corresponding one-electron energies of their highest filled orbitals intersect (inset, Figure 1).

Since $\psi_{\mathrm{s}^{2}}$ and $\psi_{\mathrm{A}^{2}}$ are both overall totally symmetric, the noncrossing rule dictates that they mix in a manner represented by the configuration interaction function $\bar{\psi}=c_{\mathrm{s}^{2}} \psi_{\mathrm{s}^{2}}+c_{\mathrm{A}^{2}} \psi_{\mathrm{A}^{2}}$. Denoting the bonding hybrids on carbons $\mathrm{C}_{1}$ and $\mathrm{C}_{4}$ by $h_{1}$ and $h_{4}$, respectively, we have $\phi_{\mathrm{S}}=h_{1}^{\mathrm{S}}+h_{4}^{\mathrm{S}}+\ldots$ and $\phi_{\mathrm{A}}=h_{1}^{\mathrm{A}}-h_{t}^{\mathrm{A}}+\ldots$, which are analogous to the $g$ and $u$ combinations of $1 s_{A}$ and $1 s_{B}$ in $H_{2}$. The dotted terms indicate the smaller contributions to $\phi_{\mathrm{S}}$ and $\phi_{\mathrm{A}}$ from other centers in the molecule. We recall that variations in the CI coefficients as a function of $R$ serve to alter the relative amounts of covalent and ionic character. In the limiting case where hybrids in $\phi_{\mathrm{S}}$ and $\phi_{\mathrm{A}}$ are identical and their overlap is neglected, the ratio of covalent and ionic contributions is given explicitly by $\left(C_{\mathrm{S}^{2}}-C_{\mathrm{A}^{2}}\right) /\left(C_{\mathrm{S}^{2}}+C_{\mathrm{A}^{2}}\right)$, and we shall employ this quantity as a rough measure of bonding character in the discussion of actual cases which follows.
ldeally, one could simultaneously obtain the orbitals for $\psi_{\mathrm{S}^{2}}$ and $\psi_{\mathrm{A}^{2}}$, as well as the coefficients $C_{\mathrm{S}^{2}}$ and $C_{\mathrm{A}^{2}}$, in a unified self-consistent procedure (multiconfiguration SCF). We have, however, taken the following, simpler approach. For small values of $R(\leq 1.648$ $\AA$ ) where the SCF energies are well separated, $\psi_{\mathrm{S}^{2}}$ is taken as the SCF solution, and $\psi_{\mathrm{A}^{2}}$ is constructed from the 58 -electron core of $\psi_{\mathrm{S}^{2}}$ and its virtual $\phi_{\mathrm{A}}$. At larger $R$ values $(\geq 1.948 \AA)$, where the $\psi_{\mathrm{s}^{2}}$ and $\psi_{\mathrm{A}^{2}}$ SCF energies become closer, we have carried out two alternative CI calculations: first with $\psi_{\mathrm{s}^{2}}$ (SCF) and $\psi_{\mathrm{A}^{2}}$ (virtual) and then with $\psi_{\mathrm{A}^{2}}$ (SCF) and $\psi_{\mathrm{S}^{2}}$ (virtual). The validity of this essentially two-electron approach is indicated by the fact that similar CI energies (constant to within $\pm \sim 3 \mathrm{kcal}$; see Figure 1) and coefficients are obtained from either choice for $\psi_{\mathrm{S}^{2}}$ and $\psi_{\mathrm{A}^{2} .}{ }^{12}$

Figure 1 plots the CI energy as a function of $R$ and clearly shows the persistence of an inner ( $1.54 \AA$ ) and outer minimum ( $2.51 \AA$ ) of similar depth, with a separating barrier at $\sim 1.95 \AA$, whose height is $\sim 29 \mathrm{kcal} /$ mol above the inner minimum. The inner well corresponds to the valence-bond structure III, in which there is $57: 43$ covalent to ionic bonding. The outer minimum at $2.54 \AA$ corresponds to $97 \%$ covalent character and is best represented in valence bond terms as the diradical

i.e., analogous to the case of $\mathrm{H}_{2}$ at large separation, we find that CI gives proper dissociation into two weakly interacting electrons, insofar as a two particle description is valid.

