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Catalytic ferrocenyl sulfides for the asymmetric transformation of aldehydes into epoxides

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Abstract—Six ferrocenyl sulfides, exhibiting planar and central chiralities, have been screened as a catalytic source of asymmetric sulfonium ylides. A one-pot reaction has been achieved, involving the addition of an aldehyde, benzyl bromide, 20% molar equivalent of the ferrocenyl sulfide, sodium iodide in a mixture of *tert*-butanol and water. The best results were observed with enantiopure sulfide **3a**, bearing a *tert*-butyl group. Good yields of stilbene oxides were obtained, with enantiomeric excesses ranging from 74% to 94%. *trans*/*cis*-Diastereomeric ratios ranged from 60:40 to 86:14. The chiral sulfide was recovered. An unexpected case of stereoconvergence was observed with diastereoisomers **3a** and **3b**. A model is proposed to account for the asymmetric induction, based on a conformation locked by the *tert*-butyl group and the interplay of planar and remote central chiralities.

1. Introduction

The search for new, efficient, and economically viable catalysts for asymmetric organic synthesis[1–3] has led to numerous investigations for the design of a variety of structures. Ferrocenes have provided[4–9] sound applications of their potential planar chirality, which can be complemented by central chirality.

We have explored ferrocenes bearing a sulfide moiety as a new source for chiral sulfonium ylides. The last 10 years[10,11] have witnessed the emergence of sulfur ylides for the asymmetric conversion of aldehydes into oxiranes.[12–23] This reaction has recently been made catalytic as far as the sulfide is concerned.[11] A few types of auxiliaries have been successfully used,[24–27] with the chiral source being either camphor or 1,4-diols. However, these successes do not yet fulfill all the requirements of a general method. Improvements are still needed in terms of catalyst loading, scope, kinetics, and diastereoselectivity. In 1998 we disclosed[17] that 2,5-dimethylthiolane was an efficient C_2-symmetric sulfide for epoxidation. It was used in a one-pot procedure, which is extremely easy to perform experimentally. We reported[25] a catalytic version (0.1–0.2 equiv) in 2001.

We are currently pursuing our efforts in this field with the exploration of new sulfide structures. Prior to our work,[28] no ferrocenyl sulfide was reported as a source of sulfonium salt and ylide for the conversion of aldehydes into oxiranes. Therefore, we first investigated the preparation and behavior of such species. We observed[28] that a reaction of benzyl bromide with ferrocenyl alkyl sulfides in a polar solvent efficiently produces sulfonium salts in a matter of hours. This reasonably rapid reaction is in line with the stabilization of a sulfonium center adjacent to the ferrocenyl nucleus, which we postulated by analogy with the ferrocenyl carbocations.[29,30]

Deprotonation of the sulfonium salt and subsequent reaction of the ylide with carbonyl compounds were achieved under our standard one-pot conditions (see Scheme 2), leading to the expected oxiranes. After having established the feasibility of the reaction, with achiral sulfides, we have screened enantiopure sulfides.

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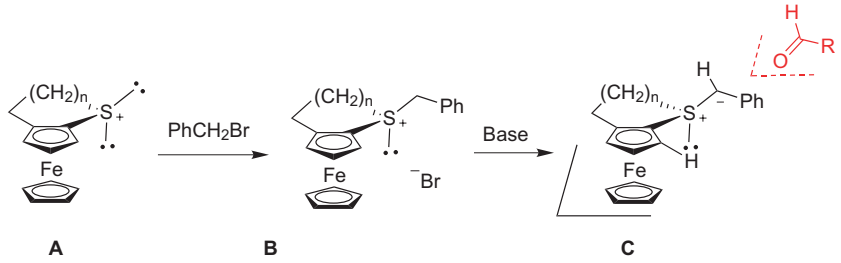


Scheme 1. Design of the auxiliaries.

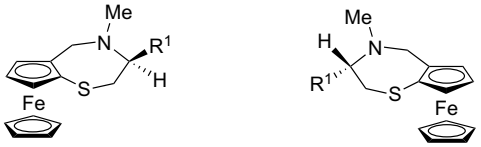
A first example (ee 67%) was included in our previous paper.[28] We now report a new series of chiral auxiliaries.

