

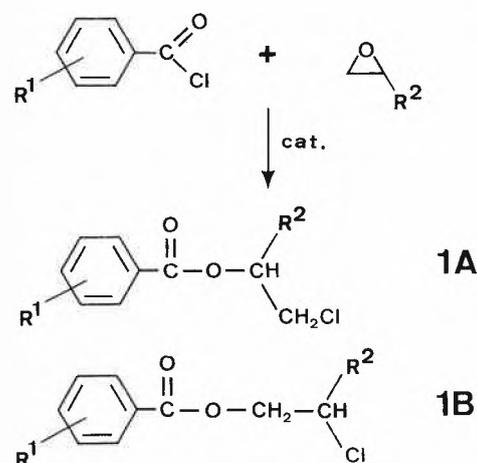
# A Transition Metal Catalyzed Reaction of Aromatic Acyl Chlorides with Epoxides

Achim Roloff\*

**Abstract:** In a transition metal catalyzed reaction of aroyl chlorides with epoxides a change from palladium to ruthenium brings about a change in regioselectivity. A participation of the transition metal in the ring opening step is now evident.

Reactions of transition metal compounds with epoxides have been reported<sup>[1]</sup>. It is known that benzoyl palladium halides will react with a number of nucleophiles such as alcohols, amines, organotin compounds, cyanides, and acetylenes to the corresponding esters<sup>[2]</sup>, amides<sup>[3]</sup>, ketones<sup>[4]</sup>, acyl cyanides<sup>[5]</sup>, and alkynyl ketones<sup>[6]</sup>.

Tanaka et al.<sup>[1d]</sup> reported a palladium catalyzed reaction of aryl halides with carbon monoxide in the presence of cyclic ethers giving halohydrin esters. We wish to report a palladium and ruthenium catalyzed reaction of aromatic acyl chlorides with epoxides. With tetrakis(triphenylphosphane)palladium or dichlorotris(triphenylphosphane)ruthenium as catalysts<sup>[7]</sup> epoxides react with aroyl chlorides in toluene solution at 100°C to give halohydrin esters in fair to excellent yield. Whereas Tanaka et al. in their communication<sup>[1d]</sup> are not sure about the mechanism of their reaction, we can clearly show that in our case a transition metal catalyzed epoxide ring opening must take place.



We find it remarkable that a change in catalyst from palladium to ruthenium brings about a change in regioselectivity.

\* Correspondence: Dr. A. Roloff  
Central Research Laboratories  
Ciba-Geigy AG  
CH-4002 Basel

changed, ruling out an acid catalyzed epoxide ring opening.

In a typical example, 100 mmol of acid chloride are dissolved in 100 mL of toluene. 100 mmol of epoxide and 1 mmol of catalyst are added to the solution, which is heated to 100°C and kept at that temperature for 10 hours. After cooling to room temperature the solvent is removed and the residue is either distilled or crystallized. It is known from the literature<sup>[2-6]</sup> that acyl-palladium compounds are excellent electrophiles. Therefore, since an acyl-palladium intermediate can be formed during the reaction, it is reasonable to propose the following reaction pathway:

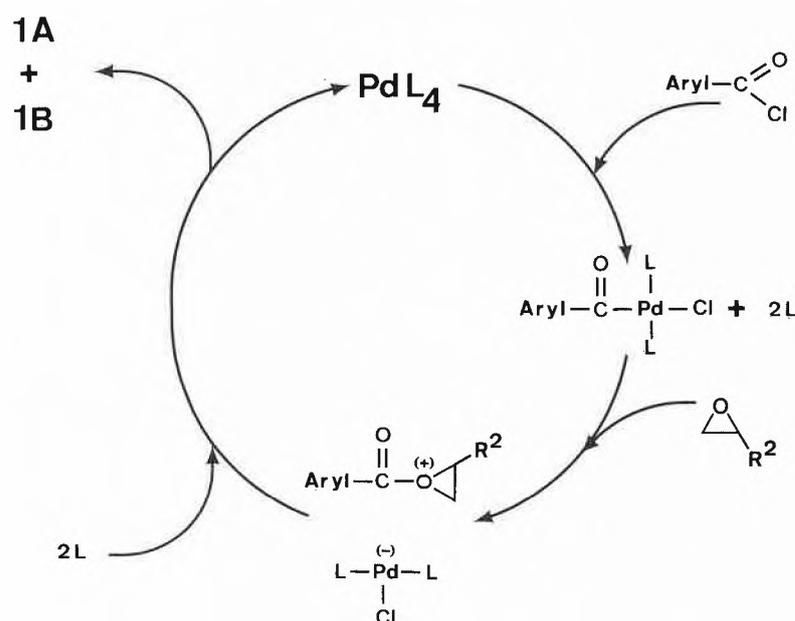


Table 1.

