Ruthenium-catalysed Prins Reaction

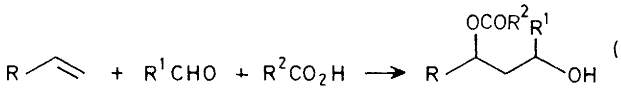
Jean Thivolle-Cazat and Igor Tkatchenko*

Institut de Recherches sur la Catalyse, 2, avenue Albert Einstein, 69626 Villeurbanne Cedex, France

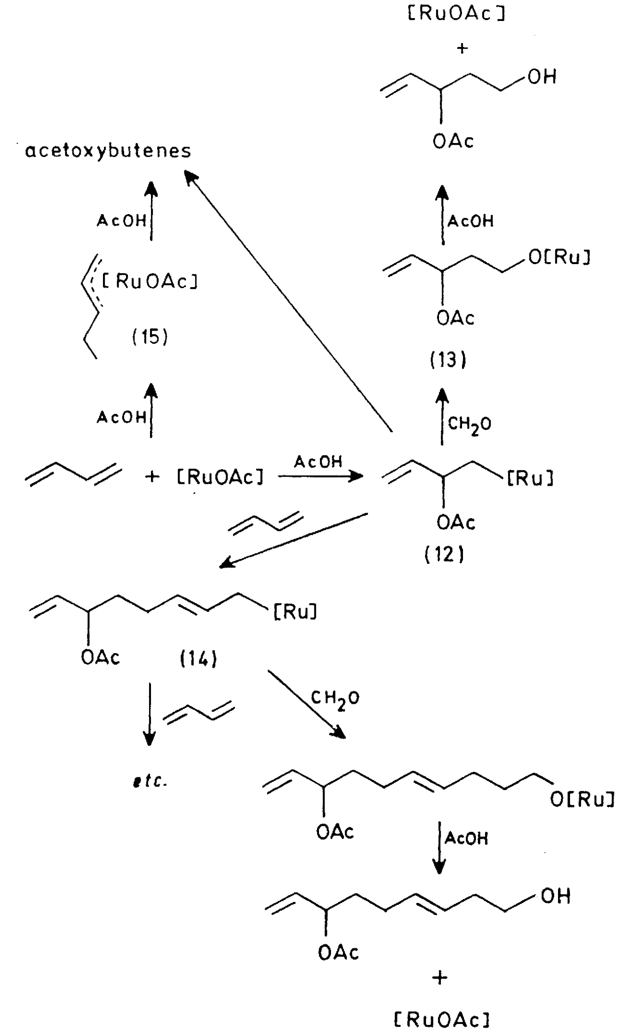
The reactions of dienes and alkenes with aldehydes and carboxylic acids leading to derivatives of 1,3-diols are catalysed by ruthenium salts under mild conditions; oxygenated compounds of higher molecular weight may also be produced by variations in the reaction conditions.

The Prins reaction, equation (1), generally occurs with formaldehyde (R^1 = H) in the presence of strong Brönsted or Lewis acids.[1] The use of metal ions has been claimed,[2,3] but drastic conditions are required which may still favour the highly electrophilic intermediate $[R^1CHOX]^+$ (X = proton, Lewis acid, or metal ion).[1]

However, aldehydes are reported to insert into alkyl– and allyl–transition metal bonds,[4] leading respectively to homoalkoxy– and homoallyloxy–transition metal bonds. Reductive elimination of the metal is known but limited to Group 8 transition metals (*e.g.*, Ru, Pd), and gives only mono-oxygenated compounds.[4] The acid cleavage of the metal–oxygen bond was reported to be a much more convenient method for the formation of alcohols. A catalytic cycle may be operative if the anion of this acid is nucleophilic enough to attack an unsaturated substrate activated by co-ordination to the metal centre, leading to the alkyl- or allyl-metal reactive species and therefore opening a route to di-oxygenated compounds (see Scheme 1). We have found that conjugated dienes and activated alkenes reacted with aldehydes and carboxylic acids in the presence of ruthenium compounds to give rise to derivatives of 1,3-diols similar to those observed for the Prins reaction.