A rational design of novel structures must follow four requirements: (i) formation of a single diastereomeric sulfonium salt; (ii) control of the ylide conformation; (iii) selective facial attack of the ylide to the aldehyde; (iv) *trans*- versus *cis*-diastereoselectivity of the oxirane formation.

From our experience and others, the inclusion of the sulfur atom in a ring brings the sound advantage of rigidity. Therefore, our first element of design here was to append a ring to the cyclopentadienyl nucleus, with a sulfur atom in an adjacent position (Scheme 1). We anticipated differentiation of the sulfur lone pairs in **A**, with the one opposite to the iron atom being more accessible. Subsequent deprotonation of the resulting benzyl sulfonium salt **B** would preferably lead to an '*anti*' ylide conformation **C**. Approach of the aldehyde from the front side of ylide **C** would be hindered by the *ortho*-cyclopentadienyl hydrogen atom, thus favoring attack from the backside.

As a strategy for the synthesis of chirally planar sulfides, we have relied on starting material bearing an acyclic side chain with central chirality (stereogenic carbon or sulfur atom) and achieving a stereodifferentiating cyclization.

Instead of having to develop a novel synthesis, we were fortunate enough that the preparation of sulfides **1**–**3** (Fig. 1) were made available[31] during the investigation of new sulfides as catalysts. Therefore, we undertook the study of their behavior toward epoxidation. We herein report that they efficiently catalyze this reaction with enantiomeric excesses up to 94%.



(S_P,S_C) **1a**: R^1 = Ph; **2a**: *i*-Pr; **3a**: *t*-Bu

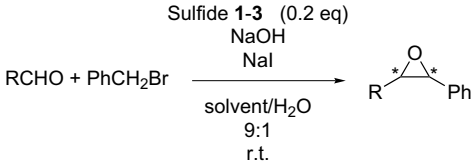
(R_P,S_C) **1b**, **2b**, **3b**

Figure 1. Ferrocenyl sulfides.

2. Results and discussion

Six sulfides **1**–**3** (Fig. 1) were prepared from three 1,2-amino alcohols: phenylglycinol, valinol, and *tert*-leucinol. It involved a sequence, reported[31] by some of us: reaction of sodium ferrocenethiolate with *N*-Boc tosyl derivatives of the aminoalcohols, deprotection of the amine, and reaction with formic acid and formaldehyde. The latter step is assumed to proceed through an iminium ion, followed by an intramolecular electrophilic attack at an *ortho*-position of the ferrocene ring, and formation of seven membered ring sulfides with diastereomeric ratios from 40% to 75% in favor of the (S_P,S_C) isomer. Isomers **a** and **b** were separated by column chromatography. It should be noted that they differ only by planar chirality, their central chirality being unchanged during the cyclization. Therefore, this investigation will raise the issue of matched or unmatched planar and central chiralities.

The six sulfides **1**–**3** were submitted to the model reaction for epoxidation under our standard conditions (Scheme 2). Synthesis of stilbene oxide was investigated from the reaction of benzaldehyde (R = Ph) and benzyl bromide (2 equiv), with sodium hydroxide (2 equiv) and sodium iodide (1 equiv),[25] in the presence of 0.2 equiv of the chiral sulfide, in a mixture of solvent and water (9:1) at ambient temperature (Table 1).



Scheme 2. Epoxidation reaction.

When using *tert*-butanol as a solvent, although the reactions were slow (6–14 days), stilbene oxide was produced in all cases. The yields were low with phenyl derivatives **1** (entries 1 and 2) and moderate with the isopropyl one **2** (entries 3 and 4). In both cases, the sulfide was not recovered during the isolation of stilbene oxide.