	R <sup>1</sup>	R <sup>2</sup>	Catalyst [a]	Physical properties [b]	Isomer distribution [c]		Yield [%]
					1A	1B	
1a	H	Phenyl-	PdL <sub>4</sub>		70	30	52
1b	H	Phenyl-	RuCl <sub>2</sub> L <sub>3</sub>	<i>b.p.</i> 121°C/0.1 Torr	–	100	30 [e]
2a	H	Chloromethyl-	PdL <sub>4</sub>	[d]	100	–	80
2b	H	Chloromethyl-	RuCl <sub>2</sub> L <sub>3</sub>	[d]	100	–	58
3a	H	Acryloxymethyl-	PdL <sub>4</sub>	[d]	100	–	75
3b	H	Acryloxymethyl-	RuCl <sub>2</sub> L <sub>3</sub>	[d]	100	–	42
4	2-Cl	Phenyl-	PdL <sub>4</sub>	<i>b.p.</i> 127°C/0.1 Torr	50	50	41
5a	4-Cl	Phenyl-	PdL <sub>4</sub>		63	37	98
5b	4-Cl	Phenyl-	RuCl <sub>2</sub> L <sub>3</sub>	<i>b.p.</i> 143°C/0.1 Torr	44	56	95
6	3,4-Cl <sub>2</sub>	Phenyl-	PdL <sub>4</sub>	[d]	51	49	90
7	4-NO <sub>2</sub>	Phenyl-	PdL <sub>4</sub>	[d]	–	100	35
8	3,5-(NO <sub>2</sub> ) <sub>2</sub>	Phenyl-	PdL <sub>4</sub>	<i>m.p.</i> 116°C	–	100	51
9	3,4,5-(OCH <sub>3</sub> ) <sub>3</sub>	Phenyl-	PdL <sub>4</sub>	[d]	70	30	77

[a] L = P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>. – [b] All compounds were identified by their <sup>1</sup>H-NMR and IR spectra and gave satisfactory elemental analysis (C, H, Cl). – [c] Isomeric mixtures were not separated. The isomer distribution was taken from the <sup>1</sup>H-NMR spectra. The O–C–H signal appears as a doublet, δ = 6.2, for all compounds of type 1A. The C–C–H signal appears as a triplet, δ = 5.2, for all compounds of type 1B. – [d] These compounds were purified by column chromatography. – [e] > 60% of starting material was recovered.

This is clearly shown in case of styrene oxide and benzoyl chloride (entry 1a and 1b in Table 1), and it is less evident in the case of styrene oxide and 4-chlorobenzoyl chloride (entry 5a and 5b in Table 1). Furthermore electron donating substituents on the aromatic ring seem to favour type 1B product formation. With addition of tertiary amines to the reaction mixture, the selectivity of the reaction remained un-

This mechanism has already been proposed by Tanaka et al.<sup>[1d]</sup>. Our results rule out the second mechanistic proposal which was made in the same paper<sup>[1d]</sup>. There a formation of acid from the acyl-palladium complex was suggested. The acid was said to react with the cyclic ether to form halohydrin esters.

Our results, especially the change in regioselectivity can only be understood, if

the transition metal is involved in the ring opening step. We furthermore added tertiary amines to our reaction mixture to avoid acid catalyzed ring opening. With these results a transition metal catalyzed ring opening of the epoxide is strongly suggested.

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- [7] Besides these two complexes we tried  $\text{PdCl}_2(\text{PPh}_3)_4$ ,  $\text{PdCl}_2(\text{NCC}_6\text{H}_5)_2$ ,  $\text{Pd}(\text{DBA})_2$ ,  $\text{Pd}(\text{OAc})_2(\text{PPh}_3)_2$ , and  $\text{RhCl}(\text{PPh}_3)_3$  as catalysts (DBA = dibenzylidene acetone); all were less efficient and product formation could hardly be seen.