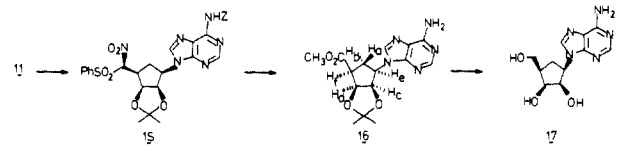
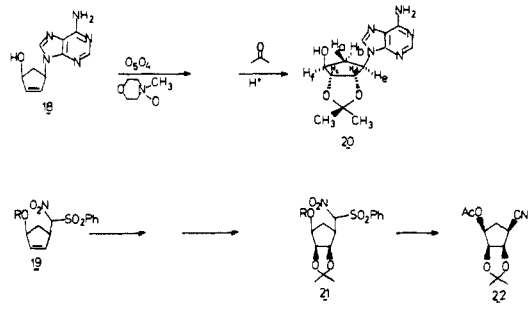
ester to the alcohol (83% yield) and aqueous hydrochloric acid hydrolysis followed by neutralization with a basic resin gave a single carbanucleoside in 66% yield. Neither the mp of the synthetic product (mp 168–70 °C) nor the spectral data (^{1}H and ^{13}C NMR) corresponded to (±)-aristeromycin.

Since the spectral data for both **13** and **11** appeared totally in agreement with the assigned structures, we considered whether the cis hydroxylation may have been "directed" to the more hindered face to give **15**.[4] A NOE study of the corresponding



methyl ester **16**[4] showed irradiation of H_b enhanced both H_e (8.3%) and H_f (5.6%) in agreement with the cis 1,4-relationship of the ester and the adenine. Irradiation of H_c enhanced both H_d and H_e indicating their cis relationship, and irradiation of H_d enhanced both H_c and H_f indicating their cis relationship. Thus, all of the structures starting from the cis hydroxylation product to the end must be reassigned as **15–17**,[4] and the final product, then, is (±)-*lyxo*-aristeromycin (**17**).[4]

To probe the source of the unusual hydroxylation stereochemistry, we hydroxylated **18** and **19**. NMR Eu(+3) induced shift studies allow assignment of the stereochemistry of **20**[4] as trans as "expected".[15] An NOE study of the nitrile **22**, derived from



the initial hydroxylation product **21** upon treatment with titanium trichloride,[8] showed the same pattern as for **16**—confirming the "abnormal" all cis orientation. Comparison of the results of the reaction of **11**, **18**, and **19** strongly implicates the nitrosulfonylmethane substituent as the director of the osmylation. Since sulfones are known not to direct osmylation,[7] it appears the source of the stereocontrol is coordination of osmium with the nitro group.

To resolve the issue of aristeromycin synthesis, we required a hydroxylation reagent that would not coordinate to the substituents present in **11**. Indeed, basic potassium permanganate[16] effects cis hydroxylation of **11** to give a product isomeric with **15**. This time, following the same sequence as before (use Scheme I), gave (±)-aristeromycin, whose spectral data is identical in all respects with an authentic sample.

The Pd-based reactions provide a very short and convenient synthesis of this carbacyclic nucleoside analogue. Other members may be readily created by similar means or through some of the intermediates reported herein. For example, introduction of a double bond in conjugation with the ester of **9** by sulfenylation–dehydrosulfenylation or the selenium equivalent followed by reduction forms neplanocin.[17] Furthermore, both the natural and the 2,3-di-epi series are available with complete stereocontrol. The unusual directive effect of the nitro group in cis hydroxylations via catalytic osmylations should prove valuable in stereocontrolled syntheses.

(15) Whereas H_a, H_c, and H_f shift by δ 1.13, 1.15, and 0.80 ppm upon adding 14.5 mol % Eu(hfc)$_3$, H_b and the two methyl groups only shift by δ 0.53, 0.17, and 0.16 under these conditions.

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Acknowledgment. We thank the National Institutes of Health, General Medical Sciences Institute, for their generous support of our programs.

