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A coherent study on the *Z*-enoate assisted Meyer–Schuster rearrangement†

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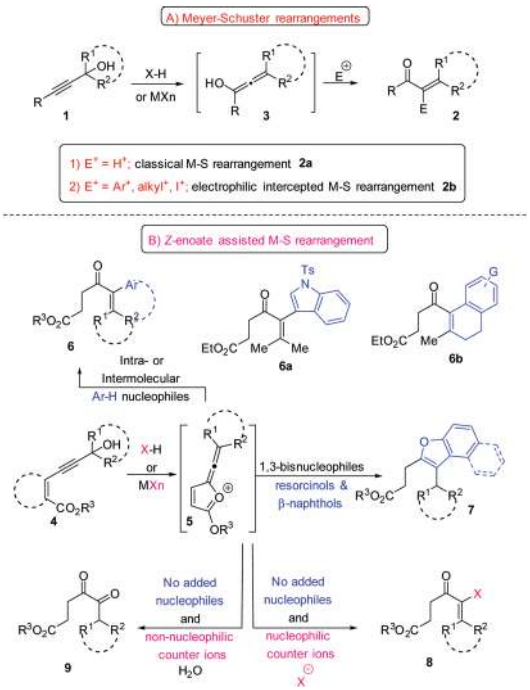
A systematic study has been performed on the *Z*-enoate assisted Meyer–Schuster rearrangement of propargylic alcohols. The impact of various factors such as temperature, solvent, concentration of a counter ion of an acid, and the nature of the arene nucleophile was studied. The relative nucleophilicity of various arenes estimated in this study is in good agreement with that of Herbert Mayr's nucleophilicity scale.

Introduction

Propargylic alcohols are the common and highly utilized synthetic building blocks with two functional groups. Among various reactions of propargylic alcohols,[1] the Meyer–Schuster (M–S) rearrangement is of significant synthetic potential in organic synthesis.[2] This rearrangement involves an isomerization of a propargylic alcohol **1** to conjugated enone **2a** *via* an allenol intermediate **3** (Scheme 1-A1). An intercepted version of this classical rearrangement has also been developed to broaden its synthetic utility.[3] In this mode, the protonation of allenol **3** was replaced by its reaction with added electrophiles (E^+), to generate α-functionalized enones **2b** (Scheme 1-A2).[4,5] Various electrophilic reagents such as, boronic acids,[6a] hypervalent iodonium salts,[6b] diazonium salts,[6c] alkyl halides *etc.* were well utilized for the synthesis of α-aryl, alkyl, and halo enones like **2b**.

In continuation of our interest in exploring the unconventional reactivity of propargylic alcohols and alkynes[7] and in contrast to these electrophilic interception approaches, recently, we designed and developed an unprecedented, conceptually novel version of the M–S rearrangement of (*Z*-enoate) propargylic alcohols **4** (Scheme 1B). In this strategy, the M–S intermediate allenol **3** was converted to be electrophilic in nature, so that nucleophiles can be employed for further functionalizations.[8] We introduced an intramolecular *Z*-enoate as an assisting (directing) group to reverse the electronic properties of the M–S intermediate allenol **3** from being nucleophilic to electrophilic **5**. This approach provided us with an opportunity to uncover the unconventional modes of reactivity of propargylic alcohols *via* a nucleophilic interception of intermediate **5**. This strategy was well described by employing



Scheme 1 (A) Classical Meyer–Schuster rearrangements of propargylic alcohols; and (B) Beeraiah-Meyer–Schuster rearrangement.

mono-nucleophilic arenes[8a] and 1,3-bisnucleophilic arenes[8b] (such as resorcinols and β-naphthols) for the synthesis of α-arylenones **6**, as well as (benzo)naphthofurans **7** respectively. Furthermore, we also evaluated the fate of the electrophilic alkoxyfuranyl-allene intermediate **5** in the absence of any added nucleophiles.[8c] During this process we discovered that the conjugate bases (X^-, such as $^-$OMs, $^-$OTs, Cl^-) of the acids can also act as nucleophiles to trap intermediate **5**, to yield α-X-enones **8**. On the other hand, when the conjugate base (X^-) is non-nucleophilic, then oxonium ion **5** was trapped with

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water (sole nucleophile), to generate the novel 4,5-dioxonoates **9** as exclusive products.

