

HOMOGENEOUS DEHYDROGENATION REACTIONS CATALYZED BY COMPLEXES OF THE PLATINUM GROUP

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Whilst the homogeneous catalysis of hydrogenation reactions by transition metal complexes has been studied extensively (1), the reverse process, dehydrogenation, has to our knowledge been investigated only with heterogeneous catalysts.

We wish to report the homogeneous catalysis of dehydrogenation reactions by $\text{RhCl}(\text{PPh}_3)_3$ (1), $\text{RhCl}_3(\text{AsPh}_3)_3$ (2), $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (3) and $\text{RuCl}_2(\text{PPh}_3)_3$ (4) at 225-265°.

The method is illustrated by the following example: A mixture of 2.5g of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene and 23mg of 3 was heated at 225°. The reaction mixture was analyzed (on a 2m x 6.4mm vpc column packed with 20% Carbowax 20 M on Chrom. P at 205°) after 1, 2, 4, 6, 9, 13, 18, 22, 27, 32, 37 and 60hr, and found to contain 2, 4, 8, 14, 17, 26, 33, 40, 46, 53, 56 and 60% of 5H-dibenzo[a,d]cycloheptene, respectively. The sample analyzed after 60hr did not contain any more starting material. The dehydrogenated hydrocarbon (mp 132°) was isolated from the reaction mixture by column chromatography on alumina.

The results of some dehydrogenation experiments using the homogeneous catalysts 1, 2, 3 or 4, and for comparison, 10% Pd/C (5), are summarized in Table I.

TABLE I. Catalytic Dehydrogenation Reactions

| No. | Starting compound | Reaction | | Products (catalyst and yield, %). |
|-----|---|----------|----------|---|
| | | Temp, °C | Time, hr | |
| 1 | Bibenzyl ^(a) | 260 | 46 | <u>trans</u> -stilbene(<u>1</u> , 37; <u>2</u> , 28; <u>4</u> , 5; <u>5</u> , 32) |
| 2 | 9,10-Dihydroanthracene | 225 | 15 | anthracene(<u>1</u> , 97; <u>2</u> , 47; <u>4</u> , 58; <u>5</u> , 45) 1,2,3,4-tetrahydroanthracene(<u>1</u> , <u>2</u> , <u>4</u> , 0; <u>5</u> , 42) |
| 3 | 10,11-Dihydro-5H-dibenzo[a,d]cycloheptene (<u>6</u>) | 225 | 13 | 5H-dibenzo[a,d]cycloheptene(<u>1</u> , 25; <u>2</u> , 14; <u>3</u> , 26; <u>4</u> , 11; <u>5</u> , 29) |
| 4 | 10,11-Dihydro-5H-dibenzo[a,d]cyclohepten-5-one | 225 | 82 | 5H-dibenzo[a,d]cyclohepten-5-one (<u>1</u> , 42; <u>3</u> , 4; <u>4</u> , 9; <u>5</u> , 54) 5H-dibenzo[a,d]cycloheptene(<u>1</u> , <u>3</u> , <u>4</u> , 0; <u>5</u> , 5) 10,11-dihydro-5H-dibenzo[a,d]cycloheptene (<u>1</u> , <u>3</u> , <u>4</u> , 0; <u>5</u> , 1) |
| 5 | 3-Bromo-10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one | 225 | 10 | 3-bromo-5H-dibenzo[a,d]cyclohepten-5-one (<u>1</u> , 5; <u>4</u> , 23; <u>5</u> , 0) 10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one (<u>1</u> , 40; <u>4</u> , 12; <u>5</u> , 1) 5H-dibenzo[a,d]cyclohepten-5-one (<u>1</u> , 13; <u>4</u> , 6; <u>5</u> , traces) |
| 6 | 5,6,11,12-Tetrahydrobenzo[a,e]cyclooctene (<u>7</u>) ^(a) | 265 | 15 | 5,6-dihydrodibenzo[a,e]cyclooctene (<u>1</u> , 17; <u>4</u> , 2; <u>5</u> , 2) dibenzo[a,e]cyclooctene(<u>1</u> , 1; <u>4</u> , <u>5</u> , 0) |
| 7 | 1,2,3,4,7,12-Hexahydrobenz[a]anthracene (<u>8</u>) ^(b) | 225 | 12 | 1,2,3,4-tetrahydrobenz[a]anthracene (<u>1</u> , 17; <u>3</u> , 0; <u>4</u> , 45; <u>5</u> , 21) benz[a]anthracene(<u>1</u> , 75; <u>3</u> , 92; <u>4</u> , 42; <u>5</u> , 58) |

