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Vinyl Triflates: A Mechanistic Study on Their Formation from Carbonyl Compounds and Triflic Anhydride

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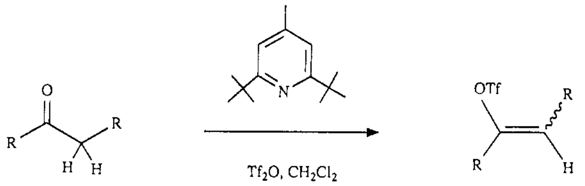
Reaction of triflic anhydride with various carbonyl compounds in the presence of a hindered base has been studied by NMR spectroscopy. In the cases of linear aldehydes exclusive formation of the *gem*-bis(triflate) occurs which then thermally decomposes to the vinyl triflate. The formation of *gem*-bis(triflate) is crucial to the success of the reaction and requires both a polar solvent such as $CHCl_3$ or 1,2-dichloroethane *and* elevated temperatures. For ketonic compounds no spectroscopic evidence was observed for a *gem*-bis(triflate) species, and, notably, nonpolar solvents such as carbon tetrachloride work well for the synthesis. It was also seen that elevated temperatures for the ketonic compounds led to good to excellent yields of vinyl triflate in very short reaction times. In general then, elevated temperatures (50 ⇒ 70 °C) and chlorinated solvents $CHCl_3$ and 1,2-dichloroethane are seen as optimal conditions for vinyl triflate preparations regardless of whether the carbonyl substrate is an aldehyde or ketone.

Introduction

Vinyl triflates[1] are valuable synthetic intermediates in transition-metal-mediated cross-coupling reactions[2] as well as useful precursors to vinyl cations.[3] Several methods exist for thier preparation,[4] most of which involve starting from a carbonyl compound and a source of Tf^+.[5] One of the more recent and general methods available involves use of the sterically hindered base 4-methyl-2,6-di-*tert*-butylpyridine (1), triflic anhydride (Tf_2O), and the appropriate carbonyl compound (eq 1).[6] We recently prepared polymer-bound 2,6-di-*tert*-butylpyridine and showed it to be very effective in vinyl triflate preparations and easily recycled for further use.[7] The yields are usually good to very good using 1; however, there is often little stereoselectivity in the reaction.[8] The problem of selectivity can be overcome by trapping metal enolates (kinetic or thermodynamic) with a source of Tf^+, but this method has been limited to the use of ketones thus far.[9]



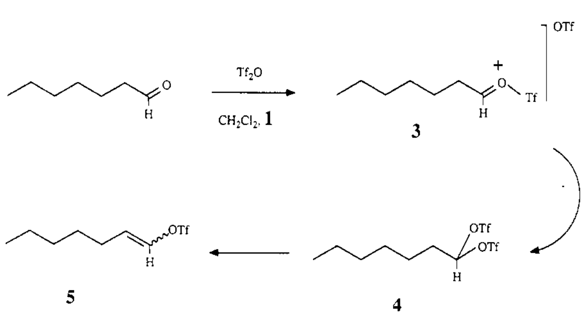
(1)

Although vinyl triflate preparations are ubiquitous in the literature, only limited attention has been focused on the mechanism of their formation. The mechanistic studies to date have centered on strained bicyclic ketones.[10] Recently *gem*-bis(triflate) species derived from aldehydes[11] have been identified spectroscopically. The purpose of the present study is to use more common carbonyl systems in a qualitative mechanistic study of vinyl triflate formation utilizing proton, carbon, and fluorine NMR spectroscopy as a nondestructive reaction probe. The results of the study should aid the synthetic chemist in designing the proper conditions for efficient vinyl triflate syntheses.

Results and Discussion

Solvent and Temperature Dependence. Converting ketones to vinyl triflates using 1 can be accomplished in a variety of organic solvents such as pentane, dichloromethane, chloroform, and carbon tetrachloride.[6] In the case of 2, carbon tetrachloride was found to be the solvent of choice because it limited a competing side reaction.[7b] In the case of hindered aldehydes, a somewhat similar range of solvents were suitable for vinyl triflate preparations.[6] In direct contrast, when employing less hindered aldehydes such as pentanal[6] or heptanal, solvents such as 1,2-dichloroethane or chloroform and elevated reaction temperatures are necessary for reasonable yields. This result has been observed for both 1 and 2 using heptanal and Tf_2O.

