Formal Transfers of Hydride from Carbon–Hydrogen Bonds. Thermolysis of 2,3-Dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole

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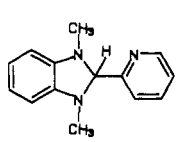
In 2,3-dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (**3**), the acidic hydrogen of a phenolic oxygen–hydrogen bond is near a carbon–hydrogen bond activated as a donor of hydride by two adjacent lone pairs in a dihydro aromatic ring. This juxtaposition does not promote the formation of molecular hydrogen. Instead, thermolysis of compound **3** appears to lead to tautomerization of the hydroxyphenyl group and heterolysis of the carbon–carbon bond to the dihydrobenzimidazole ring. These steps may then trigger intermolecular hydride and proton transfers that yield approximately equimolar amounts of the following three final products: phenol, 2,3-dihydro-1,3-dimethyl-1*H*-benzimidazole (**7**), and the inner salt **4** of 2-(2-hydroxyphenyl)-1,3-dimethylbenzimidazolium.

2,3-Dihydro-1,3-dimethyl-2-(2-pyridinyl)-1*H*-benzimidazole (**1**)[2] and the analogous dihydro-8-quinolinylbenzimidazole **2**[3] contain carbon–hydrogen bonds activated as formal donors of hydride by two adjacent lone pairs in a dihydro aromatic ring. In addition, the nitrogen atoms of the pyridine and quinoline rings can serve as receptor sites for electrophilic substrates. We hoped that the proximity of the activated carbon–hydrogen bonds and the receptor sites would allow compounds **1** and **2** to bind protons and reduce them to molecular hydrogen by an internal transfer of hydride. Unfortunately, this novel



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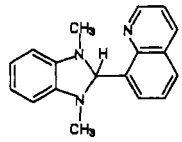

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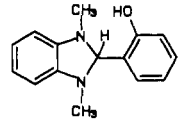

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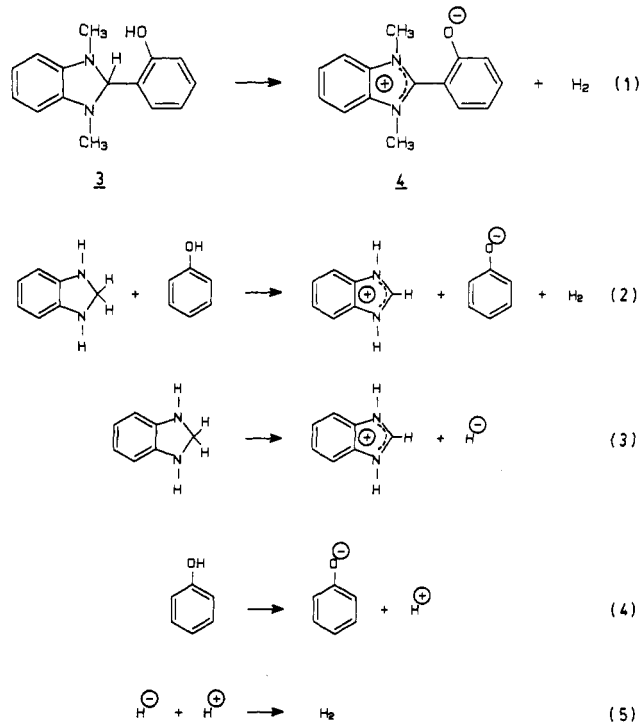
reaction does not take place, largely because it is endothermic, because salts **1**-H$^+$ and **2**-H$^+$ prefer conformations in which the hydridic carbon–hydrogen and acidic nitrogen–hydrogen bonds are not juxtaposed, and because appropriate trajectories for intramolecular protonation of the activated carbon–hydrogen bonds may be difficult to achieve. As a result, other reactions of salts **1**-H$^+$ and **2**-H$^+$ are faster, particularly those involving the pyridinium rings. We therefore decided to study the reactions of 2,3-dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (**3**),[4] a compound that incorporates some of the desirable features of dihydrobenzimidazoles **1** and **2** but does not contain the troublesome pyridine ring.

