

- anide, isocyanide, thio- and selenocarbonyl complexes.
- (7) (a) Mays, M. J.; Sears, P. L. *J. Chem. Soc., Dalton Trans.* **1973**, 1873. Fp^+Cl was prepared by a modification of this method, in which $(\text{dppe})\text{FeCl}_2$ was prepared in situ and reacted with TiCl_4 in THF. (b) Balavoine, G.; Green, M. L. H.; Sauvage, J. P. *J. Organomet. Chem.* **1977**, *128*, 247–252.
 - (8) ^{13}C NMR spectra were recorded on a JEOL FX-60Q spectrometer with internal deuterium lock and complete proton decoupling, at ambient probe temperature. Shifts are reported in parts per million downfield from Me_4Si . Generally, over 10 000 pulses were required to resolve the low-field triplets due to vinylidene α carbons, with nearly saturated (0.1–0.5 M) samples.
 - (9) $[\text{Cp}^*\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}=\text{CHPh})]\text{BF}_4$ has $\nu(\text{C}=\text{C})$ at 1675 cm^{-1} . Assignment of $\nu(\text{C}=\text{C})$ for other terminal vinylidene complexes is uncertain owing to coupling with $\nu(\text{Ph})^{2,4}$ and $\nu(\text{CN})^5$ modes, but generally falls in the range $1400\text{--}1600\text{ cm}^{-1}$.
 - (10) The equivalence of the two methyl groups in $[\text{Fp}^+\text{C}=\text{C}(\text{CH}_3)_2]\text{SO}_3\text{F}$ (Ic) in the ^1H and ^{13}C NMR spectra and the equivalence of the two H_β 's in $[\text{Fp}^+\text{C}=\text{C}(\text{CH}_2)\text{PF}_6]$ infer that the plane of the vinylidene ligand bisects the effective ^{13}C molecular symmetry plane as found for $\text{CpMn}(\text{CO})_2(\text{C}=\text{CHPh})^{4a}$ and $\text{CpMo}[\text{P}(\text{OMe})_3]_2\text{C}[\text{C}=\text{C}(\text{CN})_2]$,^{3b} or that the vinylidene ligand rotates rapidly on the NMR time scale. The invariance of the ^1H NMR spectrum from -60 to 60°C favors the former possibility.
 - (11) This low $\nu(\text{C}=\text{C})$ is common in unsubstituted transition metal acetylides, which generally have $\nu(\text{C}=\text{C})$ below 2000 cm^{-1} .¹²
 - (12) Kim, P. J.; Masai, H.; Sonogashira, K.; Hagihara, N. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 181–185.
 - (13) The conformation of the dppe-Fe chelate ring renders complexes of the type $\text{CpFe}(\text{dppe})\text{X}$ dissymmetric.¹⁴ A rapid fluxional motion of the chelate ring can account for the observation of clean triplets due to J_{PC} and J_{PH} in the NMR spectra of complexes Ic and Id and IId-e.
 - (14) (a) Riley, P. E.; Capshaw, C. E.; Pettit, R.; Davis, R. E. *Inorg. Chem.* **1978**, *17*, 408–414. (b) Hawkins, C. J. "Absolute Configuration of Metal Complexes". Wiley-Interscience: New York; 1971, Chapter 1.
 - (15) With the exception of IId⁵ and the dicyano vinylidene complexes prepared by King and Saran,³ all terminal vinylidene complexes have resulted from the $\pi \rightarrow \sigma$ rearrangement of hypothetical^{2,4b,d} or isolated^{4a,c} terminal or Ph_3Sn substituted^{4b} η^2 -phenylacetylene complexes. Thus, they contain the phenylvinylidene ($\text{C}=\text{CHPh}$) ligand.
 - (16) The titrations of Ic and IId were carried out by the addition of aqueous HCl or KOH by microliter syringe to $2 \times 10^{-3}\text{ M}$ solutions of the complexes in THF- H_2O (2:1 (v/v)) maintained under nitrogen. pH was measured with a Broadley-James Corp. glass electrode in conjunction with a Corning Model 7 pH meter. Visible spectra of the resulting solutions were obtained on a Cary 17 spectrophotometer. Plots of absorbance at 490 nm vs. pH gave well-defined titration curves.¹⁷ The midpoints of these curves were determined graphically. The pK values obtained were 7.72 ± 0.05 and 7.78 ± 0.05 for Ic and IId, respectively.
 - (17) Ewing, G. W. "Instrumental Methods of Chemical Analysis". Third ed.; McGraw-Hill: New York; 1969, Chapter 3.
 - (18) Ic was isolated from the titrations of Ic and IId by raising the pH above 12, salting out the aqueous layer, evaporating the resulting THF solution to dryness, and comparing the resulting red solid with authentic Ic (IR, ^1H NMR, mass spectrum).

