hydroxyl group and the nitrogen lone pair for the convenient inversion at the nitrogen. (For stereochemical figures see ref 3.)

The chemical shift curves show that in the trans isomer the δ_1 proton is characteristically less high field shifted than δ_2 at basic pH, whereas in the allo isomer both protons are nearly equally shifted as H_{δ_2}. In the allo isomer the β_2' proton is more high field shifted than the β_1' one at basic pH.

For the THP we have shown that in neutral solution[1] the carboxyl group is nearly coplanar with the plane defined by C^O, C^α, and N (as it is in the zwitterion crystal[5]). The trend of the curves shows that this is also true at acid pH's, but, in alkaline solution as shown by the consistent low field shift of the δ_1 proton with respect to the δ_2 proton, the carboxylic plane must pass roughly through the δ carbon. The increase of the dihedral angle (C^OOO^-, $C^OC^\alpha N$) with the pH would result from a change in the equilibrium between alternative repulsive and attractive interaction of the COO^- with the nitrogen lone pair and the NH proton, respectively. This is consistent with the behavior of the β protons which implies that the carboxyl group is nearly perpendicular to the plane defined by H_{β_1}, C_β, and H_{β_2}; the β_2 proton is high field shifted with respect to the β_1 proton, whose chemical shift is nearly constant along the whole pH range.

The magnitude of the observed chemical shift anisotropy is greater on the β than on the δ geminal proton pair as expected from its distance dependence.

For AHP the chemical shift data indicate that the carboxylic plane passes roughly through the γ-carbon at acid and neutral pH, whereas at alkaline pH it rotates slightly toward the amino group. After this rotation the carboxylic plane becomes more perpendicular to the β-carbon; the β_2 proton is high field shifted with respect to the β_1 proton. The δ protons remain roughly in the carboxylic plane; the δ_1 is low field shifted with respect to the δ_2 proton, the chemical shift difference between them increasing with the pH. This is again satisfactorily consistent with a hydrogen bond between the hydroxyl and the carboxyl groups in acid and neutral solution, whereas in alkaline solution another intramolecular hydrogen bonding possibility occurs between the hydroxyl group and the nitrogen lone pair for the convenient inversion at the nitrogen.

A further effect of this intramolecular hydrogen bond may appear in the upfield position of the γ' (and perhaps of the α') curve (allo isomer) with respect to the corresponding curve of the trans compound.

Thus, the chemical shift curves contain more information than expressed by their obvious interpretation as titration of the charged groups. They contain finer intramolecular chemical shift data which reflect structural features as the torsion angle of the carboxylic plane. Of course the reported purely qualitative interpretation should be supported by quantitative analysis. This would require data on the charge distribution in the molecule for the different ionization states and the calculation of the carboxyl anisotropy.

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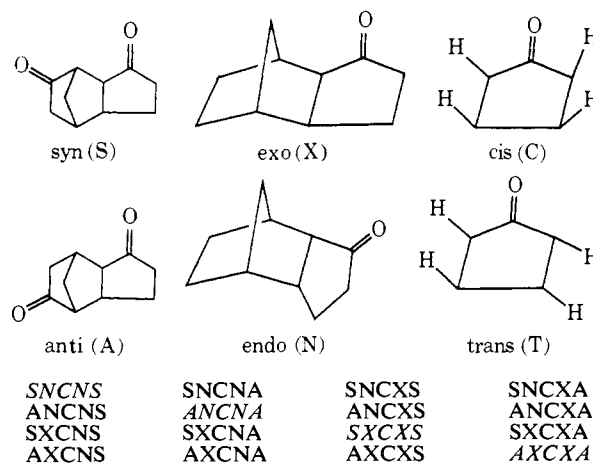
Stereochemistry of the Reaction of Strained Olefins with Iron Carbonyls
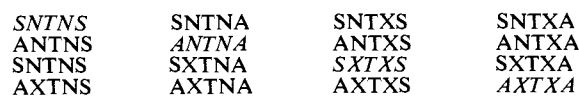
Sir:

In order to delineate further the stereochemical features of the iron carbonyl–olefin reaction that produces carbonyl-inserted dimers,[1] we have selected norbornen-5-one-2[2] as a substrate. With alkyl substitution at the 5- and 6-positions of norbornene, exo-trans-exo adducts are obtained,[1,3] while the presence of methoxy substituents on the 7-position leads to the exclusive formation of an adduct with exo-trans-endo stereochemistry.[1] Norbornenone was chosen for this study because the carbonyl group distinguishes the front from the rear. Furthermore, the homoconjugation present in the molecule, as gauged by the difference in cmr shifts between C-5 and C-6, *viz.*, 12.2 ppm, might help the metal to discriminate between insertion of CO at C-5 or at C-6.

When norbornen-5-one-2 (R,S) is treated with $Fe(CO)_5$ in refluxing *n*-heptane for 48 hr, a white crystalline solid (mp 236–237°) is isolated in 15% yield. The formula $C_{15}H_{16}O_3$ is deduced from the molecular peak in the high-resolution mass spectrum (calcd m/e 244.1099; obsd m/e 244.1113). Carbonyl bands are present in the infrared spectrum at 1725 and 1745 cm^{-1}.

