used these parameters to predict values of k_ψ which are in reasonable agreement with the experimental values (Table III).

The values of k_M cannot be compared directly with those of k_W, because they have different dimensions,[18] but they can be compared by using the volume element of reaction in the micellar pseudophase. The volume of Stern layer of 1 mol of micellized NaLS has been estimated as ca. 0.14 L,[9] and the second-order rate constant, k_2^m, written in terms of the molarity of hydrogen ions in the Stern layer, in the micellar pseudophase is given by eq 10.

$$k_2^m = 0.14k_M \quad (10)$$

Therefore $10^4k_2^m = 1.1$ and 0.8 M^{-1} s^{-1} in 0.03 and 0.1 M HCl, respectively, and the values of k_2^m are considerably smaller than that of k_W, which is 3.7×10^{-3} M^{-1} s^{-1}.[2] This low catalytic efficiency of hydrogen ions in an anionic micelle, relative to that in water, is observed in other micellar-catalyzed acid reactions[10] and can be ascribed either to deactivation by strong hydrogen bonding to the anionic head groups or to the sulfuric acid not being strong when micellized (cf. ref 11).

Significance of Negative Salt Effects. Decreases of micellar rate enhancement of ionic reactions by added salts can be explained in terms of an exclusion of a reactive counterion from the micelle because of competition with an inert counterion; e.g., a halide ion could exclude a nucleophilic anion from a cationic micelle.[7-9,22,23] But it is difficult to apply this explanation in its simplest form to the salt effects upon hydrolysis of 1 in CTABr (Table V) in terms of Scheme II.

The effect of pH is interpreted in terms of a decrease of protonating power of the solution (Scheme II); thus halide ions must inhibit the reaction in CTABr by increasing protonating power in the micellar pseudophase. Cationic micelles do not effectively bind hydrogen ions, as shown by their effects on acid rates and equilibria,[7-9] but if equilibrium between hydrogen and hydroxide ions is maintained in the micellar pseudophase (cf. ref 28) expulsion of hydroxide ions from the micelle by halide ions (Table V) will increase acidity in the micellar pseudophase and therefore slow hydrolysis (Scheme II). In other words we could interpret the salt effect in terms of a halide ion induced binding of hydrogen ions to the cationic micelle.

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Registry No. 1, 62615-78-5; NaLS, 151-21-3; CTABr, 57-09-0.

(27) These values of k_M are not very sensitive to small changes in the cmc.

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Conformational Analysis and Stability of Substituted 4-Hydrindanones. A Thermodynamic and Magnetic Resonance (^1H and ^{13}C) Study

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The relative stereochemical configurations of the 4-hydrindanones 1–6 have been determined by ^{13}C and ^1H NMR. The cis isomers **1a–6a** show ^{13}C chemical shifts of the carbonyl carbon around 214 ppm, whereas the shifts of the trans isomers **1b–4b** are around 211 ppm. These configurations are confirmed by differences in the ^1H chemical shifts of the hydrogen or methyl at C7a. The conformations of the cis isomers **1a–6a** have also been determined. The ^{13}C chemical shifts of C5 and the values of J(H3a,H3α) (when C3 is not α-substituted) show that these isomers exist at room temperature in only one or the other of the two possible conformations. The configuration of a methyl group at C3 affects the relative stabilities of the cis and trans isomers of these hydrindanones. If the methyl is in the α configuration, the trans isomer is the more stable; if it is in the β configuration, the cis isomer is favored. The entropy of the cis–trans isomerization between **3a** and **3b** has been determined.

The relative configurations and stabilities of the 4-hydrindanones 1–6 have been determined in order to analyze the stereochemistry of the hydrogenation of $\Delta^{3,3a}$-4-hydrindanones.[1] The configurations of **3b**, **5a**, and **6a** have been established by X-ray diffraction analysis using single crystals of the semicarbazones or thiosemicarbazones.[2,3] We have been able to deduce the structures of the other isomers from their ^{13}C and ^1H NMR spectra and from study of equilibrations in the presence of base. These equilibrations show that the cis isomers of **1**, **2**, **5**, and **6** (R_α = H) are more stable than their trans epimers, whereas

Table I. Results of Equilibrations in a Basic Medium

epimeric pair	composition of the equilibrated mixture: % cis	% trans
1a ⇌ **1b**	76	24
2a ⇌ **2b**	92	8
3a ⇌ **3b**	6	94
4a ⇌ **4b**	31	69
5a ⇌ **5b**	100[a]	0
6a ⇌ **6b**	100[a]	0

[a] Enolization and equilibrium are shown by incorporation of deuterium at the 3a-position in D_2O (cf. Experimental Section).

