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Palladium- and light-enhanced ring-opening of oxiranes by copper chloride

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Abstract

The yields of chlorohydrins formed by cleavage of epoxides by $CuCl_2$ is increased in the presence of small amounts of $PdCl_2(MeCN)_2$. The conversion drops dramatically on carrying out the reaction in the dark. The regiochemistry of the ring-opening is sensitive to the nature of the substituents.

Introduction

A few years ago, we reported the palladium-catalyzed oxidation of 1-(*p*-toluenesulfonyl)prop-2-ene **1** to the unsaturated alcohol **2** and the aldehyde **3** in the presence of oxygen, UV light and copper trifluoroacetate (Scheme I, path a) [1]. The best solvent was acetone and we suspected that these conditions induced the *in situ* formation of peroxy derivatives of acetone [1–3] which would facilitate the reaction path and the regeneration of an active catalyst [4,5]. Switching from trifluoroacetate to chloride as the anion associated with metals led to the chlorohydrin **4** as major product (Scheme 1, path b) [6]. These results led us to presume the epoxidation of the double bond of **1** as the intermediate step in both cases; such an epoxide would be unstable under the experimental conditions and furnish **2** and **3** in the presence of $CF_3CO_2^-$, or **4** in the presence of Cl^-. Although much more rarely observed than the Wacker process [7], the palladium-catalysed epoxidation of a double bond has been reported for a few specific compounds [8] and furthermore, ring-opening of oxiranes by stoichiometric amounts of $PdCl_2(PhCN)_2$ has been previously described [9,10]. We have already reported the unusual reactivity of **1** under some Wacker conditions [11].

As the preparation of the epoxide of **1** gave us some trouble, our propositions were tested with 1-(phenylsulfonyl)-2,3-epoxypropane, **5**. In the presence of light,

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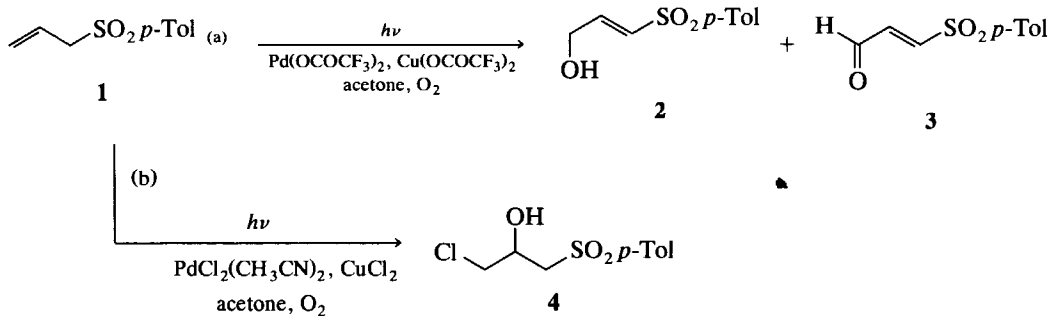
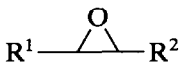

SO2 p-Tol
(a)
hν
Pd(OCOCF3)2, Cu(OCOCF3)2
acetone, O2
1
OH
SO2 p-Tol
2
H
O
SO2 p-Tol
3
(b)
hν
PdCl2(CH3CN)2, CuCl2
acetone, O2
OH
Cl
SO2 p-Tol
4

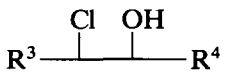
Scheme 1.

oxygen, $Cu(OCOCF_3)_2$ and small amounts of $Pd(OCOCF_3)_2$, **5** was almost unreactive, whereas under similar conditions, except that copper and palladium chlorides were then used instead of the trifluoroacetate derivatives, **5** led to the expected chlorohydrin **6** as the main product [6]. Although the formation of halohydrins from oxiranes is well known [12*], we investigated the palladium-mediated reaction of a series of epoxides since the transformation of such compounds into halohydrins with palladium has been reported only as a result of using two equivalents of $PdCl_2(PhCN)_2$ [9,10,19*,20*].



	5	**7**	**11(a)**	**15**	**16(a)**	**17(b)**	**18**	**19**	**20**
R^1	H	H	n-C_6H_{13}	H	Ph	Ph	H	H	H
R^2	CH_2SO_2Ph	n-$C_{18}H_{37}$	n-C_6H_{13}	Ph	Ph	Ph	CH_2Ph	CH_2SPh	$CH(OH)C_{17}H_{35}$

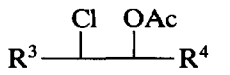
(a) *trans*-isomer, (b) *cis*-isomer



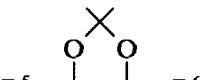
	6	**8**	**9**	**21(a)**	**25**	**26**
R^3	H	H	n-$C_{18}H_{37}$	n-C_6H_{13}	Ph	CH_2Ph
R^4	CH_2SO_2Ph	n-$C_{18}H_{37}$	H	n-C_6H_{13}	H	H

	27	**28(b)**	**31**	**32**	**38**	**39**
R^3	H	Ph	CH_2SPh	H	CH_2SO_2Ph	CH_2SO_2p-Tol
R^4	CH_2Ph	Ph	H	$CH(OH)C_{17}H_{35}$	H	H

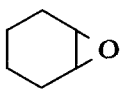
(a) *erythro*-isomer, (b) *threo*-isomer



	35	**36**	**37**	**40**
R^3	H	Ph	CH_2SPh	H
R^4	n-$C_{18}H_{37}$	H	H	CH_2SO_2p-Tol



	10	**34**	**41**
R^5	H	H	CH_2Cl
R^6	n-$C_{18}H_{37}$	CH_2SO_2Ph	n-$C_{17}H_{35}$



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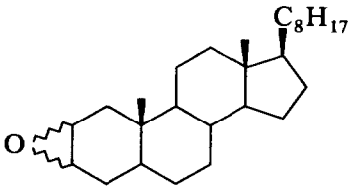
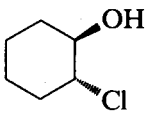


