Letter

Benzylic Ammonium Ylide Mediated Epoxidations

L. Roiser et al.

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Abstract A high yielding synthesis of stilbene oxides using ammonium ylides has been developed. It turned out that the amine leaving group plays a crucial role as trimethylamine gives higher yields than DABCO or quinuclidine. The amine group also influences the diastereoselectivity, and detailed DFT calculations to understand the key parameters of these reactions have been carried out.

Key words epoxides, ylides, diastereoselectivity, DFT calculations, diazo compounds

Onium ylides are versatile reagents for (dia)stereoselective epoxide, aziridine, and cyclopropane syntheses.^{1–10} In contrast to sulfonium ylides, which are frequently used for a variety of three-ring forming reactions,³ ammonium ylides have been less routinely used in the past.^{4–8} This is mainly because of the weaker leaving group ability of the amine group as compared to their sulfur analogues.¹⁰

We have recently succeeded in developing a high yielding and highly *trans*-selective epoxidation reaction using amide-stabilised ammonium salts **1** as ylide precursors (Scheme 1).⁷ Key to success in this transformation was the use of trimethylamine as the amine leaving group of choice, which was clearly superior to other tertiary amines such as DABCO, quinuclidine, or triethylamine. Expanding the application scope of this operationally simple method we became interested in the synthesis of stilbene oxides **5**, starting from benzylic ammonium salts **4** (Scheme 1). This transformation has been reported in the past using DABCO and quinuclidine as the amino group.⁵ However, it was found that the nature of the leaving group, as well as the electronic properties of the aryl group of the benzylic ammonium salt **4** play a crucial role hereby. While electronrich or phenyl-based ammonium salts 4 gave epoxides 5 in up to 40% yields only (with a *cis/trans* ratio depending on the leaving group ability), more stabilised ylides (with electron-withdrawing aryl substituents) allowed for higher vields and higher trans selectivities.⁵ Based on computational results, Aggarwal and co-workers explain the observed generally low yields by the high barrier to elimination, which is a consequence of the poor leaving group ability of the amine group.^{5c} They also rationalize the observed variations in diastereoselectivity according to the nature of the substrate by the degree of reversibility in betaine formation: reaction of stabilized ylides (substituted by electron-poor aryl groups) lead to reversibility of betaine formation and high trans selectivity, whilst groups that destabilize the ylide (electron-rich aryl groups) or reduce the barrier to ring closure (better amine leaving group) lead to reduced reversibility and lower diastereoselectivity.¹¹







L. Roiser et al.

Based on these observations and our excellent previous experience with trimethylamine-based ammonium salts,⁷ we became interested in investigating if the beneficial effect of this superior leaving group also holds for the synthesis of stilbene oxides **5** and evaluating the effect of Me₃N on the diastereoselectivity of this reaction.

Initial experiments to identify the best suited conditions for the reaction of the parent ammonium salt **6a** (Ar = Ph) with benzaldehyde (**2a**) showed that a combination of t-BuOK as the base and THF as the solvent clearly outperforms other base/solvent systems. With these basic conditions set, we then further fine-tuned the reaction conditions and elucidated the scope of this transformation. Table 1 gives an overview of the most significant results obtained in a rather detailed screening of different reaction conditions and substrates. As shown in Table 1, entries 1–5, the amount of base as well as the reaction temperature play a significant role. For room temperature reactions it was found best to use three equivalents of *t*-BuOK which allowed for 69% isolated yield of a 61:39 *trans:cis* mixture of **5a** (Table 1, entry 2), whereas a slightly higher temperature of 40 °C allowed us to obtain **5a** in an excellent 93% yield and a slightly higher *trans* selectivity (66:34) when using four equivalents of base (Table 1, entry 5). Noteworthy, larger or lower amounts of base reduced the yields significantly, either due to decomposition of the product or be-