Registry No. 4, 930-22-3; **5**, 54460-11-6; **6**, 111189-89-0; **7**, 111189-90-3; **8**, 13190-75-5; **9**, 111189-96-9; **10a** (diastereomer-1), 111189-94-7; **10a** (diastereomer-2), 111265-80-6; **10b** (diastereomer-1), 111189-95-8; **10b** (diastereomer-2), 111265-81-7; **11** (diastereomer-1), 111189-93-6; **11** (diastereomer-2), 111265-79-3; **12**, 111189-92-5; **13**, 111189-91-4; **15** (diastereomer-1), 111265-82-8; **15** (diastereomer-2), 111265-83-9; **16**, 111265-84-0; **17**, 72346-00-0; **20**, 111189-97-0; **22**, 111189-98-1; LiCH(NO$_2$)SO$_2$Ph, 74738-03-7; 2-pyrimidinone, 557-01-7; adenine, 73-24-5.

Supplementary Material Available: Spectral data for **6**, **7**, **8**, **9**, **11**, **13**, **16**, and **17** (2 pages). Ordering information is given on any current masthead page.

Hydrolysis Mechanisms of Alkynyl Benzoates, Tosylates, and Phosphates

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Alkynyl benzoates, tosylates, and phosphates have recently been prepared,[1a,b] and for RC≡COTs addition of protic acids HX shown to form RCH=CXOTs,[1c] while CH_3OH/K_2CO_3 gives $RCH_2CO_2CH_3$ and CH_3OTs.[1a] These compounds are of great interest for comparison to other ester types[2] and for the study of substitution of alkynyl systems,[3] and we now report that these substrates hydrolyze by several interesting mechanisms, including both electrophilic and nucleophilic attack on the triple bond.

In aqueous H_2SO_4 1-propynyl benzoate (**1**), diethyl 1-hexynyl phosphate (**2**), and 1-hexynyl tosylate (**3**) were found by ^{1}H NMR analysis of the reaction products to give the carboxylic acid corresponding to the alkynyl moiety, together with the acid derived from the acyl portion of each ester (eq 1–3). The reaction

$$CH_3C{\equiv}COBz\ (\mathbf{1}) \xrightarrow[H_2SO_4]{H_2O} CH_3CH_2CO_2H + BzOH \quad (1)$$

$$n\text{-}BuC{\equiv}COPO_3Et_2\ (\mathbf{2}) \xrightarrow[H_2SO_4]{H_2O} n\text{-}C_5H_{11}CO_2H + (EtO)_2PO_2H \quad (2)$$

$$n\text{-}BuC{\equiv}COTs\ (\mathbf{3}) \xrightarrow[H_2SO_4]{H_2O} n\text{-}C_5H_{11}CO_2H + TsOH \quad (3)$$

products from neutral aqueous solution containing CH_3CN cosolvent were reacted with CH_2N_2, and the methyl esters of the same acids were isolated and identified. The additional product

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Table I. Hydrolysis Rates of Alkynyl Esters, H_2O, 25 °C

	k_{H^+} (M^{-1} s^{-1})[a]	k_{H_2O} (s^{-1})	k_{OH^-} (M^{-1} s^{-1})	k_{H^+}/k_{D^+}	k_{H_2O}/k_{D_2O}
$CH_3C{\equiv}COBz$	3.02×10^{-5} [b]	3.42×10^{-5} [c]	73.7	2.7 ± 0.8	2.0 ± 0.0
n-$BuC{\equiv}COPO_3Et_2$	4.91×10^{-6} [d]	1.80×10^{-4} [e]	3.21	2.0 ± 0.1	2.8 ± 0.5
n-$BuC{\equiv}COTs$	1.30×10^{-5} [f]	2.40×10^{-6}	13.0	4.1 ± 1.2	

[a] log k_{H^+} taken as the intercept of a plot of log k_{obsd} versus H_0. [b] log $k_{obsd} = -1.10H_0 - 4.52$. $\Delta H^* = 20.1$ kcal/mol, $\Delta S^* = -11.8$ eu. [c] $\Delta H^* = 18.6$ kcal/mol, $\Delta S^* = -16.8$ eu. [d] log $k_{obsd} = -0.99H_0 - 5.31$. $\Delta H^* = 17.4$ kcal/mol, $\Delta S^* = -10.6$ eu. [e] $\Delta H^* = 11.1$ kcal/mol, $\Delta S^* = -38.4$ eu. [f] log $k_{obsd} = -1.38H_0 - 4.89$ ($r = 0.999$).

