higher and lower oxidized analogues and suggest analogous modes of extrusion of the sulfur-containing species. Our data reopen the question as to the nature of sulfur monoxide formed initially in thiirane oxide decompositions, a question that may ultimately only be answered by spectroscopic means. Although the observed (albeit small) crossover in our experiments tends to point to a biradical mechanism involving production of ground state species, possibly involving a stereochemically rather rigid π-thiacyclopropane oxide "biradical" of the type proposed in thiirane decompositions,[13,21] a significant contribution of a concerted process cannot be ruled out at present.[24]

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(19) **1a:** *m/e* 78 (M^+, 73%), 62 (52%), 48 (100%); IR ν_{C-D} 2260, $\nu_{S=O}$ 1050 cm^{-1}. **1b:** *m/e* 78 (M^+, 75%), 62 (61%), 48 (100%); IR ν_{C-D} 2280, $\nu_{S=O}$ 1060 cm^{-1}. For NMR spectra, see the figure. Satisfactory elemental analyses were obtained.

(20) The pyrolysis products were collected in an IR–gas cell and compared with standard deuterated ethylene mixtures (98:2, 95:5, 90:10, 85:15). Every mixture was run at six different pressures (200, 100, 50, 25, 12, 6 mm) and the corresponding series of IR spectra compared with the series of spectra depicting pyrolysis product mixtures. Compound **1a** gave a 95:5 ratio of *cis*- to *trans*-dideuterioethylene; **1b** gave an analogous ratio of 10:90. These ratios were reproduced in several duplicate pyrolyses, involving three independently prepared samples.

(21) It is interesting to note in this connection that the activation energies[22] for cleavage of the first carbon–sulfur bond in acyclic dialkyl sulfides (72 kcal/mol), sulfoxides (~57 kcal/mol, this value is a reasonable estimate based on the mean bond dissociation energies in sulfoxides[22a] and activation energies for racemization of benzyl sulfoxides, corrected for benzyl-substitution[22b]), and sulfones (62 kcal/mol) reduce by different amounts (32, 22, 34 kcal/mol, respectively) when going to the corresponding three-membered ring species,[1,13,14] and that this kinetic destabilization is close to that encountered in the corresponding hydrocarbon system (cf. central bond in *n*-butane vs. cyclopropane, $\Delta E_a = 18$ kcal/mol)[23] only in the case of sulfoxides.

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(24) Attempts to trap a biradical intermediate with di(*p*-anisyl) thioketone[8] have produced formally disproportionated adducts. Thus, thiirane oxide and a fivefold excess of thioketone in refluxing toluene gave the ethylenedithioketal of di(*p*-anisyl)ketone (identified by mass, NMR, and IR spectral data, independent synthesis by thioketalization of the corresponding ketone, and Raney-Ni desulfurization to di(*p*-methoxyphenyl)methane[25]), and the corresponding sulfone (the structure is in accord with spectral data) in low yield. None of the expected dithiolane oxide was formed. The origin of these compounds is not clear and could be connected to possible redox chemistry of SO generated in solution.[3a,7c,26]

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Nitrogen Inversion in Piperidine

Sir:

Dynamic NMR spectroscopy has not hitherto been applied successfully to the axial-equatorial NH equilibrium in piperidine (1), despite intense interest in the subject.[1-4] This failure has generally been ascribed to a fast intermolecular exchange of the NH protons in I.[2,4,5] However, conditions where NH protons exchange is slow can be achieved at low temperature (<−10 °C) as shown by the broad NMR line of the NH proton of piperidine (treated with basic alumina) in $CHFCl_2$-CHF_2Cl solutions.[6] Previous workers have been able to obtain NMR spectra of secondary amines under nonexchanging conditions for 4,4-difluoropiperidine,[7] tetrahydro-1,3-oxazines,[5] 1-methyl-1,3-diazane,[5] aziridines,[8,9] and nortropane.[4] As is shown in the present work, the barrier to nitrogen inversion in I is quite low, thus requiring both very low temperatures and high magnetic fields for its successful study by dynamic NMR.

Carbon-13 NMR spectra of I at −100 to −172 °C are shown in Figure 1. The β-carbon resonance is quite broad at about −142 °C and gives rise to a doublet in the intensity ratio of 85:15 ($\Delta G° = 0.36$ kcal/mol) at −172 °C.[10] Since entropy differences between the two conformations are likely to be small, $\Delta G°$ should be nearly independent of temperature, and population ratios can be calculated to be 80:20 at −142 °C and 65:35 at 25 °C. From a line shape analysis at −142 °C, a first-order rate constant (major form to minor form) of 240 ± 20 s^{-1} is calculated. Using the absolute rate theory, we obtain a free energy of activation ($\Delta G^{\ddagger}$) of 6.1 ± 0.2 kcal/mol. The dynamic NMR behavior of I was reproducible in many different samples of I and was unchanged when basic alumina was added directly to the solution in the NMR tube. On the other hand, addition of a trace of CF_3COOH completely wiped out the dynamic NMR effect. The ^{13}C data clearly show that two conformations are present and these can only be the equatorial (I-E) and the axial (I-A) forms of piperidine (I). However, it is not possible on this evidence alone to determine which is the major conformation.

