

LETTRES À LA REDACTION

CHIMIE

The method, as used by us, was as follows:

CDU: 547.532

PREPARATION OF SOME
TRIS(DIBENZOYLMETHANATO)
COMPLEXES BY

LIGAND-SUBSTITUTION REACTION

(Приготвување на некои трис[добензоилметананато]
комплекси со реакција на замена на лигандот)

Of the chelates of β -diketones the acetylacetonates, i. e. the chelates of acetylacetonate, Hacac (2,4-pentanedione) are the best known and most widely used and, in fact, many of them are at present commercially available. On the other hand, as shown by Van Uitert *et al.* (1), β -diketones containing aromatic rings as end-groups form more stable chelates than those having aliphatic end-groups. It is, thus, thermodynamically feasible to replace acetylacetonato ligands in a metal chelate with those of a β -diketone containing two aromatic-ring end-groups, e. g. dibenzoylmethane, HDBM (1,3-diphenyl-1,3-propanedione). The reaction is further favored by the fact that the liberated acetylacetonate is sufficiently volatile and can, consequently, be conveniently removed from the reaction system. This would, of course, displace the equilibrium towards obtaining more products, so that high yields of the desired dibenzoylmethanates are expected and have indeed been obtained (2-5).

The reaction was first suggested by Wolf *et al.* (2), who prepared dibenzoylmethanates of Fe, Ru and Rh working in an ethylbenzoate solution. The liberated acetylacetonate was carried away with a stream of CO_2 . Several modifications of this procedure have since been suggested. Charles (3) worked without a solvent, melting his reaction mixture under a nitrogen atmosphere and removing the evolved acetylacetonate by simple evaporation from the system. Korpar-Čolig (4) suggested the use of xylene (which boils close to the boiling-point of acetylacetonate) as a solvent, and this method was successfully used by one of us (5) to prepare the dioxobis(dibenzoylmethanato)tungsten(VI) complex. In all cases the ligand substitution reaction has proved to be simple for execution and giving high yields of easily purified products, particularly suitable being, in our experience, the modification using xylene as a solvent.

Since for our complex investigation of the properties and application of some tris(β -diketonato) complexes in certain polymerization processes we needed large amounts of pure products, it was decided to attempt the preparation of a number of dibenzoylmethanates of trivalent metals (both non-transitions: Al, Ga, In and first-row transition metals: V, Cr, Mn, Fe, Co), starting from the corresponding acetylacetonates, all of which except, maybe, for the Ga compound, can be commercially obtained (e. g. from *Alfa Inorganics*).

All these compounds have been previously prepared by different methods and with various yields which can sometimes be very low (thus $\text{Mn}(\text{DBM})_3$ was prepared by Wood and Jones (6) with a yield less than 16%).

In a 100 ml round-bottomed flask containing 0.06 mole dibenzoylmethane, 30 ml of dry xylene, followed by 0.02 mole of the corresponding $\text{M}(\text{acac})_3$ were added. The reaction mixture was refluxed for 30 min and the liberated acetylacetonate was distilled off under reduced pressure, together with the solvent. To the almost dry residue an additional 30 ml portion of xylene was added, the reaction mixture was heated and kept at the xylene boiling-point temperature for 15-20 min and the xylene-acetylacetonate mixture was then distilled off again. To ensure an as complete reaction as possible, the procedure was repeated once again, after which petroleum ether was added to the residue, causing the precipitation of the dibenzoylmethanate. The reaction mixture was then allowed to cool in a refrigerator, filtered off, washed with petroleum ether, and the product was recrystallized from a suitable solvent. To avoid oxydation of $\text{V}(\text{DBM})_3$ to $\text{VO}(\text{DBM})_2$, the whole procedure in the case of the V(III) chelate was carried out under nitrogen atmosphere. The compounds thus obtained were sufficiently pure after one recrystallization, although for elemental analysis they were recrystallized twice. The purity and identity of the prepared compounds were checked by elemental analysis and through their infrared spectra. The results of the elemental analysis (C, H and metal were analyzed) agreed very well with the values calculated on the basis of the formula $\text{M}(\text{DBM})_3$ while the infrared spectra, some of which are discussed in a separate publication (7), unequivocally confirmed that the obtained compounds were indeed dibenzoylmethanates. The yields were always above 90% (with respect to the amount of the employed acetylacetonate), and in some cases were close to the theoretical values.

The method has thus proved to be very suitable for the preparation of tris(dibenzoylmethanato) complexes, both because the products were obtained pure and in very high yields, and because the procedure is simple and not time-consuming.

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