

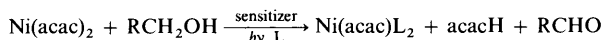
## Photochemical Generation of Nickel(I) Complexes and their Reaction with Hydrogen: Nickel Hydride Catalysed Hydrogenation of 1,5-Cyclo-octadiene

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In benzene under an atmosphere of hydrogen, triplet excited-state xanthone or acetone sensitizes the photoreduction of bis(acetylacetonato)nickel(II), Ni(acac)<sub>2</sub>, to transient nickel(I) complexes which can be detected by ESR spectroscopy in the presence of stabilizing ligands. The kinetics of these ESR signal decays prove that these nickel(I) complexes are derived from moderately co-ordinating ligands, such as tetrahydrofuran and 1,5-cyclo-octadiene (1,5-COD), and react with hydrogen in the dark to form nickel hydride complexes. An excess of 1,5-COD in the photolysate was sequentially and catalytically isomerized and hydrogenated under the irradiation conditions; *i.e.*, 1,5-COD→1,4-COD→1,3-COD→COE→COA. The nickel hydride complexes are proposed as the key species in the initiation of the catalytic cycle in which steps involving the addition and elimination of nickel hydride bonds and the hydrogenolysis of nickel complexes are assumed. As these alkene reactions cease in the dark and are quenched by a high concentration of 1,3-COD, it can be concluded that one or more steps in the catalytic cycle requires sensitized photoexcitation.

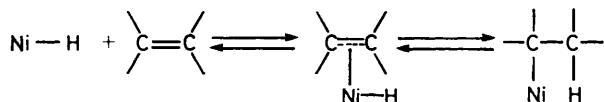
We have shown that triplet excited-state ketones with high triplet-state energy (*e.g.* xanthone and benzophenone) can sensitize the photoreduction of bis(acetylacetonato)nickel(II), Ni(acac)<sub>2</sub>, to give nickel(I) complexes and acetylacetone (acacH) in an H-atom donating solvent which is itself oxidized.<sup>1</sup> The Ni<sup>I</sup> complexes generally disproportionate to give Ni<sup>III</sup> compounds and Ni<sup>0</sup> as metallic precipitates (or its complexes in the presence of suitable ligands, L).



Scheme 1.

In our preliminary communication, we have shown<sup>2</sup> that the photoreduction conditions under hydrogen can serve as a system for the catalytic hydrogenation of alkenes under illumination. The photohydrogenation is simple to effect and shows clean chemical selectivity for unconjugated dienes.<sup>3</sup>

Transition-metal-catalysed alkene reactions<sup>4-10</sup> have attracted much interest in the past, and in recent years many of them have been shown to be enhanced or initiated by illumination.<sup>11,12</sup> Low-valence nickel complexes thermally catalyse hydrogenation,<sup>13-15</sup> double-bond migrations,<sup>16-18</sup> skeletal rearrangements,<sup>19</sup> cyclizations and oligomerizations<sup>20-22</sup> in homogeneous phases. In the majority of these cases, Ni-H complexes have been proposed, and some proven, to be the key reactive species and the addition-elimination steps depicted in Scheme 2 have been accepted to represent the basic mechanism.<sup>5-10</sup>



Scheme 2.

Interestingly, there appear to have been no reports of Ni-H catalysed alkene reactions that require photoexcitation. We wish to describe here some mechanistic studies of Ni-H complex formations and a photohydrogenation process with concurrent isomerization using *cis,cis*-1,5-cyclo-octadiene (1,5-COD) as the model compound. While the photohydrogenation of other simple alkenes is relatively straightforward,<sup>3</sup> the application of this process to 1,5-COD provides some pertinent

information with which to illuminate the hydrogenation mechanism. This report adds a new method of metal-complex-catalysed alkene reactions and some pertinent mechanistic aspects. There are a number of reports<sup>13,14,23-27</sup> on the homogeneous metal-complex-catalysed isomerization and hydrogenation of 1,5-COD.

### Results

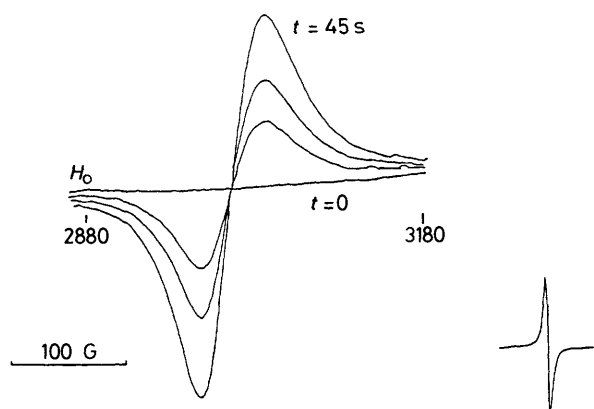
**The Photoreduction of Ni(acac)<sub>2</sub> under Hydrogen.**—Triplet-state xanthone-sensitized photoreductions of Ni(acac)<sub>2</sub> under various conditions were monitored by observing the UV absorptions at 630 nm and colour changes, and also by recording the Ni<sup>I</sup> ESR signal.<sup>1</sup> A quantitative comparison by UV measurements was not successful because of precipitation in some photoreductions. The efficiency of the photoreduction under various conditions are expressed qualitatively in Table 1; *e.g.*, rates of photoreduction in the presence of propan-2-ol were very fast, as in Experiments 6, 9, and 10. Experiments 1 and 2 clearly showed that hydrogen could act as an H-atom donor but, because of the limitation in solubility,<sup>28</sup> was less effective than propan-2-ol, tetrahydrofuran (THF), and toluene, and that as long as there was an H-atom donor in the reduction system, the photoreduction could occur. The ESR spectra recorded during irradiation were of two types: (i) the isotropic signals<sup>29-33</sup> at *ca.* *g* = 2.15–2.18 for transient Ni<sup>I</sup> complexes in the presence of good ligands, such as diglyme, phosphines and THF (see Figure 1); and (ii) broad signals at *g* = 2.3 due to paramagnetic colloidal nickel<sup>34</sup> in the absence of such ligands. While the signals due to the former type decayed rapidly, those of the latter type remained for several hours on cessation of irradiation. In the presence of 1,5-COD, neither of these signals was observed but Ni(acac)<sub>2</sub> was reduced. Since the photolysates remained clear and transparent, the Ni<sup>I</sup> complex of 1,5-COD was probably formed but was then transformed rapidly to something else under the reaction conditions. It was noted that in benzene/H<sub>2</sub> photoreduction did not generate the colloidal nickel signal though the photolysate became cloudy and dark yellow.