The free energy barrier for ring inversion in I is known to be 10.4 kcal/mol from ^1H dynamic NMR data,[11] so that ring

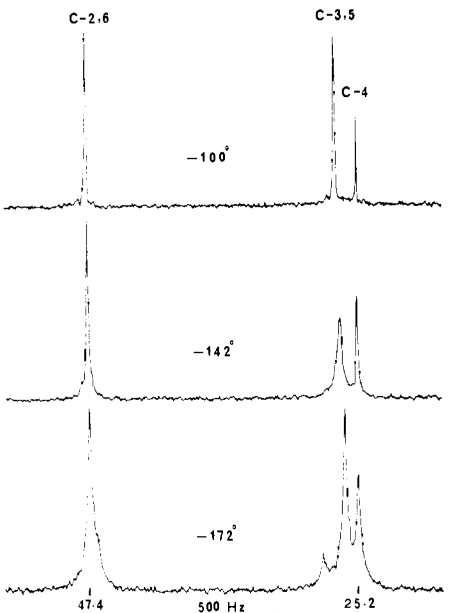
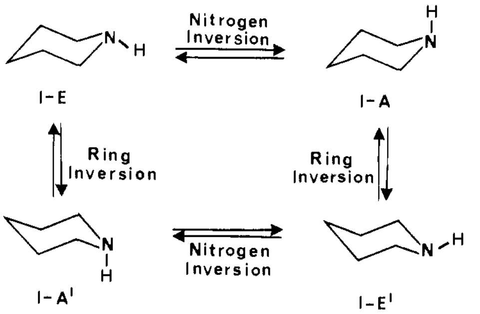


Figure 1. The 63.1-MHz ^{13}C NMR spectra of piperidine in $CHFCl_2$:CHF_2Cl (3:1), with protons noise decoupled.

Scheme I



inversion is a very slow process below −100 °C. The ring inversion process does not affect the proton-decoupled ^{13}C NMR spectrum because (a) nitrogen inversion is very rapid at temperatures (−20 to −80 °C) where, otherwise, the ring inversion process would be expected to give a dynamic NMR effect, and (b) ^{13}C NMR does not distinguish between I-E and I-E′ or between I-A and I-A′ (Scheme I). In a similar manner, it can be seen that ring inversion cannot be a very rapid process if nitrogen inversion is to give rise to a dynamic ^{13}C NMR effect.

The 251-MHz ^1H NMR spectrum of I shows a coincidence of the NH, β-CH_2, and γ-CH_2 protons at higher temperatures (>−60 °C), but it is better resolved at lower temperatures, when ring inversion becomes slow (Figure 2). A careful examination reveals that the NH band gives rise to a single resonance above −150 °C (Figure 2). Below −150 °C, this band broadens, and separates into two barely visible, but yet distinct and reproducible shoulders at −174 °C.[12] Although none of the CH_2 proton bands shows any visible effect resulting from slow nitrogen inversion, the fact that the axial α-proton band remains a 1:2:1 triplet in the temperature range of −120 to −174 °C is in agreement with an equatorial, or predominantly equatorial, NH group. The triplet arises from approximately equal couplings of the axial α proton to the equatorial α proton and to the axial β proton (vicinal couplings of the ae or ee type are too small to be resolved). If the major conformation had an axial NH group, a large vicinal diaxial NH-CH coupling constant would be expected,[13] and the axial α-CH protons should appear as an approximate 1:3:3:1 quartet rather than as a 1:2:1 triplet.

