Experimental

The proton nmr spectra were determined on a Varian HR 220-MHz spectrometer in $CDCl_3$ using tetramethylsilane as an internal reference. The chemical shifts are accurate to ±0.02 ppm. The ^{13}C spectra were obtained on a Varian XL-100 spectrometer equipped with a Digilab Fourier transform accessory, using the same solvent and reference. Chemical shifts are accurate to ±0.05 ppm.

Preparation of the Diols. Compound **1** was prepared by hydroboration of 3-methylcyclohexenone as described by Klein and Dunkelblum, mp 39–40° (reported[2] mp 39–40°).

The trans,cis diol **2** was prepared by oxidation of 3-methylcyclohexene with 30% hydrogen peroxide–90% formic acid as described for *trans*-1,2-cyclohexandiol.[17] The crude diol was crystallized from hexane and recrystallized from isooctane, mp 94–95° (reported[2] mp 91–92°). The cis,trans diol **4** was prepared by OsO_4–H_2O_2–*tert*-butyl alcohol oxidation of 3-methylcyclohexene as well as from the solvolysis of the dibromide (prepared by brominating the olefin in carbon tetrachloride at 0°) with silver acetate in acetic acid–water. The diol crystallized from hexane–ethyl acetate, mp 81–82° (reported[15] mp 81–82°).

The monobenzoate **9** and **11** were obtained by reaction of equimolar quantities of **2** or **4** and benzoyl chloride in pyridine. The monobenzoate was purified by chromatography on silica gel, yielding an oil whose proton and ^{13}C nmr spectra were consistent with the structure assigned.

The benzoate **8** was prepared from *cis*-3-methylcyclohexanol as described for **9**: ^1H nmr δ 5.00 (q, J = 3.5, 6.5 Hz), 4.00 (m), 0.98 (J = 7 hz).

The cis,cis isomer **3** was prepared using a procedure similar to that of Garanti and Marchesini[3] in which 3-methylcyclohexane-1,2-dione[16] was hydrogenated in ethanol over PtO_2. Nmr spectra of the crude diol showed it to be a mixture of cis,cis and cis,trans diols. The diol mixture, 3.783 g (2.9 mmol), was treated with benzoyl chloride, 4.51 g (3.2 mmol), in 25 ml of pyridine overnight at room temperature. The reaction mixture was poured into dilute HCl, extracted into ether, washed with aqueous $NaHCO_3$, dried, and concentrated to yield 6.569 g (97%). The monobenzoate **10** was crystallized from methanol–water to yield 4.05 g (62%): mp 82–83°; ^1H nmr δ 4.92 (m, J = 11.4, 4.8, 2.6 Hz), 3.92 (t, J = 2 Hz). *Anal.* Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.66; H, 7.61.

The monobenzoate (6.9 g) was hydrolyzed by refluxing in 50 ml of methanol, 2.5 g of KOH, and 10 ml of H_2O followed by extracting into ethyl acetate. The diol was crystallized from hexane–ethyl acetate, mp 64–65°. *Anal.* Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.37; H, 10.91.

Registry No.—**1**, 15806-70-9; **2**, 19700-12-0; **3**, 52730-58-2; **4**, 19700-14-2; **5**, 5454-79-5; **6**, 1460-57-7; **7**, 7443-52-9; **8**, 52699-45-3; **9**, 52748-17-1; **10**, 52759-91-8; **11**, 52759-90-7.

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Proton Magnetic Resonance and Stereochemical Assignments of Polycyclic Ketones and Olefins. Relative Double Bond Shielding Strengths

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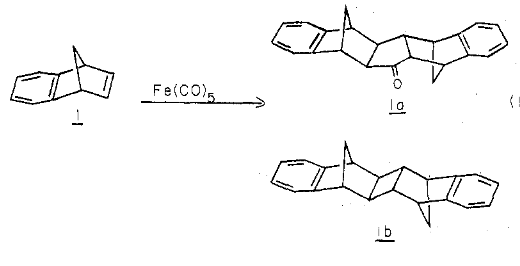
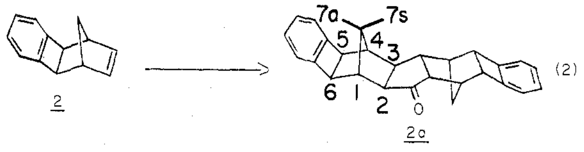
The proton magnetic resonance assignments of a series of related polycyclic cyclopentanones and their precursor olefins are compared. Stereochemical assignments are based upon observed coupling constants between bridgehead and cyclopentanone protons with iron pentacarbonyl induced coupling leading to exo-trans-exo products. The strengths of the shielding cones of ketonic and olefinic linkages are compared.

