185. *Palladous Chloride as a Dehydrogenating Agent.*

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Palladous chloride can dehydrogenate hydroaromatic and reduced heterocyclic compounds, and examples are given in which it oxidises to carboxyl a methyl group attached to an aromatic ring.

The steady growth of the chemistry of hydroaromatic compounds makes any method for their dehydrogenation worthy of investigation, more particularly if the reagents studied are efficacious at less drastic temperatures than are required in the customary oxidations by selenium and sulphur or in catalytic dehydrogenations.

Several years ago Gulland and Macrae (J., 1932, 2231) observed that a boiling aqueous solution of palladous chloride completely oxidised piperidine to pyridine, and that the weight of the resulting palladium was a measure of the extent of oxidation. It was therefore decided to investigate further this dehydrogenating action on other nitrogenous and alicylic compounds.

The results, summarised in tabular form below, show that palladous chloride is unlikely to find general application as a dehydrogenating agent, but that in some cases it may perhaps prove more acceptable than selenium, especially where small quantities of material only are available.

In addition to its dehydrogenating action on cyclic compounds, palladous chloride exhibited the unexpected property of oxidising to carboxyl a methyl group attached to the benzene ring, the examples being the conversion of toluene and *o*-cresol into benzoic and salicylic acids respectively.

This investigation is concluded.

EXPERIMENTAL.

In order to illustrate the normal procedure, the experiment marked † in the summary of results is described below in greater detail. A mixture of tetrahydronaphthalene (0·099 g.) and 2%

Summary of Results.

Substance.	Wt., mg.	2% $PdCl_2$ soln., c.c.	Time of heating, hrs.	Oxidation, % of theor.*	Product isolated.	Remarks.
Tetralin	103	40	9	28	Naphthalene (picrate)	—
„	104	20	10	35		Benzene added
„ †	99	25	33	98		—
Decalin	44	25	20	17	Nil	—
„	48	25	20	6	Nil	—
„	50	20	7	27	Naphthalene (odour only)	At 200° in sealed tube
*cyclo*Hexane	30	15	15	15	Nil	Very stable
*cyclo*Hexanol	50	20	10	35	Phenol	—
„	26	10	12	80		Confirmed by Folin-Denis estimation (*J. Biol. Chem.*, 1915, **22**, 305)
Toluene	403	170	20	28	Benzoic acid	—
„	5 c.c.	100	20	—		Large excess of toluene
Dibenzyl	105	10	12	v. slight	Nil	—
o-Cresol	170	30	16	26	Salicylaldehyde (2 : 4-dinitrophenylhydrazone). Salicylic acid	Ratio cresol used/Pd deposited = 1·29
„	953	350	30	28		p_H adjusted repeatedly. Ratio cresol used/Pd deposited = 1·19 (calc., 2·97)
2-Methyl*cyclo*hexanol	276	70	18	26	Salicylic acid	—
Methyl ethyl ketone	92	15	15	10	Nil	Decolorisation of $PdCl_2$ solution indicating formation of complex
Tetrahydrocarbazole	118	30	7	91	Carbazole	—
Tetrahydroquinoline	328	50	14	102	Quinoline (picrate)	—
„	222	45	12	66		Additional HCl present
„	134	25	15	110		—
Tetrahydro*iso*quinoline hydrochloride	208	30	15	95	*iso*Quinoline (hydroferrocyanide; Cumming, J., 1922, **121**, 1287)	—
	234	30	15	50		Additional HCl present
	289	35	22	88		p_H adjusted at 12 hours
	338	50	16	130		p_H adjusted at 5 and 8 hours
	509	70	15	119		p_H adjusted at 6 and 12 hours
2-Methyltetrahydro*iso*quinoline hydrochloride	126	25	19	114	2-Methyl-1 : 2-dihydro*iso*quinoline reineckate	—
	155	20	14	115		p_H adjusted at 10 hours
	228	50	12	105		p_H adjusted at 9 hours
	246	50	12	91		No p_H adjustment
Stilbazole	99	10	2	Nil	Nil	Yellow, crystalline complex salt deposited
Cholesterol	1000	100	20	—	—	Oxidation very slow. Chromatograph of products in ultra-violet light resembles that after Se oxidation (Diels and Rickert, *Ber.*, 1935, **68**, 267)

