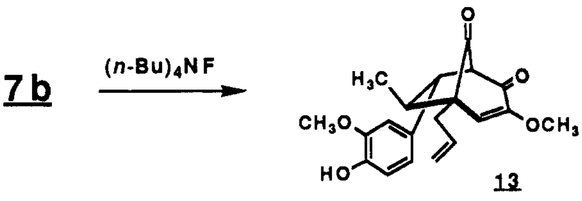
tropic rearrangement. This pathway is expected to give the observed inversion of configuration. To explore this possibility, **7b** was treated with fluoride ion [1.0 equiv $(n\text{-Bu})_4\mathrm{NF}$, THF, 25 °C] to afford **13** (mp 145.0–145.5 °C) in 78% yield with *retention* of configuration (eq 2). This result argues against a sigmatropic pathway.



(2)

The conversion of **7a** to **9** must involve the proposed biosynthetic intermediate, quinone methide β-diketone enolate **1**, which is short-lived and present in steady-state concentrations too low to be observed spectroscopically.

With the development of a selective route to the bicyclo[3.2.1]octene skeleton via the quinone methide, we sought conditions to divert the cyclization toward formation of the spiro[5.5]undecane skeleton. If the alkene is to participate in the cyclization, the nucleophilicity of the β-diketone needs to be reduced and the electrophilicity of the quinone methide increased. Accordingly, **7a** was treated with TiCl_4 (1 equiv, −78 °C, $\mathrm{CH_2Cl_2}$) to afford a 99% isolated yield of *tert*-butyldimethylsilyl ether **12** possessing the spiro[5.5]undecane skeleton (Scheme II).[9] Since the silyl group is retained, the intermediate is not the quinone methide; rather, it must be benzyl cation **11**. Thus, the complete diversion of the reaction pathway toward spiro[5.5]undecane **12** can be attributed to two reinforcing factors: (1) the benzyl cation provides a highly electrophilic intermediate for reaction with the terminal alkene, and (2) complexation of the β-diketone with Ti(IV) decreases its nucleophilicity.

To probe the possible formation of the bicyclo[3.2.1]octene in the Lewis acid mediated reaction, *tert*-butyldimethylsilyl ether **10** was treated with TiCl_4 (1.8 equiv, −78 to 25 °C, 1 h, $\mathrm{CD_2Cl_2}$) to afford a 98% yield of spiro[5.5]undecane **12**. Thus, bicyclo[3.2.1]octene **10** is a possible kinetic product in the **7a** to **12** transformation, which reversibly opens to benzyl cation **11** and ultimately affords **12** as the thermodynamic product.[12]

We have provided circumstantial chemical evidence for the intermediacy of quinone methide **1** in the formation of bicyclo[3.2.1]octene **9**. When a benzyl cation initiated the cyclization *and* the β-diketone was complexed to a Lewis acid, the cyclization was diverted toward the exclusive formation of spiro[5.5]undecane **12**. Certainly, nature might select a particular cyclization mode in a similar manner. A protonated or alkylated quinone methide/benzyl cation with the β-diketone complexed to a metal could afford futoenone, and the free quinone methide could afford the bicyclo[3.2.1]octene skeleton. Our results support Gottlieb's assertion that quinone methide **1** might serve as a precursor to neolignans with several different skeletons. Efforts to isolate quinone methide **1** are currently in progress.

Acknowledgment. We thank Dr. Dan Borchardt for assistance with the UV and low-temperature IR and NMR experiments and Professor T. H. Morton for helpful discussions. We gratefully acknowledge the National Institutes of Health (GM 39354) and the UCR Chancellor's Patent Fund (to K.D.T.) for financial support.

Supplementary Material Available: Full spectral data, including NOE data used for stereochemical assignments, for **7a**, **7b**, **9**, **12**, and **13** (4 pages). Ordering information is given on any current masthead page.

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[12] In an attempt to study the protonated quinone methide/benzyl cation under identical conditions, phenol **9** was treated with TiCl_4 (1 or 2 equiv, −78 to 25 °C, 1 h, $\mathrm{CH_2Cl_2}$) but afforded only unreacted starting material. The failure of this isomerization may be due to the complexation of Ti(IV) with the free phenol in **9**, thereby inhibiting opening of the bicyclo[3.2.1]octene.