We hoped that juxtaposition of the acidic hydrogen of the phenolic oxygen–hydrogen bond of compound **3** and the potentially hydridic hydrogen of the activated carbon–hydrogen bond would promote the formation of molecular hydrogen and the inner salt **4** of 2-(2-hydroxyphenyl)-1,3-dimethylbenzimidazolium (eq 1). Significant charge separation should make this process distinctly endothermic in the gas phase. We estimated ΔH_{298} by breaking a similar reaction (eq 2) into the three hypothetical steps of hydride generation (eq 3), proton generation (eq 4), and recombination (eq 5). The hydride affinity of benzimidazolium is approximately 200 kcal/mol,[2] the gas-phase proton affinity of phenoxide is 346 kcal/mol,[5] and combination of hydride and a proton liberates 400 kcal/mol,[5] so the overall reaction of eq 2 is endothermic by 146 kcal/mol in the gas phase. This imposes an enormous thermodynamic obstacle, but we expected the reaction of eq 1 to be aided significantly by the effects of solvation in condensed phases and by the internal charge compensation in inner salt **4**.



(1)

(2)

(3)

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Dihydrobenzimidazole **3** was easily prepared in 86% yield by the condensation[4] of salicylaldehyde with *N,N'*-dimethyl-1,2-benzenediamine.[6] Compound **3** is known to adopt the internally hydrogen-bonded structure **3a** in the solid state.[7] The five-membered ring has the expected envelope shape,[2] both nitrogen atoms have a distinctly

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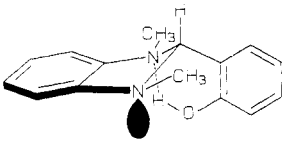
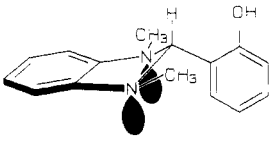


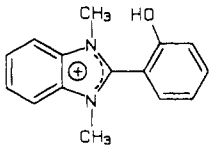
3a



3b

pyramidal hybridization, the *N*-methyl and hydroxyphenyl groups are all equatorial, and the dihedral angle defined by the average planes of the hydroxyphenyl and dihydrobenzimidazole rings is 77°. Several observations indicated that a similar structure is favored in solution. For example, the presence of Bohlmann bands[8] at 2770 and 2690 cm^{-1} in the infrared spectrum of compound **3** (CH_2Cl_2) confirms that at least one lone pair is antiperiplanar to the activated carbon–hydrogen bond at C_2 of the dihydrobenzimidazole ring. The broad phenolic OH band at about 3200 cm^{-1} does not vary when the concentration is changed from 0.9 to 0.09 M (CH_2Cl_2), providing evidence for the presence of an internal hydrogen bond. Furthermore, the signal for the phenolic hydrogen in the ^1H NMR spectrum of compound **3** (δ 9.1, 0.9 M in $CDCl_3$) is much farther downfield than that of phenol itself under similar conditions (δ 4.20), and its position is not changed significantly by tenfold dilution.[9]

The favorable orientation of the lone pairs in dihydrobenzimidazole **3** should therefore make the adjacent carbon–hydrogen bond a good formal donor of hydride.[10] As expected, compound **3** was readily oxidized by iodine in the presence of ammonia to give 2-(2-hydroxyphenyl)-1,3-dimethylbenzimidazolium iodide (**5**)[4] in 97% yield.



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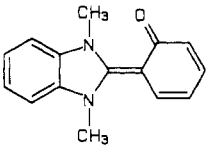

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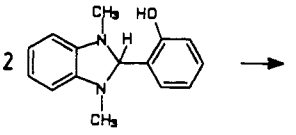
Deprotonation with methanolic potassium hydroxide produced inner salt **4** in 90% yield, and treatment of inner salt **4** with an equimolar amount of hydrogen iodide regenerated phenol **5**. The close similarity of the *N*-methyl signals in the ^1H NMR spectra of salts **4** and **5** suggests that hybrid **6** makes little contribution to the structure of salt **4**, perhaps in part because coplanarity of the dimethylbenzimidazolium and phenyl rings is sterically difficult to achieve.

