A Novel Catalytic Cycle for the Synthesis of Epoxides Using Sulfur Ylides

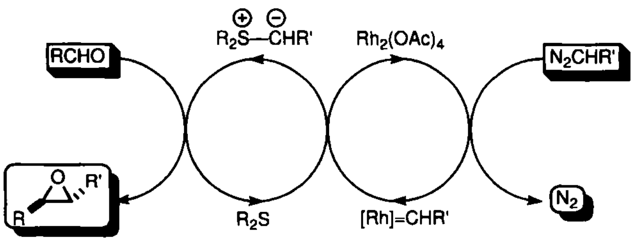
Varinder K. Aggarwal,* Hesham Abdel-Rahman, Li Fan, Ray V. H. Jones and Mike C. H. Standen

Abstract: A novel, neutral catalytic cycle for the synthesis of epoxides from carbonyl compounds and diazo compounds using catalytic quantities of transition metal salts and sulfides has been developed. In this catalytic cycle, the diazo compound is decomposed by the transition metal salt to give a metallocarbene, and this is picked up by the sulfide to give a sulfur ylide, which then reacts with the aldehyde to give an epoxide and returns the sulfide back into the catalytic cycle. To obtain good yields of epoxides it is necessary to maintain a low concentration of the diazo compound (by slow addition), otherwise dimerisation of the diazo compound is the dominant reaction. Factors affecting the outcome of the reaction were studied. The reactions are relatively insensitive to solvent, but are sensitive to the structure of the sulfide, the metal salt and the concentration. Unhindered sulfides give good yields of epoxides with any metal salt, but with hindered sulfides higher yields are obtained with $Cu(acac)_2$ than with $Rh_2(OAc)_4$. The yields of epoxides are sensitive to sulfide concentration especially when using substoichiometric amounts of sulfides. Higher concentration leads to faster rates of formation and subsequent reaction of the sulfur ylides, and consequently to higher yields. This novel catalytic cycle has also been applied to base-sensitive aldehydes. We found that our new catalytic cycle for epoxidation gives much improved yields of epoxides compared to those obtained by traditional sulfur ylide chemistry and is tolerant to a wide variety of sensitive functional groups. Ketones also participate in the catalytic cycle, although they give reduced yields of epoxides compared to aldehydes and require a slightly elevated temperature.

Keywords
catalysis · diazo compounds · epoxidations · sulfur ylides · synthetic methods

Introduction

Sulfur ylides have been extensively used for epoxidations of carbonyl compounds.[1-7] The standard conditions for this reaction utilise the original Corey method: treatment of a sulfonium salt with a strong base in the presence of an aldehyde.[1,8] We considered an alternative strategy which involved generating sulfur ylides from sulfides and diazo compounds,[9] since this would provide *neutral* reaction conditions for the epoxidation process. If sulfur ylides could be generated in the presence of an aldehyde, then the sulfide would be regenerated following epoxidation and, in principle, the reaction would be *catalytic in sulfide* (Scheme 1). The reaction of sulfides with diazo compounds to give sulfur ylides is well documented[9] and has been carried out thermolytically, photochemically[10] and more recently with transition metal catalysts.[9,11-14] Thus, there was ample precedent for the individual steps of the catalytic cycle, but none for the cycle itself. Of particular concern was the compatibility of the different reagents and the tuning of their reactivities so as to achieve the desired results. In this paper we provide a full account of this novel catalytic process.[15]



Scheme 1. Proposed catalytic cycle for epoxidation.

Results and Discussion

Development of Reaction Conditions: In attempting the catalytic process shown in Scheme 1, choice of diazo compound, catalyst and sulfide are critical. Most literature examples of sulfur ylide formation by this method use the reaction of diazocarbonyl compounds with sulfides, but the corresponding ylides are too stabilised and do not react with aldehydes.[16-19] Sulfur ylide formation with diazomethane is problematic owing to the high reactivity of this diazo compound and its tendency to dimerise very readily in the presence of transition metals.[20,21] We therefore chose phenyldiazomethane, as it is more stable than diazomethane,[22] has less of a tendency to dimerise than diazoalkanes,[23,24] and the corresponding sulfur ylide is known to react readily with aldehydes.[25] Another unwanted side reac-

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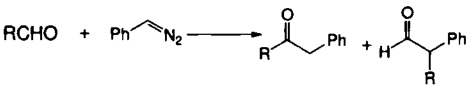
[*] V. K. Aggarwal,* H. Abdel-Rahman, L. Fan
Department of Chemistry, University of Sheffield, Sheffield S3 7HF (UK)
e-mail: v.aggarwal@sheffield.ac.uk
R. V. H. Jones, M. C. H. Standen
Zeneca FCMO, Process Technology Department
Earls Road, Grangemouth, Stirlingshire FK3 8XG (UK)

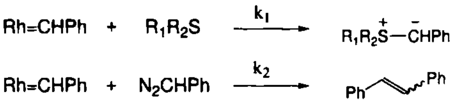
tion that could potentially occur is the direct reaction of the diazo compound with the carbonyl component to give homologated products (Scheme 2).[26] To limit the extent of this and the dimerisation of the diazo compound, it was decided to maintain a low concentration of the diazo compound by slow addition.

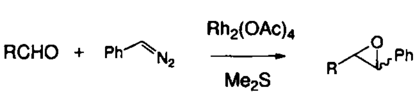

Scheme 2. Potential side reaction.

Similar problems relating to competitive dimerisation of diazo compounds during cyclopropanation of alkenes have also been solved by either using an excess of the alkene[23] or by slow addition of the diazo compound.[27]

Rhodium acetate was initially chosen as the catalyst, as this metal salt is commonly used for decomposition of diazo compounds and shown to be efficient for sulfur ylide formation in particular.[9] Diphenyl sulfide was initially chosen for convenience as it is easily manipulated and nonodorous. Stoichiometric amounts of sulfide were initially used before attempts were made to make the epoxidation process catalytic in sulfide (vide infra).