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0022-3263/81/1946-0914$01.00/0

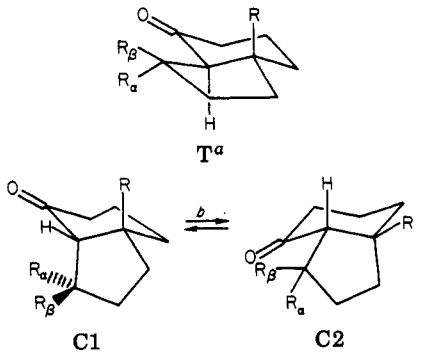
Chart I. Epimeric 4-Hydrindanones

1a, R = H; R_α = H; R_β = H
2a, R = CH_3; R_α = H; R_β = H
3a, R = H; R_α = CH_3; R_β = H
4a, R = CH_3; R_α = CH_3; R_β = H
5a, R = H; R_α = H; R_β = CH_3
6a, R = CH_3; R_α = H; R_β = CH_3

1b,[a] R = H; R_α = H; R_β = H
2b,[a] R = CH_3; R_α = H; R_β = H
3b, R = H; R_α = CH_3; R_β = H
4b, R = CH_3; R_α = CH_3; R_β = H
5b,[b] R = H; R_α = H; R_β = CH_3
6b,[b] R = CH_3; R_α = H; R_β = CH_3

[a] These compounds have not been isolated from their mixture with the cis isomers. [b] These compounds have not been observed.

Chart II. Conformations of 4-Hydrindanones



T[a]

C1 C2

[a] The rigid conformation of the trans isomers T. [b] The interconvertible conformations of the cis isomers C1 and C2.

the converse is true for **3** and **4** (R_α = CH_3; see Chart I).

It is known[4] that the *trans*-4-hydrindanones exist in a rigid conformation (T, Chart II). On the other hand, the cis isomers can exist in two potentially interconvertible forms with the six-membered ring in the chair form: C1, axial–equatorial; C2, equatorial–axial. We will show that the *cis*-4-hydrindanones **1–6** exist in only one of the C1 or C2 conformations, depending on whether R_α = H or CH_3 (C1 when R_α = H and C2 when R_α = CH_3). Finally, we will discuss the relation between these two observations.

Methods and Results

Equilibrations. The equilibrium between cis and trans isomers **1a–6a** and **1b–6b** was determined by heating **1a–6a**, **3b**, and **4b** (available as pure isomers) in solution with aqueous NaOH or KOH; the results are shown in Table I. For those compounds in which R_α = H, the cis isomer predominates in the equilibrium mixture, whereas when R_α = CH_3, the trans isomer predominates.

Thermal equilibration of **3a** and **3b** was studied by heating each of the pure isomers, sealed in Pyrex tubes at 1.3 Pa, to temperatures in the range 464–629 K. The concentrations of each isomer were measured by VPC by comparing peak areas with those of known mixtures.

The reproductibility of the measurements is about ±1%: at T_1 = 464 K we find 20 ± 1% of cis isomer, and at T_2 = 629 K we find 24 ± 1% of cis isomer, corresponding to the values K_1 = 4 ± 0.3 and K_2 = 3.15 ± 0.15 for the cis ⇄ trans equilibrium. These values are very similar to the value found by Conia.[5]

Resolution of eq 1 and 2 gives the solutions $\Delta H°$ = −3.5 ± 1.8 kJ/mol (0.85 kcal/mol) and $\Delta S°$ = 4.0 ± 3.2 J/K mol (1 eu).

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (1)$$

$$\Delta G° = \Delta H° - T\Delta S° = -RT \ln K \quad (2)$$

The trans isomer is more stable, but cis and trans isomers have about the same entropy.

When R = CH_3, the reaction is very slow, and for equilibrium **4a** ⇄ **4b**, a result was obtained only at T = 629 K (43% of cis isomer, corresponding to K = 1.32 and ΔG_{629} = −1.44 kJ/mol). The ΔS value was not accessible in this case.

^{13}C Nuclear Magnetic Resonance. The ^{13}C NMR spectra of the 4-hydrindanones are summarized in Table II. Assignment of the signals is based on classical considerations: (a) inspection of the multiplicity of the signals in the spectra without decoupling; (b) proton heteronuclear selective decoupling for the distinction between the methyl groups of **4a** and **4b**; (c) extinction of the corresponding signal in the proton-noise decoupled spectra[6] by selective deuteration at the C5 and C3a positions (deuteration in a basic medium) or at C3 (direct deuteration on Raney nickel).

^{1}H Nuclear Magnetic Resonance. The 60-MHz ^{1}H NMR spectra were determined in the presence of a chemical shift reagent, europium(III) tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate) (Eu(fod)$_3$), added to 0.2 M solutions of the ketone in $CDCl_3$.

