with vigorous stirring at such a rate that the solvent refluxed gently. When the addition was completed and the initial reaction subsided, the mixture was stirred at the reflux temperature for an additional 2 hr. The excess lithium aluminum hydride was then decomposed by the addition of water dropwise with vigorous stirring. This was followed by the addition of 12 ml of 12 *N* HCl, just sufficient to dissolve the precipitate of aluminum hydroxide. The liquid was then extracted for 7 hr with diethyl ether in a continuous extraction apparatus. The extract was stripped of ether at a final temperature of 50° in a rotary evaporator. The precipitation of colorless crystals was aided by the addition of 25 ml of CCl_4. The solid so obtained was filtered and the filtrate was reserved. The crude solid material was recrystallized from benzene to yield 2.30 g (40.5%) of colorless crystals, mp 156–157°; the ir spectrum was identical with that of *trans*-1,2-indandiol (mp 158–159°) prepared by the method of Rosen, *et al.*[6] A mixture melting point with authentic *trans*-1,2-indandiol showed no depression. The filtrate after removal of CCl_4 in a rotary evaporator at 50°, from the filtration of the crude *trans*-1,2-indandiol, was subjected to molecular distillation at 0.63 Torr and 45°. The roof of the still was cooled by ice. In 12 hr approximately 3 ml of distillate collected. The ir spectrum of the distillate was identical with that of benzyl alcohol. The residue was taken up in diethyl ether and evaporated to yield 0.350 g (6.2%) of colorless crystals, mp 94–95°. The ir spectrum of this material was identical with that of authentic *cis*-1,2-indandiol (mp 93–95°) obtained by the method of Rosen, *et al.*[6]

Registry No.—**1**, 768-22-9; **2**, 615-13-4; benzoic acid, 65-85-0; 1-bromo-2-indanol, 52148-02-4; 2-bromo-1-indanol, 5400-80-6; *cis*-1,2-indandiol, 4647-42-1; *trans*-1,2-indandiol, 4647-43-2.

References and Notes

(1) Certain preliminary work bearing on this investigation was done by John A. Hyatt, a National Science Foundation Undergraduate Research Participant (1968), NSF Grant GY 4263.
(2) A. Gagis, A. Fusco, and J. T. Benedict, *J. Org. Chem.*, **37**, 3181 (1972).
(3) The high water solubility (0.066 g/cc) of the *cis*-1,2-indandiol probably accounts for the fact that this compound was not isolated in the previous work.[2]
(4) The nmr spectrum of the crude reaction mixture points unquestionably to the presence of 2-indanone (singlet, δ 3.51) while the two doublets at δ 6.32 and 6.17 can be assigned to H on C_1 of two different hydroxy benzoates.[6] The constitution of the reaction mixture and the structure of the products actually isolated are thus in accord.
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(12) An aqueous solution of the precipitate gave a crystalline solid, mp 118.5–120°, on acidification, identified as benzoic acid.
(13) The lithium aluminum hydride reduction was undertaken at the suggestion of one of the referees.

Determination of Configuration Using Magnetic Nonequivalence of Diastereotopic Benzylic Protons

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In earlier studies it was shown that a diastereotopic relationship between the two protons of an *N*-benzyl group may, if the proper conditions are met, cause them to appear at different chemical shifts.[1] Specifically, this phenomenon has been applied to a qualitative study on the conformational analysis of *N*-benzyl-2-substituted six-membered heterocycles[2] and it has also been shown that a 3-axial, and in some cases a 3-equatorial, alkyl substituent on an *N*-benzylpiperidine causes observable nonequivalence of the benzylic methylene protons.

