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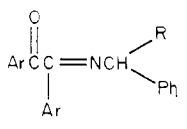
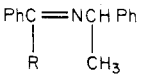
The mutarotation of substituted imines derived from optically active amines was studied for the first time in our laboratories.

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]



1



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

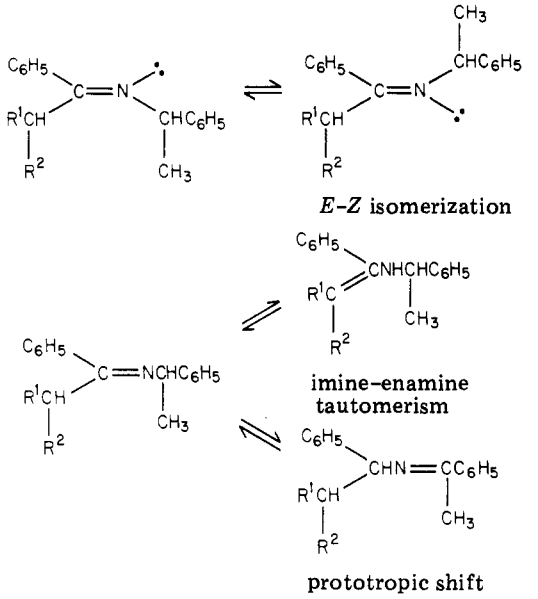
[a] Taken between 2 and 4 min after solution of imine. The solution has been prepared at least 24 h after distillation of imine.

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.

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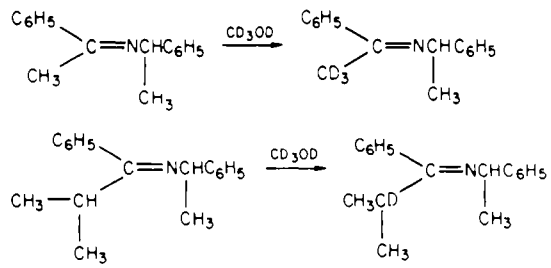
Scheme II



To this mutarotation the kinetic expression for a first-order equilibrium (eq 1)[8] is applied.

$$\ln([\alpha] - [\alpha_e]) = -(k_1 + k_{-1})t + \ln([\alpha_0] - [\alpha_e]) \quad (1)$$

In our case, plotting $\ln([\alpha_0] - [\alpha_e])$ vs. time affords a straight line (Table II) from which the value of the specific rate of approach to equilibrium and the value of $[\alpha_0]$ can be obtained. According to this, the equilibrium is established between only two species.

Three possible origins for mutarotation may now be envisaged: (a) *E–Z* isomerization;[5,9] (b) imine–enamine equilibrium;[10] (c) prototropic shift[11] (Scheme I).

Measurements of ^{1}H NMR and ^{13}C NMR both in CCl_4 and $CDCl_3$ taken along with the mutarotation experiments showed no apparent structural change of the imines. Any modifications in the *E–Z* equilibrium position will be accompanied by modification of the signals due to both isomers.[12] In CCl_4, the imine **2a** gives an *E/Z* ratio of ~95:5, and **2b** an *E/Z* ratio of ~5:95, both being unmodified with time.

With respect to possibility b, it is well-known that for primary and secondary enamines the equilibrium is considerably shifted in favor of the imine.[10] Nevertheless, the presence of the enamine has been established mainly by spectroscopic[13-16] and chemical[17,18] techniques. In our imines no ^{1}H NMR, ^{13}C NMR, or IR signals assignable to the enamine tautomer were observed either in $CDCl_3$ or in CCl_4.

Prototropic change c is not a spontaneous process in imines and requires base catalysis. Moreover, prototropy catalyzed by MeO^- or EtO^- has not been observed in the imines PhCR : NCHRPh (R = Met, Et, *i*-Pr, *t*-Bu)[19] although the imine derived from *p*-methoxyacetophenone and 1-phenylethylamine does exhibit prototropic shift if *t*-BuO^- is used as catalyst.[20] Similar results have been reported for related systems.[21,22]

However, the estimated error for ^{1}H NMR determination is ±5%. Thus, undetectable modification of the equilibrium position by ^{1}H NMR can be detectable as mutarotation; this could be true for either *E–Z* or for imine–enamine equilibrium. On these lines the narrow-range mutarotation observed for **2b** could be accounted for, but extension to **2a**, where a much wider mutarotation has been observed, is difficult to accept.