The $\delta\nu_i$ values for each proton in Tables III–V are extrapolated for a ratio of complex to ketone L_o/S_o 0.4, but the experiments were extended to ratio of about L_o/S_o = 1. This ratio was used in order to obtain sufficient signal separation to enable easy observations of splitting. The decoupling experiments (Figure 1) were run at 80 MHz.

(1) Hydrindanones 1a, 2a (Table III), and 2b. For these ketones, which do not have a methyl group at C3, the most displaced signal is assigned to H3a: it exhibits

Table II. ^{13}C Shieldings of *cis*- and *trans*-4-Hydrindanones

	δ_{CO}	δ_{C3a}	δ_{C7a}	δ_{C3}	δ_{C5}	δ_{Me3}	δ_{Me7a}
1a	214.2	53.2	43.0	26.7[a]	39.7		
1b[b]	211.4	58.2	49.8		41.5		
2a	214.0	60.4	47.2	27.1	38.9		27.4
2b[b]	211.6	[c]	48.3		41.0		
3a	214.7	55.6	41.3	37.5	42.5	18.0	
3b	211.3	64.9	50.1	31.9[d]	41.9	20.4	
4a	214.8	62.9	44.9	37.7	41.0	18.1[e]	28.8[e]
4b	211.2	67.4	49.2	29.4	41.3	20.5[e]	18.8[e]
5a	213.8	61.2[f]	42.8	36.1[d]	39.3[f]	20.0	
6a	214.0	69.3	47.3	39.0[d]	37.8[f]	20.0	27.0

[a] Partial deuteration on Pd/C gives a triplet for the CHD group at the foot residual peak. [b] Observed in the mixture with the cis isomer, after basic equilibration. [c] Not observed because of overlap with δ C3 of the cis isomer [δ (calcd) 60.7]. [d] Disappears in the product obtained by deuteration on Pd/C (Me-3 appears as a singlet in the ^{1}H NMR). [e] Attributed by selective heteronuclear decoupling. [f] Disappears in the product obtained by deuteration in a basic medium.

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Table III. Induced Chemical Shifts ($Eu(fod)_3$) and ν_0 Values for Ketones 1a and 2a at 60 MHz

	1a		2a	
	ν_0, Hz (or ppm)	δ_{ν_i}[a]	ν_0, Hz (or ppm)	δ_{ν_i}[a]
H3a	156 (2.60)	264	133 (2.22)	310
H3α[b]	120 (2.0)	225	114 (1.90)	240
H3β[b]	144 (2.40)	94	130 (2.17)	125
R(H or Me)	144 (2.40)	94	66 (1.10)	85
H5,5′	136 (2.27)	258	133 (2.22)	295
J(H3a,H3), [c] Hz	8		8	
J(H3a,H7a), [c] Hz	8			

[a] δ_{ν_i} reported values are calculated for $L_0/S_0 = 0.4$ (in hertz). [b] Assignments of H3a and H3β are based on the analogy between the ratio $\delta_{\nu_i}(H3\alpha)/\delta_{\nu_i}(H5)$ for these two ketones (0.87 and 0.81) and the *cis*-3β products **5a** and **6a** (0.74 and 0.64), which are in the same conformation (C1) with H3α very close to H5α (Chart III). [c] J values obtained from first-order AMX spectra.

equal and large coupling constants with the neighboring protons H3α and H3β and also with H7a (quartet for **1a**, R = H, and triplet for **2a**, R = CH_3). The two H5 protons are nearly equally shifted and are not separated except in double-irradiation experiments, by decoupling H6 (AB system, J(H5,H5′) = 16 Hz, Figure 1).

The signals of H3α and H3β (Table III and Figure 1) are well separated, and their assignments are based on comparison with ketones **5a** and **6a** and on molecular stereomodels that show the expected conformation of the molecule.

In the case of ketone **1a**, the proton H7a does not separate from H3β, as shown by the double-irradiation experiments (Figure 1).

The ^1H NMR spectrum of **2b** is very difficult to observe in the equilibrated mixture with **2a**. Only the sharp singlet of the methyl at position 7a is well observed at 0.53 ppm in $CDCl_3$.