Benzoquinone–Olefin Exciplexes: The Observation and Chemistry of the *p*-Benzoquinone–Tetraphenylallene Exciplex[1]

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The Paterno–Büchi reaction has traditionally been thought to proceed through a preoxetane biradical (**1** in Scheme I).[2] It has become apparent that a preoxetane biradical alone is insufficient to account for the photochemical behavior of carbonyl–olefin systems.[3] These photoadditions may involve charge-transfer (CT) exciplexes (**2**) as well as preoxetane biradicals. While preoxetane biradicals[4a–c] and triplet exciplexes,[4d] including chloranil–arene exciplexes,[4e,f] have been observed by transient spectroscopy, triplet carbonyl–olefin exciplexes have yet to be observed directly. In this account, we report the direct observation of a *p*-benzoquinone–olefin exciplex and the characterization of its chemical behavior.

Excitation of *p*-benzoquinone (PBQ) with 355- or 532-nm light[5a] in the presence of various olefins in CCl_4[5b] produces transients at 400–405 nm which decay as single exponentials in all cases studied (Table I and Figure 1A). While these transients exhibit very similar spectroscopic properties, their lifetimes vary over an appreciable range, and the allene transients are quenched by

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[1] Preliminary accounts of various aspects of this work have been presented at the following meetings: Creed, D.; Caldwell, R. A.; Rodgers, M. A. J. *Abstracts of Papers*, 194th National Meeting of the American Chemical Society, Org. Div., New Orleans, LA, Aug 30–Sept 4, 1987; American Chemical Society: Washington, DC, 1987; ORGN 87. Wilson, R. M.; Schnapp, K. A.; Ho, D. M.; Caldwell, R. A.; Creed, D. *Abstracts of the XII IUPAC Symposium*, Bologna, Italy, July 17–22, 1988; Abstract PK27. Wilson, R. M.; Schnapp, K. A.; Ho, D. M.; Caldwell, R. A.; Creed, D. *Abstracts of the 2nd Winter Conference of the Inter-American Photochemical Society*, Clearwater Beach, FL, Jan 3–7, 1989; Abstract C15.

[2] (a) Arnold, D. R. In *Advances in Photochemistry*; Noyes, Jr., W. A., Hammond, G. S., Pitts, Jr., J. N., Eds.; Interscience: New York, 1968; Vol. 6, p 301. (b) Jones, G., II. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 1. (c) Wilson, R. M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1985; Vol. 7, p 339.

[3] (a) Kochevar, I.; Wagner, P. J. *J. Am. Chem. Soc.* **1970**, *92*, 5742. (b) Kochevar, I.; Wagner, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 3859. (c) Caldwell, R. A.; Sovocool, G. W.; Gajewski, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 2549. (d) Wilson, R. M.; Outcalt, R.; Jaffe, H. H. *J. Am. Chem. Soc.* **1978**, *100*, 301 and unpublished results (Moore, C. E.; Jaffe, H. H.; Wilson, R. M.). (e) Maharaj, U.; Winnik, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 2328. (f) Wilson, R. M.; Wunderly, S. W.; Walsh, T. F.; Musser, A. K.; Outcalt, R.; Geiser, F.; Gee, S. K.; Brabender, W.; Yerino, L., Jr.; Conrad, T. T.; Tharp, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 4429. (g) Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 825 and references therein.

[4] (a) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629. (b) Freilich, S. C.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6255. (c) Freilich, S. C.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 3819. (d) Renge, I. V.; Kuzmin, V. A.; Borisevich, Y. E. *J. Photochem.* **1985**, *31*, 67 and references therein. (e) Jones, G., II; Haney, W. A.; Phan, X. T. *J. Am. Chem. Soc.* **1988**, *110*, 1922. (f) Jones, G., II; Mouli, N. *J. Phys. Chem.* **1988**, *92*, 7174.