(a) Experiments with 5 give significant amounts of degradation products. (b) The maximum accumulation of the tetrahydro-compound (52-63%) was reached by 1, 3, 4 and 5 after 2, 4, 2.5 and 1.5hr, respectively; complete transformation to benz[a]anthracene was obtained after 15, 21, 12 and 16hr, respectively. Experiments to carry out stepwise dehydrogenations were unsuccessful.

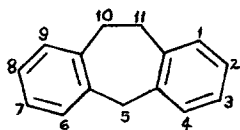
The rates of the homogeneous dehydrogenation reactions are generally of the same order as those of the heterogeneous catalyses at the same temperatures. E.g., the initial rates of formation of 5H-dibenzo[a,d]cycloheptene by 1, 2, 3, 4 and 5 are 2.3, 2.0, 3.0, 2.0 and 3.7% hr⁻¹, respectively. The homogeneous reactions are, however, more selective than the heterogeneous ones. While, e.g., the *meso* hydrogen atoms of 9,10-dihydroanthracene are transferred by Pd/C (5) to the external ring to give 1,2,3,4-tetrahydroanthracene (2) (up to 50% after 4.5 hr at 225°), the rhodium (III) and ruthenium (II) complexes (2 and 4) lead to almost quantitative evolution of hydrogen gas, anthracene being the sole product. The rhodium (I) catalyst causes hydrogen transfer to a limited extent (up to 9% after 7.5hr) (3). 10,11-Dihydro-5H-dibenzo[a,d]cyclohepten-5-one is smoothly converted to the trienone by the homogeneous catalysts studied; palladium causes the formation of additional products (see Table I).

Unlike Pd/C (5), the complexes 1 and 4 dehydrogenate 3-bromo-10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one. This reaction is accompanied by some dehalogenation.

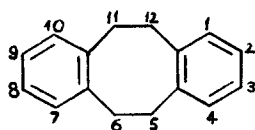
The dehydrogenation reactions proceed in the same manner in argon or in air; the rhodium (I)-catalyzed reactions are, however, faster in the presence of oxygen (initial rates of removal of hydrogen from 9,10-dihydroanthracene are 8.0 and 2.2% hr⁻¹ in the presence and absence of oxygen, respectively), probably due to the oxygen promoted enhanced dissociation of RhCl(PPh₃)₃ to the reactive RhCl(PPh₃)₂ (4-6).

The occasional formation of hydrido-metal complexes during the dehydrogenation with rhodium and ruthenium catalysts (proven by ir spectroscopy) might suggest a "reversal of hydrogenation" mechanism. A stable complex of the formula [HRuCl(PPh₃)_n] [Calcd C, 54.2; H, 4.0; Cl, 8.9; P, 7.8. Found: C, 54.2; H, 4.3; Cl, 9.5; P, 7.7; ir (Nujol)(Ru-H) 1955cm⁻¹] was isolated when RuCl₂(PPh₃)₃ (4) was treated with 10,11-dihydro-5H-dibenzo[a,d]cycloheptene at 140° (both in the presence and absence of mesitylene). The complex dissociates into the monomer when dissolved in benzene. However, as 9,10-dihydroanthracene failed to give an isolable hydrido-complex with 4, we assume that [HRuCl(PPh₃)_n] is a secondary product and not a reaction intermediate.

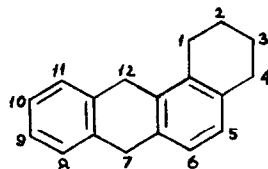
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