Reaction of 1 or 2 with heptanal and Tf_2O in refluxing 1,2-dichloroethane for 2 h produced the expected vinyl triflate 5 as a mixture of *Z* and *E* isomers (eq 2). When



(2)

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Table I. List of ^{19}F Resonances[a]

compd	^{19}F resonance (ppm)	compd	^{19}F resonance (ppm)
1·HOTf	74.2	4	78.5
TfOH	76.7	(*Z*)-5	78.8
Tf_2O	80.8	(*E*)-5	79.2

[a] Spectra were run in $CDCl_3$ and resonances are reported in δ referenced externally to CF_3CO_2H at δ 76.5 ppm.

utilizing 2, freshly distilled Tf_2O is recommended as we have observed a tendency for 2 to readily catalyze the aldol condensation of the aldehyde, whereas for 1, using identical Tf_2O, this was not a problem.[12] The polymer-bound base and 1 gave moderate selectivity for the (*Z*)-vinyl triflate, with an *E*/*Z* ratio of 1/4, respectively.

Reactions involving 1 or 2, Tf_2O, and heptanal in dichloromethane (ambient and refluxing) produce complex mixtures with only small amounts of vinyl triflate observed. It should be pointed out that if the reaction was carried out at 0 °C the major product isolated was the *gem*-bis(triflate) 4.[11] Furthermore, carbon tetrachloride gave complex product mixtures whether the reactions were run at ambient or elevated temperatures. Reaction of heptanal, 1 or 2, and Tf_2O in tetrachloroethene at 80 °C also gave only minor amounts of the desired vinyl triflate. When utilizing 1, for all three solvents, the reaction mixture quickly becomes heterogeneous and remains so throughout the reaction period. It is clear from the results above that temperature alone is not the only factor making 1,2-dichloroethane or chloroform the solvents of choice.

If 1,2-dichloroethane was employed at ambient temperatures with 1 or 2, only small amounts of 5 were produced in the reaction. As with the solvents above, the reaction mixture was heterogeneous throughout the reaction period. These results demonstrated that neither the elevated temperature or the solvents (i.e. $CDCl_3$ or 1,2-dichloroethane) individually can produce 5 in good yield, but the combination of the two conditions works well. The data above suggested that conversion of heptanal to 5 proceeds through a unique reaction pathway relative to ketones and even closely related but more hindered aldehydes.

Mechanistic Information via NMR Spectroscopy. To gain further insight into the mechanism of vinyl triflate formation we utilized variable temperature ^{13}C, ^{19}F, and ^{1}H NMR spectroscopy. Although *gem*-bis(triflates) like 4 have been isolated and characterized,[11] their intermediacy in the formation of vinyl triflates is unclear.

A 1,2-dichloroethane solution of heptanal, Tf_2O, and 1 was prepared in a NMR tube and placed in the NMR probe already heated to 70 °C. Within 2 min *all* the ^{13}C resonances for heptanal were absent, and new signals corresponding to the *gem*-bis(triflate) 4 appeared.[11] Continued heating of the sample at 70 °C showed disappearance of the signals for 4 and 1 with concomitant appearance of resonances for 1·HOTf and (*E*)- and (*Z*)-5. The reaction was complete in 40 min with no change in the spectra thereafter.

We have also examined the reaction of heptanal, Tf_2O, and 1 using ^{19}F NMR spectroscopy. In Table I we have displayed the positions for ^{19}F resonances for the starting materials and products, including the *gem*-bis(triflate) 4. All signals show base-line separation, and the spectra are easily obtained in approximately 30 s.

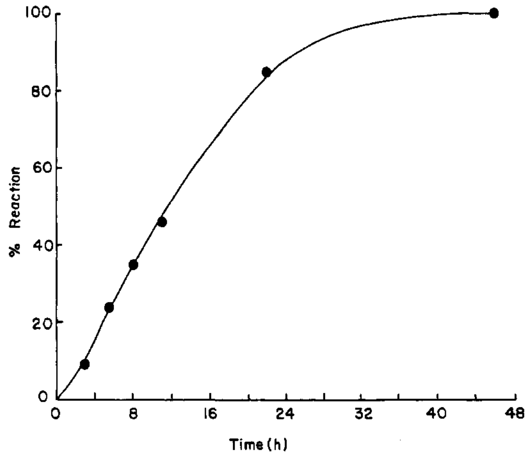

Figure 1. Relative rate plot for the reaction of heptanal with 1 and Tf_2O at 50 °C in $CDCl_3$.