[5] (a) Unfocused, third- and second-harmonic, Q-switched, Nd:YAG laser pulses, 10 ns fwhm, ca. 10 and 30 mJ, respectively, were used in this study. (b) In CCl_4, these transients are readily observed without the interference from the semiquinone radical. Ketyl radical interference may have been a significant factor in the failure to observe related species in previous studies: Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393.

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Table I. Properties of *p*-Benzoquinone–Olefin Transients in CCl_4[a]

quinone–olefin system	transient λ_{max}, nm	τ, ns (23 °C)	A, s^{-1}	E_a, kcal/mol	k_q (O_2), M^{-1} s^{-1}	ΔG electron transfer,[b] kcal/mol
(1) *p*-benzoquinone/*tert*-butylethylene (PBQ/TBE)[c]	400	3–4				
(2) *p*-benzoquinone/tetramethylallene (PBQ/TMA)	405	140	1.45×10^{10}	4.5	1.5×10^9	3.5[d]
(3) *p*-benzoquinone/tetraphenylallene (PBQ/TPA)	400	51	1.96×10^{10}	4	ca. 1×10^8	−5.7[e]

[a] k_q ^{3}[*p*-benzoquinone] by tetramethyl- and tetraphenylallene ca. 3×10^9 M^{-1} s^{-1}. [b] For PBQ, E_T = 50 kcal/mol and E_{Rd} = −0.47 V versus an Ag/AgCl electrode. [c] Reference 7. [d] Estimated from the oxidation potential of trimethylallene, E_{ox} = 1.85 V versus an Ag/AgCl electrode, ref 8. [e] For TPA, E_{ox} = 1.45 V versus an Ag/AgCl electrode, ref 9.

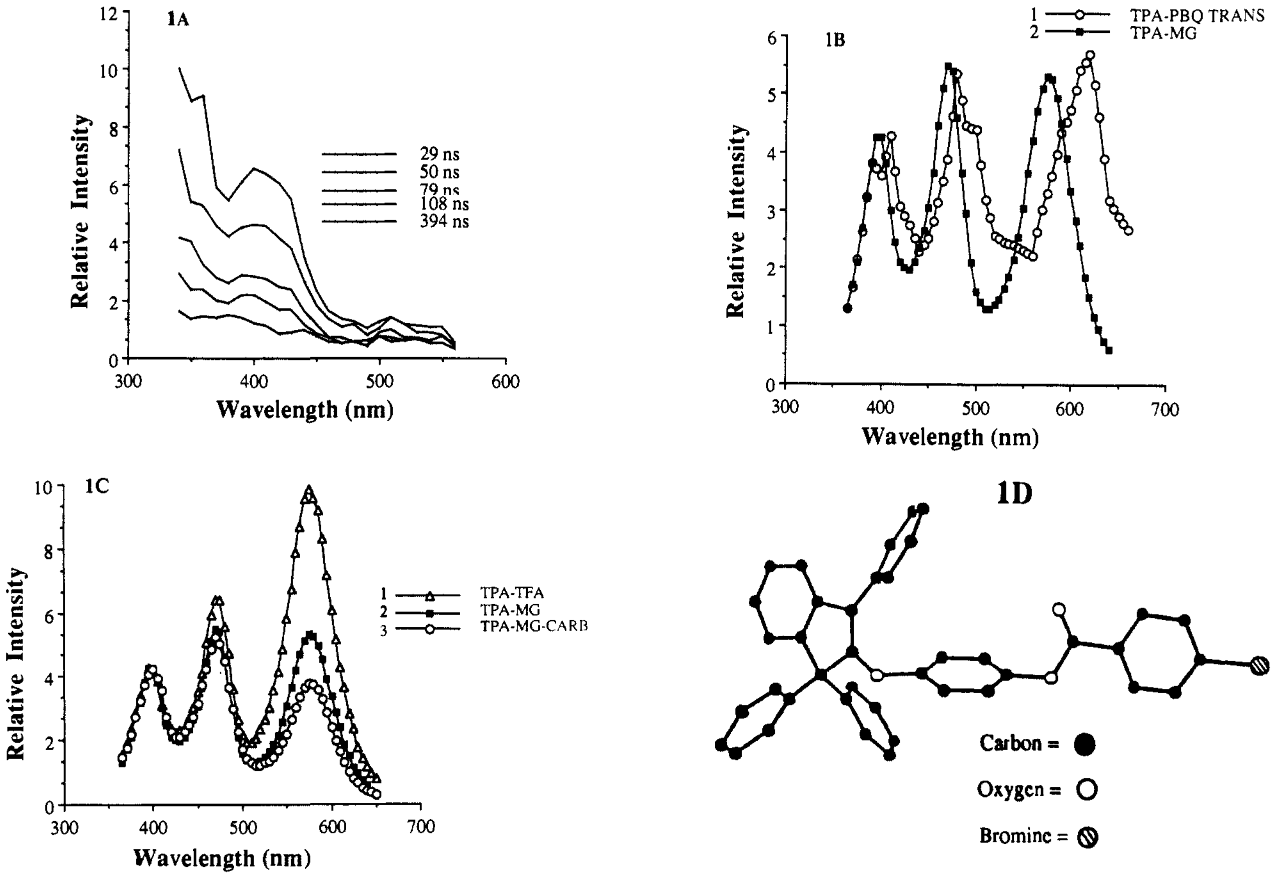
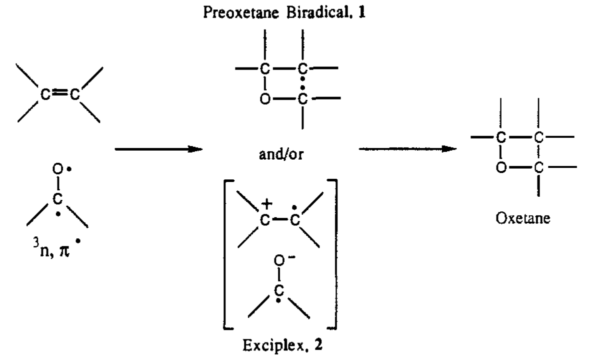


