JOC*Note*

A Versatile and Highly Stereoselective Access to Vinyl Triflates Derived from 1,3-Dicarbonyl and Related Compounds

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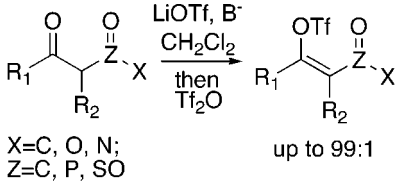
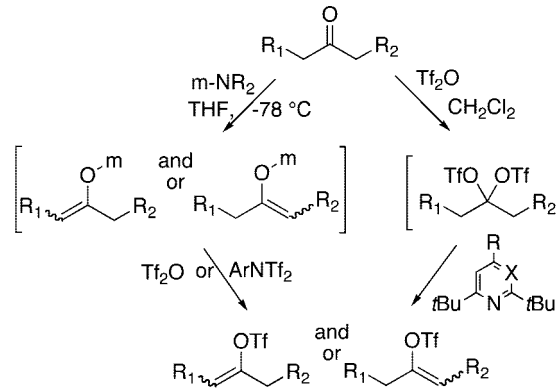


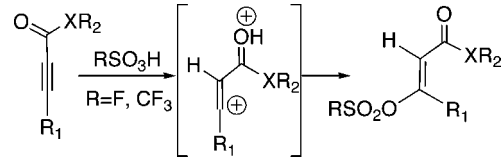
1,3-Dicarbonyl derivatives, such as 1,3-diketones, β-ketoaldehydes, β-ketoesters, β-ketoamides, β-ketophosphonates and β-ketosulfones were efficiently converted to the corresponding *Z* vinyl triflates with high stereoselectivity. Precoordination with lithium triflate in dichloromethane and enolization with mild bases such as trialkylamines or DBU followed by trapping with triflic anhydride probably accounted for such high selectivity, achieved even at 0 °C. This method offers the first direct route to vinyl triflates from β-ketoamides, β-ketophosphonates and β-ketosulfones.

Vinyl triflates are important building blocks in organic synthesis.[1] They are involved in many processes such as elimination giving alkynes,[2] sp^2-sp^3 coupling reactions with cuprates[3] and mainly sp^2-sp and sp^2-sp^2 coupling reactions, usually promoted by palladium catalysts.[4] Their preparation from simple ketones commonly relies on two protocols, each involving a different mechanistic pathway (Scheme 1). One of them is based on enolization with strong bases followed by trapping with triflic anhydride or equivalents.[1,5] In this sequence, the enolization step controls the regio- and stereoselectivity of the overall process. On the other hand, triflic anhydride addition to ketones provides *gem*-bis-triflyloxy intermediates,[6] which evolve to vinyl triflates by elimination upon treatment by hindered pyridines or pyrimidines.[7] With this method, almost no regio- nor stereocontrol could be achieved.[8]

SCHEME 1. Two Conventional Methods for the Synthesis of Vinyl Triflates from Ketones



SCHEME 2. Direct Route to Vinyl Triflates from Alkynes



A third protocol has been developed based on a completely different process, i.e., the direct addition of triflic acid to acetylene derivatives (Scheme 2).[9]

Although the latter method provided a highly regio- and stereoselective access to vinyl triflates derived from 1,3-dicarbonyl compounds, it cannot allow to access to vinyl triflates derived from cyclic or 2-substituted 1,3-dicarbonyl compounds. In contrast, the two other methods could in principle be applied to such substituted derivatives. However, these routes were complicated by the possible formation of mixtures of regioisomers and (*E*)- and (*Z*)-stereoisomers and most reports seem specific for particular cases.[8,10] A general solution is clearly needed in this area.

Facing such problems in several total syntheses, we designed new conditions that allow for a convenient and highly regio- and stereoselective access to *Z*-vinyl triflates derived from any 1,3-dicarbonyl compounds. Since this method proved quite general, we detail here our results.

