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FACILE CATALYTIC METHODS FOR INTERMOLECULAR GENERATION OF ALLYLIC OXONIUM YLIDES AND THEIR STEREOSELECTIVE [2,3]- SIGMATROPIC REARRANGEMENT

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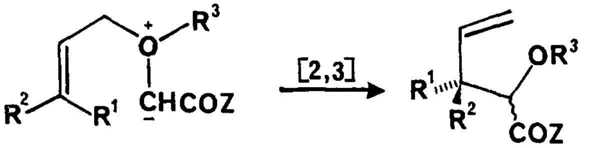
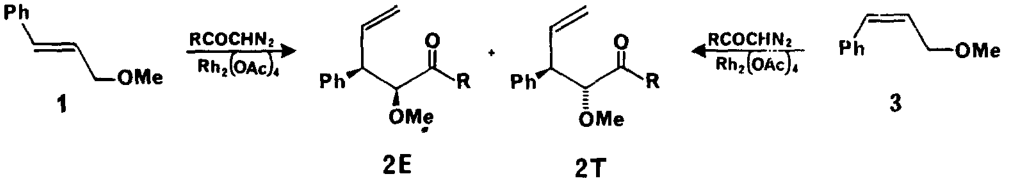
Summary: Allylic oxonium ylides, generated by rhodium(II) acetate-catalyzed decomposition of diazo carbonyl compounds in the presence of allyl methyl ethers, undergo the [2,3]-sigmatropic rearrangement with a high degree of diastereoselectivity.

The selective formation of allylic oxonium ylides by intermolecular reactions between allyl ethers and catalytically generated metal carbenoid intermediates has been elusive.[1] Their generation provides the molecular framework for the [2,3]-sigmatropic rearrangement (eq. 1), but competitive carbenoid addition to the carbon-carbon double bond has prevented its synthetic utilization. Both photochemical and copper(II) sulfate catalyzed reactions of ethyl diazoacetate with allyl methyl ethers lead to complex mixtures consisting of cyclopropane products along with those from the [2,3]-sigmatropic rearrangement and from [1,2]-insertion.[2] In addition, preliminary results from $Rh_2(OAc)_4$-catalyzed reactions have shown an overwhelming preference for cyclopropanation.[3] We have previously reported that allyl acetals are amenable to ylide generation and rearrangement in $Rh_2(OAc)_4$-catalyzed reactions with ethyl diazoacetate or dimethyl diazomalonate but, even in the best case, ylide generation is favored by only a factor of three over cyclopropanation.[4] More recently, Pirrung and Werner[5] and Roskamp and Johnson[6] have independently demonstrated the feasibility of intramolecular generation of allylic oxonium ylides from diazocarbonyl compounds with $Rh_2(OAc)_4$ catalysis, and their success has prompted us to reexamine its intermolecular counterpart.



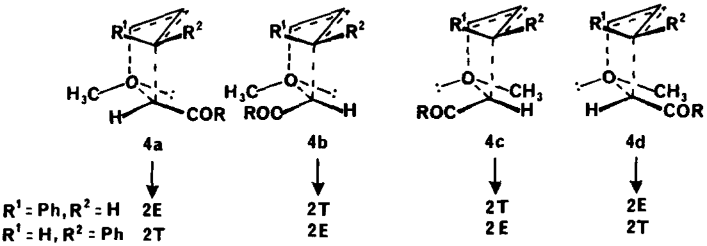
(1)

Treatment of cinnamyl methyl ether **1** at room temperature with ethyl diazoacetate (EDA) in the presence of $Rh_2(OAc)_4$ (reactant mole ratio = 1.7:1.0:0.01) resulted in the production of two diastereomeric ylide-derived [2,3]-sigmatropic rearrangement products (**2**) in high yield (eq. 2, R = OEt).[7] The erythro isomer **2E** was favored over the threo isomer **2T** by nearly 5:1. Similar treatment of the cis-cinnamyl ether **3** with EDA using $Rh_2(OAc)_4$ produced the diastereomeric mixture in which the threo isomer dominated by more than 16:1. As in prior evaluations of diastereo-



(2)