Since the ESR signals of transient Ni<sup>I</sup> complexes show the same line width under the same conditions as shown in Figure 1,

**Table 1.** The xanthone sensitized photoreduction of Ni(acac)<sub>2</sub>; ESR parameters for Ni<sup>I</sup> complexes<sup>a</sup>.

Experiment	Conditions	Photoreduction	ESR signal <sup>b</sup>
1	Benzene, N <sub>2</sub>	–	None
2	Benzene, H <sub>2</sub>	+	None <sup>c</sup>
3	Benzene, H <sub>2</sub> , PBU <sub>3</sub>	+	$g = 2.153, \Delta H = 35 \text{ G}^d$
4	Benzene, H <sub>2</sub> , diglyme	+	$g = 2.182, \Delta H = 44 \text{ G}^d$
5	Benzene, H <sub>2</sub> , 1,5-COD	+	None <sup>d</sup>
6	Benzene-Pr <sup>i</sup> OH (19:1), N <sub>2</sub> or H <sub>2</sub> , PBU <sub>3</sub>	+++	$g = 2.155, \Delta H = 35 \text{ G}^d$
7	Toluene, PBU <sub>3</sub> , H <sub>2</sub> or N <sub>2</sub>	++	$g = 2.158, \Delta H = 31 \text{ G}^d$
8	THF, N <sub>2</sub> or H <sub>2</sub>	++	$g = 2.188, \Delta H = 46 \text{ G}^d$
9	Benzene-Pr <sup>i</sup> OH (19:1), H <sub>2</sub> , 1,5-COD	+++	None <sup>d</sup>
10	Benzene-Pr <sup>i</sup> OH, N <sub>2</sub>	+++	$g = 2.268, \Delta H = 920 \text{ G}^e$
11	Toluene, H <sub>2</sub>	++	$g = 2.3, \Delta H = 900 \text{ G}^e$

<sup>a</sup> Solution containing Ni(acac)<sub>2</sub> (0.010 mol dm<sup>-3</sup>) and xanthone (0.015 mol dm<sup>-3</sup>) placed in the ESR cavity were photolysed at 24 ± 1 °C. <sup>b</sup> ΔH values represent peak-to-peak widths/G. <sup>c</sup> The yellow photolysate became cloudy in prolonged irradiation. <sup>d</sup> These photolysates remained clear during photolysis. <sup>e</sup> Precipitates of metallic nickel were obtained.

**Figure 1.** The ESR spectra recorded from irradiation of a THF solution containing Ni(acac)<sub>2</sub> (0.010 mol dm<sup>-3</sup>) and xanthone (0.015 mol dm<sup>-3</sup>) under hydrogen at 15 s intervals.

the peak-to-peak amplitudes of the waves are proportional to absorption intensities which are, in turn, proportional to Ni<sup>I</sup> complex concentrations.<sup>35</sup> Therefore, by monitoring signal heights at a fixed field strength (at the maximum position of the wave) against time, we can study the dynamics of Ni<sup>I</sup> complex decompositions; such kinetic traces are shown in Figure 2.

The kinetic traces of Ni<sup>I</sup> complex decomposition were analysed as double-exponential decay curves, according to our previous observations<sup>1</sup> that such decompositions contained first- and second-order components, as in equation (1), where *A* is the recorded signal height at time *t*.

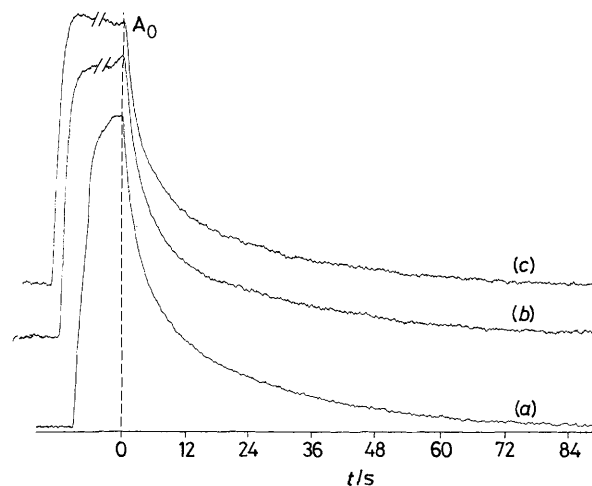
$$-(dA/dt) = k_1A + k_2A^2 \quad (1)$$

The details of experiments and the method of analysis were given in the thesis presented by H. Li.<sup>3</sup> The rate constants are summarized in Table 2. It should be mentioned that the

