

NCH(Ph)CO), 3.90 and 3.20 (dd,  $J = 12$  Hz, 4 H, Ar CH<sub>2</sub>N),  $[\alpha]^{20}_D$   $\lambda$  ( $c$  1.3, DMF) +223.1° (589), +232.3° (578), +258.7° (546), +330.9° (436); MS,  $m/e$  428 (M<sup>+</sup>). Anal. Calcd for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O: C, 84.08; H, 5.65; N, 6.54. Found: C, 83.86; H, 5.57; N, 6.54.

The mother liquor was concentrated on a hot plate to ca. 300 cm<sup>3</sup> and left at room temperature. The obtained crystals [4.44 g; 74%;  $[\alpha]^{20}_{546} -368^\circ$  ( $c$  1.2, DMF); corresponding to ca. 82% (*RR*)-**3B**, 18% (*SR*)-**3A** by <sup>1</sup>H NMR] were recrystallized from ethyl acetate to give 2.76 g (46%) of pure (*RR*)-**3B**: mp 263-266 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>/Me<sub>4</sub>Si)  $\delta$  8.1-7.2 (m, 17 H, Ar H), 4.09 (s, 1 H, NCH(Ph)CO), 3.62 and 3.13 (dd,  $J = 12$  Hz, 4 H, Ar CH<sub>2</sub>N);  $[\alpha]^{20}_D$  ( $c$  1, DMF) -356.1° (589), -372.8° (578), -422.4° (546), -638.5° (436), +190.2° (365). Anal. Calcd for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O: C, 84.08; H, 5.65; N, 6.54. Found: C, 83.79; H, 5.50; N, 6.63.

A similar reaction using optically pure (*S*)-**1**<sup>6</sup> (0.220 g; 0.5 mmol) and (*R*)-**2** (0.16 g; 1.1 mmol) led after crystallization from dichloromethane/ethyl acetate, to (*SR*)-**3A**: 0.146 g (68%); mp 278-280 °C; <sup>1</sup>H NMR (vide supra);  $[\alpha]^{20}_D$  ( $c$  1, DMF) +225.7° (589), +234.7° (578), +261.0° (546), +333.7° (436).

A similar reaction using optically pure (*R*)-**1**<sup>6</sup> (0.220 g; 0.5 mmol) and (*R*)-**2** (0.16 g; 1.1 mmol) led after crystallization to (*RR*)-**3B**: 0.085 g (39%); mp 262-264 °C; <sup>1</sup>H NMR (vide supra);  $[\alpha]^{20}_D$  ( $c$  1, DMF) -353.0° (589), -367.7° (578), -417.0° (546), -626.0° (436).

**$\alpha$ -[2,7-Dihydrodinaphtho[2,1-*c*:1',2'-*e*]azepinyl]- $\alpha$ -phenylacetonitriles (*S,R*)-**4A** and (*RR*)-**4B**.** To 4.44 g (10.4 mmoles) of  $\alpha$ -amino amide (*SR*)-**3A** in 100 cm<sup>3</sup> of DMF at 0 °C was added drop by drop a large excess of POCl<sub>3</sub> (10 cm<sup>3</sup>) during a period of 1 h. The resulting solution was magnetically stirred at 0 °C and then at room temperature overnight and poured into water (2 L). The resulting precipitate was filtered, washed with water, air-dried, dissolved in 100 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub>, and chromatographed on a column of SiO<sub>2</sub> (Kieselgel 60) made up with CH<sub>2</sub>Cl<sub>2</sub>. Elution with CH<sub>2</sub>Cl<sub>2</sub> led to pure (*SR*)-**4A** as a white crystalline solid: 4.0 g (94%); mp 215-218 °C (not recrystallized); <sup>1</sup>H NMR (CDCl<sub>3</sub>/Me<sub>4</sub>Si)  $\delta$  8.1-7.0 (m, 17 H, Ar H), 4.87 (s, 1 H, NCH(Ph)CN), 3.75 and 3.45 (dd,  $J = 12$  Hz, 4 H, Ar CH<sub>2</sub>N);  $[\alpha]^{23}_D$  ( $c$  1.2, CHCl<sub>3</sub>) +382.0° (589), +399.0° (578), +453.1° (546), +731.1° (436); MS,  $m/e$  410 (M<sup>+</sup>). Anal. Calcd for C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>: C, 87.77; H, 5.40; N, 6.82. Found: C, 86.93; H, 5.25; N, 7.00.

