

Decarbonylation of Sugars by Chlorotris(triphenylphosphine)rhodium

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Unprotected aldose sugars are smoothly decarbonylated by 1 equiv. of chlorotris(triphenylphosphine)rhodium in *N*-methylpyrrolidin-2-one at 130 °C to give the next lower alditol and carbonylchlorobis(triphenylphosphine)rhodium; ketose sugars undergo more complex dehydration-decarbonylation reactions.

As part of a new, long-range study designed to explore routes to metal-catalysed biomass conversion, we were led to examine the decarbonylation of sugars. Reactions of this type appear to have synthetic utility in the carbohydrate field, but have been demonstrated only rarely.¹ In particular, while chlorotris(triphenylphosphine)rhodium and related compounds are well known aldehyde decarbonylation agents,² the only documented reports of their use with carbohydrates involve protected sugars.³ We attribute this to (a) the difficulty of finding a suitable solvent for both free sugars and metal complexes, and (b) the masking of the aldehyde functionality in free sugars as a hemiacetal (Scheme 1). For example, the equilibrium free aldehyde content of aqueous glucose at room temperature is only 0.002%.⁴

We have nevertheless found that it is possible to decarbonylate smoothly all aldose sugars examined with chlorotris(triphenylphosphine)rhodium⁵ in *N*-methylpyrrolidin-2-one (NMP) at 130 °C (Table 1). No significant side-products or decomposition are normally detected and the stereochemistry of the sugar is, as expected,⁶ rigorously maintained. The reaction rates appear to be qualitatively correlated with the percentage of free aldehyde in solution, if we assume that these parallel those known for aqueous solution.⁴ Although initial attempts to make the decarbonylation catalytic^{2c} have not yet proved successful, the rhodium can be recycled.⁷ These results constitute a new method for degrading sugars by a single carbon atom and complement existing procedures⁸ by yielding the next lower alditol instead of the next lower aldose.

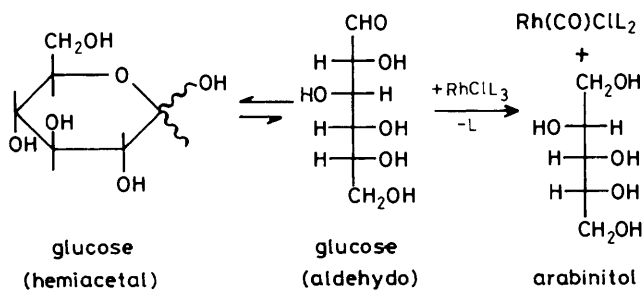
An example of the potential utility of this reaction is provided by the one-step conversion of commercial 2-deoxyribose into 1-deoxyerythritol, for which the best literature preparation involves seven steps from glucose.⁹

Since chlorotris(triphenylphosphine)rhodium has been reported to effect decarbonylation of activated ketone functionalities,¹⁰ the reaction of ketose sugars has also been examined. Surprisingly, fructose yields furfuryl alcohol as the major product (130 °C, 2 h, 79%), while 1,3-dihydroxyacetone reacts with an excess of reagent to give 1.8–1.9 equiv. of

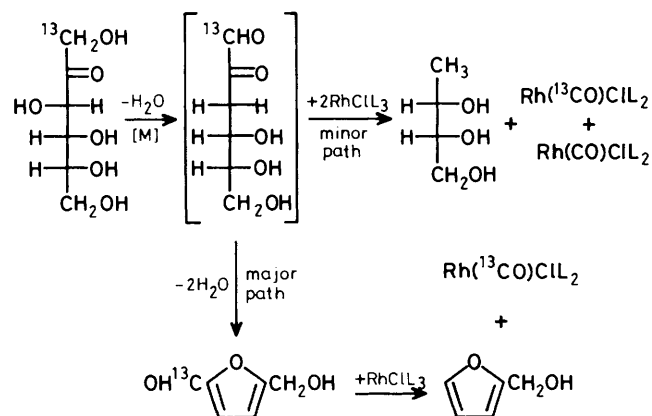
Table 1. Decarbonylation of aldose sugars by RhCl(PPh₃)₃.^a

Aldose	Time (h)	Product ^b	Yield(%) ^c
D-glycero-D-gulo-Heptose	3.5	Glucitol	88
Glucose	5.0	Arabinitol	88
Arabinose	2.0	Erythritol	84
2-Deoxyribose	0.5	1-Deoxyerythritol	90
Glyceraldehyde	0.5	Ethylene glycol	95
Glycolaldehyde ^d	0.3	Methanol	83

^a Typical reaction conditions: RhCl(PPh₃)₃ (150 μmol), sugar (150 μmol), NMP (5 ml), 130 °C, under nitrogen. ^b Identified by g.l.c., g.l.c.-mass spectrometry, and/or ¹H n.m.r. ^c Determined by g.l.c. after silylation of samples with trimethylsilylimidazole/pyridine. ^d Dimethylacetamide as solvent.



Scheme 1. Glucose equilibria and decarboxylation.



Scheme 2. Proposed mechanism for fructose decarboxylation.

carbonylchlorobis(triphenylphosphine)rhodium and *ca.* 0.9 equivalents of methane (8 h). While these ketose decarboxylation products could be explained by mechanisms that begin with transfer of the ketose carbonyl group to the rhodium, treatment of [1-¹³C]fructose with chlorotris(triphenylphosphine)rhodium yields Rh(¹³CO)Cl(PPh₃)₂ and unlabeled furfuryl alcohol. A suggested explanation for this result is given in Scheme 2. The first step consists of a rhodium(I)-assisted dehydration of fructose to 5-hydroxymethylfurfural.[†] This

[†] Dehydration of fructose to 5-hydroxymethylfurfural is well known.¹¹ In the present case, however, Rh^I catalysis must be involved since thermolysis of fructose alone in NMP at 130 °C for 3 h gave only *ca.* 10% conversion, into unidentified products. In support of the possibility of metal catalysis, we find that the Pd^{II} complex Pd(MeCN)₂Cl₂ (0.2 equiv.) is an efficient catalyst for the conversion of fructose into 5-hydroxymethylfurfural (2 h, 80 °C).

¹³C-labelled aldehyde would then be readily decarbonylated to give the observed products. Further evidence for the proposed α-oxo aldehyde intermediate is provided by the formation of 1-deoxyerythritol (*ca.* 5%), derivable from double decarbonylation of the furfural precursor. In the case of 1,3-dihydroxyacetone, dehydration would yield pyruvaldehyde (MeCOCHO), which in turn would be readily doubly decarbonylated to give methane.

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