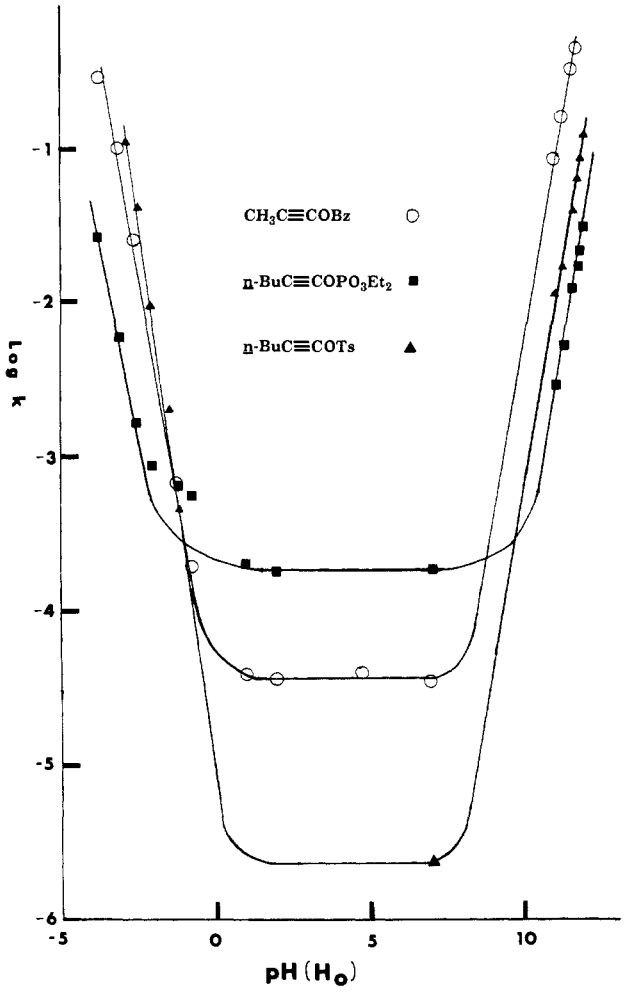

Figure 1. Rates of hydrolysis of $CH_3C{\equiv}COBz$ (**1**), n-$BuC{\equiv}COPO_3Et_2$ (**2**), and n-$BuC{\equiv}COTs$ (**3**) as a function of pH (H_0 below pH 1).

CH_3COCH_2OBz was formed in 46% yield from **1** under these conditions.

The kinetics of the reactions shown in reactions **1–3** in aqueous solutions were followed by UV spectroscopy, and the derived rate constants for hydrolysis are summarized in Table I, together with derived solvent isotope effects and activation parameters. Full kinetic data are given in Supplementary Tables II–IV. The rate measurements were also made by conductivity in certain cases, and satisfactory agreement between rate constants obtained by the two different methods was observed.

The variations of the rate of hydrolysis of **1–3** as a function of pH (H_0 below pH 1) are shown in Figure 1.

The acid-catalyzed reactions of **1–3** are interpreted as proceeding through the Ad_E2 mechanism of rate-limiting proton transfer to the β-carbon of the triple bond in each case (eq 4 and 5). This mechanism resembles the pathway established for the

$$RC{\equiv}COR' \xrightarrow[\text{slow}]{H^+} RCH{=}\overset{+}{C}OR' \xrightarrow[\text{fast}]{H_2O} RCH{=}C(\overset{+}{O}H_2)OR' \quad (4)$$

$$RCH{=}C(\overset{+}{O}H_2)OR' \longrightarrow RCH_2\overset{O}{\overset{\|}{C}}OR' \longrightarrow RCH_2CO_2H + HOR' \quad (5)$$

hydration of many alkynes,[4] with the further feature that mixed acid anhydrides that may be intermediates in the process are rapidly hydrolyzed further to the acids.

