The lesser reactivity of nitranions than carbanions denoted by the displacement of the carbazole–phenothiazine line to the right of the (extended) 9-CO_2Me-Fl$^-$ line, which we have adopted as a model for the least sterically demanding of the 9-G-Fl$^-$ carbanions,[5] cannot be due to a steric effect since carbazole anions have *less* steric demands than fluorenyl anions. (They lack the 9-substituent.) On the other hand, the sixfold lower reactivity of a diphenylamine nitranion than a carbazole–phenothiazine nitranion of the same basicity probably *is* a steric effect since it parallels the fourfold lower reactivity of PhC(Ph)CN$^-$ carbanions, relative to the 9-CO_2Me-Fl$^-$ line.[6]

The near equality in β_{Nu} values for carbanions, oxanions, and nitranions suggests that the transition-state structures for these reactions are closely related, despite the different kinds of atoms that are being bonded to carbon. The near equality of slopes is a useful feature since it allows comparison of the nucleophilicity of different kinds of anions at constant basicity.[4]

The vertical gap between the 9-CO_2Me-Fl$^-$ and carbazole–phenothiazine family lines indicates that the carbanions are 80 times more nucleophilic than the corresponding nitranions of the same basicity.[7] When combined with data from earlier studies,[4] this result leads to the nucleophilicity order: $S^- \gg C^- > O^- > N^-$ for anions of similar structure and the same basicity.[9] Factors that may be important in determining this order include bond distance (average bond distances are as follows: S–C, 1.82; C–C, 1.54; O–C, 1.43; N–C, 1.47), bond strength (average bond strengths are 65, 83, 86, and 83 kcal/mol, respectively), and electronegativity (S, 2.5; C, 2.5; N, 3.0; O, 3.5). The much higher nucleophilicity of thianions[4] can be correlated with the longer S–C bond distance, together with the low electronegativity of sulfur. The higher nucleophilicity of carbanions, relative to oxanions and nitranions, can also be correlated with the longer C–C bond length and the low electronegativity of carbon. (The longer S–C and C–C bond distances could serve to decrease steric interactions in the transition state, TS.) The lower electronegativity of S and C could serve to decrease solvation and thus decrease the amount of solvent reorganization required in the TS; lower electronegativity can also be correlated with greater anion polarizability and with the availability of molecular orbitals of higher energy, which may provide the proper HOMO–LUMO combination to lower the energy of the TS. The greater nucleophilicity of oxanions than nitranions is not expected on any of these grounds, however.[9]

The size of Brønsted β values has generally been taken as a measure of the extent of bond formation in the TS.[10] Bell has pointed out that (for proton transfer) this could be related to (a) the geometrical position of the proton, (b) the orders of force constants of the two bonds holding the proton, (c) the distribution of charge, or (d) the free-energy change in the overall reaction.[11] In the S_N2 reactions under consideration here one would expect the geometries, force constants, and $\Delta G°$ values for the overall reaction to change appreciably as the kind of atom bonded to carbon is changed. We conclude from the near constancy of β_{Nu} values for S$^-$, C$^-$, O$^-$, and N$^-$, however, that these changes are not causing appreciable changes in TS structures for these anionic nucleophiles. Instead, the size of β_{Nu} in these reactions appears to be almost entirely substrate dependent.[7] If β_{Nu} values provide a measure of the fraction of charge transferred from the anion to the substrate in the transition state,[12] then our results show that, for a given substrate reacting with delocalized anions, the same fraction of charge is transferred from anions of different structure over a wide range of basicity.

