There is a strong bromide common-ion effect on the reaction of **4**;[10] the pseudo-first-order rate constants for the disappearance of **4** decrease from $k_{solv} = 6.2 \times 10^{-4}$ s^{-1} at zero NaBr to $k_{obsd} = 1.3 \times 10^{-4}$ s^{-1} at 0.083 M NaBr. The addition of 0.083 M NaN_3 or NaCl has no effect on k_{obsd}. A plot of k_{solv}/k_{obsd} against [NaBr] is linear with a slope $k_{Br}/k_s = 38$ M^{-1}.

These results show that 1-(4-methoxyphenyl)-2,2,2-trifluoroethyl derivatives react by an S_N1 mechanism (Scheme I) through a common carbocation intermediate which shows an appreciable selectivity in its reaction with strong nucleophiles and solvent. The azide selectivity $k_{az}/k_s = 95$ M^{-1} for the reaction of **5** is not significantly different than the value of 105 M^{-1} for **1** capture.[11,12] The k_{az} values for the reactions of **1** and **5** must also be similar, since k_{az} for **1** is diffusion-limited and insensitive to further increases in cation reactivity.[11,12] A value of 5×10^7 s^{-1} for both **1** and **5** reaction with solvent can be calculated from the experimental k_{az}/k_s values and an estimated diffusional rate constant of 5×10^9 M^{-1} s^{-1} for k_{az}.[13] Since **1** and **5** show the same reactivity with solvent, it is concluded that the decreased equilibrium stability of **5** compared to **1** is essentially entirely expressed as the difference in the rate constants for the formation of **5** and **1** by S_N1 solvolysis of precursors with the same leaving group.[3]

The absence of an α-CF_3 substituent effect on k_s is surprising, since in a number of other systems carbocation reactivity has been observed to increase substantially with decreasing stability.[12,14] There are at least two explanations for the small substituent effect on k_s.

(1) The transition state for the reaction of **1** and **5** with solvent is very early. This is unlikely because structure–reactivity studies on the reactions of ring-substituted 1-phenylethyl carbocations show that there is significant bonding between the hydroxylic solvent and the α-carbon in the transition state for solvent addition.[12]

(2) A more likely explanation is that the inductive-destabilizing effect of the α-CF_3 group is partially offset by greater 4-methoxyphenyl stabilization of **5**,[15] and the transition state for cation reaction is unbalanced with respect to the fractional change in ground-state inductive and resonance interactions. The change in k_s is given by eq 2,[16] where $(K/K_o)_I$ is the large equilibrium

$$\log (k/k_o)_s = p_I{}^n \log (K/K_o)_I + p_R{}^n \log (K/K_o)_R \qquad (2)$$

inductive effect of the α-CF_3 group, $(K/K_o)_R$ is a measure of the extent to which inductive destabilization is offset by increased resonance delocalization into the 4-methoxyphenyl ring, and $p_I{}^n$ and $p_R{}^n$ are the fractional expression of these effects in the reaction transition state. If the transition state is unbalanced ($p_R{}^n > p_I{}^n$), then the magnitude of the opposing resonance and inductive effects may be equal, and k_s unchanged.

The results reported here should be added to a diverse list of novel structure–reactivity effects that can be explained by a transition-state imbalance in the progression of two processes.[12,17] Taken as a whole, these novel effects provide good evidence that imperfect transition-state synchronization[17b] often plays an important role in determining the effect of changing reactant structure on reactivity.

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[10] The reaction of **4** was followed by monitoring the decrease in A_{290}.

[11] Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 4689.

[12] Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361.

[13] Reference 12, footnote 45.

[14] Diffenbach, R. A.; Sano, K.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 4747. Arnett, E. M.; Hofelich, T. C. *Ibid.* **1983**, *105*, 2889. Young, P. R.; Jencks, W. P. *Ibid.* **1977**, *99*, 8238.

[15] The observation that a resonance-electron-donating 4-methoxy ring substituent causes a (4×10^7)-fold increase in k_{solv} for 1-phenyltrifluoroethyl tosylate reaction,[2b] but only a (6×10^4)-fold increase in k_{solv} for 1-phenylethyl chloride[3] is good evidence that cation stabilization by resonance is greater in the 1-phenyltrifluoroethyl system.

[16] Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288.