The bases of the mechanistic assignment in acid include the slope of the log k_{obsd} versus H_0 plots, the magnitude of the isotope effects k_{H^+}/k_{D^+}, and the magnitude of the activation parameters (Table I). All of these are consistent with values obtained for reactions of alkenes[5] and other alkynes[4] assigned as proceeding through Ad_E2 pathways and are different from the values characteristic of other conceivable mechanisms, particularly preequilibrium protonation followed by rate-limiting water attack.

Supportive of the above conclusion is that k_{H^+} for n-$BuC{\equiv}COPO_3Et_2$ exceeds k_{H^+} for $CH_2{=}CHOPO_3Et_2$[2j] by a factor of 80, compared with the ratio $k_{H^+}(HC{\equiv}COMe)/k_{H^+}(CH_2{=}CHOMe)$ of 40. Both of these methyl ethers also react by this mechanism.[4]

The values of k_{H^+} for the alkynyl esters **1–3** are each about 10^5 greater than that for $CH_3C{\equiv}CCH_3$ but 10^5 less than that for $CH_3C{\equiv}COEt$, consistent with the known[2j] diminished electron donor power to carbocations of acyloxy groups compared to alkoxy groups.

Mixed acid anhydrides are postulated as reaction intermediates following the rate-limiting steps in eq 5 but from the known behavior of such species[6] are expected to hydrolyze rapidly to the acids under these conditions.

Three distinctly different mechanisms for the neutral and base reactions merit consideration, namely nucleophilic attack on the acyl group or on either carbon of the alkynyl moiety, as illustrated for H_2O attack in eq 6–8, respectively. Analogoues of all three mechanisms have been observed in reactions in alkynyl halides.[3a]

$$RC{\equiv}COX + H_2O \longrightarrow [RC{\equiv}CO{\cdots}X{\cdots}OH_2] \longrightarrow \text{products} \quad (6)$$

4

$$\longrightarrow [R\bar{C}{=}C(\overset{+}{O}H_2)OX] \longrightarrow \text{products} \quad (7)$$

$$\longrightarrow [R(H_2\overset{+}{O})C{=}\bar{C}OX] \longrightarrow \text{products} \quad (8)$$

Comparative rate data show that the neutral and base reactions of the alkynyl esters **1–3** are accelerated by factors of 10^2–10^5 relative to the analogoues PhOAc, $(PhO)_3PO$, and PhO_3SCH_2Ph, respectively.[7,8] These latter three all react by eq 6, and the accelerations for **1–3** could be provided by breaking of the O–X bond in a rate-limiting transition state **4** or by a change in mechanism to those of eq 7 or 8. The occurrence of the process in eq 8 as one path for the neutral reaction of $CH_3C{\equiv}COBz$ is

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(7) Comparative rate constants are k_{H_2O} (s^{-1}): PhOAc (2×10^{-8}),[8a] $(PhO)_3PO$ ($<5 \times 10^{-7}$)[8b] (estimated using a conversion factor $k(4\text{-}O_2NC_6H_4OPO_3Ph_2)/k[(PhO_3PO) = 20)$,[8b] and PhO_3SCH_2Ph (10^{-9})[8c,d] (estimated by using $k_{OH^-}/k_{H_2O} = 4.27 \times 10^4$ for PhOMs[8d] and k_{OH^-} for PhO_3SCH_2Ph);[8c] k_{OH^-} (M^{-1} s^{-1}): PhOAc (1.27),[8a] $(PhO)_3PO$ (1.6×10^{-2}),[8b] and PhO_3SCH_2Ph (4.94×10^{-5}).[8c]
(8) (a) Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622–2637. (b) Bunton, C. A.; Farber, S. J.; Fendler, E. J. *J. Org. Chem.* **1968**, *33*, 29–33. (c) Zaborsky, O. R.; Kaiser, E. T. *J. Am. Chem. Soc.* **1966**, *88*, 3084–3087. (d) Bunton, C. A.; Welch, V. A. *J. Chem. Soc.* **1956**, 3240–3242.

demonstrated by the formation of CH_3COCH_2OBz in 46% yield in this reaction. Further experimental studies designed to establish the details of these reactions are in progress.