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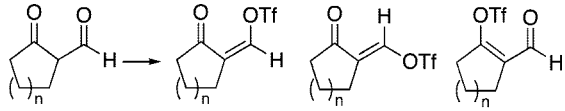
TABLE 1. Screening of Conditions for the Triflation of 2-Formylcycloalkanones[a]



entry	cyclic 1,3-diketones	base	solvent	reagent	product yields[b] (%) *Z*-**2**	*E*-**2**	**3**[c]
1	*n*=1,**1a**	*t*-BuLi	THF	Tf_2O	42	24	6
2	*n*=1,**1a**	*t*-BuLi	THF	Tf_2NPh	40	25	7
3	*n*=1,**1a**	*n*-BuLi	THF	Tf_2O	40	26	7
4	*n*=1,**1a**	*n*-BuLi	THF	Tf_2NPh	38	26	7
5	*n*=1,**1a**	*n*-BuLi	Et_2O	Tf_2O	28	25	17
6	*n*=1,**1a**	*n*-BuLi	Et_2O	Tf_2NPh	27	24	16
7	*n*=1,**1a**	*n*-BuLi	CH_2Cl_2	Tf_2O	76	0	0
8	*n*=1,**1a**	*n*-BuLi	CH_2Cl_2	Tf_2NPh	74	0	0
9	*n*=2,**1b**	*n*-BuLi	CH_2Cl_2	Tf_2O	75	0	0

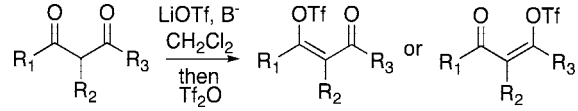
[a] Reaction at −78 °C. [b] Yields of isolated pure products. [c] **3a** proved to be a extremely sensitive compound, highly prone to degradation.

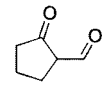
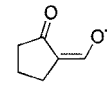
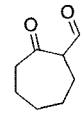
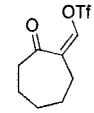
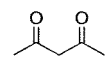
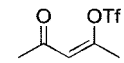
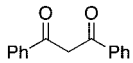
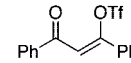
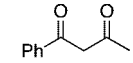
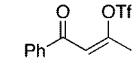
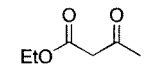
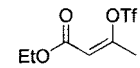
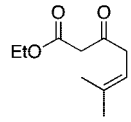
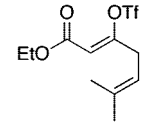
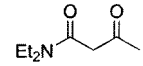
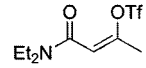
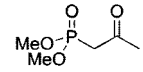
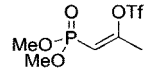
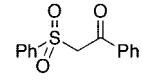
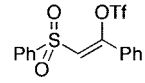
We first screened conditions on cyclic 1,3-diketones (Table 1), for which only two reports are known.[10i,j]

Applying conditions described for the selective formation of *Z*-2-triflyloxymethylenecyclopentanone,[10j] we obtained a mixture of regio- and stereoisomers (entry 1). Shifting to a milder triflating agent did not change the product distribution (entry 2 vs 1). A more aggregate base did not change the product ratio, regardless of the triflating agent used (entries 3, 4 vs 1, 2). Running the reaction in a less coordinating solvent surprisingly increased the amount of the more hindered endocyclic regioisomer **3a** to the detriment of the *Z* exocyclic regioisomer *Z*-**2a**. Here again, the nature of the triflating agent did not play any role (entries 5, 6 vs 3, 4). Decreasing further the coordination ability of the solvent could favored the *Z* isomer compared to the *E*, but the regioselectivity might be difficult to control as revealed with the latter examples. Gratifyingly, the reaction performed in dichloromethane gave the best results, since only the *Z*-2-triflyloxymethylenecyclopentanone *Z*-**2a** was detected and isolated whatever the triflating agent (entries 7, 8). Moreover, these conditions could be applied to the 6-membered ring analog **1b**, leading to the expected *Z*-2-triflyloxymethylenecyclohexanone *Z*-**2b** with the same high regio- and stereoselectivity (entry 9). However, applied to noncyclic derivatives, these conditions led to the *Z*-stereoisomer in good yields but the *E* isomer could be detected and isolated (*Z*/*E* 10:1).