**Table 2.** Decay rate constants of nickel(I) complexes.<sup>a</sup>

	$k_1/10^{-3} \text{ s}^{-1}$	$k_2/10^3 \text{ s}^{-1}$ (unit) <sup>-1</sup>
Benzene-Pr <sup>i</sup> OH (19:1), PBU <sub>3</sub> (0.05 mol dm <sup>-3</sup> ), N <sub>2</sub>	0.5 ± 0.8	5.7 ± 1.2
Benzene-H <sub>2</sub> , PBU <sub>3</sub> (0.05 mol dm <sup>-3</sup> )	0.2 ± 0.1 <sup>b</sup>	5.1 ± 0.5
Benzene-Pr <sup>i</sup> OH (19:1), diglyme (0.05 mol dm <sup>-3</sup> ), N <sub>2</sub>	0.8 ± 1.0	4.8 ± 2.0
Benzene-H <sub>2</sub> , diglyme (0.05 mol dm <sup>-3</sup> )	0.6 ± 1.3	5.9 ± 1.7
Benzene-Pr <sup>i</sup> OH (19:1), (Ph <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> (0.03 mol dm <sup>-3</sup> ), N <sub>2</sub>	0.5 ± 1.1	5.9 ± 1.6
Benzene-H <sub>2</sub> , (Ph <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> (0.03 mol dm <sup>-3</sup> )	0.6 ± 1.3	5.6 ± 2.0
THF-N <sub>2</sub>	0.3 ± 2 <sup>b</sup>	34 ± 3
THF-H <sub>2</sub>	6.3 ± 0.2 <sup>b</sup>	19 ± 2
THF-N <sub>2</sub> , 1,5-COD (0.06 mol dm <sup>-3</sup> )	0.4 ± 3 <sup>b</sup>	20 ± 3
THF-H <sub>2</sub> , 1,5-COD (0.06 mol dm <sup>-3</sup> )	4.2 ± 0.1 <sup>b</sup>	13 ± 2
	3.1 ± 0.6 <sup>c</sup>	14 ± 3 <sup>c</sup>
	1.7 ± 0.8 <sup>c</sup>	15 ± 3 <sup>c</sup>

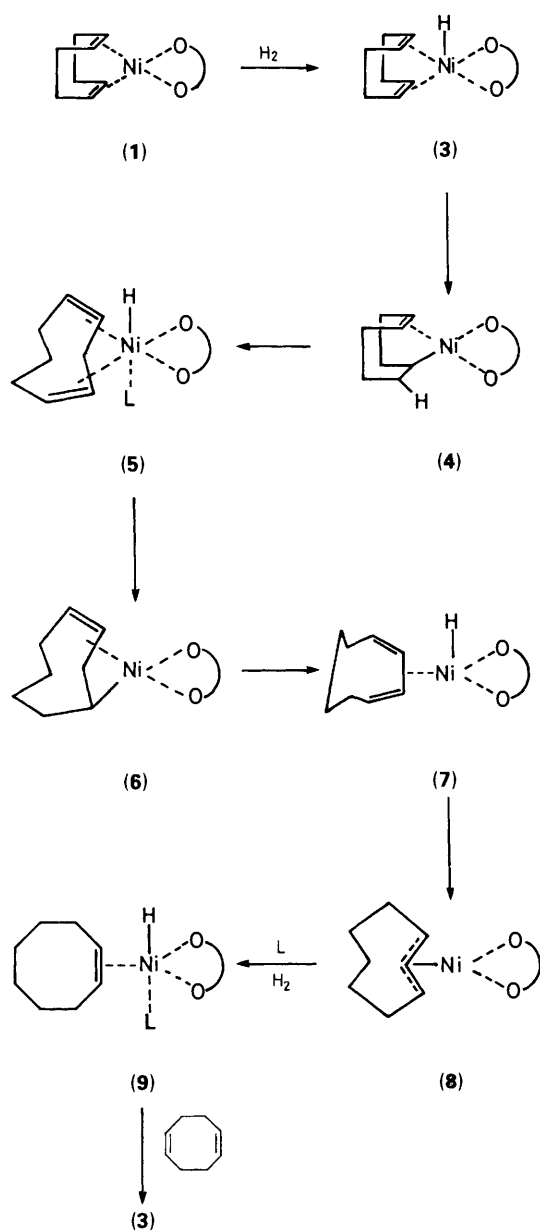
<sup>a</sup> Solutions containing Ni(acac)<sub>2</sub> (0.010 mol dm<sup>-3</sup>) and xanthone (0.015 mol dm<sup>-3</sup>) placed in an ESR tube were photolysed at the cavity temperature of 24 ± 1 °C. <sup>b</sup> These data are the average of several consecutive runs; other data are one standard deviation from single runs. <sup>c</sup> The solution shown above was photolysed 5 and 10 min, respectively, before the kinetic runs were recorded.

**Figure 2.** The formation and decay of the Ni<sup>I</sup> ESR signal using a THF solution containing Ni(acac)<sub>2</sub> (0.010 mol dm<sup>-3</sup>), xanthone (0.015 mol dm<sup>-3</sup>), and 1,5-COD (0.06 mol dm<sup>-3</sup>) under hydrogen at 24 °C; curves (a), (b), and (c) were recorded after the solution had been irradiated for 10 s, 5 min, and 10 min, respectively (see the last three Experiments in Table 2).

bimolecular rate constants are not absolute values owing to the unavailability of Ni<sup>I</sup> complex concentrations and to variations in the ESR spectrometer settings from one experiment to the other. However, within the same series of experiments under the same conditions, *k*<sub>2</sub> values can be compared (see Table 2). It is clear that Ni<sup>I</sup> complexed with diglyme or phosphines have small and comparable unimolecular rate constants, *k*<sub>1</sub>, under either nitrogen or hydrogen. The *k*<sub>1</sub> values in THF or in the presence of 1,5-COD under hydrogen were considerably larger than those under nitrogen, and the *k*<sub>1</sub> values under hydrogen decrease significantly after a period of irradiation, *i.e.*, after a portion of hydrogen has been consumed, as shown in Table 2 (the last three Experiments). Both observations indicated that the Ni<sup>I</sup> complex of 1,5-COD reacted with hydrogen efficiently and that these *k*<sub>1</sub> values represented pseudo-first-order rate

constants since the hydrogen concentration must be several orders of magnitude higher than the  $\text{Ni}^{\text{I}}$  concentration. It should be noted that the bimolecular reaction rate constants in this same series of reactions were about the same in spite of variations in the  $k_1$  values (the last three Experiments in Table 2). Since the kinetic conditions were approximately comparable and the ESR settings were the same, this indicated the absence of pseudo-second-order reactions involving hydrogen.