[17] (a) Kresge, A. J. *Can. J. Chem.* **1974**, *52*, 1897. (b) Bernasconi, C. F. *Tetrahedron* **1985**, *41*, 3219. (c) Hupe, D. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 451. (d) Hupe, D. J.; Wu, D. *Ibid.* **1977**, *99*, 7653. (e) Jencks, W. P.; Brandt, S. R.; Gandler, J. R.; Fendrich, G.; Nakamura, C. *Ibid.* **1982**, *104*, 7045. (f) Jencks, D. A.; Jencks, W. P. *Ibid.* **1977**, *99*, 7948.

Direct Observation of *o*-Xylylene (*o*-Quinodimethane) in Solution. Dimerization Kinetics of Some *o*-Quinodimethanes[1]

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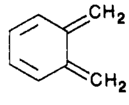
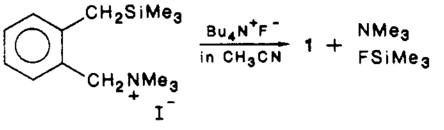
o-Xylylene (**1**), also called *o*-quinodimethane (*o*-QDM), is a reactive molecule that has been extensively studied, both theoretically[2,3] and experimentally.[3,4] Although **1** is very reactive, some direct evident for its existence has been reported. It has been observed directly by UV–visible spectroscopy both in solution[5] and in a low-temperature matrix[3,6] and by IR, Raman, fluorescence, and fluorescence excitation spectroscopy in a low-temperature matrix.[6] The UV-photoelectron spectrum of **1** in the gas phase has also been published.[7] The reported observation of **1** in solution involved the generation of **1** by flash photolysis.[5] Recently, the generation of *o*-QDM's based on the fluoride ion induced 1,4-elimination from [*o*-[α-(trimethylsilyl)alkyl]benzyl]trimethylammonium halides was reported.[4,8] We now wish to report that we have found this reaction to be very fast, and it provides a simple and efficient method for generating *o*-QDM's under conditions which allow them to be detected by UV–visible spectroscopy.



1

When an acetonitrile solution of [*o*-[(trimethylsilyl)methyl]benzyl]trimethylammonium iodide (**2**) (10^{-3} M) was treated with an acetonitrile solution of tetrabutylammonium fluoride (TBAF, 10^{-1} M) at room temperature in a UV–visible cell, a species with a λ_{max} of 367 nm was produced which rapidly decayed following second-order kinetics. These observations are consistent with very rapid formation of **1**. The value of the λ_{max} of the reactive species is similar to the reported λ_{max} of **1** in a rigid glass (373 mm)[6] and in benzene (369 nm).[5] Further support for the rapid formation of **1** under the conditions used in the UV–visible spectroscopy experiments was obtained by product studies under these conditions and under conditions which differed only by the presence of an excess of methyl acrylate. In the absence of methyl acrylate, the known[9] [4 + 2] (**3**) and [4 + 4] (**4**) dimers were produced in a ratio of 11:1. However, with added excess methyl acrylate, the Diels–Alder adduct of **1** and methyl acrylate (**5**) was obtained instead of dimers **3** and **4**.



2

The very rapid formation of **1** under the conditions used in the UV–visible spectroscopy experiments allows the rate of dimeri-

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[1] (a) Presented in part at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept, 1985; paper ORGN 152. (b) Based on work by J.R.M. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

[2] (a) Baudet, J. *J. Chim. Phys. Physichochim. Biol.* **1971**, *68*, 191. (b) Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941.

[3] Michl, J.; Flynn, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 5802 and references cited therein.

[4] Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1982**, *104*, 7609 and references cited therein.

[5] Roth, W. R.; Biermann, M.; Dekker, H.; Jochems, R.: Mosselman, C.; Hermann, H. *Chem. Ber.* **1978**, *111*, 3892.

[6] Michl, J.; Tseng, K. L. *J. Am. Chem. Soc.* **1977**, *99*, 4840.

[7] Kreile, J.; Munzel, N.; Schulz, R.; Schweig, A. *Chem. Phys. Lett.* **1984**, *108*, 609.

[8] Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 863.