The substantial thermodynamic barrier that opposes loss of molecular hydrogen from dihydrobenzimidazole **3** (eq 1) is augmented by kinetic problems, since the preferred hydrogen-bonded structure **3a** does not place the hydridic carbon–hydrogen bond and acidic oxygen–hydrogen bond in close proximity. No alternative reaction seemed likely, however, so we expected heating to break the internal hydrogen bond and make structure **3b** accessible, and we hoped that this structure would be stereoelectronically inclined to produce hydrogen by intramolecular protonation of the activated carbon–hydrogen bond.

In fact, compound **3** decomposes when neat samples or solutions in CH_3CN are heated, and inner salt **4** is a major product. Unfortunately, however, no hydrogen could be detected.[11] Instead, thermolysis produces an approximately 1:1:1 mixture of inner salt **4**, 2,3-dihydro-1,3-dimethyl-1*H*-benzimidazole (**7**),[12] and phenol (eq 6). For



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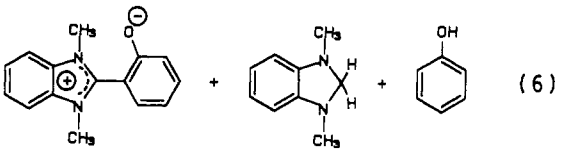

4 7 (6)

example, when neat dihydrobenzimidazole **3** was heated in vacuo at 165 °C for 6 h, compounds **4**, **7**, and phenol could be isolated in 62%, 64%, and 78% yields, respectively.

We propose that these products arise from the unanticipated reactions summarized in Scheme I. Tautomerization of the hydroxyphenyl group of dihydrobenzimidazole **3**, followed by heterolysis of the carbon–carbon bond to the dihydrobenzimidazole ring, would produce the phenoxide salt of 1,3-dimethylbenzimidazolium (eq 7). This hypothetical reaction is reasonable since it resembles the known thermal decarboxylation of salicyclic acid.[13] It is effectively irreversible, since an independently prepared mixture of 1,3-dimethylbenzimidazolium iodide[14] and lithium phenoxide in CD_3CN did not regenerate detectable amounts of dihydrobenzimidazole **3** or any other covalent adduct. Transfer of hydride from dihydrobenzimidazole **3** to 1,3-dimethylbenzimidazolium would then yield the observed dihydrobenzimidazole **7** (eq 8). This process, presumably nearly thermoneutral, may be driven to completion by the final step (eq 9), in which phenoxide exothermically deprotonates the cationic and more acidic phenol **5**. This proton transfer yields the other two observed products, inner salt **4** and phenol. As expected, an independently prepared mixture of dihydrobenzimidazole **3** and 1,3-dimethylbenzimidazolium phenoxide in CD_3CN was slowly converted at 25 °C into the three observed products. The reactions of eq 8 and 9 therefore appear to be faster than the initial tautomerization and heterolysis of eq 7.

The failure of dihydrobenzimidazole **3** to produce molecular hydrogen is disappointing but instructive. It underscores the significant thermodynamic and kinetic ob-

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(11) No hydrogen could be trapped by our standard procedure[2] in which effluent gases are passed into a mixture of *trans*-stilbene and palladium on charcoal.

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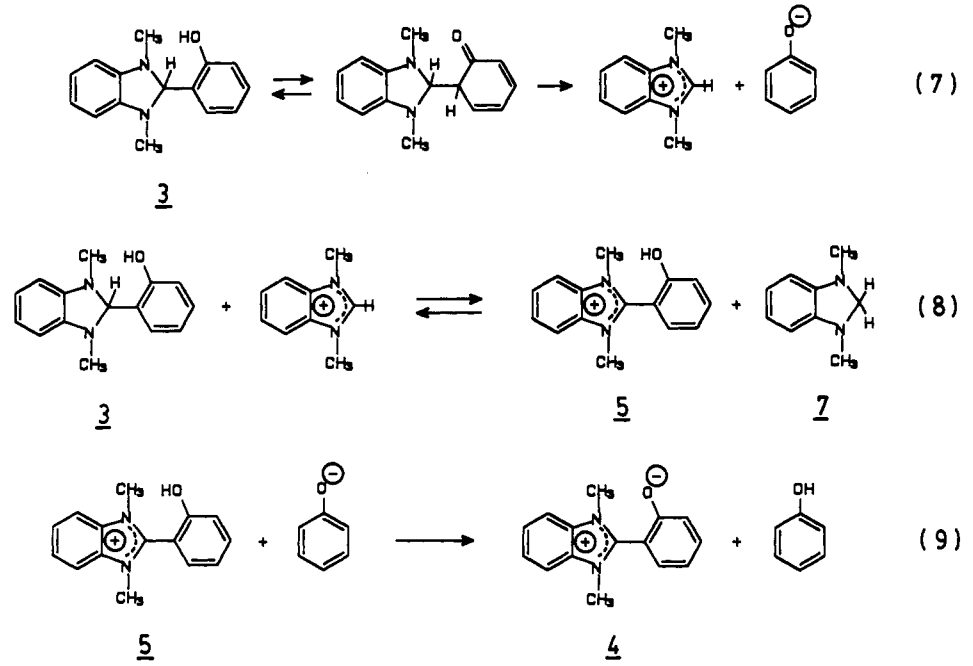
Scheme I