In the same manner, treatment of (*RR*)-**3B** (2.63 g; 6.1 mmol) with POCl<sub>3</sub> led after chromatography to pure (*RR*)-**4B** as a white solid foam: 2.37 g (94%); mp  $\approx$  105-115 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>/Me<sub>4</sub>Si)  $\delta$  8.1-7.0 (m, 17 H, Ar H), 4.70 (s, 1 H, NCH(Ph)C 3.75 and 3.38 (dd,  $J = 12$  Hz, 4 H, Ar CH<sub>2</sub>N);  $[\alpha]^{23}_D$  ( $c$  1.1 CHCl<sub>3</sub>) -217.5° (589), -228° (578), -258.8° (546), -391° (436). Anal. Calcd for C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>: C, 87.77; H, 5.40; N, 6.82. Found: C, 87.55; H, 5.21; N, 6.83.

**2,7-Dihydrodinaphtho[2,1-*c*:1',2'-*e*]azepine (*S*)-**5** and (*R*)-**5**.** To a solution of  $\alpha$ -amino nitrile (*SR*)-**4A** (0.41 g; 1 mmol) in 50 cm<sup>3</sup> of THF was rapidly added 20 cm<sup>3</sup> of aqueous AgNO<sub>3</sub> (0.5 N). The mixture was stirred at room temperature overnight. After addition of CH<sub>2</sub>Cl<sub>2</sub> (50 cm<sup>3</sup>)/Et<sub>2</sub>O (350 cm<sup>3</sup>), the organic phase was separated, washed with water, and dried (MgSO<sub>4</sub>). The solvents were removed on a rotary evaporator, and the residue was dissolved in ether. The ether solution was extracted twice with 20% HCl and the acid phase made basic with an excess of aqueous KOH. Extraction with ether led to pure amine (*S*)-**5** as a pale yellow solid foam: 0.181 g (58%); <sup>1</sup>H NMR (CDCl<sub>3</sub>/Me<sub>4</sub>Si)  $\delta$  8.1-7.0 (m, 12 H, Ar H) 3.77 and 3.42 (dd,  $J = 12$  Hz, 4 H, Ar CH<sub>2</sub>N), 2.40 (s, 1 H, NH);  $[\alpha]^{20}_D$  ( $c$  0.7, CHCl<sub>3</sub>) +574.8° (589), +601.8° (578), +689.3° (546), +1196.7° (436); MS,  $m/e$  295 (M<sup>+</sup>). Anal. Calcd for C<sub>22</sub>H<sub>17</sub>N: C, 89.45; H, 5.80; N, 4.74. Found: C, 89.25; H, 5.97; N, 4.66.

In the same manner, from (*RR*)-**4B** (0.41 g; 1 mmol) was obtained pure (*R*)-**5**: 0.207 g (69%);  $[\alpha]^{23}_D$  ( $c$  1, CHCl<sub>3</sub>) -592.9° (589) -621.5° (578), -714.5° (546), -1242.5° (436). Anal. Calcd for C<sub>22</sub>H<sub>17</sub>N: C, 89.45; H, 5.80; N, 4.74. Found: C, 89.20; H, 5.86; N, 4.79.

**Asymmetric Nucleophilic Acylations.** The following is a representative procedure for nucleophilic addition of the  $\alpha$ -amino nitrile anions to aldehydes: In a flame-dried three-necked round-bottomed flask equipped with septums and kept under an argon atmosphere were introduced by syringe, at 0 °C, 10 cm<sup>3</sup> of THF freshly distilled over sodium benzophenone ketyl, 250  $\mu$ L (1.8 mmol) of diisopropylamine and 1.3 cm<sup>3</sup> of *n*-BuLi (1.38