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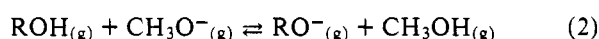
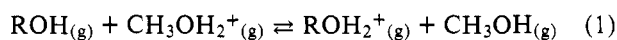
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Regarding the Separation of Polarizability and Inductive Effects in Gas- and Solution-Phase Proton-Transfer Equilibria¹

Sir:

The inductive effects of dipolar substituents on both experimental and theoretically calculated gas-phase acidities have been found to be generally consistent with the σ_1 scale from solution acidities.² However, major apparent exceptions occur with alkyl substituents at saturated (sp^3) carbon in both gas phase³ and in solution.⁴ Although gas-phase acidities are free from steric hindrance to ionic solvation that (with other factors) may interfere frequently with the observation of the very small inductive effects of alkyl substituents in solution, the polarizability effects of hydrocarbon substituents completely dominate any inductive effects in gas-phase proton-transfer equilibria,³ e.g.



where R is any group derived by substitution for the H's of the CH_3 group.

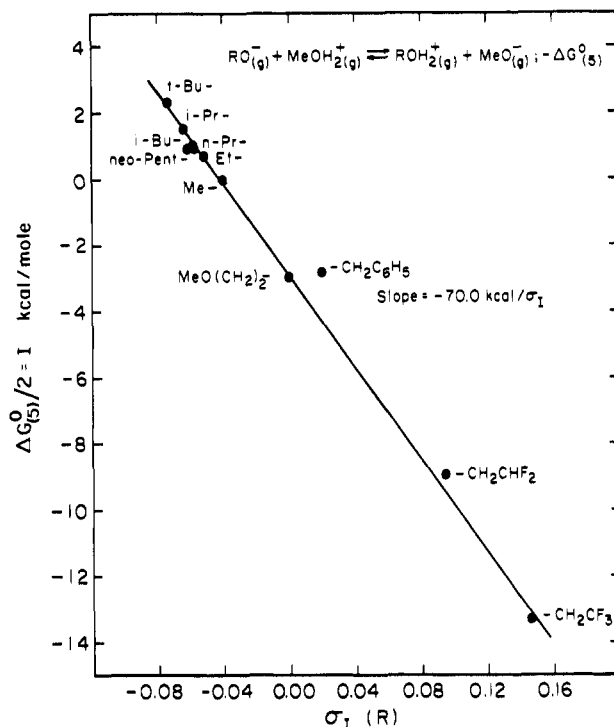


Figure 1. Correlation of gas-phase inductive effects with σ_1 parameters.