In our early attempts, a solution of phenyldiazomethane was added over three hours to a solution of PhCHO, Ph_2S and $Rh_2(OAc)_4$, but only stilbene was isolated. We were encouraged, however, by the lack of formation of homologated products, which indicated that direct addition of the diazo compound to the aldehyde was not a serious side reaction in this process. The formation of stilbene instead of epoxide indicated that the intermediate metallocarbene was being intercepted by the diazo compound at a faster rate than capture by sulfide ($k_2 > k_1$) (Scheme 3). Whilst it may have been possible to reduce the rate of dimerisation (k_2) further by even slower addition of phenyldiazomethane, this would have required inordinately long addition times for success. Instead, in an attempt to influence k_1, we used dimethyl sulfide rather than the less nucleophilic diphenyl sulfide,[28] and we were pleased to find clean epoxidation with essentially no stilbene formation (Scheme 4).


Scheme 3. Reactions of the rhodium carbenoid.


Scheme 4. Process of epoxidation.

A range of aldehydes were tested in the catalytic cycle and the results are summarised in Table 1. It was found that all aldehydes gave good yields of epoxides, but as mixtures of diastereomers. Aromatic aldehydes gave much higher ratios of *trans* epoxides than aliphatic aldehydes. Factors affecting the outcome of *cis–trans* selectivity in epoxidation has not been previously studied.

Table 1. Yields and ratios of epoxides formed from aldehydes (Scheme 4) [a].

Entry	Aldehyde	% Yield	*trans*:*cis*
1	benzaldehyde	70	88:12
2	*p*-nitrobenzaldehyde	79	>98:2
3	*p*-chlorobenzaldehyde	81	84:16
4	cyclohexane carboxaldehyde	66	79:21
5	isobutyraldehyde	64	60:40
6	valeraldehyde	55	56:44
7	ethyl-2-formyl-1-cyclopropane carboxylate	72	50:50

[a] Procedure: a solution of phenyldiazomethane (1.5 mmol in 6 mL *t*BuOMe) was added over 3 h to a solution of aldehyde (1 mmol), dimethyl sulfide (1 mmol) and $Rh_2(OAc)_4$ (0.01 mmol) in CH_2Cl_2 (4 mL), and the reaction mixture was stirred at RT for 18 h.

We confirmed that all the reagents were necessary for the operation of the catalytic cycle. Thus, in the absence of sulfide, only stilbenes were isolated, and in the absence of rhodium acetate only homologated products were obtained.

Solvent Effects: Reactions were carried out with both *p*-chlorobenzaldehyde and valeraldehyde in a variety of different solvents to determine the solvent effect on yield and diastereoselectivity of epoxidation, and the results are summarised in Table 2.

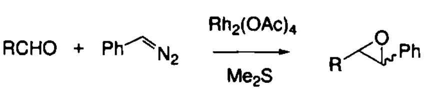
Table 2. Influence of solvent on the reaction in Scheme 4 [a].

Entry	Solvent	Aldehyde	% Yield	*trans*:*cis*
1	DMF	p-ClC_6H_4CHO	62	97:3
2	DMSO	p-ClC_6H_4CHO	52	100:0
3	MeCN	p-ClC_6H_4CHO	60	94:6
4	Me_2CO	p-ClC_6H_4CHO	56	95:5
5	$CHCl_3$	p-ClC_6H_4CHO	60	94:6
6	$PhCH_3$	p-ClC_6H_4CHO	80	94:6
7	DMF	n-C_4H_9CHO	60	89:11
8	DMSO	n-C_4H_9CHO	14	100:0
9	MeCN	n-C_4H_9CHO	58	86:14
10	Me_2CO	n-C_4H_9CHO	56	86:14
11	CH_2Cl_2	n-C_4H_9CHO	55	56:44
12	$PhCH_3$	n-C_4H_9CHO	70	83:17

[a] Procedure: a solution of phenyldiazomethane (1.5 mmol in 6 mL of solvent) was added over 3 h to a solution of aldehyde (1 mmol), dimethyl sulfide (1 mmol) and $Rh_2(OAc)_4$ (0.01 mmol) in solvent (4 mL), and the reaction mixture was stirred at RT for 18 h.

It was found that good yields were obtained in most solvents, and higher ratios of *trans* epoxides were obtained in more polar solvents. This observation suggests that there is an increasing degree of reversibility in betaine formation when the reactions are conducted in solvents of increasing polarity. In less polar solvents the rate of ring closure of the betaine is expected to be enhanced, and therefore the possibility of reversal back to the ylide and aldehyde is reduced.

Use of Catalytic Amounts of Sulfide: The reaction represented by Scheme 1 can, in principle, be catalytic in sulfide. However, with decreasing amounts of sulfide, we observed a corresponding reduction in the yield of epoxide and increase in the yield of stilbenes (Scheme 5). This indicated that sulfide was not turning over within the catalytic cycle and was being held up at either the sulfur ylide stage (slow reaction of the ylide with the aldehyde) or the betaine stage (slow ring closure of the betaine to release sulfide). In order to solve this problem we needed to either increase the rates of reactions of the sulfur ylide or allow the reactions more time to go to completion before the next addition of diazo compound. We elected to allow the reactions to go to



Me_2S (eq.)	yield of epoxide
0.1	0%
0.2	14%
0.5	42%
1.0	70%

Scheme 5. Attempts to use catalytic amounts of sulfide.

completion by slower addition of the diazo compound over a longer period of time. We were pleased to find that addition of phenyldiazomethane over 24 hours with 0.2 equivalents of sulfide gave stilbene oxide in good yield. A range of aldehydes were investigated, and the results are summarised in Table 3.

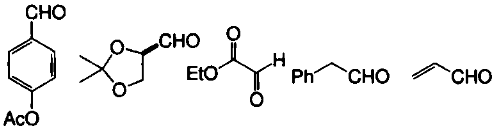
Table 3. Yields and ratios of epoxides formed from aldehydes with 0.2 equiv of dimethyl sulfide [a].

