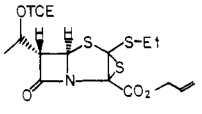
J. Am. Chem. Soc. 1982, 104, 6139–6140

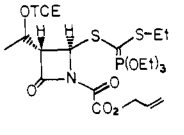
with excess triethyl phosphite to form the ylide **10b**. The reduction product **9** probably arises via reaction of **6b** with solvent.

Regarding the mechanism for the formation of penem **1b**, we propose that the carbene in **6b** adds intramolecularly to the thione group[14] to form an intermediate episulfide **11**. Since episulfides are readily desulfurized to olefins by triethyl phosphite,[15] the second molecule of the latter reagent used in the reaction desulfurizes **11** to form **1b**. The fact that **1b** is the major product when the reaction is run according to the conditions described earlier[13] implies that, among the pathways available for the carbene in **6b** to react, the rate of addition to the thione group is fast provided the intermolecular process leading to **10b** is physically controlled by adjusting the rate of addition of triethyl phosphite.



11

On the basis of precedents, there are two other possible mechanisms for the cyclization reaction. One of them involves an ylide intermediate **12**. Cyclic trithiocarbonates react quantitatively with triethyl phosphite to generate phosphite ylides.[16] Conceivably, if the oxalimide **3** had reacted according to this precedent to form **12**, the ylide could undergo an internal Wittig cyclization at the reactive oxalimido carbonyl to form **1b**. However, the intermediacy of **12** was ruled out on the basis of the stability of trithiocarbonates **3b**, **4b**, and **9** to further reaction with triethyl phosphite. The other mechanism is an intramolecular Wittig cyclization involving the phosphite ylide **10b**, which was isolated as a major byproduct of the reaction. No penem **1b** formation was detectable when a solution of **10b** was heated under the present reaction conditions.



12

In conclusion, the above described oxalimide cyclization reaction offers many advantages over Woodward's phosphorane cyclization for the synthesis of penems.[17]

Acknowledgment. We thank Professor J. Meinwald for helpful discussions on the mechanistic aspects of this work and Dr. M. Puar, R. Novotny, P. Bartner, and Dr. B. Pramanik for the spectral data.

Registry No. 1b, 80629-48-7; (±)**2**, 83248-84-4; (±)**3a**, 83248-85-5; **3b**, 83248-88-8; (±)**4a**, 83290-88-4; **4b**, 83290-89-5; **7**, 83248-86-6; **8**, 83248-87-7; **9**, 83248-89-9; **10b**, 83248-90-2; P(OEt)$_3$, 122-52-1; (allyloxy)oxalyl chloride, 74503-07-4.

Supplementary Material Available: Tables of atomic positional and thermal parameters, interatomic distances and angles, and crystal data, a view of the solid-state conformation of **4a**, and physical data of the compounds described (8 pages). Ordering information is given on any current masthead page.

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(14) A. Schoenberg, B. Koenig, and E. Singer, *Chem. Ber.*, **100**, 767 (1967).

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(17) For example, the conversion of **2** to **1b** by the Woodward route[12] requires four separate intermediate steps, three chromatographies, and proceeds in approximately 25% overall yield. C$_5$ epimer formation and the number of days needed for completion of this reaction sequence are important drawbacks in the phosphorane route. The present oxalimide cyclization is essentially a one-step operation, since **8** need not be isolated, it proceeds in high yields with no epimer formation, and the process can be completed in a few hours.

An Ion Gate Membrane: Electrochemical Control of Ion Permeability through a Membrane with an Embedded Electrode

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Resistance to transport of ions across membranes, classically studied by dc resistance[1] and ac impedance methods,[2] is influenced by many factors, including the ion size, charge and concentration, the presence of carrier species (i.e., antibiotics in lipid bilayers), and of course the nature of the membrane. A membrane can be fabricated to have certain characteristics such as low resistance to transport of small ions and high resistance to large ions (dialysis), but once prepared, the membrane characteristics are fixed. Until now, no membrane has been devised whose resistance to ion transport between two contacting solutions could be varied in situ without altering the contacting solution conditions such as changing pH or adding carrier species. We report here development of a membrane in which the ionic resistance as measured by impedance methods can be dynamically varied by electrochemical control of redox states within the membrane.