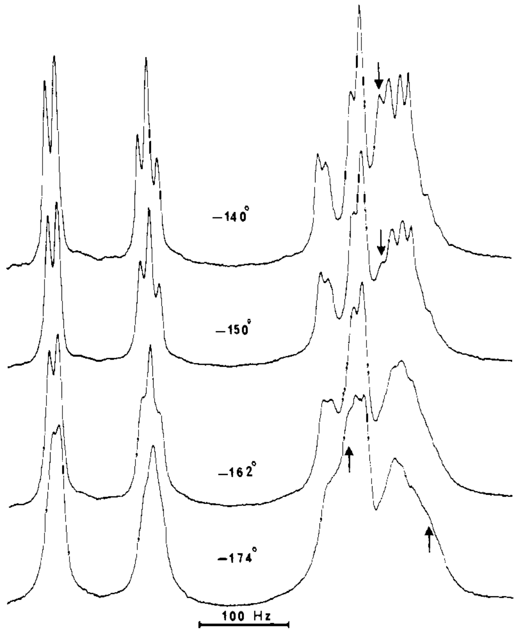


Figure 2. The 251-MHz ^1H NMR spectra (frequency-sweep) of piperidine in $CHFCl_2$:CHF_2Cl (1:1). The peaks marked with arrows belong to the NH group.

The only previous dynamic NMR data on a simple six-membered secondary amine is that on 4,4-difluoropiperidine in acetone solution, where the $\Delta G^{\ddagger}$ for nitrogen inversion was found to be 9.7 kcal/mol,[7] substantially higher than in piperidine itself. At present, we have no good explanation for this difference, which we find puzzling,[14] although it is possible that the *gem*-difluoro grouping is responsible for the observed effect. A $\Delta G^{\ddagger}$ of 7.8 kcal/mol has been found recently in nortropane,[4] which can be considered as a piperidine derivative bridged in the 2,6 positions by two methylene units. The bridged structure is expected to increase the barrier to nitrogen inversion,[1] and thus the observed value of $\Delta G^{\ddagger}$ for this compound is understandable.

The present work strongly supports the view[2] that the more stable conformation of piperidine has the N–H group equatorial, and not axial, as has been claimed.[3,11]

Acknowledgment. This work was supported by the National Science Foundation.

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(10) The ^{13}C NMR chemical shifts in $CHFCl_2$:CHF_2Cl (3:1) in parts per million downfield from internal tetramethylsilane at −100 °C are: 47.7 (α-^{13}C), 27.3 (β-^{13}C), and 25.2 (γ-^{13}C). At −172 °C, the shifts are: 47.4 (α-^{13}C), 28.2 (β-^{13}C, minor form), 26.4 (β-^{13}C, major form), and 25.2 (γ-^{13}C). The conditions for the FT pulse experiment are such that saturation effects on intensities should be very small.
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(13) J_{aa}(NH–CH) = 13 Hz in tetrahydro-1,3-oxazines and in 1-methyl-1,3-diazane, compounds that exhibit axial NH groups as a result of the anomeric effect.[5]
(14) Yousif and Roberts[7] present good evidence that acetone was not involved chemically with the amine. We have not found any reaction between I and acetone, as determined by ^{13}C NMR in the temperature range of +20 to −80 °C. The addition of acetone (2 equiv) to $CHFCl_2$ solutions of I had no observable effect on the nitrogen inversion process, as observed by ^{13}C NMR.

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Metal Clusters in Catalysis.[1] 10. A New Fischer-Tropsch Synthesis

Sir:

We wish to report a new Fischer-Tropsch synthesis in which a catalytic hydrogenation of carbon monoxide yielded a set of aliphatic hydrocarbons with ethane the *primary* reaction product. Reactions rates at 180 °C and 1–2 atm were relatively high with average turnover times of about 10–15 min. The catalyst or catalyst precursor was tetrairidium dodecacarbonyl, $Ir_4(CO)_{12}$.

Earlier we demonstrated[2] a homogeneous methanation[3] reaction, eq 1,

$$3H_2 + CO \rightarrow CH_4 + H_2O \qquad (1)$$

for hydrogen and carbon monoxide at 130–160 °C and 1–3 atm using toluene solutions that contained certain transition metal clusters;[4] all mononuclear complexes investigated were found to be inactive. The most effective metal cluster in this reaction was $Ir_4(CO)_{12}$ and, with this cluster, the sole hydrocarbon product detected was methane.[5] Unfortunately, the rates in this reaction system proved so inordinately low that mechanistic studies have been precluded.

The guiding hypothesis[2,6] in our search for soluble catalysts for the hydrogenation of carbon monoxide has been that optimal activation of carbon monoxide for reduction would be achieved in a state where there is extensive interaction of both the carbon and oxygen atoms of carbon monoxide with metal atoms. Such a state[7] would be distinguished by a substantially lower carbon–oxygen bond order and a potentially facile mechanism for carbon–oxygen bond scission. An exemplary surface model is the dissociative chemisorption of carbon monoxide on some metals which include those that can catalyze either the methanation reaction or Fischer-Tropsch[8] syntheses. This hypothesis led to the initial selection of metal cluster catalysts and, now in our new modification, to the use of aluminum chloride for a possibly substantial oxygen–aluminum interaction (M-C-O-Al).[9]