These results clearly emphasized the preeminent role of coordination in such triflation reactions. In order to get even milder conditions, we envisaged to precoordinate the two carbonyl groups of the 1,3-diketone moiety. In analogy with the Evans enolization with boryl triflate,[11] we reasoned that such precoordination should first preorganize the system and second, increase the polarization of the C−O bonds and acidify the adjacent proton. A rapid screening revealed that lithium triflate in dichloromethane was the perfect choice,[12] allowing mild amine bases to efficiently provide the *Z* isomer with excellent stereoselectivity even at 0 °C (Table 2). The premixing time

TABLE 2. Stereoselective Triflation of 1,3-Dicarbonyl Derivatives in the Presence of LiOTf, Amines, and Triflic Anhydride at rt[a]



	Substrate		Triflates		Base	Yield (%)[b]	*Z*:*E*[c] Ratio
1		**1a**		**2a**	NEt_3	63	8:1
2					N*i*Pr Et$_2$	64	10:1
3		**1b**		**2b**	NEt_3	69	20:1
4					N*i*Pr Et$_2$	87	60:1
5		**1c**		**2c**	NEt_3	89	≥99:1
6					N*i*Pr Et$_2$	97	≥99:1
7		**4a**		**5a**	NEt_3	56	≥99:1
8					N*i*Pr Et$_2$	47	≥99:1
9		**4b**		**5b**	NEt_3	41	≥99:1
10					N*i*Pr Et$_2$	58	≥99:1
11		**4c**		**5c**	NEt_3	84	90:1
12					N*i*Pr Et$_2$	87	40:1
13		**6a**		**7a**	NEt_3	74	≥99:1
14					N*i*Pr Et$_2$	88	≥99:1
15		**6b**		**7b**	NEt_3	60	≥99:1
16					N*i*Pr Et$_2$	89	≥99:1
17		**8**		**9**	DBU	75	≥99:1
18		**10**		**11**	DBU	90	≥99:1
19		**12**		**13**	DBU	42[d]	≥99:1

[a] Conditions: LiOTf, base in dichloromethane, then Tf_2O at 0 °C. [b] Yields of isolated *Z* products after chromatography; the starting materials usually accounted for mass balance. [c] The stereoisomeric ratio was determined by ^1H NMR on the crude mixture. [d] The product was instable on silica gel; the yield of crude product was 65%.

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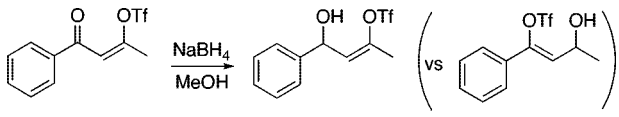
(12) Other lithium salt such as LiCl and Li_2CO_3 did not give satisfactory results; 2 equiv of LiOTf was required to achieve high selectivity.

SCHEME 3



before adding the triflating agent proved to be critical for stereoselectivity, since without it, a mixture of stereoisomers was formed.

Indeed, when 2-formylcyclopentanone **1a** was successively submitted to lithium triflate, triethylamine, and after 20 min to triflic anhydride in dichloromethane, the expected *Z*-2-triflyloxymethylene cyclopentanone *Z*-**2a** was obtained in good yield, but the other isomer could nevertheless be detected (entry 1). Interestingly, a slightly stronger base increased both yield and selectivity (entry 2). The 2-formylcyclohexanone **1b** only gave slightly better results in term of yields, but the selectivity was twice to four times better (entries 3, 4 vs 1, 2). Since the ring size seemed to play a role in the coordination due to geometrical constrains, we submitted the homologous 2-formylcycloheptanone **1c** to the same conditions. Indeed, stereoselectivity and yield were the highest of the series (entries 5, 6 vs 3, 4 vs 1, 2). It is worth noting that this yield is far better than the reported one (91 vs 53%[13]).

Using acyclic 1,3-diketones, these conditions also led to the formation of the corresponding triflates with excellent stereoselectivity (entries 7−12). The simplest acetylacetone **4a** gave the corresponding *Z*-4-triflyloxypent-3-en-2-one ***Z*-5a** with selectivity as high as 99:1 whatever the base used (entries 7, 8). The stereochemistry was secured by spectroscopic analysis, especially NOE experiments.

The symmetrical 1,3-diphenyl-1,3-propanedione **4b** also gave a single vinyl triflate, and here also, the more basic amine gave a higher yield (entry 10 vs 9). However, assigning its stereochemistry was far from obvious since NMR spectra revealed high shifts for the vinylic proton (7.18 ppm), but without literature precedent, it was not easy to refer this shift to the deshielding effect of the carbonyl group common in this series or to π-effect due to phenyl rings. Fortunately, we were able to grow crystals from this compound and the X-ray diffraction pattern unambiguously indicated Z stereochemistry for this compound (see the Supporting Information).