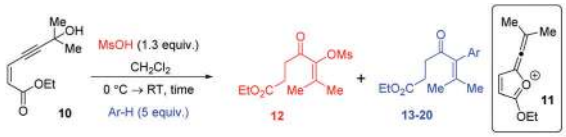
In continuation of exploring the novel reactivity of propargylic alcohols *via Z*-enoate assisted *i.e.*, the Beeraiah–Meyer–Schuster rearrangement, we performed a systematic study to understand the factors that control the reaction outcome and also to estimate the relative nucleophilicity of various external as well as internal nucleophiles (such as arenes, $^{-}$OMs, $^{-}$OTs, Cl^{-}, H_2O *etc.*) in this novel reaction. The observations and conclusions constitute the body of the current manuscript.

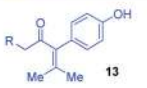
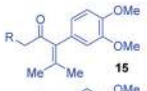
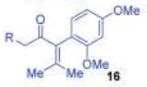
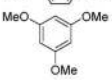
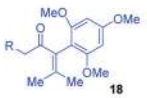
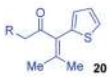
Results and discussion

To begin with, initially a competitive study among various external aromatic nucleophiles was performed employing the mesylate ion ($^{-}$OMs) as the standard nucleophile (Table 1). We chose propargylic alcohol **10** as the model substrate, and 1.3 equiv. of MsOH, 0 °C, CH_2Cl_2, 5 equiv. of the arene nucleophile as standard conditions. Some of the very commonly used aromatics such as phenol, anisole, 1,2- 1,3- and 1,4-dimethoxybenzenes, 1,3,5-trimethoxybenzene, mesitylene, and thiophene were employed. Most of the aromatics trapped intermediate **11** in competition with the mesylate ion (–OMs) and offered a separable mixture of α-OMs-enone **12** and the corresponding α-arylenones **13–20** in varying amounts. Based on the ratios of isolated products, the following conclusions have been derived. Among all the aromatics tested, only 1,3,5-trimethoxybenzene (1,3,5-TMB) was found to be a stronger nucleophile (when used in 5 equivalents) than mesylate to afford the aromatic trapped product **18** exclusively (entry 6). Anisole, 1,4-dimethoxybenzene and mesitylene (Table 1, entries 2, 5 and 7) were found to be very poor nucleophiles in comparison with mesylate and they did not result in any of the corresponding aromatic trapped products **14**, **17** & **19**, instead resulted in the exclusive formation of **12**. Phenol (entry 1) was found to be a better nucleophile than anisole & 1,2-dimethoxybenzene (entry 3), and a weaker nucleophile than thiophene (entry 8) and 1,3-dimethoxybenzene (entry 4) as it resulted in an isolated mixture (1 : 0.83) of **12** *vs.* **13**. Interestingly, the relative nucleophilicity of the three regioisomeric dimethoxybenzenes (entries 3–5) is found to be in the order of 1,4- < 1,2- < 1,3-. The nucleophilicity order found in the *Z*-enoate M–S rearrangement reaction for various aromatics was compared with the well known Herbert Mayr's nucleophilicity chart.[9] It is noteworthy to mention here that the found nucleophilicity trend is in good agreement with that of the Herbert Mayr's for similar arenes.

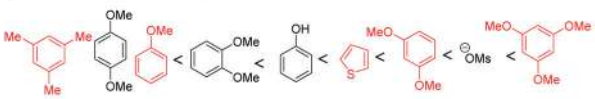
Having the best external nucleophile (1,3,5-TMB, at the 5 equiv. scale) in hand, we next turned our attention to evaluate the effect of the acid amount (*i.e.*, counter ion concentration), solvent, and temperature on this intermolecular trapping process. Initially, the acid amount was varied keeping 5 equiv. of 1,3,5-TMB, 0 °C–RT, and CH_2Cl_2 as conditions (Table 2). When **10** was treated with 0.25 equiv. of MsOH (entry 1) at 0 °C, the reaction was very slow and after 60 h, it resulted in a

Table 1 (A) Estimation of the relative nucleophilicity of various aromatics in the *Z*-enoate M–S rearrangement; (B) Herbert Mayr's nucleophilicity trend for the same and similar aromatics. (a) All the yields and ratios are for isolated compounds



Entry	Ar-H	Time (h)	12	Yield	13–20	Ratio (OMs : Ar)
1		24	36%	30%	 13	(1 : 0.83)
2		6	77%	—	—	(1 : 0)
3		5	54%	34%	 15	(1 : 0.63)
4		4	10%	68	 16	(1 : 7)
5		6	79%	—	—	(1 : 0)
6		6	—	75%	 18	(0 : 1)
7		7	81%	—	—	(1 : 0)
8		2	40%	39%	 20	(1 : 1)

Relative nucleophilicity of aromatics in the *Z*-enoate M–S rearrangement (wrt the mesylate ion)