N) in hexane (1.8 mmol). The mixture was cooled at -78 °C for 0.5 h, and a solution of 0.615 g (1.5 mmol) of amino nitrile (*SR*)-**4A** in 10 cm<sup>3</sup> of THF was slowly added. The purified sample was submitted to <sup>1</sup>H NMR (CDCl<sub>3</sub>); integration of the two methoxy signals) and GC (capillary column SIL S, 10 m), both methods indicating a 50  $\pm$  2% diastereoisomeric excess. The resulting dark red solution was magnetically stirred at -78 °C for 1 h, and a solution of 0.108 g (1.5 mmol) of butyraldehyde in 5 cm<sup>3</sup> of THF was slowly added. The solution was stirred at -78 °C for 3 h, quenched with 20 cm<sup>3</sup> of saturated aqueous NH<sub>4</sub>Cl, and allowed to warm up at room temperature. After addition of dichloromethane, the organic phase was washed with water, dried over MgSO<sub>4</sub>, filtered, and evaporated. A solution of 20 cm<sup>3</sup> of aqueous AgNO<sub>3</sub> (0.5 N) was added to the residue, previously dissolved in 20 cm<sup>3</sup> of THF, and the mixture was stirred at room temperature overnight. After addition of CH<sub>2</sub>Cl<sub>2</sub> (50 cm<sup>3</sup>) and ether (250 cm<sup>3</sup>), the organic phase was washed with water, extracted twice with 100 cm<sup>3</sup> of aqueous 20% HCl, washed with water, dried (MgSO<sub>4</sub>), and evaporated under vacuum to give crude  $\alpha$ -ketol **8** (R = *n*-Pr). The acidic extract was made basic with an excess of aqueous KOH, and extraction with ether led to the amine (*S*)-**5** (0.268 g; 61%). The crude  $\alpha$ -ketol was chromatographed on a preparative TLC plate (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>), giving a pure sample: 0.150 g (56%);  $[\alpha]^{23}_{546}$  ( $c$  2.5; 95% EtOH) +10.4°. According to Mosher's procedure,<sup>10</sup> 0.041 g (0.23 mmol) of pure ketol, 0.120 g (0.5 mmol) of (-)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetic acid chloride, CCl<sub>4</sub> (15 drops), and dry pyridine (15 drops) were introduced in a test tube and left at room temperature for 24 h. Extraction with ether led to a crude sample, which was chromatographed on a preparative TLC plate (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>). Care was taken in order to avoid any fractionation of the diastereoisomeric mixture of esters.

**Registry No.** (*S*)-**1**, 37803-02-4; (*R*)-**1**, 86631-56-3; ( $\pm$ )-**1**, 64091-25-4; (*R*)-**2**, 6485-67-2; (+)-**3A**, 97551-07-0; (-)-**3B**, 97590-56-2; (+)-**4A**, 97551-08-1; (-)-**4B**, 97590-57-3; (*S*)-**5**, 97551-09-2; (*R*)-**5**, 97551-10-5; (*S*)-**6A** (lithium salt), 97551-11-6; (*R*)-**6B** (lithium salt), 97551-12-7; **7** (R = Me), 97551-13-8; **7** (R = Pr), 97551-14-9; **7** (R = Pr-*i*), 97551-15-0; **7** (R = CH<sub>2</sub>Ph), 97551-16-1; (*S*)-**8** (R = Me), 65646-07-3; (*R*)-**8** (R = Me), 65646-06-2; (*R*)-**8** (R = Pr), 97551-17-2; (*S*)-**8** (R = Pr), 97551-18-3; (*R*)-**8** (R = Pr-*i*), 97551-19-4; (*S*)-**8** (R = Pr-*i*), 97551-20-7; (*R*)-**8** (R = CH<sub>2</sub>Ph), 69897-44-5; MeCHO, 75-07-0; PrCHO, 123-72-8; *i*-PrCHO, 78-84-2; PhCH<sub>2</sub>CHO, 122-78-1; (*S*)-*i*-PrCH(OH)CO<sub>2</sub>H, 17407-55-5.

### Stable Simple Enols. 12.<sup>1</sup> Molecular Mechanics Structure and Dipole Moment of (*Z*)-1,2-Dimesityl-2-phenylethenol