Table I
Nmr Results on the Determination of Stereochemistry of 1-Benzyl-3-methyl-4-acetoxy-4-Substituted Piperidines (1) Using the Diastereotopic *N*-Benzyl Protons

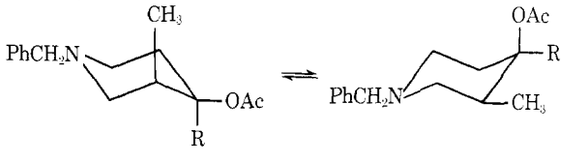
Compd 1	Isomer	*N*-Benzyl protons ($\Delta\nu_{AB}$, ±0.5 Hz)
a R = CH_3	Trans	Singlet
b, R = CH_3	Cis	Singlet
c, R = CH_2CH_3	Trans	Singlet
d, R = CH_2CH_3	Cis	11.7 Hz[a]
e, R = Ph	Trans	Singlet
f, R = Ph	Cis	13.8 Hz[a]
g, R = *o*-tolyl	Trans	Singlet
h, R = *o*-tolyl	Cis	

[a] Calculated from coupling constants obtained on a Jeolco MH-100 at a sweep width of 270 Hz.

To study further the "3-axial alkyl effect," 1-benzyl-3-methyl-4-acetoxy-4-substituted piperidines (1) were prepared to (1) determine the conformational limits for observing benzylic methylene nonequivalence when a third substituent was present on the piperidine ring and (2) determine what effect an anisotropic carbonyl would have on the magnetic nonequivalence. Since the configurational assignments of some 1-alkyl-4-aryl-3-methylpiperidin-4-ols (2) and their corresponding alkoxy esters have been previously determined by X-ray crystallography[3] and other pmr methods,[4] facile verification of stereochemical assignments was possible.

Alkyllithium addition to 1-benzyl-3-methyl-4-piperidone (3)[5] followed by acetylation of the resulting tertiary alcohol with acetyl chloride in $CHCl_3$ yielded the desired 4-acetoxy derivatives. In each case a mixture of diastereomers resulted with the trans isomer being predominant. The stereochemistry of each isomer was preliminarily assigned on the basis of its thin layer chromatographic retention time on silica gel, with the trans isomer always being the slower eluate as previously noted by Casy.[6,7]

From steric considerations, the conformational equilibrium for the trans isomers of **1** should favor the equatorial 3-methyl conformer by 1.2–1.4 kcal/mol[8,11] (R = CH_3, the smallest group studied). This prediction was confirmed by their nmr spectra (see Table I), which show singlets for the benzylic protons as expected when the 3-methyl group is equatorial and not axial.

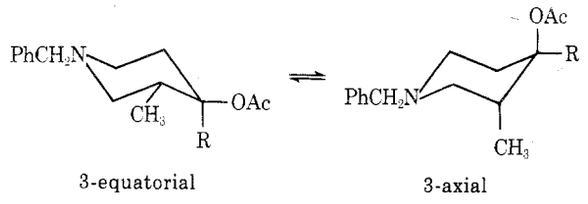


3-axial 3-equatorial

trans-**1a**, R = CH_3
c, R = CH_2CH_3
e, R = Ph
g, R = *o*-tolyl

Steric consideration of the cis isomer **1b** shows that there is very little (0.3–0.5 kcal/mol) difference in free energy between its two conformers. The nmr signal for its benzylic protons appears as a singlet, since the equatorial 3-methyl conformer is present in the conformational equilibrium by as much as 40%. However, for the cis isomer of **1** when R is

larger than a methyl group, the *N*-benzyl protons appear as a detectable AB quartet (see Table I), therefore indicating that the percentage of the axial 3-methyl conformer had increased while that of the equatorial 3-methyl conformer decreased with greater steric bulk at the 4 position. Further



3-equatorial 3-axial

cis-**1b**, R = CH_3
d, R = CH_2CH_3
f, R = Ph
h, R = *o*-tolyl

evaluation of the data presented in Table I also shows that the benzylic nonequivalence is not only detectable, but increases (~2 Hz) as the steric strain caused by the 4 substituent increases. This correlates well with the calculated percentages of ~65 and ~95% for the 3-axial conformer in the equilibrium of **1d** and **1f**, respectively.

To provide an answer for the second objective, the nmr spectrum of *cis*-1-benzyl-3-methyl-4-phenylpiperidine (**4**) shows a chemical shift separation of ~13 Hz for the *N*-benzyl protons (see Experimental Section), the magnitude of which is similar to those observed for the corresponding 4-acetoxy derivatives listed in Table I. This suggests that the 4-acetoxy has very little influence, other than steric, on the nonequivalence of the *N*-benzyl protons.