Herbert Mayr's nucleophilicity of aromatics

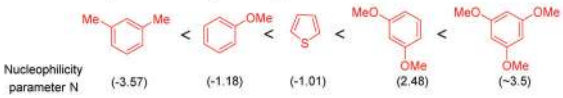
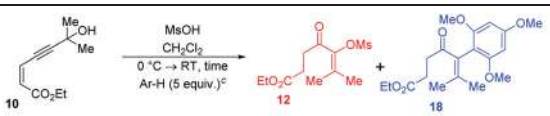


Table 2 Estimation of the effect of the acid amount



Entry	Equiv.	Time (h)	12 yield[d] (%)	18 yield[d] (%)	Ratio (12 : 18)
1[a]	0.25	60	16	15	1.07 : 1
2[b]	0.5	60	29	32	0.91 : 1
3	1.3	6	0	75	0 : 1
4	3	3.5	0	81	0 : 1

[a] 50% of **10** was recovered. [b] 20% of **10** was recovered. [c] Ar-H = 1,3,5-trimethoxybenzene. [d] All the yields and ratios are for isolated compounds.

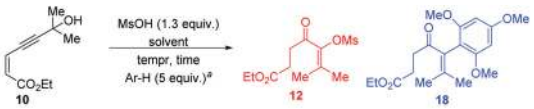
~1.1 : 1 mixture of mesylate and aryl trapped products (**12 : 18**) respectively along with 50% of unreacted **10**. With 0.5 equiv. of MsOH (entry 2), the conversion rate was better and a small reduction in the relative amount of mesylated product **12** (0.9 : 1) was also observed. Surprisingly, both 1.3 and 3 equiv. of MsOH resulted in the exclusive formation of the arylated trapped product **18** in excellent yields (entries 3 & 4). No traces of **12** were detected. This may be due to the fact that when an acid is employed in stoichiometric amounts, the concentration of the counter ion present in the reaction mixture at any time of the reaction might be low.

In continuation, the reaction was studied in various chlorinated solvents like CH_2Cl_2, 1,2-DCE and 1,2-DCB keeping 1.3 equiv. of MsOH, 5 equiv. of 1,3,5-TMB and 0 °C to RT as the standard conditions to understand the effect of solvent if any (Table 3). Interestingly, a smooth improvement in the preference for the mesylate trapped product **12** from $CH_2Cl_2$to 1,2-DCE to 1,2-DCB (0 : 1 to 0.13 : 1 to 0.56 : 1; **12 : 18**) was observed. On the other hand, when the reaction was performed at 55 °C in the same solvents (entries 4–6), in the case of CH_2Cl_2 (entry 4), there was a big change in the preference for the mesylate trapped product **12** when compared to that at 0 °C (entry 1). But there was no considerable change observed in the ratio of **12** and **18**, at 55 °C in the case of 1,2-DCE (entry 5) and 1,2-DCB (entry 6) when compared to their 0 °C counterparts. In addition we performed this reaction in non-chlorinated solvents such as toluene (entry 7), acetonitrile (entry 8) and nitromethane (entry 9) as well. In toluene, a 1 : 1.3 mixture of **12** and **18** was observed after 20 h at 0 °C to RT. In polar solvents the preference increases towards the aromatic trapped product **18** as the found ratio of **12 : 18** is 1 : 2.8 for acetonitrile and exclusively **18** for nitromethane.

Further, we performed the reaction in 1,2-DCB at various temperatures keeping 1.3 equiv. of MsOH, and 5 equiv. of 1,3,5-TMB as the standard conditions (Table 4). As the temperature increases gradually from 0 °C–RT to 55 °C to 100 °C to 150 °C (entries 1–4), the preference for the mesylate trapped product **12** gradually increases over the preference for the aryl trapped product **18** as described by the change in the ratio of **12 : 18** from (0.56 : 1) to (1.45 : 1). This observation suggests that at higher temperatures the ionization of the acid may be more and hence the concentration of the mesylate counter ion is relatively higher than that at lower temperatures. It is noteworthy here that when only 1.3 equiv. of MsOH are used for the reaction, the maximum amount of mesylate ions can be generated at any temperature, whereas the external arene nucleophile 1,3,5-TMB is present in 5 equivalents. Therefore, when compared to an equimolar mixture of both mesylate and 1,3,5-TMB, the mesylate possibly will be a stronger nucleophile than 1,3,5-TMB (see entries 3 and 4).