Table 1 Syntheses of Epoxides 5 Using Trimethyl Amine Based Ammonium Salts 6

$Ar \xrightarrow{(+)}{NMe_3} + RCHO \xrightarrow{t-BuOK, THF} Ar \xrightarrow{(+)}{3 \text{ h, temp}} Ar \xrightarrow{(+)}{5} R$											
Entry	Ar	R	5	<i>t</i> -BuOK (equiv)	Temp (°C)	trans:cisª	Yield (%) ^b				
1	Ph	Ph	5a	2	25	61:39	42				
2	Ph	Ph	5a	3	25	61:39	69				
3	Ph	Ph	5a	4	25	61:39	36				
4	Ph	Ph	5a	3	40	63:37	37				
5	Ph	Ph	5a	4	40	66:34	93				
6	Ph/DABCO salt	Ph	5b	4	40	80:20	41				
7	Ph/Et ₃ N salt	Ph	5b	4	40	89:11	31				
8	$4-O_2NC_6H_4$	Ph	5b	4	40	n.d.¢	0 ^d				
9	$4-O_2NC_6H_4$	Ph	5b	3	25	95:5	19 ^d				
10	$4-F_3CC_6H_4$	Ph	5c	4	40	> 99:1	97				
11	4-BrC ₆ H ₄	Ph	5d	4	40	91:9	89				
12	$4-FC_6H_4$	Ph	5e	4	40	55:45	94				
13	3-MeOC ₆ H ₄	Ph	5f	4	40	73:27	97				
14	4-MeC ₆ H ₄	Ph	5g	4	40	47:53	52 ^e				
15	Ph	4-MeOC ₆ H ₄	5h	4	40	68:32	88				
16	Ph	$2-MeOC_6H_4$	5i	4	40	41:59	83				
17	Ph	$4-Me_2NC_6H_4$	5j	4	40	86:14	99				
18	Ph	$4-MeC_6H_4$	5g	4	40	60:40	16				
19	Ph	$4-MeC_6H_4$	5g	3	25	64:36	66				
20	Ph	$4-BrC_6H_4$	5d	4	40	60:40	90				
21	Ph	4-CIC ₆ H ₄	5k	4	40	64:36	81				
22	Ph	4-NCC ₆ H ₄	51	4	40	50:50	26				
23	3-MeOC ₆ H ₄	$4-BrC_6H_4$	5m	4	40	66:34	84				
24	$4-F_3CC_6H_4$	$4-BrC_6H_4$	5n	4	40	97:3	55				
25	Ph	Су	5o	4	40	62:38	8				

В

^a Determined by ¹H NMR on the crude product.

^b n.d. = not determined.

^c Isolated yield of the mixture of both diastereomers.

^d Epoxide **5b** decomposition under the basic conditions.

 $^{\rm e}$ Partial oligomerization of ${\bf 6g}$ under the basic conditions. $^{\rm 12}$

L. Roiser et al.

cause of insufficient reactivity when using less base. In addition, longer reaction times usually had no positive effect, even in those cases where conversion was slow.

To illustrate the different leaving group ability of trimethylamine compared to DABCO and triethylamine, we also used the analogous ammonium salts under the optimized conditions (Table 1, entries 6 and 7). These experiments clearly demonstrate the significantly higher yield using trimethylamine but also showed that with this more reactive system the diastereoselectivity slightly decreases, giving increasing amounts of the *cis* epoxides.

Having identified simple conditions that allowed for high vields within a short reaction time, we next tested a variety of differently substituted ammonium salts 6 (Table 1. entries 8–14) and various aromatic aldehydes 2 (Table 1. entries 15-24). Except in the case of electron-poor aryl groups (Table 1, entries 8 and 9) and/or electron-poor aryl aldehvdes (Table 1, entry 22), for which **2** and **5** are prone to decomposition under the basic conditions, a variety of differently substituted aryl groups are well accepted in this reaction. Yields for epoxides 5 starting from electron-rich and electron-neutral substrates were equally high, apart for 5g synthesized from ammonium salt 6g (Table 1, entry 14), which tends to oligomerize under the basic reaction conditions.¹² As expected, the diastereoselectivity strongly depends on the electronic properties of the ammonium salt, with more stabilized ylides (obtained from 6 with electronpoorer aryl groups) gave higher trans selectivities. The opposite (but less pronounced) trend was observed by changing the nature of the aldehyde 2. Hereby, less reactive electron-rich aryl groups (i.e., Table 1, entries 15 and 17) give a higher *trans* selectivity than electron poorer ones (Table 1, entry 20). Unfortunately, using cyclohexane carbaldehyde as the acceptor mainly resulted in decomposition, giving only minute amounts of the corresponding epoxide 50 (Table 1. entry 25).