* The figures in this column are calculated from the weight of palladium deposited,

aqueous palladous chloride solution (excess, actually 25 c.c.) containing the lowest possible concentration of hydrochloric acid consistent with retention of the palladous chloride in solution, was boiled under reflux for 33 hours. The precipitated palladium (0·1568 g. when dried) was collected, and both precipitate and filtrate were extracted thoroughly with benzene. The benzene was dried and evaporated, and the residue was dissolved in a little alcohol and mixed with alcoholic picric acid. Crystalline naphthalene picrate separated, m. p. 149°, not depressed by an authentic specimen.

The actual method of separation of the organic from the inorganic products of reaction varied in different cases. Sometimes extraction with organic solvents was used as described above; in other cases, notably those of the basic nitrogenous compounds, the palladochlorides were decomposed by excess of alkali, and the bases volatilised in steam.

It will be observed in the table that certain of the oxidations do not proceed so smoothly or so completely as that just described. The reasons for these incomplete oxidations are not entirely clear, but several factors seem to be in operation. In the first place successive oxidations under apparently similar conditions do not always proceed to the same extent, as is shown by the two experiments with *cyclo*hexanol.

Secondly, some oxidations come to a standstill while the mixture still contains considerable quantities of unchanged reactants. There are at least two reasons for such incomplete oxidation, which are discussed below. One is the presence of too high a concentration of hydrogen chloride, either in the initial solution of palladous chloride (experiments with tetrahydroquinoline and tetrahydro*iso*quinoline) or produced as a result of the oxidation. Some reactions are more easily inhibited than others by this acidity, and in order to bring these to completion the hydrogen-ion concentration was adjusted to be just acid to Congo-red by the addition of small quantities of dilute sodium hydroxide solution at intervals during the reaction. Such adjustments must be done carefully, because in absence of sufficient hydrogen chloride palladous oxide, formed by hydrolysis, is precipitated and subsequently weighed with the palladium, thus giving rise to yields of apparently over 100%. Such hydrolysis became very marked when an attempt was made to control the acidity by additions of an excess of calcium carbonate to the mixture.

The other cause of incomplete oxidation is simply a cessation of oxidation after a definite percentage of material has been oxidised, irrespective of the concentration of acid, its neutralisation, the concentration of reactants, and the duration of heating. An example of this effect is found in the experiments with *o*-cresol, in which unchanged palladous chloride and *o*-cresol were recovered from the mixtures. The phenomenon finds a parallel in the peak efficiency at 30% recorded by Stiller and Rosenheim (J., 1938, 353) in the oxidation of cholestanone to cholestane-2 : 3-dione by selenium dioxide, where a large excess of the oxidant remained and unchanged cholestanone could be recovered.

Unsuccessful efforts were made to increase the rates of oxidation of substances which are sparingly soluble in water by the addition of organic solvents to the oxidation mixture. Alcohol is oxidised by palladous chloride, acetone and pyridine form non-reducible complexes with it, and benzene failed to improve the rate of oxidation of tetralin. Some attempts were made to use dry organic solvents in the case of such water-insoluble substances. Palladous chloride is not readily soluble in such liquids, but solutions in boiling phenol and nitrobenzene, although very dilute, might be used and have the advantage of boiling at high temperatures. A boiling ethyl benzoate solution of palladous chloride deposited the metal, but a solution in ethyl acetate (0·68 g. of palladous chloride in 100 g. of solvent) was more satisfactory, although the results were not superior to those obtained with an aqueous solution.

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