The plot for the reaction of heptanal, 1, and Tf_2O in $CDCl_3$ is presented in Figure 1. The aldehyde carbonyl group appears to react very quickly with the triflic anhydride to form the *gem*-bis(triflate), which then decomposes to 5 with loss of triflic acid. The exact path for the loss of triflic acid is not known, although from data discussed below it would appear that a polar intermediate or transition state is involved in the process. We find that base concentration does not affect the relative rate of formation for 5 which is consistent with previous studies.[10]

At 50–70 °C in 1,2-dichloroethane or chloroform, the reaction sequence appears quite straight forward; however, how can the more complex reactivity pattern be explained when using CCl_4 and $Cl_2C{=}CCl_2$ or when the reaction is run at lower temperatures? To answer these important questions, we have collected ^{1}H and ^{19}F NMR data in various solvents and at different temperatures for the reaction of heptanal, 1, and Tf_2O. If the reaction (eq 2, solvent = $CDCl_3$) was performed at 25 °C, we observe the following results: (i) formation of 4 is slow; (ii) concomitant with the formation of 4 is an aldol product of heptanal; (iii) after 7 h of reaction only *gem*-bis(triflate) and aldol-type products are present.

From the above data, it can then be visualized that at the lower temperatures an aldol-type reaction successfully competes with *gem*-bis(triflate) formation, hence decreasing the yield of the desired vinyl triflate. If the reaction is run at 0 °C in CH_2Cl_2 though, it appears that formation of 4 becomes the dominant reaction again, and moderate yields of 4 can be isolated without contamination by large amounts of aldol-type byproducts.[11]

Monitoring the reaction (eq 2, solvent = CCl_4) by ^{1}H NMR at 50 °C gave similar results as the reaction run at 25 °C in $CDCl_3$. The formation of the *gem*-bis(triflate) was slowed down considerably in the nonpolar solvent. This would suggest that a polar intermediate or transition state (e.g. 3) is involved in the formation of 4. Compound 4 was prepared and then subjected to decomposition in the presence of 1 in both $CDCl_3$ and CCl_4 solutions. The latter solvent gave only minor conversion to product and very slow decomposition at 50 °C, whereas in $CDCl_3$ compound 4 eliminated triflic acid to afford 5 in good yield. These data indicate that not only is the formation of 4 solvent dependent but the decomposition as well.

A key point for the success in converting heptanal to 5 is the rapid and complete conversion to the intermediate *gem*-bis(triflate) 4, and this requires a relatively polar

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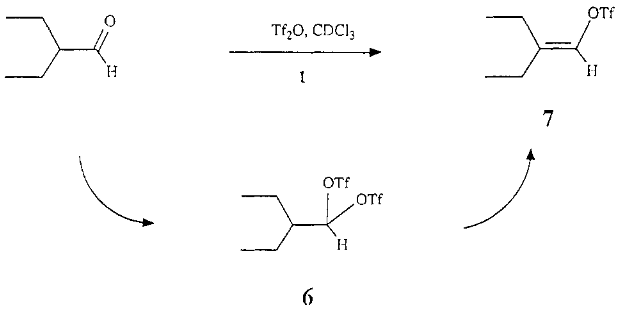
(12) Previously we observed a majority of aldol-type products using 2 as the base (ref 7b above) and discovered recently that this was due to using triflic anhydride that was several days old. Freshly distilled triflic anhydride gave the expected vinyl triflate from heptanal by employing 2 as the acid scavenger. The "older" triflic anhydride and 1 were found to promote clean conversion of heptanal to 5 using the conditions of Stang and Treptow.[5]