In deuteriated benzene or THF under hydrogen, the xanthone-sensitized photolysis of  $\text{Ni}(\text{acac})_2$  in the presence of 1,5-COD showed  $^1\text{H}$  NMR signals at  $-15.2$  and  $-16.9$  ppm, respectively. In both cases, an unresolved signal at  $-1.3$  ppm was also recorded. The high field signals were obviously derived from the Ni-H bond, in agreement with those reported<sup>36-38</sup> for nickel hydride complexes at  $-25$  to  $-15$  ppm. The latter signal at  $-1.3$  ppm was assigned to the resonance of the Ni-CH proton of the known nickel complex,  $(\eta^1, \eta^2\text{-cyclo-octenyl})\text{nickel acetylacetonate}$ <sup>20-22</sup> [(4), (see Scheme 3)]. The signal in the 15-17 ppm region was not observed when the photolysis was run in



Scheme 3.

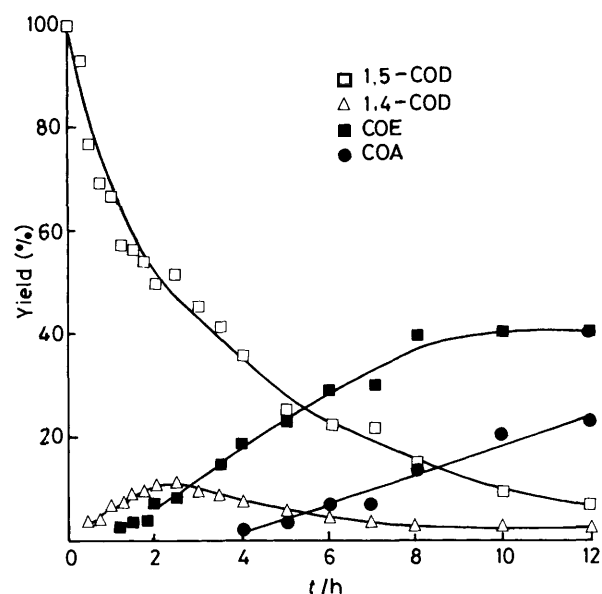


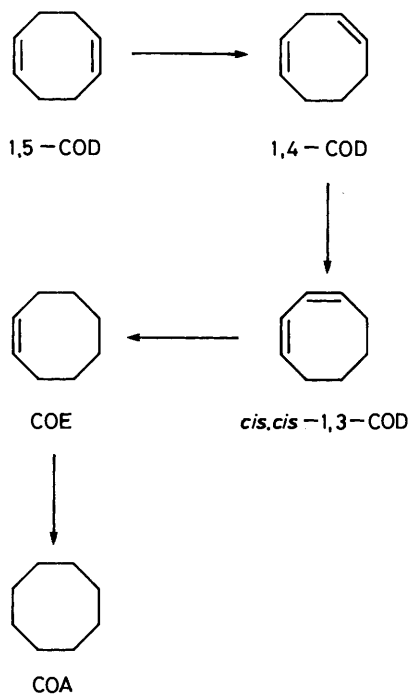
Figure 3. The percentage variations of  $\text{C}_8$ -hydrocarbons in photolysis of a benzene solution containing  $\text{Ni}(\text{acac})_2$  ( $5.6 \times 10^{-3} \text{ mol dm}^{-3}$ ), xanthone ( $8.5 \times 10^{-3} \text{ mol dm}^{-3}$ ), and 1,5-COD ( $4.4 \times 10^{-2} \text{ mol dm}^{-3}$ ) under hydrogen at room temperature.

a benzene-propan-2-ol mixture (19:1, v/v) under nitrogen, though the reduction of  $\text{Ni}(\text{acac})_2$  had clearly occurred as shown by the disappearance of the green colour.

**Photohydrogenation of 1,5-COD.**—Under a variety of conditions conducive to sensitized photoreduction of  $\text{Ni}(\text{acac})_2$ , alkenes could be hydrogenated if the photoreactions were carried out under hydrogen.<sup>3</sup> In the presence of 1,5-COD, the sensitized photoreduction of  $\text{Ni}(\text{acac})_2$  under hydrogen caused the rapid migration of double bonds followed by hydrogenation under a variety of conditions. This series of reactions occurred whether acetone, xanthone or benzophenone was used as a sensitizer, or propan-2-ol, THF, toluene, or hydrogen was used as an H-atom donor as long as the photolysates were purged with a slow stream of hydrogen. Similar photolysis under nitrogen gave no reaction of 1,5-COD even in the presence of these H-atom donors, though photoreduction had occurred. A mixture of acetone-propan-2-ol (4:1, v/v) was an efficient system with which to carry out photohydrogenation but caused rapid precipitation of metallic nickel. THF and benzene were better solvents since they prevented the precipitation of metallic nickel, but photolysis in these solvents for longer periods also started precipitation. Photohydrogenation of 1,5-COD with  $\text{Ni}(\text{acac})_2$  in acetone-propan-2-ol under hydrogen gave 1,4-cyclo-octadiene (1,4-COD), cyclo-octene (COE), and cyclo-octane (COA) as shown by GC analysis. The percentages of  $\text{C}_8$ -hydrocarbons were determined against an internal standard, and the variations of the absolute percentages were very similar to that shown in Figure 3 except that the 1,4-COD percentages were significantly lower at all points of analysis. The products were identified by co-injection with authentic samples and by comparisons of their mass spectra with those reported. In other solvent and H-atom donating systems, the products were the same but the patterns of percentage changes were different. The control experiments showed that in the absence of a sensitizer or  $\text{Ni}(\text{acac})_2$  no isomerization and hydrogenation occurred.

