J. Org. Chem. **1998,** *63,* 2850−2853

Dynamic NMR Study of Cyclopropanecarbaldehyde. Comparison of the Conjugating Abilities of the Cyclopropyl and Phenyl Groups

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Received September 18, 1997

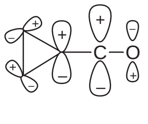
The NMR spectrum of cyclopropanecarbaldehyde (**1**) shows two chemical shifts for the aldehyde proton at −169.2 °C, separated by 1.71 ppm. The populations of the two conformations at this temperature are 0.012 and 0.988, corresponding to the aldehyde hydrogen cis (**1a**) or trans (**1b**) to the methine hydrogen, respectively. From the averaged chemical shift at room temperature, populations of **1a** and **1b** were estimated to be 0.27 and 0.73. Free-energy barriers of 5.03 kcal/mol (**1a** → **1b**) and 5.95 kcal/mol (**1b** → **1a**) were determined for the compound at −169.2 °C. Comparison of these barriers with the barrier for benzaldehyde indicates that the π-donating ability of the cyclopropyl group is lower than for phenyl.

Introduction

The bonding in cyclopropanes is unique among the cycloalkanes, due to the small CCC bond angles. Two bonding descriptions are in common use for cyclopropane, and each of these has an analogy in the bonding of ethylene. In both descriptions, the carbon uses sp^2 hybrid orbitals to bond to hydrogen, as in ethylene.[1] The stronger C−H bonds in cyclopropane, relative to those in larger rings, have been suggested[2] to partially compensate for the angle strain in the three-membered ring. In the Walsh model,[3] each carbon has an additional sp^2 hybrid orbital pointing toward the center of the ring and a p-orbital in the plane of the ring with its axis perpendicular to the HCH plane. Addition of the three sp^2 hybrid orbitals gives the lowest energy orbital of cyclopropane (Chart 1), which is comparable to the σ-bond of ethylene. The other two occupied orbitals are derived from combinations of the p-orbitals and are comparable to the π-bond of ethylene (Chart 1). The bent bond model of bonding in cyclopropane is similar to the τ-bond model for bonding in ethylene and uses sp^5 or similar hybrid orbitals for the C−C bonds.[2−4]

As in the case of a vinyl or phenyl group, the three-membered ring can function as an electron donor. This effect is shown, for example, by the high reactivity of cyclopropylcarbinyl halides toward solvolysis.[5,6] Relative rates of solvolysis are shown in Chart 2 for several tertiary *p*-nitrobenzoates.[6]

The vacant π* orbital of a carbonyl group can also serve as an electron acceptor, and the relevant orbitals for these systems are shown below. Maximum overlap of the two



orbitals will occur in either of the two bisected conformations, as shown for cyclopropanecarbaldehyde (**1**).

Chart 1. Occupied Walsh Orbitals of Cyclopropane

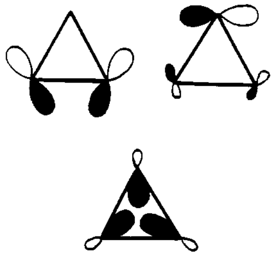
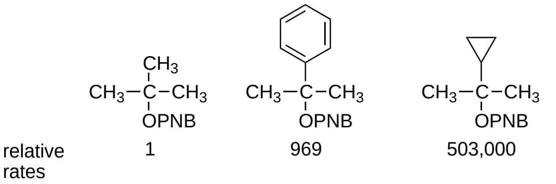
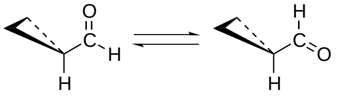


Chart 2



This paper describes a dynamic NMR study of the equilibrium for this parent carbonyl compound, and comparison of the barriers for **1** with the value for



1a **1b**

benzaldehyde provides a measure of the relative conjugating abilities of the cyclopropyl and phenyl groups.