As an extension of these arguments imines obtained from 1-phenylethylamine and either pivalophenone or aromatic aldehydes were tested in the polarimeter. These imines cannot undergo imine–enamine tautomerism and they show no mutarotation.

Then ^{1}H NMR spectra in CD_3OD of **2a** and **2b** were recorded. Deuteration was detected by the disappearance of the signal for the methyl (**2a**) or isopropyl H group (**2b**) (Scheme II). This means that both imines are equilibrating species with the enamine tautomer (and perhaps also between imine geometrical isomers[24]). Possibility c can now be definitively ruled out since the proton of the amine moiety did not undergo deuteration.

Deuteration precluded the direct detection of the enamine tautomer by ^{1}H NMR. But additional and valuable information has been obtained from the ^{13}C NMR spectra of **2a** and **2b** in CD_3OD. Although in $CDCl_3$ the ^{13}C NMR spectrum of **2a** is that expected for the imine,[25] in CD_3OD imine signals are very slight and the recorded spectrum is practically that expected for the enamine. However, for **2b** the imine spectrum was found both in $CDCl_3$ and in CD_3OD.

To proceed to kinetic determinations we suppose that both for **2a** and **2b** only one species is present at the outset. This allows us to deduce the specific rate for the direct process k_1.[26] On the other hand, the steady-state approach for the deuteration[27,28] allows us also to calculate the value of k_1. These values are $k_1(\text{mut})(CD_3OD) = 4.47 \times 10^{-4}$ s^{-1} at 25 °C and $k_1(\text{deut})(CD_3OD) = 4.78 \times 10^{-4}$ s^{-1} at 28 ± 3 °C for **2a**, and $k_1(\text{mut})(CD_3OD) = 8.00 \times 10^{-6}$ s^{-1} at 30 °C and $k_1(\text{deut})(CD_3OD) = 7.95 \times 10^{-6}$ s^{-1} at 28 ± 3 °C for **2b**. As deduced from Table II, $K_{eq} = k_1/k_{-1}$ is very high for **2a**, in agreement with the observation of the signals of the enamine tautomer in the ^{13}C NMR spectrum. The opposite is true for **2b**, with a low value of K_{eq}.

These results confirm that the origin of mutarotation is an imine–enamine tautomerism.

Experimental Section

Imines **2a** and **2b** were prepared by standard procedures.[5] The amine and the carbonyl compound were refluxed in xylene for

(8) Meyer, J. *Z. Phys. Chem.* **1908**, *62*, 68. See also: Huisgen, R. In "Ausführung Kinetischer Versuche", Houben-Weyl Ed. 111/1; 1955; p 135.
(9) Reviews: Mc Carthy, G. In "The Chemistry of the carbon-nitrogen double bond"; Patai, S., Ed.; Wiley Interscience: London, 1970; p 363. Lehn, M. *Forschr. Chem. Forsch.* **1970**, *15*, 311. Kalinowsky, O.; Kessler, H. *Top. Stereochem.* **1973**, *7*, 295.
(10) Reviews: Gilbert Cook, A., Ed. "Enamines: Synthesis, Structure and Reactivity"; Marcel Dekker: New York, 1969. Hickmott, P. W. *Tetrahedron* **1982**, *38*(23), 3363, 3410–3416.
(11) Review: Layer, R. W. *Chem. Rev.* **1963**, *63*, 489.
(12) The assignment of configuration for this imine is based on the widely substantiated fact that the protons of the *N*-alkyl group are shifted to higher field in the *Z* isomer. See ref 5 and: Abramovitch, R. A.; Kyba, E. P. *J. Am. Chem. Soc.* **1974**, *96*, 480. Wurmb-Gerlich, D.; Vögtle, F.; Mannschrenck, A.; Staab, H. A. *Liebigs Ann. Chem.* **1967**, *708*, 35.
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(21) Richer, J.; Perelman, D. *Can. J. Chem.* **1970**, *48*, 570.
(22) Smith, P. A. S.; Van Dang, Ch. *J. Org. Chem.* **1976**, *41*, 2013 and references therein.
(23) There is considerable experimental evidence showing that imines derived from aromatic aldehydes exist as unique isomers at room temperature. See, for example: (a) Pérez-Ossorio, R.; Sánchez del Olmo, V. *Tetrahedron Lett.* **1961**, 737. (b) Al-Tai, A. S.; Hall, D. M.; Mears, A. R. *J. Chem. Soc., Perkin Trans. 2* **1976**, 133. Imine derived from benzaldehyde and (-)-1-phenylethylamine show $[\alpha] = 35.84$. Imine derived from pivalophenone and the same amine have $[\alpha] = 104.7$. Both values do not change with time.
(24) Jennings and Boyd have proposed that the interconversion of ketimines proceeds through the enamine tautomer. See: Jennings, W. B.; Boyd, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7187.
(25) Garcia-Ruano, J. L.; Pascual, C.; Pérez-Ossorio, R. *Afinidad* **1978**, *31*, 200.
(26) For a similar treatment of the mutarotation of monoimines of 1,2-dicarbonyl compounds, see: (a) García-Ruano, J. L.; Henao, M.; Molina, D.; Pérez-Ossorio, R.; Plumet, J. *Tetrahedron Lett.* **1979**, 3123. (b) García-Ruano, J. L.; Henao, M.; Molina, D.; Pérez-Ossorio, R.; Plumet, J. *An. Quim.* **1980**, *76C*, 260.
(27) Laidler, K. J. "Reaction Kinetics"; Pergamon Press: New York, 1970; Vol. 2.
(28) A similar treatment of an enolization process can be seen in Werstink, M. H.; Taifeller, R.; Banerjee, S. *Can. J. Chem.* **1978**, *56*, 1140.

