

Synthesis with Zerovalent Metals: Conversion of Thionocarbonates to Alkenes with Bis(1,5-cyclooctadiene)nickel(0).

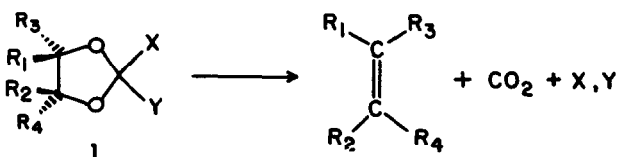
M.F. Semmelhack and R.D. Stauffer

Department of Chemistry, Cornell University, Ithaca, New York 14850

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We wish to report that bis(1,5-cyclooctadiene)nickel<sup>1,2</sup>  $[\text{Ni}(\text{COD})_2]$  reacts with the thionocarbonates (1; X, Y=S) of vicinal diols under mild conditions to produce alkenes with high efficiency and high stereospecificity; preliminary results suggest that the transient intermediate involved in the reaction is a carbene-nickel complex.

In the last decade, several approaches to the regiospecific and stereospecific generation of double bonds from vicinal diols have been reported,<sup>3-6</sup> all proceeding from decomposition of an intermediate symbolized as 1. To be practical for the preparation of delicate natural products,

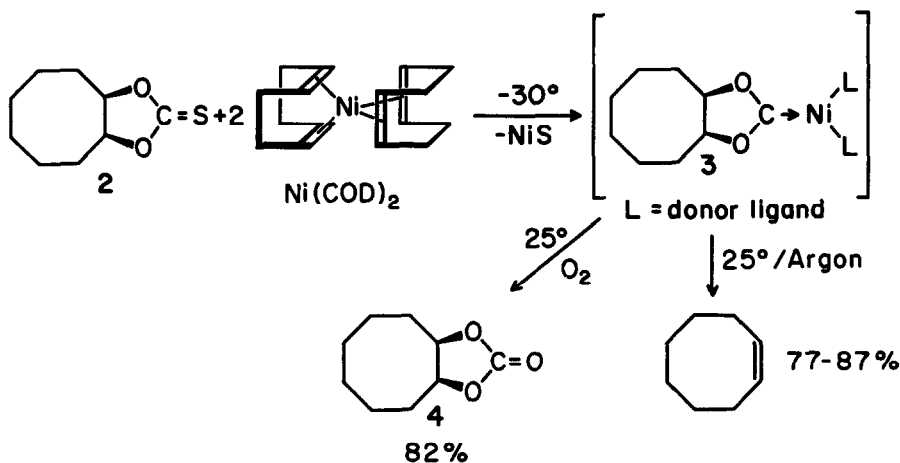


the technique must be compatible with a variety of functional groups and proceed at moderate temperatures. Each of the existing methods has serious limitations due to the reactivity of the reagent necessary to generate the  $\pi$ -bond (e.g., organolithiums for 1, X=phenyl, Y=H)<sup>3</sup> or due to the elevated temperatures necessary for reasonable rates (e.g., refluxing trimethylphosphite with 1, X, Y=S)<sup>4</sup>. The high reactivity of nickel catalysts for sulfur and our interest in zerovalent nickel reagents in organic synthesis<sup>7,8</sup> led us to consider  $\text{Ni}(\text{COD})_2$ , a highly reactive source of zerovalent nickel, as an agent for promoting the disassembling of thionocarbonates.

Although all of the examples reported here are from small scale preliminary experiments, the following typical procedure exemplifies the method in some detail. To a suspension of  $\text{Ni}(\text{COD})_2$  (278 mg, 1.02 mmol)<sup>9</sup> in 10 ml of dimethylformamide frozen at  $-78^\circ$  under argon was added, as a solid, the thionocarbonate 2 of cis-cyclooctan-1,2-diol (92 mg, 0.49 mmol).<sup>4a</sup> The solution was allowed to warm to  $25^\circ$  over one hr; a black solid appeared at  $-30^\circ$ . After additional stirring at  $25^\circ$  for 2 hr, the volatile material was flash-distilled at  $25^\circ/0.001$  Torr into a trap cooled to  $-196^\circ$ . An internal standard was added to the distillate, and the yield of cis-cyclooctene was determined to be 82% by glpc analysis.<sup>10</sup>

The reaction is viewed as rapid initial attack by nickel on the sulfur atom to produce an intermediate (here represented as 3, a carbene-nickel complex) which slowly fragments to produce the alkene. The existence of an unstable intermediate with properties consistent with structure 3 is suggested by the following observations. A mixture of  $\text{Ni}(\text{COD})_2$  and 2 were mixed in ether at

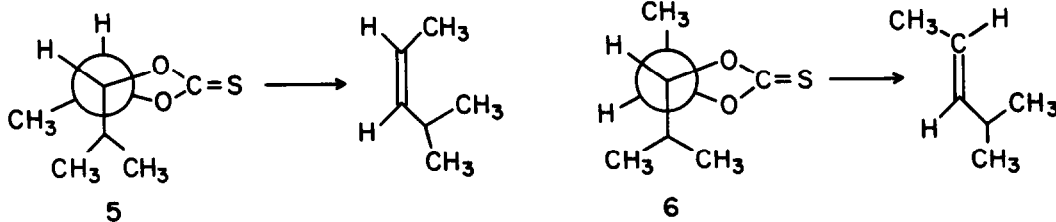
-78° under argon and allowed to warm to -30° to 25° for 3 hr; the resulting black suspension was carefully filtered at -78°, and the filtrate was flash distilled at 25°/0.001 Torr. The yield of *cis*-cyclooctene in the distillate was <2% by glpc analysis. The residue was stirred with dimethylformamide for two hr at 25°, flash distilled, and the distillate was analyzed to reveal *cis*-cyclooctene in 77% yield. Isolation of a discrete intermediate from the residue has not yet been possible, although colored nickel-containing species, which slowly decompose to give *cis*-cyclooctene, can be extracted into xylene or tetrahydrofuran. After the residue was exposed to oxygen<sup>11</sup> for short periods at 25°, trituration with ether gave a colorless solution which contained the carbonate<sup>14</sup> (4) of *cis*-cyclooctane-1,2-diol in 82% yield. The fate of the CO<sub>2</sub> fragment is not known in detail, but it is likely to be associated with nickel; the black precipitate after complete formation of the alkene contains 58% nickel (calculated for Ni<sub>2</sub>CO<sub>2</sub>S: 61% Ni). Attempts to intercept the proposed carbene ligand by addition to methyl acrylate<sup>15</sup> failed; reaction of Ni(COD)<sub>2</sub> with 2 at 65-90° in xylene and excess methyl acrylate led to the formation of *cis*-cyclooctene in 99% yield.