Entry	Aldehyde	% Yield	*trans*:*cis*
1	benzaldehyde	76	88:12
2	*p*-nitrobenzaldehyde	89	>98:2
3	*p*-chlorobenzaldehyde	76	84:16
4	cyclohexane carboxaldehyde	51	79:21
5	valeraldehyde	45	56:44
6	ethyl-2-formyl-1-cyclopropane carboxylate	54	50:50

[a] Procedure: a solution of phenyldiazomethane (1.5 mmol in 6 mL *t*BuOMe) was added over 24 h to a solution of aldehyde (1 mmol), dimethyl sulfide (0.2 mmol) and $Rh_2(OAc)_4$ (0.01 mmol) in CH_2Cl_2 (4 mL).

Application to Base-Sensitive Aldehydes: One of the significant features of this catalytic cycle is the neutral conditions for effecting epoxidation of carbonyl compounds, and this has been highlighted by carrying out the epoxidation of base-sensitive aldehydes.[29] A number of base-sensitive aldehydes (**1**–**5**) were subjected to epoxidation by the two traditional methods (KOH/NaOH[30, 31] in wet acetonitrile or dimsyl sodium in DMSO[1]) and by our newly developed catalytic cycle; the results are summarised Table 4.

Table 4. Yields and ratios of epoxides formed from aldehydes **1**–**5** under different conditions.



1 **2** **3** **4** **5**

Entry	Aldehyde	% Yield Me_2S [a]	 DMSO [b]	 KOH [c]	Ratio [d] (*trans*:*cis*)
1	**1**	73 (54 [e])	33	–	>95:5
2	**2**	78 (63 [e])	34	–	33:33:33 [f]
3	**3**	55 (45 [e])	53	–	100:0
4	**4**	83 (69 [e])	43	–	90:10
5	**5**	75 (43 [e])	23	16 [g]	92:8

[a] Procedure: a solution of phenyldiazomethane (1.5 mmol in 6 mL *t*BuOMe) was added over 24 h to a solution of aldehyde (1 mmol), dimethyl sulfide (0.5 mmol) and $Rh_2(OAc)_4$ (0.01 mmol) in CH_2Cl_2 (4 mL). [b] Dimsyl sodium in DMSO and dimethylbenzylsulfonium perchlorate (ref. [1]). [c] KOH in wet acetonitrile and dimethylbenzylsulfonium perchlorate (ref. [31]). [d] Ratio of epoxide diastereomers from the Me_2S reaction (determined by NMR integration). [e] 0.2 equiv of dimethyl sulfide. [f] *trans*–*trans*:*trans*–*cis*:*cis*–*cis* ratio of epoxy diastereoisomers. [g] Obtained from ref. [25].

For all the aldehydes tested, no epoxide was obtained with the KOH method, owing to their base sensitivity (except a low GC yield for acrolein[25]). The dimsyl sodium method gave lower yields of epoxides than our new catalytic cycle. Particularly noteworthy are the successes with glyoxylate **3** and acrolein **5** as these provide important epoxides with useful functionality for further manipulation.

Effect of Sulfide Structure and Metal Catalyst: The effect of sulfide structure on yield and diastereoselectivity in epoxidation was investigated, and the results are shown in Table 5. It was found that increasing steric hindrance of the sulfide resulted in reduced yields of epoxides and increased yields of stilbenes. Evidently, less nucleophilic sulfides were less able to react with the rhodium carbene (Scheme 3, top), and the dominant reaction became the reaction of the rhodium carbene with further diazo compound (Scheme 3, bottom).

Table 5. Yields and ratios of epoxides formed from aldehydes using different sulfides in the catalytic cycle [a].

Entry	Aldehyde	Sulfide	% Yield	*trans*:*cis*
1	*p*-ClC_6H_4CHO	Me_2S	81	86:14
2	*p*-ClC_6H_4CHO	THT [b]	84	86:14
3	*p*-ClC_6H_4CHO	EtS*i*Pr	56	(97:3)
4	*p*-ClC_6H_4CHO	*i*Pr_2S	24	100:0
5	*n*-C_4H_9CHO	*i*Pr_2S	0	–
6	PhCHO	MeSPh	0	–
7	PhCHO	Ph_2S	0	–

[a] Procedure: a solution of phenyldiazomethane (1.5 mmol in 6 mL *t*BuOMe) was added over 3 h to a solution of aldehyde (1 mmol), sulfide (1 mmol) and $Rh_2(OAc)_4$ (0.01 mmol) in CH_2Cl_2 (4 mL), and the reaction mixture was stirred at RT for 18 h. [b] Tetrahydrothiophene.

In order to influence the relative rates of the two equations shown in Scheme 3 (with the aim of increasing k_1 at the expense of k_2), we decided to alter the ligands around the rhodium, particularly since it had previously been shown that, in the case of intramolecular reactions, partitioning of reaction pathways can be dramatically influenced by altering ligands around rhodium.[32–35] A range of rhodium salts were therefore prepared and tested in the catalytic cycle. The results are summarised in Table 6.

It was found that changing ligands on rhodium did not substantially affect the relative rates of these processes. With hindered sulfides (entries 5, 6) only very low yields of epoxides were obtained (8–15%), but with unhindered sulfides (entries 1, 2, 4) much higher yields resulted (64–98%). Rhodium mandelate was a much less effective catalyst than any of the other rhodium

Table 6. Yields of epoxide formed from *p*-chlorobenzaldehyde using different rhodium salts [a].