Recently, reports[1,2] of iron carbonyl coupling of olefins leading to cyclopentanone derivatives of the type illustrated in reactions 1, 2, and 3 have appeared and the mechanism[3] of this reaction considered. A particularly important aspect of the reaction, both synthetically and as it relates to mechanistic considerations, is product stereochemistry. Olefin reactivity and product stereochemistry are sensitive to the presence of bulky groups[1a] and complexing groups[2a] at the 7 position of **1** with significant stereochemical changes being observed when 7,7-dimethoxybenzonor-





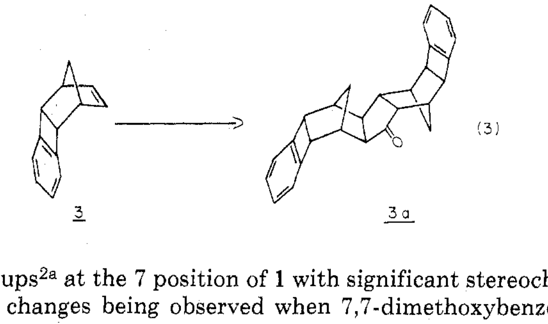


Table I
Chemical Shift (τ) and Coupling Constant[a] (Hz) Assignments

	Compound		
Proton	**1**	**2**	**3**
Aromatic	2.92, $J_{1,2} = 2.0$	2.76, $J_{1,2} = 1.7$	3.06, $J_{1,2} = 1.9$
1,4	6.17, $J_{1,7} = 1.6$	7.22, $J_{1,7a} = 2.0$	7.05, $J_{1,7} = 1.4$
2,3	3.25, $J_{2,7a}$ (vs)	3.84, $J_{2,7a}$ (vs)	4.38, $J_{5,7s} < 1.0$
5,6	$J_{7a,7s} = 8.0$	6.82, $J_{5,7s}$ (vs)	6.31, $J_{7a,7s} = 8.4$
7a	7.83	9.12, $J_{7a,7s} = 9.0$	8.39
7s	7.70	8.71	8.08
	1b	**2a**	**3a**
Aromatic	2.90, $J_{1,7s} = 1.5$	2.84, $J_{2,3} = 7.5$	2.87, $J_{2,3} = 7.9$
1	6.85, $J_{7a,7s} = 9.5$	7.46, $J_{7a,7s} = 11.0$	7.40, $J_{1,6} \sim 4.5$
2	8.31	7.87	8.29, $J_{7a,7s} = 10.5$
3	8.31	8.11	8.85
4	6.85	7.64	7.67
5,6		6.75	6.47
7a	8.42	9.16	8.58
7s	7.98	9.16	8.77

[a] vs = very small but observable.

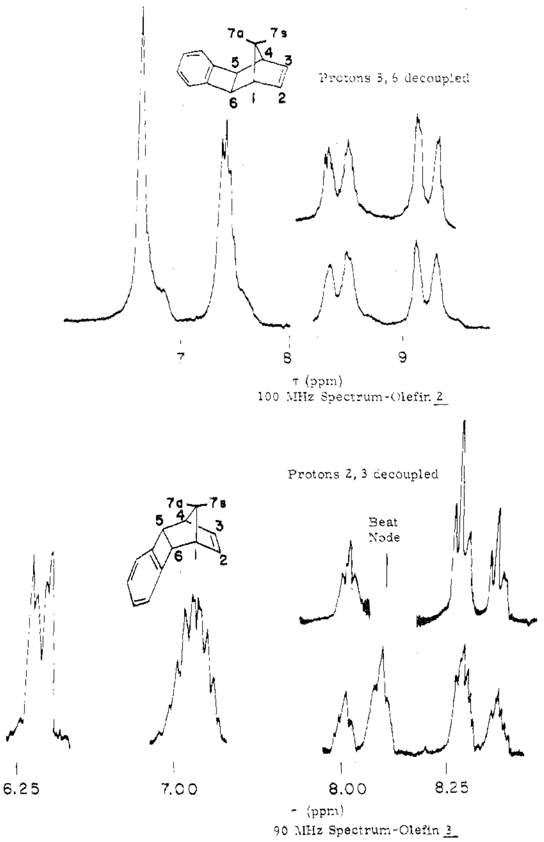


Figure 1. Olefin spectra. Aromatic and olefinic regions not shown.

