The identity of the above signals was established by adding a small amount of each compound to the hot solution and observing the signal grow in intensity. Benzyl chloride and o-chlorotoluene were also identified by their gc retention times on a 20% SE-30 on 40/60 Chromosorb W column. In addition to the above CIDNP signals, strong polarizations in the aromatic proton region and weak polarizations in the aryl methyl region were observed.

Thermolysis of Benzoyl Peroxide with Toluene in HCA Solution. CIDNP from an HCA solution of 60 mg of benzoyl peroxide and 25 mg of toluene was measured at 115° in the manner described above. The methylene protons of 6 exhibited strong emission signals in this sample.

Registry No.—1, 22904-44-5; 2, 2154-56-5.

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Ring Opening of Indene Oxide with Benzoic Acid[1]

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A stereochemical study on the ring opening of indene oxide with benzoic acid was recently reported by Gagis, Fusco, and Benedict.[2] We find that in addition to trans-1,2-indandiol, cis-1,2-indandiol[3] is also formed on hydrolysis of the hydroxy benzoates initially produced. A third product, not hitherto reported in this context, is 2-indanone, which is formed concurrently with the hydroxy benzoates and can be isolated directly from the reaction mixture.[4] This parallels our findings for the reaction of indene oxide with formic acid in chloroform where the cis and trans esters together with 2-indanone are formed in a ratio of about 2:2:1.[5] The least equivocal evidence for the simultaneous formation of the cis and trans benzoates we think lies in the appearance of the nmr doublets at δ 6.32 and 6.17 in the raw reaction mixture. These must almost certainly be assigned to the C_1 proton in the benzoates from the analysis of analogous compounds by Rosen, et al.[6]

These results give credence to a carbonium ion or ion-pair mechanism in which positive charge is localized on the benzylic carbon. The formation of both cis and trans benzoates can be associated with the susceptibility of such a benzylic carbon to attack on either side of the ring. The formation of 2-indanone may be attributed to hydride ion transfer.

Our work supports that of Brewster,[7] and of Berti and Bottari.[8]

Experimental Section

All melting points were taken on a Mel-Temp apparatus and are uncorrected. Infrared spectra were taken on a Beckman IR-5 spectrophotometer as Nujol mulls. Nmr spectra were obtained on a Varian A56/60 spectrometer, using tetramethylsilane in $CHCl_3$ as an external standard.

Preparation of Chloroform.[9] To remove the ethyl alcohol which is present as a preservative, 250 ml of Fisher certified grade chloroform was washed with three 100-ml portions of concentrated sulfuric acid followed by 100-ml portions of water until the washings were neutral to litmus. The chloroform was dried over anhydrous calcium chloride and distilled. The chloroform was further dried by passing over Linde 4A molecular sieve just before using.

Preparation of Indene Oxide (1). A solution of 100 g of indene bromohydrin (prepared by the method of Suter and Milne)[10] in 900 ml of 95% ethanol was cooled to 5°. To this was added slowly, with stirring, 55 g of 85% potassium hydroxide in 95% ethanol, keeping the temperature below 10°. The reaction mixture was poured over 2000 g of ice and the crude indene oxide was taken up in ~200 ml of diethyl ether, washed twice with water, and dried over anhydrous sodium sulfate. After removal of the ether on a rotary evaporator the crude oxide was sublimed at 5 Torr with a cold-finger temperature of 0–10°: mp 30–31°; ir 1230, 1005, 986 cm^{-1} (lit.[11] mp 31°).

Reaction of Indene Oxide with Benzoic Acid. A solution of 0.037 mol (4.88 g) of 1 and 0.037 mol (4.51 g) of benzoic acid in 60 ml of chloroform was allowed to stand for about 72 hr at room temperature (25°). The solution was washed with 50 ml of 10% sodium bicarbonate twice and with 50 ml of water and dried over anhydrous sodium sulfate. The chloroform was removed on a rotary evaporator at about 50° and the product was transferred to a sublimation apparatus. Sublimation of the viscous liquid at 5 Torr and with a cold-finger temperature of 0–10° gave in about 3 hr 0.4 g of colorless crystals (2) and a residue of 5.3 g of a viscous liquid. Nmr analysis (CCl$_4$) showed that the separation of indanone was incomplete.