Entry	Catalyst	Sulfide	% Yield
1	$Rh_2(O_2CCF_3)_4$	Me_2S	98
2	$Rh_2(CF_3CONH)_4$	Me_2S	94
3	$Rh_2(mandelate)_4$	Me_2S	17 (0% *ee*)
4	$Rh_2((5S)\text{-}MEPY_4)$ [b]	Me_2S	64 (0% *ee*)
5	$Rh_2(O_2CCF_3)_4$	*i*Pr_2S	8
6	$Rh_2(CF_3CONH)_4$	*i*Pr_2S	15
7	$Rh_2(mandelate)_4$	*i*Pr_2S	0

[a] Procedure: a solution of phenyldiazomethane (1.5 mmol in 6 mL CH_2Cl_2) was added over 3 h to a solution of aldehyde (1 mmol), sulfide (1 mmol) and rhodium salt (0.01 mmol) in CH_2Cl_2 (4 mL), and the reaction mixture was stirred at RT for 18 h. [b] Methyl 2-oxapyrrolidine-(5*S*)-carboxylate. [36]

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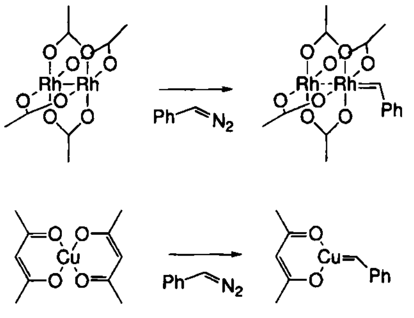
salts investigated (entries 3, 7). Chiral carboxamide ligands on rhodium were also investigated in the catalytic cycle, owing to their ability to induce high enantioselectivity in related cyclopropanation and C–H insertion reactions.[36] However, no enantioselectivity was obtained in epoxidation; this indicated that the sulfur ylide had probably dissociated from the metal at the time of reaction with the aldehyde.

We have interpreted our results in the following manner. It is believed that the rhodium carbene retains the ligands around rhodium and so presents a wall of ligands to an incoming nucleophile.[37] Therefore, the rate of reaction of the nucleophile with the metal carbenoid will be highly sensitive to the steric encumbrance of the nucleophile (Scheme 6). Thus, with increasing steric hindrance of the sulfide, k_1 will be reduced relative to k_2 (Scheme 3) and ultimately dimerisation of the diazo compound dominates. Changing the ligands around rhodium still leaves a wall of ligands around the carbenoid and evidently does not drastically alter the relative rates of the two processes. To allow efficient carbene transfer to hindered sulfides, less crowded metal carbenoids are therefore required. In principle, copper salts are ideal, as copper(II) is reduced to copper(I), and one of the charged ligands dissociates prior to formation of the carbenoid (Scheme 6).[38] The copper carbenoid should thus present a less sterically sensitive moiety to incoming nucleophiles. We therefore investigated various Cu salts, and the results are presented in Table 7.



Scheme 6. Carbenoids from Rh and Cu salts.

Table 7. Yields of epoxides formed from *p*-chlorobenzaldehyde and dimethyl sulfide in the presence of different copper salts [a].

Entry	Copper salts	% Yield
1	$Cu(OTf)_2$	30
2	$Cu(acac)_2$	97
3	$Cu(t_facac)_2$ [b]	84
4	$Cu(h_facac)_2$ [c]	44

[a] Procedure: a solution of phenyldiazomethane (1.5 mmol in 6 mL CH_2Cl_2) was added over 3 h to a solution of aldehyde (1 mmol), dimethyl sulfide (1.0 mmol) and Cu^{II} salt (0.1 mmol) in CH_2Cl_2 (4 mL), and the reaction mixture was stirred at RT for 18 h. [b] $Cu(trifluoroacetoacetate)_2$. [c] $Cu(hexafluoroacetoacetate)_2$.

Of the copper salts investigated, $Cu(acac)_2$ gave the highest yields in the epoxidation process. The lower yields obtained with the more electron deficient ligands around copper could be due to stronger complexation of the sulfide to the metal, resulting in a coordinatively saturated metal complex, thereby limiting its ability to effect decomposition of the diazo compound. We investigated the use of $Cu(acac)_2$ with various sulfides and *p*-chlorobenzaldehyde and the results are presented in Table 8.

Table 8. Yields of epoxides formed from *p*-chlorobenzaldehyde with $Cu(acac)_2$ and different sulfides [a].

Entry	Sulfide	% Yield of epoxide	*trans*:*cis*
1	Me_2S	97	90:10
2	Et*Si*Pr	53	100:0
3	iPr_2S	44	100:0
4	MeSPh	60	77:23

[a] Procedure: a solution of phenyldiazomethane (1.5 mmol in 6 mL CH_2Cl_2) was added over 3 h to a solution of *p*-chlorobenzaldehyde (1 mmol), sulfide (1.0 mmol) and $Cu(acac)_2$ (0.1 mmol) in CH_2Cl_2 (4 mL), and the reaction mixture was stirred at RT for 18 h.

It was found that higher yields of epoxides were indeed obtained with $Cu(acac)_2$ compared to $Rh_2(OAc)_4$ for all sulfides, and that the Cu complex was less sensitive to the steric and electronic nature of the sulfide used. Notably, thioanisole gave epoxide in 60% yield (Table 8, entry 4), whereas no epoxide was obtained in the corresponding reaction using $Rh_2(OAc)_4$ (Table 5, entry 6). It was also noted that higher *trans*:*cis* ratios of epoxides were obtained with more hindered sulfides. However, surprisingly, thioanisole gave a much poorer *trans*:*cis* ratios than the dialkyl sulfides.[40]

Attempts at carrying out the reaction with catalytic amounts of Et*Si*Pr (used as a representative hindered sulfide) resulted in epoxidation but with reduced yields (23%; Table 9, entry 1).

Table 9. Yields and ratios of epoxides formed from aldehydes.

Entry	Aldehyde	% Yield	*trans*:*cis*
1	$p\text{-}ClC_6H_4CHO$	23 [a]	100:0
2	$p\text{-}ClC_6H_4CHO$	90 [b]	100:0
3	$p\text{-}ClC_6H_4CHO$	94 [c]	100:0
4	PhCHO	73 [c]	98:2
5	$p\text{-}NO_2C_6H_4CHO$	82 [c]	100:0
6	$cyclo\text{-}C_6H_{11}CHO$	64 [c]	67:33
7	$n\text{-}C_4H_9CHO$	61 [c]	67:33

[a] A total volume of 10 mL of CH_2Cl_2 was used. [b] Procedure: a solution of phenyldiazomethane (1.5 mmol in 1 mL CH_2Cl_2) was added over 16 h to a solution of aldehyde (1 mmol), ethyl isopropyl sulfide (0.2 mmol) and $Cu(acac)_2$ (0.1 mmol) in CH_2Cl_2 (1ml). [c] As in [b] but addition over 3 h.

