

Regioselective Monoepoxidation of 1,3-Dienes Catalysed by Transition-metal Complexes

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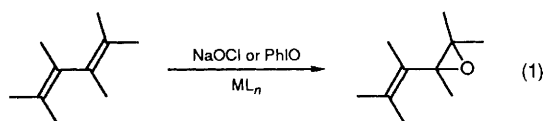
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A procedure for regioselective monoepoxidation of mainly the less substituted double bond of 1,3-dienes with sodium hypochlorite or iodosylbenzene using various metal complexes as catalysts is presented; the results obtained are different from those found when applying the usual epoxidation reagents.

Transition-metal complexes are effective catalysts for the oxidation of alkenes to epoxides,¹ both of which are fundamental intermediates in organic synthesis. The investigations of transition-metal catalysed epoxidations have been restricted mainly to isolated alkenes.^{1c} Only a few reports on attempts to epoxidize conjugated dienes have been published.²⁻⁴ Mo(CO)₆ and OV(acac)₂ have been shown to catalyse the epoxidation of buta-1,3-diene, penta-1,3-diene and isoprene with hydroperoxides as oxygen donors.² Hydroquinone was added in order to avoid polymeric materials when oxidizing buta-1,3-diene.^{2a} The epoxidation of isoprene gave 3,4-epoxy-3-methylbut-1-ene and 3,4-epoxy-2-methylbut-1-ene in a 4:1 molar ratio,^{2a} *i.e.* the more substituted double bond is most reactive towards these epoxidation reagents. When using *m*-CPBA as epoxidation reagent, mixtures of the possible epoxides are obtained together with polymeric materials.^{2a} Isoprene has been used as a model substrate for studying the regioselectivity in epoxidations catalysed by manganese porphyrins—a model system for the cytochrome P-450 enzymes, but no high regioselectivity was obtained.^{3b} Mn(salen) complexes have very recently been found to catalyse the enantioselective monoepoxidation of cyclo-octa-1,3-diene and (*E,Z*)-hexa-2,4-dienoic-acid-*tert*-butyl ester.⁴ In this communication we show that ML_{*n*} (M = Mn^{III}, Fe^{III}; L_{*n*} = salens, porphyrins) can act as effective catalysts

with sodium hypochlorite as well as iodosylbenzene as oxygen donor for the regioselective monoepoxidation of a variety of conjugated 1,3-dienes [reaction (1)]. The present method gives high yields of the corresponding monoepoxide and shows generally a high regioselectivity for epoxidation of the less substituted double bond of the 1,3-diene system—a regioselectivity which is significantly different from the results obtained by epoxidation with *m*-CPBA.

Treatment of the 1,3-dienes, 1–6, with sodium hypochlorite or iodosylbenzene as the terminal oxidant in the presence of Mn(tpp)Cl, Mn(tppCl₈)Cl, Mn(salen)Cl, Mn(salen-Bu^{*t*})Cl,⁵ 7, or Fe(tpp)Cl[†] as catalysts produces the corresponding



† Abbreviations: Hacac: pentane-2,4-dione; *m*-CPBA: *m*-chloroperbenzoic acid; tpp: *meso*-tetraphenylporphyrin; tppCl₈: *meso*-2,6-dichloro-tetraphenylporphyrin; salen: *N,N'*-ethylenebis(salicylidene-amino); salen-Bu^{*t*}: *N,N'*-ethylenebis-3,3'-di-*tert*-butyl-5,5'-dimethyl-salicylidene-amino).

Table 1 Results for the metal catalysed monoepoxidations of 1,3-dienes using sodium hypochlorite as oxygen donor. The total yield of epoxides is listed together with the relative distribution of the epoxides.

