1,4-Diaminopentane Dihydrochloride (5a). Reduction of crude **4a** gave (50%) pure biscarbamate **6a**: mp 130–131 °C. Anal. Calcd for $C_{21}H_{26}N_2O_4$: C, 68.1; H, 7.1; N, 7.6. Found: C, 68.2; H, 7.2; N, 7.5. Hydrogenolysis of **6a** afforded 98% of **5a** dihydrochloride:[16] mass spectrum, *m/e* 102 (4, M^+), 44 (100, $M^+ - CH_2CH_2NH_2$); ^{13}C NMR (D_2O) δ 39.8 (CH_2NH_2), 48.1 ($CHNH_2$).

1,4-Diaminohexane Dihydrochloride (5b). Reduction of crude **4b** gave 51% of **6b**: mp 117–118 °C. Anal. Calcd for $C_{22}H_{28}N_2O_4$: C, 68.7; H, 7.3; N, 7.3. Found: C, 68.6; H, 7.2; N, 7.4. Hydrogenolysis of **6b** afforded 98% of **5b** dihydrochloride:[16] mass spectrum, *m/e* 116 (4, M^+), 58 (100, $M^+ - CH_2CH_2NH_2$); ^{13}C NMR δ 40.1 (CH_2NH_2), 53.6 ($CHNH_2$).

1,4-Diaminoheptane Dihydrochloride (5c). Reduction of crude **4c** gave 48% of **6c**: mp 117–118 °C. Anal. Calcd for $C_{23}H_{30}N_2O_4$: C, 69.3; H, 7.5; N, 7.0. Found: C, 69.2; H, 7.4; N, 7.1. Hydrogenolysis of **6c** gave 95% of **5c** dihydrochloride: mass spectrum, *m/e* 130 (4, M^+), 70 (100, pyrrolenine cation); ^{13}C NMR δ 39.8 (CH_2NH_2), 51.9 ($CHNH_2$).

1,4-Diaminooctane Dihydrochloride (5d). Reduction of crude **4d** gave 46% of **6d**: mp 110–111 °C. Anal. Calcd for $C_{24}H_{32}N_2O_4$: C, 69.9; H, 7.7; N, 6.8. Found: C, 70.0; H, 7.8; N, 6.7. Hydrogenolysis of **6d** gave 98% of **5d** dihydrochloride: mass spectrum, 144 (4.5, M^+), 70 (100); ^{13}C NMR δ 40.1 (CH_2NH_2), 52.3 ($CHNH_2$).

1,4-Diaminononane Dihydrochloride (5e). Reduction of crude **4e** gave 42% of **6e**: mp 104–105 °C. Anal. Calcd for $C_{25}H_{34}N_2O_4$: C, 70.4; H, 8.0; N, 6.5. Found: C, 70.4; H, 7.9; N, 6.5. Hydrogenolysis of **6e** gave 98% of **5e**: mass spectrum, *m/e* 158 (4.7, M^+), 70 (100); ^{13}C NMR δ 41.8 (CH_2NH_2), 54.1 ($CHNH_2$).

1,4-Diaminodecane Dihydrochloride (5f). Reduction of crude **4f** gave 52% of **6f**: mp 112–113 °C. Anal. Calcd for $C_{26}H_{36}N_2O_4$: C, 70.9; H, 8.2; N, 6.4. Found: C, 70.8; H, 8.1; N, 6.3. Hydrogenolysis of **6f** gave 98% of **5f**: mass spectrum, *m/e* 172 (8, M^+); ^{13}C NMR δ 39.8 (CH_2NH_2), 52.1 ($CHNH_2$).

1,4-Diaminoundecane Dihydrochloride (5g). Reduction of crude **4g** gave 57% of **6g**: mp 112–113 °C. Anal. Calcd for $C_{27}H_{38}N_2O_4$: C, 71.4; H, 8.4; N, 6.2. Found: C, 71.2; H, 8.3; N, 6.1. Hydrogenolysis of **6g** gave 95% of **5g**; mass spectrum, *m/e* 186 (8, M^+), 70 (100); ^{13}C NMR δ 40.0 (CH_2NH_2), 52.3 ($CHNH_2$).