Experimental Section

Melting points were determined in a Mel-Temp apparatus in open capillaries and are uncorrected. The nmr spectra were obtained on either a Jeolco MH-100, Perkin-Elmer R-32A, Varian T-60, or a Hitachi R-20A in $CDCl_3$ with tetramethylsilane as an internal standard. Infrared absorption spectra were determined using a Perkin-Elmer 237B spectrophotometer. Elementary analyses were performed by Chemalytics, Inc., Tempe, Ariz. Thin layer chromatography (tlc) was done on precoated silica gel GF-254 plates (Analtech, Inc., Newark, Del.); spots were developed in an iodine chamber. Isomeric ratios were determined by nmr electronic integration.

General Procedure for Preparation of 1-Benzyl-3-methyl-4-acetoxy-4-substituted Piperidines (1). The *N*-benzyl-3-methyl-4-piperidone (**3**)[5] (50 mmol) was added dropwise with stirring to a cooled ether solution of the appropriate organometallic reagent (70 mmol). The mixture was stirred under reflux for 24–48 hr and then added to cold dilute hydrochloric acid. The acid solution was washed with ether and then basified with aqueous ammonia and extracted with ether. After drying over K_2CO_3, the ether was removed under reduced pressure to yield the crude mixture of diastereomeric 4-piperidinols which was then distilled and dissolved in $CHCl_3$. The reaction flask was cooled in an ice–water bath and 50 mmol of acetyl chloride was added slowly with stirring. The solution was then allowed to stand for 12 hr, and after concentration under reduced pressure, the resulting residue was basified with K_2CO_3 and extracted with ether (in some cases the residue was recrystallized before basification to yield the pure trans isomer as its hydrochloride salt; see below). The ether extracts were combined and dried over K_2CO_3 and the solvent was removed to yield the crude isomeric mixture of 4-acetoxy derivatives. The following *N*-benzylpiperidines were prepared by this method.

***trans*-1-Benzyl-3-methyl-4-acetoxy-4-methylpiperidine (1a)** was the major isomer (80%) and was isolated by recrystallization of its crude esterification mixture from ethanol–ether: mp (HCl) 204–205°, mp (base) 48–50°; ir (neat) 1716 cm^{-1}; nmr ($CDCl_3$) δ 0.85 (d, 3 H, J = 6.0 Hz), 1.5 (s, 3 H), 1.96 (s, 3 H), 1.4–2.8 (m, 7 H), 3.45 (s, 2 H), 7.28 (s, 5 H).

Anal. Calcd for $C_{16}H_{24}ClNO_2$: C, 64.53; H, 8.12; N, 4.70. Found: C, 64.04; H, 8.18; N, 4.50.

***cis*-1-Benzyl-3-methyl-4-acetoxy-4-methylpiperidine (1b)** was the minor isomer (20%) and was separated from the slower moving trans isomer **1a** (R_f 0.3) by thick layer chromatography over a 0.5-mm plate of silica gel, R_f 0.5 (90% benzene–10% ethyl acetate): mp (HCl) 201–202°; bp 94° (0.02 mm); ir (neat) 1718 cm^{-1}; nmr ($CDCl_3$) δ 0.90, (d, 3 H, J = 6.4 Hz), 1.26 (s, 3 H), 1.80 (s, 3 H), 1.5–2.6 (m, 7 H), 3.4 (s, 2 H), 7.2 (s, 5 H).

Anal. Calcd for $C_{16}H_{24}ClNO_2$: C, 64.53; H, 8.12; N, 4.70. Found: C, 64.54; H, 8.30; N, 4.64.

***trans*-1-Benzyl-3-methyl-4-acetoxy-4-ethylpiperidine (1c)** was the major isomer (68%) and was isolated by recrystallization of its crude esterification mixture from ethanol–ether: mp (HCl) 194–195°, mp (base) 42–45°; ir (neat) 1721 cm^{-1}; nmr ($CDCl_3$) δ 0.90 (m, 6 H), 1.2–2.8 (m, 9 H), 2.0 (s, 3 H), 3.5 (s, 2 H), 7.4 (s, 5 H).