13 β-epoxide
14 α-epoxide



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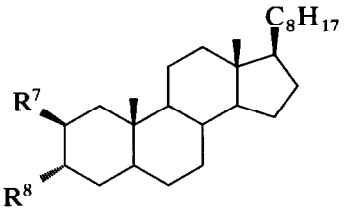
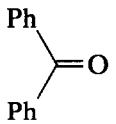


23 $R^7 = OH$, $R^8 = Cl$

24 $R^7 = Cl$, $R^8 = OH$



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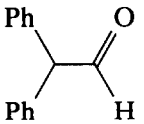

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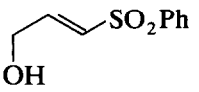

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Results

A large variety of experimental conditions was analysed with the readily available 1,2-epoxyeicosane, **7**, as starting material. Representative results obtained using first palladium and copper chlorides are reported in Table 1.

Table 1

Influence of $PdCl_2(MeCN)_2$, light and solvent on the efficiency of the opening of **7** [a]

Run	Solvent	$PdCl_2(MeCN)_2$ equiv.	$CuCl_2$ equiv.	Time (h)	Conversion (%)	Yield% [b]		
						8	**9**	**10**
1 [c]	acetone	0.1	1.2	92	85	49	24	6
2 [c,d]	acetone	0.1	1.2	92	79	33	28	16
3 [c]	acetone	0	1.2	96	80	28	13	37
4 [e]	acetone	0.1	1.2	92	27	15	9	trace
5 [e]	acetone	0	1.2	96	56	13	11	9
6 [c]	CH_2Cl_2	0.1	1.2	40	89	33	50	–
7 [f]	CH_2Cl_2	0.01	1.2	120	96	35	44	–
8 [d,f]	CH_2Cl_2	0.01	1.2	120	96	31	50	–
9 [c]	CH_2Cl_2	0	1.2	120	65	21	21	–
10 [e]	CH_2Cl_2	0.1	1.2	40	55	20	28	–
11 [e]	CH_2Cl_2	0	1.2	120	25	9	8	–
12 [f]	CH_2Cl_2	0.5	0	120	18	5	3	–
13 [c,d,g]	CH_2Cl_2	0.01	1.2	120	56	19	11	–
14 [c]	PhH	0.1	1.2	46	98	49	43	–
15 [c,h]	PhH	0.1	1.2	92	18	trace	trace	–
16 [f]	PhH	0.01	1.2	120	85	34	32	–
17 [c]	PhH	0	1.2	120	47	9	12	–
18 [c]	MeOH	0.1	1.2	96	53	17	4	–
19 [c]	MeCN	0.1	1.2	92	65	27	22	–

[a] Reaction carried out at room temperature under oxygen. [b] Yield calculated on the amount of epoxide introduced. [c] Reaction carried out in daylight. [d] Reaction carried out under argon. [e] Reaction carried out in the dark. [f] Reaction carried out under irradiation by visible light (200W). [g] PPh_3 (0.01 equiv.) was added to the reaction mixture. [h] Reaction carried out in the presence of H_2O (50 equiv.).

Table 2

Influence of the metallic species on the efficiency of the opening of **7** [a]

Run	Metallic species (equiv.)	Time (h)	Conversion (%)	Yield% [b]		
				8	**9**	**10**
Solvent: acetone						
20 [c]	$PdCl_2(MeCN)_2(0.1)+CuCl(2)$	92	38	6	6	20
21 [c]	$PdCl_2(MeCN)_2(0.1)+LiCl(5)$	120	44	43	0	0
22 [c]	CuCl(2.4)	95	36	18	9	8
23 [c]	$MgCl_2(1.2)$	96	19	trace	trace	trace
24 [c]	$NiCl_2(1.2)$	95	20	10	9	trace
25 [c]	$SnCl_2(1.2)$	95	90	7	9	46
Solvent: CH_2Cl_2						
26 [d]	$Pd(OAc)_2(0.05)+CuCl_2(1.2)$	158	45	13	10	–
27 [d]	$Pd(OCOCF_3)_2(0.05)+CuCl_2(1.2)$	158	46	11	11	–

[a] Reaction carried out at room temperature under oxygen. [b] Yield calculated on the amount of epoxide introduced. [c] Reaction carried out in daylight. [d] Reaction carried out in air and irradiation by visible light (200W).

Chlorohydrins **8**, and **9**, and the acetal **10** were obtained when acetone was used as solvent (runs 1 to 5). The Lewis acid-induced formation of such an acetal from an epoxide has been previously reported [21]. The chlorohydrins **8** and **9** were not transformed to **10** under the experimental conditions. From runs 1 and 2, it appeared that the efficiency of the opening of **7** was not greatly influenced by an oxygen or argon atmosphere. In contrast, the conversion decreased greatly when the reaction was performed in the dark (runs 4 and 5). The presence or the absence of the palladium complex did not greatly influence the conversions of the daylight-reactions (runs 1 and 3) but strongly modified the ratio of **8**:**9**:**10**, the acetal becoming the main product when the palladium was omitted.

The results were different with methylene chloride as solvent (runs 6 to 13). High yields of chlorohydrins were obtained in the presence of light and of both palladium and copper chlorides (runs 6 to 8). The conversion remained high even with a small quantity of palladium complex (runs 7 and 8) but decreased in the dark or in the absence of either chloride (runs 9 to 12). The addition of triphenylphosphine as a good ligand inverted the regioselectivity but reduced the percentage of conversion (run 13).

The Pd–Cu system in daylight also gave high yields of chlorohydrins in dry benzene as solvent (runs 14 and 16), but the presence of water in this solvent or the absence of the Pd complex then led to the inhibition of the ring-opening of **7** (runs 15 and 17). A lower efficiency was observed in methanol or acetonitrile (runs 18 and 19).