1,4-Diaminotetradecane Dihydrochloride (5h). Reduction of crude **4h** gave 50% of **6h**: mp 109–110 °C. Anal. Calcd for $C_{30}H_{44}N_2O_4$: C, 72.6; H, 8.9; N, 5.6. Found: C, 72.4; H, 8.8; N, 5.7. Hydrogenolysis of **6h** gave 97% of **5h**: mass spectrum, *m/e* 228 (8, M^+), 70 (100); ^{13}C NMR δ 40.0 (CH_2NH_2), 52.3 ($CHNH_2$).

1,4-Diaminohexadecane Dihydrochloride (5i). Reduction of crude **4i** gave 45% of **6i**: mp 109–110 °C. Anal. Calcd for $C_{32}H_{48}N_2O_4$: C, 73.3; H, 9.2; N, 5.3. Found: C, 73.4; H, 9.2; N, 5.3. Found: C, 73.4; H, 9.3; N, 5.2. Hydrogenolysis of **6i** gave 98% of **5i**: mass spectrum, *m/e* 256 (7, M^+), 70 (100); ^{13}C NMR δ 39.9 (CH_2NH_2), 52.3 ($CHNH_2$).

Acknowledgment. This work was made possible by a grant (GM-11973) from the National Institutes of Health (PHS).

Registry No. **1b**, 127-19-5; **1c**, 758-96-3; **1d**, 760-79-2; **1e**, 6225-06-5; **1f**, 5830-30-8; **1g**, 1115-96-4; **1h**, 14433-76-2; **1i**, 3007-53-2; **2a**, 1003-29-8; **2b**, 1072-83-9; **2c**, 1073-26-3; **2d**, 61480-97-5; **2e**, 89789-53-7; **2f**, 89789-54-8; **2g**, 73252-31-0; **2h**, 89789-55-9; **2i**, 89789-56-0; **3a**, 636-41-9; **3b**, 1551-06-0; **3c**, 1551-08-2; **3d**, 1551-10-6; **3e**, 1551-12-8; **3f**, 1551-14-0; **3g**, 878-12-6; **3h**, 89789-57-1; **3i**, 1216-25-7; **4a**, 89789-58-2; **4b**, 89789-59-3; **4c**, 89789-60-6; **4d**, 89789-61-7; **4e**, 89789-62-8; **4f**, 89789-63-9; **4g**, 89789-64-0; **4h**, 89789-65-1; **4i**, 89789-66-2; **5a**, 89789-67-3; **5b**, 89789-68-4; **5c**, 89789-69-5; **5d**, 89789-70-8; **5e**, 89789-71-9; **5f**, 89789-72-0; **5g**, 89789-73-1; **5h**, 89789-74-2; **5i**, 89789-75-3; **6a**, 89789-76-4; **6b**, 89789-77-5; **6c**, 89789-78-6; **6d**, 89789-79-7; **6e**, 89789-80-0; **6f**, 89789-81-1; **6g**, 89789-82-2; **6h**, 89789-83-3; **6i**, 89789-84-4; $CH_3CH_2C(O)Cl$, 79-03-8; $CH_3(CH_2)_2C(O)Cl$, 141-75-3; $CH_3(CH_2)_3C(O)Cl$, 638-29-9; $CH_3(CH_2)_4C(O)Cl$, 142-61-0; $CH_3(CH_2)_5C(O)Cl$, 2528-61-2; $CH_3(CH_2)_8C(O)Cl$, 112-13-0; $CH_3(CH_2)_{10}C(O)Cl$, 112-16-3; Me_2NH, 124-40-3; $NH_2OH{\cdot}HCl$, 5470-11-1; pyrrole, 109-97-7.

(16) Previously obtained from aliphatic precursors: Vita, G.; Bucher, G. *Chem. Ber.* **1966**, *99*, 3387.