All thionocarbonates studied began to react with Ni(COD)<sub>2</sub> at ca. -30° (in ether, tetrahydrofuran, xylene, or dimethylformamide) to produce a black suspension, but the rate of appearance of alkene depends on the structure of the alkene. The thionocarbonate<sup>14</sup> of *exo, exo*-2,3-dihydroxybicyclo[2.2.1]heptane produces bicyclo[2.2.1]hept-2-ene in 99% yield only after 38 hr at 65-70° in dimethylformamide. In contrast to 2, the thionocarbonate of *trans*-cyclooctan-1,2-diol<sup>4a</sup> produces *cis*-cyclooctene in only 12% yield after 3 hr at 25° in dimethylformamide; after 45 hr at 65-70°, the yield is 99%.<sup>16</sup> The apparent *trans*-elimination may be due to initial formation of *trans*-cyclooctene followed by nickel-catalyzed isomerization.<sup>17</sup> When a mixture of the thionocarbonate of *trans*-cyclooctan-1,2-diol and Ni(COD)<sub>2</sub> (2.1 mole-eq.) is stirred in dimethylformamide at 20° for 3 hr and then exposed to air, the carbonate<sup>19</sup> of *trans*-cyclooctan-1,2-diol is the only product, indicating that epimerization or isomerization occurs during or after the

second stage of the reaction.

In a comparison where the geometric isomers of the alkene products are of similar thermodynamic stability, the reactions are >99% stereospecific. The thionocarbonates<sup>14</sup> (5 and 6) of erythro- and threo-4-methylpentan-2,3-diol react with  $\text{Ni}(\text{COD})_2$  in dimethylformamide over 46 hr at 65° to give cis-4-methyl-2-pentene from erythro (79% yield, < 1% trans<sup>20</sup>) and trans-4-methyl-2-pentene from threo (99% yield, < 0.2% cis<sup>20</sup>).



Variation in solvent has no significant effect on the direction of the reaction but does reveal a substantial solvent effect on the rates of formation of the alkene. The thionocarbonate 2 affords cis-cyclooctene in only 12% yield after 2 hr at 25° in ether; addition of triphenylphosphine does not accelerate the reaction. Dimethylformamide and tetrahydrofuran provide rates 10-100 times faster than those in ether or benzene.

In related work, carbonate 4 shows very low reactivity towards  $\text{Ni}(\text{COD})_2$ ; even after several days at 60-70° in dimethylformamide, the yield of cis-cyclooctene is less than 10%, and the starting material was recovered (90%). Cyclohexene sulfide is reactive toward  $\text{Ni}(\text{COD})_2$ , producing cyclohexene in 67% yield after 5 hr at 30° in dimethylformamide (80% from reaction in xylene, 0.5 hr, 80°) using an equimolar quantity of the nickel reagent. The reaction of excess nickel carbonyl with 2 at 60° for 24 hr in dimethylformamide produced only a trace of cyclooctene (< 2%) and left the thionocarbonate largely unreacted.

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- (9) Two molar-equivalents of  $\text{Ni}(\text{COD})_2$  were found necessary to provide complete conversion of the thionocarbonates.
- (10) Experiments using other solvents (tetrahydrofuran, ether) or longer reaction times in dimethylformamide (3.5, 5.5, 28 hr) gave similar yields:  $82 \pm 5\%$ .
- (11) Although the reaction of oxygen with well-characterized carbene-metal complexes has not been reported,<sup>12</sup> related species, such as phosphorous ylides, undergo cleavage of the bond to the heteroatom ( $\text{R}_2\text{C}=\text{PR}_2$ ) to give the carbonyl compound (e.g.,  $\text{R}_2\text{C}=\text{O}$  and  $\text{R}_3\text{P}=\text{O}$ )<sup>13</sup>.
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- (14) This compound has been characterized by satisfactory combustion analysis, and it shows <sup>1</sup>H nmr, ir, and low resolution mass spectral data consistent with the structure.
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- (16) The cis-cyclooctene was isolated by preparative glpc (minimum thermal conditions) and identified by comparison with an authentic sample.
- (17) The thermal stability of trans-cyclooctene<sup>18</sup> precludes simple thermal isomerization under the reaction conditions.
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- (19) The trans-carbonate showed ir, <sup>1</sup>H nmr, and mass spectral properties consistent with the structure; the <sup>1</sup>H nmr and (mp 79-81°) serve to distinguish it from the corresponding cis-isomer (mp 105-105.5°).
- (20) The cis and trans-4-methyl-2-pentenes were identified by comparison of retention times on two different glpc columns with authentic samples of the separate isomers.
- (21) We wish to acknowledge a National Institutes of Health Postdoctoral Traineeship to R.D.S. Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.