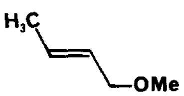
selectivity for [2,3]-sigmatropic rearrangements of the comparable dimethylammonium ylides,[8] the results that we have obtained with oxonium ylides can be explained by steric and/or electronic influences on transition state structures **4a-d**. We rationalize that **4b** and **4d** are of higher energy than **4a** and **4c** because of eclipsing interactions between the O-methyl and COR groups. Accordingly, the observed diastereoselectivity is a function of the relative transition state energies for **4a** and **4c** with **4c** dominant in product selection.. Compared to the diastereoselectivities observed with



the analogous ammonium ylides, which were 2:1 and 1:2, respectively,[8] those from rearrangements of oxonium ylides were significantly greater, presumably because of the additional differentiation provided to transition state structures by the methyl substituent of the methyl-oxonium ion.

Cyclopropane formation is the major competing process in reactions of cinnamyl methyl ethers with EDA. However, even this competitive reaction is minimized when α-diazoacetophenone, a more selective carbenoid reagent, is used in place of EDA. Whereas **1** formed **2** and cyclopropane products with EDA in relative yields of 73% and 27%, respectively, with α-diazoacetophenone (DAP) their relative yields were 94% and 6%. Likewise, **3** formed **2** and cyclopropane products with EDA in relative yields of 74% and 26%, respectively, but DAP favored the ylide products by 91% and 9% for cyclopropantion. Similar results were obtained with *p*-methoxy-α-diazoacetophenone (MDA).

Results from $Rh_2(OAc)_4$-catalyzed reactions of representative allyl methyl ethers (**1**, **3**, **5-7**) with EDA, DAP, and MDA are reported in Table I. Reactions were performed by the slow addition of the diazo compound in dichloromethane through a syringe pump to the allyl ether and 1.0 mol %, based on the limiting reagent, of $Rh_2(OAc)_4$ in dichloromethane under nitrogen at 25°C.



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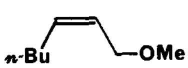

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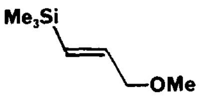

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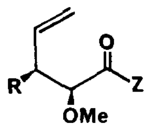
8E



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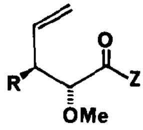

Table I. Selectivity in $Rh_2(OAc)_4$-Catalyzed Reactions of Diazo Compounds with Allyl Methyl Ethers^a

Allyl ether	Diazo compound	Ratio^b	R =	Z =	product yield, %	relative yield, %		rel. yield %	
						8	cyclopropane	**8E**	**8T**
1	EDA	1.6	Ph	OEt	95	73	27	83	17
1	DAP	1.7	Ph	Ph	86	94	6	91	9
1	MDA	1.5	Ph	*p*-$MeOC_6H_4$	85	96	4	91	9
3	EDA	1.7	Ph	OEt	95	74	26	6	94
3	DAP	1.6	Ph	Ph	70	91	9	19	81
5	EDA	5.4	Me	OEt	86	92	8	79	21
5	DAP	3.0	Me	Ph	95	98	2	82	18
5	MDA	3.0	Me	*p*-$MeOC_6H_4$	90	97	3	82	18
6	DAP	1.5	n-Bu	Ph	87	95	5	20	80
7	EDA	2.5	Me_3Si	OEt	68	94	6	97	3

[a] Reactions were performed with the diazo compound as the limiting reagent, usually on a 2.0 mmol scale. [b] Mole ratio of reactant allyl ether to diazo compound.

Diastereoisomers were assigned from the vicinal coupling constant to the proton on the methoxy-substituted carbon in **8** by evaluating relative conformer populations in accordance with the Karplus equation ($J_{anti} > J_{gauche}$).[9] As can be seen from the data, ylide-derived [2,3]-sigmatropic rearrangement products **8E** and **8T** are formed to the near exclusion of olefinic cyclopropanation products in most cases. Since the rate for cyclopropanation of styrene using EDA is nearly four-times greater than that for cyclopropanation of 1-hexene,[10] the greater yield of cyclopropane products in $Rh_2(OAc)_4$-catalyzed reactions of EDA with **1** or **3**, relative to **5-7**, is understandable. Furthermore, the [2,3]-sigmatropic rearrangement of oxonium ylides occurs with a high degree of diastereoselectivity, which with **7** and its bulky trimethylsilyl substituent results in the nearly exclusve formation of **8E** even from reactions with EDA.[11]. Products from direct insertion into the allyl carbon-methoxide bond of these allyl methyl ethers (Stevens [1,2]-rearrangement) were observed, but their yields, even with **1** or **3**, were less than 4% of the total and could be further minimized by performing these reactions at lower temperatures.[3]