Heats of Formation of 1,3-Dioxolenium Ions from Ortho Ester Precursors in Sulfuric Acid Solution: Methyl vs. Phenyl Substitution at the *pro*-Acyl Carbon Atom

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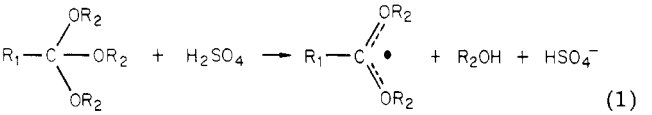
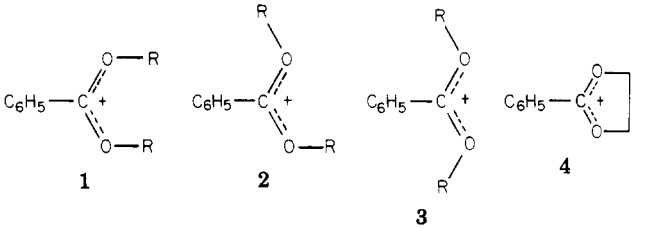
Recent calorimetric measurements have shown that the formation of methyl-substituted oxocarbonium ions in strongly acidic media is generally more exothermic than the formation of their phenyl-substituted analogues, contrary to the widely held idea that phenyl is a better carbocation-stabilizing group than methyl.[2] Among the substrates examined in this work were the ortho esters, trimethyl and triethyl orthoacetate and orthobenzoate; these substances, upon introduction into concentrated sulfuric acid, react to give the corresponding methyl- and phenyldialkoxycarbonium ions, eq 1. The heat evolved



$R_1 = CH_3, C_6H_5; R_2 = CH_3, C_2H_5$ (1)

in these exothermic reactions was found in each case to be greater for the methyl than for the phenyl analogue, by 3.8 kcal mol^{-1} in the methyl ortho ester series and by 4.6 kcal mol^{-1} in the ethyl ortho ester series.

These results, however, could have been complicated by steric interactions which inhibit the normal resonance effect of the phenyl group. Such steric inhibition of resonance has been demonstrated in the hydrolysis of trialkyl orthobenzoates under conditions where generation of dialkoxycarbonium ion intermediates is rate determining.[3] In these reactions, substitution of phenyl for hydrogen at the *pro*-acyl carbon atom produces rate retardations, in contrast to the strong acceleration shown by the phenyl group in the analogous hydrolysis reactions of acetals. This phenomenon was interpreted as the consequence of unfavorable interactions in all three of the completely planar conformations of the phenyldialkoxycarbonium ion: in the cis,cis conformation **1**, there is interference between the



1 **2** **3** **4**

alkoxy alkyl groups, and in the cis,trans **2** and trans,trans **3** conformations, there is interference between these alkyl groups and the ortho hydrogens of the benzene ring. When the steric interaction in the cis,cis conformation is relieved by joining the interfering alkyl groups together in a small

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(2) Larsen, J. W.; Bouis, P. A.; Riddle, C. A. *J. Org. Chem.* **1980**, *45*, 4969.

(3) Chiang, Y.; Kresge, A. J.; Salomaa, P.; Young, C. I. *J. Am. Chem. Soc.* **1974**, *96*, 4494.

0022-3263/84/1949-2622$01.50/0

Table I. Heats of Ionization and Solution of 2-Alkoxy-1,3-dioxolanes

substrate	$\Delta\bar{H}_{s,acid}$,[a] kcal mol^{-1}	$\Delta\bar{H}_{s,CCl_4}$, kcal mol^{-1}	$\Delta\bar{H}_{R^+}$, kcal mol^{-1}
2-methoxy-1,3-dioxolane	−21.3 ± 0.8	0.56 ± 0.03	−21.9
2-methyl-2-methoxy-1,3-dioxolane	−25.0 ± 0.9	0.34 ± 0.04	−25.3
2-phenyl-2-methoxy-1,3-dioxolane	−28.5 ± 0.7	0.78 ± 0.07	−29.3

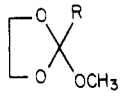
[a] In 97% H_2SO_4.

ring, as in the 2-phenyl-1,3-dioxolenium ion, **4**, phenyl substitution is indeed found to give a rate acceleration.

We have now examined this matter further by performing calorimetric measurements on the cyclic ortho ester precursors of the relevant dioxolenium ions and have found that in this series the methyl and phenyl group effects are in fact reversed.