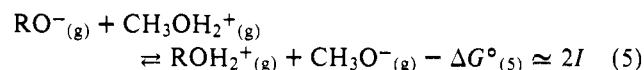
We report a separation of polarizability and inductive effects contributing to the values of $-\Delta G^\circ$ for reactions 1 and 2. The polarizability effect³ (P) for R relative to CH_3 arises from greater charge-induced dipole stabilization of both the cation or anion, i.e., ROH_2^+ relative to CH_3OH_2^+ and RO^- relative to CH_3O^- . An inductive electron-releasing effect of $\text{R}(\text{I})^5$ will stabilize ROH_2^+ relative to CH_3OH_2^+ but will destabilize RO^- relative to CH_3O^- . We make the simplifying assumption (in view of the nature of reactions 1 and 2) that the magnitudes of these effects will be approximately equal,⁶ i.e., for reaction 1

$$-\Delta G^\circ_{(1)} \approx I + P \quad (3)$$

and for reaction 2

$$-\Delta G^\circ_{(2)} \approx -I + P \quad (4)$$

where I is the inductive effect of R compared to CH_3 (opposite in sign for reactions 1 and 2) and P is the stabilizing polarizability effect of R compared to CH_3 (+ for both reactions 1 and 2). Subtracting (2) from (1) gives an equilibria (hypothetical) between four ions, for which the polarizability effect has been minimized or eliminated, i.e., $(1) - (2) = (5)$.



The results obtained from our combined studies by the pulsed ion cyclotron resonance equilibrium constant method⁷ are given in Table I. It is immediately apparent that the values of I obtained from the double proton-transfer equilibria, eq 5, are in the classical inductive order. The quantitative correlation of the I values with σ_1 values is shown in Figure 1. For alkyl substituents the σ_1 values used are based upon the method of Ingold^{5a} and Taft^{5b,c} involving alkaline- and acid-catalyzed ester ($\text{RCH}_2\text{CO}_2\text{Et}$) hydrolysis transition states.

For alkyl substituents, the electron-releasing inductive effects of R relative to CH_3 are substantial, i.e., up to 2.3 kcal/mol for $t\text{-Bu}$, but, nonetheless, these are three to seven times smaller than for the corresponding predominant polarizability (P) effects. As expected for inductive electron-withdrawing substituents, I values are negative but P values are positive.⁸

Table I. Evaluation of Inductive and Polarizability Effects' Contribution to $-\Delta G^\circ$ Values for Reactions 1 and 2

R	$-\Delta G^\circ_{(1)}^a$	$-\Delta G^\circ_{(2)}^b$	$-\Delta G^\circ_{(5)}^c$	I^d	P^e	σ_1 (lit.)	σ_1^f
<i>t</i> -Bu	10.8 ^g	6.2	4.6	2.3	8.5	-0.074 ^{h,i}	-0.073
<i>i</i> -Pr	8.0 ^g	5.1	2.9	1.5	6.5	-0.056, ^h	-0.062
neopent	9.1 ^g	7.3	1.8	0.9	8.2	-0.062 ⁱ	-0.053
<i>i</i> -Bu	8.0 ^g	6.1	1.9	1.0	7.0	-0.065 ⁱ	-0.055
<i>n</i> -Pr	6.5 ^g	4.8	1.7	0.9	5.6	-0.058, ^h	-0.061 ⁱ
Et	4.5 ^g	3.1	1.4	0.7	3.8	-0.052, ^h	-0.051
Me	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	-0.045, ^h	-0.040
C ₆ H ₅ CH ₂	4.8	10.3	-5.5	-2.8	7.6	0.036 ^h	0.000
MeO(CH ₂) ₂	1.0	7.0	-6.0	-3.0	4.0	0.00 ^j	0.003
F ₂ CHCH ₂	-4.3	13.4	-17.7	-8.9	4.6	0.094 ^k	0.087
CF ₃ CH ₂	-10.0	16.6	-26.6	-13.3	3.3	0.144 ^h	0.150