The use of other metallic species was disappointing (Table 2). In acetone, low conversions were induced in the presence of LiCl [22*], CuCl, $MgCl_2$, or $NiCl_2$, whereas $SnCl_2$ caused a high conversion with preferential formation of acetal **10** (run 25). This last compound was not formed in the presence of LiCl (run 21). In methylene chloride, switching from palladium chloride (runs 6, 7 and 8) to

* Reference number with asterisk indicates a note in the list of references.

Table 3

Reaction of epoxides **5** and **11–20** [a]

Epoxide	$PdCl_2(MeCN)_2$ equiv.	Time (h)	Conversion (%)	Products (% yield [b])
11	0.01	96	53	**21**(52)
12	0.01	40	96	**22**(87)
13	0.1	48	100	**23**(86)
14	0.1	48	88	**24**(64)
15	0.01	120	89	**25**(73)
16	0.01	17	95	**28**(46) + **29**(16) + **30**(26)
17	0.01	15	100	**28**(57) + **30**(28)
18	0.01	120	92	**26**(8) + **27**(26)
19	0.01	16	95	**31**(92)
20	0.01	15	94	**32**(89)
5 [c]	0.01	113	100	**6**(67) + **33**(9) + **34**(13)

[a] Reaction carried out in CH_2Cl_2 at room temperature in air with visible irradiation in the presence of $PdCl_2(MeCN)_2$ (0.01 or 0.1 equiv.) and $CuCl_2$ (1.2 equiv.). [b] Yield calculated on the amount of epoxide introduced. [c] Reaction carried out in acetone.

palladium acetate or palladium trifluoroacetate decreased the yield of chlorohydrins (runs 26 and 27).

From the experiments reported in Tables 1 and 2, we can conclude that the opening of an oxirane ring to give a chlorohydrin benefits from a synergistic effect between $PdCl_2$ and $CuCl_2$, is enhanced by visible light, and is best carried out in methylene chloride as solvent.

Following these observations, the reactivity of epoxides **11** to **20** was examined in the presence of $PdCl_2(MeCN)_2$ and $CuCl_2$ in CH_2Cl_2 in air and visible light irradiation. From the results summarized in Table 3, it appears that the opening of oxiranes is generally highly regioselective under these conditions. Indeed, often only one chlorohydrin was formed, and furthermore in high yield, allowing for the starting material recovered. The orientation of the cleavage of monosubstituted epoxides giving 1,2- or 2,1-chlorohydrin depends on the nature of the substituent: 1,2-chlorohydrin was preferentially or selectively obtained when the oxirane was substituted by a $PhCH_2$ or CHOHR group (epoxides **18** and **20**) while the Ph and CH_2SPh groups (epoxides **15** and **19**) induced the formation of the regioisomer. The *trans*-epoxide **11** led to the *erythro*-chlorohydrin **21**. *trans*-Chlorohydrins were obtained from **12**, **13** and **14**, but *trans*- and *cis*-1,2-diphenylepoxyethanes, **16** and **17**, furnished the same chlorohydrin **28**. The epoxide **16** also led to benzophenone **29** and diphenyl acetaldehyde **30**, but its isomer, **17**, gave **30** but no **29**. However, we observed first that small changes of the reaction temperature modified the ratio **29**:**30**, and secondly, that **30** was completely transformed to **29** at 40–50°C under the reaction conditions.

In contrast to the thioether **19**, 1-(phenylsulfonyl)-2,3-epoxypropane, **5**, did not react in CH_2Cl_2 as solvent. In acetone, **5** led mainly to the chlorohydrin **6**, accompanied by the elimination product **33** and the usual acetal **34**.

Determination of the structure of the chlorohydrins

The *erythro*-structure was attributed to **21** because of its conversion to the epoxide **11** under basic conditions. The configuration of the *trans*-chlorohydrins