With the nonsymmetrical 1-phenyl-1,3-butanedione **4c**, regio- and stereoisomers could be expected. Gratifyingly, the precoordination conditions also led to the formation of a *single* triflate, with the same yield improvement using stronger amine (entry 12 vs 11). In order to secure its regiochemistry, the vinyl triflate ***Z*-5c** was reduced in the presence of sodium borohydride in methanol. The corresponding alcohol clearly exhibited in its ^{1}H NMR spectra a singlet for the methyl group and a doublet for the vinylic and the benzhydryl protons, as expected for the 2,3 regioisomer, clearly different from one would expect from the other regioisomer (Scheme 3). Crystals could also be obtained from ***Z*-5c**, and X-ray diffraction confirmed its structure and *Z* stereochemistry (see the Supporting Information). The present method thus offers high regioselectivity in the case of nonsymmetrical 1,3-diketones.

Due to the current focus on the cheaper vinyl tosylates,[14] we also performed some experiments with **4a**−**c** replacing triflic anhydride by tosyl derivatives. However, no more than 20−30% of the expected products could be obtained. These conditions are therefore limited to triflation reactions.

We then extended the scope of our triflation method to other 1,3-dicarbonyl derivatives. For comparison with other conventional triflation methods, ethyl acetoacetate **6a** was submitted to these conditions. The expected *Z*-ethyl 3-triflyloxybut-2-enoate **7a** was exclusively produced and isolated in high yield (entry 13). As with 1,3-diketo derivatives, the use of diisopropylethylamine instead of triethylamine significantly improved the yield without altering stereocontrol (entry 14 vs 13). It is also worth noting that this yield is again better than the reported one (88 vs 62%[10g]). Another β-ketoester **6b** with a longer chain, which included a double bond at a suitable position for a possible cyclization, behaves in the same way, giving the corresponding triflate **Z-7b** as a single stereoisomer whatever the base used (entries 15, 16). The latter result confirmed the noncationic nature of the reaction mechanism.

The good correlation observed between the lower acidity of β-ketoesters and the strength of bases suggested that other related compounds could also be triflated in these conditions but shifting from triethylamine to diisopropylethylamine or to even stronger bases. We thus submitted β-ketoamides to the same conditions and screened some bases. With the simple *N,N*-diethyl acetylacetamide **8**, DBU proved to be the best choice,[15] leading to the corresponding triflate **9** in high yield and with excellent stereoselectivity (entry 17).

Since β-ketophosphonates and β-ketosulfones have pK_a values close to those of β-ketoamides, and due to the analogy between P═O and S═O bonds with carbonyls, we reasoned that such compounds might also be triflated in our conditions. Indeed, β-ketophosphonate **10** and β-ketosulfone **12** were efficiently converted to the corresponding vinyl triflates **11** and **13**, respectively. Interestingly, the same excellent *Z* stereoselectivity (>99:1) was observed (entries 18, 19).

In conclusion, we have reported a new and direct route toward vinyl triflates derived from a large variety of 1,3-dicarbonyl derivatives, such as 1,3-diketones, β-ketoaldehydes, β-ketoesters, β-ketoamides, β-ketophosphonates, and β-ketosulfones. Moreover, a single regioisomer and stereoisomer was produced with excellent *Z* selectivity, except for cyclic β-ketoaldehydes for which the selectivity, still high, varied upon ring size.

Further work is now underway to understand this reaction and its scope.

Experimental Section

General Procedure 1 for Triflation. To a 2-formylcycloalkanone (1 equiv) in dry solvent (15 mL/mmol) at −78 °C was added a hexane solution of *n*-BuLi (1.1 equiv), turning the colorless solution to a bright yellow mixture. After 10 min of stirring, the triflating agent (1.1 equiv) was added, discharging the bright color of the solution. The reaction mixture was further stirred at −78 °C for 10−30 min depending on the reaction scale. A saturated solution of ammonium chloride (30 mL/mmol) and dichloromethane (30 mL/mmol) were then added. After the mixture was warmed at room temperature, the aqueous layer was extracted with dichloromethane (3 × 30 mL/mmol) and the combined organic layers were dried over sodium sulfate, filtered, and evaporated.

(*Z*)-2-Triflyloxymethylenecyclopentanone (*Z*-2a).[10i,j] Following the general procedure 1 using trifluoromethanesulfonic anhydride,

(13) Brückner, S.; Abraham, E.; Klotz, P.; Suffert, J. *Org. Lett.* **2002**, *4*, 3391–3393.