Experimental Section

Cyclopropanecarbaldehyde was purchased from Aldrich Chemical Co. and was purified by distillation under reduced pressure using a water aspirator. A small residue, mostly cyclopropanecarboxylic acid, remained at the end of the distillation. A 5% solution of **1** was prepared in 3:1:1 CHClF$_2$/

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S0022-3263(97)01752-0 CCC: $15.00 © 1998 American Chemical Society
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Table 1. Chemical Shifts, Coupling Constants, and Populations of Cyclopropanecarbaldehyde at Various Temperatures

T (°C)	chemical shifts (Hz)		coupling constants (Hz)	populations of **1a**[a] (%)	populations of **1a**[b] (%)
22.7	2665.7[c]		5.89[d]	17.5	27.4
−60.5	2603.2[c]		6.71[d]	10.4	15.3
−100.9	2568.7[c]		7.35[d]	6.5	8.6
−111.0	2560.5[c]		7.45[d]	5.6	7.0
−121.4	2553.3[c]		7.42[d]	4.7	5.6
−130.9	2544.9[c]		7.17[d]	3.8	4.0
−136.9				3.3	
−142.8				2.9	
−150.9				2.3	
−154.7				2.1	
−160.9			8.00[g]	1.6	
−162.8	3037.0[e]	2523.4[f]	8.09[g]	1.5	
−166.6	3038.5[e]	2523.7[f]	8.00[g]	1.3	
−169.2	3040.0[e]	2524.2[f]		1.2	
−171.4	3040.0[e]	2524.5[f]		1.1	

[a] The population of **1a** at −169.2 °C was measured directly, and the other populations were estimated with the assumption that $\Delta G°$ does not change with temperature. [b] The populations in this column were calculated from the relationship $\nu = p_1\nu_1 + p_2\nu_2$, where ν is the averaged chemical shift and ν_1 and ν_2 are the chemical shifts of **1a** and **1b**, which were measured at −169.2 °C. [c] Averaged chemical shifts. [d] Averaged coupling constants. [e] Chemical shifts of minor conformation. [f] Chemical shifts of major conformation. [g] Coupling constants of major conformation.

$CHCl_2F/CF_2Cl_2$. A small amount of TMS was added to this solution as an internal reference, and the NMR tube was then sealed under vacuum.

NMR spectra of **1** were taken without spinning on a General Electric wide-bore GN-300 NMR spectrometer, operating at 300.54 MHz for protons. A pulse width of 4.2 μs was used with a delay time between pulses of 8 s. The number of acquisitions was 200 ± 50, and the sweep width and block size were ±3000 Hz and 64 000.

Temperatures were measured by replacing the sample with an NMR tube containing pentane[7] and a copper−constantan thermocouple. Rate constants at temperatures from −160.9 to −171.4 °C were determined by matching the experimental spectra of the exchange-broadened formyl hydrogen peak of the minor conformation with computer-generated spectra.[8] The spectra were treated approximately as a two-spin system, and input for the calculations included the chemical shifts, populations, coupling constant, the mean lifetime, τ, for conversion of the minor conformation to the major conformation, and the line widths, which were taken to be the same as for TMS. Chemical shifts of 3040.0 and 2524.2 Hz were measured for the minor and major conformations at −169.2 °C, and a chemical shift of 540.6 Hz was used in each calculation for the methine hydrogen. Populations of 0.012 and 0.988 were obtained at −169.2 °C by the cut-and-weigh method, and populations at the other temperatures were estimated by assuming that $\Delta G°$ does not change with temperature (Table 1). A coupling constant of 8.09 Hz for the major conformation was measured at −162.8 °C, and the coupling constant for the minor conformation was estimated to be 0.1 Hz by a procedure described in the next section. On the basis of the coupling constants, the minor and major conformations can be assigned to structures **1a** and **1b**, respectively.