1,3-Diene	Epoxide	Mn(tpp)Cl		Mn(tppCl ₈)Cl		Mn(salen)Cl		Mn(salen-Bu ^t)Cl	
		Yield (%)	Distribution	Yield (%)	Distribution	Yield (%)	Distribution	Yield (%)	Distribution
Buta-1,3-diene, 1	3,4-Epoxybut-1-ene	61	—	—	—	40	—	50	—
Isoprene, 2	3,4-Epoxy-3-methylbut-1-ene (ms)	45 ^b	60	80 ^b	67	34	100	89 ^b	63
	3,4-Epoxy-2-methylbut-1-ene (ls)	—	40	—	33	—	0	—	37
2,4-Dimethylpenta-1,3-diene, 3	4,5-Epoxy-2,4-dimethylpent-2-ene (ls)	91 ^{b,c}	85	42 ^{b,c}	80	^d	—	100	88
	3,4-Epoxy-2,4-dimethylpent-1-ene (ms)	—	15	—	20	—	—	—	12
<i>(E)</i> -Hexa-1,3-diene, 4	1,2-Epoxy- <i>(E)</i> hex-3-ene (ls)	89 ^b	71	50 ^b	87	12 ^b	64	100 ^b	76
	<i>(E)</i> -3,4-Epoxyhex-1-ene (ms) ^a	—	29	—	13	—	36	—	24
1,4-Diphenylbuta-1,3-diene, 5	<i>(E)</i> -3,4-Epoxy-1,4-diphenyl- <i>(E)</i> -but-1-ene	100 ^b	92	—	—	78 ^b	80	100	84
	<i>(Z)</i> -3,4-Epoxy-1,4-diphenyl- <i>(E)</i> -but-1-ene	—	8	—	—	—	20	—	16
2,3-Dimethylbuta-1,3-diene, 6	3,4-Epoxy-2,3-dimethylbut-1-ene	—	—	—	—	13	—	75	—

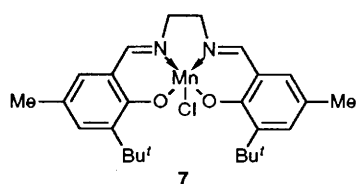
^a Traces of *(Z)*-3,4-epoxyhex-1-ene are seen. ^b Reaction temperature of 45–50 °C used. ^c Approximately 10% over oxidized products.

^d No epoxides observed after 24 h.

Table 2 Results for the metal catalysed monoepoxidations of 1,3-dienes using iodossylbenzene as oxygen donor. The total yield of epoxides is listed together with the relative distribution of the obtained epoxides.

1,3-Diene	Epoxide	Mn(tpp)Cl		Mn(tpp-Cl ₈)Cl		Fe(tpp)Cl		Mn(salen)Cl		Mn(salen-Bu ^t)Cl	
		Yield (%)	Distribution	Yield (%)	Distribution	Yield (%)	Distribution	Yield (%)	Distribution	Yield (%)	Distribution
Buta-1,3-diene, 1	3,4-Epoxybut-1-ene	87	—	—	—	—	—	92	—	71	—
Isoprene, 2	3,4-Epoxy-3-methylbut-1-ene (ms)	100	55	80	67	25	64	100	71	92	74
	3,4-Epoxy-2-methylbut-1-ene (ls)	—	45	—	33	—	36	—	29	—	26
2,4-Dimethylpenta-1,3-diene, 3	4,5-Epoxy-2,4-dimethylpent-2-ene (ls)	86	85	81	89	40	75	64	77	76	92
	3,4-Epoxy-2,4-dimethylpent-1-ene (ms)	—	15	—	11	—	25	—	23	—	8
<i>(E)</i> -Hexa-1,3-diene, 4	1,2-Epoxy- <i>(E)</i> hex-3-ene (ls)	87	77	59	86	39	74	87	71	59	85
	<i>(E)</i> -3,4-Epoxyhex-1-ene (ms) ^a	—	23	—	14	—	26	—	29	—	15
1,4-Diphenylbuta-1,3-diene, 5	<i>(E)</i> -3,4-Epoxy-1,4-diphenyl- <i>(E)</i> -but-1-ene	65	87	25	100	11 ^b	99	84	89	51	81
	<i>(Z)</i> -3,4-Epoxy-1,4-diphenyl- <i>(E)</i> -but-1-ene	—	13	—	0	—	1	—	11	—	19
2,3-Dimethylbuta-1,3-diene, 6	3,4-Epoxy-2,3-dimethylbut-1-ene	47	—	73	—	28	—	57	—	61	—

^a Traces of *(Z)*-3,4-epoxyhex-1-ene are seen. ^b Reaction temperature of 45–50 °C used.



monoepoxides.⁵ Tables 1 and 2 show the yields and regioselectivity for the epoxidation of the dienes, **1–6**, with the above catalysts and sodium hypochlorite (Table 1), respectively iodossylbenzene (Table 2) as oxygen donor.‡

