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Transformation of organic compounds in the presence of metal complexes

VI *. Reactions of cyclic acetals with alcohols in the presence of $RuCl_2(PPh_3)_2$

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Abstract

In the presence of $RuCl_2(PPh_3)_2$ 1,3-dioxolanes and 1,3-dioxanes react with alcohols R^1R^2CHOH ($R^1 = R^2$ = alkyl or H) to give 2-R^1,R^2-1,3-dioxolanes and 2-R^1,R^2-1,3-dioxanes, respectively, with practically 100% selectivity. This paper discusses the reaction route of the transacetalization and the role of the catalyst.

Introduction

A number of general works [1–3] report in detail on the theoretically and practically important chemistry of cyclic acetals (1,3-dioxacycloalkanes). Since these compounds can be prepared via the acid-catalyzed reactions of the corresponding diols and oxo compounds, much information is to be found in the literature on the mechanism of formation of acetals and on transacetalization (the transformation of 1,3-dioxacycloalkanes with alcohols and carbonyl compounds). These data are summarized in ref. 4.

We have already made a number of new observations [5,6] on the transformation of 1,3-dioxacycloalkanes on transition metals. These findings, together with the known tendency of 1,3-dioxacycloalkanes to undergo complex formation with metal ions (e.g. ref. 7 and 8), led us to initiate a study of the transformations of the compounds in question on the action of certain transition metal complexes.

As the first research task, we have chosen the reactions between cyclic acetals and alcohols, with the well-known complex $RuCl_2\mathbf{P}_3$ ($\mathbf{P} = PPh_3$) as catalyst [9–12]. This research topic has hardly been described in the literature; according to a Japanese

* For Part V see ref. 22.

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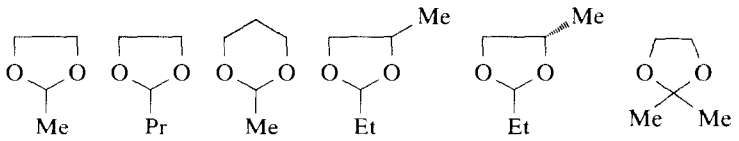
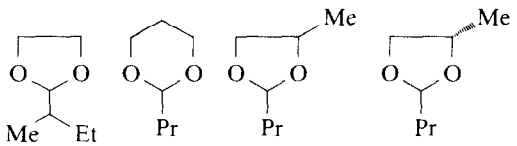
patent, acetal formation is catalyzed by Rh complexes [13], while the reactions of alcohols and carbonyl compounds are catalyzed by $RuCl_2P_3$ [14–17].

Results and discussion

The 5- and 6-membered cyclic acetals investigated are depicted below.



(1) (2) (3) (4) (5) (6)



(7) (8) (9) (10)

Some characteristic experimental results are listed in Tables 1 and 2. As eqs. 1–4 show, the use of primary and secondary alcohols in excess results in transacetaliza-

Table 1

Reaction of 1,3-dioxacycloalkanes (**1**, **2**, **3**, **6**) with alcohols [a] in the presence of $RuCl_2P_3$

Entry	Comp. (A)	Alcohol (B)	Time (h)	Conversion (%)	Product [b]
1	**1**	BuOH	1	55	**2**
2	**1**	BuOH	2.5	80	**2**
3	**1**	BuOH	5	85	**2**
4	**2**	EtOH	5	90	**1**
5	**1**	BuOH [c]	5	16	**2**
6	**3**	BuOH	5	83	**8**
7	**1**	2-Butanol	2.5	60	**7**
8	**1**	2-Butanol	5	77	**7**
9	**6**	BuOH	5	80	**2**
10	**6**	2-Butanol	5	83	**7**

[a] Experimental conditions: see Experimental. [b] Selectivities are ca 100%. [c] A/B = 1/1.