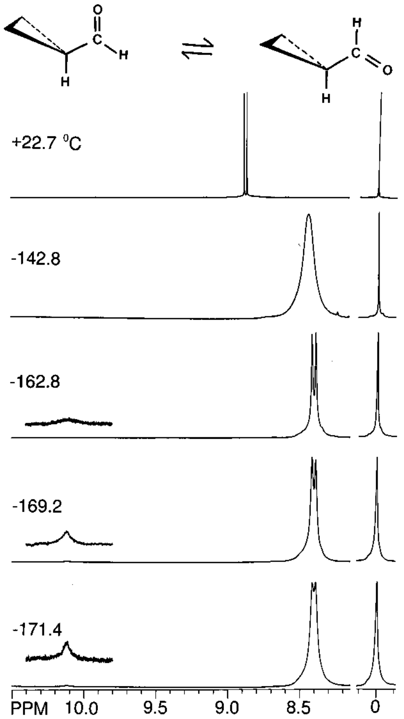

Figure 1. NMR spectra of TMS and the formyl hydrogen of cyclopropanecarbaldehyde, taken at different temperatures.

Results

The proton NMR spectrum of cyclopropanecarbaldehyde at room temperature (22.7 °C) in 3:1:1 $CHClF_2/CHCl_2F/CF_2Cl_2$ shows the formyl hydrogen as a doublet from coupling to the methine hydrogen, and the chemical shift is δ 8.87. The averaged coupling constant (5.89 Hz at room temperature) increases at lower temperatures, as noted earlier by Karabatsos,[9,10] and the chemical shift moves to lower frequency. These properties are consistent with an increase in the population of the major conformation (**1b**), which has the formyl and methine hydrogens trans to one other. The formyl proton chemical shifts and coupling constants of **1** for various temperatures are summarized in Table 1. The doublet broadens at lower temperatures, and by −143 °C individual lines are no longer seen. The two lines of the doublet reappear below −143 °C, although viscosity broadening at still lower temperatures causes the line widths to increase again. Figure 1 shows the formyl proton NMR spectra of cyclopropanecarbaldehyde over a range of temperatures. The chemical shifts at −169.2 °C are δ 10.11 for **1a** and δ 8.40 for **1b**.

Populations of **1a**, determined by two methods, are also shown in Table 1. The population of 1.2% at −169.2 °C was measured directly by the cut-and-weigh procedure, and the other populations in this column were estimated by assuming that the $\Delta G°$ of 0.91 kcal/mol does not change with temperature. In the second method, populations in the temperature range +22.7 to −130.9 °C were estimated from the relationship $\nu = p_1\nu_1 + p_2\nu_2$, where ν is the averaged chemical shift and ν_1 and ν_2 are the chemical shifts of **1a** and **1b**, which were measured at −169.2 °C. The two methods are in good agreement at

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[7] Because pentane solidifies below −130 °C, the calibration was later checked with the thermocouple immersed in 3:1:1 $CHClF_2/CHCl_2F/CF_2Cl_2$, and the temperatures in the region −160 to −171 °C were within 0.4 °C of those obtained for a new calibration using pentane and within 1.1 °C of the previous temperatures obtained using pentane.

[8] Spectra were calculated with a VAX computer connected by a modem to a PC equipped with a Radio Shack TRS-80 plotter-printer, using a dynamic NMR program written by: Binsch, G.; Kleier, D. A. *QCPE* **1969**, *11*, 140.

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Table 2. Some Conformational Studies of Cyclopropanecarbaldehyde[a]

method used	solvent or phase	T (°C)	% **1a**	energy difference **1b** − **1a** (kcal/mol)	barrier **1a** → **1b** (kcal/mol)	barrier **1b** → **1a** (kcal/mol)	ref
b	gas		55 ± 10		>2.5	>2.5	15
c	gas	−78 °C to rt		−0.029 ± 0.057	4.38 ± 0.41	4.43 ± 0.41	16
d	(gas)			0.8	5.4	4.6	17
e	CS_2		34				18
e	neat liquid		29				18
e	CD_3CN		23				18
e	solid	−130	0				19
e	gas			0.17 (ΔH)			20
f	gas				4.35	4.20	20
e	neat liquid			−1.16 (ΔH)			20
g	(gas)			0.66			21
h	(gas)			0.53			21
i	(gas)			1.17			22
j	(gas)			0.33	5.82	5.49	22
k	(gas)			−0.25	5.46	5.71	23
l	*m*	−169.2	1.2	−0.91 ($\Delta G°$)	5.03 ($\Delta G^{\ddagger}$)	5.95 ($\Delta G^{\ddagger}$)	this work