Rhodium(II) perfluorobutyrate, $Rh_2(pfb)_4$,[12] used in place of $Rh_2(OAc)_4$ for reactions of EDA or DAP with **5**, did not change the diastereoselectivities of the [2,3]-sigmatropic rearrangement from those reported in Table I. These results indicate that the [2,3]-sigmatropic rearrangement occurs from the free ylide rather than a metal-associated ylide. However, an increased yield of cyclopropane products resulted from $Rh_2(pfb)_4$-catalyzed decomposition of EDA in the presence of **5** (17% versus 8% with $Rh_2(OAc)_4$), although a similar increase was not observed with DAP or MDA. With allyl ethyl ether and EDA, $Rh_2(pfb)_4$ causes an increase in the relative yield of the ylide-derived product (**8**, R = H) to 45% from the 10% yield obtained from the $Rh_2(OAc)_4$-catalyzed reaction.

Given the reactivity enhancement for cyclopropanation caused by alkyl and phenyl substituents on a carbon-carbon double bond,[10] the increased selectivities for ylide generation found with cinnamyl and crotyl methyl ethers over that observed with allyl ethyl ether are unlikely to be due to steric or electronic factors which disfavor cyclopropanation. Rather, these substituents appear to promote intramolecular trapping of the intermediate ylide which, as we have previously proposed,[4] exist in equilibrium with the metal-associated ylide formed by equilibrium association of the metal carbene and ether.

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(7) ^{1}H NMR of **2E** ($CDCl_3$, 300 MHz): δ 7.35-7.20 (m, 5H), 6.18 (d of d of d, *J* = 17.1, 10.3, 8.2 Hz, 1H), 5.17 (d, *J* = 10.3 Hz, 1H), 5.09 (d, *J* = 17.1 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, $OC\mathit{H}_2CH_3$) 3.98 (d, *J* = 5.8 Hz, C*H*OMe), 3.73 (d of d, *J* = 8.2, 5.8 Hz, C*H*Ph), 3.38 (s, OMe), and 1.12 (t, *J* = 7.1 Hz, $OCH_2C\mathit{H}_3$). ^{1}H NMR of **2T** ($CDCl_3$, 300 MHz): δ- 7.35-7.20 (m, 5H), 6.06 (d of d of d, *J* = 17.6, 9.6, 8.3 Hz, 1H), 5.12 (d, *J* = 17.6 Hz, 1H), 5.11 (d, *J* = 9.6 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, $OC\mathit{H}_2CH_3$), 4.02 (d, *J* = 7.4 Hz, C*H*OMe), 3.72 (d of d, *J* = 8.3, 7.4 Hz, C*H*Ph), 3.33 (s, OMe), and 1.21 (t, *J* = 7.1 Hz, $OCH_2C\mathit{H}_3$). Diastereoisomer assignments were made on the basis of vicinal proton coupling constants between CHOMe and CHPh in **2**.

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(9) Assumption is made that R is larger than vinyl. **8E**: *J* = 5.8 Hz (R = Ph, Z = OEt), 5.7 Hz (R = Ph, Z = Ph), 5.1 Hz (R = CH_3, Z = OEt), 6.2 Hz (R = CH_3, Z = Ph), 4.8 Hz (R = *n*-Bu, Z = Ph), and 4.5 Hz (R = Me_3Si, Z = OEt). **8T**: *J* = 7.4 Hz (R = Ph, Z = OEt), 8.2 Hz (R = Ph, Z = Ph), 5.7 Hz (R = CH_3, Z = OEt), 6.2 Hz (R = CH_3, Z = Ph), and 6.8 Hz (R = *n*-Bu, Z = Ph).

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(11) Similar reactions with the cis isomer of **7** resulted in a complex mixture of products.

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