acts as a general acid catalyst by partially protonating the carbonyl oxygen atom of the substrate. Since polar substituents in the carboxylic acid will affect the proton-donating powers of the hydroxyl function and the proton-withdrawing powers of the carbonyl oxygen atom in opposite fashions, it would be anticipated that the catalytic constants would be independent of the nature of such substituents. In other words, α should be smaller than 0.35. This is in contrast with the observed value of α (0.90) and rules out this explanation.

The possibility of rate-determining proton transfer from the carboxylic acid to the zwitterionic addition compound[4,5] is also inconsistent with the data since such reactions are expected to be diffusion controlled or nearly so and, hence, have rate constants independent of the acidity of the catalyst. In addition, unusual mechanisms for phenylhydrazone formation from pyrrole-2-carboxaldehyde seem unlikely since the reactivity of this compound is consistent with that expected on the basis of its relatives (see below).

We are left without a satisfactory explanation for the unusually large value of α for this reaction. It evidently depends on having the proton on the heterocyclic nitrogen atom and may or may not depend on the bifunctional character of the carboxylic acid. Further studies will be required to settle this point.

B. Free Energy Relationships. In this work we have found a linear free energy relationship between the reactivity of derivatives of aromatic heterocyclic rings, viz., furan, thiophene, and pyrrole, and the acidity of the corresponding acids.

The sensitivity of the attack reaction of phenylhydrazine on the aromatic heterocyclic aldehydes is highest when the reaction is water catalyzed ($\gamma = 1.2$), intermediate when the reaction is catalyzed by carboxylic acids ($\gamma = 1.0$), and smallest when the reaction is catalyzed by the hydronium ion ($\gamma = 0.27$). The variation of the γ values with the acidity of the general acid catalyst together with the considerations concerning variation in transition state structures as function of reactivity is in accord with the considerations of Hammond,[21] Leffler,[22] and Swain and Thornton.[23]

Acknowledgment. The author is indebted to Dr. Eugene H. Cordes for helpful comments concerning this work.

Registry No.—Phenylhydrazine, 100-63-0; furfural, 98-01-1; 2-thiophenecarboxaldehyde, 98-03-3; pyrrole-2-carboxaldehyde, 1003-29-8; *N*-methylpyrrole-2-carboxaldehyde, 1192-58-1; *N*-methylpyrrole-2-carboxylic acid, 6973-60-0; acetic acid, 64-19-7; β-bromopropionic acid, 590-92-1; formic acid, 64-18-6; chloroacetic acid, 79-11-8; cyanoacetic acid, 372-09-8; phenylhydrazinium ion, 55668-06-9.

Supplementary Material Available. Tables I, II, III, and VI that report full determination of the acidity constants data for *N*-methylpyrrole-2-carboxylic acid, acetic acid, bromopropionic acid, formic acid, chloroacetic acid, cyanoacetic acid, and phenylhydrazinium ion (4 pages). Ordering information is given on any current masthead page.

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Stereochemistry of Photochemical Cycloadditions: Addition of Ethylene to a Δ^9-1-Octalone[1]

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Photochemical cycloaddition of ethylene and 1 gave only **2**, a result consistent with the Wiesner model for photoaddition of olefins to cyclohexenones.

The photochemical cycloaddition of olefins to enones is a synthetically useful reaction. Wiesner[2] has rationalized the stereochemistry of such additions to cyclohexenones in terms of an excited enone in which the β carbon becomes nearly tetrahedral with an electron-rich orbital in a pseudoaxial orientation. This model is consistent with a large number of cycloadditions to cyclohexenones of the cholestenone type. We report here the first test of the Wiesner model in a Δ^9-1-octalone.

The enone **1**[3] underwent photochemical cycloaddition with ethylene in methylene chloride solution at −60 °C to give exclusively **2** in 82% yield. The structure of **2** was established by single-crystal x-ray diffraction analysis of the *p*-bromobenzoate **3b**.