Since the sulfide is involved in the rate-limiting steps, reduced concentration of sulfide would necessarily reduce rates. We therefore decided to maintain the original concentrations by reducing the volume of solvent by the same factor as the reduction in the amount of sulfide used. Following this change we were pleased to find significantly improved yields in the epoxidation process (Table 9, entry 2). Under these more concentrated conditions we also found that the addition of the diazo compound could be conducted over a shorter period of time without suffering from reduced yields (Table 9, entry 3). These are now the conditions of choice for the catalytic epoxidation process and were applied to a range of aldehydes (Table 9, entries 4–7).

Application to Ketones: It is known that dimethylbenzylsulfonium ylide reacts with ketones to give epoxides, but the reactions require elevated temperatures (60 °C).[25] We therefore investigated reactions with cyclohexanone at various temperatures (Table 10, entries 1–3). In order to allow variation in reaction temperature, we decided to use the higher boiling sulfide tetrahydrothiophene instead of dimethyl sulfide. It was found that optimum yields were obtained at 35 °C. Presumably, at lower temperature the ylide does not react rapidly enough, and at elevated temperature the ylide may suffer decomposition. Several other ketones were studied at 35 °C, and moderate yields of epoxides were obtained (Table 10, entries 4, 5).

Table 10. Yield of epoxides formed from ketones with 1.0 equiv of tetrahydrothiophene [a].

Entry	Ketone	T/°C	% Yield
1	cyclohexanone	RT	10
2	cyclohexanone	35	45
3	cyclohexanone	60	0
4	*p*-nitroacetophenone	35	62
5	acetophenone	35	38

[a] Procedure: a solution of phenyldiazomethane (1.5 mmol in 1 mL CH_2Cl_2) was added over 3 h to a solution of ketone (1 mmol), tetrahydrothiophene (1.0 mmol) and $Cu(acac)_2$ (0.1 mmol) in CH_2Cl_2 (1ml) at 35 °C.

Sulfide–Rhodium Complexes: Sulfides are well known to poison transition metal catalysts. Indeed, upon addition of dimethyl sulfide to a suspension of $Rh_2(OAc)_4$, the metal salt dissolved completely and the colour changed from green to red; this indicated that the sulfide had complexed to rhodium[41] (through the vacant axial coordination sites). However, this would give rise to a coordinatively saturated complex, which would not be capable of decomposing a diazo compound. We therefore studied the rate of decomposition of phenyldiazomethane in the presence of $Rh_2(OAc)_4$ with and without dimethyl sulfide. We found that, in the absence of dimethyl sulfide, rapid evolution of nitrogen occurred at −20 °C; in the presence of sulfide, decomposition was slower by at least an order of magnitude.

The nature of the complex between dimethyl sulfide and $Rh_2(OAc)_4$ was studied by ^1H NMR. Dimethyl sulfide was titrated into a solution of $Rh_2(OAc)_4$, and ^1H NMR spectra were recorded (Fig. 1). The peak at $\delta = 1.9$ corresponds to the methyl signal of $Rh_2(OAc)_4$ and remains invariant throughout the NMR study. It was found that, when the sulfide concentration was increased up to a 1:2 ratio of $Rh_2(OAc)_4$:Me_2S, a single peak for Me_2S was observed at $\delta = 2.58$ (Fig. 1, spectra a,b). This species corresponded to sulfide bound to rhodium. Above this concentration, the Me_2S peak shifted upfield, but only one peak was observed (Fig. 1, spectra c–f). This indicated that a time-averaged signal for free and bound Me_2S was obtained and that free and bound Me_2S were in rapid equilibrium. Thus, decomposition of the diazo compound can occur when the sulfide decomplexed from the rhodium, and the much slower rate of decomposition of the diazo compound in the presence of sulfide is due to the much lower concentration of sulfide-free metal.

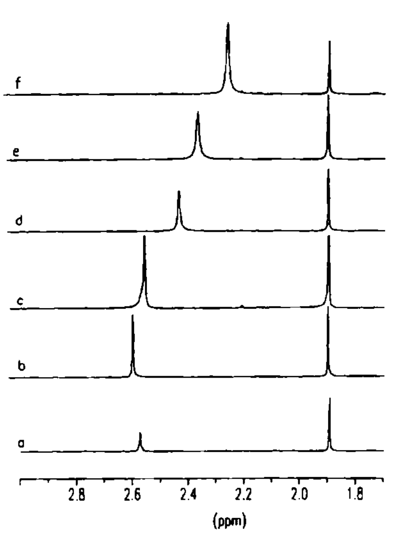


Fig. 1. ^1H NMR spectra of the titration of Me_2S into a solution of $Rh_2(OAc)_4$ in $CDCl_3$. The ratio of $Rh_2(OAc)_4$:Me_2S was a) 1:1, b) 1:2, c) 1:3, d) 1:4, e) 1:5 and f) 1:10.

Conclusion

We have found conditions under which epoxides can be obtained from aldehydes using catalytic quantities of sulfides. The reactions are relatively insensitive to solvent, but are sensitive to sulfide structure, metal salt and concentration. Unhindered sulfides give good yields of epoxides with any metal salt, but with hindered sulfides higher yields of epoxides are obtained with $Cu(acac)_2$. The yields of epoxides are sensitive to sulfide concentration especially when using substoichiometric amounts of sulfides. Higher concentrations lead to faster rates of formation and subsequent reaction of the sulfur ylides and consequently to higher yields. This novel catalytic cycle has also been applied to base-sensitive aldehydes. We found that our new catalytic cycle for epoxidation gives much improved yields of epoxides compared to those obtained by traditional sulfur ylide chemistry and is tolerant to a wide variety of sensitive functional groups. Ketones also participate in the catalytic cycle although they give reduced yields of epoxides compared to aldehydes and require a slightly elevated temperature.