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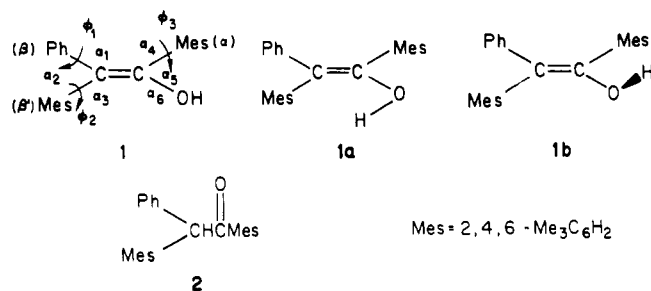
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Several crowded mesityl-substituted diaryl- and triarylethenols exist in the enol form and their isomerization to the carbonyl  $\rightleftharpoons$  enol equilibrium mixture is relatively slow even under acid-catalysis.<sup>1-3</sup> Some noteworthy features of their chemistry are as follows: (i) When the crowding is high the enol form is *more stable* than the corresponding carbonyl<sup>4</sup> form. For example, (*Z*)-1,2-dimesityl-2-phenylethenol<sup>5</sup> (**1**) is more stable by 0.6 kcal mol<sup>-1</sup> in hexane and by 1.1 kcal mol<sup>-1</sup> in PhCl than the corresponding keto form (**2**).<sup>2a</sup> (ii) Both in solution<sup>6</sup> and in the solid state<sup>7</sup> these enols exist in a chiral propeller conformation where all the rings are twisted in the same sense. (iii) In solution the conformation of the OH is syn

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planar (**1a**) in hydrogen-bond-nonaccepting solvents due to OH...( $\beta'$ -Mes) hydrogen bonding, while in hydrogen-bond-accepting solvents it is anti clinal (**1b**) due to OH...solvent hydrogen bonding.<sup>8</sup> (iv) The cation radicals of **1<sup>9a</sup>** and of **2<sup>9b</sup>** were shown to undergo a reciprocal methyl/hydrogen transfer where one  $\alpha$ -o-Me group is the migration origin and the ipso carbon of the  $\beta$ -phenyl ring is the migration terminus.<sup>9</sup>

In order to assess the influence of crowding on the structural details, the crystal structures of **1** and other enols were examined by X-ray diffraction.<sup>7</sup> Unfortunately, crystals of **1** are disordered, the ethylenic portion of ca. a quarter of the molecules being rotated at 90° with respect to the rest. Whereas the structural data for most other enols were reasonably reliable, the greater uncertainty in the crystal data of **1** prompted us to calculate its structure by molecular mechanics.<sup>10,11</sup>

### Results and Discussion

The molecular structure of **1** was calculated by the MMP2 program<sup>12</sup> in which Allinger and Dodziuk's recent parameters<sup>13</sup> are incorporated. In the computational procedure the input atomic coordinates were those determined by X-ray diffraction, assuming tetrahedral positions for the oxygen lone pairs. In the first stage only hydrogens were let relax, while the carbons and oxygen

Table I. Selected Bond Lengths (Å) and Angles (deg) for **1**

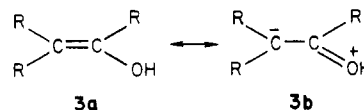
coordinate <sup>a</sup>	calcd	exptl <sup>b</sup>
C(1)-C(2)	1.35	1.26 (1)
C(1)-C(ipso $\alpha$ -Mes)	1.50	1.561 (8)
C(2)-C(ipso $\beta$ -Ph)	1.48	1.508 (8)
C(2)-C(ipso $\beta'$ -Mes)	1.51	1.546 (7)
C(1)-O	1.36	1.454 (9)
O-H	0.97	1.03
$\alpha_1$	126	119.3 (8)
$\alpha_2$	116	126.3 (7)
$\alpha_3$	118	114.4 (8)
$\alpha_4$	121	120 (1)
$\alpha_5$	118	113.2 (7)
$\alpha_6$	121	126.8 (9)
C(2)-C(1)-O-H	-0.4	
$\phi_1$	39	38.3
$\phi_2$	74	74.4
$\phi_3$	67	79.0

<sup>a</sup> For definition of the  $\alpha$ 's and  $\phi$ 's, see structure **1**.

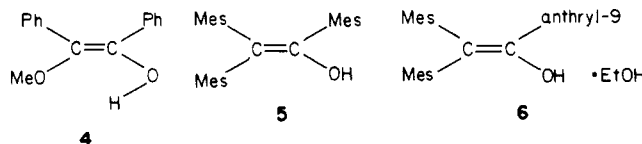
<sup>b</sup> Experimental (input values) are listed in ref 7.

were restricted at their crystallographic positions. Relaxation at this stage lowered the initial energy by ca. 500 kcal mol<sup>-1</sup>. Most of this amount is simply a consequence of inaccuracies in the crystallographic positions of hydrogens, besides reflecting the gearing of molecular-mechanical geometries to electron-diffraction geometries in the vapor.<sup>14,15</sup> In the second stage, the molecule was let relax in all degrees of freedom, resulting in an additional gain of 12 kcal mol<sup>-1</sup>. The calculated conformation has a syn arrangement of the C=C-OH grouping with a torsional angle of 0.4° (Table I).