[a] Some early calculations for **1**, not listed in the table, are described in refs 11−14. [b] Electron diffraction. [c] Microwave spectroscopy. [d] SCF-LCAO-MO calculations, INDO. [e] Raman spectroscopy. [f] Far-infrared. [g] MO calculations, extended 4-31G, G 86. [h] MO calculations, extended 6-31G, G 86. [i] MO calculations, 3-21G, G 86. [j] MO calculations 6-31G*, G 86. [k] MO calculations, CBS-4 method. [l] NMR spectroscopy. [m] 3:1:1 $CHClF_2/CHCl_2F/CF_2Cl_2$.

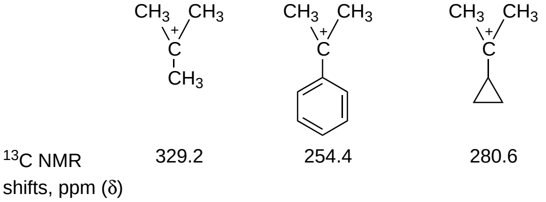
−130.9 °C, but at higher temperatures the difference in the estimated populations of **1a** increases. For calculations of the barriers, populations estimated by the first method were used, but the second method is considered to be more accurate and is used where applicable, including room temperature (27.4% at 22.7 °C). From the room-temperature populations, the coupling constant for **1b** (8.09 Hz), and the averaged coupling constant at room temperature (5.89 Hz), the coupling constant of **1a** was calculated to be 0.1 Hz from the relationship $J = p_1 J_1 + p_2 J_2$.

A rate constant of 55 s^{-1} was determined for the conversion of **1a** to **1b** at −169.2 °C, corresponding to a barrier of 5.03 kcal/mol. The rate constant for the reverse process was estimated as 55 (0.012/0.988) = 0.67 s^{-1}, and the calculated barrier for **1b** → **1a** at this temperature is 5.95 kcal/mol. Five barriers determined for **1a** → **1b** at temperatures between −160.9 and −171.4 °C ranged from 5.03 to 5.15 kcal/mol.

Discussion

The results of some previous conformational studies of **1** are summarized in Table 2. In the gas phase, conformation **1a** is slightly more stable than **1b**. An enthalpy difference for **1a** and **1b** of 0.17 kcal/mol was determined for this phase by Raman spectroscopy.[20] Only the microwave study[16] indicated a smaller energy for **1b** under these conditions, and the estimated experimental error in this experiment was larger than the energy difference. Molecular orbital calculations also have been used to study the conformations of **1**; in recent calculations, **1b** was estimated[23] using the CBS-4 method to have an energy 0.25 kcal/mol lower than **1a**, with a transition state 5.7 kcal/mol above **1b**.

Chart 3



The conformational preference found experimentally for the gas phase is reversed in the condensed phase, and **1b** was determined in a Raman study of the neat liquid to be more stable than **1a** by an enthalpy difference of 1.16 kcal/mol.[20] The population of 1.2% found by us for **1a** at −169.2 °C in the mixture of Freons corresponds to a free-energy difference of 0.91 kcal/mol. Our best estimate of 27.4% for the population of **1a** in this solvent mixture at 22.7 °C was derived from the averaged and slow-exchange chemical shifts and corresponds to a free-energy difference of 0.57 kcal/mol. Only conformation **1b** was found in a Raman study[19] to be present in the solid state.

The rotational barriers of 5.03 and 5.95 kcal/mol for **1** provide a measure of the electron-donating ability of the cyclopropyl group in this compound. The relative conjugating abilities for cyclopropyl and phenyl groups have been of interest for a long time, and conflicting conclusions have been reported.[6,24] Solvolysis studies of *p*-nitrobenzoates described earlier (Chart 2) were interpreted[6] to indicate that the cyclopropyl group is a better electron donor than phenyl. However, the chemical shifts of the C^+ in the cations derived from the three nitrobenzoates (Chart 3) were explained[24] in terms of greater electron donation by phenyl than by cyclopropyl in these systems.