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Table I. Second-Order Rate Constants for the Dimerization of *o*-QDM's **1**, **6**, and **7** in Acetonitrile[a]

temp, °C	k_1, L mol^{-1} s^{-1} [b]	k_6, L mol^{-1} s^{-1} [c]	k_7, L mol^{-1} s^{-1} [d]
25	9.94 ± 0.32 × 10^3	3.90 ± 0.15 × 10^3	5.59 ± 0.21 × 10^3
35	12.1 ± 0.41 × 10^3	5.24 ± 0.18 × 10^3	7.89 ± 0.30 × 10^3
45	15.4 ± 0.51 × 10^3	6.78 ± 0.24 × 10^3	10.1 ± 0.38 × 10^3

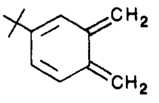
[a] For all reactions the concentration of TBAF was 5.00×10^{-2} M and the concentration of **1**, **6**, or **7** was 5.00×10^{-4} M. Rate constants were obtained from an average of at least nine kinetic runs. [b] $\Delta H_1^\ddagger = 3.5 \pm 0.13$ kcal mol^{-1}, $\Delta S_1^\ddagger = -29 \pm 1.1$ cal mol^{-1} K^{-1}. [c] $\Delta H_6^\ddagger = 4.8 \pm 0.17$ kcal mol^{-1}, $\Delta S_6^\ddagger = -26 \pm 1.0$ cal mol^{-1} K^{-1}. [d] $\Delta H_7^\ddagger = 4.9 \pm 0.20$ kcal mol^{-1}, $\Delta S_7^\ddagger = -25 \pm 1.0$ cal mol^{-1} K^{-1}.

zation of **1** and other reactive *o*-QDM's to be measured using the stopped-flow technique. Since the rate of dimerization is a second-order process, measurement of the rate constant requires knowledge of the concentration of **1** and this can be obtained by knowing the ϵ_{max} of **1**. Michl estimated the ϵ_{max} of **1** in a frozen matrix to be >3000,[3] and Roth used Michl's estimated value of 3000 in his flash photolysis study.[5] We have determined the ϵ_{max} for **1** in the following manner. Several runs were carried out[10] in which the concentration of **2** was kept constant but the fluoride ion concentration was varied from 5×10^{-3} to 1 M. As the concentration of fluoride ion increased, the maximum absorbance of the intermediate did not continue to increase but leveled off at a fluoride ion concentration of 0.025 M. We assumed that when the fluoride ion concentration was at least 0.025 M, **2** was converted quantitatively to **1** before much of **1** had dimerized. Knowing the concentration of **2**, we calculated ϵ_{max} to be 3015.

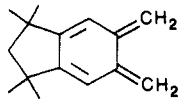
Rate constants for the dimerization of **1** from 25 to 45 °C were measured and these are reported in Table I. Both the values of the *k*'s and the temperature dependence of the reaction are in good agreement with Roth's data: $k_1 = 9.85 \times 10^3$ L mol^{-1} s^{-1} at 22.3 °C, $\Delta H^\ddagger = 5.3$ kcal/mol, and $\Delta S^\ddagger = -24.3$ eu.[5]

Some previous work in our laboratory on the corresponding 2,3-dimethylene-2,3-dihydrofuran system suggests that *o*-QDM dimerizations proceed via a stepwise mechanism involving a diradical intermediate.[11] It is believed that in forming the diradical intermediate, the *o*-QDM monomers prefer a non-endo approach.[12]

o-QDM's such as **6** and **7** contain alkyl substituents which introduce steric bulk on the ring away from the reactive site without significantly changing the electronic nature of the molecule. If, *o*-QDM monomers prefer an endo approach when undergoing dimerization, the bulky substituents on **6** and **7** would be expected to repel one another, resulting in significantly reduced rates of dimerization for these *o*-QDM's. Alternatively, if a non-endo approach is preferred, one would expect similar rates of dimerization for **1**, **6**, and **7**. When iodides[13] **8** and **9** were treated with fluoride ion in acetonitrile, *o*-QDM's **6** and **7**,[16] respectively, were generated. Rate constants for the dimerization of **6** and **7** are listed in Table I. Clearly the differences in rate constants for the dimerization of **1**, **6**, and **7** are small and this supports the non-endo approach of monomers.