**Bond Lengths.** One of the more important pieces of data is the enolic C=C bond length. Two factors that would act to elongate this bond in a sterically hindered enol in comparison with a simple alkenic C=C bond are the steric crowding and the contribution of the resonance form **3b**. Data on the C=C bond length of simple enols are



relatively scarce. For vinyl alcohol itself, Saito<sup>16</sup> determined the C=C bond length by microwave spectroscopy as 1.33 Å, whereas several calculations by Radom and co-workers afforded values of 1.312,<sup>17a</sup> 1.339<sup>17b</sup> and 1.314<sup>17c</sup> Å. For enol **4**, McGarrity et al.<sup>18</sup> obtained by X-ray diffraction a C=C bond length of 1.29 (1) Å, but no explanation was given for the shorter C=C bond in comparison with the previously cited data. Our calculated bond length



for **1** is 1.354 Å, longer than the reference value that the VESCF-stage affords (1.342 Å) and much longer than the experimental value of 1.26 Å. The calculated value is in the range of the bond lengths<sup>7</sup> found by X-ray diffraction for enol **5** and for the ethanolate **6**: 1.362 (7) and 1.343

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(10) We meant originally to calculate the structures and energies of both **1** and **2** in order to evaluate  $\Delta H^\circ$  for the enol  $\rightleftharpoons$  ketone equilibrium. Unfortunately, there is no molecular mechanical program that can deal with both aryl ketones and enols. The ketone was therefore calculated by the MMPI (not MMP2) program (using as input the crystallographic parameters) so that comparison of results for **1** and **2** cannot serve to estimate their relative stabilities. In the calculated structure of **2** certain bond lengths and angles deviate from values considered as "normal", as well as from the crystallographic parameters. Notably, the calculated (O=C)-C(ipso  $\alpha$ -Mes) length came out as 1.41 Å (measured value 1.518 Å), while the calculated C(ipso)-C(ortho) bond lengths in the  $\alpha$ -ring are 1.45 Å, as compared with the observed values of 1.38 and 1.41 Å. The calculated dipole moment is 2.83 D, and we have now measured an experimental value of 2.71 D.<sup>22</sup> Further improvement of the calculation was not attempted.

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(7) Å for two crystallographic forms of **5** and 1.339 (6) Å for **6**. It seems therefore that in spite of the unrealistic input value, the calculation converges on a realistic C=C bond length, and the value clearly shows C=C elongation which reflects the relief of steric congestion. Similarly, all the calculated C(Aryl)-C(double bond) bond lengths are in the normal range 1.48-1.51 Å (the average bond length between single-bonded sp<sup>2</sup> carbons is 1.48 Å),<sup>19</sup> while the calculated C(1)-O bond length is 1.36 Å. Again, these values are similar to the corresponding distances found<sup>7</sup> for enols **6** and **7**.

**Bond Angles.** The calculated double bond angles are found to be in agreement with the crystallographic values for related enols (compare the  $\alpha$  values in Table I with Table I in ref 7). Among the  $\alpha$  values  $\alpha_4$  is unusual since it is calculated to be 121° (input 126.8°), lower than that expected by comparison with the crystallographic values for related enols (129-130°).<sup>7</sup> While the reason for this discrepancy is unclear to us, we note that  $\alpha_4$  values in 2,2-dimesityl-1-alkyl enols are linearly correlated with the bulk of the alkyl substituents.<sup>20</sup> Hence, the smaller  $\alpha_4$  value may be a consequence of the less severe repulsion between the  $\alpha$ -mesityl and the less bulky  $\beta$ -aryl (as compared with the  $\beta$ -mesityl) groups. Moreover, a systematic analysis of double bond angles in tri- and tetraarylvinyl systems reveals that  $\alpha_4$  values as small as 122° occur in systems of the type Ar'Ar'C=C(Et)Ar.<sup>21</sup>

**Torsional Angles.** The torsional angles calculated for **1** are similar to those found by X-ray diffraction.<sup>7</sup> The values are closer for the  $\beta$ -mesityl and phenyl rings (calculated values 74° and 39°; experimental values 74° and 38°, respectively) than for the  $\alpha$ -mesityl ring (67° vs. 72°). The difference may reflect the intervention of packing forces. A gratifying aspect is that our calculation stresses that the propeller conformation represents a minimum energy conformation, at least local, for an isolated triarylvinyl molecule in the gas phase. This is complementary of previous evidence in solution which is based on NMR<sup>6</sup> and on the analysis of the solid by X-ray diffraction.<sup>7</sup>