A better case was observed with *t*-butyl derivatives **3**, with yields of 66–80% (entries 5 and 9). The sulfides were detected in the crude product and could be recovered. In order to reduce the reaction time, the epoxidation was attempted at a temperature of 60 °C. After 6.5 days

Table 1. Catalytic epoxidation reaction of benzaldehyde with ferrocenyl sulfides **1**–**3**

Entry	Sulfide (0.2 equiv)	R^1	Solvent 9:1	Time (d)	Yield (%)	Dr[a] *trans*/*cis*	Ee (%)[b] *trans* (*R*,*R*)	Sulfide recovery (%)
1	**1a**	Ph	*t*-BuOH/H_2O	14	<10	75:25	37	No
2	**1b**	Ph	*t*-BuOH/H_2O	14	<10	72:28	41 (*S*,*S*)	No
3	**2a**	*i*-Pr	*t*-BuOH/H_2O	14	14	69:31	28	No
4	**2b**	*i*-Pr	*t*-BuOH/H_2O	14	32	63:37	31 (*S*,*S*)	No
5	**3a**	*t*-Bu	*t*-BuOH/H_2O	14	66	76:24	83	78
6	**3a**	*t*-Bu	*t*-BuOH/H_2O at 60 °C	6.5	56	77:23	79	76
7	**3a**	*t*-Bu	DMSO/H_2O	14	8	65:35	0	No
8	**3a**	*t*-Bu	CH_2Cl_2/H_2O	13	37	83:17	74	77
9	**3b**	*t*-Bu	*t*-BuOH/H_2O	14	80	72:28	77	75

[a] Ratio determined by ^1H NMR of the crude product.
[b] Enantiomeric excess determined by HPLC (Daicel ChiralPak AD-H column 250 × 4.6 mm (L × ID) 5 μm, 90% *n*-heptane/10% *i*-PrOH, 1 mL min^{-1}, 20 °C).

(entry 6), a slightly lower yield (56%) was obtained. Two other solvent mixtures were tested at room temperature. A mixture of DMSO and water (entry 7) led to a mediocre yield, probably due to decomposition of the sulfide. Reaction in dichloromethane and water (entry 8) led to epoxidation, but with no benefit.

Significant variations of enantiomer ratios were observed versus the sulfides. With the **1a** and **2a** isomers of the phenyl and isopropyl sulfides (entries 1 and 3) the ee's were 37% and 28%, respectively, in favor of the (*R*,*R*)-stilbene oxide.

Similar data were observed with the **1b** and **2b** isomers (41% and 31% ee, respectively), but *in the opposite sense* (entries 2 and 4): the (*S*,*S*)-oxide is predominant. Therefore the control here is in direct relationship to the planar chirality.

For the *tert*-butyl sulfides **3**, much better enantioselectivities were observed (entries 5 and 9). Isomer **3b** gave 77% ee and isomer **3a** afforded 83%, the highest for stilbene oxide in this series. An unexpected result is that the absolute sense of control is *the same* for both **3a** and **3b** isomers, which differ by planar chirality. The situation is thus opposite to that of Ph and *i*-Pr sulfides **1** and **2**!

Other observations have been made with sulfide **3a**. The reaction carried out at 60 °C (entry 6) caused only a small drop of selectivity (79% vs 83%). The epoxidation performed in CH_2Cl_2/H_2O (entry 8) took place with an enantioselectivity only slightly lower (74%) than in *t*-BuOH/H_2O (83%). In DMSO/H_2O, a racemic oxirane was obtained, in connection with a mediocre yield and decomposition of the sulfide.

In terms of diastereoselectivity, the results are analogous to those observed[28] with achiral ferrocenyl alkyl sulfides. *trans*/*cis*-Ratios range from 63:37 to 83:17. For the best example **3a** in terms of enantioselectivity (entry 5), the diastereomeric ratio is 76:24, and for its planar diastereoisomer **3b** it is 72:28 (entry 9).

Having established that **3a** is an efficient sulfide in our standard reaction conditions, we have examined the reaction of other aldehydes (Table 2). With 4-nitrobenzaldehyde (entry 4), traces of oxirane were isolated with 72% ee. 2-Furaldehyde led to a nice 88% ee, but with a poor yield (entry 3). With 2-thienaldehyde a 50% oxirane yield and 90% ee were obtained (entry 2). In this series, the highest stereocontrol was observed with cinnamaldehyde: 94% ee. For all these examples, sulfide **3a** could be recovered.

We have shown that ferrocenes bearing an adjacent ring with a sulfur atom can be used as catalysts for sulfur ylide epoxidation. Chemical efficiency is achieved with sulfides **3a** and **3b**, bearing a *tert*-butyl group on the carbon adjacent to the nitrogen atom. This group brings steric hindrance with two possible effects: protection of the nucleophilic character of the nitrogen center versus benzyl bromide, and therefore inhibition of the subsequent ring cleavage of the ammonium salt. Indeed with R = *i*-Pr, Ph, sulfides **1** and **2** were not recovered under the epoxidation conditions.