Table 2

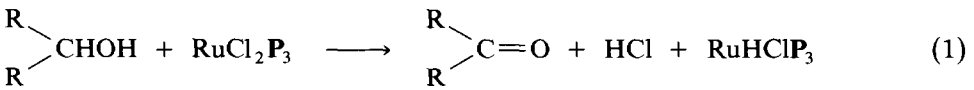
Reaction of 1,3-dioxolanes (**4** + **5**) with 1-butanol [a] in the presence of $RuCl_2P_3$

Entry	Time (h)	Conversion (%)			Product composition	
		4 + **5**	**4**	**5**	**4**/**5**	**9**/**10**
1	0	0	0	0	70/30	0/ 0
2	1	37	45	19	61/39	67/33
3	2	52	63	28	55/45	68/32
4	3	60	72	33	50/50	66/34
5	5	75	85	52	42/58	66/34

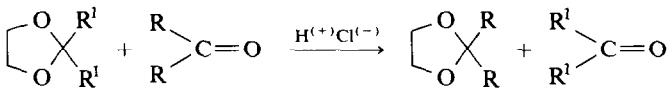
[a] Experimental conditions: see Experimental.

tion with high selectivity. Preliminary experiments had demonstrated that no reaction occurs either with the alcohol or with the corresponding carbonyl compound in the absence of the catalyst. With carbonyl compounds, no reaction takes place even in the presence of the catalyst. Under the given experimental conditions, the quantity of catalyst (5, 10 or 15 mg) had no essential effect on the conversion. On transacetalization, the carbonyl compounds formed from 1,3-dioxacycloalkanes are mainly hydrogenated to the corresponding alcohols (2–5% of the open-chain acetals are also formed).

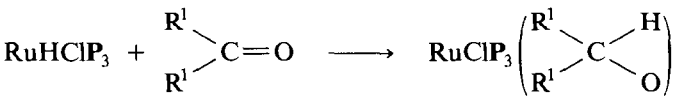
The transformations of 1,3-dioxacycloalkanes with alcohols in the presence of $RuCl_2P_3$ are interpreted according to eqs. 1–4.



(1)



(2)



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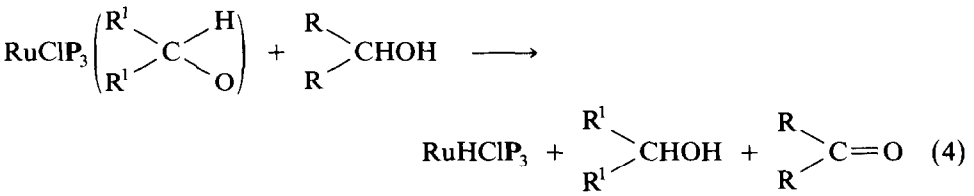


(4)

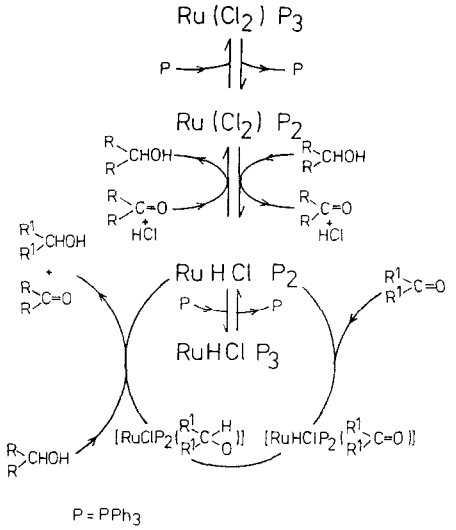
($P = PPh_3$)

$RuCl_2P_3$ reacts with alcohols to yield a catalytically active species $RuHClP_3$, which is required for subsequent reaction [9,10], together with a carbonyl compound and the hydrochloric acid whose catalytic effect leads to transacetalization (eqs. 1 and 2). A transfer hydrogenation catalyzed by $RuHClP_3$ takes place between the carbonyl compound formed in the latter reaction and the excess starting alcohol (eqs. 3 and 4). Thus, the role of $RuCl_2P_3$ is to provide a continuous supply of the carbonyl compound and the catalyst (HCl) for the transacetalization of the cyclic acetal. Scheme 1 shows the formation, the reaction and the regeneration of the catalytically active complex necessary for the process.