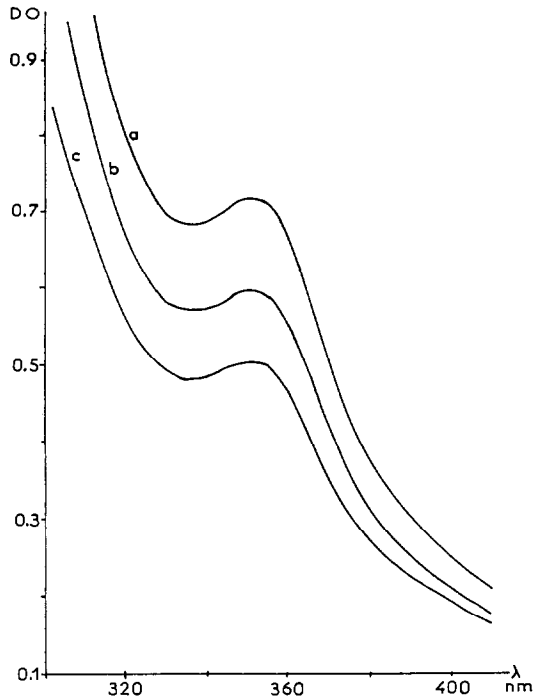
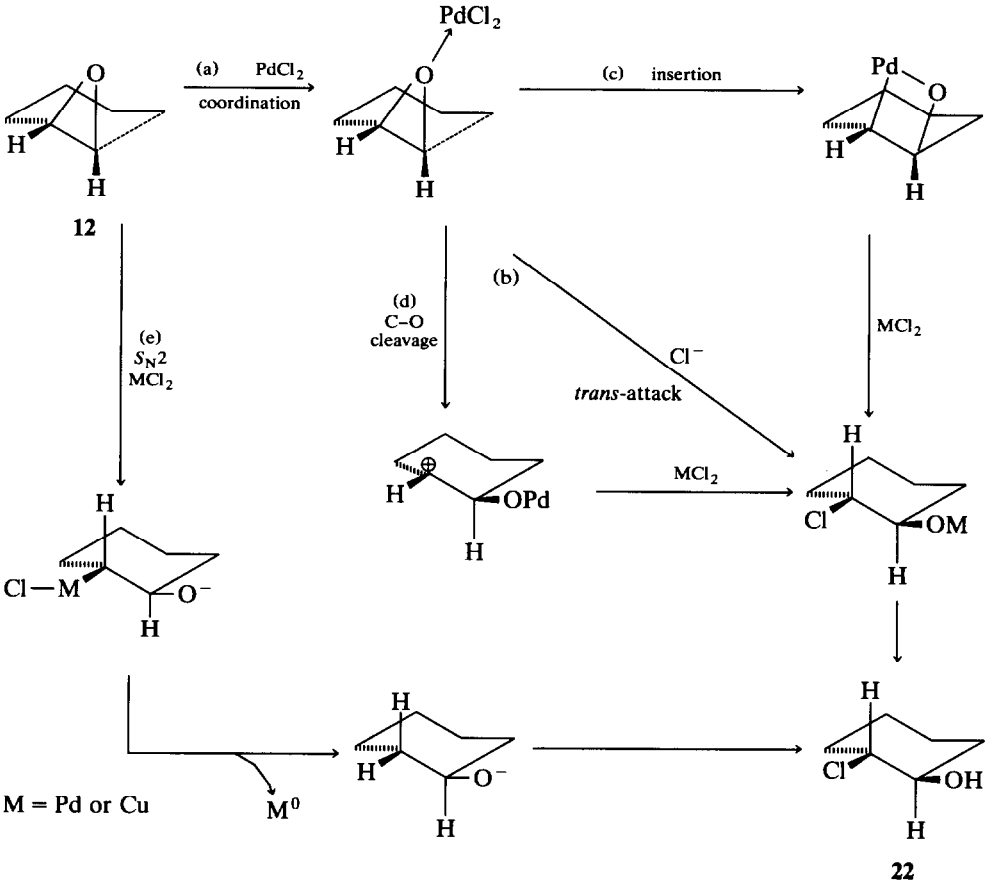


Fig. 1. Development of the UV spectrum of a methylene-chloride solution of $PdCl_2(MeCN)_2$ ($0.45 \cdot 10^{-3}$ $M \cdot l^{-1}$) in the presence of the epoxide **7** ($4.46 \cdot 10^{-3}$ $M \cdot l^{-1}$). For significance of curves a, b and c, see text.

22, **23** and **24** was determined by comparison with literature data [23,24]. The acetoxylation of the hydroxy group of **8**, **25**, and **31** led to **35**, **36** and **37**, respectively. The comparison of the NMR spectra of these hydroxy and acetoxy compounds allowed us to determine whether the hydroxy and chloro-substituents were *gem* to one or two hydrogen atoms and thus, to establish the regioselectivity of the opening step. Furthermore, the structures of **8** and **25** have been confirmed by very recently reported NMR data [18]. Based on these data the structures of **9**, **26** and **27** were established by NMR correlations. The oxidation of **31** by *m*-chloroperbenzoic acid afforded **38**. As the structure of **31** has been previously determined, the structures of **38** and then **6** were also established. The *threo*-structure was assigned to **28** by comparison of melting points with literature data (mp_{threo} = 42–43°C [25,26], $mp_{erythro}$ = 76–79°C [25,27] and synthesis of *cis*-1,2-diphenylepoxyethane, **17**, from **28** under basic conditions [26]. The structure of **32** was deduced after acetalisation of this α-diol to give **41**.

Mechanistic interpretation

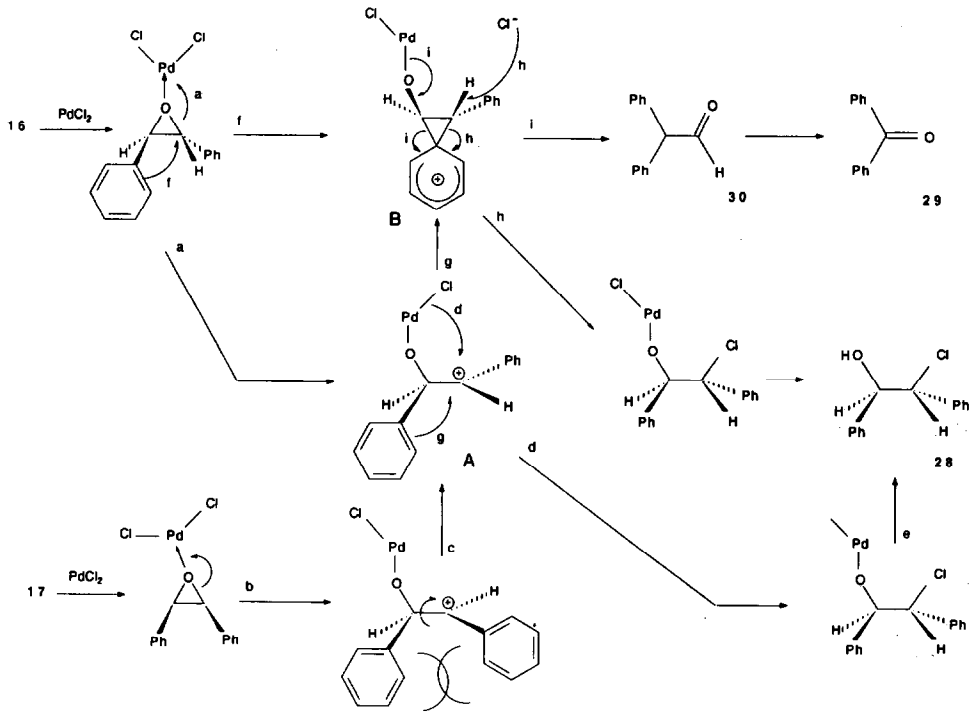
A UV study has been undertaken in methylene chloride to unravel the mechanism of the reaction (Fig. 1). The UV spectra of $PdCl_2(MeCN)_2$ has a strong band at $\lambda < 400$ nm (curve a). The addition of an excess of the epoxide **7** immediately induced a decrease in these absorptions (curve b). They continued to decrease during 10–15 min, finally changing to curve c which remained unchanged with



Scheme 2.

time. Similar spectra were obtained when the UV cell was irradiated by daylight or when some $CuCl_2$ (almost insoluble) was added. The decrease of the UV absorption of $PdCl_2(MeCN)_2$ upon addition of **7** can be interpreted as due to an interaction (coordination or/and reaction) between palladium and the epoxide.