Results

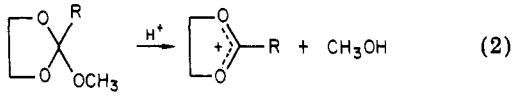
Three substrates were investigated: 2-methoxy-1,3-dioxolane (**5**, R = H), 2-methyl-2-methoxy-1,3-dioxolane (**5**,



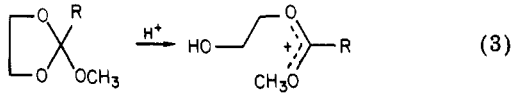
5

R = CH_3), and 2-phenyl-2-methoxy-1,3-dioxolane (**5**, R = C_6H_5). These substances were dissolved in 97% H_2SO_4 and the heat given off by this process, $\Delta\bar{H}_{s,acid}$, was measured. Most of the energy change in a process such as this is the enthalpy of ionization for the reaction of eq 1, $\Delta\bar{H}_{R^+}$, but there is also a small contribution from the heat of solution of the unionized substrate in the sulfuric acid medium. This was estimated by measuring the heats of solution of the substrates in the nonreactive solvent CCl_4, $\Delta\bar{H}_{s,CCl_4}$, and enthalpies of ionization were then calculated as the difference between the two measured quantities: $\Delta\bar{H}_{R^+} = \Delta\bar{H}_{s,acid} - \Delta\bar{H}_{s,CCl_4}$. The data are summarized in Table I.

The acid-promoted ionization of a cyclic ortho ester such as **5** can, in principle, occur either by loss of the exocyclic group, eq 2, or by cleavage of the dioxolane ring, eq 3.

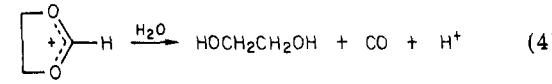


(2)



(3)

Several lines of evidence indicate that exocyclic group loss is the predominant if not exclusive reaction when R = phenyl,[4] and this was confirmed in the present study by the observation of proton NMR spectra characteristic of 1,3-dioxolenium ions[5] in both D_2SO_4 and CF_3SO_3H solution. NMR spectra also indicated predominant exocyclic group loss from the methyl (R = CH_3) and unsubstituted (R = H) substrates in these acids. The dioxolenium ion formed from the unsubstituted substrate, however, was unstable in D_2SO_4: it decomposed slowly over a period of several days in a reaction which formed ethylene glycol and gave off carbon monoxide gas, eq 4. This process is reminiscent of the well-known decarbonylation of formic acid in concentrated sulfuric acid.[6] The process requires 1 equiv of water, which is present in the 97% D_2SO_4 used but is not available in CF_3SO_3H.



(4)

Discussion

The evidence presented above indicates that all three of the cyclic ortho esters examined here undergo rapid acid-promoted exocyclic group loss to give 1,3-dioxolenium ions in the 97% H_2SO_4 solvent employed for the calorimetric measurements. The phenyl- and methyl-substituted dioxolenium ions so formed are stable in this medium; the unsubstituted ion, on the other hand, undergoes a subsequent reaction, but this is slow and will have no significant influence on the heat of ionization determined here.

The results presented in Table I show that the ionization of 2-methyl-2-methoxy-1,3-dioxolane to the 2-methyl-1,3-dioxolenium ion is more exothermic by 3.4 kcal mol^{-1} than is the ionization of the unsubstituted compound, and replacement of methyl by phenyl makes the process still more exothermic by another 4.0 kcal mol^{-1}. The phenyl-substituted cation is thus clearly more stable relative to the precursor ortho ester than is the methyl-substituted ion relative to its ortho ester precursor. It is unlikely that this superiority of phenyl over methyl is due to a countervailing initial state effect, inasmuch as the starting ortho esters are saturated uncharged molecules in which substituents will have little effect on stability. This, of course, is opposite to the effect of phenyl vs. methyl found in the acyclic methyl and ethyl ortho esters,[2] and that difference can be ascribed to steric inhibition of resonance in the acyclic phenyl-substituted ions.

