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REACTION OF 1,3,5-CYCLOHEPTATRIENE WITH DICARBONYL-(PENTANE-2,4-DIONATO)RHODIUM

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SUMMARY

Contrary to a published report, 1,3,5-cycloheptatriene has been shown not to give bicyclo[2.2.1]hepta-2,5-diene(pentane-2,4-dionato)rhodium on treatment with dicarbonyl(pentane-2,4-dionato)rhodium.

INTRODUCTION

A number of molecular rearrangements promoted by metal complexes have been described during the past several years[1]. Among these, the reaction of dicarbonyl-(pentane-2,4-dionato)rhodium (I) with 1,3,5-cycloheptatriene has been reported by Bonati and Wilkinson[2] to give, as a single product, bicyclo[2.2.1]hepta-2,5-diene-(pentane-2,4-dionato)rhodium (II). Our studies of this reaction, however, suggest that (II) does not arise from rearrangement of cycloheptatriene but is formed instead from bicyclo[2.2.1]heptadiene (III), which is present in small amounts in commercial samples of cycloheptatriene. The presence of 3% of (III) in samples of cycloheptatriene is readily detected by gas chromatography and this amount is sufficient to account for the apparent formation of the complex (II) in moderate yield from cycloheptatriene and (I), since a large excess of the triene was used. Furthermore, the diene is irreversibly consumed when such samples of cycloheptatriene are treated with (I) under conditions in which the complex (II) is formed. Careful purification of cycloheptatriene employing a spinning band column gives a product free of the diene (III). Such samples do not lead to the formation of complex (II), even when the reactants are heated in refluxing toluene or in a sealed tube at 140° for prolonged periods of time.

EXPERIMENTAL

Except for the preparation of $Rh_2(CO)_4Cl_2$[3], all reactions were carried out under nitrogen. All liquid reagents were distilled under nitrogen immediately before use.

Dicarbonyl(pentane-2,4-dionato)rhodium, (I)

Bonati and Wilkinson[2] used petroleum ether (b.p. 65–70°) as the solvent for

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preparation of $(C_5H_7O_2)Rh(CO)_2$, but by using a higher boiling solvent the reaction period needed for preparation of this substance may be greatly shortened. In a typical reaction, tetracarbonyldichlorodirhodium[3] (0.85 g), acetylacetone (2 ml), and barium carbonate (2.9 g) in decalin (25 ml) were heated at 110–120° under nitrogen for 13 h with stirring. Thin layer chromatography (silica gel, solvent: petroleum ether, b.p. 65–70°) indicated that all of the $Rh_2(CO)_4Cl_2$ had been consumed. The filtered solution, on cooling in an ice bath, yielded red-green dichroic needles, which were washed with cold methanol. Yield, 0.94 g. By vacuum-concentration of the mother liquor, an additional 62 mg of the compound was obtained. The combined product was recrystallized from petroleum ether (b.p. 65–70°). The melting point (153°) and IR and NMR spectra of the compound were identical with dicarbonyl(pentane-2,4-dionato)-rhodium (I) obtained by refluxing the same starting materials in petroleum ether (b.p. 65–70°) for 1 week.

Bicyclo[2.2.1]*hepta-2,5-diene(pentane-2,4-dionato)rhodium,(II), from cycloheptatriene*

Dicarbonyl(pentane-2,4-dionato)rhodium (0.30 g, 1.2 mmoles) and cycloheptatriene (Shell Chemical Company, 1.5 ml, 24 mmoles) in petroleum ether (b.p. 65–70°; 30 ml) were refluxed for 2 days, according to the preparation described by Bonati and Wilkinson[2]. After removal of the solvent, the residue was chromatographed on a silica gel column and eluted with methylene chloride. The product (0.16 g; m.p., after recrystallization from petroleum ether, 170–173°) was obtained in 47% yield, and the unreacted pentanedionate (I) was recovered quantitatively. The mixed melting point of the yellow product with the compound prepared from norbornadiene, following the procedure of Bonati and Wilkinson[2], was 177–178.5°. The IR and NMR spectra of the two products were identical.

By gas chromatography using an SE-30 column, the cycloheptatriene used for the previous reaction was found to contain *ca.* 3% norbornadiene (as well as some toluene). Refluxing of cycloheptatriene in petroleum ether (b.p. 65–70°) for 2 days did not change the concentration of norbornadiene. However, when cycloheptatriene and (I) (same amounts as above) were refluxed in petroleum ether, the norbornadiene originally present in the cycloheptatriene was removed from the solvent after *ca.* 11 h. (Norbornadiene)rhodium pentanedionate (II) and unreacted (I) were isolated from the reaction mixture by chromatography on silica gel.

Fractional distillation of the cycloheptatriene using a spinning band column (Nester–Faust, 24 inch, 28 theoretical plates) removed the norbornadiene impurity, as indicated by gas chromatography. Refluxing this purified cycloheptatriene (1.5 ml) with (I) (283 mg) under the same conditions as before produced no (II), as shown by thin layer chromatography and column chromatography (alumina) of the reaction mixture. Unreacted (I) was recovered.

The reaction was also carried out at a higher temperature in boiling toluene as the solvent instead of petroleum ether. Although (I), when refluxed in toluene, leaves a metallic mirror on the walls of the flask, the decomposition is slow, and after 18 h only an insignificant amount of the compound was destroyed. (I) (0.14 g) and norbornadiene-free cycloheptatriene (1.5 ml) in toluene (25 ml) were refluxed, and aliquots were removed after 20 and 60 h. No norbornadiene complex (II) could be detected by thin layer chromatography. Although the reaction mixture had blackened considerably, indicating serious decomposition, (I) was still present after 60 h.

A further reaction was carried out in a sealed tube. The reaction containing 1.2 ml of purified cycloheptatriene and 0.20 g of (I) in 15 ml of benzene were placed in a carius tube, degassed, and the tube was sealed *in vacuo*. The tube was heated for 14 h at 140°. No norbornadiene complex (II) could be detected by thin layer chromatography.

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