Scheme I



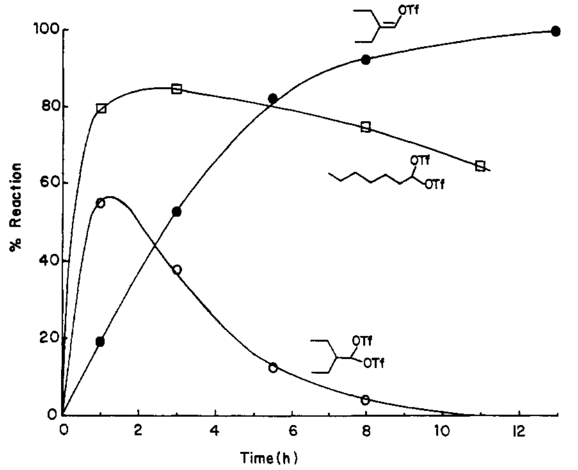


Figure 2. Relative rate plot for the reaction of 2-ethylbutanal with 1 and Tf_2O in $CDCl_3$ at 50 °C. A plot showing the relative disappearance of 4 is included for comparison purposes.

solvent. The subsequent conversion of 4 to 5 also requires a polar solvent such as chloroform or 1,2-dichloroethane *and* the elevated temperature.

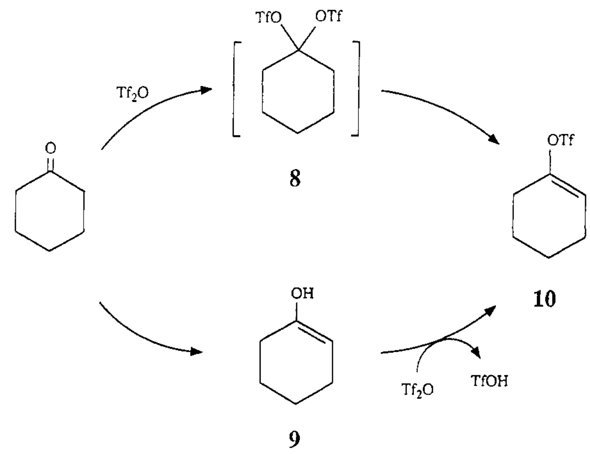
Studying yet another aldehyde, but now adding an alkyl group on the α-carbon, induces some intriguing changes. The 2-ethylbutanal can be converted to the vinyl triflate 7 (Scheme I) in very high yield, in most of the typical solvents, and at temperatures ranging from 25 to 70 °C!

The data in Figure 2 show that formation of the *gem*-bis(triflate) 6 was nearly as fast as for heptanal, but the relative rate at which 6 decomposed was faster in comparison to 4. Steric hindrance near the *gem*-bis(triflate) would be expected to accelerate loss of a triflate group. Recently Norton and co-workers[13] prepared $CH_3CH(OTf)_2$ [from CH_3CHI_2 and AgOTf] and found the compound could be isolated in pure form and was noted as being reasonably stable. The observed stability of the latter compound can be interpreted as indirect evidence showing that a decrease in steric crowding increases the stability of the *gem*-bis(triflate) species.

With the *gem*-bis(triflate) observed as an intermediate in the path to 7, it was not surprising that vinyl triflate formation slowed down considerably when the reaction was carried out in CCl_4. For example, at 50 °C in $CDCl_3$ the conversion of 2-ethylbutanal to 7 was complete in 13 h, whereas in CCl_4, after 13 h of reaction we observed only a 6% conversion to product!

The success of 2-ethylbutanal in the vinyl triflate synthesis at lower temperatures would appear to rely on the alkyl substitution at the α-carbon slowing down aldol-type reactions and having the opposite effect (i.e. rate enhancement) on vinyl triflate formation. The major reaction path does appear to involve formation of the *gem*-bis(triflate) 6 and its decomposition to vinyl triflate.