Anal. Calcd for $C_{17}H_{26}ClNO_2$: C, 65.47; H, 8.40; N, 4.49. Found: C, 65.56; H, 8.50; N, 4.40.

***cis*-1-Benzyl-3-methyl-4-acetoxy-4-ethylpiperidine (1d)** was the minor isomer (32%) and was separated from the slower moving trans isomer **1c** by column chromatography over neutral alumina using petroleum ether–ether (4:1) as the eluent: mp (HCl) 151–153°; ir (neat) 1717 cm^{-1}; nmr ($CDCl_3$) δ 0.80 (m, 3 H), 1.10 (d, 3 H, J = 6.5 Hz), 1.4–2.7 (m, 9 H), 1.9 (s, 3 H), 3.4 (q, 2 H, J_{AB} = 13.0, $\Delta\nu_{AB}$ = 11.7 Hz), 7.3 (s, 3 H).

Anal. Calcd for $C_{17}H_{26}NO_2$: C, 65.47; H, 8.40; N, 4.49. Found: C, 65.60; H, 8.51; N, 4.73.

***trans*-1-Benzyl-3-methyl-4-acetoxy-4-phenylpiperidine (1e)** was the major isomer (72%) and was obtained pure by recrystallization of its crude esterification mixture from ethanol–ether: mp (HCl) 214.5–216°, mp (base) 88–89°; ir (neat) 1724 cm^{-1}; nmr ($CDCl_3$) δ 0.65 (d, 3 H, J = 6.0 Hz), 2.0–3.3 (m, 7 H), 2.10 (s, 3 H), 3.55 (s, 2 H), 7.2–7.5 (m, 10 H).

Anal. Calcd for $C_{21}H_{26}ClNO_2$: C, 70.08; H, 7.28; N, 3.89. Found: C, 70.41; H, 7.15; N, 3.88.

***cis*-1-Benzyl-3-methyl-4-acetoxy-4-phenylpiperidine (1f)** was the minor isomer (28%) and was separated from the slower moving trans isomer **1e** (R_f 0.55) by thick layer chromatography over a 0.5-mm plate of silica gel, R_f 0.70 (90% benzene–10% ethyl acetate): mp (HCl) 207–208°; ir (neat) 1718 cm^{-1}; nmr ($CDCl_3$) δ 0.75 (d, 3 H, J = 6.8 Hz), 2.0 (s, 3 H), 2.0–2.7 (m, 7 H), 3.58 (q, 2 H, J_{AB} = 13.5, $\Delta\nu_{AB}$ = 13.8 Hz), 7.4 (s, 5 H).

Anal. Calcd for $C_{21}H_{26}ClNO_2$: C, 70.08; H, 7.28; N, 3.89. Found: C, 69.76; N, 7.03; H, 3.84.

***trans*-1-Benzyl-3-methyl-4-acetoxy-4-*o*-tolylpiperidine (1g)** was the major isomer (84%) and was obtained pure by recrystallization of the crude isomeric alcohol mixture from ether–hexane: mp (HCl) 198–199°; ir (neat) 1709 cm^{-1}; nmr ($CDCl_3$) δ 0.85 (s, 3 H), 1.8–3.2 (m, 7 H), 2.05 (s, 3 H), 2.4 (s, 3 H), 3.45 (s, 2 H), 7.0–7.3 (m, 9 H).

Anal. Calcd for $C_{22}H_{28}ClNO_2$: C, 70.67; H, 7.55; N, 3.78. Found: C, 70.60; H, 7.54; N, 4.17.

***cis*-1-Benzyl-3-methyl-4-acetoxy-4-*o*-tolylpiperidine (1h)** was the minor isomer (16%) and was separated from the slower moving trans isomer **1g** by column chromatography over neutral alumina using petroleum ether–ether (4:1) as the eluent. However, this material was found to be thermally unstable and an analytically pure sample could not be obtained.