The results in Tables 1 and 2 show that buta-1,3-diene, **1**, is epoxidized to 3,4-epoxybut-1-ene in high yields, when using Mn(tpp)Cl, Mn(salen)Cl or Mn(salen-Bu^t)Cl as catalysts and most efficient is iodossylbenzene as oxygen donor. Generally, the results in Tables 1 and 2 indicate that Mn(salen-Bu^t)Cl with sodium hypochlorite is the most effective system for formation of the monoepoxides. All the used manganese

complexes are better catalysts than the iron porphyrin complex, and the latter is deactivated when sodium hypochlorite is the terminal oxidant.

We will define a regioselectivity index calculated as the ratio between the yields of the less-substituted epoxide (ls) and the more-substituted epoxide (ms). All the catalysts give ls:ms regioselectivity ratios of about 0.5–0.8 with isoprene, **2**, as substrate. An exception is oxidation with Mn(salen)Cl and sodium hypochlorite, which shows a high regioselectivity for epoxidation of the more-substituted double bond without the formation of the less-substituted epoxide. Epoxidation of isoprene with *m*-CPBA gives a ls:ms regioselectivity of 0.16.

The catalyst Mn(salen-Bu^t)Cl has been found to be particularly successful in the epoxidation of 2,4-dimethylpenta-1,3-diene, **3**, as the regioselectivity for oxidation of the terminal double bond is found to be as high as 12, which is higher than the results obtained with the other catalysts. Epoxidation of *(E)*hexa-1,3-diene, **4**, shows high regioselectivity, and best are Mn(salen-Bu^t)Cl and Mn(tppCl₈)Cl as ls:ms ratios of ca. 6 are obtained, which compares with ratios of 1.8–3.3 with Mn(tpp)Cl, Mn(salen)Cl and Fe(tpp)Cl as catalysts. Traces of *(Z)*-3,4-epoxyhex-1-ene are also observed in these reactions. Epoxidation of **4** with *m*-CPBA gives a ls:ms epoxide ratio of 0.75. 1,4-Diphenyl-*(E,E)*buta-1,3-diene, **5**, is epoxidized to a mixture of the *(E,E)* and *(Z,E)* epoxides, where the *(E,E)*:*(Z,E)* epoxide ratio depends on the catalyst; Mn(salen)Cl with sodium hypochlorite gives a *(E,E)*:*(Z,E)* ratio of 4, whereas no isomerisation is observed with Mn(tppCl₈) and iodossylbenzene. Isomerisation of an *E*-isomer to the *Z*-epoxide is only observed very rarely in

‡ The following procedure for the monoepoxidations has been used: 1 mmol of the 1,3-diene is dissolved in 5–10 ml of CH₂Cl₂ or CDCl₃ (buta-1,3-diene is bubbled through the solvent) containing 0.025 mmol of the catalyst. A solution of commercial available sodium hypochlorite at a pH value of about 11.3 (2.5 mmol) using a Na₂HPO₄ buffer solution or 1.5 mmol iodossylbenzene is then added. The iodossylbenzene reactions are filtered through celite, and for the sodium hypochlorite reactions the organic phase is separated from the aqueous phase and filtered through celite. The products are analysed by ¹H NMR.

transition-metal catalysed epoxidations of isolated alkenes,⁶ and has also been observed in one case in the epoxidation of conjugated enynes using chiral Mn(salen) catalysts.⁴ Attempts to epoxidize **5** with *m*-CPBA at room temperature leads to polymerisation of either the diene or the epoxide and one has to perform the epoxidation with *m*-CPBA at -78°C to obtain the corresponding epoxide in good yields. The epoxidation of **5** using a sodium hypochlorite solution at different pH values (9.7–12.0) showed that the yield of the monoepoxide is highest at pH values between 10.6–11.3, and that the *E* to *Z* isomerisation is independent of the pH value of the sodium hypochlorite solution. 2,3-Dimethylbuta-1,3-diene, **6**, can also be monoepoxidized by the present catalytic method.

Work is in progress to develop catalysts that further optimize the regioselectivity of the epoxidation of conjugated dienes, but also metal complexes that can result in both regioselective and enantioselective monoepoxidation of selected double bonds in 1,3-dienes.

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