Figure 1. (A) Transient absorption spectra of the prompt 400-nm PBQ–TPA transient in CCl_4. (B) Transient absorption spectra generated from TPA by (1) irradiation in the presence of PBQ in 10% $AcOH/CCl_4$ and (2) treatment with magic green (MG). (C) Transient absorption spectra generated from TPA by treatment with (1) trifluoroacetic acid (TFA), (2) MG, and (3) MG and Na_2CO_3 (MG–CARB). (D) X-ray structure of the *p*-bromobenzoate of **3**.

Scheme I



oxygen at significantly different rates. What appears to be a PBQ–TMA preoxetane biradical has been trapped by oxygen to form a peroxide.[3f] However, no trapping products were observed for the PBQ–TPA system even at 8 atm of oxygen. This failure to observe trapping with oxygen in the PBQ–TPA system may be due to the more favorable ΔG for electron transfer (Table I) which should favor exciplex rather than preoxetane biradical formation.[6]

The low-intensity irradiation of PBQ-TPA in either CCl_4 or 10% $AcOH/CCl_4$ affords the indene **3** (Scheme II) as the only photoproduct.[10] However, if this reaction is conducted in 10% CH_3OH/CCl_4, 2-methoxy-1,1,3-triphenylindene and 3-methoxy-1,1,3,3-tetraphenylpropene are isolated as well as the indene **3**.

The transient absorption of PBQ–TPA in CCl_4 (Figure 1A) is substantially altered in CH_3CN, where it exhibits two bands, a sharp band at 440 nm which can reasonably be assigned to the PBQ radical anion and a broad band with λ_{max} = ca. 720–760 nm which, although weak, resembles the absorption assigned to the TPA radical cation (**4** in Scheme II).[11] Furthermore, in 10%

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(6) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(7) Creed, D.; Caldwell, R. A. *J. Am. Chem. Soc.*, submitted.