Table 2. Catalytic epoxidation reaction[a] of aldehydes with ferrocenyl sulfide **3a**

Entry	Aldehyde R	Time (d)	Yield (%)	Dr[a] *trans*/*cis*	Ee (%)[b] *trans* (*R*,*R*)	Sulfide recovery (%)
1	Ph	14	66	76:24	83	78
2	2-Thienyl	7	50	81:19	90 (2*S*,3*R*)	94
3	2-Furyl	2.5	<10	74:26	88 (2*S*,3*R*)	80
4	4-$NO_2C_6H_4$	14	<5	—	72	82
5	2-Naphthyl	14	67	82:18	90	75
6	*trans*-Cinnamyl	14	47	60:40	94	77

[a] Reactions conducted in *t*-BuOH/H_2O 9:1 at room temperature.
[b] Enantiomeric excess determined by HPLC (Daicel ChiralPak AD-H column 250 × 4.6 mm (L × ID) 5 μm, 90% *n*-heptane/10% *i*-PrOH, 1 mL min^{-1}, 20 °C).

The best asymmetric induction was observed with sulfide **3a**. We propose that (*R*,*R*)-stilbene oxide is produced predominantly through the following selective steps. Reaction of benzyl bromide presumably takes place with the pseudo-equatorial sulfur lone pair (*anti* to the sandwich iron atom). Information on the ground state conformation (Fig. 2) of the seven membered ring sulfide is fortunately available[31] from the X-ray analysis of sulfide **3a**.

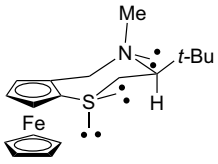


Figure 2. Conformation of sulfide **3a**.

Whereas a seven membered ring is rather flexible, compound **3a** is constrained by the connection to the *Cp* ring (four atoms in a plane) and the pseudo-equatorial *t*-butyl group. The five non *Cp* members of the ring exhibit a pseudo-chair conformation with sulfur and two carbon groups being located upward, relative to iron. To relieve the steric interaction of a pseudo-diequatorial arrangement (torsion angle of 5°–10°, to be calculated on X-ray), the *N*-methyl group occupies an axial position (torsion angle around 90°–100°). Consequently, the two sulfur lone pairs are nicely differentiated. Attack of the benzyl bromide toward the bottom lone pair is hindered by its axial position, in favor of the equatorial top sulfur doublet, providing formation of the sulfonium salt **B** (Scheme 3).

By ^{1}H NMR we examined the alkylation of sulfide **3a** (0.2 equiv) with benzyl bromide (2 equiv) in a CD_3CN/D_2O 9:1 solution. We have observed the formation of a single new signal in *t*-butyl region, at 0.99 ppm, assigned to the sulfonium salt. After 4 h, the reaction composition did not change (Fig. 3, red curve). It is slightly slower than with FcSMe (black curve). The main difference is the ratio between the sulfonium salt and the sulfide, which is here only 20%, at equilibrium, in contrast to 95% with FcSMe. This probably contributes to a slower overall reaction.

