_5H_7O_2)_2$.

For comparison with the compound described by Gach we prepared molybdic trioxide dihydrate by adding successively to a 15%

solution of ammonium molybdate, 30% nitric acid, and ammonium nitrate until the solution contained 10% of this salt. After 8 days a small amount of dihydrate had separated, and precipitation was hastened by scratching the sides of the containing vessel (Found : Mo, 53·2. Calc. for $MoO_3,2H_2O$: Mo, 53·3%). Six grams of this dihydrate were heated for 4 hours with 7 g. of acetylacetone in alcoholic solution. The solution, filtered from blue oxide, yielded canary-yellow crystals insoluble in water but soluble in acetone, acetylacetone, benzene, or chloroform. From these media the product crystallised in six-sided plates melting at 175° and decomposing above 230° (Found : C, 36·7 ; H, 4·0 ; Mo, 29·5%). A mixed melting-point determination with the preparation from Gach's experiment showed that the two products were identical. In both experiments a portion of the trioxide was reduced to blue oxide, which, when suspended or dissolved colloidally in the yellow alcoholic solution, rendered this liquid green. If the product is crystallised from this solution, it may become contaminated with blue Mo_3O_8, only 8% of which would be required to give a molybdenum content of 32·90% corresponding with Gach's determination of the metal. Moreover, this impurity in the molybdyl bisacetylacetone induces thermal decomposition at a temperature much lower than the melting point of the pure substance.

Molybdyl Bispropionylacetone, $MoO_2(Et{\cdot}CO{\cdot}CH{\cdot}COMe)_2$.—When molybdenum trioxide (1·4 g.) and 2·2 g. of propionylacetone were heated together on the water-bath, a viscid mass resulted which was washed with ether and dissolved in chloroform; the product was precipitated from this solution by addition of light petroleum. When crystallised from alcohol, the substance separated in small, brown, rhombic crystals melting at 185°, whereas from hot chloroform more fusible green crystals separated (m. p. 130°). The *compound* was soluble in alcohol, chloroform, benzene, or acetone, but insoluble in water, ether, or light petroleum (Found : C, 40·5 ; H, 5·3 ; Mo, 27·0. $C_{12}H_{18}O_6Mo$ requires C, 40·7 ; H, 5·1 ; Mo, 27·2%).

Molybdyl Bisdipropionylmethane, $MoO_2(Et{\cdot}CO{\cdot}CH{\cdot}COEt)_2$.—A mixture of 1·4 g. of molybdenum trioxide and 2·5 g. of dipropionylmethane was heated until the trioxide had disappeared. The brown, viscid mass was washed with ether and extracted with alcohol. The alcoholic solution gave brown, six-sided plates, m. p. 78°, which were soluble in alcohol, acetone, chloroform, benzene, or toluene (Found: C, 44·25 ; H, 5·9 ; Mo, 25·4. $C_{14}H_{22}O_6Mo$ requires C, 44·0 ; H, 5·8 ; Mo, 25·1%).

Molybdyl Bis-3-ethylacetylacetone, $MoO_2(Me{\cdot}CO{\cdot}CEt{\cdot}COMe)_2$.—On heating together molybdenum trioxide and 3-ethylacetylacetone, the mixture became brown and set to a viscid mass. Extraction as in previous examples removed a brown, crystalline solid, soluble in alcohol, acetone, chloroform, or benzene (Found: C, 43·3; H, 5·1; Mo, 25·8. $C_{14}H_{22}O_6Mo$ requires C, 44·0; H, 5·8; Mo, 25·1%).

Molybdyl Bisbenzoylacetone, $MoO_2(Ph{\cdot}CO{\cdot}CH{\cdot}COMe)_2$.—A mixture of 1·5 g. of molybdenum trioxide and 3·25 g. of benzoylacetone was warmed on the water-bath until the oxide had disappeared; the melt was then allowed to cool to a viscid mass. This, after being washed with ether, was extracted with alcohol; the extract yielded brown, rhombic crystals, m. p. 98°, soluble in acetone, chloroform, benzene, or toluene, but insoluble in water, ether, or light petroleum (Found: C, 53·8; H, 4·1; Mo, 21·3. $C_{20}H_{18}O_6Mo$ requires C, 53·3; H, 4·0; Mo, 21·3%).

Molybdyl Bisdibenzoylmethane, $MoO_2(Ph{\cdot}CO{\cdot}CH{\cdot}COPh)_2$.—On heating together 1·5 g. of molybdenum trioxide and 4·5 g. of dibenzoylmethane, a dark brown solid resulted which was washed successively with ether and alcohol, and the residue extracted with chloroform. From the cold extract a substance separated in light brown needles, m. p. 112°, soluble in alcohol, acetone, benzene, and toluene, but not in water, ether, or light petroleum (Found: C, 62·1; H, 4·3; Mo, 16·6. $C_{30}H_{22}O_6Mo$ requires C, 62·7; H, 3·8; Mo, 16·7%).

Molybdenyl Acetylacetone, $MoO(Me{\cdot}CO{\cdot}CH{\cdot}COMe),2\frac{1}{2}H_2O$.—By heating together for several hours 1·5 g. of molybdenyl chloride, $MoOCl,4H_2O$ (Wardlaw and Wormell, *loc. cit.*), and 1 g. of acetylacetone in alcoholic solution, a deep red liquid was obtained which on evaporation furnished brown, cubical crystals of hydrated *molybdenyl acetylacetone*. This product was recrystallised from alcohol and dried out of contact with air. It was soluble in water, but insoluble in anhydrous organic media. The dark red solution in alcohol or water was decolorised by dilute acids or alkalis; warm potassium ferrocyanide developed a yellowish-green fluorescence which changed to greenish-blue on cooling. The aqueous solution reduced cold silver nitrate and a valency determination indicated tervalent molybdenum. The compound decomposed indefinitely at about 150° (Found: C, 23·6; H, 4·2; Mo, 37·2; H_2O, 17·7. $C_5H_7O_3Mo,2\frac{1}{2}H_2O$ requires C, 23·4; H, 4·7; Mo, 37·5; H_2O, 17·6%). The water was estimated by heating the compound at 120° in a stream of nitrogen, the water evolved being collected in sulphuric acid.

In an endeavour to estimate the water by difference the compound was heated in the air at 120°; oxidation occurred slowly and a green residue was left. This substance, which was hygroscopic in air, decomposed at 150° and dissolved to a green solution in water, alcohol, chloroform, or benzene (Found: C, 26·3; H, 3·8; Mo, 42·7. $C_5H_7O_4Mo$ requires C, 26·4; H, 3·1; Mo, 42·3%). Accordingly these data correspond with a derivative of quinquevalent molybdenum.

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