The sizable barrier between roughly symmetric wells of $\sim 29 \mathrm{kcal} / \mathrm{mol}$ suggests that III could be expected to have a lifetime of several hours at room temperature within the inner well. ${ }^{13}$ Since our calcu-
(12) CI calculations using orbitals from triplet SCF calculations yield a singlet $C I$ energy curve roughly parallel to that in Figure 1 for $R \geq 1.9 \AA$ and a few kilocalories lower in energy. We feel, however, that at the level of approximation adopted, the singlet SCF orbitals provide the best overall basis for studying the bridgeheadbridgehead interaction in III.
(13) The least-energy path must cross the singlet barrier, since the tripiet energy is $>1 \mathrm{eV}$ above the singlet at $R \sim 1.95 \AA$. At the crossing point, which occurs for a substantially greater value of $R(\sim 2.3 \AA)$,
lated barrier must be considered uncertain by at least a few kilocalories per mole, a precise estimate of the lifetime is not possible. At any rate, the barrier seems rather low for a process which is symmetry forbidden in the orbital sense, ${ }^{6}$ thus demonstrating how useful quantitative calculations can be in complementing predictions based on orbital symmetry. The stability of the inner minimum species is important, since the interconversion of the outer minimum diradical to dimethylenecyclohexane symmetry is symmetryallowed, and, though the barrier for this process is of unknown magnitude, most synthetic attempts at [2.2.2]propellane do, in fact, give this latter Grob fragmentation product. ${ }^{2}$

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the triplet must lie below the singlet, in the level of approximation used here. ${ }^{14}$
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## A Flexible and Directed Synthesis of Azoxyalkanes ${ }^{1}$

Sir:
Azoxyalkanes are currently of great interest. Four naturally occurring examples, macrozamin, ${ }^{2}$ cycasin, ${ }^{3}$ elaiomycin, ${ }^{4}$ and LL-BH872 $\alpha,{ }^{5}$ exhibit potent biological properties; the initial three are carcinogenic, ${ }^{6}$ the latter possesses antifungal qualities. ${ }^{5,7}$ Recently, studies of the photolytic closure of azoxyalkanes to oxadiaziridines have appeared, ${ }^{8,9}$ and photoisomerization now makes acyclic cis-azoxyalkanes available. ${ }^{9.10}$
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(10) Oxidation of cis-azoalkanes can also be used. ${ }^{9 a}$ Previous reports of ciz-azoxyalkanes are discussed by Woodward and Wintner. ${ }^{11}$ Cyclic

Table I. Azoxyalkanes, $\mathrm{RN}=\mathrm{N}(\mathrm{O}) \mathrm{R}^{\prime}$, from Alkylation $\left(\mathrm{R}^{\prime} \mathrm{X}\right)$ of Alkane Diazotates ( $\mathrm{RN}=\mathrm{NO}^{-} \mathrm{K}^{+}$)