In order to investigate the origin of the observed better yield and lower diastereoselectivity using the trimethylamine-based ylide, as compared to DABCO, quinuclidine, and Et₃N derivatives, we carried out DFT calculations. We have computed the free energy profile of the reaction of PhCHNMe₃ ylide with benzaldehyde at the B3LYP-D3/6-311+G**(DCM)//B3LYP/6-31G*(DCM) level of theory (Table 2 and Figure 1).¹³ For purpose of comparison with Aggarwal's results, we also considered DABCO and quinuclidine derivatives.^{5c}

Our calculations are in good agreement with the previously predicted (partial) reversibility of betaine formation in reaction of quinuclidine-based ylide and the less or nonreversible addition step in the case of Me₃N and DABCO derivatives.¹⁴ While for trimethylamine-based ylides this reduced reversibility in betaine formation can be accounted for by a better leaving group ability (see free energy barriDownloaded by: University of Kentucky. Copyrighted material.



Figure 1 Calculated free energy profile (kcal/mol) for the epoxidation reaction between PhCHNMe₃ ylide and benzaldehyde. See Supporting Information for the estimation of free energy barrier to addition.

ers from *anti*-betaine in brackets in Table 2), for DABCO derivatives the main reason is in fact a more exothermic betaine formation.

Accordingly, the generally low diastereoselectivity observed in reaction of trimethylamine-based ylides can be accounted for by a less reversible addition step which is therefore the selectivity determining step. This latter involving no significant barrier,¹⁵ it is expected to occur with no (or very low) selectivity. Conversely, for quinuclidinebased ylides the addition is predicted to be (partially) reversible, meaning that selectivity must be determined at the elimination step, which explains the high preference for *trans*-epoxides in this case.⁵

The observed increase in *trans* diastereoselectivity with electron-withdrawing character of ylide substituents (see Table 1, entries 7–9) can be explained by their impact on the degree of reversibility of addition, and hence on the origin of the selectivity-determining step. Indeed, stabilization of the ylide by EWG increases addition reversibility because of a less exothermic betaine formation and an increased free energy barrier to elimination¹⁶ (Figure 2). In the case of EWG substitution, selectivity is thus determined at the elimination step, and the predicted relative higher stability of *trans*-TSelim over its *cis* isomer (by 1.9 kcal/mol for 4- $F_3CC_6H_4CHNMe_3$ ylide) accounts for the observed high selectivity.

In terms of yield, the better results obtained for reaction of Me₃N-based ylides, as compared to DABCO and quinuclidine derivatives, can be explained by the higher reactivity toward epoxidation of the former due to a better leaving group ability, which then decreases the occurrence of competitive degradation reactions.¹⁷

One very versatile strategy to carry out ylide-mediated epoxidations without the need of strong basic conditions relies on the use of diazo compounds as ylide precursors. This strategy is commonly used for sulfonium ylide mediat-

Syn lett

L. Roiser et al.

Letter

Table 2 Computed Relative Free Energies (kcal/mol)