It is interesting that this increased stability of the 2-phenyl-1,3-dioxolenium ion over its methyl-substituted counterpart, as expressed by the 4 kcal mol^{-1} difference in their heats of ionization, is not realized in the specific rates of formation of these ions. These specific rates have been measured as rates of hydrolysis of the cyclic ortho ester precursors catalyzed by the hydronium ion under conditions where dioxolenium ion formation is rate determining. The results, k_{H^+} = 175 M^{-1} s^{-1} for the unsubstituted ion,[3] k_{H^+} = 22 000 M^{-1} s^{-1} for the methyl derivative,[7] and k_{H^+} = 5400 M^{-1} s^{-1} for the phenyl substrate,[8] show the expected rate-accelerating effect of phenyl over hydrogen in the absence of steric complications, but they also show that generation of the phenyl-substituted ion is some 4 times slower than formation of its methyl analogue. The reason for this reversal is not clear. It may be due to a lagging developement of the cation-stabilizing conjugative effect of phenyl, which might run behind developement of the destabilizing inductive effect of this group because the π-system through which the conjugative effect must operate is not yet fully formed at the transition state of this reaction. A similar argument has been used to explain differences in the relative contributions of conjugative and inductive effects to the stability of transition and final states in the ionization of nitroalkanes.[9]

(4) Ahmaad, M.; Bergstrom, R. G.; Cashen, M. J.; Kresge, A. J.; McClelland, R. A.; Powell, M. F. *J. Am. Chem. Soc.* **1977**, *99*, 4827. Ahmad, M.; Bergstrom, R. G.; Cashen, M. J.; Chiang, Y.; Kresge, A. J.; McClelland, R. A.; Powell, M. F. *J. Am. Chem. Soc.* **1979**, *101*, 2669.

(5) Tomalia, D. A.; Hart, H. *Tetrahedron Lett.* **1966**, 3383, 3389.

(6) See, e.g.: Liler, M. "Reaction Mechanisms in Sulfuric Acid and Other Strong Acid Solutions"; Academic Press: New York, 1971; pp 253–258.

(7) Chiang, Y; Kresge, A. J.; Lahti, M. O.; Weeks, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 6852.

(8) Bergstrom, R. G.; Cashen, M. J.; Chiang, Y.; Kresge, A. J. *J. Org. Chem.* **1979**, *44*, 1639.

(9) Kresge, A. J. *Can. J. Chem.* **1974**, *52*, 1897.

There still remain a number of other reactions for which heats of ionization indicate methyl to be superior than phenyl at stabilizing a cationic center and from which steric effects are quite probably absent, e.g., the ionization of acyl chlorides which gives the linear RC≡O$^+$ ions.[2] In many of these systems, the ion precursors are unsaturated molecules, which could be stabilized more by phenyl than by methyl substituents. The initial-state substituent effects in these systems, however, would have to be stronger than the effects in the ion products in order to produce an inverted overall effect on the reaction. This seems unlikely, and the relative carbocation-stabilizing ability of methyl vs. phenyl is therefore still an incompletely solved problem.

Experimental Section

The 2-methoxy-1,3-dioxolanes were prepared by transesterification from the corresponding trimethyl ortho esters.[3,8] All other materials were best available commercial grades. Calorimetric measurements were performed as described previously.[10]

Acknowledgment. We are grateful to Dr. J. F. McGarrity for help with the NMR spectra and to the Natural Sciences and Engineering Research Council of Canada and to the donors of Petroleum Research Fund, administered by the American Chemical Society, for their support of this research.

Registry No. 5 (R = H), 19693-75-5; 5 (R = CH_3), 19798-71-1; 5 (R = C_6H_5), 19798-73-3; 2-phenyl-1,3-dioxolenium, 45888-13-9; 2-methyl-1,3-dioxolenium, 45380-51-6; 1,3-dioxolenium, 6680-54-2.

(10) Arnett, E. M.; Bentrude, W. G.; Burke, J. J; Duggleby, P. M. *J. Am. Chem. Soc.* **1965**, *87*, 1541. Arnett, E. M.; Larsen, J. W. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1968; Vol. 1, p 441.

Origin of Mutarotation in Some N-Substituted Ketimines

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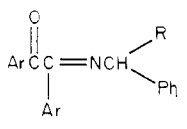
The mutarotation of substituted imines derived from optically active amines was studied for the first time in our laboratories.