| Compd | R | $\mathrm{R}^{\prime}$ | Method ${ }^{\text {a }}$ | Yield, \% ${ }^{\text {b }}$ | $\mathrm{Ir}, \mathrm{cm}^{-1 \mathrm{c}}$ | Uv, $\mathrm{nm}^{\text {d }}$ | Nmr, ${ }^{\text {e }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $n-\mathrm{C}_{8} \mathrm{H}_{17}$ | $\mathrm{C}_{2} \mathrm{H}_{5}$ | A, B | 48, 44 | 1505,1320 | 217.5 (3.87) | 3.32 t (7), 4.12 q (7) |
|  |  |  |  |  |  | 280.0 (1.71) |  |
| 2 | $n-\mathrm{C}_{8} \mathrm{H}_{17}$ | $n-\mathrm{C}_{4} \mathrm{H}_{9}$ | B | 46 | 1510, 1320 | $217.5(3.88)$ | 3.30 t (7), 4.07 t (7) |
| 3 | $\begin{aligned} & n-\mathrm{C}_{8} \mathrm{H}_{17} \\ & \sec -\mathrm{C}_{4} \mathrm{H}_{9} \end{aligned}$ | $\sec -\mathrm{C}_{4} \mathrm{H}_{0}$ <br> $\mathrm{C}_{2} \mathrm{H}_{5}$ | B | 32 | 1510, 1320 | 285.0 (1.83) 222.5 (3.80) | 3.27 t (7), 4.14 sextet (7) |
| 4 |  |  | A ${ }^{\text {a }}$ | 48 | 1500, 1320 | 220.0 (3.72) | $\sim 3.9$ sextet ( 6 ), 4.07q(7) ${ }^{\text {g }}$ |
|  |  |  |  |  |  | 280.0 (1.62) |  |
| 5 | $\mathrm{sec}-\mathrm{C}_{8} \mathrm{H}_{17}$ | $\mathrm{C}_{2} \mathrm{H}_{5}$ | A | 64 | 1495, 1310 | 221.5 (3.85) | $h, 4.08 \mathrm{q}$ (7) |
|  |  |  |  |  |  | 270.0 (2.68) |  |
| 6 | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CHCH}_{3}$ | $\mathrm{C}_{2} \mathrm{H}_{3}$ | A, ${ }^{\prime}$ B | 46, 28 | 1490, 1320 | $208.5^{i}(4.19)$ | $5.00 \mathrm{q}(7), 4.09 \mathrm{q}(7)^{\text {a }}$ |
| 7 | $\mathrm{C}_{6} \mathrm{H}_{3} \mathrm{CHCH}_{3}$ | $n-\mathrm{C}_{4} \mathrm{H}_{9}$ | B | 33 | 1505, 1330 | $j$ | $5.06 \mathrm{q}(7), 4.10 \mathrm{t}$ (7) |
| 8 | $\mathrm{C}_{6} \mathrm{H}_{3} \mathrm{CHCH}_{3}$ | ${ }_{i} \mathrm{i}_{3} \mathrm{C}_{7} \mathrm{H}_{7}$ | $\mathrm{B}^{k}$ | 36 | 1490, 1292 | $j$ | $5.03 \mathrm{q}(7), 4.23 \mathrm{~m}(7)^{l}$ |
| 9 | $t$ - $\mathrm{C}_{8} \mathrm{H}_{17}$ | $\mathrm{C}_{2} \mathrm{H}_{5}$ | A | $4^{m}$ | 1505,1310 | 224.0 (3.77) | None, 4.07 q (7) |
|  |  |  |  |  |  | 280.0 (1.58) |  |

${ }^{a}$ See text. ${ }^{b}$ Yields, based on $N$-alkyl- $N$-nitrosourethane diazotate precursors, were determined by gc. ${ }^{c}$ Neat liquid. The characteristic azoxy bands ${ }^{2 d}$ are listed. ${ }^{d}$ Recorded as $\lambda_{\max }(\log \epsilon), \lambda_{\text {inf1 }}(\log \varepsilon) .{ }^{2 d}$ Solvents: 6, cyclohexane; others, ethanol. e Reported are the $\alpha$ protons ( R ) and the $\alpha^{\prime}$ protons ( $\mathrm{R}^{\prime}$ ) determined on $\mathrm{CCl}_{4}$ solutions. Other signals and integrals were in accord with structures. Fine splitting, often observed in $\alpha$ and $\alpha^{\prime}$ resonances, could reflect through-azoxy coupling. ${ }^{3 b}$ Accidentally degenerate upfield signals of 6 and 8 $\left(\mathrm{CCl}_{4}\right)$ were resolved in $\mathrm{C}_{6} \mathrm{H}_{6}$. A modest $( \pm 0.05 \mathrm{ppm})$ concentration dependence was observed in the spectra of $6\left(\mathrm{CCl}_{4}\right)$. $J$ values, in
 absortion buries the azoxy absorption. iNot determined. ${ }^{k} i-\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{Br}$. ${ }^{l}$ The isopropyl methyls are nonequivalent (nmr in benzene) but only a doublet is observed in $\mathrm{CCl}_{4}$. ${ }^{m}$ Major product was 2,4,4-trimethylpentene-1 (23\%).

Given this abundance of concern and accomplishment, it is striking that there exists no general synthesis of unsymmetrical azoxyalkanes. ${ }^{14}$ We consider that such a synthesis must be (1) flexible, or applicable to a wide variety of unsymmetrical azoxyalkanes; (2) directed, affording a single, structurally predictable azoxyalkane; (3) proceed from readily available starting materials; and (4) accommodate constraints on chirality at the $\alpha$ and $\alpha^{\prime}$ carbon atoms.