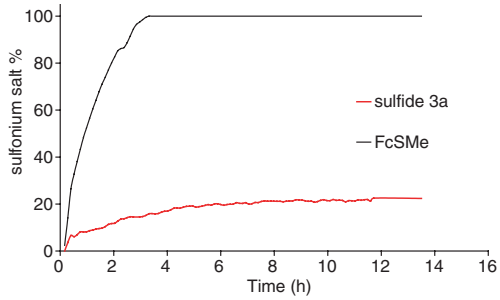
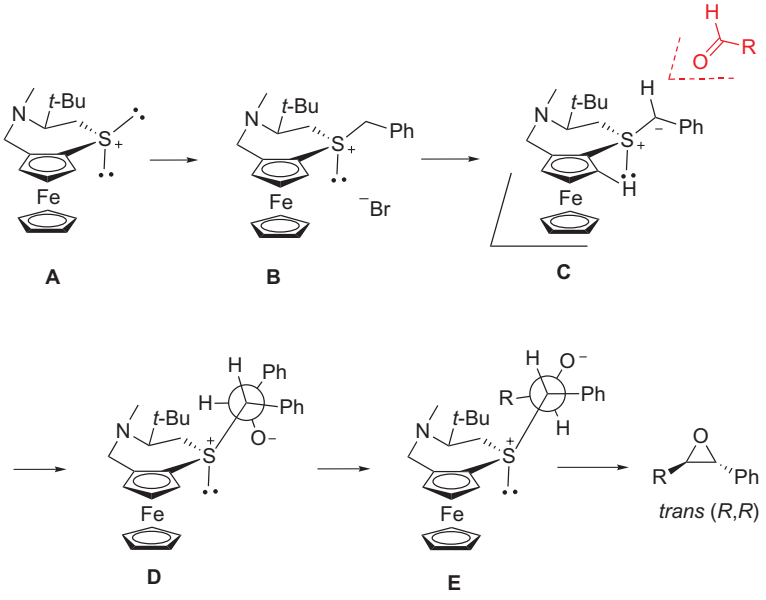


Figure 3. Conversion (%) of sulfides into sulfonium salts versus time (h).

Deprotonation of sulfonium salt **B** provides two possible conformations. As for other examples of cyclic sulfide ylides,[11,18,27] we believe there is a strong preference for *anti*-conformation **C** (phenyl opposite to the sulfur ring, and the ylidic hydrogen opposite to the available lone pair).

The two faces of approach[32] of the ylide **C** by the aldehyde are clearly different. Attack from the ferrocene side will cause severe interaction by *ortho* C–H of the cyclopentadienyl ring, as assumed previously. The approach from the CH_2 side (adjacent to sulfur) takes place in a more open space and is very probably favored, to lead to betaine **D**, which after proper C–C bond rotation, provides an *anti*-betaine **E**, set for nucleophilic displacement, and *trans*-oxirane formation.



Scheme 3. Proposed approaches with sulfide **3a**.

A similar model may be proposed for sulfides **1a** and **2a** (R = *i*-Pr, Ph), for which the enantioselectivity has the same sense [(*R*,*R*)-oxirane] but a lower amplitude. The R group exerts a lower conformation control than for a *t*-butyl.

Application of the present model to diastereomeric sulfide **3b**, differing by planar chirality, should lead to the (*S*,*S*)-enantiomeric oxirane, provided that the presence of a substituent on the saturated ring does not play a key role. This is indeed true for the other sulfides **1b** and **2b** (R^1 = Ph, *i*-Pr). An opposite (*S*,*S*)-enantioselectivity was experimentally observed, with a similar magnitude.

With compound **3b** (R = *t*-Bu), an unexpected observation was made: the same (*R*,*R*)-enantiomeric oxirane was obtained as with **3a**. It is the remote asymmetric center, which dictates the stereochemistry of the product. A clue to this intriguing result was given by careful examination of sulfide **3b** conformations. We could not perform an X-ray structure analysis. We propose that it adopts a conformation of the seven membered ring similar to **3a** and typical of cycloheptene:[33] a cyclohexene chair in which one of the ring's CH_2 is replaced by the C=C moiety (Fig. 4). The *t*-butyl group must take a pseudo-equatorial position. This will orient the 7-membered ring below the *Cp* ring in the half space, where the iron atom is located.

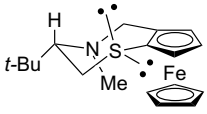
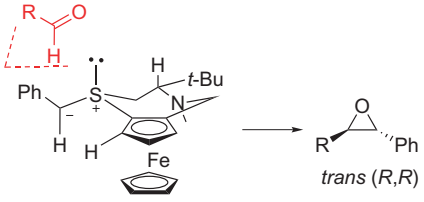


Figure 4. Proposed conformation for sulfide **3b**.

This creates for **3b** an arrangement around the sulfur atom, which is different from sulfide **3a**. The axial lone pairs will now be located up (relative to iron), and the equatorial one will be down. As previously observed for **3a**, benzyl bromide will prefer to attack the equatorial lone pair. The two faces of the *anti*-ylide will again differ by an *ortho*-cyclopentadienyl hydrogen and a CH_2 group, in favor of the latter. Thus, the two faces of approach (*Si* for the aldehyde and *Re* for the ylide) are the same for both sulfides **3a** and **3b** (Scheme 4).