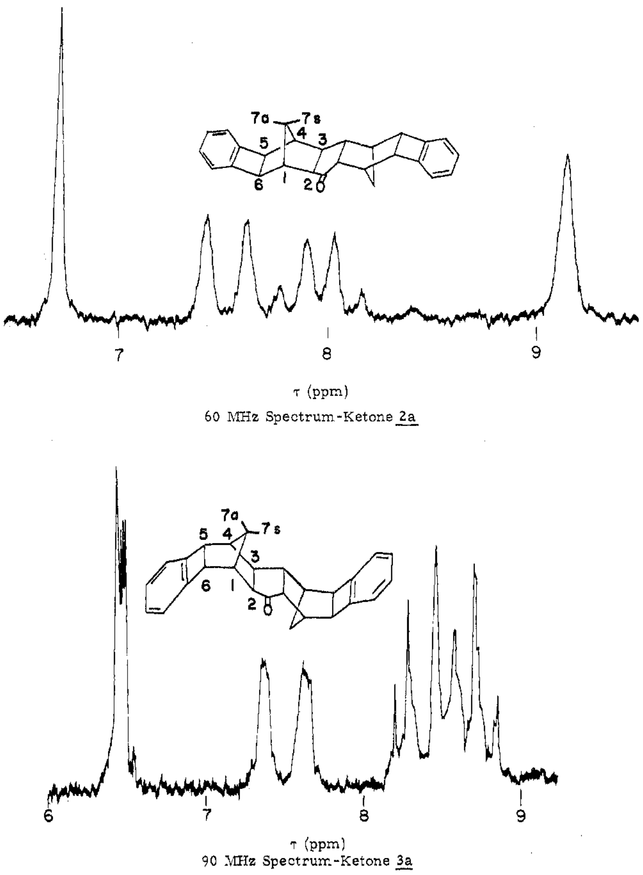


Figure 2. Ketone spectra. Aromatic and olefinic regions not shown.

bornadiene rather than 1 is the reactive olefin. It is remarkable[2b] that norbornen-5-one-2 yields but one isomer.

In the following discussion we present the data and arguments which lead to the conclusion of the stereochemical assignments illustrated in reactions 2 and 3. Proton magnetic resonance assignments appropriate to reactions 2 and 3 are compared to those of reaction 1. The indicated series of seven compounds permits one to draw conclusions regarding the effect of ring strain and relative shielding strengths of olefinic and carbonyl bonds on chemical shifts.

Results and Assignments

Chemical-shift assignments along with available coupling constants are reported in Table I. Partial assignments have been previously reported for olefins[4] 2 and 3 as well as for dimer **1b**;[5] to the extent that interpretations overlap, our conclusions agree with literature assignments. Compound **1a** has been reported.[1,2a] Representative spectra are shown in Figures 1 and 2.

The spectrum of olefin 2 is relatively simple. Protons 5 and 6 appear as a slightly broadened singlet at τ 6.82 only minimally coupled to the 1,4-bridgehead protons as predicted by the Karplus[6] relation for endo protons. When the 5,6 protons are exo to the norbornyl ring as in **3**, they are more strongly coupled to protons 1 and 4 causing the resonance assigned to the 5,6 protons of **3** to be significantly split. In each case, bridgehead protons 1,4 are coupled to bridge protons 7a and 7s with coupling constants of 2 Hz or less and are further coupled to the olefinic protons. Thus, the multiplet assigned to the 1,4 protons of olefin **3** at τ 7.05 shows additional complexity in comparison to that of olefin **2**. Coupling between protons 1,4 on the one hand and 2,3 on the other is apparent in the triplet character of olefinic resonances.

Assignments of protons 7a and 7s for **2** and **3** result from decoupling studies and from the observation of relative complexity of the 7a,7s AB pattern. Long-range (W rule) coupling between 7a and 2,3 is expected to be sufficient to complicate the resonance of the 7a portion of the AB pattern beyond that which would occur from coupling of the 7a,7s protons to the 1,4 protons alone. Long-range coupling between the 5,6 protons and 7s is to a large extent determined by molecular geometry. Such coupling will not be observable for exo protons, as in **3**, but is expected to be significant when the 5,6 protons are endo as in **2**. The high-field portion of the AB pattern of **3** shows the greater complexity of the two portions and is assigned to the 7a proton. Irradiation of the 2,3 protons (Figure 1, 90 MHz, olefin **3**) removes long-range coupling between protons 2,3 and 7a, degrading the high-field portion to a pattern of triplets arising from coupling between 1,4 and 7. The low-field portion of the AB pattern is thus assigned to the 7s proton. Irradiation of protons 2,3 of compound **2** induces loss of complexity of the high-field portion of the AB pattern while irradiation of the 5,6 protons (Figure 1) reduces the complexity of the low-field portion. Thus, the high-field portion of **2** is assigned to the 7a proton and the low-field portion to the 7s proton.