Syntheses ${ }^{14}$ in which the ultimate precursors or intermediates possess linked nitrogens of identical oxidation states do not generally satisfy requirements 1 and 2 (e.g., the oxidation of azoalkanes, and the reduction of $C$-nitrosoalkane dimers ${ }^{14}$ ). The condensation of $C$ nitrosoalkanes with $N$-alkylhydroxylamines has been largely restricted to tert - $^{15}$ or perfluoroalkyl ${ }^{16} \quad C$ nitrosoalkanes, and examples from the aromatic series ${ }^{17}$ suggest that N -symmetrized intermediates can intervene, leading to a violation of 2 . Similar objections apply to the reduction of nitro compounds, and the oxidation of amines or hydroxylamines, which presumably involve related intermediates. Finally, such methods as the reaction of Grignards with azoxy tosyl-
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ates ${ }^{18}$ and azoxy fluorides ${ }^{19}$ do not afford purely aliphatic azoxy compounds.

Now we report that the alkylation of alkane diazotates to give unsymmetrical azoxyalkanes ${ }^{20}$ is capable of broad generalization, and that the flexibility, directedness, and simplicity of the generalized process approach the above requirements for a general azoxyalkane synthesis.
The basic reactions are shown in eq 1 and 2 , and the

azoxyalkanes synthesized accordingly are collected in Table I. ${ }^{22}$ The alkane diazotates were prepared from aminoalkanes, ${ }^{23}$ and allowed to react with Meerwein's reagent as $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ suspensions, or with alkyl halides as hexamethylphosphoric triamide solutions. Experiments with the latter method suggest that iodide is the halide of choice, and that 7 hr at $40^{\circ}$ constitute good, if not optimal, reaction parameters.
Azoxyalkanes were purified by gc. Their identity follows from analyses, mass spectra ( $\mathrm{M}^{+}$or $\mathrm{M}^{+}-17$ ),
 The latter also fix the location of the oxygen atom. ${ }^{15 a}$

The major competing process in reactions 1 and 2 is O -alkylation, followed by nitrogen loss, and the formation of carbonium ion products, such as ethers and ole-

[^0]fins. ${ }^{24}$ The yield of azoxyalkane is thus limited, but variation of reaction conditions may permit augmented N -alkylation and better yields. Note that alkylation of the diazotates' other nitrogen (yielding $N$-alkyl- $N$ nitrosoamines) is a minor process. Synthesis of the authentic $N$-nitrosoamines, followed by gc analysis of the crude reaction mixtures accompanying 1 and 6 , limit $N$-nitrosoalkane formation to less than $5 \%$.

By uver, ${ }^{9 a, b}$ and $n m r,{ }^{9,12}$ our azoxyalkanes are trans (see eq 1 and 2). ${ }^{25}$ Because the diazotates from which they come are probably of syn configuration, ${ }^{26}$ reactions 1 and 2 could lead directly to trans-azoxyalkanes by nucleophilic attack of the diazotate on RX, with retention of the $\mathrm{N}=\mathrm{N}$ configuration.

The new axoxyalkane synthesis meets generality requirements 1-3. Our synthesis of ( $S$ )-4 from ( $S$ )-butane-2-diazotate (method 1) shows that it can partly meet the chirality requirement, 4 . The CD spectrum of (S)-4 closely resembled those of (S)-ONN-1cyclohexylazoxyethane ${ }^{91}$ and elaiomycin. ${ }^{5 b}$ We are studying stereospecific synthetic routes to azoxyalkanes in thich the chiral center is bonded at the $=\mathrm{N}(\mathrm{O})$ position.

Our synthesis generates primary and secondary trans-azoxyalkanes of varied structure. Superior syntheses of tert-azoxyalkanes ${ }^{15}$ complement our work. Coupled with photoisomerization, ${ }^{8,9}$ we can gain access to new O-position isomers, cis-azoxyalkanes, and oxadiaziridines as well. The potential for the synthesis of naturally occurring azoxyalkanes is patent, and we are exploring such possibilities.