Palladium(II) is a better Lewis acid than copper(II) [28]. Thus, when $PdCl_2(MeCN)_2$ and $CuCl_2$ are both present, the first step could be a coordination to palladium rather than to copper of the oxirane oxygen (scheme II, path a). The formation of *erythro*-chlorohydrin, **21**, and *trans*-chlorohydrins **22**, **23**, and **24**, from such a complex could be explained by the following pathways (Scheme 2): a *trans* attack of a chloride anion (path b) [29], or an insertion of Pd into a C–O bond leading to metallaoxetane (path c) [30,31], or the cleavage of a C–O bond with formation of a carbocation (path d). The reaction of the intermediates of paths c and d with MCl_2 (M = Pd or Cu) would give the thermodynamic chlorohydrin. Instead of a coordination of palladium by the oxiran oxygen, an S_N2 type reaction of MCl_2 on the oxirane ring [31] can also be envisaged (Scheme 2, path e). With these mechanistic interpretations, the regioselectivities obtained from steroids **13**



Scheme 3.

and **14** are easily understood in considering the steric interactions shown by use of Dreiding models [9].

On the other hand, these reaction pathways do not help to rationalize the transformation of *trans*- and *cis*-1,2-diphenylepoxyethanes into the *threo*-chlorohydrin, **28**. The selective formation of **28** from both **16** and **17** is not common; indeed, with tetrabutylammonium dihydrogentrifluoride as reagent, the *erythro* fluorohydrin has been obtained from **16**, and the *threo* isomer from **17** [15]. Under our conditions, a common carbocation **A** may then be envisaged (Scheme 3, paths a, b and c) which would evolve toward **28** from its less crowded conformation through the internal delivery of Cl^- from the palladium chloride molecule already coordinated by the oxygen atom [29] (paths d and e). However, such an explanation contradicts the stereospecific formation of *trans*-chlorohydrins from **12**, **13** and **14**, as previously established. A more satisfactory interpretation for the formation of **28** from both **16** and **17** can be developed for these particular compounds by considering the parallel formation of benzophenone **29** and diphenyl acetaldehyde **30**. Indeed, this stereospecificity could be due to a phenonium ion **B** as intermediate (Scheme 3) [32]. Such an intermediate would be directly accessible from *trans*-1,2-diphenylepoxyethane *via* phenyl participation (path f), whereas its formation from *cis*-1,2-diphenylepoxyethane would require C–O bond cleavage and a rotation around the C–C bond (paths b, c and g). As envisaged by Detty and Seidler [32], the intervention of a phenonium ion suggests a late involvement of the nucleophile Cl^-, leading to **28** (path h). The isolation of large amounts of **30** supports this interpretation (path i).

The low regioselectivity of the opening of **7** in methylene chloride has not been observed using other methods with similar compounds [15,16,18]. The formation of **24** from **14** has already been described using stoichiometric amounts of $PdCl_2(PhCN)_2$ [9]. Stilbene oxide led to **25** with a selectivity and a yield which both seem to be higher than with other epoxide-opening methods [15–18]. The regioselective formation of **32** from **20** is in agreement with the recently described opening of a variety of epoxy alcohols by stoichiometric amounts of both $Ti(O-^iPr)_4$ and iodide (or bromine) [13] but contrasts with the low regioselectivity obtained from *trans*-2,3-epoxypentan-1-ol in using Pd^0/NH_4Cl [20]. Although the regioselective opening of **20** can be explained by coordination of the hydroxy group to the palladium atom already bound to the oxirane oxygen [10], similar coordination is unsatisfactory to rationalise the other regioselectivities observed. Nevertheless, it is obvious that both steric and electronic factors play important roles in determining the regioselectivity of the opening of oxiranes.

Conclusion

$PdCl_2(MeCN)$ provides a large synergetic effect for the oxirane ring-opening to a chlorohydrin by $CuCl_2$ in CH_2Cl_2. This reaction, whose the regioselectivity depends on the nature of the substituents and is generally high, is enhanced by light.

Experimental

The NMR spectra (δ ppm) were recorded with tetramethylsilane as internal reference, in $CDCl_3$ solution using Bruker AC300 or CW80 spectrometers. The IR spectra (cm^{-1}) were recorded in $CHCl_3$ solution in using a Philips SP3-300 instrument. Melting points were determined with a Büchi apparatus. Combustion analyses were performed at the microanalysis facility of the University of Champagne-Ardenne. Metal salts were prepared as previously described [1]. 2β,3β-Epoxy-5α-cholestane, **13** [33], was prepared from 2α-bromo-5α-cholestan-3-one [34]. 2α,3α-Epoxy-5α-cholestane **14** [35] was prepared from 5α-cholestan-3-one [36]. "Visible light" means tungsten filament radiation.

Preparation of epoxides

Epoxides, **7**, **11**, **16–18**, and **20**: *m*-Chloroperbenzoic acid was added gradually to a stirred methylene chloride solution of alkene cooled at 0°C. The mixture was then stirred overnight at room temperature. After conventional work-up with an aqueous sodium bicarbonate solution and evaporation of the solvent, the epoxide was purified by flash-chromatography eluted with a mixture of ethyl acetate and petroleum ether.