Experimental Procedure

General: All reactions were run under a nitrogen atmosphere. Melting points were determined on a Reichert hot stage micro melting point apparatus and are uncorrected. ^1H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded in $CDCl_3$ on a Bruker AC-250 instrument unless otherwise noted. Chemical shifts (δ) are given in ppm units relative to $CHCl_3$. Infrared spectra were run on a Perkin-Elmer 684 Spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyser. Commercially available inorganic reagents were used without further purification. Rhodium trifluoroacetamide [42], rhodium trifluoroacetate [43], rhodium mandelate [44], copper acetylacetonate [45] and phenyldiazomethane [46] were prepared according to literature procedures. Compounds were purified by flash column chromatography on silica gel 40–63 mesh. All liquid aldehydes and ketones were distilled prior to use. Solid aldehydes and ketones were used without further purification. Tetrahydrofuran (THF) was distilled from K-benzophenone ketyl under nitrogen. Dichloromethane and 1,2-dichloroethane were distilled from CaH_2. When epoxides were obtained as a mixture of diastereoisomers, then superscripted c = *cis* and superscripted t = *trans*.

Preparation of epoxides using 1 equiv of dimethyl sulfide: Phenyldiazomethane (1.5 mmol in 6 mL of *t*BuOMe) was added to a solution of $Rh_2(OAc)_4$ (0.01 mmol), dimethyl sulfide (1 mmol) and aldehyde (1 mmol) in CH_2Cl_2 (4 mL) over 3 h by means of a syringe pump. After the addition was complete the reaction mixture was stirred at room temperature for 18 h. The solvent was removed in vacuo, and the residue was chromatographed over silica to give the corresponding epoxide.

***trans*-Stilbene oxide**: After chromatography [eluent CH_2Cl_2:petroleum ether (2:3), $R_f = 0.35$] the epoxide was obtained in 70% yield as a white solid, m.p. 67–68 °C (ref. [47]: 69 °C). ^1H NMR ($CDCl_3$): $\delta = 7.35$ (m, 10H, ArH), 3.85^t (s, 2H, 2 × CH).

***trans*-2-(4-Nitrobenzenyl)-3-phenyloxirane**: After chromatography [eluent CH_2Cl_2:petroleum ether (2:3), $R_f = 0.25$] this epoxide was obtained in 79% yield as a white solid, m.p. 126–128 °C (ref. [47]: 127 °C). ^1H NMR ($CDCl_3$): $\delta = 8.30$ (m, 2H, ArH), 7.30 (m, 7H, ArH), 3.98 (d, $^3J(H,H) = 1.9$ Hz, 1H, CH), 3.85 (d, $^3J(H,H) = 1.9$ Hz, 1H, CH). IR ($CHCl_3$): $\tilde{\nu} = 2290$, 1600, 1510, 1460, 1350, 1100, 860, 840 and 760 cm^{-1}.

2-(4-Chlorobezenyl)-3-phenyloxirane: After chromatography [eluent CH_2Cl_2:petroleum ether (2:3), $R_f = 0.35$] this epoxide was obtained (84:16, *trans*:*cis*) in 81% yield as a white solid, m.p. 90–91 °C (ref. [48]: 91–93 °C). ^1H NMR ($CDCl_3$): $\delta = 7.04$–7.50 (m, 9H, ArH), 4.37^c (d, $^3J(H,H) = 4.6$ Hz, 1H, CH), 4.31^c (d, $^3J(H,H) = 4.6$ Hz, 1H, CH), 3.85^t (d, $^3J(H,H) = 1.8$ Hz, 1H, CH),

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3.82^{t} (d, ^{3}J(H,H) = 1.8 Hz, 1 H, CH). IR ($CHCl_3$): $\tilde{\nu}$ = 3030, 1495, 1460, 1420, 1090, 1010, 820 and 750 cm^{-1}.

2-Cyclohexyl-3-phenyloxirane: After chromatography [eluent CH_2Cl_2:petroleum ether (2:3), R_f = 0.30] this epoxide was obtained (79:21, *trans*:*cis*) in 66% yield as a clear oil. ^{1}H NMR ($CDCl_3$): δ = 7.20 (m, 5 H, ArH), 4.08^{c} (d, ^{3}J(H,H) = 4.2 Hz, 1 H), 3.68^{t} (d, ^{3}J(H,H) = 2.1 Hz, 1 H), 2.91^{c} (dd, ^{3}J(H,H) = 8.9 Hz, ^{3}J(H,H) = 4.2 Hz, 1 H, CH), 2.76^{t} (dd, ^{3}J(H,H) = 6.8 Hz, ^{3}J(H,H) = 2.1 Hz, 1 H, CH), 2.09–0.76 (m, 10H, 5xCH_2). ^{13}C NMR ($CDCl_3$): δ = 138.18 (C), 135.18 (C), 128.42 (CH), 127.97 (CH), 127.91 (CH), 127.35 (CH), 126.33 (CH), 125.50 (CH), 67.43 (CH), 63.92 (CH), 57.46 (CH), 40.53 (CH), 34.92 (CH), 30.33 (CH_2), 29.62 (CH_2), 29.02 (CH_2), 28.10 (CH_2), 26.29 (CH_2), 26.20, (CH_2), 25.71 (CH_2), 25.56 (CH_2), 25.27 (CH_2). IR ($CHCl_3$): $\tilde{\nu}$ = 2980, 1450, 1400, 1320, 1180, 1090, 1040, 870 and 750 cm^{-1}. Calcd. for $C_{12}H_{16}O$, C 81.77, H 9.15; found C 81.54, H 9.35.