stacles that oppose the liberation of hydrogen from apparently well-designed molecules like dihydrobenzimidazoles 1-H$^+$, 2-H$^+$, and 3. Future efforts to design molecules that can bind a proton and reduce it to molecular hydrogen can now be guided by the following principles: the molecule formed by loss of hydrogen should have a hydride affinity at least as low as 200 kcal/mol; the proton affinity of the receptor should be as low as possible, preferably not above 200 kcal/mol; and the molecule should be extremely robust, so that no undesirable thermal reactions can take place before hydrogen is evolved.

Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 783 spectrometer. A Bruker WH-400 spectrometer was used to obtain ^{1}H nuclear magnetic resonance (NMR) spectra. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane (δ). Low-resolution mass spectra were recorded on a V.G. Micromass 12-12 quadrupole spectrometer using chemical ionization (CI) mass spectrometry or on a Kratos MS-50 TA spectrometer using fast atom bombardment (FAB) mass spectrometry. High-resolution mass spectra were recorded on a Kratos MS-50 TA spectrometer using electron impact (EI) mass spectrometry at 70 eV. Galbraith Laboratories, Knoxville, TN, performed all elemental analyses. Melting points were recorded on a Thomas-Hoover capillary apparatus and are not corrected. Solvents were deoxygenated when necessary by sparging with dry argon.

2,3-Dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (3).[4] A solution of *N,N'*-dimethyl-1,2-benzenediamine[6] (4.25 g, 31.2 mmol), salicylaldehyde (4.26 g, 34.9 mmol), and (±)-10-camphorsulfonic acid (20 mg) in benzene (20 mL) was heated at reflux for 4 h under N_2 in an apparatus fitted with a Dean–Stark trap containing 4-Å molecular sieves. The mixture was then extracted with cold, deoxygenated 10% aqueous NaOH, and the organic phase was washed with brine, dried, and decolorized. Solvent was removed by evaporation under reduced pressure. Recrystallization of the residue from benzene yielded large yellow rhombs of 2,3-dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (3; 6.47 g, 26.9 mmol, 86.2%). Sublimation at 120–140 °C (0.02 Torr) provided an analytically pure sample: mp 150–152 °C (lit.[4] mp 150 °C); IR (KBr) 3055, 2950, 2900 (br), 2870, 2800, 2770, 2690, 1595, 1490 (br), 1360, 1280, 1250, 1115, 1100, 1015, 875, 765 (br), 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (s, 6 H), 4.70 (s, 1 H), 6.60 (m, 2 H), 6.83 (m, 2 H), 6.89 (td, $J_{34} = J_{45} = 7.4$ Hz, $J_{46} = 1.0$ Hz, H_4), 6.94 (d, $J_{56} = 8.2$ Hz, H_6), 7.08 (dd, $J_{34} = 7.4$ Hz, $J_{35} = 1.4$ Hz, H_3), 7.32 (td, H_5), 9.1 (br s, 1 H); mass spectrum (CI, isobutane), *m/e* 241, 240, 225, 147. Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.79; H, 6.74; N, 11.45.