(2) Hydrindanones with a Methyl Group at C3 (Table IV and V). Compounds **3a**, **3b**, and **5a**, with R7a = H, show large coupling constants J(H3a,H7a) (J = 9 Hz for the cis isomers, **3a** and **5a**, and J = 11 Hz for the trans

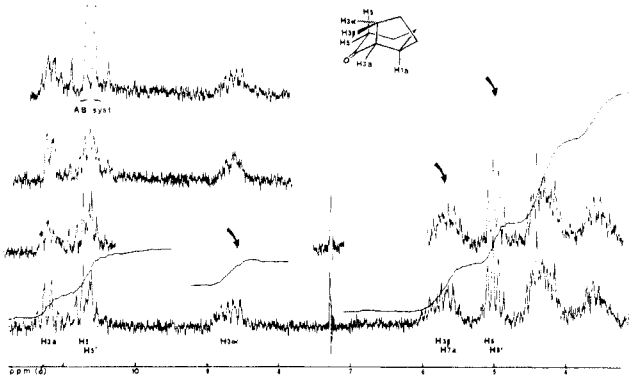


Figure 1. ^1H NMR spectrum of **1a** obtained with a chemical shift reagent (ratio of L_0/S_0 of 1) and double-irradiation experiments (at 80 MHz).

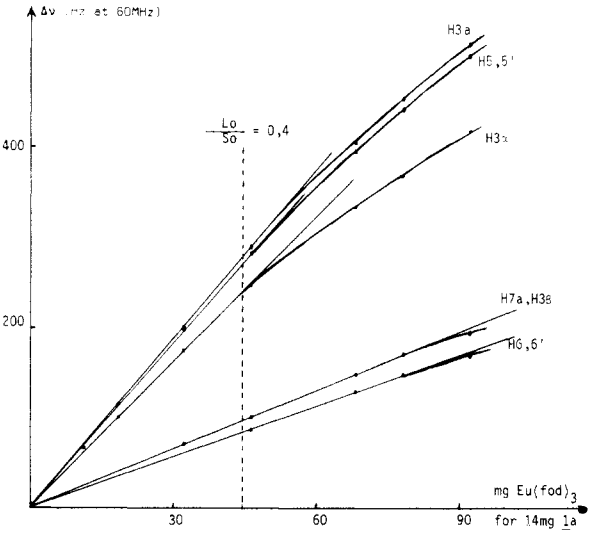


Figure 2. Chemical shifts of **1a** in the presence of $Eu(fod)_3$.

Table IV. Induced Chemical Shifts and ν_0 Values[c] for Ketones 3a, 3b, and 5a (Series R = H)

	3a		3b		5a	
	ν_0, Hz (or ppm)	δ_{ν_i}	ν_0, Hz (or ppm)	δ_{ν_i}	ν_0, Hz (or ppm)	δ_{ν_i}
CH_3(3)	55.5 (0.92)	150	57 (0.95)	113	56 (0.93)	97
H7a	148 (2.46)	93	110 (1.83)	141	138 (2.30)	101
H3a	169 (2.82)	298	120 (2.0)	204	137 (2.28)	248
H3	151 (2.52)	136	142 (2.36)	221	140 (2.33)	170
H5 (ax)	144 (2.40)	278	142 (2.36)	221	143 (2.38)	229
H5 (eq)	144 (2.40)	278	153 (2.55)	236	143 (2.38)	229
J(H3a,H7a), Hz	9[a]		11[b]		9[a]	
J(H3,H3a), Hz	9[a]		11[b]		9[a]	

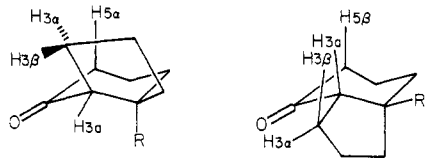
[a] Coupling obtained by inspection of first-order AMX spectra. [b] Splitting observed on the H3a triplet neighboring the H3 signal (AB part of an ABX system). [c] The δ_{ν_i} values are calculated for $L_0/S_0 = 0.4$ at 60 MHz.

Table V. Induced Chemical Shifts[a] and ν_0 Values for Ketones 4a, 4b, and 6a (Series R = Me)

	4a		4b		6a	
	ν_0, Hz (or ppm)	δ_{ν_i}	ν_0, Hz (or ppm)	δ_{ν_i}	ν_0, Hz (or ppm)	δ_{ν_i}
CH_3(3)	53 (0.88)	154	55 (0.92)	121	55 (0.92)	105
CH_3(7a)	59 (0.98)	79	38 (0.63)	140	58.5 (0.98)	81
H3a	150 (2.50)	324	134 (2.23)	226	112.5 (1.88)	300
H3	154 (2.57)	146	144 (2.40)	256	133 (2.22)	164
H5 (ax)	148 (2.47)	278	144 (2.40)	256	135 (2.25)	256
H5 (eq)	148 (2.47)	278	144 (2.40)	256	135 (2.25)	256
J(H3,H3a), Hz	10		10		10	

[a] The δ_{ν_i} are calculated values for $L_0/S_0 = 0.4$ at 60 MHz.