^a From ref 7c. In kcal/mol; precision, ± 0.2 kcal/mol. ^b From ref 7d. In kcal/mol; precision, ± 0.2 kcal/mol. ^c $-\Delta G^\circ_{(5)} = -\Delta G^\circ_{(1)} + \Delta G^\circ_{(2)}$, kcal/mol. ^d $I = (1/2)(-\Delta G^\circ_{(5)})$, kcal/mol. ^e $P = -\Delta G^\circ_{(1)} - I$, kcal/mol. ^f Intrinsic $\sigma_1(R)$ values obtained from Figure 1 as $\sigma_1 = (I + 2.84)/-70.0$. ^g Ab initio calculations at the 4-31G level give the following: *t*-Bu (11.2), *i*-Pr (7.7), Et (3.9), neopent (4.8), *i*-Bu (5.1), *n*-Pr (5.6); cf. ref 19: ^h $\sigma_1(R) = 0.45\sigma^*$ (RCH₂-), cf. ref 5c. ⁱ L. S. Levitt and H. F. Widing, *Prog. Phys. Org. Chem.*, **12**, 119 (1976). ^j M. Charton, private communication. ^k Estimated from σ^* values of CF₃ and HCF₂.

I values are nearly additive in the two series:⁹ Me, Et, *i*-Pr, *t*-Bu, and Et, CH₂CHF₂, CH₂CF₃, whereas *P* values show that saturation occurs in the former series (increments of 3.8, 2.7, and 2.0 kcal^{10,11}) and in the latter series *P* is approximately constant. The introduction of CH₃ substituents for H on the β carbon gives *I* values which are the same within the combined experimental errors, whereas *P* values increase substantially.¹⁰ Evidently, the conformations with β -alkyl substituents "bent around" are favored to obtain optimal stabilization by the polarizability effect (giving, for example, $P_{t\text{-Bu}} \approx P_{\text{neopent}}$).

The regression line of Figure 1 may be used to define inherent σ_1 values, which are free from solvation effects: $\sigma_1 = (I + 2.84)/-70.0$. The values obtained are in the last column of Table I. However, eq 5, $-\Delta G^\circ_{(5)} \approx 2I$, is not applicable to the H substituent on oxygen, i.e., for H₂O, since there is hyperconjugative stabilization of alkoxides compared with hydroxide.¹² Small differential stabilizations of the alkoxide ions due to differing C-H and C-C hyperconjugative interactions probably contribute to $-\Delta G^\circ_{(2)}$ values, but these and *P* contributions have evidently nearly cancelled in the $-\Delta G^\circ_{(5)}$ (or σ_1) values.

While the substituent effects for reactions 1 and 2 are composites of *I* and *P* effects, corresponding or analogous proton transfer equilibria for alkoxide ions or ammonium ions in aqueous solutions have been shown by correlations with only σ_1 values^{13,14} to involve predominant but reduced inductive effects. The correlations are as follows. For reaction 2, $-\Delta G^\circ_{(g)} = -70.0(\Delta\sigma_1) + (1.00)P$ ($R = 0.999$, $n = 11$); $-\Delta G^\circ_{(aq)} = -23.2(\Delta\sigma_1) - 0.03$ ($R = 0.990$, $n = 4$). For the reaction



$-\Delta G^\circ_{(g)} = -64.2(\Delta\sigma_1) + (0.67)P$ ($R = 0.998$, $n = 10$); $-\Delta G^\circ_{(aq)} = -38.9(\Delta\sigma_1) - 0.40$ ($R = 0.975$, $n = 10$); $\Delta H^\circ_{(aq)} = -25.6(\Delta\sigma_1) - 0.01$ ($R = 0.980$, $n = 9$).

The dependence on $\Delta\sigma_1$ values is reduced by factors of 2-3 in aqueous solution compared with the corresponding gas-phase values. The dependence on *P* values is reduced to such an extent in aqueous solution as to be negligible. These results may be understood in terms that the specific binding of solvent molecules to the ions¹⁵ acts to disperse charge to the H-bonded solvent, attenuating both the *I* and *P* effects.^{2a,16} A much larger solvent attenuation factor for *P* than for *I* effects is anticipated by the simple electrostatic models for these effects: charge-induced dipole interaction, $E = -\alpha e^2/2Dr^4$ and charge-dipole interaction, $E = \pm e\mu \cos \theta/Dr^2$, respectively. The dispersal of charge accompanying specific binding of H-bonded solvent molecules leads to an appreciable increase in the distance (*r*) between the centroids of charge (*e*) and polarizability (α) or dipole moment (μ). Since *P* effects fall

off with the fourth power of distance (*r*), whereas *I* effects fall off only with the second power of distance, the consequence is a much larger solvent attenuation factor for *P* than *I* effects. This solvent effect differentiation for oxonium, ammonium, and alkoxide ions provides an important means for identifying these structural effects.^{2a} The reverse order of acidities of aliphatic alcohols in the gas phase and in hydroxylic solvents is explained since *P* effects determine the gas phase acidity order,³ but the *I* effects of the opposite order (reduced but not eliminated by solvation) determine the solution acidity order.¹³