1,2-Epoxyeicosane, **7**. Yield = 82%. m.p. = 45°C. ^1H NMR (80 MHz, $CDCl_3$) = 0.71–1.69 (37H), 2.40 (1H, dd, J = 2.4, 5), 2.71 (1H, dd, J = 4.5, 5), 2.88 (1H, m). IR ($CHCl_3$) = 2940, 2860, 1460. Anal. Found: C, 81.20; H, 13.42. $C_{20}H_{40}O$ calcd.: C, 81.01; H, 13.60%.

trans-7,8-Epoxytetradecane, **11**. Yield = 90%, oil. ^1H NMR (300 MHz, $CDCl_3$) = 0.87 (6H, t, J = 6.7), 1.18–1.38 (16H), 1.42 (2H, m), 1.49 (2H, m), 2.62 (2H, dt, J = 2, 4.4, 5). ^{13}C NMR (75 MHz, $CDCl_3$) = 13.96, 22.50, 25.96, 29.07, 31.71, 32.09,

58.80. IR ($CHCl_3$) = 2900, 1448, 1370, 1215. Anal. Found: C, 78.97; H, 13.19. $C_{14}H_{28}O$ calcd.: C, 79.18; H, 13.29%.

trans-1,2-Diphenylepoxyethane, **16**. The epoxidation was carried out in diethyl ether instead of methylene chloride. Yield = 90%. m.p. = 65–66°C (lit. [37]. m.p. = 65–67°C). ^1H NMR (80 MHz, $CDCl_3$) = 3.82 (2H, s), 7.29 (10H, m). IR ($CHCl_3$) = 3000, 1605, 1480, 1442.

cis-1,2-Diphenylepoxyethane, **17**. The epoxidation was carried out in diethyl ether instead of methylene chloride. Yield = 92%, oil. ^1H NMR (80 MHz, $CDCl_3$) = 4.29 (2H, s), 7.08 (10H, m). IR ($CHCl_3$) = 3018, 1650, 1490, 1450, 1408.

Benzylepoxyethane, **18**. Yield = 74%, oil. ^1H NMR (300 MHz, $CDCl_3$) = 2.53 (1H, dd, J = 2.25, 4.6), 2.83 (1H, dd, J = 6.6), 2.85 (1H, dd, J = 5.7), 2.96 (1H, dd, J = 6, 15), 3.19 (1H, m), 7.33–7.41 (5H). IR ($CHCl_3$) = 3000, 1610, 1450, 1260, 1135. Anal. Found: C, 80.39; H, 7.64. $C_9H_{10}O$ calcd.: C, 80.56; H, 7.51%.

1,2-epoxyeicosan-3-ol **20**. Eicos-1-en-3-ol, the starting alkene, was obtained by oxidation of eicosene by the SeO_2-^{t}BuOOH procedure [38]. Yield = 87%. m.p. = 58–59°C. ^1H NMR (80 MHz, $CDCl_3$) = 0.75–1.69 (35H), 1.74 (1H, exchanged with D_2O), 2.75 (2H, m), 2.97 (1H, m), 3.43 (1H, m). IR ($CHCl_3$) = 3595, 3490, 2925, 1470. Anal. Found: C, 76.89; H, 12.80. $C_{20}H_{40}O_2$ calcd.: C, 76.86; H, 12.90%.

Epoxides **5** and **19**: 3-benzenesulfonyl-1,2-epoxypropane, **5**. Epoxide **19** in methylene chloride was treated with *m*-chloroperbenzoic acid (3 equiv.) at 0°C. Yield = 86%. m.p. = 133–134°C. ^1H NMR (80 MHz, $CDCl_3$) = 2.43 (1H, m), 2.80 (1H, m), 3.32 (3H, m), 7.40–8.20 (5H). IR ($CHCl_3$) = 3025, 1450, 1330, 1235. Anal. Found: C, 54.83; H, 4.95. $C_9H_{10}SO_3$ calcd.: C, 54.53; H, 5.08%.

3-Phenylthio-1,2-epoxypropane, **19**, was obtained by reaction between thiophenate and epichlorohydrin [39]. Yield = 85%. b.p. = 152–154°C/9 mmHg (lit. [39] b.p. = 111–113°C/4 mmHg). ^1H NMR (80 MHz, $CDCl_3$) = 2.50 (1H, dd, J = 2, 5), 2.75 (1H, dd, J = 4, 5), 2.85–3.39 (3H), 7.12–7.61 (5H). IR ($CHCl_3$) = 3075, 3015, 1590, 1442, 1215. Anal. Found: C, 65.09; H, 6.19. $C_9H_{10}OS$ calcd.: C, 65.02; H, 6.06%.

Opening of oxiranes

General procedure: The epoxide was added to a stirred suspension of metal chlorides and solvent (25 ml/100 mg of substrate). At the end of the reaction, the mixture was washed successively with water and a saturated solution of sodium chloride. After drying over $MgSO_4$, the solvent was removed under reduced pressure. Purification of the residue was carried out on preparatory thin-layer-chromatography plates.

1-Benzenesulfonyl-3-chloropropan-2-ol, **6**. m.p. = 62–63°C. ^1H NMR (80 MHz, $CDCl_3$) = 3.42 (2H, d, J = 7), 3.5 (1H, exchanged with D_2O), 3.65 (2H, d, J = 5), 4.45 (1H, m), 7.52–8.20 (5H). IR ($CHCl_3$) = 3665, 3100, 1330, 1165, 1100. Anal. Found: C, 46.62; H, 4.99. $C_9H_{11}ClO_3S$ calcd.: C, 46.05; H, 4.72%.