Chart III. Dihedral Angles in the Conformations of *cis*-4-Hydrindanones



(a) conformation C1	(b) conformation C2
H3a-H3α, 150-160°	H3a-H3α, ~90°
H3a-H3β, 20-30°	H3a-H3β, 20-30°
H3a-R, <20-30°	H3a-R, <20-30°

isomer **3b**, Table IV). Such large values are generally attributed to the trans configuration. However, the structure of the two cis ketones **3a** and **5a** has been determined by X-ray diffraction analysis of the semicarbazones of **5a** and of the epimeric trans isomer **3b**. It therefore appears that the coupling constant is not a good tool for distinguishing cis and trans structures in the 4-hydrindanones (same observation with J_{cis}(H3a,H7a) = 8 Hz for **1a**, Table III).

Discussion

In the ^{13}C NMR spectra of each pair of epimeric ketones, we observe that the ^{13}C resonance of the carbonyl group occurs at 211 ppm for one isomer and at 214 ppm for the other (Table II). In the three cases where the structures have been assigned by X-ray diffraction (**3**, **5**, and **6**) we observe that the cis isomers give the signal at 214 ppm (**3a**, **5a** and **6a**) and the trans isomer the signal at 211 ppm (**3b**).

In the case of the epimeric pair **1a** and **1b**, Hückel and Doll have shown[7] that the cis isomer is more stable than the trans isomer. Now, the more stable isomer **1a** in our equilibration gives its signals at 214 ppm and the less stable **1b** near 211 ppm (Table II). We have generalized these observations to assign the cis and trans structures in the two last pairs **2a** ⇄ **2b** and **4a** ⇄ **4b**, assuming that *in the 4-hydrindanone series the ^{13}C resonance of the carbonyl group occurs near 214 ppm for the cis isomers and near 211 ppm for the trans isomers.*

Conformational Analysis of the *cis*-4-Hydrindanones without a Methyl Group at the C3 Position (1a and 2a). Dreiding models of **1a** and **2a** show an important difference between the two conformations C1 and C2 (equilibrium b, Chart II).

In the conformation C1 (ax–eq), the dihedral angles around the C3–C3a bond with hydrogen H3a and hydrogen H3α or H3β are, respectively, 150–160° and 20–30° (Chart III). According to the Karplus rule, J(H3a,H3α) and J(H3a,H3β) should be both large coupling constants, and we have observed coupling constants of 8 Hz in the NMR spectra of **1a** and **2a** (Table III).

In the conformation C2 (eq-ax, Chart III), the situation is quite different, as we observe a dihedral angle between H3a and H3α near 90°, corresponding to a small coupling constant. Only the other coupling constant, J(H3a,H3β), should be larger as it corresponds to a dihedral angle of 20–30°.

It is clear that the *cis*-hydrindanones **1a** and **2a** are largely or entirely in the C1 conformation; if the C2 conformation had a noticeable contribution to the conformational equilibrium at room temperature, we should find one of the J(H3a,H3) coupling constants lower than the other, as J(H3a,H3α) would decrease with any significant contribution from the C2 conformation.

Conformational Analysis of *cis*-4-Hydrindanones with a Methyl Group at the C3 Position (3a, 4a, 5a, and 6a). In the C1 conformation of *cis*-hydrindanones **1a** and **2a** (Chart III), we observe that the 3α-hydrogen is very close to axial 5α-hydrogen, whereas the 3β-hydrogen does not have significant interaction with any of the substituants on the cyclohexanone ring. If a methyl group is introduced at the 3β-position, one may infer that the isomers **5a** and **6a** should also exist in the C1 conformation. In fact, the NMR spectra with Eu(fod)$_3$ show that these two *cis*-hydrindanones exhibit large J(H3a,H3α) coupling constants (9 Hz for **5a**, Table IV, and 10 Hz for **6a**, Table V). We conclude that these two hydrindanones are in an essentially pure C1 conformation, since a contribution of the C2 conformation would decrease this coupling constant significantly.

The problem of the isomers **3a** and **4a** is more difficult because the dihedral angle of H3a with H3β is small in both the C1 and C2 conformations (20–30°), and the coupling constant J(H3a,H3β) would be large in either case. The observed large constants (9 Hz for **3a** and 10 Hz for **4a**, Tables IV and V) therefore do not give any conformational information.

Dreiding models show that a methyl group in the 3α-position interacts strongly with H5α (axial) in the C1 conformation and with the carbonyl group in the C2 conformation.

In fact, the slightly positive ΔS value, measured for the equilibrium **3a** ⇄ **3b** (~4 J K^{-1} mol^{-1}), indicates that the cis isomer is a little more rigid than the trans one. The cis-hydrindanone **3a** (and probably also **4a**) exists in a pure C1 or C2 conformation which is a little more rigid than the T conformation of the trans isomer **3b** (or **4b**).