This mutarotation has different origins for different types of imines. For the imines derived from α-dicarbonyl compounds **1**, the mutarotation is considered to be due to rotation around the chiral axis N=CC=O as deduced from kinetic and thermodynamic data.[1-4]



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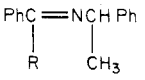


2

(1) López Mardomingo, C.; Pérez-Ossorio, R.; Plumet, J. *J. Chem. Res., Synop.* **1983**, 150.
(2) Alcaide, B.; Lago, A.; Pérez-Ossorio, R.; Plumet, J. *J. Chem. Res., Synop.* **1982**, 173.

Table I. Change of Rotatory Power with Time for Imines 2a and 2b

imine	solvent	T, K	$[\alpha_0]^a$ (exptl)	$[\alpha_e]$
2a	CD_3OD	298	41.34	2.34
		313	80.25	47.73
2b	CD_3OD	303	160.03	151.30
		313	155.70	146.64

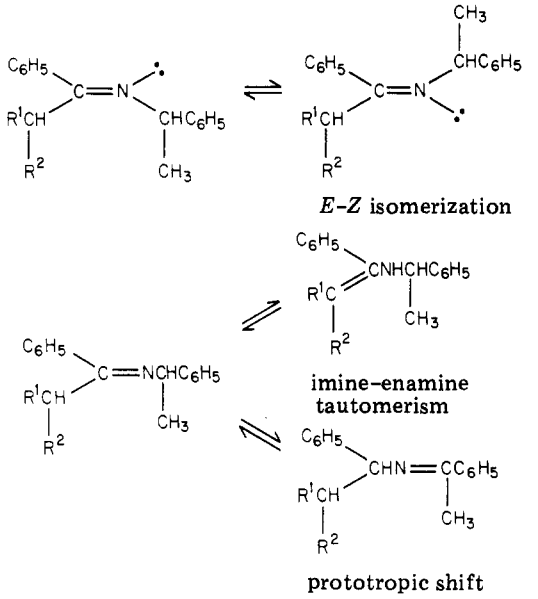
[a] Taken between 2 and 4 min after solution of imine. The solution has been prepared at least 24 h after distillation of imine.

Table II. Specific Rates of Approach to Equilibrium and Initial Rotatory Power (Calculated) for the Mutarotation of Imines 2a and 2b

imine	solvent	T, K	$(k_1 + k_{-1})10^5$,[a] s g^{-1}	$[\alpha_0]^a$	r[b]
2a	CD_3OD	298	47.6	41.33	0.998
		313	121.0	88.81	0.999
2b	CD_3OD	303	7.68	160.03	0.991
		313	29.0	155.69	0.999

[a] Obtained from eq 1. [b] Correlation coefficient for at least 15 experimental points.

Scheme I



For the imines derived from propiophenone (like **2**, with R = Et), the mutarotation observed as neat liquids just after distillation is due mostly, although perhaps not exclusively, to an *E–Z* isomerization.[5,6]

In the present paper we report the observed mutarotation of imines derived from aromatic monocarbonyl compounds and optically active 1-phenylethylamine (**2**, R = Me, *i*-Pr)[7] in CD_3OD solution.

Mutarotation Experiments

The imines **2** (**a**, R = Me; **b**, R = *i*-Pr) show mutarotation when observed polarimetrically in CD_3OD (Table I).

(3) Fonseca, I.; García Blanco, S.; Martínez Carrera, S. *Acta Crystallogr., Sect. B* **1979**, *35*, 2643.
(4) García Ruano, J. L.; Haro, R.; Pascual, C.; Pérez-Ossorio, R.; Plumet, J. *An. Quim.* **1979**, *75*, 165.
(5) Meléndez, E.; Pérez-Ossorio, R.; Sánchez del Olmo, V. *An. Quim.* **1970**, *66*, 87.
(6) García Ruano, J. L.; Pérez-Ossorio, R. *An. Quim.* **1975**, *71*, 93.
(7) The imine **2** (R = Et) has not been studied as yet due to the difficulties associated with *E–Z* isomerism.

0022-3263/84/1949-2624$01.50/0