18 (**2a**) and 50 (**2b**) h in the presence of a catalytic amount of the complex $ZnCl_2$–1-phenylethylamine by using a Dean–Stark device for water separation.

***N*-(1-Phenylethyl)-1-phenylethanimine (2a)**: bp 123 °C (1.0 mm); yield, 85%; IR ν_{max} (neat) 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (d, J = 7 Hz, CH_3CH), 2.10 (s, $CH_3C{=}N$); 4.80 (q, J = 7 Hz, $CHCH_3$); 7.30 (m, Ar); ^{13}C NMR ($CDCl_3$) δ 162.79 (C=N), 59.14 (CHMePh), 24.83 (*Me*CHPh), 15.10 (*Me*C=N); ^{13}C NMR (CD_3OD) δ 145.60 ($C{=}CD_2$), 60.60 ($CD_2{=}C$), 59.69 (CHMePh), 24.05 (CH_3CHPh).

***N*-(1-Phenylethyl)-1-phenyl-2-methylpropanimine (2b)**: bp 121 °C 0.4 mm); yield, 52%; IR ν_{max} (neat) 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (d, J = Mz, CH_3CH), 1.15 (d, J = 7 Hz, CH_3CHCH_3), 1.20 (d, J = 7 Hz, CH_3CHCH_3), 2.70 (septet, J = 7 Hz, CH_3CHCH_3), 4.20 (q, J = 7 Hz, CHN), 7.15 (m, Ar); ^{13}C NMR ($CDCl_3$) δ 174.06 (C=N), 60.22 CHMePh), 39.09 (CHC=N), 25.04 (*Me*CHPh), 20.13 (CH_3CHCH_3); ^{13}C NMR (CD_3OD) δ 177.41 (C=N); 61.17 (CHMePh), 39.93 (CHC=N), 24.28 (*Me*CHPh), 20.41 (CH_3CHCH_3).

Mutarotation Experiments. A Perkin-Elmer 141 polarimeter was used. The temperature was maintained constant to ±5 °C. Imine concentration was chosen to make the range of rotations as large as possible.

NMR Measurements. ^1H NMR. A Varian T-60 spectrometer was used. The temperature was maintained within ±3 °C. The disappearance of the signal due to the methyl group was measured by double integration on the spectrum conveniently enlarged.

^{13}C NMR. A Varian FT-80 spectrometer was used. The CD_3OD spectra were recorded at least 24 h after solution of the imine.

Registry No. **2** (R = Me), 25102-87-8; **2** (R = *i*-Pr), 29412-61-1.

Hydrogenation of Nitro Compounds with an Anthranilic Acid Polymer-Bound Catalyst

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Heterogeneous catalysts capable of hydrogenating nitroaromatics are commonplace. In contrast to this, relatively few homogeneous catalysts demonstrate activity with nitro compounds. Among the more successful soluble catalysts are $RuCl_2(PPh_3)_3$[1] and $Co(CN)_5^{3-}$[2] and $RhCl_2(BH_4)(DMF)(py)_2$.[3] An interface area between use of classical heterogeneous catalysts and homogeneous catalysts, involving the use of polymer-bound catalysts, has seen even fewer applications with respect to the hydrogenation of nitro groups. Besides our own reports of nitrobenzene hydrogenation using rhodium[4] or palladium[5] derivatives of anthranilic acid on polystyrene, there seems to be only the report by Jiang and associates.[6] They used a silica-supported polyacrylonitrile complex of palladium.