The ^{13}C NMR spectra of **3a** and **4a** provide an indication that these cis isomers exist in the C2 conformation. Table II shows that the C5 chemical shifts for those cis isomers that are known to be in the C1 conformation (**1a**, **2a**, **5a**, and **6a**) are around 39 ppm. The C5 shifts for the trans isomers **1b**–**4b** are 41–42 ppm. The steric compression[8] between H3α and H5α (Chart III) may be responsible for deshielding the C5 atoms of these cis isomers compared to the trans isomers. In trans isomers (Chart II, conformation T) as well as in the C2 conformation of cis isomers (Chart III) there is no compression of this kind at carbon C5. Since the cis isomers **3a** and **4a** show C5 chemical shifts of 42.5 and 41.0 ppm, respectively, we conclude that they must be in the C2 conformation.

The chemical shift of the C3 methyl group for the trans isomers **3b** and **4b** and for the cis isomers **5a** and **6a** is about 20 ppm. However, for the cis isomers **3a** and **4a** this shift is only about 18 ppm. We attribute this change to deshielding by interaction of the methyl group with the carbonyl oxygen in the C2 conformation of the latter two isomers. It is also probably this interaction which is responsible for the loss of the free rotation of the methyl group in **3a** (compared to **3b**), giving the observed ΔS positive value. Having established the C1 and C2 conformations for the cis isomers, we have to explain the large values observed for the coupling constants J(H3a,H7a) = 8–9 Hz (Tables III and IV) which are unusual for a cis coupling constant in the cyclohexane series. Dreiding models show that the cyclopentane ring exerts a strain which distorts the cyclohexane ring so that the dihedral angle between H3a and H7a is 20–30° in both the C1 and C2 conformations (**1a**, **5a**, and **3a**). It is not necessary to invoke any supplementary strain to explain the excep-

(7) Hückel, W.; Doll, W. *Justus Liebigs Ann. Chem.* **1936**, *526*, 103.

(8) Conia, J. M.; Moinet, G. *Bull. Soc. Chim. Fr.* **1969**, 500.

tionally large J_{cis} observed values.

Conformational Analysis of *trans*-4-Hydrindanones (1–4b). These *trans*-hydrindanones exist in a single rigid conformation, T (Chart II). It is of interest to compare the proton chemical shifts of the angular substituent R7a (H or CH_3) with those of the cis isomers.

When R = CH_3, the signal appears at higher field (δ 0.53 for **2b** or 0.63 for **4b**) for trans isomers than for cis isomers (δ 1.1 for **2a** and 0.98 for **4a** and **6a**). The same observation is possible with the extrapolated ν_0 values of proton H7a in the experiments with Eu(fod)$_3$. Trans isomer **3b** has its resonance signal at ν_0 = 1.83 ppm, at higher field than the values for cis isomers (2.40 ppm for **1a**, 2.30 ppm for **5a**, and 2.46 ppm for **3a**; Tables III and IV).

The angular substituent R (methyl or hydrogen) is deshielded by about 0.5 ppm in the trans isomers compared to the cis isomers. This deshielding reflects the position of the R group toward the cone of anisotropy of the carbonyl group. In the trans isomers, R is axial near the carbon of the carbonyl group while in the cis isomers R is equatorial in the C2 conformation and in a distorted axial position in the C1 conformation. This proximity of R to the carbonyl in the trans isomers is also responsible for their large δ_{vi} observed values (R = Me, δ_{vi} (Me) 140 Hz for **4b** compared with δ_{vi} (Me) 85 Hz for **2a**, 79 Hz for **4a**, and 81 Hz for **6a**; R = H, δ_{vi} (H7a) 141 Hz for **3b** compared with 94 Hz for **1a**, 93 Hz for **3a**, and 101 Hz for **5a**; Table III–V).

Influence of the 3-Methyl Substituent on the Relative Stabilities of Cis and Trans Isomers. When there is no methyl group at the C3 position, it has been observed (by heating[7] and by equilibrating in basic medium) that the cis isomers in the C1 conformation (**1a** or **2a**) are more stable than the trans isomers **1b** or **2b** (Table I).

The methyl group at the 3β-position (H3β of a in Chart III) in cis isomers is free from any strain in conformation C1. Comparison of the results of the equilibration between ketones **1** or **2** and **5** or **6**, which are in the same conformation, shows that a 3β-methyl favors the formation of the cis isomer.

In contrast, a 3α-methyl favors the trans isomers: a methyl in this position has strong interaction with axial H5 (H5α) in the conformation C1 and also significant interaction with the carbonyl group in the alternative conformation C2; here the trans isomer appears to be more stable than its cis epimer.