For mechanistic studies on 1,5-COD photohydrogenation, irradiation of  $\text{Ni}(\text{acac})_2$  and xanthone in benzene containing a large excess of 1,5-COD was carried out under a slow stream of hydrogen. Xanthone had the advantage over other comparable triplet sensitizers in having an intense absorption peak in the

320 nm region and a high triplet energy<sup>39</sup> ( $E_T$  74 kcal mol<sup>-1</sup>) and  $\phi_{ISC} = 1$ . Unfortunately it also reacted with these C<sub>8</sub>-alkenes to form a small amount of the corresponding oxetane. These oxetanes detected by GC were minor amounts and did not interfere with GC analysis of C<sub>8</sub>-hydrocarbons. The percentage changes of C<sub>8</sub>-hydrocarbons in the photohydrogenation of 1,5-COD in the Ni(acac)<sub>2</sub>-xanthone-benzene-hydrogen system are plotted in Figure 3. The lagging times required for the formation of COE and COA as well as the rise and fall of the 1,4-COD percentages were indications of the sequential transformation shown below except that the presence of *cis,cis*-1,3-cyclo-octadiene (*cis,cis*-1,3-COD) has not been proven.



For a prehydrogenated benzene solution of 1,5-COD, either interruption of irradiation or imposition of a GWV filter (cut-off < 380 nm) caused cessation of the percentage changes of C<sub>8</sub>-hydrocarbons as shown in Figure 4, although small residual changes in the percentages were noted. Resumption of irradiation through a Pyrex filter started the reaction normally. The photohydrogenation of 1,4-COD under similar conditions provided the missing link of *cis,cis*-1,3-COD in the transformation, as shown in Figure 5. In this photohydrogenation, 1,5-COD was not formed. A small peak of *cis,cis*-1,3-COD in the photolysate after the initial 15–30 min period was confirmed by GC co-injection, GC-MS analysis, as well as by HPLC analysis using a 254 nm UV monitor; this peak rapidly decreased and appeared as a small shoulder close to the emerging peak of COE. This, together with rapid formation of COE, attested to the fact that *cis,cis*-1,3-COD, being a conjugated diene, was hydrogenated rapidly under the conditions. In the photohydrogenation of 1,5-COD (Figure 3), *cis,cis*-1,3-COD was certainly formed but could not be detected owing to its low concentration.

The quenching effects of *cis,cis*-1,3-COD on the photohydrogenation of 1,5-COD was studied using the same Ni(acac)<sub>2</sub>-xanthone-benzene-hydrogen system. For a benzene solution, prehydrogenated for 1 h, the addition of 0.0025 mol dm<sup>-3</sup> 1,3-COD did retard slightly the percentage changes of 1,5-COD and 1,4-COD, but caused a rapid formation of COE as

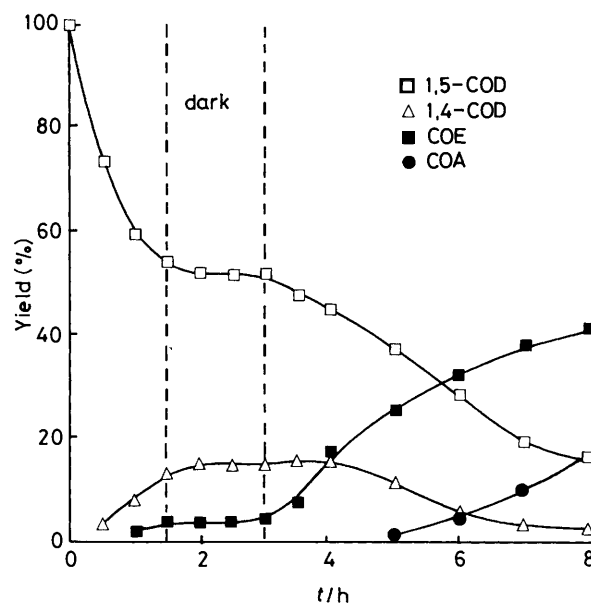


Figure 4. The same conditions as shown in Figure 3 except for the interruption of irradiation after 1.5 h and a resumption at 3 h.