Subsequently, we also focused to evaluate the relative nucleophilicity of the counter ions (Cl^-, $^-$OTs and $^-$OMs) of commonly employed acids (Table 5). For this study, we chose 1,3,5-TMB as the standard nucleophile. Accordingly, we separately treated the propargylic alcohol **10** in dichloromethane, with 1.3 equiv. of each $BiCl_3$, *p*TSA and MsOH at 55 °C, in the presence of 5 equiv. of 1,3,5-TMB. Interestingly, the tosylate ion gave a 1.5 : 1 ratio of the tosylate trapped product **21** *vs.*

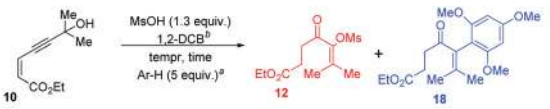
Table 3 Estimation of the solvent effect on the product distribution



Entry	Solvent	Temp. (°C)	Time (h)	**12** yield[f] (%)	**18** yield[f] (%)	Ratio (**12 : 18**)
1	DCM[c]	0 to RT	6	0	75	0 : 1
2	1,2-DCE[d]	0 to RT	5	8	61	0.13 : 1
3	1,2-DCB[e]	0 to RT	6	27	48	0.56 : 1
4	DCM	55	4	41	49	0.84 : 1
5	1,2-DCE	55	2	10	63	0.16 : 1
6	1,2-DCB	55	3.25	26	54	0.5 : 1
7	Toluene	0 to RT	20	32	36	1 : 1.3
8	CH_3CN[b]	0 to RT	72	10	28	1 : 2.8
9	CH_3NO_2	0 to RT	21	0	67	0 : 1

[a] Ar-H = 1,3,5-trimethoxybenzene. [b] 25% of unreacted **10** was recovered. [c] DCM = dichloromethane. [d] 1,2-DCE = 1,2-dichloroethane. [e] 1,2-DCB = 1,2-dichlorobenzene. [f] All the yields and ratios are for isolated compounds.

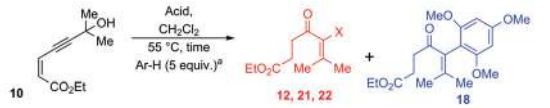
Table 4 Estimation of the temperature effect on the product distribution



Entry	Temp. (°C)	Time (h)	**12** yield[c] (%)	**18** yield[c] (%)	Ratio (**12 : 18**)
1	0 to RT	60	27	48	0.56 : 1
2	55	60	26	54	0.5 : 1
3	100	3	36	33	1.1 : 1
4	150	2.5	32	22	1.45 : 1

[a] Ar-H = 1,3,5-trimethoxybenzene. [b] 1,2-DCB = 1,2-dichlorobenzene. [c] All the yields and ratios are for isolated compounds.

Table 5 Relative nucleophilicity measurement among tosylate, mesylate and chloride ions



Entry	Acid	Equiv.	Time (h)	Yield[b] (%)	**18** yield[b] (%)	Ratio (X : Ar)
1	MsOH	1.3	4	41 (**12**)	49	0.84 : 1
2	*p*TSA	1.3	6	47 (**21**)	32	1.45 : 1
3	$BiCl_3$	1.3	6	28 (**22**)	40	0.7 : 1

The relative nucleophilicity order is: chloride < mesylate < aryl < tosylate

[a] Ar-H = 1,3,5-trimethoxybenzene. [b] All the yields and ratios are for isolated compounds.

aryl trapped product **18**. In the case of MsOH, the mesylate trapped product **12** *vs.* aryl trapped product **18** ratio was found to be 0.84 : 1. With $BiCl_3$, the ratio of the counter ion (chloride) trapped product **22** *vs.* aryl trapped product **18** further decreased to 0.7 : 1. Hence, based on the relative ratio of the counter ion trapped products *vs.* aryl trapped products, the increasing order of nucleophilicity among these three counter ions is chloride < mesylate < tosylate.

After performing a systematic study on the competitive product distribution among various intermolecular nucleophiles during the *Z*-enoate M–S rearrangement, next, we compared the nucleophilicity of the mesylate ion with an intramolecular nucleophile, *i.e.*, *p*-chlorophenyl group (Table 6). With 1.3 equiv., of MsOH at 0 °C, the propargylic alcohol **23** resulted in the formation of the cyclized product **24** (62%) along with 15% of α-OMs product **25**. As we increase the amount of MsOH from 1.3 to 2.5 (entry 2) the formation of **25** is more (48%) compared to **24** (32%). A further increase in the acid amount to 5 equiv. (entry 3) reverted the preference towards cyclized product **24** over **25**.