Other examples of this type of inversion of stability between *cis*- and *trans*-hydrindanones according to the α or β-position of a methyl substituent,[8] to the position of the carbonyl group,[9] or to the substituent effect in polycyclic systems[10] may be explained in the same way.

Conclusion

In this work, we have shown that it is possible to determine by NMR (^{13}C and ^1H) the relative configuration of *cis*- and *trans*-4-hydrindanones and the conformation of the cis isomers. The NMR coupling constants and the measurements of equilibrium at various temperatures prove in every case that the cis isomers are in only one of the two interconvertible conformations, C1 or C2, depending on the configuration of the methyl at the 3-position. When the 3-methyl is in the α configuration the *cis*-hydrindanone lies in the conformation C2 (eq–ax), and the trans isomer is predominant at equilibrium. When the 3-methyl is in the β configuration the *cis*-hydrindanone is in conformation C1 (ax–eq), and only the cis isomer exists at equilibrium. Without a 3-methyl substituent, the *cis*-hydrindanones are the predominant isomers at equilibrium, and their conformation is exclusively C1 (ax–eq).

Table VI[a]

R_{7a}	R_3	catalyst	temp, °C	product	yield, %	t_r
H	H	Ni	20	1a	100	
CH_3	H	Ni	20	2a	98	
H	CH_3	Pd	20	3a	45	1.13
				5a	55	1
CH_3	CH_3	Ni	50	4a	18	1.15
				6a	74	1

[a] Separation of **3a–5a** and **4a–6a** is obtained by VPC on silicone or Apiezon at 180 °C with the indicated t_r (relative retention times).

Experimental Section

^1H NMR spectra were obtained with a Varian A60 spectrometer and ^{13}C spectra with a Varian XL-100 spectrometer.

The $\Delta^{3,3a}$-4-hydrindanones were synthesized by hydrodimerization of a mixture of cyclohex-2-en-1-one or 3-methylcyclohex-2-en-1-one with acrolein or methyl vinyl ketone[1a].

These compounds were hydrogenated over Raney Nickel or 10% Pd on charcoal with the results shown in Table VI.

The trans isomers **1b–4b** were prepared by isomerization of the cis isomer with base, as described in the following experiments on equilibration.

Equilibration in a Basic Medium. (I) *cis*- and *trans*-4-Hydrindanone (1a ⇄ 1b; R = H). A stirred solution of 10 mL of tetrahydrofuran (THF), 2 mL of H_2O, 2 mL of EtOH, 200 mg of NaOH, and 200 mg of **1a** was refluxed 24 days. We believe this to be long enough, as in a preliminary 3-day experiment, incorporation of about 50% of deuterium in the 3a-position was determined by mass spectroscopy. Thus 24 days represents 8 times the half-reaction time. After extraction and evaporation of the solvents at room temperature, the composition of the product was determined by integration of the ^{13}C NMR spectrum. Since the peak areas are significant only if relaxation processes are fast enough, this integration was done in the presence of the relaxation reagent chromium(III) acetylacetonate (Cr(acac)$_3$) with a pulse interval of about 5 s.[11] The integration of all signals gave a composition of 76% of cis epimer **1a** and 24% of the trans epimer **1b**. This analytical method was used because VPC and ^1H NMR techniques did not give any result in this case.

(II) *cis*- and *trans*-4-Hydrindanones (2a ⇄ 2b; R = Me). A stirred solution of 10 mL of C_6H_6, 1 mL of H_2O, 7 mg of NaOH, and 250 mg of **2a** was heated to reflux. After 7 days the composition of the mixture was stabilized. The extracted product was analyzed by ^1H NMR (peak of the methyl group) or by VPC on silicone and gave 92% of cis isomer **2a** and 8% isomer **2b**.

(III) 3-Methyl-4-hydrindanones (R = H). (a) Epimers 3a ⇄ 3b. A solution of 80 mg of **3a** in 5 mL of THF was added to 0.5 mL of 2 N aqueous potassium hydroxide solution. The stirred mixture was heated at 66 °C until its composition remains constant (4 days). The samples are then analyzed by VPC on silicone. The equilibrium was 94% of trans ketone **3b** and 6% of cis ketone **3a**.

This equilibrated mixture was extracted with ether, dried, and then fractionated by VPC on silicone at 180 °C (relative retention times: **3b**, t_r = 1; **3a**, t_r = 1.25).

Equilibration of **3b** under the same conditions gives the same result.

(b) Epimers 5a ⇄ 5b. Treatment of **5a** in base as described for **3a** did not give any detectable **5b**. However, the cis ketone was observed to enolize in a deuteration experiment in a basic medium.