Scheme II



In a similar fashion as above, cyclohexanone was reacted with Tf_2O and 1 in $CDCl_3$ over a range of temperatures (Scheme II). There are several notable changes in going from the aldehydes to the cyclohexanone. In all the reactions we have studied thus far for cyclohexanone, we do not observe any spectroscopic evidence for a *gem*-bis(triflate) intermediate analogous to 4 and 6. The lack of spectroscopic evidence for the *gem*-bis(triflate) of ketonic compounds with α-hydrogens could be attributed to the formation of the *gem*-bis(triflate) being rate determining and the elimination step becoming relatively fast; hence, there may never exist a sufficient concentration of the *gem*-bis(triflate) for detection by NMR spectroscopy. It is also conceivable that steric hindrance may preclude formation of a *gem*-bis(triflate), and elimination occurs from a cationic species related to 3. The latter explanation would be consistent with the mechanism proposed for the bicyclic ketones studied previously.[10]

In the aldehyde cases studied above we found conversion to the desired vinyl triflate was considerably slowed down or made impossible by a change to a nonpolar solvent such as CCl_4. On the other hand, conversion of cyclohexanone in CCl_4 (50 °C, Tf_2O, and 1) to 10 was only mildly impeded relative to the other solvents. The ability to successfully utilize CCl_4 for ketone compounds might reflect a shift in the mechanism whereby trapping the enol tautomer by Tf_2O becomes competitive or even dominate over the formation and decomposition of a cationic–triflic anhydride complex. The formation of vinyl triflates via reaction of an enol with Tf_2O was previously suggested by Stang, Hanack, and Subramanian,[5] and this study provides experimental proof that indeed such a mechanism for ketones is quite plausible.

Concluding Remarks

For the successful conversion of aldol-susceptible carbonyl compounds it is critical to use a more polar chlorinated solvent and higher reaction temperature. Conversion of the carbonyl group to the *gem*-bis(triflate) has been shown to be very temperature and solvent dependent. With carbonyl compounds less prone to aldol condensation type reactions the higher temperature and more polar solvent are not required for successful conversion to vinyl triflate. But nevertheless, the latter reaction conditions lead to shorter reaction times and no overall change in isolated yields. Ketonic compounds may form a significant amount of product through the reaction of an enol tau-

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tomer with triflic anhydride without serious concomitant formation of aldol-type byproducts.

Experimental Section

General. All manipulations of compounds and solvents were carried out using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying reagents. Spectroscopic measurements utilized the following instrumentation: ^{1}H NMR, Varian XL 300; ^{13}C NMR, Varian XL 300 (75.4 MHz); ^{19}F NMR, Varian XL 300 (282.2 MHz). NMR chemical shifts are reported in δ vs Me_4Si assigning the $CDCl_3$ resonance in ^{13}C spectra to be at 77.00 ppm; C_6D_6 resonance in ^{13}C spectra to be at 128.00 ppm. ^{19}F chemical shifts are reported in δ vs CF_3CO_2H at 76.53 ppm. Carbonyl compounds were purchased and used as follows; heptanal from Eastman Kodak and bulb-to-bulb transferred before use; 2-ethylbutyraldehyde from Aldrich, distilled before use; cyclohexanone from Matheson Coleman & Bell, distilled before use. Tf_2O was prepared from TfOH distilled from P_2O_5 and Celite. *Important*: The Tf_2O should be freshly (ca. within 2–3 days) distilled from P_2O_5 before use and stored under N_2 for the best and most consistent results.

General Method for Vinyl Triflate Preparations Using Polymer-Bound 2,6-Di-*tert*-butylpyridine (2). A small flask was charged with the appropriate solvent (14.5 mL), polymer-bound 2,6-di-*tert*-butylpyridine (4.9 mmol, 2.08 g), the corresponding aldehyde or ketone (4.7 mmol), and Tf_2O (4.75 mmol, 1.34 g). The reaction mixture was stirred at room temperature or refluxed depending on the system investigated. Upon the completion of the reaction the mixture was diluted with pentane (50 mL). The pentane solution was decanted from the polymer-bound base and washed with water (50 mL) and then brine (25 mL). The organic layer was filtered through basic alumina with pentane elution, and then the sovents were removed by rotary evaporation to yield the appropriate vinyl triflate. The polymer-bound base was regenerated for further use using previously published procedures.[7b]