2-(2-Hydroxyphenyl)-1,3-dimethylbenzimidazolium Iodide (5).[4] A stirred suspension of 2,3-dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (3; 233 mg, 0.970 mmol) in methanol (15 mL) containing concentrated aqueous ammonia (70 μL, 15 M, 1.0 mmol) was treated dropwise at 25 °C with a solution of iodine (248 mg, 0.977 mmol) in methanol (15 mL). The resulting mixture was kept at 25 °C for 12 h. Volatiles were then removed by evaporation under reduced pressure, and the residual solid was washed with chloroform. Crystallization of the insoluble portion from water (10 mL) gave off-white needles of 2-(2-hydroxyphenyl)-1,3-dimethylbenzimidazolium iodide (5; 346 mg, 0.945 mmol, 97.4%). Three additional recrystallizations from water provided an analytically pure sample: mp 267–269 °C dec (lit.[4] mp 265 °C); IR (KBr) 3110 (br), 1615, 1525, 1520, 1490, 1475, 1455, 1340, 1305, 1265, 755, 745 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ 3.95 (s, 6 H), 7.18 (dd, H_6), 7.20 (ddd, H_4), 7.65 (dd, H_3), 7.68 (ddd, H_5), 7.75 (m, 2 H), 8.00 (m, 2 H); mass spectrum (FAB, glycerol), *m/e* 239, 148, 134. Anal. Calcd for $C_{15}H_{15}IN_2O$: C, 49.20; H, 4.13; N, 7.65. Found: C, 48.93; H, 4.25; N, 7.54.

Inner Salt 4 of 2-(2-Hydroxyphenyl)-1,3-dimethylbenzimidazolium. A solution of 2-(2-hydroxyphenyl)-1,3-dimethylbenzimidazolium iodide (5; 636 mg, 1.74 mmol) in methanol (25 mL) was treated with methanolic KOH (25 mL, 0.093 N, 2.3 mequiv), and the mixture was stirred at 25 °C for 12 h. Volatiles were then removed by evaporation under reduced pressure, and the residue was extracted with dichloromethane. Removal of solvent from the filtered extracts by evaporation in vacuo left a spectroscopically pure residue of the inner salt 4 of 2-(2-hydroxyphenyl)-1,3-dimethylbenzimidazolium as a yellow solid (373 mg, 1.57 mmol, 90.2%). Sublimation at 155–160 °C (0.02 Torr) gave an analytically pure sample: mp 245–247 °C; IR (KBr) 1605, 1535, 1520, 1510, 1490, 1485, 1480, 1270, 770, 760, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 6 H), 6.33 (t, $J_{34} = 7.8$ Hz, $J_{45} = 7.0$ Hz, H_4), 6.83 (d, $J_{56} = 8.7$ Hz, H_6), 6.97 (dd, $J_{34} = 7.8$ Hz, $J_{35} = 1.9$ Hz, H_3), 7.29 (ddd, $J_{35} = 1.9$ Hz, $J_{45} = 7.0$ Hz, $J_{56} = 8.7$ Hz, H_5), 7.57 (m, 4 H); mass spectrum (CI, isobutane), *m/e* 239, 238; high-resolution mass spectrum (EI), calcd for $C_{15}H_{14}N_2O$, 238.1106, found, 238.1090.

Pyrolysis of 2,3-Dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (3). 2,3-Dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (3; 254 mg, 1.06 mmol) was sealed in vacuo (0.03 Torr) in a bent Pyrex tube. The end of the tube holding the solid was submerged in an oil bath and heated at 165 °C for 6.5 h. The tube was then opened under N_2

and the upper part was washed out with ether. The ether washings were extracted with deoxygenated aqueous KOH (1 N) and dried. Removal of solvent from the ether phase by evaporation under reduced pressure left a residue of 2,3-dihydro-1,3-dimethyl-1*H*-benzimidazole (**7**; 50.1 mg, 0.338 mmol, 63.8%), which was identical by IR and NMR with an authentic sample.[12b] Solvent was removed from the basic aqueous extracts by evaporation in vacuo, and the residue was redissolved in water (0.1 mL). The solution was then acidified, saturated with NaCl, and extracted with ether. Careful removal of solvent from the dried ether extracts by evaporation under reduced pressure left a residue of pure phenol (39.1 mg, 0.415 mmol, 78.3%), which was identified by its ^{1}H NMR spectrum.