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Registry No. Benzyl chloride, 100-44-7; 9-(methoxycarbonyl)-fluorenyl anion, 12565-94-5; 2-bromo-9-(methoxycarbonyl)fluorenyl anion, 73838-71-8; 2,7-dibromo-9-(methoxycarbonyl)fluorenyl anion, 73838-70-7; 2-naphthoxide anion, 15147-55-4; 6-bromo-2-naphthoxide anion, 78232-03-8; 4,6-dibromo-2-naphthoxide anion, 78232-04-9; carbazole nitranion, 23560-25-0; 3-chlorocarbazole nitranion, 80010-03-3; 3,6-dibromocarbazole nitranion, 79990-92-4; phenothiazine nitranion, 76069-04-0; 2-chlorophenothiazine nitranion, 79990-93-5; 3,7-dibromophenothiazine nitranion, 79990-94-6; diphenylamine nitranion, 61057-05-4; *N*-(3-chlorophenyl)benzene amine nitranion, 78525-46-9; bis(4-bromophenyl)amine nitranion, 79990-95-7.

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(9) In a later paper we will show that the size, extent of delocalization, and nature of delocalization of carbanions such as PhC(CN)$_2^-$, 9-CN-Fl$^-$, MeC(CN)$_2^-$, and the like do not affect the linear basicity–nucleophilicity correlation. This gives us confidence that the present comparison of carbanion and nitranion nucleophilicities is valid. On the other hand, the fact that the nucleophilic atom in thianions and oxanions is on the periphery of the anion, whereas that for carbanions and nitranions is more centrally located, may be a factor affecting their nucleophilicities.
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New Penem Synthesis via a Novel Pummerer Rearrangement Process

Summary: The olefinic group of the penem ring system has been introduced via a Pummerer rearrangement of the penam sulfoxide **11** by utilizing trifluoroacetic anhydride–lutidine.

Sir: The novel penem β-lactam ring system **2** has recently been described by the Woodward group and others.[1] In their sequence, the C-2 olefin was constructed by Wittig reaction of the phosphorane **1** (Chart I). Recently, conversion of clavulanic acid (**3**) and penicillanic acid (**4**) into the penem system has been reported by Cherry[2] and Beels[3]

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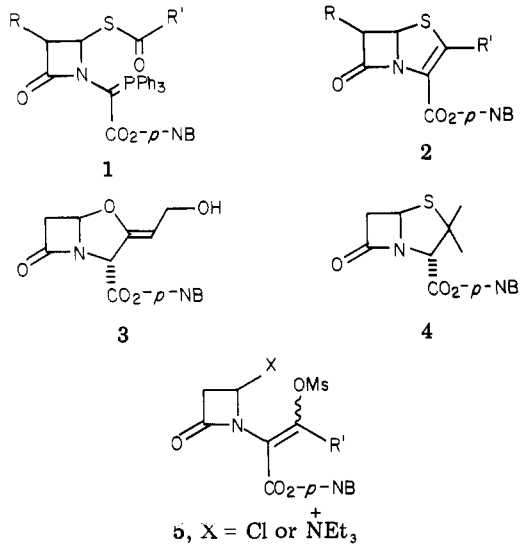
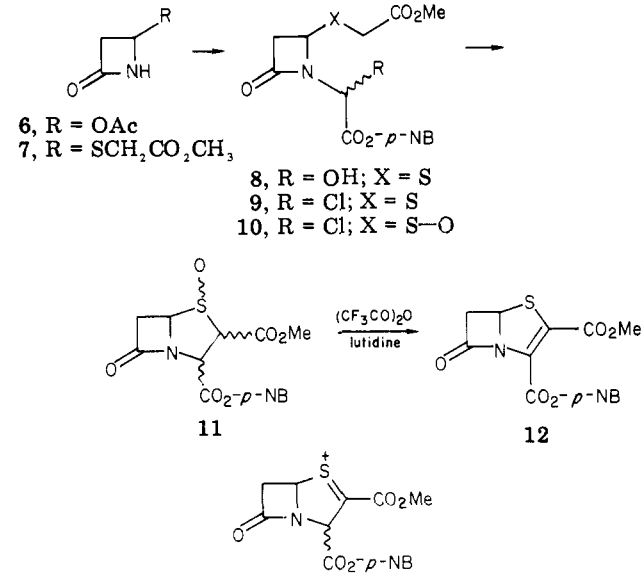
Chart I[a]



[a] p-NB = p-nitrobenzyl.

Scheme I



via the treatment of the intermediate **5** with hydrogen sulfide and triethylamine.