With the help of decoupling and shift reagent data, pmr resonance assignments observed for ketones **2a** and **3a** are quite straightforward, typical spectra being shown in Figure 2. Once again, when exo, as in **3a**, the 5,6 protons are characterized by a multiplet resulting from strong coupling to the 1,4-bridgehead protons. This is to be contrasted with the endo 5,6 protons of **2a**. As coupling between the 1,4 protons and the 2,3 protons of all three ketones is also unobserved, the 2,3 protons must be endo, as illustrated.

The AB pattern centered at τ 7.99 for ketone **2a** is assigned to the cyclopentanone ring protons, an assignment confirmed by the observation that the lower field portion of this pattern is the most sensitive resonance in the spectrum to the presence of Eu(fod)$_3$. This experiment also confirms the differentiation between protons 2 and 3. While certainly expected, the observed 2,3 coupling constant of 7.5 Hz confirms cis fused rings. Finally, the presence of a C_2 symmetry axis in the molecule, implied by the simplicity of the spectrum, leads to the exo-trans-exo stereochemistry illustrated in reaction 2. The possibility of exo-cis-exo stereochemistry is excluded on the basis of steric hindrance and analogy arguments presented in previous communications.[1]

The accidental magnetic degeneracy of 7a and 7s in **2a** may be lifted by addition of Eu(fod)$_3$, the chemical shift of 7s being more sensitive to shift reagent than that of 7a as a consequence of its greater proximity to the europium coordination site. Upon addition of the shift reagent, the reported 7a,7s coupling constant of 11.0 Hz is observed. Differentiation between resonances resulting from protons 1 and 4 of **2a** also derives from relative motion of chemical shifts of these protons in the presence of the shift reagent although one would certainly anticipate the appearance of 1 at lower field than 4 since it is closer to the electron-withdrawing carbonyl group.

Assignment of resonances to protons 1 and 4 of ketone **3a** is straightforward with the lower field resonance being assigned to proton 1; however, because cyclopentanone ring protons 2,3 and bridge protons 7a,7s resonate in the same region (between τ 7.40 and 8.85), differentiation of these proton resonances required a quantitative shift reagent study. Assignments are based upon relative slopes of the linear chemical-shift change *vs.* added shift reagent plots in combination with decoupling and coupling constant results. Proton chemical-shift sensitivity to shift reagent was observed to be in the order: $2 > 1 > 7s > 3 > 4 > 7a > 5,6$. The coupling constant of 4.5 Hz reported for the interaction of protons 1 and 6 (as well as 4 and 5) is estimated from the splitting of the 1 and 4 protons in the presence of large amounts of shift reagent. While probably a good estimate, this value is not to be taken literally due to the fact that protons 5 and 6 are undoubtedly strongly coupled to one another as well as to 4 and 1. Nevertheless, this coupling constant is consistent with the 5,6 protons being exo to the norbornyl ring. Arguments entirely analogous to those described for **2a** lead to the stereochemistry illustrated in reaction 3.

Previously reported[5] pmr assignments of hydrocarbon dimer **1b** did not include differentiation of the 7a and 7s protons. Our assignments, reported in Table I, are similar to literature assignments with the addition of 7a,7s differentiation. While the geometry is correct for long-range coupling between 2,3 and 7a, no such coupling may perturb proton 7s, implying that the 7s resonance should be less complex than that of 7a. Although the low-field side of the high-field portion of the 7a,7s AB pattern is partially buried under the 2,3 resonance at 90 MHz, the high-field side is readily observed. Comparison of this resonance with the corresponding side of the low-field portion of the AB pattern shows it to be somewhat broadened and less well resolved. Thus, the high-field portion is subject to coupling beyond coupling to 1,4 and is assigned to proton 7a. This assignment may be compared to that of ketone **1a**. One would expect the carbonyl group to significantly shield the 7s proton in **1a** with respect to **1b** while not strongly affecting proton 7a; the assignment is at least consistent with this expectation.

Discussion

In general, addition of the rigid, planar[7] five-membered ring to any of the olefins induces diamagnetic shielding, the one exception being the 5,6 protons of **2** → **2a**. The average resonance of these protons is slightly (0.07 ppm) deshielded, a long-range effect presumably resulting from ring conformation modifications. Of significance is the observation that the relative shielding parameters of 7a and 7s are reversed in the ketonic coupling products from the corresponding olefins. A strong contribution to this reversal from the 2′–3′ single bond or from the 2′,3′ protons acting on 7s may be immediately ruled out by observing that, while a similar affect might be expected from these interactions in **1a** and **1b**, the relative shielding of 7a and 7s in **1b** is the same as in **1**. Thus, the shielding cone of the carbonyl group is dominant in establishing 7s at higher field than 7a, as is certainly expected.

