Pergamon

Tetrahedron Letters 39 (1998) 8811–8812

TETRAHEDRON LETTERS

EFFECT OF CATALYST ON THE DIASTEREOSELECTIVITY OF METHYL PHENYLDIAZOACETATE CYCLOPROPANATIONS

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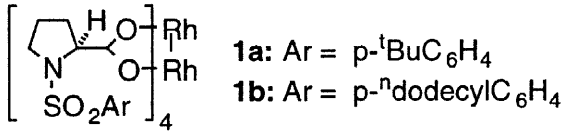
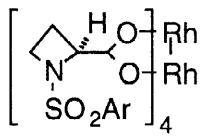
Received 10 July 1998; accepted 17 September 1998

Abstract: In contrast to previously published studies, the diastereoselectivity of phenyldiazoacetate cyclopropanations is not greatly altered by the type of rhodium carboxylate catalyst that is used.

In 1993, we communicated that Rh_2(S-TBSP)$_4$ (**1a**) is an excellent catalyst for asymmetric cyclopropanations by vinyldiazoacetates.[1] Subsequently, a full paper on this work demonstrated that in order to achieve high asymmetric induction, the N-sulfonated amino acid ligand needed to be a cyclic system.[2] Catalysts derived from acyclic amino acids resulted in low asymmetric induction while the azetidinecarboxylate **2** and the picolinate complex gave reasonable asymmetric induction, although neither was as effective as the prolinate catalysts. In 1996, two groups reported that methyl phenyldiazoacetate behaved analogously to the vinyldiazoacetates,[3] resulting in highly diastereoselective and enantioselective cyclopropanations on decomposition by either Rh_2(*S*-TBSP)$_4$ (**1a**) or Rh_2(*S*-DOSP)$_4$ (**1b**). Recently, Zwanenburg and co-workers[4] reported that the cyclopropanation of styrene by methyl phenyldiazoacetate occurred with lower enantioselectivity but much better diastereoselectivity when catalyzed by **2** rather than **1a**. The conclusions with regard to diastereoselectivity[4] were not in accord with our general observations on the effect of catalysts on vinyldiazoacetate cyclopropanations.[2] Moreover, some of the reported diastereoselectivity seemed very unusual. For example,[4] the E/Z ratio changed from >99 : 1 to 97.6 : 2.4 to >99 : 1 as the mole equivalent of catalyst **2** changed from 4.3% to 1% to 0.1%. Consequently, we have carried out a systematic study to re-evaluate the effect of catalyst on the diastereoselectivity of phenyldiazoacetate cyclopropanations and the results of this study are described herein.



1a: Ar = p-^{t}BuC$_6$H$_4$
1b: Ar = p-^{n}dodecylC$_6$H$_4$



2: Ar = p-^{t}BuC$_6$H$_4$

In order to evaluate the effect of the catalysts, the decomposition of methyl phenyldiazoacetate (**3**) in the presence of styrene (5 equiv.) using 1 mol% of catalyst at room temperature was used as the standard reaction (Table 1). In addition to the chiral catalysts **1** and **2**, bulky catalysts such as Rh_2(OPiv)$_4$ and Rh_2(TPA)$_4$, and the highly electron deficient catalyst Rh_2(TFA)$_4$ were examined. The diastereoselectivity was measured by

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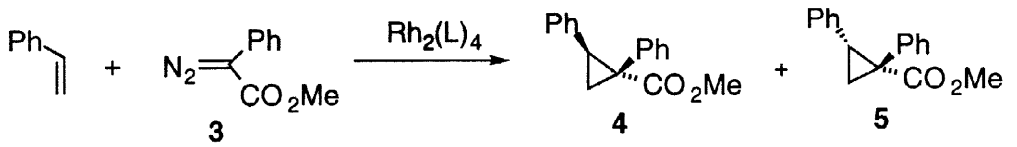
Table 1. **Stereoselectivity of cyclopropanations by methyl phenyldiazoacetate.**



Entry	Catalyst	solvent	E/Z ratio	Yield, %	ee of **4**, %
1	Rh_2(S-TBSP)$_4$	CH_2Cl_2	98 : 2	65	67 (61[4])
2	Rh_2(S-TBSP)$_4$	pentane	97 : 3	72	86 (85[4])
3	Rh_2(S-DOSP)$_4$	CH_2Cl_2	98 : 2	69	69
4	Rh_2(S-DOSP)$_4$	pentane	97 : 3	79	91
5	**2**	CH_2Cl_2	98 : 2	55	32 (35[4])
6	**2**	pentane	97 : 3	74	47 (49[4])
7	Rh_2(OAc)$_4$	CH_2Cl_2	98 : 2	69	-
8	Rh_2(OPiv)$_4$	CH_2Cl_2	98 : 2	61	-
9	Rh_2(TPA)$_4$	CH_2Cl_2	98 : 2	71	-
10	Rh_2(TFA)$_4$	CH_2Cl_2	99 : 1	70	-

integration of the methoxy signals in the NMR of the crude reaction mixtures. The minor *Z* isomer **5** is readily identified because the methoxy group is shielded by the adjacent phenyl ring and occurs at 3.32 ppm. In all instances the diastereoselectivity was between 97 : 3 and 99 : 1. Changing the mole equivalent of **2** from 0.1% to 5% had no effect on the *E/Z* ratio. A very slight solvent effect was seen in these reactions and the highest diastereoselectvity was seen using Rh_2(TFA)$_4$ in CH_2Cl_2. The enantioselectivity was readily determined by HPLC on a chiraldex OJ column and was in very close agreement with the published values.[3,4]

In summary, this study demonstrates that the rhodium catalyst structure has minimal effect on the diastereoselectivity of cyclopropanation of styrene by methyl phenyldiazoacetate. The azetidinecarboxylate catalyst **2** has no advantage over Rh_2(*S*-TBSP)$_4$ (**1a**) or Rh_2(*S*-DOSP)$_4$ (**1b**) with regard to diastereocontrol[5] and is an inferior catalyst in terms of asymmetric induction.

Acknowledgment: Financial support of this work by the National Science Foundation (CHE 9726124) is gratefully acknowledged.

References and Notes

1. Davies, H. M. L.; Hutcheson, D. K. *Tetrahedron Lett.* **1993**, *34*, 7243.
2. Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897.
3. (a) Davies, H. M. L.; Bruzinski, P. R.; Fall, M. J. *Tetrahedron Lett.* **1996**, *37*, 4133. (b) Doyle, M. P.; Zhou, Q. -L.; Charnsangavej, C.; Longoria, M. A.; McKervey, M. A.; Garcia, C. F. *Tetrahedron Lett.* **1996**, *37*, 4129.
4. Starmans, W. A. J.; Thijs, L.; Zwanenburg, B. *Tetrahedron* **1998**, *54*, 629.
5. It is difficult to rationalize the cause of the difference between the diastereoselectivity results reported here and those in Ref. 4. In our studies the diasteroselectivity was measured by NMR, which gave an excellent indicator for the minor diastereomer, while the studies in Ref. 4 used GC analysis.