**The OH Conformation.** In addition to the input crystallographic syn conformation of the C=C-OH moiety, the positions of the lone pairs and proton on oxygen were permuted, resulting in two other input structures, both nonplanar anti conformations. On optimization, each of the three input structures relaxed into that planar conformation, syn or anti, that was closer to it. This is irremediable in the present version of the force field, since both planar conformations have one syn and one anti C(sp<sup>2</sup>)C(sp<sup>2</sup>)OH combination, and the program takes C=C-OH and C(aryl)-C(=C)-OH to be torsionally equivalent. The geometry with anti C=C-OH came out higher by 0.1 kcal mol<sup>-1</sup> in energy than the syn. Bond lengths and bond and dihedral angles (apart from C=C-OH) are similar in the two final structures. Since the program does not take hydrogen bonding into account, neither intramolecular to the aryl cis to OH nor to the external solvent, comparison with solution OH conformation, which is determined mainly by these interactions,<sup>8</sup> is of little value. However, we note that the planar conformations are more stable than the gauche conformation and that in the solid state the conformation of the OH is syn periplanar.<sup>7</sup>

**Dipole Moment.** The MM2 force field predicted for vinyl alcohol<sup>13</sup> a dipole moment of 1.24 D, in good agreement with the measured value of 1.016 ± 0.009 D.<sup>16</sup> Calculation for **1** afforded again 1.24 D, which is not unexpected since the C(sp<sup>2</sup>)-C(sp<sup>3</sup>) bond moments for the two mesityl rings would roughly cancel on vectorial summation, due to their mutual trans arrangement. In order to check the prediction, the dipole moment of **1** was measured,<sup>22</sup> and the value obtained is 1.08 D.

**Conclusions.** The conformation and bond lengths and angles for (*Z*)-1,2-dimesityl-2-phenylethenol (**1**) were calculated by molecular mechanics. The results are complementary to previous findings on the structure and conformation in the solid state and in solution of crowded triarylethenols and provide structural parameters that seem more reliable than those obtained from the X-ray diffraction of the disordered crystals of **1**. The calculated dipole moment is in good agreement with the experimental value.

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(22) Measurement was conducted in benzene at 30 °C, according to: Halverstadt, I. F.; Kumler, J. *J. Am. Chem. Soc.* 1942, 64, 2988. The measured molar refraction  $R_m$  is 116.592 cm<sup>3</sup> for **1** and 111.978 cm<sup>3</sup> for **2**. The polarizations  $P$  are respectively 138.898 and 260.159 cm<sup>3</sup>.

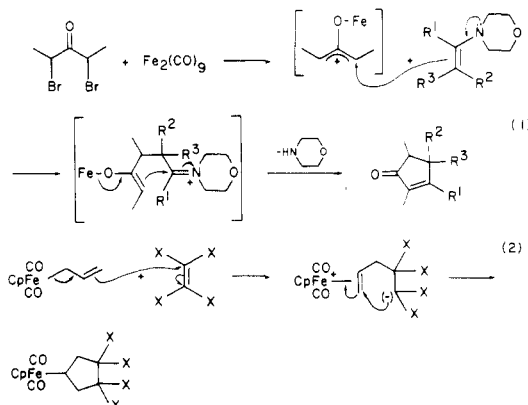
### Synthesis of Carbocycles by the Interaction of Ambiphilic Reagents. Reactions of Cationic Oxyallyl-Iron(II) Complexes with $\eta^1$ -Allyliron(II) Complexes and with *N*-Tosyl Enamines

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Ambiphilic reagents are useful for reactions involving the sequential formation of two bonds since they can alternately function as nucleophiles and electrophiles. Many organometallic complexes are ambiphilic and several that effect efficient carbocycle formation have been developed. For example, cationic oxyallyl-iron complexes, from the reaction of  $\alpha,\alpha'$ -dihalo ketones with Fe<sub>2</sub>(CO)<sub>9</sub>, react with enamines—first as an electrophile and then as a nucleophile—to annelate a five-membered ring to the enamine (eq 1).<sup>1</sup> Similarly,  $\eta^1$ -allyl(cyclopentadienyl)iron



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