***cis*-1-Benzyl-3-methyl-4-phenylpiperidine (4a).** To 5 g (1.8 mmol) of the isomeric mixture of alcohols obtained from the phenyllithium addition to **3** was added 66 ml of concentrated hydrochloric acid and 124 ml of acetic acid. The solution was stirred under reflux for 24 hr and then concentrated to dryness. The resulting residue was dissolved in 50 ml of ethanol and 100 mg of PtO_2 was added to the flask. The reaction vessel was placed on the Parr apparatus, kept under hydrogen at 45–50 psi for 48 hr, and then concentrated to dryness. The residue obtained was basified with aqueous K_2CO_3 and extracted with ether. The combined ether extracts were dried over K_2CO_3 and then concentrated to yield a mixture (by nmr) of 1-benzyl-3-methyl-1,2,5,6-tetrahydropyridine (**5**, 40%), *cis*-**4a** (25%), and *trans*-1-benzyl-3-methyl-4-phenylpiperidine (**4b**, 35%). An examination of the nmr signals for the *N*-benzyl protons in the mixture shows singlets at δ 3.64 and 3.54 for *trans*-**4b** and **5**, respectively, and also a partially obscured AB quartet at δ 3.50 for *cis*-**4a** (J_{AB} = 13, $\Delta\nu$ ~13 Hz). Further attempts to effect complete catalytic hydrogenation of the 3,4 double bond (using Pt) without debenzylation and reduction of the 4-phenyl were futile.

Acknowledgment. The author is grateful to Dr. R. Lyle's research group of the University of New Hampshire,

Dr. E. White, V, of Smith, Kline and French Laboratories, and Dr. Ned Heindel of Lehigh University for nmr spectra. The author is especially grateful to Dr. Lyle for his consultation and encouragement.

Registry No.—**1a,** 52195-27-4; **1a** hydrochloride, 52195-28-5; **1b** hydrochloride, 52195-29-6; **1c,** 52195-30-9; **1c** hydrochloride, 52195-31-0; **1d** hydrochloride, 52195-32-1; **1e,** 52195-33-2; **1e** hydrochlorides, 52195-34-3; **1f** hydrochloride, 52195-35-4; **1g** hydrochloride, 52195-36-5; **1h,** 52195-37-6; **3,** 34737-89-8; **4a,** 52195-38-7; **4b,** 52195-39-8; **5,** 40240-24-2.

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(7) In addition to the nmr methods summarized in ref 4, an X-ray crystallographic analysis[3] of the slower eluting major isomer obtained from phenyllithium addition to 1,3-dimethyl-4-piperidone (**6**) established the 4-Ph/3-Me stereochemistry as trans. Our stereochemical assignments were then made on the warranted assumption that replacement of the *N*-methyl group by *N*-benzyl does not reverse the preferred pathway of lithium reagent attack. Additionally, these stereochemical assignments and nmr results are in accord with those reported earlier for similar piperidines obtained by catalytic hydrogenation of the parent pyridines.[1]
(8) Free-energy differences between conformers were calculated using a decrease of 0.6–0.8 kcal/mol in the unfavorable axial methyl interaction on replacement of one syn-axial hydrogen by the nitrogen free pair[9] and the best $-\Delta G$x values listed by Hirsch.[10]
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(11) As one referee has correctly suggested, there are several hazards in making predictions on conformational equilibria based on additive free energies of substituent groups when two or more are present.[12] In our case, conformational distortions are considered to be negligible.
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Hydration of 3-Methyl-3-buten-2-one (Isopropenyl Methyl Ketone)

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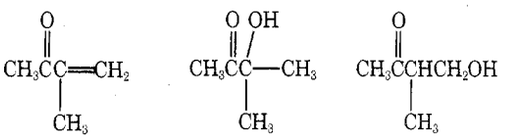
Experience shows that the acid-catalyzed addition of water to a carbon–carbon double bond conjugated with a carbonyl group occurs such that hydrogen appears on the α carbon atom and hydroxyl on the β. Thus methyl vinyl ketone affords 4-hydroxy-2-butanone,[1] and acrylaldehyde and acrylic acid yield respectively 3-hydroxypropionaldehyde and 3-hydroxypropionic acid.[2] This direction of addition can be rationalized in terms of the strong electron-withdrawing influence of the carbonyl group, especially when protonated by the mineral acid catalyst.[2]