6



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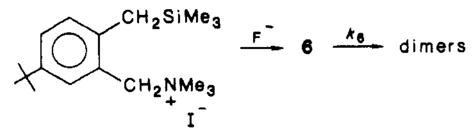

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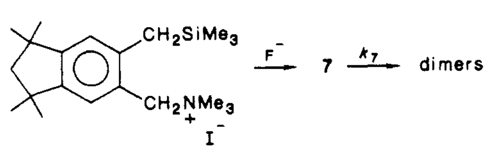

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The 1,4-elimination from [*o*-[α-(trimethylsilyl)alkyl]benzyl]trimethylammonium halides seems well suited for generating *o*-QDM's for the purpose of spectroscopic investigation. This method makes it possible to study many substituted *o*-QDM's, the precursors of which are readily prepared from simple starting materials.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-ENG-82. We thank J. H. Espenson, C. B. Steffan, and M. S. Ram for assistance with the kinetics measurements.

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(9) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949.

(10) The progress of the reactions was monitored with use of a Canterbury SF-3A stopped-flow spectrophotometer and OLIS Model 3820 computer.

(11) Chou, C.-H.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1986**, *108*, 1438.

(12) Chou, C.-H. Ph.D. Dissertation, Iowa State University, Ames, IA, 1985.

(13) Iodide **8**[14] was prepared from [*p-tert*-butylbenzyl]trimethylammonium bromide in a manner analogous to that used for the parent system.[4] Iodide **9**[15] was prepared as follows: Sommelet–Hauser rearrangement of [3,4-(1,1,3,3-tetramethyltrimethylene)benzyl]trimethylammonium chloride produced a mixture of two isomeric (pentamethylindanyl)dimethylamines which were separated on silica gel. Conversion of the appropriate amine to **9** was analogous to the sequence used for the parent system.[4]

(14) **8**: mp 205–206 °C; IR (KBr) 2940, 1470, 1240 cm^{-1}; ^{1}H NMR (CD_3CN; Me_4Si as an external reference) δ –0.05 (s, 9 H), 1.33 (s, 9 H), 2.30 (s, 2 H), 3.06 (s, 9 H), 4.43 (s, 2 H), 7.2–7.6 (m, 3 H). Anal. Calcd for $C_{18}H_{34}INS$: C, 51.54; H, 8.17, N, 3.34. Found: C, 51.62; H, 8.22; N, 3.27.

(15) **9**: mp 204–205 °C; IR (KBr) 2940, 1484, 1460, 1240 cm^{-1}; ^{1}H NMR (CD_3CN, Me_4Si as an external reference) δ –0.03 (s, 9 H), 1.31 (s, 12 H), 1.91 (s, 2 H), 2.31 (s, 2 H), 3.04 (s, 9 H), 4.40 (s, 2 H), 6.96 (s, 1 H), 7.20 (s, 1 H). Anal. Calcd for $C_{21}H_{38}INS$: C, 54.88; H, 8.33; N, 3.05. Found: C, 54.81; H, 8.35; N, 3.01.

(16) Uv–visible data: **6**, $\lambda_{max} = 381$ nm, $\epsilon_{max} = 2120$; **7**, $\lambda_{max} = 378$ nm, $\epsilon_{max} = 2390$.

Direct Determination of the Barrier to Edge Inversion at Trivalent Phosphorus: Verification of the Edge Inversion Mechanism

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We now report the direct determination of the barrier to edge inversion at a trivalent 8-electron phosphorus center (8-P-3).[1] The experimentally determined $\Delta H^\ddagger$ of 23.4 kcal/mol for **1c** is in excellent agreement with a large basis set ab initio calculation of a barrier height of 28.1 kcal/mol for **1a**. These results verify the operation of the recently recognized edge inversion process proceeding through transition state **2** at suitably substituted 8-P-3 centers.[2]

In a previous report we presented evidence that the classical vertex inversion process, e.g., NH_3 inversion, should not be expected for the inversions of all 8-Pn-3 (Pn = pnictogen P, As, Sb, Bi) centers.[2] Substitution of the pnictogen center by electronegative groups (σ-acceptors) and π-donors can lead to a pref-

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(1) The *N*-X-*L* nomenclature system has previously been described (Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753). *N* Valence electrons about a central atom X, with *L* ligands.

(2) Dixon, D. A.; Arduengo, A. J., III; Fukunaga, T. *J. Am. Chem. Soc.* **1986**, *108*, 2461.

0002-7863/86/1508-6821$01.50/0