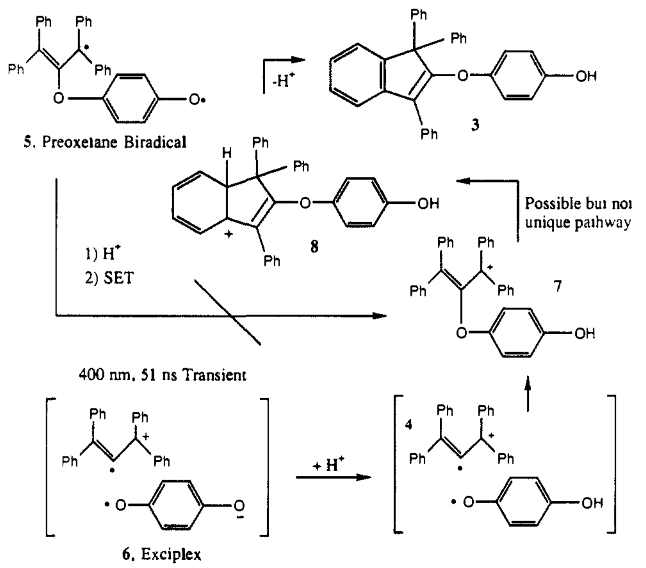
(8) Becker, J. Y.; Zinger, B. *J. Chem. Soc., Perkin Trans. 2* **1982**, 395.

(9) Schlegel, G.; Schäfer, H. J. *Chem. Ber.* **1983**, *116*, 960.

(10) The structure of **3** has been confirmed by an X-ray crystal study of its *p*-bromobenzoate derivative (Figure 1D). For experimental details of this crystal study, see the supplementary material paragraph at the end of the paper.

(11) The TPA radical cation has been generated by 355-nm flash photolysis of ceric ammonium nitrate in the presence of TPA in CH_3CN and displays a broad absorption centered at ca. 740 nm: Khanna, R. K.; Creed, D., unpublished results.

Scheme II



AcOH/CCl$_4$, drastic alterations in transient behavior are observed (Figure 1B, curve 1). In this case, decay of the initially formed 400-nm band [$(4.2 \pm 0.3) \times 10^7$ s^{-1}] and synchronous growth of the band at 610 nm [$(4.7 \pm 0.3) \times 10^7$ s^{-1}] are observed. The resulting three-maximum spectrum (λ_{max} = 400, 490, and 610 nm) persisted for the duration of the experiment (1 μs). Both trifluoroacetic acid (TFA) and magic green[12,13] [MG, tris(2,4-dibromophenyl)aminium hexachloroantimonate] produce similar and, thus, apparently related three-maximum spectra (Figure 1C, λ_{max} = 400, 475, and 590 nm) from TPA in the dark in CCl$_4$. In contrast, AcOH fails to afford a similar spectrum in the dark. While no rigorous assignments can be made for the species that afford the spectra in Figure 1, parts B and C, the strong similarities in these spectra indicate that the photochemical transient (Figure 1B, curve 1) is derived from electrophilic attack on the TPA.[14]

The preoxetane biradical **5** (Scheme II) was excluded as the initially observed transient (Figure 1A), since there is no obvious reason why **5** should be prone to rapid protonation under such mild conditions. Instead, a charge-transfer exciplex **6** would seem to be the more likely structure for this prompt transient. Protonation of the basic PBQ radical anion moiety should lead to a neutral semiquinone radical, which can couple with the TPA moiety at its central carbon atom either within a cage or following diffusion. The exact sequence of events leading from exciplex **6** to the product **3** is not clear; acid-assisted coupling of the PBQ and TPA moieties may precede cyclization to the indene skeleton as illustrated in Scheme II, or alternatively, cyclization may precede coupling. Furthermore, the bands of the long-lived transient spectrum (Figure 1B, curve 1) might be due to some combination of the open cation **7**, the cyclized cation **8**, or other closely related species. The tentative mechanism outlined in Scheme II is supported by the previous observation of reactions of CT exciplexes with Brönsted[2c] and Lewis acids,[15] as well as salt effects in Paterno–Büchi reactions.[3g] Finally, this photochemical cyclization to **3** closely parallels the efficient, thermal cyclization of TPA to 1,1,3-triphenylindene in TFA.

In summary, this work provides transient spectroscopic evidence for exciplex intermediacy in at least one photoreaction of a carbonyl compound with an olefin. Additional work directed toward the interception of related exciplexes with acids should further characterize these carbonyl–olefin intermediates and probably lead to novel chemistry as well.