Our new cluster-based synthesis comprised the following reagents and conditions. The synthesis gas was 3:1 H_2:CO,[10] the cluster catalyst reagent was $Ir_4(CO)_{12}$ in a 1:100 cluster:CO ratio and the solvent was molten $NaCl{\cdot}2AlCl_3$ in a 1000:1 Al:Ir ratio. All reactions were effected in sealed glass tubes at 180 °C and 1.5 atm, and, at reaction temperature, there was a yellow to amber solution and no solid phase evident on visual examination. Analyses of product gases were based on gas chromatography and high resolution mass spectrometry.[11] Conversion of carbon monoxide to hydrocarbon was essentially complete after 12–24 h, although detectable traces of carbon monoxide were present after reaction periods of up to 5 days and iridium carbonyl was detectable by IR analysis of the solidified reaction melt after such 5-day reaction periods. In the absence of the iridium carbonyl cluster, the reaction system produced no hydrocarbons in reaction times of 3 days. Iridium metal generated by reductive pyrolysis of the carbonyl cluster[12] and a very fine iridium dust were inactive as a catalyst substitute for the carbonyl cluster in our specific reaction system. An extensive, but not exhaustive, exploration of catalyst alternatives to $Ir_4(CO)_{12}$ was relatively nonproductive. Essentially inactive[13] were $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Re_2(CO)_{10}$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Os_3(CO)_{12}$, $Co_2(CO)_8$, $Co_4(CO)_{12}$, and $NiCl_2$. Most notably, Na_3IrCl_6 was inactive; hence, the catalyst or catalyst precursor was not a chloroiridate complex. $Rh_6(CO)_{16}$ and $Rh_4(CO)_{12}$ were as active or slightly more active than $Ir_4(CO)_{12}$. However, because this rhodium-based system was heterogeneous at 180 °C, we do not know whether this catalytic reaction was wholly or even partially a solution phase process.[14b] $Ru_3(CO)_{12}$ was very active and appeared homogeneous in the early reaction stages. Slightly active were H_2PtCl_6 and $PdCl_2$, but both gave heterogeneous reaction systems.

The detectable hydrocarbon products of this relatively fast catalytic hydrogenation with $Ir_4(CO)_{12}$ were methane, ethane, propane, and isobutane. The latter two were invariably minor constituents. Interestingly, the relative amounts of methane and ethane varied rather significantly with reaction time. The ethane to methane ratio in the product gas fell from a 10:1 to 4:1 range after 3 h to ~1:2 after 0.5 to 3 days; the lowest observed ratio was about 1:2.5. This lowest ratio is far larger than that calculated from the equilibrium constant for reaction 2.

$$C_2H_6 + H_2 \rightleftharpoons 2CH_4 \qquad (2)$$

Since aluminum chloride is a quite effective catalyst for carbonium ion-based alkane isomerization and fragmentation,[15] this type of secondary catalytic reaction could explain the observed decrease in the C_2H_6:CH_4 ratio with reaction time increase. However, we found methane formation from ethane and hydrogen under our reaction conditions in the absence of the iridium cluster catalyst to be too slow to account for the product variation in the catalytic reaction, although, in the presence of the iridium cluster, there appeared to be a slightly more rapid fragmentation[16] (methane proved nonreactive under these conditions). In any case, our preliminary results raise the possibility of a high yield ethane synthesis.

We have evidence that the $Ir_4(CO)_{12}$ catalyst is not, at least wholly, converted to other complexes under the reaction conditions.[17] The reaction solution on cooling yielded solid phases including a minor one that had the characteristic yellow $Ir_4(CO)_{12}$ color. In the infrared spectrum of this phase, there were the characteristic CO stretching absorptions of $Ir_4(CO)_{12}$. Attempts to isolate the cluster in pure form from reaction mixtures have not been successful yet.

The $Ir_4(CO)_{12}$ catalyzed reactions were homogeneous[18] by the light scattering criterion. However, the possibility that very small *metal* aggregates were the actual catalyst cannot be excluded with the scattering criterion. Vannice's[19] kinetic expression for the iridium metal[20] catalyzed methanation reaction was used to calculate a rate for iridium metal catalysis at 180 °C. This calculated rate was slightly too low to account for our observed turnover rates with an assumption that all the $Ir_4(CO)_{12}$ was converted to metal aggregates in which *every* metal atom was catalytically active. In addition, a fine iridium metal dust[21] was examined as a catalyst for the CO hydrogenation reaction at 180 °C with a $NaCl{\cdot}2AlCl_3$ reaction medium and without the salt medium. The dust was slightly ac-