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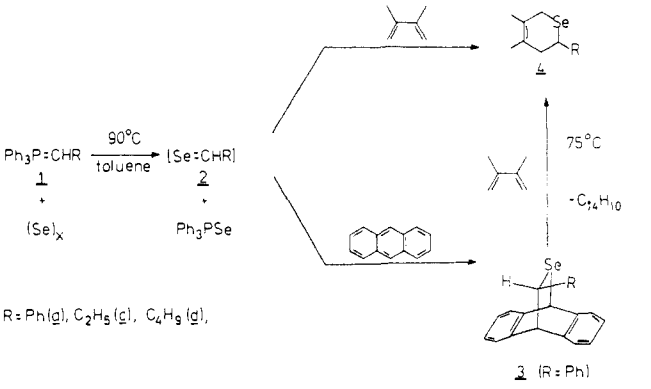
Supplementary Material Available: Tables II-IV containing rate constants and solvent isotope effect calculations for **1-3** (5 pages). Ordering information is given on any current masthead page.

Scheme I



Reaction of Phosphorus Ylides with Elemental Selenium: Generation of Selenoaldehydes and Selenium-Catalyzed Ph_3P=CHR Cleavage To Give RHC=CHR and Triphenylphosphine

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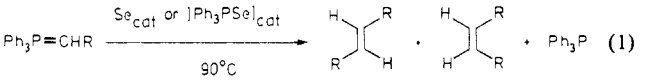
Selenoaldehydes (RCHSe) **2** are more reactive than their oxygen analogues RCHO. With very few exceptions, this has prevented the isolation of the monomeric RCHSe species.[1-3] The enhanced and often different reactivity makes selenoaldehydes objects of general interest and indicates some special synthetic potential. In situ generated selenocarbonyl compounds **2** undergo thermally induced [4 + 2] cycloaddition reactions with conjugated dienes to form 3,6-dihydro-2*H*-selenapyran derivatives **4**.[4] When carried out with aldehydes, the analogous reactions require strong acid catalysis.[5]

Several methods to generate selenoaldehydes have been reported, most of which are variants of 1,2-elimination reactions employing suitably substituted precursors X-RCHSe-Y.[2,4] We report here a fundamentally different way of generating the RCHSe species **2** by treating alkylidene triphenylphosphoranes Ph_3P=CHR **1** with elemental selenium.[6]

The reaction between elemental selenium (2.1 equiv) and Ph_3P=CHR was carried out at 90 °C with use of an excess of a conjugated diene as a Diels-Alder trapping agent (Scheme I). Typically, a red solution of benzylidene triphenylphosphorane **1a** (12 mmol, in 50 mL of toluene) was added dropwise over a period of 48 h to a hot (90 °C) mixture of 2,3-dimethylbutadiene (177 mmol) and Se (2.0 g) in 50 mL of toluene. Decolorization of the ylide occurred rapidly, and Ph_3PSe precipitated. 3,6-Dihydro-4,5-dimethyl-2-phenyl-2*H*-selenapyran **4a** was isolated from the solution (41% yield after chromatography).[7] The corresponding heterocycles **4c** and **4d** were identified by NMR from the reaction of the ylides Ph_3P=CHR (R=C_2H_5, C_4H_9) with selenium and 2,3-dimethylbutadiene. An analogous reaction was carried out employing Ph_3P=CHPh and anthracene to give **3** (21%).[7] Compound **3**, when heated to 75 °C in chloroform in the presence of excess 2,3-dimethylbutadiene, decomposed and transferred the selenobenzaldehyde unit to give **4a** and anthracene.