Identification of 2 as 2-Indanone. The nmr spectrum showed only two resonances at δ 7.11 and 3.32 (CCl$_4$). The melting point was 56–56.5° (lit.[11] mp 57–59°); 2,4-dinitrophenylhydrazone mp 196.5–197.5° (lit.[6] mp 198–198.5°).

Saponification of Benzoate. The 5.3 g of liquid from the reaction of indene oxide with benzoic acid was treated under reflux with 1.3 g of potassium hydroxide in 50 ml of 95% ethanol. The solution quickly turned dark brown and a precipitate gradually formed. After 3 hr the precipitate was removed by filtration,[12] 50 ml of water was added, and the solution was extracted with four 100-ml portions of diethyl ether. The extract was washed with water, dried over anhydrous sodium sulfate, and evaporated to dryness in a rotary evaporator at about 50°. The solid so obtained was recrystallized from benzene, after treatment with Norite, to yield 1.6 g (40.5%) of 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] The mother liquor from the recrystallization was evaporated to a viscous liquid which on sublimation at 90° and 5 Torr gave 0.4 g (6.2%) of colorless crystals, mp 92–93°. The ir spectrum of this material was identical with that of authentic sublimed cis-1,2-indandiol (mp 93–95°) obtained by the method of Rosen, et al.[6]

Nmr Spectrum of Reaction Mixture. A sample of the reaction mixture was withdrawn after about 72 hr and the nmr spectrum (CHCl$_3$) was obtained on the untreated mixture: δ 8.12 (m, ArH), 7.4 (m, ArH), 6.7 (m), 6.32 (d), 6.17 (d), 5.7–4.5 (m), 3.51 (s), 3.3 (m). The relative intensities of the doublets at δ 6.32 and 6.17 and the singlet at δ 3.51 were estimated from the peak heights and half-widths to be roughly in the ratio 15:115:200, respectively. The overall spectrum was that expected from the work of Rosen, et al.[6]

Reaction of Indene Oxide with Benzoic Acid.[13] A solution of 0.0378 mol (5.0 g) of 1 and 0.0420 mol (5.13 g) of benzoic acid in 60 ml of chloroform (purified only by distillation and passing over Linde 4A molecular sieve) was allowed to stand for 72 hr at room temperature (25°). The solution was washed with a 5% sodium bicarbonate solution and then with water, dried, and concentrated on a rotary evaporator at about 50° to yield 9.21 g of an oily liquid which proved difficult to crystallize. Sublimation of the viscous liquid at 5 Torr with a cold-finger temperature of 0–10°, water-bath temperature of 35–40°, gave in about 3 hr 0.40 g of colorless crystals (2) and a residue of 7.75 g of a viscous liquid.

Reduction of Benzoate. A 250-ml two-necked round-bottomed flask was fitted with a reflux condenser, a dropping funnel, a magnetic stirrer, and a heating mantle. In the flask were placed 2.0 g of pulverized lithium aluminum hydride and 50 ml of tetrahydrofuran which had been dried over lithium aluminum hydride and distilled. A solution of the 7.75 g of residue from the sublimation apparatus in 20 ml of dry tetrahydrofuran was then added slowly

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.

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(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.
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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

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.

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.

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.
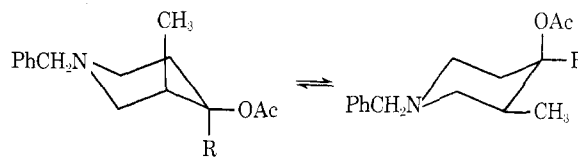
3-axial   3-equatorial

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