The values of $-\Delta G^\circ_{(1)}$ for benzyl and for branched-chain alcohols have been obtained indirectly since their ROH₂⁺ are too unstable for direct equilibrium constant determination. Using methane as a chemical ionization source, mixtures of 2-propanol with a series of reference bases, B, of increasing strength, were utilized in the spectrometer to form *i*-PrOH₂⁺ and BH⁺. It was determined using double resonance that propanethiol did not deprotonate *i*-PrOH₂⁺, but ethyl formate and propionitrile did. Based upon these results,^{7c} a value of $-\Delta G^\circ_{(1)}$ for *i*-PrOH of 9.0 ± 0.5 kcal can be assigned. More generally $-\Delta G^\circ_{(1)}$ values have been obtained (as given in Table I) from the highly precise linear relationships between the relative gas-phase basicities for aliphatic ethers, ROME (relative to Me₂O),¹⁷ and aliphatic amines, RNH₂ (relative to MeNH₂),^{2a} compared with ROH (relative to MeOH).^{7c} The conjugate acids of the branched-chain members of the former two series are stable and their gas-phase basicities have been directly determined. The results for these compounds are converted to $-\Delta G^\circ_{(1)}$ values, using the slopes of the linear correlations obtained from the results for the straight-chain alkyl groups in all three series.

Ab initio molecular orbital calculations of $-\Delta G^\circ_{(1)}$ values have been carried out at the 4-31G level¹⁸ (cf. Table I, note g, and ref 19). The calculated values are in very satisfactory agreement with the results obtained above for the series Me, Et, *i*-Pr, *t*-Bu, but (inexplicably) are in poor agreement for the series *n*-Pr, *i*-Bu, neopent.

Acknowledgment. We are pleased to acknowledge the helpful comments of Dr. Leo Radom.

References and Notes

- (1) This work was supported in part by grants from the National Science Foundation.
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- (6) The *I* and *P* effects for reaction 1 are probably more accurately proportional to rather than equal to the corresponding *I* and *P* effects for reaction 2. However, the assumption of equality expressed in eq 3 and 4 is simpler and is sufficiently adequate for all of the major points of concern in this paper.
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- (9) The opposite directions of the effects of CH₃ and F substituents are in accord with the greater first ionization potential and electron affinity of -F than -H, and the smaller of both of these quantities for -CH₃ than -H.
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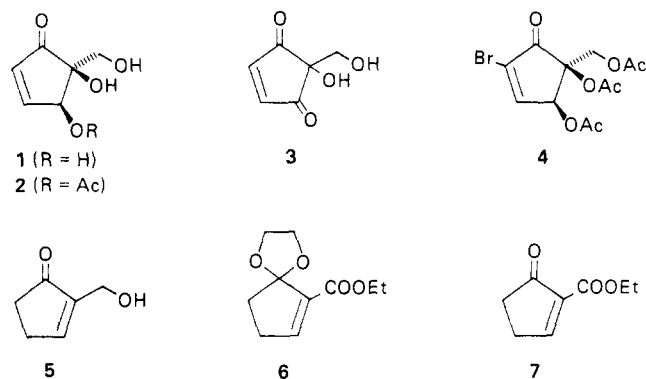
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A Stereospecific Total Synthesis of (±)-Pentenomycin I, (±)-Pentenomycin II, and Dehydropentenomycin I Exploiting a Versatile Latent α -Ketovinyl Anion Equivalent