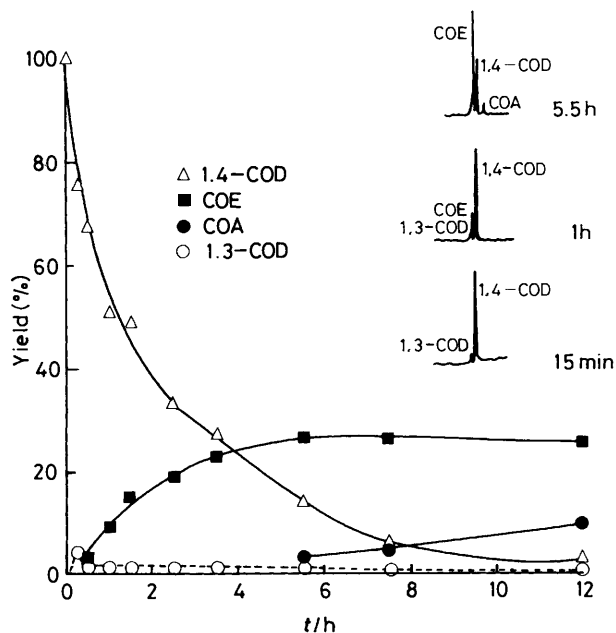
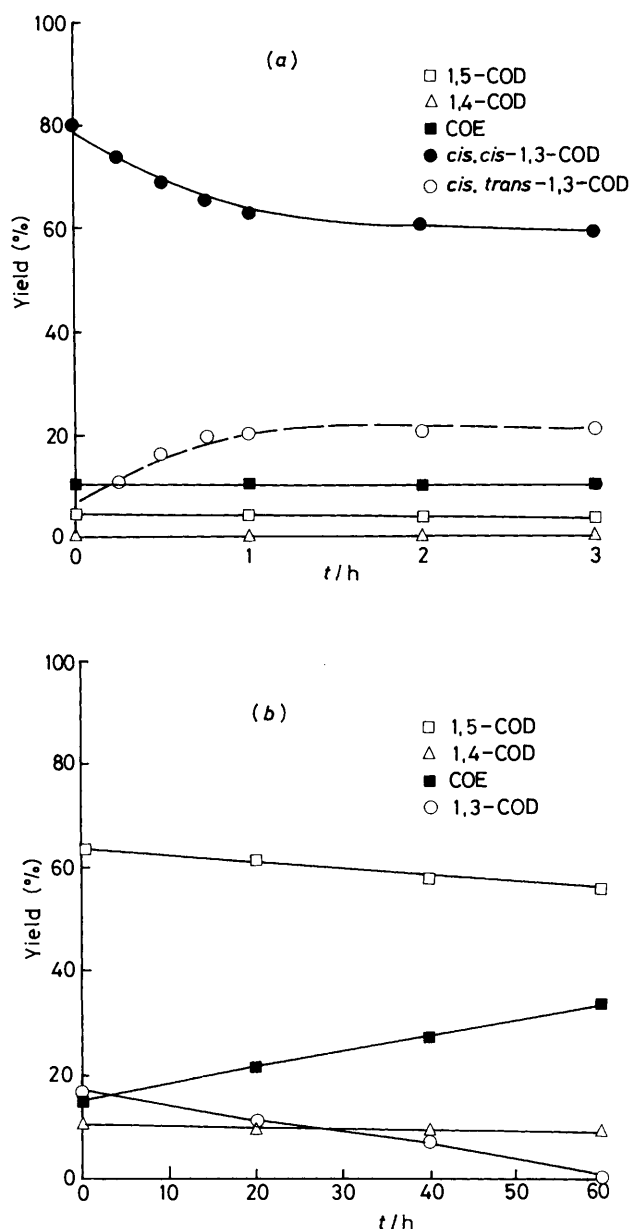


Figure 5. The percentage variations of C<sub>8</sub>-hydrocarbons in photolysis of a benzene solution containing Ni(acac)<sub>2</sub> ( $6 \times 10^{-3}$  mol dm<sup>-3</sup>), xanthone ( $9 \times 10^{-3}$  mol dm<sup>-3</sup>), and 1,4-COD ( $2 \times 10^{-2}$  mol dm<sup>-3</sup>) under hydrogen at room temperature. Inset: The GC traces.

expected [Figure 6(b)]. However, the addition of a higher concentration of *cis,cis*-1,3-COD at 0.05 mol dm<sup>-3</sup> completely stopped the percentage changes of 1,5-COD, 1,4-COD, and COE; the only reaction observed was added *cis,cis*-1,3-COD being photolytically isomerized to *cis,trans*-1,3-cyclo-octadiene (*cis,trans*-1,3-COD) [Figure 6(a)]. This isomerization has been known for some time<sup>40</sup> and was shown to occur by triplet-state ketone sensitization in the control experiments. COE was photohydrogenated in a similar system to give COA (74%).

A solution of Ni(acac)<sub>2</sub>, xanthone and 1,5-COD in benzene was photolysed under deuterium to give deuteriated 1,4-COD, COE, COA, and acetylacetone but 1,5-COD was not deuteriated (Table 3). Acetylacetone was monodeuteriated at the



**Figure 6.** The effects of the addition of *cis,cis*-1,3-COD at (a)  $5 \times 10^{-2}$  mol dm<sup>-3</sup>, and (b)  $2.5 \times 10^{-3}$  mol dm<sup>-3</sup> to a prephotolysed benzene solution of Ni(acac)<sub>2</sub> ( $5.7 \times 10^{-3}$  mol dm<sup>-3</sup>), xanthone ( $8.7 \times 10^{-3}$  mol dm<sup>-3</sup>), and 1,5-COD ( $5.0 \times 10^{-2}$  mol dm<sup>-3</sup>) for 1 h.

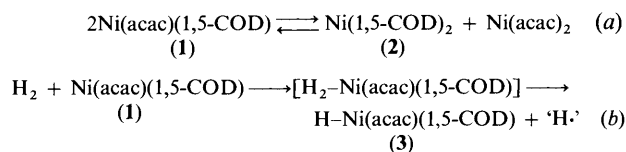
> 95% level. The percentages of deuterated species for each compound were determined by GC-MS techniques, as described in the Experimental section. Although the number of deuterium incorporation spread considerably in COE and COA, the major isotopomers were [<sup>2</sup>H<sub>2</sub>]COE and [<sup>2</sup>H<sub>4</sub>]COA in the respective products. The isolated COE isotopomer mixture showed <sup>2</sup>H NMR signals at 5.60, 2.04, and 1.43 ppm, in the ratio 2.2:6.5:10.5, indicating deuterium incorporation at the alkenic positions and a slightly higher incorporation at the allylic positions than the alkanic ones.

### Discussion

The observations presented above lead to the following conclusions derived from the experiments. First, a wide range of conditions can be used photolytically to reduce Ni(acac)<sub>2</sub> to Ni<sup>I</sup> complexes, Ni(acac)L<sub>2</sub> (L = ligands), so long as a high-energy

triplet-state sensitizer and H-atom donor are present. Second, Ni(acac)L<sub>2</sub>, where L = alkene or THF, reacts with hydrogen to generate nickel hydride complexes, H-Ni(acac)L<sub>2</sub>. Third, in the presence of excess 1,5-COD the photoreduction conditions under hydrogen serve to isomerize and hydrogenate sequentially, in the order shown in Scheme 4.