To a solution of 100 mg of **5a** in 3 mL of dried THF was added 1 mL of a solution of 5% potassium hydroxide in D_2O. The mixture was stirred and refluxed at 66 °C. Successive mass spectra at 11 eV showed that equilibrium was reached after 10 days; the

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following isotopic composition of the product was obtained: 12% dideuterated, 88% trideuterated.

(IV) 3,7a-Dimethyl-4-hydrindanones (R = H). (a) Epimers 4a ⇄ 4b. Isomerization of **4a** under the conditions used for **3a** required 2 weeks to reach equilibrium. We therefore used the following procedure. To solution of 420 mg of **4a** in 6 mL of EtOH was added 2.5 mL of aqueous 2 N KOH. After 3 h of reflux, the extracted product was analyzed by VPC, indicating 69% **4b** and 31% **4a**.

(b) Epimers 6a ⇄ 6b. Under the same conditions as for **4a**, **6a** did not give any detectable **6b**. However, enolization at the C3a position was shown by a deuteration experiment as for **5a**. The isotopic composition of the product was 2% underated and 13% mono-, 46% di-, and 39% trideuterated. During the deuteration, the ^1H NMR spectra with $Eu(fod)_3$ show that H5 and H5′ protons disappear before the H3a proton.

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Registry No. 1a, 3513-11-9; **1b**, 20480-53-9; **2a**, 75961-73-8; **2b**, 75961-74-9; **3a**, 22647-02-5; **3b**, 22646-98-6; **4a**, 75961-75-0; **4b**, 75961-76-1; **5a**, 14800-19-2; **6a**, 75961-77-2; cyclohex-2-en-1-one, 930-68-7; 3-methylcyclohex-2-en-1-one, 1193-18-6; acrolein, 107-02-8; methyl vinyl ketone, 78-94-4.

Sigmatropic Rearrangements of 1,1-Diarylindenes.[1-3] Migratory Aptitudes of Aryl Migration in the Ground and Electronically Excited States

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The photochemical and thermal rearrangements of 1,1-diarylindenes to give 2,3-diarylindenes have been investigated. Migratory aptitudes of *p*-X-phenyl vs. phenyl were determined for X = Br, CN, and OCH_3 in the photochemical and thermal migrations. The identities of the products of these rearrangements were established by unambiguous synthesis, and the synthetic work is described. Product ratios were generally determined by NMR techniques, but VPC and isotope dilution were also used in the case of 1-(*p*-cyanophenyl)-1-phenylindene reactions. The excited-state reactions (direct and triplet sensitized) are highly selective, migration of the substituted phenyl group being favored for all three substituents. The thermal reactions, in contrast, are quite unselective, phenyl migrating almost as readily as the substituted phenyl group in all cases. Quantum yields for the rearrangement in the case of 1,1-diphenylindene and 1-(*p*-cyanophenyl)-1-phenylindene were 0.80 and 0.46, respectively (direct irradiation), and 0.43 and 0.53 (sensitized reactions). The results of the thermal reactions and results from the literature are discussed in terms of bond-dissociation energies and transition-state-delocalization energies calculated by using the Hückel theory. Neither approach led to a satisfactory interpretation. The excited-state migrations are consistent with charge-transfer stabilization of the transition state, which can be estimated from oxidation and reduction potentials by using Weller's equation.

For a number of years we have been studying various aspects of the thermal rearrangements and photorearrangements of 1,1-diarylindenes.[1,2] These reactions are of interest for several reasons. First of all, since the migration of phenyl occurs in the ground and excited states[3-5] (i.e., on thermolysis[6,7] and photolysis[1,2,8,9]), studies with suitably substituted indenes allow a comparison of migratory aptitudes in the two electronically different states.[1b] Also, photorearrangement of 1,1-diphenylindene (**1a**) has been proposed to proceed via an isoindene intermediate[1] (**2a**; see Scheme I). The photoreaction thus promised to be a way of generating various isoindenes for further study.

We have pursued both lines of research, and in the present paper we describe the synthesis and reactions of various 1,1-diarylindenes (**1a-d**). In a related paper,[2] studies of the isoindene species are described, the latter being observed as transient intermediates. Migratory aptitudes have proved useful in characterizing excited-state properties,[3-5] and the present work provides a comparison between migrations in the ground and excited states.

Migratory Aptitude Studies

Syntheses. (a) Preparation of 1-(*p*-X-Phenyl)-1-phenylindenes (1). The 1,1-diarylindenes **1** were prepared by the route shown in Scheme II. The bromo compound **1b** was prepared from 1-(*p*-bromophenyl)-1,1-diphenylpropionic acid (**5**) by a route similar to the synthesis of 1,1-diphenylindene.[10]

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