As part of a program aimed at the total synthesis of derivatives of compound **2**, we have investigated and developed a new penem synthesis via a Pummerer rearrangement of a penam sulfoxide **11**. The carbomethoxy group was chosen for the R′ of compound **2** because it was anticipated that it would enhance the acylating power of the β-lactam by conjugation through the penem double bond. Increased acylation power is felt to be associated with increased antibacterial potency in the case of β-lactam antibiotics (e.g., the cephalosporins[4]). The required penam sulfoxide **11** was obtained from the racemic azetidinone **6** by a five-step synthesis (Scheme I). Treatment of **6** with methyl thioglycolate gave the thioazetidinone **7**[5] in 87% yield. Condensation of **7** with *p*-nitrobenzyl glyoxylate[6] in refluxing benzene for 12 h gave the hydroxy compound **8** in 92% yield as a 1:1 diastereoisomeric mixture. Treatment of **8** with thionyl chloride–lutidine in methylene chloride at 0 °C produced the chloro compound **9** in a quantitative yield. Satisfactory generation of the sulfoxide **10** was achieved in 75% yield by exposure of **9** to *m*-chloroperbenzoic acid (1.1 equiv in CH_2Cl_2, O °C), followed by a fast silica gel column chromatography. Treatment of the sulfoxide **10** with lithium diisopropyl amide (1.1 equiv in THF, −78 °C) furnished the cyclized azetidinone **11** in 53% yield as an oily diastereoisomeric mixture.[7] A high IR β-lactam carbonyl frequency (1790 cm^{-1}) of **11** is in accord with the formation of the bicyclic azetidinone.[8] Although **11** existed as a complex diastereoisomeric mixture, the Pummerer rearrangement of **11** converted all isomers into a single product, **12**. Thus, exposure of **11** to $(CF_3CO)_2O$–lutidine at 25 °C overnight produced the penem **12** as a gum in 37% yield after silica gel column chromatography.[9]

The penem **12** had the following properties: IR ($CHCl_3$) 1805, 1740, 1725 cm^{-1}; UV (EtOH) λ_{max} 262 nm (ϵ 12 200), and 322 (5800); NMR ($CDCl_3$) δ 3.60 (1 H, dd, J = 2.5, 16.0 Hz, C-6H), 3.75 (3 H, s, OMe), 3.90 (1 H, dd, J = 3.0, 16.0 Hz, C-6H), 5.30 (2 H, s, OCH_2Ph-*p*-NO_2), 5.82 (1 H, dd, J = 2.5, 3.0 Hz, C-5H), 7.5 (2 H, J = 9.0 Hz, aromatic protons), 8.3 (2 H, J = 9.0 Hz, aromatic protons). A reasonable reaction pathway from **11** to **12** might involve a stepwise sequence through the intermediate **13**, followed by the migration of the double bond to furnish the penem **12**. In conclusion, it has been demonstrated that a highly activated penem system can be readily constructed via a Pummerer rearrangement process of a penam sulfoxide. The further application of this methodology for the synthesis of novel penems will be reported in due course.

Registry No. (±)-**6**, 64804-09-7; (±)-**7**, 79970-18-6; (±)-**8** (isomer 1), 79970-19-7; (±)-**8** (isomer 2), 79970-20-0; **9**, 79970-21-1; **10**, 79970-22-2; **11**, 79970-23-3; (±)-**12**, 79970-24-4; methyl thioglycolate, 2365-48-2; *p*-nitrobenzyl glyoxylate, 64370-35-0.

(9) Spectral properties of all new compounds were in accord with the proposed structure.

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A Stereospecific Synthesis of Trisubstituted Alkenes via Hydridation of Dialkylhaloboranes Followed by Hydroboration–Iodination of Internal Alkynes

Summary: Dialkylvinylboranes, prepared conveniently via the hydridation of dialkylhaloboranes in the presence of an internal alkyne, react with iodine under basic conditions to produce trisubstituted alkenes of established stereochemistry, providing a general synthesis of trisubstituted alkenes with unambiguous stereochemistry.

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