At the fixed amount of MsOH (1.3 equiv.), with the increase in temperature from 0 °C to 55 °C to 80 °C to 120 °C (entries 1 & 4–6), there was a gradual increase in the relative amount of formation of **25**, but surprisingly, the overall yield of the process decreased. A further increase in temperature to 150 °C (entry 7) resulted in a lowered preference towards the α-OMs product **25**, and gave a ratio of 2.6 : 1 of products **25** and **24**. At 80 °C and with 3 equiv. of MsOH (entry 8), the relative ratio of both **25** and **24** (6.4 : 1) was similar to that at 80 °C and with 1.3 equiv. of MsOH (entry 5). This means that the preference for **25** is higher by the increase in temperature than that by the increase in the acid amount.

In summary, we have performed a systematic study to estimate the relative nucleophilicity of various external nucleophiles during the *Z*-enoate assisted Meyer–Schuster rearrangement. It was found that among various arene nucleophiles screened, 1,3,5-trimethoxybenzene (at the 5 equiv. scale) was found to be the strongest when compared with the mesyloxy group. Among mesylate, tosylate, and chloride, the order of nucleophilicity was found to be chloride < mesylate < tosylate. Interestingly, the significant effect of the acid concentration (counter ion), temperature and the nature of the solvent was observed on the product distribution when a competitive study was performed between mesylate and 1,3,5-trimethoxybenzene nucleophiles. Similar effects were also observed when an intramolecular arene nucleophile was compared with the mesylate ion. The results of this study may assist in further development of the *Z*-enoate assisted Meyer–Schuster rearrangement.

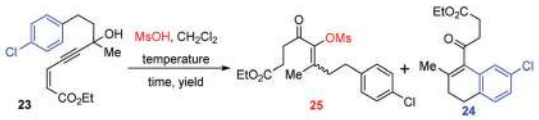
Experimental section

Reactions were monitored by thin-layer chromatography (TLC) carried out on Merck silica plates using UV light and anisaldehyde or potassium permanganate stains for visualization. Column chromatography was performed on silica gel (60–120 mesh) using hexanes and ethyl acetate as eluents. NMR data were recorded on 400 and 500 MHz spectrometers. ^{13}C and ^{1}H chemical shifts in NMR spectra were referenced relative to the signals of $CDCl_3$ (δ 7.263 ppm for ^{1}H and 77.16 ppm for ^{13}C). Chemical shifts δ and coupling constants J are given in ppm (parts per million) and Hz (hertz), respectively. Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet) or m (multiplets). HRMS were recorded by the electron spray ionization (ESI) method on a Q-TOF Micro with a lock spray source. Known compounds' data have been compared with the reported data, and references were given appropriately. Characterization data for new compounds are given below. ^{1}H and ^{13}C (proton decoupled) NMR spectra for all new compounds are given in the ESI.† Reagents were purchased from chemical companies.

General experimental procedure for the *Z*-enoate assisted Meyer–Schuster rearrangement

To a solution of the *Z*-enoate-propargylic alcohol[7] (1 equiv.) and the arene (5 equiv.) in dichloromethane (5 mL/0.2 mmol,

Table 6 Comparing the relative nucleophilicity of an intramolecular arene nucleophile with that of the mesylate ion, and the effect of concentration and temperature



Entry	Acid	Equiv.	Temp. (°C)	Time	25 yield[b] (%)	24 yield[b] (%)	Ratio (25 : 24)
1	MsOH	1.3	0 to RT	2 h	15	62	0.24 : 1
2	MsOH	2.5	0 to RT	1.5 h	48	32	1.5 : 1
3	MsOH	5	0 to RT	45 min	27	53	0.51 : 1
4	MsOH	1.3	55	1 h	20	58	0.35 : 1
5	MsOH	1.3	80	45 min	65	10	6.5 : 1
6[a]	MsOH	1.3	120 °C	45 min	52	7	7.4 : 1
7[a]	MsOH	1.3	150 °C	40 min	52	20	2.6 : 1
8	MsOH	3	80 °C	40 min	51	8	6.4 : 1

[a] 1,2-DCB as the solvent. [b] All the yields and ratios are for isolated compounds.

0.04 M) under a nitrogen atmosphere was added an acid (1.3 equiv.). The reaction tube was stirred at the prescribed temperature (0 °C or 55 °C or higher temperature) for 1–8 h. After completion of the reaction (by TLC analysis), saturated $NaHCO_3$ and DCM were added to reaction mixture and extracted with DCM. The combined organic layer was washed with brine, dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The crude material was purified by flash column chromatography using a hexane–ethyl acetate mixture as an eluent to yield the corresponding α-OMs or α-OTs or α-Cl-enone derivatives and arene trapped products.

For full details of all experiments, spectroscopic data and ^{1}H & ^{13}C-NMR data of all new compounds, see the ESI.†

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