$\Delta G°$ values for the isodesmic reactions shown in eqs 1 and 2 were obtained[25] for the gas phase by cyclotron

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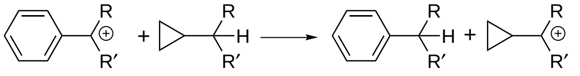
resonance, and ΔE values for eqs 1−3 were estimated[25] using STO-3G calculations. The reaction for the tertiary



eq 1 $R = R' = CH_3$
eq 2 $R = CH_3$; $R' = H$
eq 3 $R = R' = H$

system (eq 1) was found to be essentially thermoneutral in the gas phase by both methods, and the authors concluded that in solutions this reaction would be exothermic, with the cyclopropyl-substituted cation having the lower energy. Reactions 2 and 3, however, were determined to be endothermic in the gas phase, with the STO-3G calculations indicating that the phenyl group is the more effective substituent by 20 kcal/mol in the primary system and by half this amount in the secondary system.

The decreasing stability of the benzyl cations in eqs 1−3 with increasing methyl substitution on C^+ was interpreted[25] as being a consequence of a greater interaction between the phenyl π-system and the vacant p-orbital in all three benzyl cations, relative to the corresponding interaction in the cyclopropylcarbinyl cations involving the Walsh orbital of the cyclopropyl group, as shown by the change in energy for eq 3. The increased orbital splitting in the benzyl systems was suggested to decrease the ability of added methyl groups to stabilize the cation.

Rotational barriers could also provide information about the relative stabilizing abilities of cyclopropyl and phenyl. Barriers obtained for cyclopropylboron difluoride,[26] vinylboron difluoride,[27] and phenylboron difluoride[28] (Chart 4) by infrared, Raman, and microwave spectroscopy, respectively, indicate that phenyl is a poorer donor than cyclopropyl or vinyl, but the barriers determined by dynamic NMR spectroscopy for cyclopropanecarbonyl fluoride,[29] acryloyl fluoride,[30] and benzoyl fluoride[31] (Chart 5) indicate the reverse order. The discrepancy could be explained by an error in one or more of the barriers for the boron difluorides. In particular, the value for phenylboron difluoride may be low.

Chart 4

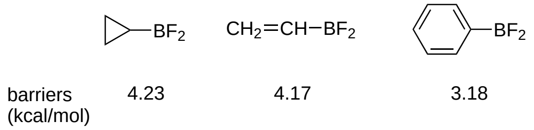
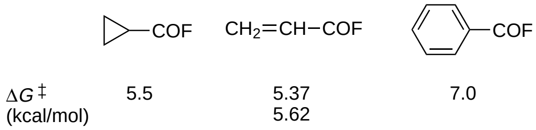


Chart 5



The barriers for **1** and benzaldehyde should provide a good measure of the relative π-donating abilities of the cyclopropyl and phenyl groups. No electron donor to π^* other than cyclopropyl or phenyl exists in these compounds, and the CHO group is small, so that steric effects should be unimportant. Katrizky[32] has suggested that the differences in steric interactions for planar and perpendicular benzaldehyde are negligible and that $\sigma°_R$ for the transition state to rotation in this compound is also close to zero; therefore, the barrier should accurately represent the resonance energy. A free-energy barrier of 7.9 kcal/mol[33] in vinyl chloride solvent was obtained for benzaldehyde using ^1H NMR spectroscopy and an approximate equation for the rate constant. Later studies using ^{13}C NMR spectroscopy and complete line shape analysis gave values of 7.61 kcal/mol[34] in a mixture of $CHCl_2F$ and CF_2Cl_2 and 7.76 to 7.65 kcal/mol[35] in dimethyl ether as solvent. The close agreement of the results from different laboratories demonstrates the reliability of barriers obtained by dynamic NMR spectroscopy. Comparison of the barrier for benzaldehyde with those for cyclopropanecarbaldehyde provides evidence that phenyl is the better donor in these simple systems.

Acknowledgment. We thank the National Science Foundation (Grant No. RII-9005618) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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