As a sensitizer, acetone has the disadvantage of possessing a low absorption > 300 nm at which Ni(acac)<sub>2</sub> absorbs strongly. Its triplet excited state is efficiently quenched by Ni(acac)<sub>2</sub> preventing oxetane formation with C<sub>8</sub>-alkenes. For preparative photohydrogenation, volatile acetone is the obvious choice as a sensitizer. The ability of hydrogen to act concurrently as an H-atom donor in the photoreduction of Ni(acac)<sub>2</sub> is advantageous, although this ability is not as efficient as that of propan-2-ol (compare Experiments 3 and 6, Table 1) for the obvious reason that the solubility of hydrogen is relatively low and calculated to be *ca.* 0.003 mol dm<sup>-3</sup> in benzene.<sup>28</sup> The Ni<sup>I</sup> species obtained under the photoreduction conditions could be stabilized long enough to show its isotropic ESR signal in the presence of good ligands such as phosphines, THF, and diglyme; otherwise, it decomposed rapidly, primarily by a bimolecular reaction (*vide infra*) to give colloidal nickel. With 1,5-COD as the ligand, Ni(acac)(1,5-COD) in benzene apparently does not possess sufficient stability to show an ESR signal but probably disproportionates rapidly [path (a), Scheme 5] or reacts with hydrogen to give nickel hydride (3) [path (b), Scheme 5].



**Scheme 5.**

Experimentally, the occurrence of disproportionation is confirmed by the observation that the green colour of Ni(acac)<sub>2</sub> is restored when a partially bleached photolysate under nitrogen is allowed to stand at room temperature without exposure to the air. This also explains the formation of nickel(0) complexes (NiL<sub>4</sub>) from Ni(acac)L<sub>2</sub> where L = phosphines and phosphites.<sup>1,3</sup>

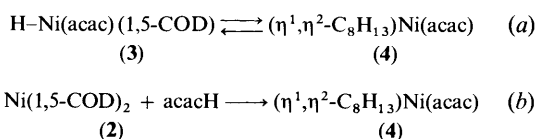
In the literature, some Ni<sup>I</sup> complexes are generated as transients,<sup>29-32</sup> but other Ni<sup>I</sup> species stabilized with phosphines are isolable.<sup>16,33,41</sup> As they have a 17-electron configuration, they should be reactive species; analogous reactions to path (b), Scheme 5 have been suggested, but the detailed mechanism remains obscure.<sup>7-10,42-44</sup> In the same series of experiments carried out under hydrogen with comparable conditions (Table 2, the last three Experiments), the approximate constancy of the second-order rate constants *k*<sub>2</sub> as compared with the decrease in the first-order rate constants *k*<sub>1</sub> with diminishing size of hydrogen concentration is a good indicator of the Ni<sup>I</sup> reactivity patterns under these conditions. The former suggests that the often-suspected termolecular reactions of Co and Rh complexes with 17-electron configurations<sup>7-10</sup> do not occur in Ni<sup>I</sup> complexes. The latter naturally confirms the reactions shown in Scheme 5 to be a pseudo-first-order reaction, although it is not possible to pinpoint exactly which species is the acceptor of the extra H-atom. One possibility is that bulk Ni(acac)<sub>2</sub> may scavenge this H-atom to give another Ni<sup>I</sup> complex and acetylacetone. The failure of Ni(acac)L<sub>2</sub>, where L<sub>2</sub> is diglyme or phosphines, to react with hydrogen in benzene (Experiments 1-6 in Table 2) is related to the ability of these complexes to give ESR signals, and indicates that these Ni<sup>I</sup> complexes are more stable (and therefore less reactive) than Ni(acac)(1,5-COD) whose ESR spectrum cannot be obtained in benzene (see Table 1).

**Table 3.** Relative percentages of deuteriated C<sub>8</sub>-hydrocarbons in the photohydrogenation of 1,5-COD under deuterium.<sup>a</sup>

	Relative percentages			
	1,5-COD	1,4-COD	COE	COA
[ <sup>2</sup> H <sub>0</sub> ]	100	44	0	0
[ <sup>2</sup> H <sub>1</sub> ]	0	56	10	0
[ <sup>2</sup> H <sub>2</sub> ]	0	0	48	<1
[ <sup>2</sup> H <sub>3</sub> ]	0	0	27	24
[ <sup>2</sup> H <sub>4</sub> ]	0	0	15	45
[ <sup>2</sup> H <sub>5</sub> ]	0	0	0	29
[ <sup>2</sup> H <sub>6</sub> ]	0	0	0	3

<sup>a</sup> A solution of Ni(acac)<sub>2</sub> (0.68 mmol), xanthone (1.0 mmol), and 1,5-COD (11.8 mmol) in benzene (12 cm<sup>3</sup>) was photolysed under deuterium for 6 h.

Nickel hydride compounds are stabilized by complexing with bulky phosphines and a number of these have been reported.<sup>36–38</sup> In solution the Ni–H complex of 1,5-COD, compound (3), is most likely to be in equilibrium with the known Ni–alkyl complex (4) [path (a), Scheme 6] and shows weak high-field <sup>1</sup>H NMR signals at *ca.* –16 and –1.3 ppm.<sup>21,22</sup> The complex (4) has been prepared from Ni(1,5-COD)<sub>2</sub> and acetylacetone [path (b), Scheme 6] and characterized, and has been used as an oligomerization catalyst by Keim *et al.*<sup>20–21</sup> Attempts to isolate the Ni–alkyl complex (4) have not been successful, but the presence of (4) is indicated by the presence of the reported proton signal of the Ni–CH moiety at –1.3 ppm.<sup>21,22</sup>

**Scheme 6.**

By analogy with the accepted addition–elimination mechanism for Ni–H complex catalysed alkene reactions,<sup>4–10</sup> the observed isomerization and hydrogenation of 1,5-COD can be mechanistically represented as shown in Scheme 3 for the convenience of discussion; while complexes (4) and (8) have been described in the literature,<sup>22</sup> others are assumed. However, [RhCl(1,5-COD)]<sub>2</sub> catalysed isomerization of 1,5-COD to 1,4-COD under illumination has been proved to follow a different mechanism: an irreversible [1,3]-hydrogen shift.<sup>27</sup> The hydrogenation of COE to COA occurs in the late stage of photolysis and follows the standard addition and hydrogenolysis steps;<sup>8–10</sup> this is not shown in Scheme 3. For the steps (6)→(7)→(8), the ease of addition and elimination involving conjugated dienes and metal hydrides are well established in the literature,<sup>10,23</sup> and are also shown by the facile reaction of 1,3-COD in Figures 3–5.