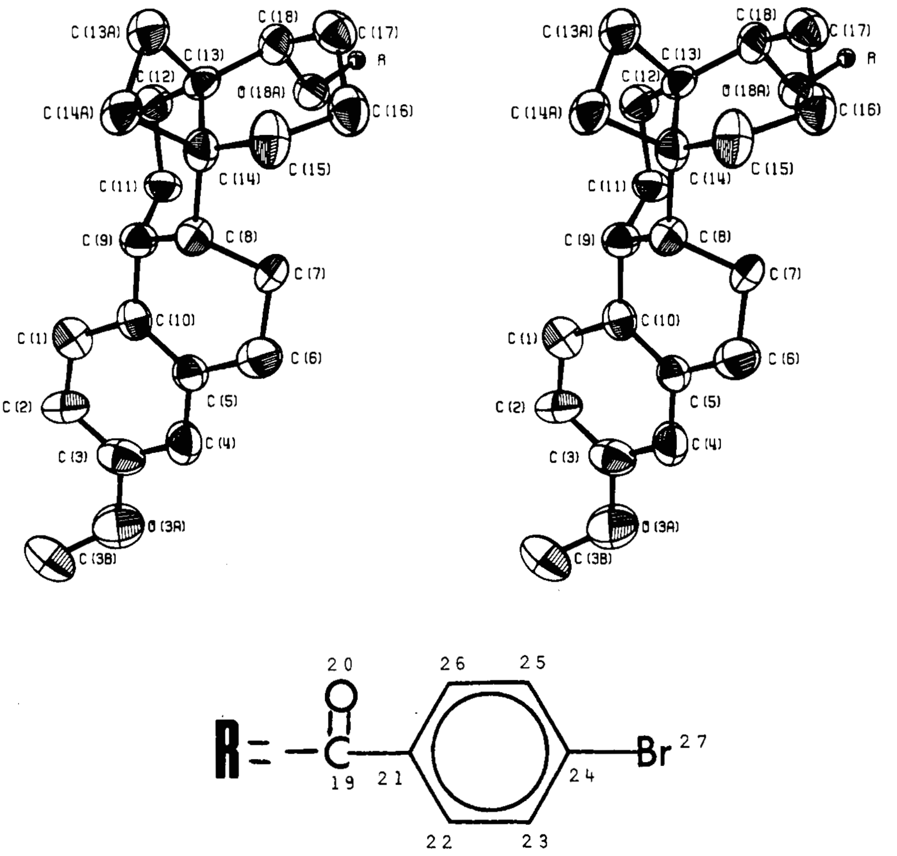
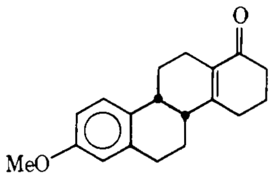
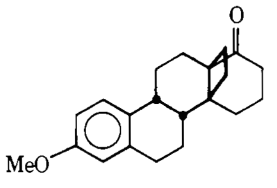


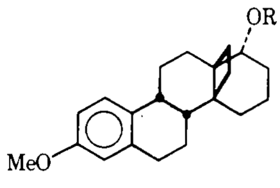
Figure 1. Stereoview of **3b.**



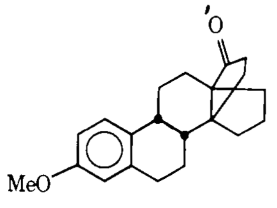
1



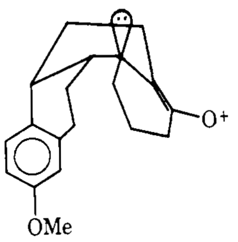
2



3a, R = H
b, R = p-BrC_6H_4CO



8



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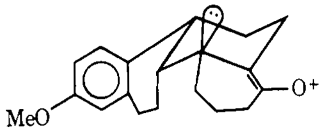