2-(1-Methylethyl)-3-phenyloxirane: After chromatography [eluent CH_2Cl_2:petroleum ether (2:3), R_f = 0.28] this epoxide was obtained (60:40, *trans*:*cis*) in 64% yield as a clear oil. ^{1}H NMR ($CDCl_3$): δ = 7.35 (m, 5 H, ArH), 4.05^{c} (d, ^{3}J(H,H) = 4.2 Hz, 1 H, CH), 3.60^{t} (d, ^{3}J(H,H) = 2.2 Hz), 2.85^{c} (dd, ^{3}J(H,H) = 4.2 Hz, ^{3}J(H,H) = 2.2 Hz, 1 H, CH), 2.70^{t} (dd, ^{3}J(H,H) = 4.2 Hz, ^{3}J(H,H) = 2.2 Hz, 1 H, CH), 1.64 (m, 1 H, CH), 1.02 (d, ^{3}J(H,H) = 6 Hz, 3 H, CH_3), 0.90 (d, ^{3}J(H,H) = 6 Hz, 3 H, CH_3) [ref. [49]: 4.10^{c} (d, ^{3}J(H,H) = 4.15 Hz, 1 H, CH), 3.66^{t} (d, ^{3}J(H,H) = 2.22 Hz, 1 H, CH), 2.86^{c} (d, ^{3}J(H,H) = 4.15 Hz, 1 H, CH), 2.76^{t} (d, ^{3}J(H,H) = 2.22 Hz, 1 H, CH]. ^{13}C NMR ($CDCl_3$): δ = 138.05 (C), 135.85 (C), 128.43 (CH), 127.97 (CH), 127.38 (CH), 126.32 (CH), 125.52 (CH), 68.36 (CH), 65.18 (CH), 57.79 (CH), 57.65 (CH), 30.984 (CH), 25.87 (CH), 19.91 (CH_3), 19.04 (CH_3), 18.43 (CH_3), 17.91 (CH_3).

2-*n*-Butyl-3-phenyloxirane: After chromatography [eluent CH_2Cl_2:petroleum ether (2:3), R_f = 0.28] this epoxide was obtained (56:44, *trans*:*cis*) in 55% yield as a clear oil. ^{1}H NMR ($CDCl_3$): δ = 7.35 (m, 5 H, ArH), 4.08^{c} (d, ^{3}J(H,H) = 4.3 Hz, 1 H, CH), 3.61^{t} (d, ^{3}J(H,H) = 2.1 Hz, 1 H, CH), 3.15^{c} (m, 1 H, CH), 2.95^{t} (dt, ^{3}J(H,H) = 2.1, 5.5 Hz, 1 H, CH), 1.90–0.90 (m, 7 H, n-C_3H_7). ^{13}C NMR ($CDCl_3$): δ = 137.98 (C), 135.82 (C), 128.58 (CH), 128.44 (CH), 127.98 (CH), 127.43 (CH), 126.49 (CH), 125.53 (CH), 63.12 (CH), 62.85 (CH), 59.57 (CH), 58.64, 57.46 (CH), 32.08 (CH_2), 28.18 (CH_2), 28.02 (CH_2), 22.55 (CH_2) 14.02 (CH_3), 13.89 (CH_3). Calcd. for $C_{14}H_{18}O$, C 83.12, H 8.97; found C 83.24, H 8.68.

Epoxide derived from ethyl-2-formyl-1-cyclopropanecarboxylate: After chromatography [eluent CH_2Cl_2:petroleum ether (2:3), R_f = 0.30] this epoxide was obtained (50:50, *trans*:*cis*) in 72% yield as a clear oil. ^{1}H NMR ($CDCl_3$): δ = 7.25 (m, 5H, ArH), 4.2 (m, 2 H, CH_2), 3.65^{c} (d, ^{3}J(H,H) = 1.8 Hz, 1 H, CH), 3.60^{t} (d, ^{3}J(H,H) = 1.8 Hz, 1 H, CH), 2.95^{c} (dd, ^{3}J(H,H) = 2.0 Hz, ^{3}J(H,H) = 3.5 Hz, 1 H, CH), 2.8^{t} (dd, ^{3}J(H,H) = 2.0 Hz, ^{3}J(H,H) = 4.7 Hz, 1 H, CH), 1.75 (m, 2 H, CHCH), 1.25 (m, 5 H, CHCH + CH_3). Calcd. for $C_{14}H_{16}O_3$, C 72.39, H 6.94; found C 72.51, H 6.73.

***trans-p*-Acetoxy stilbene oxide**: After chromatography [eluent CH_2Cl_2:petroleum ether (2:3), R_f = 0.35] this epoxide was obtained in 73% yield as a white foam. ^{1}H NMR ($CDCl_3$): δ = 7.10–7.45 (m, 9 H, ArH), 3.86 (d, ^{3}J(H,H) = 1.7 Hz, 1 H, CH), 3.83 (d, ^{3}J(H,H) = 1.7 Hz, 1 H, CH) 2.25 (s, 3 H, CH_3). Calcd. for $C_{16}H_{14}O_3$, C 75.58, H 5.55; found C 75.64, H 5.68 .

1-Phenyl-1,2-anhydro-3,4-isopropylidene erythritol: After chromatography [eluent CH_2Cl_2:petroleum ether (2:3), R_f = 0.35] this epoxide was obtained (33:33:33, *trans*:*trans*:*cis*) in 78% yield as a clear oil. ^{1}H NMR ($CDCl_3$): δ = 7.40–7.20 (m, 5 H, ArH), 4.30–$3.90^{c,t}$ (m, 3 H, CH + CH_2), 3.80–$3.10^{c,t}$ (m, 2 H, CH + CH), 1.30 (s, 3 H, CH_3) 1.25 (s, 3 H, CH_3). Calcd. for $C_{15}H_{13}O_3$, C 70.89; H 7.32; found C 70.91; H 7.10.

Ethyl-2,3-epoxy-3-phenyl propionate: After chromatography [eluent CH_2Cl_2:petroleum ether (2:3), R_f = 0.33] this epoxide was obtained in 55% yield as a white foam. ^{1}H NMR ($CDCl_3$): δ = 7.3–7.1 (m, 5 H, ArH), 4.30 (m, 2 H, CH_2), 4.12^{c} (d, ^{3}J(H,H) = 2.0 Hz, 1 H, CH), 3.50^{t} (d, ^{3}J(H,H) = 2.0 Hz, 1 H, CH), 1.25 (t, ^{3}J(H,H) = 7.0 Hz, 3 H, CH_3) [ref. [50]: 4.00 (d, 1 H, CH), 3.34 (d, 1 H, CH) in CCl_4].