1-Chloroeicosan-2-ol, **8**. m.p. = 58–59°C. ^1H NMR (80 MHz, $CDCl_3$) = 0.79–1.65 (37H), 2.1 (1H, exchanged with D_2O), 3.49 (2H, m), 3.74 (1H, m). IR ($CHCl_3$) = 3600, 3420, 2950, 1465. Anal. Found: C, 72.20; H, 14.44. $C_{20}H_{41}ClO$: C, 72.13; H, 12.41%.

2-Chloroeicosan-1-ol, **9**. m.p. = 45°C. ^1H NMR (80 MHz, $CDCl_3$) = 0.69–2.07 (37H), 1.90 (1H, exchanged with D_2O), 3.73 (2H, m), 3.99 (1H, m). IR ($CHCl_3$) =

3595, 3430, 2915, 2850, 1455. Anal. Found: C, 72.08; H, 12.26. $C_{20}H_{41}ClO$: C, 72.13; H, 12.41%.

2,2-Dimethyl-4-octadecyl-1,3-dioxolane, **10**. m.p. = 38°C. ^1H NMR (300 MHz, $CDCl_3$) = 0.89 (3H, t, $J = 6$), 1.16–1.44 (32H), 1.36 (3H, s), 1.42 (3H, s), 1.48 (1H, m), 1.65 (1H, m), 3.50 (1H, dd, $J = 7, 7$), 4.05 (2H, m). IR ($CHCl_3$) = 2980, 2850, 1470, 1215, 1160. Anal. Found: C, 78.04; H, 13.12. $C_{23}H_{46}O_2$ calcd.: C, 77.90; H, 13.07%.

Compound **10** was also obtained by reaction between **7** (112 mg) and acetone (5 ml) in the presence of BF_3-Et_2O (2 drops) at 0°C [21]. Yield = 71%.

8-Chlorotetradecan-7-ol, **21**. Oil. ^1H NMR (80 MHz, $CDCl_3$) = 0.87 (6H, m), 1.02–1.85 (23H), 1.94 (1H, exchanged with D_2O), 3.74 (1H, m), 3.99 (1H, m). IR ($CHCl_3$) = 3600, 3480, 2945, 2875, 1468. Anal. Found: C, 67.19; H, 11.69. $C_{14}H_{29}ClO$ calcd.: C, 67.57; H, 11.75%.

trans-2-Chlorocyclohexan-1-ol, **22** [37,40,41]. Oil. ^1H NMR (80 MHz, $CDCl_3$) = 0.97–2.43 (8H), 2.98–4.13 (2H). IR ($CHCl_3$) = 3510, 3420, 3000, 1445, 1220.

3α-Chloro-2β-hydroxy-5α-cholestane **23**. m.p. = 108°C (lit. [23,24] m.p. = 109–111°C). $[\alpha]_D = +52°$ ($c = 4.4$, $CHCl_3$) (lit. [19] $[\alpha]_D = +53°$).

2β-chloro-3α-hydroxy-5α-cholestane **24**. m.p. = 121–123°C (lit. [9,23,24] m.p. = 120–122°C). $[\alpha]_D = +39°$ ($c = 6.0$, $CHCl_3$) (lit. [19] $[\alpha]_D = +39°$).

2-chloro-2-phenylethan-1-ol, **25** [18]. Oil. ^1H NMR (80 MHz, $CDCl_3$) = 2.26 (1H, exchanged with D_2O), 3.93 (2H, d, $J = 6.5$), 4.99 (1H, t, $J = 6.5$), 7.18–7.52 (5H). IR ($CHCl_3$) = 3600, 3440, 3010, 2930, 1495. Anal. Found: C, 61.16; H, 5.92. C_8H_9ClO calcd.: C, 61.35; H, 5.79%.

2-Chloro-3-phenylpropan-1-ol, **26**. Oil. ^1H NMR (80 MHz, $CDCl_3$) = 2.12 (1H, exchanged with D_2O), 3.09 (2H, d, $J = 7$), 3.70 (2H, m), 4.21 (1H, m), 7.26 (5H, m). IR ($CHCl_3$) = 3600, 3450, 3080, 1210, 1080. Anal. Found: C, 63.25; H, 6.62. $C_9H_{10}ClO$ calcd.: C, 63.34; H, 6.50%.

1-Chloro-3-phenylpropan-2-ol, **27**. Oil. ^1H NMR (80 MHz, $CDCl_3$) = 2.32 (1H, exchanged with D_2O), 2.87 (2H, d, $J = 7$), 3.50 (2H, dd, $J = 2, 4$), 4.04 (1H, m), 7.24 (5H, m). IR ($CHCl_3$) = 3595, 3450, 3015, 1455, 1380. Anal. Found: C, 63.13; H, 6.57. $C_9H_{10}ClO$ calcd.: C, 63.34; H, 6.50%.

threo-2-Chloro-1,2-diphenylethan-1-ol, **28** [25–27]. m.p. = 42–43°C (lit. [26] m.p. = 47°C). ^1H NMR (300 MHz, $CDCl_3$) = 3.07 (1H, exchanged with D_2O), 4.93 (1H, d, $J = 8.1$), 5.01 (1H, d, $J = 8.1$), 7.04–7.35 (10H). ^{13}C NMR ($CDCl_3$) = 138.71, 137.65, 128.43, 128.05, 127.90, 126.69, 78.65, 70.50. IR ($CHCl_3$) = 3590, 3430, 3080, 1455, 1190.

2-Chloro-3-phenylthiopropan-1-ol, **31**. Oil. ^1H NMR (80 MHz, $CDCl_3$) = 2.02 (1H, exchanged with D_2O), 3.31 (2H, d, $J = 7$), 3.87 (2H, m), 3.57–4.22 (1H), 7.04–7.59 (5H). IR ($CHCl_3$) = 3610, 3460, 3075, 1610, 1440, 1385, 1270. Anal. Found: C, 53.43; H, 5.53. $C_9H_{11}ClOS$ calcd.: C, 53.30; H, 5.47%.