(14) (a) Nakatsuji, H.; Ueno, K.; Misaki, T; Tanabe, Y *Org. Lett.* **2008**, *10*, 2131–2134. (b) Baxter, J. M.; Steinhuebel, D.; Palucki, M.; Davies, I. W. *Org. Lett.* **2005**, *7*, 215–218.

(15) Simple amines only returned the starting materials.

2-formylcyclopentanone **1a** (0.505 g, 4.5 mmol) gave the Z-vinyltriflate ***Z*-2a** (0.835 g, 3.4 mmol) after 15 min of stirring and purification on silica gel column chromatography using pentane/ether (9:1 to 2:1). This compound is extremely sensitive and could only be stored in dichloromethane solution or better, in benzene matrix at 0 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.60 (1H, t, $J = 2.3$ Hz), 2.69 (2H, dt, $J = 2.3$, 7.2 Hz), 2.40 (2H, t, $J = 7.7$ Hz) 2.01 (2H, quint, $J = 7.4$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 201.75, 133.45, 126.27, 118.43 (q, $J = 321.0$ Hz), 39.37, 27.01, 20.33.

General Procedure 2 for Triflation. A solution of β-dicarbonyl compound (1 equiv) and lithium trifluoromethanesulfonate (2 equiv) in dichloromethane (30 mL/mmol) was cooled to 0 °C, and the base (1.1 equiv) was then added. After 20 min of stirring at 0 °C, trifluoromethanesulfonic anhydride (1.1 equiv) was added, and the reaction mixture was further stirred at this temperature upon reaction completion (followed by TLC). A saturated solution of ammonium chloride (30 mL/mmol) and dichloromethane (10 mL/mmol) were then added, and the aqueous phase was extracted twice with dichloromethane (2 × 30 mL/mmol). The resulting organic layers were dried over sodium sulfate and evaporated.

***N,N*-Diethyl (*Z*)-3-Triflyloxybut-2-enamide 9.** Following general procedure 2 using 8-diazabicyclo[5.4.0]undec-7-ene, *N,N*-diethyl-3-oxobutanamide **8** (0.158 mL, 1 mmol) gave the *Z*-vinyl triflate **9** after 30 min of stirring and purification on silica gel column chromatography using pentane/ether (2:1 to 1:2) as a colorless oil (0.216 g, 75%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.92 (1H, s), 3.41 (2H, q, $J = 7.1$ Hz), 3.33 (2H, q, $J = 7.1$ Hz), 2.15 (3H, s), 1.16 (3H, t, $J = 7.1$ Hz), 1.13 (3H, t, $J = 7.1$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 162.17, 150.29, 118.37 (q, $J = 319.5$ Hz), 115.02, 42.58, 39.73, 20.58, 14.31, 12.77; HRMS (ESI) calcd for $C_9H_{14}O_4NF_3S$ + Na 312.0488, found 312.0470.

Dimethyl (*Z*)-2-Triflyloxyprop-1-enephosphonate 11. Following the general procedure using 8-diazabicyclo[5.4.0]undec-7-ene, dimethyl 2-oxopropylphosphonate **10** (0.166 g, 1 mmol) gave the Z-vinyl triflate **11** after 30 min of stirring. Since the product decomposed on silica gel, the organic layers were washed with 2 × 30 mL of 5% HCl solution, then with 30 mL of water and 30 mL of brine, dried over Na_2SO_4, and evaporated to afford **11** as a colorless oil (0.268 g, 90%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.51 (1H, qd, $J = 0.9$, 6.4 Hz), 3.77 (6H, d, $J = 11.5$ Hz), 2.24 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.63 (d, $J = 5.6$ Hz), 118.34 (q, $J = 320.1$ Hz), 108.92 (d, $J = 191.1$ Hz), 52.96 (d, $J = 5.6$ Hz), 21.92 (d, $J = 13.0$ Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 13.13 (s, 1P); HRMS (ESI) calcd for $C_6H_{10}O_6F_3PS$ + Li 305.0042, found 305.0044.

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Supporting Information Available: Experimental procedures, characterization data, and NMR spectra of compounds **2a**−**c**, **5a**−**c**, **7a**,**b**, **9**, **11**, and **13**; X-ray diffraction structures of ***Z*-5b** and ***Z*-5c** and their separate CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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