Ion movement through membranes containing fixed ionic sites is dependent on the nature and number of such charged sites; changing these factors will change the membrane ionic resistance. If the charge on an ionic polymer site is altered by an electrochemical reaction, such an electrochemical reaction can be made the basis for changing the membrane resistance. The most drastic effect is expected on going between charged and neutral membranes. Poly(vinylferrocene), poly(tetrathiafulvalene), and poly(pyrrole) are examples of redox polymers whose films, deposited on solid electrodes, can be cycled electrochemically between charged-site and neutral states. All of these materials show electrochemical evidence of ion exclusion upon reduction to the neutral polymer.[3-6] Impedance measurements[5] of a film of poly(pyrrole) electrochemically polymerized onto platinum show that the neutral (reduced) polymer has a much higher resistance in 1.0 M aqueous KCl solution than the charged (oxidized) polymer.

The preceding films[3-6] were deposited on solid, nonporous electrodes. If a porous electrode is instead embedded *inside* a redox polymer membrane, and this membrane/electrode is used to separate two pools of electrolyte solution, control of the ion flow *through* the membrane can be achieved by control of the polymer redox state. To demonstrate this, we used a gold minigrid sheet (Buckbee-Mears 2000 lpi), epoxied between two glass slides predrilled with 0.24-cm^2 area holes, as the porous electrode and electropolymerized poly(pyrrole) as the redox membrane. Anodic polymerization of pyrrole as described by Diaz[6] (except with 0.1 M TEAP instead of 0.1 M TEABF$_4$ as supporting electrolyte) was carried out for ca. 6 min to fill the holes in the gold minigrid with polymer as seen by optical and scanning electron microscopy (total thickness ca. 15 μm). The resulting freshly prepared electrode/membrane was mounted in the cell (see Figure 1), and the change in its in-phase impedance at 2 Hz (which is proportional to the ionic resistance) was monitored by using two large area Pt electrodes (a) and a PAR HR-8 lock-in amplifier. As shown by Buck and co-workers,[2] a cell like this with pools of non-redox-active ionic conductors (electrolyte solution) blocking

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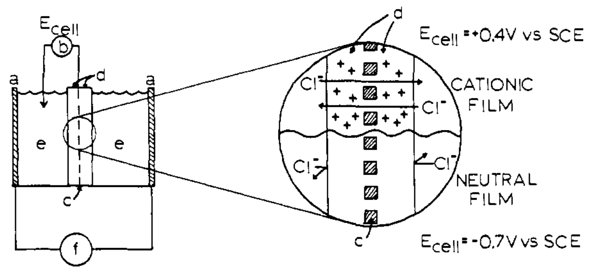

Figure 1. (Left) experimental setup for impedance measurement with electrochemical control of membrane impedance: platinized platinum electrodes (a); constant voltage power supply (b); gold minigrid electrode (c); poly(pyrrole) film (d); 1.0 M KCl(aq) solution (e); constant current ac circuit, which consists of a frequency generator, lock-in amplifier, and a 50 K Ω series resistor to maintain constant ac current to cell (f). (Right) microscopic view of membrane, illustrating effect of membrane potential on ionic resistance.

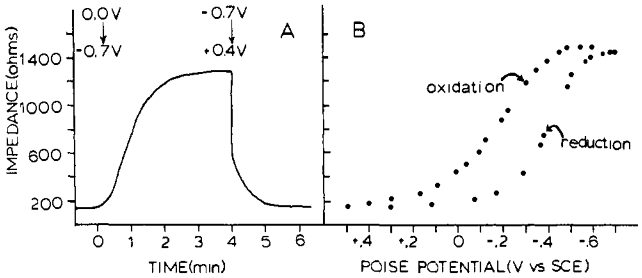

Figure 2. (A) Plot of in-phase impedance (Z) in ohms vs. time in minutes after initial −0.7-V step for a freshly prepared polypyrrole electrode. (B) Plot of in-phase impedance (Z) vs. poise potential for same electrode as in A.

the membrane from *electronic* conduction with the Pt electrodes, specifically measures the ionic, as opposed to the electronic conductivity, in a membrane at dc or low ac frequencies (<2000 Hz).[7]

Typical results are seen in Figure 2A. Upon stepping the potential applied to the electrode/membrane from 0.0 V vs. SCE to −0.7 V, the in-phase impedence of the virgin electrode at 2 Hz increases from 132 to 1280 Ω in approximately 4 min.[8] The impedance continues to rise very slowly after the initial jump; in an hour it reaches 1500 Ω. Stepping back to 0.0 V lowers the impedance but is not a sufficient potential to oxidize all the reduced polypyrrole. Stepping instead to +0.4 V brings the impedance back to its original value, as seen in Figure 2A. With oxygen excluded from the cell, this pattern can be cyclically repeated many times. Neither a gold minigrid electrode alone nor a membrane/electrode whose holes are incompletely filled produces a change in impedance (constant at 115 Ω) upon stepping from +0.4 to −0.7 V and back.

