Tetrahedron Letters No.38, pp. 3665-3668, 1967. Pergamon Press Ltd. Printed in Great Britain.

OXIDATION OF ALKYLBENZENES, CATALYZED BY CHLOROTRIS(TRIPHENYLPHOSPHINE)RHODIUM

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(Received in UK 26 June 1967)

Recent studies of the catalytic activity of chlorotris(triphenylphosphine)rhodium, $RhCl(PPh_3)_3$, have given some unexpected results. It has been shown in our laboratory that this organometallic compound causes decarbonylation of various carbonyl compounds and desulfonylation of aromatic sulfonyl chlorides (1-3). Equally, it is capable of extracting nitrogen from suitable organic compounds containing the N=N linkage (4). Further examples showing the activity of this rhodium complex as hydrogenation catalyst are given in recent papers (5-8).

We wish to report the homogeneous catalysis of the α-oxidation of alkylbenzenes by the rhodium compound. When a mixture of 20 g. of ethylbenzene and 100 mg. of the rhodium complex was treated for 5 hrs. at 130° with a current of air (undried, 1 liter per 3 mins.), the only product which was isolated by distillation was acetophenone. It was formed in at least 90% yield, calculated on the amount of ethylbenzene that entered into reaction. The conversion under these conditions was 17-23%, and the ethylbenzene, that had not reacted, could be recovered practically without loss.

The results of our experiments are summarized in the following Table. In experiments 1-5 the yields exceeded 90%.

TABLE I

Oxidation of Hydrocarbons in the Presence of $RhCl(PPh_3)_3$

(20 g. hydrocarbon; 100 mg. rhodium compound; reaction time 5 hrs.)

No.	Hydrocarbon	Temp. °C	Product	Conversion (%)	Hydroperoxide (%) in the absence of the catalyst
1	acenaphthene	115	acenaphthenone	9-10	traces
2	ethylbenzene	130	acetophenone	17-23	1-4.5
3	fluorene	130	fluorenone	10	3-4
4	n-propylbenzene	130	propiophenone	17	2
5	tetralin	55	α-tetralone	48-60	1-2
6	p-xylene	120	p-tolualdehyde p-toluic acid	2.8-3.4 0.9	traces

Toluene and 2-methylnaphthabene are not oxidized under these conditions. p-xylene (No. 6) is oxidized rather slowly to p-tolualdehyde and p-toluic acid (4% after 5 hrs.) which are contaminated with various oxidation products to an extent of 0.5%. In that experiment no terephthaldehyde or terephthalic acid was formed.

The temperatures indicated in the Table may not be the optimum ones; they were chosen so as to minimize secondary reactions. At 150°, e.g., propylbenzene yields some benzoic acid, and the oxidation product of acenaphthene contains five constituents (by gas chromatography).

Parallel oxidation experiments in the absence of the rhodium complex did not give any ketonic products (infrared spectrum); small amounts of hydroperoxides were formed, which did not appear in the presence of the catalyst. The quantities of these hydroperoxides are also indicated in the Table.

The following observations, made in the case of ethylbenzene, will characterize the method more fully: If pure oxygen is used instead of air, the conversion rises under the same conditions from 17-23 to 33%. After 1, 2, 3, 4, 5 and 6 hrs., the conversion is 6, 12, 18, 26, 33 and 40% respectively.

Some experiments were carried out with other potential catalysts: palladous chloride, rhodium trichloride (trihydrate), chlorocarbonylbis(triphenylphosphine)rhodium, chlorocarbonylbis(triphenylphosphine) iridium, and the new compounds trichlorotris(triphenylarsine)rhodium, $RhCl_3(AsPh_3)_3$, [m.p. 219-220°, Calcd.: C, 57.5; H, 4.0; Cl, 9.5. Found: C, 57.2; H, 4.1; Cl, 9.8], and trichlorotris(triphenylstibine) rhodium, $RhCl_3(SbPh_3)_3$, [m.p. 155-156°, Calcd.: C, 51.2; H, 3.6; Cl, 8.4. Found: C, 51.1; H, 3.6; Cl, 8.7]. With the exception of chlorocarbonylbis(triphenylphosphine)rhodium, which gave a conversion of 7%, these compounds only gave 4% conversion of ethylbenzene to acetophenone, that is, the same amount which is formed as hydroperoxide without any added catalyst. We assume, therefore, tentatively, that these compounds only catalyze the transformation of the hydroperoxide formed into acetophenone, whilst chlorotris(triphenylphosphine)rhodium and to a lower extent the chlorocarbonyl complex catalyse both the formation and the transformation of the hydroperoxides.

Two surprising facts emerge from these experiments: firstly, the arsenic and antimony containing rhodium complexes are inert in the oxidation, whilst they have been shown to be active as decarbonylation catalysts (9). Secondly, chlorocarbonylbis(triphenylphosphine)iridium is not an active oxidation catalyst, although its transformation to the oxygen complex, $O_2IrCl(CO)(PPh_3)_2$, is well known (10).

We have succeeded in isolating both at room temperature and at 130°, an oxido-rhodium complex $(O_2RhClPPh_3)_n$ [Calcd.: C, 49.9; H, 3.5; Cl, 8.2. Found: C, 49.8; H, 3.6; Cl, 8.2]; it shows in the infrared spectrum the -O-O- absorption at 875 cm^{-1} (Nujol) (11).

The study of the structures of this oxido-complex and of other rhodium compounds formed during the oxidation process is now in hand.

Acknowledgement. The authors are indebted to the Authority for Research and Development of the Hebrew University for partial support of this investigation.

REFERENCES

(1) J. Blum, Tetrahedron Letters, 1605, 3041 (1966).

(2) J. Blum, E. Oppenheimer and E. D. Bergmann, J. Am. Chem. Soc., **89**, 2338 (1967).

(3) J. Tsuji and K. Ohno, Tetrahedron Letters, 4713 (1966).

(4) J. Blum, Israel J. Chem. **4**, 15 p (1966).

(5) J-F. Biellmann and H. Liesenfelt, Compt. Rend., **263**, 251 (1966); Bull. Soc. Chim. France, 4029 (1966).

(6) A. J. Birch and K. A. M. Walker, J. Chem. Soc., C, 1894 (1966).

(7) D. N. Lawson, A. Osborn, J. F. Young and G. Wilkinson, J. Chem. Soc., A, 1711 (1966).

(8) F. H. Jardin and G. Wilkinson, J. Chem. Soc., C, 270 (1967).

(9) Unpublished results.

(10) L. Vaska, Science, 140, 809 (1963).

(11) Cf. J. T. Mague and G. Wilkinson, J. Chem. Soc., A, 1736 (1966).