Sir:

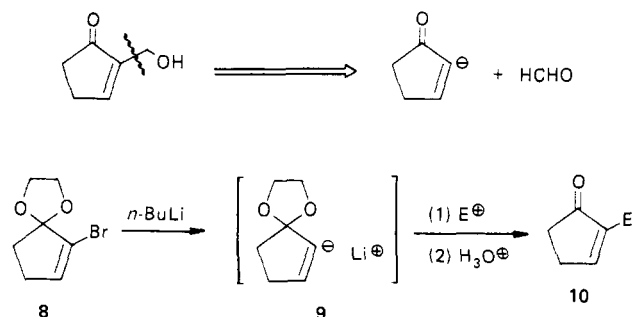
In this communication we report an efficient, stereospecific total synthesis of three novel cyclopentenoid antibiotics, pentenomycin I (**1**), pentenomycin II (**2**), and dehydropentenomycin I (**3**) exploiting a versatile latent α -ketovinyl anion equivalent. Pentenomycins I and II were isolated by Umino and co-workers in 1973 from culture broths of *Streptomyces erytherrimus* and assigned structures **1** and **2**, respectively, based on a combination of spectroscopic techniques² including X-ray crystallographic analysis³ of the derived bromotriacetate **4**. More recently (1978) Noble et al. reported the isolation of antibiotic G-2201-C (**3**), a simple oxidation product of pentenomycin I, from *Streptomyces cattleya*⁴ which we have termed dehydropentenomycin I.^{5,6} Our interest in these synthetic



targets was prompted both by their demonstrated activity against Gram-positive^{1,4} and Gram-negative^{1,4} bacteria including *Neisseria gonorrhoeae*¹ as well as by the potential pharmacological importance of the cyclopentenone structural unit recently suggested to be the reactive functionality in a variety of structurally complex antitumor agents.⁷ Our synthetic route is particularly attractive in that it is short, stereospecific, highly efficient (i.e., proceeds in 25, 22, and 11% overall,⁸ respectively, for **1-3** from cyclopentenone) and has led to the development of new methodology for α,β -enones.

From a retrosynthetic perspective, α -hydroxymethylcyclopentenone **5** appeared to be an ideal intermediate for the elaboration of **1-3**. Although merely an olefinic positional isomer of the enolic form of α -formylcyclopentanone, examination of the literature revealed, somewhat surprisingly, no previous report for this compound. Furthermore, α -hydroxymethyl- α,β -enones are, in general, not common to the chemical literature. With these considerations in mind we set out to devise a viable approach to **5**.

Initial successful construction of **5**,⁹ albeit expensive and multistep, employed the low-temperature Dibal reduction of ketal **6**⁹ followed by careful deketalization (HOCCOOH/aqueous CH₂Cl₂). Ketal **6** in turn was readily available in 82% yield⁸ from 2-carbethoxy-2-cyclopentenone (**7**) (1.2 equiv HOCH₂CH₂OH/catalyst:HOOCC=CHCOOH/C₆H₆/-H₂O via the Dean-Stark procedure),¹⁰ the latter prepared from commercially available 2-carbethoxycyclopentanone as reported by Reich and co-workers (i.e., α -phenylselenenylation followed by oxidative-elimination).¹¹ Although available in 53%⁸ yield from **7**, the demand for large quantities of **5** coupled with the expense of phenylselenenyl chloride necessitated the development of an alternate route. To this end we envisioned the hypothetical reaction illustrated below. Equivalent to this transformation appeared to be metalation¹² of bromo ketal **8**; addition of CH₂O and deketalization would then afford **5**. Indeed, treatment of **8**^{9,13} with *n*-butyllithium (-78 °C, THF)



led to vinyl anion **9**, which could be efficiently captured with a variety of electrophilic reagents; for the case at hand careful addition of predistilled gaseous CH₂O and subsequent deketalization afforded **5** (mp 68-69 °C) in 84% yield.^{8,14} The efficiency of this approach to **5** demonstrates, we believe, that