By choice of other value of potential steps, it can be shown that a polymer redox reaction must occur to produce a change in membrane impedance. Thus, if the potential of a virgin electrode is stepped from 0.0 to +0.5 V, no change in impedance occurs. If after stepping to −0.7 V and allowing the impedance to rise to a fairly constant level the potential is returned to −0.5 V, again no impedance change is seen. These observations suggest that the impedance change is a result of the change in oxidation state of poly(pyrrole), whose electrochemistry is centered at $E_{1/2}$ = ca. −0.26 V in H_2O.

A plot of the poise potential (the potential at which the redox polymer is poised at open circuit) vs. impedance is shown in Figure 2B to more clearly illustrate the influence of the polymer redox state on the impedance of the film. Varying the potential from +0.4 to −0.7V and back in 0.1-V increments, with measurement of poise potential at open circuit[9] after each increment, results in a poise potential vs. impedance curve that remarkably resembles a current–potential curve for a redox species. The potentials corresponding to half the impedance changes occuring during reduction and oxidation, −0.4 and −0.17 V, respectively, are in fact nearly the same as slow potential scan cyclic voltammetric peak potential values, −0.33 and −0.20 V, respectively. The separation between oxidation and reduction potentials in each case must correspond to some degree of electrochemical irreversibility, possibly due to a nonequilibrium distribution of the oxidized and reduced forms in the very thick polymer film.

The facts that the impedance varies nonlinearly with applied potential and that plots of impedance vs. rest potential resemble *i–E* curves for reduction and oxidation of the poly(pyrrole) redox species demonstrates, we believe, that the ionic resistance of the membrane is electrochemically controlled via the oxidation state of the redox sites within the polymer. We term this phenomenon an "ion gate", since the resistance is varied from low to high and vice versa by a step voltage. Further work, elucidating the nature of ion transport as well as development of methods to increase the difference in impedance between the charged and neutral membrane, is currently is progress.

Registry No. Au, 7440-57-5; KCl, 7447-40-7; poly(pyrrole), 30604-81-0.

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[7] Poly(pyrrole) is known[5,6] to be an electronic as well as an ionic conductor, so this type of cell is necessary to distinguish the two. The frequency dependence of the in-phase and out-of-phase components of the ac signal in the cell of Figure 1 has been measured down to dc, and the impedance behavior is consistent with an ionic conduction pathway through the cell.

[8] This relatively slow time is a consequence of the relatively thick poly(pyrrole) film that is being reduced and oxidized. Possibly, all of the polypyrrole is not reduced.

[9] These potentials are stable at least for 2 min, the time taken to make these measurements.

Orchestrated Silylene to Silene to Silylene Rearrangement. The Unusual Behavior of C_3H_5 Silylsilylenes

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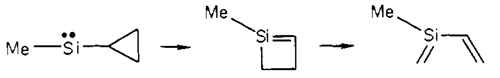
In 1980 we first proposed a thermally induced isomerization of a silene to a silylene when we suggested that the origin of 1,3-disilacyclobutane **3** (Scheme I) from the pyrolysis of allylpentamethyldisilane was the cyclization of β-silylsilylene **2** formed from 1,2-silyl migration in silene **1**.[1] Later we were able to present confirming evidence for this sequence[2] and in unpublished work have again demonstrated the rearrangement of a silene to a silylene when **1** was generated through pyrolysis of **4**.

Most recently we have presented evidence for the first thermally induced silylene to silene rearrangement when we demonstrated that cyclopropylsilylene **5** (eq 1) underwent ring expansion to silene **6**, which in turn opened to 2-sila-1,3-butadiene **7**.[3]



5 6 7 (1)

We now report that these rearrangements can be combined to produce a predictable sequence of silylene to silene to silylene rearrangements. The desired starting material for this sequence,

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