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## Geometry of Nickel(II) Complexes

Sir:
Nickel(II) forms many complexes with octahedral, square-planar, and tetrahedral geometries and a smaller number of five-coordinate compounds ${ }^{1}$ with other stereochemical arrangements. It is generally considered that a combination of steric and electronic factors determines which of the three common geometries is assumed by a given compound. Steric factors clearly operate in the sense that bulky ligands are most favorable to tetrahedral geometry and least favorable to octahedral geometry. The mode of operation of the electronic effects is much less clear in spite of ex-
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tensive discussion of the subject. ${ }^{2-4}$ We wish to present some new data on the structure of thiourea (tu) complexes of nickel(II) in solution and to suggest a simple rationale for their geometries.

Measurements of visible spectra, magnetic moments, conductivity, and molecular weights of nickel(II) complexes of thiourea and substituted thiourea at room temperature have been reported ${ }^{2,5}$ and have provided evidence for all three geometries. We have undertaken nmr and other studies of a number of these complexes over a wide range of temperature primarily to elucidate ligand exchange mechanisms. We report here data on four complexes chosen to illustrate the geometric possibilities. $\mathrm{Ni}(\mathrm{tu})_{6}\left(\mathrm{ClO}_{4}\right)_{2}$ gives conducting solutions in acetone and has a magnetic moment ranging from 2.3 $\left(+27^{\circ}\right)$ to $3.2 \mathrm{BM}\left(-90^{\circ}\right)$, and the nmr spectrum indicates fast ligand exchange involving a paramagnetic complex at room temperature. In the presence of excess ligand the exchange is barely frozen out at $-90^{\circ}$. (The dimethylthiourea complex is similar but the ligand exchange is slow at $-90^{\circ}$ giving complexed resonances at $-101.4,-19.9$, and -12.1 ppm from TMS.) All data are consistent with octahedral $\mathrm{Ni}(\mathrm{tu})_{6}{ }_{6}{ }^{2+}$ being the only species present at $-90^{\circ}$ with some dissociation to square-planar $\mathrm{Ni}(\mathrm{tu})_{4}{ }^{2+}$ at higher temperatures. Solutions of $\mathrm{Ni}(\mathrm{tu})_{4} \mathrm{Cl}_{2}$ in acetone are nonconducting at all temperatures and the magnetic moment varies from 3.5 $\left(+27^{\circ}\right)$ to $3.8 \mathrm{BM}\left(-90^{\circ}\right)$. The nmr of this complex shows fast exchange with dissociated ligand at $+27^{\circ}$, but at $-90^{\circ}$ one of the two complexed tu protons (chemical shift -104.8 ppm ) which result from restricted rotation about the $\mathrm{C}-\mathrm{N}$ bond is no longer exchanging with free ligand. Free ligand and the second complexed ligand proton give an averaged resonance at -11.3 ppm . The species present is tetrahedral $\mathrm{Ni}(\mathrm{tu})_{2} \mathrm{Cl}_{2}$ at all temperatures. $\mathrm{Ni}(\mathrm{tu})_{6} \mathrm{Br}_{2}$ in acetone has a moment varying from 3.6 BM at $+27^{\circ}$ to 1.2 BM at $-94^{\circ}$. It has a small conductivity at room temperature which increases at low temperature. The nmr spectrum at $-90^{\circ}$ has four resonances. Two show contact shifts ( -110.3 and -20.2 ppm ) and are attributed to tetrahedral $\mathrm{Ni}(\mathrm{tu})_{2} \mathrm{Br}_{2}$. One arises from free ligand ( -8.9 ppm ) and the fourth at -9.3 ppm is assigned to a diamagnetic complex. This latter compound must be ionic since its formation is accompanied by an increase in conductivity. The concentration of the analogous iodide complex is decreased by addition of $\left(\mathrm{CH}_{3}\right)_{4} \mathrm{NI}$ (experiment carried out at $-50^{\circ}$ in the fast exchange region). On the other hand it cannot be $\mathrm{Ni}(\mathrm{tu})_{4}{ }^{2+}$ since at $-90^{\circ}$ in the presence of excess ligand this species is completely converted to $\mathrm{Ni}(\mathrm{tu})_{8}{ }^{2+}$. It must therefore be square-planar $\mathrm{Ni}(\mathrm{tu})_{3} \mathrm{Br}^{+} .{ }^{6} \quad \mathrm{Ni}(\mathrm{tu})_{6} \mathrm{I}_{2}$ has a
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