In the absence of the diene scavenger, a different reaction was observed. At 90 °C Ph_3P=CHPh (**1a**) reacted smoothly with excess selenium to yield stilbene and triphenylphosphine selenide[8] (eq 1). Surprisingly, Ph_3PSe itself is capable of inducing the



R = Ph (a), CH_3 (b), C_2H_5 (c), C_4H_9 (d), C_5H_{11} (e)

cleavage of nonstabilized ylides Ph_3P=CHR **1a-e** to give the alkylidene coupling product RCH=CHR and triphenylphosphine. This indicated that alkylidene triphenylphosphoranes Ph_3P=CHR can be catalytically cleaved by elemental selenium to give RCH=CHR and 2 equiv of PPh_3.[9] We were able to demonstrate this by reacting benzylidene triphenylphosphorane (58 mmol) in 100 mL of toluene with 5.8 mmol of selenium. Reaction took place rapidly. After 6-h reaction time and usual workup, stilbene (64%) and PPh_3 (70%) were isolated. Similar results were obtained reacting ylides Ph_3P=CHR **1a-e** each with $^1/_{10}$ equiv of gray selenium or Ph_3PSe in toluene solution. In each case a near-to-thermodynamic mixture of the two geometric isomers of the expected olefin was obtained [(cis/trans ratio (yield): stilbene (**a**) 16/84 (64%); 2-butene (**b**) 20/80 (53%); 3-hexene (**c**) 17/85

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(7) 3,6-Dihydro-4,5-dimethyl-2-phenyl-2*H*-selenapyran (**4a**) (oil after chromatography, silica/petrol): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.66, 1.75 (s, 3 H each, CH_3), 2.43, 2.64, 4.00 (ABX, ^2J = 15.8 Hz, ^3J = 11.4 and 3.8 Hz, 1 H each, H2, H3, H3'), 3.00, 3.34 (AB, ^2J = 16.3 Hz, 1 H each, H6, H6'), 7.1-7.3 (m, 5 H, phenyl); ^{13}C (50.3 MHz, $CDCl_3$) δ 19.9, 20.7 (methyl-C), 24.1 (t, 140 Hz, C3), 38.5 (d, 142 Hz, C2), 40.8 (t, 127 Hz, C6), 124.7 (C4), 126.8, 127.4, 128.5, 143.5 (phenyl-C), 129.3 (C5); MS (70 eV), *m/z* for M^+ = 252.0418, theoretical 252.0417. Anal. C, H. **3**: ^{1}H NMR ($CDCl_3$) δ 7.4-6.7 (m, Ph), 5.35 (s), 4.77 (d, 4.0 Hz), 4.34 (d, 1 H each); see ref 4b for a comparison.
(8) Analogous reactions of ylides with molecular oxygen are well known: Bestmann, H. J.; Kratzer, O. *Chem. Ber.* **1963**, *96*, 1899. For some recent work on ylide oxidation, see: Ricci, A.; Fiorenza, M.; Degl'Innocenti, A.; Seconi, G.; Dembeck, P.; Witzgall, K.; Bestmann, H. J. *Angew. Chem.* **1985**, *97*, 1068 and references cited therein.
(9) To our knowledge, a pairwise exchange mechanism (of the type R_3P=CHR^a + $R_3'P$=CHR^b ⇌ R_3P=CHR^b + $R_3'P$=CHR^a) had only once been proposed in the literature (Bestmann, H. J.; Snyder, J. P. *J. Am. Chem. Soc.* **1967**, *89*, 3936). Since this interpretation was later corrected in favor of a trans ylidation mechanism (Crew, P. *J. Am. Chem. Soc.* **1968**, *90*, 2961. Bestmann, H. J.; Liberda, H,. G.; Snyder, J. P. *J. Am. Chem. Soc.* **1968**, *90*, 2963. See, also: Schmidbaur, H.; Tronick, W. *Angew. Chem.* **1967**, *79*, 412), a pairwise ylide alkylidene exchange reaction appears not to have been observed yet experimentally. In view of the close mechanistic similarity to the olefin metathesis reaction[10] one might therefore be tempted to use the term "ylide metathesis" for the here described $2R_3P$=CHR → $2R_3P$ + RCH=CHR transformation.

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