The 36 stereoisomers that can be seriously envisaged are presented below in matrix form, according to whether they belong to the syn (S) or anti (A) series, with exo (X) or endo (N) substitution, and with a cis (C) or trans (T) cyclopentanone central ring

syn (S) exo (X) cis (C)

anti (A) endo (N) trans (T)

SNCNS	SNCNA	SNCXS	SNCXA
ANCNS	*ANCNA*	ANCXS	ANCXA
SXCNS	SXCNA	*SXCXS*	SXCXA
AXCNS	AXCNA	AXCXS	*AXCXA*

cis series, four *meso* isomers plus six pairs of enantiomers

SNTNS	SNTNA	SNTXS	SNTXA
ANTNS	*ANTNA*	ANTXS	ANTXA
SNTNS	SXTNA	*SXTXS*	SXTXA
AXTNS	AXTNA	AXTXS	*AXTXA*

trans series, four pairs of enantiomers with a C_2 *axis* plus six pairs of enantiomers.

We were greatly helped in the elucidation of this stereochemical maze by the observation that the 300-MHz pmr spectrum is made of eight multiplets, each corresponding to two protons, and that the cmr spec-

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(2) P. K. Freeman, D. M. Balls, and D. J. Brown, *J. Org. Chem.*, **33**, 2211 (1968).
(3) J. Mantzaris and E. Weissberger, *Tetrahedron Lett.*, 2815 (1972).

Table I. Nmr Spectra of the Adduct

	H-1	H-3x	H-3n	H-4	H-5	H-6	H-7s[a]	H-7a
Pmr (CDCl₃, δ ±0.01 ppm) ($|J|$, ±0.1 Hz)	2.87 $^2J_{3x,3n} = 18$; $^3J_{3x,4} = 4.5$;	2.14 $^2J_{7s,7a} = 11.5$ $^3J_{5n,6n} = 7.5$;	1.96 $^4J_{3n,7a} = 4$	2.77	2.23	2.48	1.69	1.50

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
Cmr (CDCl₃, δ ±0.1 ppm)	54.1	211.9	44.1	43.5 (or 48.9)	48.9 (or 43.5)	53.1	33.8	217.3

[a] Syn to the C-2 carbonyl.

trum contains only eight carbon resonances (Table I). It should be noted here in passing that cmr with its resolution is an extremely powerful tool for the identification of symmetrical structures. In this case, it rules out *all* the off-diagonal stereoisomers. Analysis of the ¹H spectrum at 300 MHz is straightforward; exo-exo substitution is indicated by the lack of observable coupling between the endo 5- and 6-protons and the bridgehead 1- and 4-protons.[4] A cis cyclopentanone is excluded because the vicinal $^3J_{5,5'}$ (or $^3J_{6,6'}$) coupling constant has an upper limit of 2 Hz as shown by computer simulation of the AA′BB′ system observed for the 5,5′- and 6,6′-protons.[5] Finally, it is possible to choose between the remaining SXTXS and AXTXA structures from the dipole moment; the calculated values are 4.7 ± 0.7 and 1.5 ± 0.5 D, respectively, while the measured[6] value is 4.6 ± 0.3 D.

The adduct formed is thus the SXTXS stereoisomer.
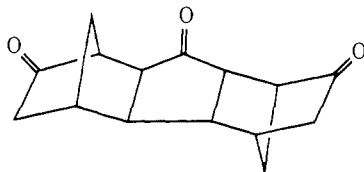
Outside of starting material and polymers, it is the only organic material we could isolate by column chromatography from the reaction mixture. Since (*R*,*S*)-norbornen-5-one-2 was used, the finding of the single pair of enantiomers (SXTXS, SXTXS) is equivalent to the statement that the (*R*) enantiomer of norbornen-5-one-2 combines only with another (*R*) enantiomer, and that the (*S*) enantiomer likewise recognizes another (*S*) enantiomer. This rather unusual observation of asymmetric induction at the level of the first organometallic complex formed is an important clue to the mechanism of the reaction. Further experiments are now in progress to test our working hypothesis of a trigonal bipyramidal intermediate or transition state with the two olefins as equatorial ligands, and the inserted carbonyl originating from an axial position.

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Reduction of α,β-Unsaturated Carbonyl Compounds by "ate" Complexes of Copper(I) Hydride

Sir:

We would like to report the results of our studies on the selective reduction of α,β-unsaturated carbonyl compounds by complexes of Cu¹H. Whitesides and San-Fillipo's initial studies showed that solubilized Cu¹H is capable of functioning as a reducing agent.[1] More recently, Masamune and coworkers demonstrated that a complex of Cu¹H can cleanly effect the reductive removal of halide and tosylate groups. However, the presence of aluminum salts clouds the exact nature of the reducing species.[2]

As a part of our program aimed at generalizing the preparation of enolate species containing copper,[3] we have prepared a series of "ate" complexes (1-3) analogous to the diorganocuprate alkyl transfer reagents prepared by Corey and Posner.[4,5] We anticipated that selective transfer of hydride in the 1,4 sense would occur, and this has been realized.

The Cu¹H was prepared free of other salts[1] and then solubilized utilizing the lithio derivative of the nontransferable ligand. This eliminates the necessity of dealing with additional solubilizing ligands which may interfere with subsequent purification procedures. The structure

$$\overset{+}{\text{Li}}\overset{-}{\text{CuHR}}$$

1, R = 1-pentyne
2, R = O-*t*-Bu
3, R = SPh
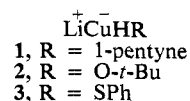
of the reducing species in this case is presumably similar

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(5) F. A. L. Anet, *Can. J. Chem.*, **39**, 2316 (1961); S. Forsén, B. Gestblom, R. A. Hoffman, and S. Rodmar, *J. Mol. Spectrosc.*, **21**, 372 (1966).
(6) According to G. Hedestrand, *Z. Phys. Chem.*, *Abt. B*, **2**, 428 (1929).