The experimental data in Table 2 reveal that transacetalization was not accompanied by epimerization. This is illustrated by the following reaction route. The reaction is directed by thermodynamic control. Consequently, an isomeric mixture is formed whose *cis–trans* composition is identical with that of the starting equilibrium mixture [18] (Scheme 2).

The driving force of the process is the ability of the semi-acetal to achieve stability. The mechanism of this reaction step is influenced fundamentally by the degree of substitution of the C atom bearing the aldehyde that is eliminated [19].

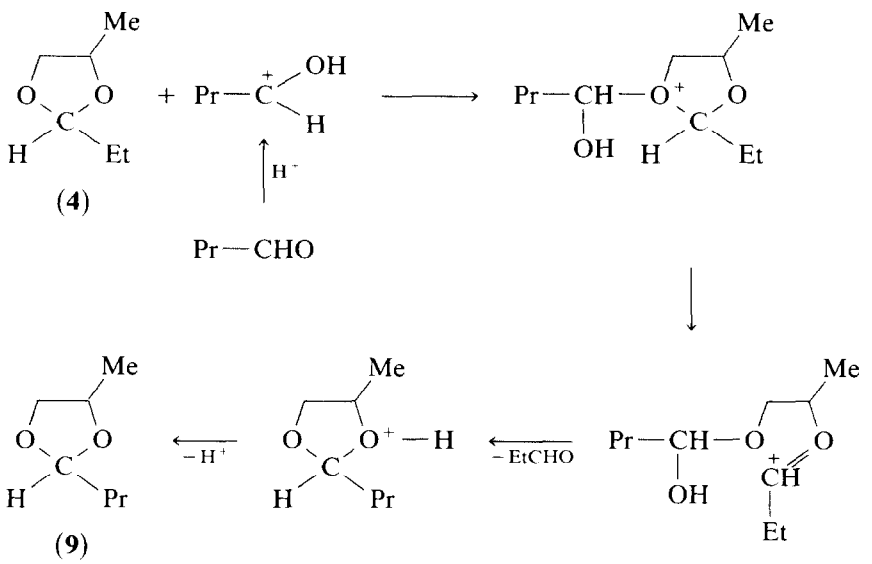
Earlier investigations demonstrated that the complex $HRuClP_3$ (and its precursor $RuCl_2P_3$) can be used as catalysts for a variety of catalytic reactions in synthetic organic chemistry. James has reviewed this topic in detail [10]. Such reactions are



Scheme 1. Formation of intermediate complexes between $RuCl_2\mathbf{P}_3$ and alcohols.

widely applied commercially [20]. Our earlier findings on the isomerization of unsaturated alcohols [21] and the cyclization of aminoalcohols [22] have contributed to the broadening of this field.

The experimental results in our present paper draw attention to some new properties of $RuCl_2\mathbf{P}_3$: its role in the transacetalization of acetals with alcohols, and transfer hydrogenation between carbonyl compounds and alcohols.



Scheme 2. Reaction scheme of acid-catalysed transacetalization.

Experimental

1,3-Dioxacycloalkanes were prepared as described previously [23]. Their purity was controlled by means of GC. The alcohols were Fluka products, while the $RuCl_2P_3$ was a Strem product.

A mixture of 1,3-dioxacycloalkane (0.1 ml), alcohol (0.5 ml) and $RuCl_2P_3$ (5 mg) was heated for 1–5 h under argon in a sealed glass tube. The reaction temperature was 150 °C. After cooling, the reaction mixture was subjected to GC examination with a Fractovap 2101 chromatograph coupled to an Autolab integrator (Spectra-Physics), on a 2 m 15% PEG 20M/Chromosorb P column; temperature 120–140 °C; carrier gas 30 ml hydrogen/min.

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