Here we report more fully the reactions of our palladium derivative of anthranilic acid on polystyrene. We have investigated the hydrogenation of a variety of nitro compounds and have examined steric and electronic effects.

Results and Discussion

Catalyst preparation for this study is as reported previously.[7] Highly cross-linked polystyrene beads (Rohm and Haas XAD-4) were chloromethylated, the pendant anthranilic acid ligand was attached via substitution, and the ligand beads were treated with palladium chloride (Scheme I).

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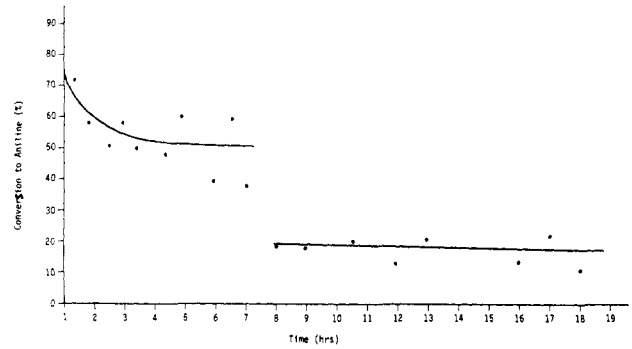
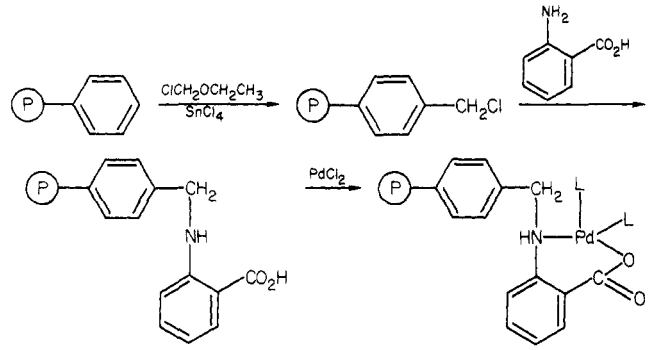


Figure 1. Conversion of nitrobenzene to aniline with a flow reactor.

Scheme I



Hydrogenation was performed normally at 400–1500 psi and 60–90 °C, though this was a matter of convenience. Nitrobenzene was observed to hydrogenate at room temperature and 60 psi [Table I]. Solvents are not required for liquid aromatic nitrocompounds. The solvents ethanol, ethyl acetate, and glacial acetic acid all result in high amine yields.

In Table I the results of our investigation are summarized. For *p*-chloronitrobenzene it is necessary to perform the reaction at low temperature or the halide is stripped from the ring. The catalyst is not effective for selectively reducing one nitro group in *m*-dinitrobenzene. Other atoms that could coordinate with palladium, as in *p*-nitrophenol and 5-nitroquinoline, do not interfere with the reaction.

The catalyst displays remarkable stability. Nitrobenzene, 20 g (161 mmol) was hydrogenated for 3 h at 100 °C and 500 psi without a solvent, employing 1.00 mmol of catalyst. GC analysis showed the conversion of nitrobenzene to aniline was 76% complete under these conditions. No other products were in evidence. This level of activity represents an average of 40 mol of aniline/mol of Pd/h. The catalyst from this batch run was thoroughly washed with acetone and returned to the reactor and recycled with fresh nitrobenzene; there was a modest drop in activity. After five recycles the activity of the beads had leveled off at 50% of the original activity. The six runs represented a total of 440 mol of aniline/mol of Pd.

The same general performance curve was obtained when a tube reactor was employed. Feeding nitrobenzene at 210 °C under 100 psi of hydrogen, WHSV = 14.3, initially gave

(1) (a) Knifton, J. F., *Tetrahedron Lett.* **1975**, 2163; (b) *J. Org. Chem.* **1975**, 40, 519; (c) **1976**, *41*, 1200.
(2) Murabami, M.; Kawai, R.; Suzuhi, K. *J. Chem. Soc. Jpn.* **1963**, *84*, 669.
(3) Jardine, I.; McQuillin, F. J. *J. Chem. Soc. D* **1970**, 626.
(4) Holy, N. L. *J. Org. Chem.* **1979**, *44*, 239.
(5) Holy, N. L. *J. Chem. Soc.; Chem. Commun.* **1978**, 1074.
(6) Li, Y. J.; Jiang, Y. Y.; *J. Catalysis* **1981**, *2*, 42.
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0022-3263/84/1949-2626$01.50/0