The conditions of the pyrolysis were modified slightly to simplify isolation of the inner salt **4** of 2-(2-hydroxyphenyl)-1,3-dimethylbenzimidazolium. 2,3-Dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (**3**; 93.7 mg, 0.390 mmol) was heated at 165 °C for 5 h in vacuo (0.01 Torr) in an open tube. Under these conditions, phenol and 2,3-dihydro-1,3-dimethyl-1*H*-benzimidazole (**7**) distilled from the tube. Sublimation of the residue at 150 °C (0.015 Torr) removed a small amount of unreacted starting material. Further sublimation at 150–190 °C (0.007 Torr) then yielded the inner salt **4** of 2-(2-hydroxyphenyl)-1,3-dimethylbenzimidazolium (28.9 mg, 0.121 mmol, 62.1%), which was identified by its IR and ^{1}H NMR spectra.

Control Reaction of 2,3-Dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (3) with 1,3-Dimethylbenzimidazolium Phenoxide. A mixture of 2,3-dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (**3**; 9.4 mg, 0.039 mmol), 1,3-dimethylbenzimidazolium iodide[14] (11 mg, 0.040 mmol), and lithium phenoxide (3.7 mg, 0.037 mmol) was treated with CD_3CN (1.5 ml), and lithium iodide was removed by filtration. After 28 h at 25 °C, the inner salt **4** of 2-(2-hydroxyphenyl)-1,3-dimethylbenzimidazolium and 2,3-dihydro-1,3-dimethyl-1*H*-benzimidazole (**7**) could be detected in the filtrate by ^{1}H NMR spectroscopy.

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Registry No. **3**, 3652-93-5; **4**, 113036-44-5; **7**, 3204-31-7; PhOH, 108-95-2.

1,2-Dioxetanes Derived from 4,5-Dimethyl-2,3-dihydrofuran and 4,5-Dimethyl-2,3-dihydrothiophene: Synthesis via Photooxygenation, Activation Parameters, and Excitation Properties

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Photooxygenation of 4,5-dimethyl-2,3-dihydrofuran (**1a**) and 4,5-dimethyl-2,3-dihydrothiophene (**1b**) in a variety of solvents gave the respective 1,2-dioxetanes **2a,b** ([2 + 2] cycloaddition) as major products (82–90%) and the allylic hydroperoxides **3a,b** and **4a,b** (ene reaction) as minor products (10–18%). The 2,3-dihydrofuran-derived dioxetane **2a** shows higher thermal stability ($\Delta G^{\ddagger}$ = 28.1 ± 1.0 kcal/mol at 343 K) compared to other known alkoxy-substituted dioxetanes; but more remarkable is the 2,3-dihydrothiophene derivative **2b** ($\Delta G^{\ddagger}$ = 22.7 ± 1.2 kcal/mol at 343 K), the most stable sulfur-substituted dioxetane to date, isolable by molecular distillation. Concerning their excitation properties, both dioxetanes afford preferentially triplet excited state products during thermal decomposition, e.g. Φ^T = 3.2 ± 0.5% for **2a** and $\Phi^T \sim$ 0.002% for **2b**, the latter being the first triplet excitation yield (Φ^T) for a sulfur-substituted dioxetane. Mechanistic rationales for the 1000-fold lower efficiency of generating excited states for the 2,3-dihydrothiophene dioxetane **2b** are presented.

Introduction

Numerous examples of 1,2-dioxetanes bearing heteroatom substituents directly at the four-membered ring have been isolated and characterized.[1] Whereas oxygen-substituted dioxetanes are moderately stable and can be handled at ambient temperatures,[2] only a few sulfur-substituted examples have been described.[3] The synthesis of these labile derivatives utilized photooxygenation of the corresponding thio enol ethers, instead of the Kòpecky route[4] (cyclization of β-bromo hydroperoxides). Since these substrates do not possess allylic hydrogens, competing ene reaction[5] with singlet oxygen presented no problems. Normally, for substrates with allylic hydrogens the ene reaction becomes a serious side reaction and in many cases the dominant pathway. For example, for simple enol ethers such as (*E*)- and (*Z*)-2-methoxy-2-butene, ene reaction takes place exclusively.[6] Increasing solvent polarity

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