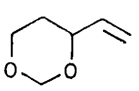
(1)



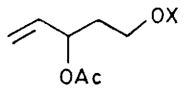
Scheme 1

Reaction of paraformaldehyde and acetic acid with butadiene yields mainly the compounds (**1**)—(**3**). Of all the Group 8 complexes studied, those of ruthenium lead to the best results. The lack of activity of carbonyl and phosphine complexes like $Ru_3(CO)_{12}$, $[Ru(CO)_3Cl_2]_2$, and $RuHCl(CO)(PPh_3)_3$ is noteworthy. In fact, the yields of (**2**) and (**3**) decrease when the reactions are run under an atmosphere of carbon monoxide or hydrogen and/or in the presence of more than one equiv. of triphenylphosphine. Conversely, addition of sodium acetate to '$RuCl_3.3H_2O$' improves the conversion of butadiene, but the highest selectivities for the formation of (**2**) and (**3**) are observed with $[Ru_3O(OAc)_6(H_2O)_3]OAc$.[6] Variable amounts of acetoxybutenes and higher molecular weight compounds of general structure (**4**) are also produced. As shown in Table 1, selectivities >65% are observed under optimum conditions for the difunctionalized products (**2**) and (**3**). Similarly, the ratio [(**2**) + (**3**)]: (**4**) can be modified by changing the amounts of butadiene and reagents present.

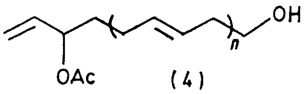
The reaction proceeds with isoprene, albeit at a lower rate, leading to the adducts (**5**)—(**7**) in addition to dimers and



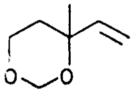
(1)



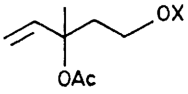
(2) X = H
(3) X = Ac



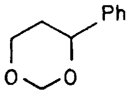
(4)



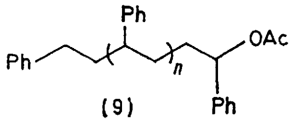
(5)



(6) X = H
(7) X = Ac



(8)

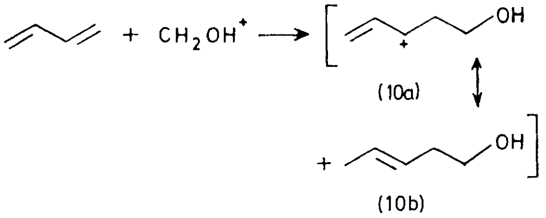


(9)

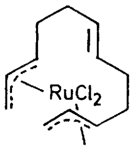
Table 1. Catalytic reactions of unsaturated hydrocarbons with paraformaldehyde and acetic acid.[a]

Hydrocarbon/ mmol	$(CH_2O)_n$ /mmol	$MeCO_2H$ /mmol	Catalyst /mmol	Additive	Reaction time/h	Hydro-carbon conver-sion, %	Product selectivity, %		
							Oligo-mers	Mono-oxygen-ated	Di-oxygenated
Butadiene (400)	400	400	$RuCl_3.3H_2O(1)$	—	3	51	25	8	(**1**) 5.5; (**2**) 66; (**3**) 6; (**4**) 12
Butadiene (400)	400	400	$RuCl_3.3H_2O(1)$	—	20	85	5	10	(**1**) 5; (**2**) 53; (**3**) 10; (**4**) 17
Butadiene (400)	400	400	$RuCl_3.3H_2O(1)$	dioxan	20	67.5	3	11	(**1**) 10; (**2**) 49; (**3**) 7; (**4**) 20
Butadiene (600)	300	300	$RuCl_3.3H_2O(1)$	dioxan	20	62	7.5	19	(**1**) 12; (**2**) 34.5; (**3**) 7; (**4**) 20
Butadiene (600)	200	50	$RuCl_3.3H_2O(1)$	dioxan	20	38	20	14	(**1**) 25; (**2**) 14; (**4**) 27
Butadiene (400)	400	400	$RuCl_3.3H_2O(1)$	H_2,10 bar	20	76	9	12	(**1**) 6; (**2**) 38.5; (**3**) 8.5; (**4**) 26
Butadiene (400)	400	400[b]	$RuCl_3.3H_2O(1)$	CO,10 bar	20	72	15	—	(**1**) 32; (**2**) 4.5[b]; (**3**) 7.5[b]; (**4**)2[b]
Butadiene (400)	400	400	$RuCl_3.3H_2O(1)$	AcONa,10mmol	20	100	5.5	23	(**1**) 2.5; (**2**) 39; (**3**) 6; (**4**) 24
Butadiene (400)	400	400	$Ru_3O(OAc)_7.3H_2O(0.33)$	—	20	93	6	14.5	(**1**) 2; (**2**) 59; (**3**) 4.5; (**4**) 14
Isoprene (400)	400	400	$RuCl_3.3H_2O(1)$	—	20	50	31	8	(**5**) 10; (**6**) 22; (**7**) 4
Styrene (200)	200	200	$RuCl_3.3H_2O(1)$	—	20	73	3[c]	—	(**8**) 41; (**9**) 56

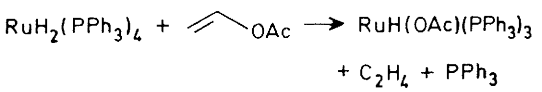
[a] All the reactions were performed in a glass-lined, 300 ml autoclave heated at 80 °C. [b] Formic acid was used; the corresponding formates are formed, in addition to pent-2-en-1,5-diyl diformate. [c] Ethylstyrene.