It has been reported that 3-methyl-3-buten-2-one (isopropenyl methyl ketone, **1**) behaves abnormally in this reaction, yielding 3-hydroxy-3-methyl-2-butanone (**2**) instead of the anticipated 4-hydroxy-3-methyl-2-butanone (**3**).[3] The formation of this unexpected product has been explained in terms of a possible methyl migration in **1** subsequent to protonation,[3] or of Markovnikov addition of water to the enolic form of **1**.[4]



1 **2** **3**

Since there appeared to be no compelling reason why **1** should be hydrated in this unusual manner, we have carefully reinvestigated the reaction, and our findings show that in fact the sole product of the addition (aside from polymeric material and unchanged ketone) is the expected 4-hydroxy-3-methyl-2-butanone (**3**). None of the isomeric ketol **2** could be detected.

3-Methyl-3-buten-2-one (**1**) was prepared by reaction between ethyl methyl ketone and formaldehyde,[5] leading to **3**, the ir and nmr spectra of which (see Experimental Section) were in complete agreement with the assigned structure; dehydration of the ketol with anhydrous oxalic acid[6] afforded **1**. The structure **1** was in harmony with its spectral properties, and the melting points of the 2,4-dinitrophenylhydrazones of both ketol and enone were in agreement with values in the literature (see Experimental Section).

The hydration of **1** was effected at 100 and at 50°, by simply mixing the ketone and 2 *N* sulfuric acid and heating under reflux at these temperatures. At the higher temperature the major product was polymeric material; volatile material consisted of unchanged ketone and 4-hydroxy-3-methyl-2-butanone (**3**), separable by fractional distillation and identified by their 2,4-dinitrophenylhydrazones and by comparison of their ir and nmr spectra with those of authentic specimens. Glc of the volatile product showed three peaks; two of these had retention times identical with those of authentic samples, and the third small peak was not identified. There was no peak corresponding to 3-hydroxy-3-methyl-2-butanone. At 50° for a longer period a similar result was obtained, except that there was very little polymeric material formed, and most of the ketone was recovered unchanged. Two glc peaks were observed with the volatile product; these corresponded exactly in retention times with unchanged ketone and 4-hydroxy-3-methyl-2-butanone. Neither of the peaks corresponded with 3-hydroxy-3-methyl-2-butanone, which could not be detected in the product.

We conclude that the hydration of isopropenyl methyl ketone occurs in the expected manner, to yield 4-hydroxy-3-methyl-2-butanone (**3**). It would seem almost certain that this was also the product encountered in the original report,[3] since the 2,4-dinitrophenylhydrazone of the product there described had mp 192°, which coincides with that of isopropenyl methyl ketone, and 4-hydroxy-3-methyl-2-butanone is known to yield this derivative under the acid conditions normally used for 2,4-dinitrophenylhydrazone formation.[7] Further, 3-hydroxy-3-methyl-2-butanone (**2**) with 2,4-dinitrophenylhydrazine in alcoholic acid media yields not the simple derivative, but that of the *O*-alkyl ketone $CH_3CO(CH_3)_2OR$.[8] Finally, the *p*-nitrobenzoates of both isomeric alcohols **2** and **3** were prepared. The former had mp 123–123.5°, as opposed to the reported[3] value of 194°, and the latter had mp 54°, in agreement with that reported.[5]

Experimental Section

Gas chromatography was conducted on a Carbowax column at 150°, on an F and M Model 810 apparatus. Nmr measurements were carried out using a Hitachi Perkin-Elmer R-24 Instrument, in deuteriochloroform solution, and using TMS as internal standard. Analyses are by Galbraith Laboratories, Inc., Knoxville, Tenn.