One may estimate the effect of the carbonyl group on 7s for each of the three ketones if one assumes that the effect of the carbonyl group on 7a is minimal, that the diamagnetic shift of the 7a protons in progressing from olefins to ketones is a consequence of addition of the strained ring, and that the ring strain effect will be the same on 7a and 7s. The range of values thus calculated is less than 0.2 ppm. While this calculation is approximate at best, it does indicate that the 7s proton is being strongly and similarly shielded by the carbonyl function in each case.

It is interesting to note that the syn methyl group of the isopropyl bridge of β-pinene is shielded with respect to the same methyl group of α-pinene by 0.13 ppm. This has been interpreted[8] as arising from the fact that the syn methyl group lies closer to the C_2 axis of the double bond for the β isomer than for the α isomer. The external double bond is more effective at shielding the syn methyl group than is the internal double bond.

A related contrast may be drawn between the shielding of 7s by a carbonyl group as in the three ketones under consideration and an olefinic double bond as in the three corresponding olefins. As reversal of relative chemical shifts occurs between these two systems, it appears that the carbonyl shielding cone is far more effective at influencing the 7s proton than is the olefinic double bond. Exact quantitative shifts for the series of compounds in question comparable to that mentioned for the pinene isomers cannot be determined due to the structural insertion of the five-membered ring. Nevertheless, the estimated shifts lie between 0.3 and 0.5 ppm, values well in excess of the symmetry effect observed for the pinenes. Although there is undoubtedly a contribution to this enhanced shielding from the greater proximity of the 7s proton to the double bond C_2 axis in the ketone system than in the olefin system, the change is too great to be explained on this basis alone. Hence we conclude that the carbonyl shielding cone is the stronger of the two.

The shielding effect of the aromatic ring current is observable from the relative chemical shifts of the 2,3 protons for ketones **2a** and **3a**. Disposal of the ring so as to shield these protons induces a diamagnetic shift in proton 2 of 0.42 ppm, a shift not far different from the 0.54-ppm diamagnetic shift observed for the 2,3 protons of the olefins; however, the difference observed is of opposite sign to that expected from the relative geometries of the two compounds. In all likelihood, the small ring shielding of 2 is a consequence of this proton already being strongly affected by the shielding cone of the carbonyl function. The electron density at proton 2 is thus primarily influenced by the ketone and is not subject to substantial further change. The observation of a greater shift (0.74 ppm) for proton 3 is consistent with this presentation.

An inverse but similar effect may be active in bringing about the magnetic equivalency of 7a and 7s in ketone **2a**. Proton 7a is already strongly affected by the aromatic ring in 2 and is not subject to significant shielding upon introduction of the five-membered ketone ring. On the other hand, 7s is much more weakly influenced by aromatic ring current and may be strongly influenced by the carbonyl group thus bringing it into degeneracy with 7a. Consistent with this argument is the observation that both 7a and 7s are shifted to a greater degree between **3** and **3a** than between **2** and **2a**.

Experimental Section

All synthetic procedures have been previously described and the physical properties of the compounds reported. Olefin **1** was prepared according to Wittig and Knauss,[9] olefin **2** according to Simmons,[4] and **3** according to Cava and Mitchell.[10] *o*-Fluorobromobenzene was purchased from Aldrich Chemical Co. and solvents were distilled prior to use. As implied by previous workers, the preparation of **2** leads to a mixture of products which codistill and which are difficult to separate. We employed liquid chromatography (Waters Associates, Milford, Mass.) to effect purification of **2** using four 2 ft × ⅜ in. lengths of Porasil A and eluting with hexanes (Fisher Scientific, ACS, certified reagent). Six passes for a total of 48 ft of column *via* recycling procedures were necessary to effect base-line separation of the six-component mixture obtained from distillation. After three passes, the first three components were removed so as to prevent remixing. Components 4, 5, and 6 were dominant (differential refractometer) with 4 being the desired olefin. Flow rates of 5 ml/min and initial retention times of slightly in excess of 50 ml were observed. The column dead volume was found to be approximately 48 ml.

Nuclear magnetic resonance spectra were obtained in $CDCl_3$ against an internal TMS standard. Spectra were observed on Varian A60A, Brucker 90-MHz, and Jeol 100-MHz instruments.

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Registry No.—**1**, 4453-90-1; **1b**, 10026-43-4; **2**, 27297-14-9; **2a**, 51799-95-2; **3**, 27297-13-8; **3a**, 51830-09-2.

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