1-Chloroeicosan-2,3-diol, **32**. m.p. = 81–82°C. ^1H NMR (300 MHz, $CDCl_3$) = 0.9 (3H, t, $J = 7.1$), 1.12–1.63 (32H), 2.0–2.7 (2H, exchanged with D_2O), 3.55–3.82 (4H). IR ($CHCl_3$) = 3595, 3400, 2930, 2862. Anal. Found: C, 68.99; H, 11.72. $C_{20}H_{41}ClO_2$ calcd.: C, 68.83; H, 11.84%.

3-Benzenesulfonylpent-2-en-1-ol, **33**. m.p. = 138–139°C. ^1H NMR (80 MHz, $CDCl_3$) = 2.08 (1H, exchanged with D_2O), 4.34 (2H, m), 6.59 (1H, d, $J = 14.5$), 7.01 (1H, t, $J = 3$, 14.5), 7.40–7.91 (5H). IR ($CHCl_3$) = 3550, 2950, 1313. Anal. Found: C, 54.50; H, 5.14. $C_9H_{10}O_3S$: calcd.: C, 54.53; H, 5.08%.

4-Benzensulfonylmethyl-2,2-dimethyl-1,3-dioxolane, **34**. m.p. = 131–132°C. ^{1}H NMR (80 MHz, $CDCl_3$) = 1.27 (6H), 3.3 (2H, m), 3.75 (1H, dd, J = 5, 9), 4.04 (1H, dd, J = 6, 9), 4.28 (1H, m), 7.32–7.95 (5H). IR ($CHCl_3$) = 3020, 2960, 1460, 1385, 1320. Anal. Found: C, 56.13; H, 6.11. $C_{12}H_{16}O_4S$ calcd.: C, 56.23; H, 6.29%.

3-Benzensulfonyl-2-chloropropan-1-ol, **38**. m.p. = 48°C. ^{1}H NMR (80 MHz, $CDCl_3$) = 2.85 (1H, exchanged with D_2O), 3.60 (2H, dd, J = 7,7), 3.88 (2H, d, J = 4), 4.70 (1H, m), 7.37–8.01 (5H). IR ($CHCl_3$) = 3520, 3030, 2925, 1600, 1315.

3-(*p*-Tosyl)-2-chloropropan-1-ol, **39**. ^{1}H NMR (80 MHz, $CDCl_3$) = 2.35 (1H, exchanged with D_2O), 2.45 (3H, s), 3.57 (1H, d, J = 7), 3.67 (1H, d, J = 7), 3.94 (2H, d, J = 4), 4.41 (1H, m), 7.39 (2H, d, J = 8), 7.82 (2H, d, J = 8).

Other compounds and reactions

The acetoxylations of chlorohydrins were carried out in the presence of pyridine and acetic anhydride.

2-Acetoxy-1-chloroeicosane, **35**. ^{1}H NMR (80 MHz, $CDCl_3$) = 0.75–1.85 (37H), 2.01 (3H, s), 3.58 (2H, d, J = 4.5), 5.02 (1H, m). IR ($CHCl_3$) = 2918, 1722, 1450, 1210.

1-Acetoxy-2-chloro-2-phenylethane, **36**. Oil. ^{1}H NMR (80 MHz, $CDCl_3$) = 2.05 (3H, s), 4.45 (2H, d, J = 7), 5.06 (1H, t, J = 7), 7.06–7.53 (5H). IR ($CHCl_3$) = 2995, 1745, 1495, 1458. Anal. Found: C, 60.28; H, 5.73. $C_{10}H_{11}ClO_2$ calcd.: C, 60.46; H. 5.58%.

1-Acetoxy-2-chloro-3-phenylthiopropane, **37**. Oil. ^{1}H NMR (80 MHz, $CDCl_3$) = 2.02 (3H, s), 3.36 (2H, d, J = 6.5), 4.11 (1H, m), 4.36 (2H, m), 7.05–7.48 (5H). IR ($CHCl_3$) = 3028, 1745, 1600, 1380, 1150.

2-Acetoxy-3-chloro-1-(*p*-tosylpropane), **40**. ^{1}H NMR (80 MHz, $CDCl_3$) = 1.90 (3H, s), 2.46 (3H, s), 3.51 (2H, d, J = 6), 3.71 (2H, d, J = 4), 5.41 (1H, m), 7.32 (2H, d, J = 8), 7.79 (2H, d, J = 8). IR ($CHCl_3$) = 3030, 1745, 1600, 1320, 1145, 1085. Anal. Found: C, 49.79; H, 5.46. $C_{12}H_{15}ClO_4S$ calcd.: C, 49.47; H, 5.20%.

2,2-Dimethyl-5-chloromethyl-4-heptadecyl-1,3-dioxolane, **41**. An acetone solution of **32** containing a catalytic amount of *p*-toluenesulfonic acid, was stirred at room temperature for 2 h. After removal of solvent, the residue was purified by thin-layer chromatography (eluant: ethyl acetate/petroleum ether: 5/95). Yield = 95%. m.p. = 52–53°C. ^{1}H NMR (300 MHz, $CDCl_3$) = 0.88 (3H, t, J = 6.7), 1.17–1.67 (32H), 1.41 (3H, s), 1.43 (3H, s), 3.61 (2H, d, J = 4.5), 3.88 (2H, m). IR ($CHCl_3$) = 2980, 2880, 950. Anal. Found: C, 71.32; H, 11.76. $C_{23}H_{45}ClO_2$ calcd.: C, 71.0; H, 11.66%.

Benzophenone, **29**. A mixture of **30** (262 mg), $PdCl_2(CH_3CN)_2$ (3.4 mg, 0.01 equiv.) and $CuCl_2$ (245 mg, 1.2 equiv.) in CH_2Cl_2 (50 ml) was kept at 40–50°C under visible light irradiation for 17 h. The work-up was carried out as for the reaction with epoxides. Conversion: 98%. Yield: 88%.

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