Scheme 4. Proposed approach with sulfide **3b**.

For isomers **1b** and **2b**, a boat conformation will be tolerated for the cycloheptene ring, placing the ring up relative to the iron metal. The more reactive sulfur lone pair might be the equatorial upper one, leading to an *anti*-ylide with a *Si* face now being more reactive.

The diastereoselectivity observed herein differs notably from that reported with aliphatic sulfides, which lead to the *trans*-stilbene oxide, usually in ratios higher than 90:10. It has been proposed, and demonstrated experimentally with dimethyl sulfide derivatives, that the formation of the *syn*-betaine is reversible.[34,35] The *anti*-betaine is produced irreversibly, so that the substrate nature and reaction conditions may lead to the major formation of the *trans*-oxirane. In our first report[28] on the epoxidation reaction with simple ferrocenyl sulfides, we also obtained untypical *trans*- and *cis*-mixtures of stilbene oxide, with ratios ranging from 60:40 to 80:20. Monitor experiments revealed only a minor equilibration of the *syn*-betaine. So, the aromatic nature of the ferrocenyl substituent to sulfur strongly reduces the reversibility.

Here the observations are similar to those with simple alkyl ferrocenyl sulfides. For stilbene oxide the *trans*/*cis* ratio with **3a** in *t*-BuOH/H_2O is 76:24. It is higher than with FcSMe (62:38) and lower than with FcSCy (80:20) or FcS-*t*-Bu (81:19).

The ratios also depend upon the aldehyde: *trans*-cinnamaldehyde gave a 60:40 dr and 2-naphthaldehyde the highest dr observed in the present series, 82:18. A steric factor is clearly playing a role in the latter case, in favor of the *trans*-oxide, probably by enhanced reversibility of the *syn*-betaine.

3. Conclusion

We have investigated ferrocenyl derivatives, bearing an adjacent sulfur atom included in a fused ring, for the epoxidation reaction of aldehydes. Using available structures, we have shown that sulfide **3a** nicely catalyzes the formation of stilbene oxides in a simple one-pot procedure. The reactions however are not as rapid as expected, despite the fact that the formation of the sulfonium salt, with a positive charge in an α-position of a ferrocene cyclopentadienyl, is probably accelerated.[28] The stability of the subsequent ylide might lower the kinetic rate of the overall sequence.

Enantiomeric excesses up to 94% have been achieved. Significantly, the same enantiomer of the product is obtained with both the (*SS*)- and (*SR*)-diastereomers of the *t*-butyl sulfide **3**. Thus, the remote central chirality dictates the outcome. The effect of planar chirality is reversed from diastereomer **3a** to **3b**, by the necessity for the *t*-butyl group to adopt a pseudo-equatorial position on the seven membered ring.

Diastereoselectivity remains an issue to be controlled. Mixtures of isomers are obtained with ratios from 60:40 to 82:18, in favor of the *trans*-oxirane.

Ferrocenes are being extensively investigated for catalytic asymmetric synthesis.[4,6–9] Sulfur derivatives[36] have

recently emerged for stereocontrolled dialkylzinc addition to aldehydes,[7,37,38] allylic alkylations,[31,39–42] and Diels–Alder cycloadditions.[43] We have shown herein that the sulfur ylide epoxidation can be made asymmetric with a catalytic amount of ferrocenyl sulfides, and the first applications of planar chirality to this reaction.

4. Experimental

4.1. Typical epoxidation procedure

To a solution of sulfide (17 mg, 0.05 mmol) in *t*-BuOH/H_2O 9:1 (415 μL) was added benzyl bromide (60 μL, 0.50 mmol), aldehyde (0.25 mmol), NaI (38 mg, 0.25 mmol), and NaOH (20 mg, 0.50 mmol). The reaction mixture was stirred at room temperature and monitored by TLC using *n*-heptane/ethyl acetate (v/v: 9:1). Water (1 mL) was then added and the aqueous phase was extracted with dichloromethane (3×2 mL). The combined organic phases were dried over $MgSO_4$ and concentrated to dryness. Column chromatography using *n*-heptane/ethyl acetate afforded the desired oxirane.[25,27]

Acknowledgements

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