(2)



(11)


$RuH_2(PPh_3)_4$ + OAc ⟶ $RuH(OAc)(PPh_3)_3$ + C_2H_4 + PPh_3 (3)

analogues of (**4**). In the case of styrene, only the dioxan (**8**) which is the main product formed in the classical Prins reaction[7] and oligomers of gross structure (**9**) are observed with the HCHO–AcOH couple. The reaction occurs also with the couples HCHO–HCO_2H, MeCHO–HCO_2H, or PhCHO–HCO_2H and butadiene. The corresponding 1,3-dioxans and 1,2-diol derivatives are formed but in lower ratios with respect to the higher molecular weight compounds. The reaction performed with paraformaldehyde and water leads mainly to (**1**) and, as yet uncharacterized, higher molecular weight products.

The presence of a ruthenium catalyst is essential for the observation of the specified reaction and for the product distributions reported. Although the reaction of paraformaldehyde and formic acid with butadiene proceeds smoothly at room temp.,[8] a noticeable amount of the 1,4-diester is obtained. The formation of this adduct can be explained by the reaction of the protonated species CH_2OH^+ with butadiene leading to the allyl cation structures (**10a,b**), equation (2). The lack of formal 1,4-adducts in the case of the ruthenium-catalysed reaction suggests that an η-but-2-enylruthenium species is not involved. In fact, by contrast with the case of nickel,[5] we observed no reaction of complex (**11**)[9] with paraformaldehyde. The formation of the 1,2-adducts may proceed first by a process similar to acetoxypalladation,[10] *i.e.* the addition of ruthenium and acetoxy-species to one double bond (Scheme 1). In support of this first step, only the reverse reaction, equation (3), has been reported in the case of ruthenium. Insertion of HCHO into the [Ru]–C bond of (**12**) will ensue, leading to the alkoxy-intermediate (**13**). This in turn is protonated and gives rise to the 1,2-adduct which can react further with AcOH to produce the diacetate or with formaldehyde to give the 1,3-dioxan. The formation of higher molecular weight products can be explained by competition between formaldehyde [*viz.* (**13**)] and butadiene [*viz.* (**14**)] for 'insertion' into the [Ru]–C bond. The lack of catalytic activity observed where palladium compounds are used suggested that in this case β-elimination strongly competes with the 'insertion' of the aldehyde. The formation of acetoxybutenes may involve either potonolysis of (**12**) or an η^3-but-2-enylruthenium species (**15**), formed by the reverse mode of addition of the ruthenium species, as invoked in the case of palladium.

We thank the Societé Nationale Elf-Aquitaine for support of this work.

Received, 6th July 1982; Com. 782

References

1 D. R. Adams and S. P. Bathnagar, *Synthesis*, 1977, 661.
2 G. Foster and P. Johnson, B.P. 1 205 397 1967; *Chem. Abstr.*, 1970, **73**, 131809; T. Kazumi, M. Tervo, and M. Masahiro, G.P. 2 049 049/1969; *Chem. Abstr.*, 1971, **75**, 37597; C. M. Starko, U.S. P. 3 813 043/1969; *Chem. Abstr.*, 1974, **81**, 63140.
3 S. Sakai, Y. Kamashima, Y. Takahashi, and Y. Ishii, *Chem. Commun.*, 1967, 1073.
4 P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' Academic Press, New York, 1975, Vol. 2, ch. 2 and 5; J. Tsuji, 'Organic Synthesis by Means of Transition Metal Complexes,' Springer Verlag, Berlin, 1975, ch. 4.
5 R. Baker, B. N. Blackett, R. C. Cookson, R. C. Goss, and P. Madden, *J. Chem. Soc., Chem. Commun.*, 1972, 343; J. Thivolle-Cazat and I. Tkatchenko, *Tetrahedron Lett.*, 1979, 345.
6 A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1972, 1570.
7 R. C. Shriner and P. R. Ruby, *Org. Synth.*, 1963, Coll. Vol., **4**, 786.
8 J. K. Sutherland, G. Pratt, R. Battaglia, and J. J. S. Bajorek, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1243.
9 J. K. Nicholson and B. L. Shaw, *J. Chem. Soc.*, 1966, 807.
10 P. M. Henry, 'Palladium Catalyzed Oxidation of Hydrocarbons,' D. Reidel, Dordrecht, 1980, ch. 2.