Acknowledgment. K.A.S. thanks the University of Cincinnati Summer Research Council, the Procter & Gamble Company, the Research Associates Program, and the Center for Laser Chemistry for stipend support. We thank the National Science Foundation for partial support of this work (R.M.W., CHE-8312691 and CHE-8409628; R.A.C., CHE-8516534 and CHE-8820268). Kinetic absorption spectroscopy was performed at the Center for Fast Kinetic Research at the University of Texas at Austin, supported by NIH Grant RR-00886 from the Biotechnology Branch of the Division of Research Resources and by the University of Texas.

Registry No. 3, 126035-47-0; **6**, 126035-49-2; *p*-benzoquinone, 106-51-4; *p*-benzoquinone radical anion, 3225-29-4; tetraphenylallene, 1674-18-6; tetraphenylallene radical anion, 126035-48-1; 2-methoxy-1,1,3-triphenylindene, 126035-50-5; 3-methoxy-1,1',3,3'-tetraphenylpropene, 86477-15-8; 2-(4-(4-bromobenzoyloxy)phenoxy-1,1,3-triphenylindene, 126035-51-6.

Supplementary Material Available: Figure showing the atomic numbering scheme, X-ray experimental description, X-ray structure determination summary, and X-ray data tables for the *p*-bromobenzoate derivative of **3**, including Table 3-1 of atomic positional parameters, Table 3-2 of anisotropic temperature factors, Table 3-3 of hydrogen positional parameters, Table 3-4 of bond distances, and Table 3-5 of bond angles (13 pages). Ordering information is given on any current masthead page.

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[12] Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, 2719.

[13] Wilson, R. M.; Dietz, J. G.; Shepherd, T. A.; Ho, D. M.; Schnapp, K. A.; Elder, R. C.; Watkins, J. W., II; Geraci, L. S.; Campana, C. F. *J. Am. Chem. Soc.* **1989**, *111*, 1749.

[14] Presumably the spectrum of the photochemical transient (Figure 1B, curve 1) is shifted to slightly longer wavelength by the hydroquinone substituent.

[15] Bowman, R. M.; Chamberlain, T. R.; Huang, C. W.; McCullough, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 4106.

Immobilizing the Gate of a Tartaric Acid–Gramicidin A Hybrid Channel Molecule by Rational Design

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The ability to control the gating of ion-conducting channel molecules represents an important step toward the goal of producing molecular switches. Recently we developed a transmembrane ion channel motif based on tartaric acid–gramicidin A hybrids.[1,2] By covalent linkage of two gramicidin A (gA) monomers, the problem of channel disruption seen in the native channel can be removed.[3] Single-channel ion conductance measurements of **1** and **2** (Figure 1) demonstrated that the ion-conducting properties of these molecules are dependent on the stereochemistry of the tartaric acid derived linker element, in accord with the predictions of a structural model based on a β-helix secondary structure. In this model, the *S,S* stereochemistry of the dioxolane is matched with respect to the helix geometry, whereas the (*R,R*)-dioxolane linker is a stereochemical mismatch. Importantly, it was noted that diastereomer **2** exhibited rapid interruptions in current (flickers), a property suggestive of a gating mechanism. A structural basis for the diastereospecific gating was proposed that involves the movement of the dioxolane ring in **2** into and out of the ion-conducting pore, resulting in the closed and open form of the channel. A prediction of this model is that the introduction of sterically demanding substituents at the acetal

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[1] Heinemann, S. H.; Stankovic, C. J.; Delfino, J. M.; Schreiber, S. L.; Sigworth, F. J. *Biophys. J.* **1989**, *55*, 505a.

[2] Stankovic, C. J.; Heinemann, S. H.; Delfino, J. M.; Sigworth, F. J.; Schreiber, S. L. *Science* **1989**, *244*, 813-817.

[3] (a) Urry, D. W.; Goodall, M. C.; Glickson, J. D.; Mayers, D. F. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 1907-1911. (b) Bamberg, E.; Janko, K. *Biochim. Biophys. Acta* **1977**, *465*, 486-499.

0002-7863/90/1512-3702$02.50/0