1,3-Diphenyl-2,3-epoxypropane: After chromatography [eluent CH_2Cl_2:petroleum ether (2:3), R_f = 0.35] this epoxide was obtained (90:10, *trans*:*cis*) in 83% yield as a clear oil. ^{1}H NMR ($CDCl_3$): δ = 7.3–7.1 (m, 10 H, ArH), 4.15^{c} (d, ^{3}J(H,H) = 4.5 Hz, 1 H, CH), 3.7^{t} (d, ^{3}J(H,H) = 2.0 Hz, 1 H, CH), 3.45^{c} (dt, ^{3}J(H,H) = 4.5 Hz, ^{3}J(H,H) 6 Hz, 1 H, CH), 3.20^{t} (dt, ^{3}J(H,H) = 6 Hz, ^{3}J(H,H) = 2.0 Hz, 1 H, CH), 3.10 (d, ^{3}J(H,H) = 6 Hz, 2 H, CH_2), 2.8^{c} (dd, ^{3}J(H,H) = 6, 4.5 Hz, 1 H, C*H*CH), 2.55^{c} (dd, ^{3}J(H,H) = 6, 4.5 Hz, 1 H, CHCH), [ref. [51] 4.11^{c} (d, ^{3}J(H,H) = 4.5 Hz, 1 H, CH), 3.64^{t} (d, ^{3}J(H,H) = 2.0 Hz, *1 H*, CH)].

2-Phenyl-3-vinyloxirane: After chromatography [eluent CH_2Cl_2:petroleum ether (2:3), R_f = 0.28] this epoxide was obtained (92:8, *trans*:*cis*) in 75% yield as a clear oil. ^{1}H NMR ($CDCl_3$): δ = 7.20 (m, 5 H, ArH), 5.75 (m, 1 H, CH), 5.50 (dd, ^{3}J(H,H) = 2 Hz, ^{3}J(H,H) = 12 Hz, 1 H, CH), 4.85 (dd, ^{3}J(H,H) = 2 Hz, ^{3}J(H,H) = 9 Hz, 1 H, CH), 3.55 (d, ^{3}J(H,H) = 2 Hz, 1 H, CH), 3.30 (dd, ^{3}J(H,H) = 2 Hz, ^{3}J(H,H) = 6 Hz, 1 H, CH) [ref. [52] 3.30 (dd, ^{3}J(H,H) = 2 Hz, ^{3}J(H,H) = 6 Hz, 1 H, CH].

Preparation of epoxides using Cu(acac)$_2$ and 0.2 equiv of ethyl isopropyl sulfide: Phenyldiazomethane (1.5 mmol in 1 mL of CH_2Cl_2) was added to a solution of Cu(acac)$_2$ (0.1 mmol), sulfide (0.2 mmol) and aldehyde (1 mmol) in CH_2Cl_2 (1 mL) over 3 h by means of a syringe pump. After the addition was complete the reaction mixture was stirred at room temperature for 18 h. The solvent was removed in vacuo, and the residue chromatographed over silica to give the corresponding epoxide. Yields and diastreoselectivities with various aldehydes are given in the text. The products had the same data as those obtained from reactions carried out previously.

Epoxides derived from ketones: The following general procedure was used in all of the reactions. To a stirred solution of dimethyl sulfide (1.0 mmol), Cu(acac)$_2$ (0.1 mmol) and the ketone (1 mmol) in CH_2Cl_2 (1 mL) was added a solution of phenyldiazomethane (1.5 mmol in 1 mL of CH_2Cl_2) at 25–35 °C over a period of 3 h. After the addition was complete the solvent was removed in vacuo and the residue was chromatographed over silica [eluent CH_2Cl_2:petroleum ether (2:3)].

Epoxide derived from cyclohexanone: Following the procedure above and after chromatography [eluent CH_2Cl_2:petroleum ether (2:3), R_f = 0.30] this epoxide was obtained in 45% yield as a clear oil. ^{1}H NMR ($CDCl_3$): δ = 7.41–7.20 (m, 5H, ArH), 3.88 (s, 1 H, CH), 1.91–1.18 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ = 136.35 (C), 127.94 (CH), 127.23 (CH), 126.33 (CH), 65.50 (C), 64.54 (CH), 35.45 (CH_2), 28.39 (CH_2), 25,49 (CH_2), 25.34 (CH_2) 24.53 (CH_2). IR ($CHCl_3$): $\tilde{\nu}$ = 2975, 1455, 1400, 1325, 1180, 1090, 1040, 870 and 750 cm^{-1}.

***trans*-2-(4-Nitrobenzenyl)-2-methyl-3-phenyloxirane**: Following the procedure above and after chromatography [eluent CH_2Cl_2:petroleum ether (2:3), R_f = 0.25] this epoxide was obtained in 62% yield as a yellow solid, m.p. 126–128 °C. ^{1}H NMR ($CDCl_3$): δ = 8.05 (m, 2 H, ArH), 6.95–7.45 (m, 7 H, ArH), 4.25 (s, 1 H, CH), 1.8 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 145.81 (C), 134.46 (CH_3), 127.96 (CH), 127.90 (CH), 127.79 (CH), 123.17 (CH), 65.68 (CH), 65.26 (C), 24.77 (CH_3). IR ($CHCl_3$): $\tilde{\nu}$ = 2290, 2920, 1600, 1520, 1450, 1350, 1250, 1050, 1010 and 860 cm^{-1}. Calcd. for $C_{15}H_{13}NO_3$, C 70.58; H 5.13; N 5.05 found C 70.26; H 5.16; N 4.87.

***trans*-2,3-Diphenyl-2-methyloxirane**: Following the procedure above and after chromatography [eluent CH_2Cl_2:petroleum ether (2:3), R_f = 0.30] this epoxide was obtained in 38% yield as a white solid, m.p. 46–47 °C (ref. [25]: 45–47 °C). ^{1}H NMR ($CDCl_3$): δ = 7.50–7.00 (m, 10 H, ArH), 4.20 (s, 1 H, CH), 1.80 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 138.37 (C), 135.56 (C), 127.80 (CH), 127.61 (CH), 127.31 (CH), 127.07 (CH), 126.99 (CH), 126.52 (CH), 66.08 (C), 65.59 (CH), 25.75 (CH_3).

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