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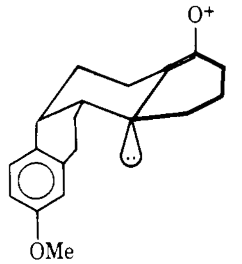
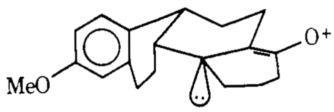


6



7

According to the Wiesner model, four excited forms of **1** may be considered: **4, 5, 6,** and **7.** In two of these, **4** and **7,** ring C is held in the boat conformation and these are presumed to be considerably less important than **5** or **6.** Cycloaddition with **6** must occur from the α face, which is severely hindered by rings A and B. No obstacles impede cycloaddition with the remaining species, **5.** Thus, the formation of **2** as the sole product of cycloaddition of ethylene and **1** is adequately rationalized in terms of the Wiesner model and intermediate **5.**

Reduction of **2** with lithium tri-*tert*-butoxyaluminum hydride gave only **3a.** Conversion of this alcohol into its p-bromobenzoate **3b** gave a crystalline derivative suitable for x-ray analysis.

When **2** was heated with p-toluenesulfonic acid in boiling benzene for 2 h, a new cyclopentanone **8** was isolated in 64% yield. The structure of **8** follows from spectral data and ample precedent.[4]

Experimental Section[5]

Cycloaddition of Ethylene and 1. An irradiation apparatus equipped with a Hanovia 450-Watt Type L mercury vapor lamp and a Pyrex probe cooled by circulating ethanol maintained at ca. −60 °C by a dry ice–isopropyl alcohol bath was charged with a solution of 7.25 g of **1** in 130 ml of methylene chloride. The apparatus was cooled in a dry ice–isopropyl alcohol bath and ethylene was bubbled through the solution during irradiation. After 1 h of irradiation all the starting material had reacted. The solvent was removed and the resulting solid was recrystallized from methanol to yield 5.03 g of **2,** mp 131.5–133 °C. The mother liquors yielded another 1.49 g of **2** (total 82.1% yield), ir (CH_2Cl_2) 1690 cm^{-1}.

Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 80.94; H, 8.08.

Reduction of 2. To a solution of 1.20 g (5.83 mmol) of lithium tri-*tert*-butoxyaluminum hydride in 6 ml of dry tetrahydrofuran was

Table I

A. Crystal Parameters	
Formula	$C_{28}H_{31}O_3Br$ (495.5)
Crystal size, mm	0.2 × 0.2 × 0.3
Cell dimensions	a = 11.874 (2) Å b = 7.520 (1) Å c = 27.095 (5) Å β = 101.08 (1)° V = 2374.3 (7) Å^3
Space group	$P2_1/c$
Molecules/unit cell	4
Density observed, g/cm^3	1.35
Density calculated, g/cm^3	1.386
Linear absorption coefficient (μ), cm^{-1}	28.1
B. Refinement Parameters	
Number of reflections	2443
Nonzero reflections	2038
R index ($R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$)	0.061
Weighted R ($R' = \omega(F_o^2 - F_c^2)^2/\Sigma\omega F_o^4$)	0.010
Final shifts	$<0.3\sigma$

added a solution of 600 mg (1.94 mmol) of **2** in 6 ml of dry tetrahydrofuran. The resulting mixture was stirred at 0 °C for 75 min. After the usual workup alcohol **3a** was isolated as a white solid (570 mg, 94.5%, mp 153–159 °C). Recrystallization from methanol gave material of mp 158.5–160 °C; ir (CH_2Cl_2) 3630, 3500 cm^{-1}. Alcohol **3a** was converted into the *p*-bromobenzoate **3b** by treatment with *p*-bromobenzoyl chloride in dioxane-pyridine. The crystalline product obtained after usual workup was recrystallized twice from benzene-hexane: mp 175.5–177 °C; ir (CH_2Cl_2) 1710, 1615 cm^{-1}. This material was used for x-ray diffraction analysis.