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R ₃ N =	Me ₃ N			quinuclidine		DABCO	
	trans	cis	trans	cis	trans	cis	
TSadd	_ ^a	_a	_a	_a	_a	_ ^a	
<i>syn</i> betaine	-7.7	-7.9	-8.8	-9.1	-15.8	-15.9	
TSrot	1.6	-0.3	n.d. ^b	n.d. ^b	n.d. ^b	n.d. ^b	
anti betaine	-2.1	-1.2	-3.6	-2.6	-10.3	-9.1	
TSelim	1.8 (3.9) ^c	3.1 (4.3) ^c	2.8 (6.4) ^c	5.5 (8.2) ^c	-4.2 (6.1) ^c	–1.4 (7.7) ^c	
Epoxide + R ₃ N	-26.3	-23.1	-22.8	-19.6	-31.5	-28.3	

^a Betaine formation occurs without enthalpic barrier.¹⁵

^b n.d. = not determined.

^c Free energy barrier from *anti* betaine reported in brackets.

ed epoxidations, where the diazo compound can be used to obtain ylides in situ upon reaction with a metal catalyst (usually Rh- or Cu-based) and a (catalytic amount of) sulfide as was impressively shown by Aggarwal's group.¹⁸ Interestingly, it was also shown that by changing from sulfonium to tellurium ylides,¹⁹ the corresponding alkenes are obtained instead of the epoxides. Much to our surprise (and to the best of our knowledge) no analogous reports for ammonium ylides have been reported so far. We thus tested



Figure 2 Effect of EWG substitution. Calculated free energy profile (kcal/mol) for the epoxidation reaction between 4- $F_3CC_6H_4CHNMe_3$ ylide and benzaldehyde.

the feasibility of such a transformation by using phenyldiazomethane **7** in combination with $Rh_2(OAc)_4$ and DABCO (**8**) as the amine component (Scheme 2). After thorough screening of different conditions, we found that such a reaction is possible in principle, albeit with low yield only. These low yields can mainly be attributed to rather pronounced side-reactions such as the dimerization of the diazo compound to stilbene derivatives or different carbene insertion products. Also, variations of the metal catalyst or the in situ generation of the diazo species under phasetransfer conditions (as reported previously^{18d}) were not beneficial. Attempts to use the amine component in a catalytic fashion also were not very successful. Thus, it can be concluded that, although possible, the use of diazo com-





pounds as ammonium ylide precursors for epoxide formations is not as effective as the comparable use for sulfonium ylide mediated reactions.

In conclusion, a high-yielding protocol for the synthesis of stilbene oxides using ammonium ylides has been developed.^{19,20} The nature of the amine leaving group plays a crucial role herein and it was found that trimethylamine gives significantly higher yields than DABCO or quinuclidine. The nature of the amine group also influences the diastereoselectivity in these reactions. A detailed DFT study allows understanding the different yields and selectivities when using different amine leaving groups and aryl substituents.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1562344.

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L. Roiser et al.

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(20) General Epoxidation Procedure

Ammonium salt **6** (1 equiv) was suspended in dry THF (0.05 M) and stirred at 40 °C. *t*-BuOK (4 equiv) was added, and the

mixture was stirred vigorously. After 10 min, 2 equiv of aldehyde **2** were added, and the mixture was stirred for 3 h at 40 °C. The reaction was then quenched by addition of a half-saturated NaCl solution. After phase separation, the aqueous phase was extracted three times with CH_2Cl_2 , and the combined organic phases were dried with Na_2SO_4 and evaporated to dryness. Purification by column chromatography (gradient of heptanes and EtOAc) gave the corresponding epoxides in the reported yields as a mixture of diastereomers.

Compound **5a**: Obtained in 93% (*trans/cis* = 66:34) on a 0.5 mmol scale as a white solid. Analytical data match those reported previously.^{5,21}

Selected Data

¹H NMR (300 MHz, δ, CDCl₃, 298 K):*trans* isomer: 3.94 (s, 2 H), 7.36–7.49 (m, 5 H);*cis* isomer: 4.42 (s, 2 H), 7.18–7.28 (m, 5 H) ppm. ESI-HRMS: *m*/zcalcd for $C_{14}H_{12}O$: 197.0961 [M + H]⁺; found: 197.0961.

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