Spectroscopic data for **5**: Assignments of stereochemistry were based upon the coupling pattern for the vinyl protons in the two isomers. (*Z*)-**5** isomer: ^{1}H NMR ($CDCl_3$) δ 6.48 (d, J = 5 Hz, =CHOTf, 1 H), 5.21 (dt, J = 5, 8 Hz, CH$_2$C*H*=, 1 H), 2.20–2.10 (m, C*H*$_2$CH=, 2 H), 1.40–1.00 (m, CH$_2$'s, 6 H), 0.80 (t, J = 7 Hz, CH$_3$, 3 H); ^{13}C NMR ($CDCl_3$) δ 135.2 (=CHOTf), 120.9 (CH=), 118.6 (q, CF, J = 320 Hz), 31.2, 28.2, 24.1, 22.3 (CH$_2$'s), 13.9 (CH$_3$). (*E*)-**5** isomer: ^{1}H NMR ($CDCl_3$) δ 6.44 (d, J = 12 Hz, =CHOTf, 1 H), 5.72 (dt, J = 12, 7 Hz, CH$_2$C*H*=, 1 H), 2.04–1.94 (m, C*H*$_2$CH=, 2 H), 1.40–1.00 (m, CH$_2$'s, 6 H), 0.80 (t, J = 7 Hz, CH$_3$, 3 H); ^{13}C NMR ($CDCl_3$) δ 135.8 (=CHOTf), 122.9 (CH=), 31.0, 28.4, 26.5 (CH$_2$'s), remaining signals overlapped with the *Z* isomer.

Relative Rate Experiments. Stock solutions were prepared by weighing out a calculated amount of solvent and reagent necessary to yield a 1.0 M stock solution of each reagent (i.e. carbonyl compound, base, and Tf_2O). The NMR tube was charged with the base solution 0.33 mL) and the appropriate aldehyde or ketone solution (0.33 mL). At this point NMR spectra were obtained to verify starting material purities and concentrations in the reaction mixture. Finally, the Tf_2O solution (0.33 mL) was added to the NMR tube to yield a reaction that was 0.33 M in each reactant. The progress of the reactions were then monitored by either ^{1}H, ^{13}C, or ^{19}F NMR techniques to obtain data on the reaction rates. Variable-temperature NMR spectra were collected in the temperature-controlled probe at the specified temperature. When reaction times exceeded 4 h the sample was placed in constant temperature bath in between collection of spectra. In the cases where the pyridinium salt was not in solution, usually when the reaction temperature was less than 40 °C, the NMR sample was centrifuged to move the solid to the top of the solution and out of the receiver coils in the probe to obtain maximum resolution.

Decomposition of *gem*-Bis(triflate) 4 in $CDCl_3$ and CCl_4. *gem*-Bis(triflate) was prepared following the procedure of Martinez and co-workers.[11] Stock solutions were prepared by weighing out a calculated amount of the appropriate solvent and *gem*-bis(triflate) with enough base (0.411 g) to yield a ~1.0 M stock solution. The NMR tubes were charged to give 0.5 M samples. ^{19}F NMR techniques were used to follow the decomposition of the *gem*-bis(triflate) in the appropriate solvent.

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Cephalosporins from Glycinic Esters. 1. Total Synthesis of the Cephamycin Framework[†]

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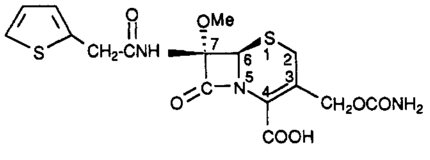
Δ^3 and Δ^2 N-protected 7-methoxycephem isomers are synthesized from thiazabutadiene derived from methoxyglycinate, in three major steps: hetero Diels–Alder cycloaddition, functional conversions, and lactamization.

During the past two decades, numerous semisynthetic cephalosporins have been prepared by varying the side chains at the 3- and 7-positions of 7-aminocephalosporinic acid or its analogues. These studies have generated compounds of broader antibacterial activity and improved pharmacokinetic properties.[1,2] Since the discovery of cefoxitin,[3] semisynthetic derivatives have been developed which benefit from the β-lactamase stability conferred by the 7-position α-methoxy functionality.



Cefoxitin

Here, we report a new and widely applicable total synthesis which affords Δ^3 or Δ^2 7-methoxy cephalosporin

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[†] Dedicated to Emeritus Professor Noël Lozac'h on the occasion of his 73rd birthday.

(1) Flynn, E. H. *Cephalosporins and Penicillins*; Academic Press: New York and London, 1972.