Anal. Calcd for $C_{28}H_{31}O_3Br$: C, 67.87; H, 6.31; Br, 16.14. Found: C, 67.63; H, 6.21; Br, 16.32.

Acid-Catalyzed Isomerization of 2. A solution of 500 mg (1.64 mmol) of **2** and 1.5 g of *p*-toluenesulfonic acid monohydrate in 125 ml of benzene was refluxed for 2 h. The resulting mixture was washed with aqueous $NaHCO_3$ and water, and dried ($MgSO_4$). Removal of solvent gave 540 mg of a dark oil. A solution of this oil in methanol was stirred with activated charcoal, filtered and concentrated to yield 320 mg (64%) of crystalline **8**, mp 119–120 °C. Two additional recrystallizations from methanol gave an analytical sample: mp 120–121 °C; ir (CH_2Cl_2) 1735, 1615 cm^{-1}.

Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.07; H, 8.26.

X-Ray Analysis of 3b. The crystal structure of this compound was concluded in a routine manner. Suitable crystals were grown from a mixture of benzene and hexane. The crystals were surveyed and a 1-Å intensity data set (maximum sin θ/λ = 0.5) was obtained on a Syntex P$\bar{1}$ diffractometer using copper radiation (λ = 1.5418 Å) at room temperature. The crystal density was measured by the flotation technique in aqueous KI. Final unit cell dimensions were obtained using 15 high angle reflections ($2\theta > 40°$). The diffractometer was equipped with a graphite incident beam monochromator mounted in the perpendicular mode. During data collection a θ–2θ scan technique was employed, the scan rate was 2°/min in 2θ, the scan range was 1.0° above Kα_2 and 1.0° below Kα_1, and the background was counted for half the scan time on each side of the peak. A single check reflection was monitored every 30 reflections and indicated no crystal damage since it was reproducible within counting statistics.

The diffractometer output was processed using subprograms of the CRYM crystallographic computer system.[6] The processing included corrections for background, Lorentz, and polarization effects. The polarization effect due to the graphite monochromator was included in these corrections.[7] No corrections were made for absorption. The data processing also included calculation of the F^2 value and its standard deviation for each reflection. The standard deviations were assigned on the basis of the equation

$$\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2$$

where S is the scan count, B_1 and B_2 are the background counts, d is an empirical constant equal to 0.02, and α is the scan time to total background time ratio. All intensities with values less than three times the standard deviation were set equal to zero with zero weight. The data set was placed on an approximately absolute scale by means of Wilson statistics. Crystal parameters are summarized in Table I.

Determination of Structure and Refinement. A trial structure for **3b** was obtained by conventional Patterson and Fourier techniques. This trial structure refined routinely to an acceptable R index (see Table I). The latter stages of the refinement procedure included a full matrix least-squares treatment of all nonhydrogen coordinates in one matrix, and anisotropic temperature factors and scale factor in a second matrix. Methylene and methine hydrogen positions were calculated; all other hydrogen positions were located by difference Fourier techniques. While hydrogen parameters were added to the structure factor calculation in the latter stage of refinement, they were not refined. The quantity minimized by the least-squares procedure was $\Sigma\omega(F_o^2 - F_c^2)^2$, where $\omega = 1/\sigma^2(F_o^2)$. A final difference Fourier revealed no missing or misplaced electron density. A stereoplot of **3b** is given in Figure 1. Atomic parameters and bond distances and angles appear in Tables II and III.[8]

Acknowledgment. This work was supported by HEW (Grant AM18802).

Registry No.—**1**, 60428-06-0; **2**, 60428-07-1; **3a**, 60428-08-2; **3b**, 60428-09-3; **8**, 60428-10-6; ethylene, 74-85-1; *p*-bromobenzoyl chloride, 586-75-4.

Supplementary Material Available. Tables II and III, atomic parameters and bond distances and angles (2 pages). Ordering information is given on any current masthead page.

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(8) See paragraph at end of paper regarding supplementary material.