The rapid formation of the downstream products from 1,4-COD and 1,3-COD (Figures 4 and 6) clearly suggests that the regioselectivity for the addition and elimination steps in the early stages of Scheme 3 [*e.g.*, (3)→(4)→(5)→(6)] favours the same direction, probably directed by conformational factors in the co-ordination of nickel complexes. This is supported by two observations. First, the lack of formation of 1,5-COD in the photohydrogenation of 1,4-COD indicates that either one or both of the reverse processes, (5)→(4) and (4)→(3), does not occur. Second, the failure to incorporate deuterium in 1,5-COD in the catalysed photohydrogenation with D<sub>2</sub> may suggest—but does not confirm—the irreversibility of (3)→(4) since many addition and elimination steps catalysed by metal hydrides are

known to be stereospecific.<sup>10</sup> While 1,4-dienes are known to have some special reactivity in Ni complex catalysed thermal hydrogenations,<sup>14</sup> this can not be easily rationalized. It is noted that transition metal complex catalysed thermal 1,5-COD reactions<sup>13,23–26</sup> in the literature show similar reactivity patterns, except that induction periods for downstream products are not as distinct as those shown in Figures 3–5. The wide spread of deuterium numbers in COE and COA in Table 3 suggests a complex reaction pattern. However, the major components of isotopomer [<sup>2</sup>H<sub>2</sub>]COE and [<sup>2</sup>H<sub>4</sub>]COA clearly indicate that once the addition step (3)→(4) starts, the subsequent reactions are practically intramolecular up to the formation of (9). The labelling pattern of <sup>2</sup>H<sub>0</sub>/<sup>2</sup>H<sub>1</sub> of *ca.* 1:1 for recovered 1,4-COD indicates that for every reaction of a Ni–D species, a Ni–H species is formed.

What is the role played by photoexcitation? The efficient quenching by 1,3-COD (Figure 6) clearly suggests that triplet excited state xanthone, but not direct excitation of the nickel complexes, is accelerating the isomerization–hydrogenation processes. The rapid cession of C<sub>8</sub>-alkene reactions in the dark in Figure 4 (ignoring small variations) undoubtedly indicates that one or more steps of the catalytic cycle of Scheme 3 requires sensitized excitation. Owing to the overlap of the generation of Ni–H complexes and photohydrogenation reactions, the complex pattern does not allow the study of more quantitative aspects of these processes. Because of the rather lengthy irradiation time required, the photohydrogenation is most likely a so-called ‘photoassisted’ reaction rather than a true photocatalytic reaction. Many thermal alkene reactions catalysed by transition metal complexes share the same product formation patterns with the corresponding light-promoted reactions<sup>11,12</sup> and, in fact, illumination often changes the mode of reaction very little but does enhance the rate. In this work, the addition steps (3)→(4) and (7)→(8) are shown to occur easily under thermal conditions, the former by kinetic ESR and <sup>1</sup>H NMR spectroscopy and the latter by the 1,3-COD formation patterns in Figure 4 and other similar examples;<sup>7,10,24</sup> the analogous process (5)→(6) is also assumed to be fast in the dark. Both nickel complexes (4) and (8) are thermally stable<sup>20</sup> and the latter is unreactive towards alkenes.<sup>21,22</sup> This led us to suggest that the elimination step (4)→(5) and/or the hydrogenolysis step (8)→(9) require sensitized excitation in order to create a vacant co-ordination site so that the subsequent reaction can proceed.

In spite of the fact that certain reported thermally catalysed 1,5-COD reactions are promoted by phosphine complexes of transition metals,<sup>13,14,17</sup> the addition of PBu<sub>3</sub> to a pre-hydrogenated solution of Ni(acac)<sub>2</sub>, xanthone and 1,5-COD under hydrogen stops the alkene reactions promptly. It appears that a better co-ordinating ligand, PBu<sub>3</sub>, completely displaces C<sub>8</sub>-alkenes in the Ni-complexes. This agrees with the observation that Ni(acac)(PBu<sub>3</sub>)<sub>2</sub> lacks reactivity with hydrogen (Table 2).

The detection of the isotropic spectra of Ni<sup>1</sup> samples during the catalysed 1,5-COD reaction led us to believe that these catalytic reactions occur in a homogeneous phase using soluble nickel complexes, shown in Scheme 3, as the carriers. The occurrence of precipitation in the later phase of photolysis and the probability of forming colloidal nickel as shown by ESR spectroscopy, however, restrain us from making a premature conclusion as to the question of homogeneity. The possibility of the involvement of a colloidal metal in the catalysis of alkene reactions is a particularly difficult question to answer as shown in the recent literature,<sup>45–48</sup> and the concurrence of this cannot be confidently excluded during the irradiation in the present case. Whatever phases are involved, the photohydrogenation processes using Ni(acac)<sub>2</sub> and a sensitizer in the benzene–hydrogen system work and show unusual selectivity.

## Experimental

**General Conditions and Materials.**—General experimental conditions and equipment are the same as those published.<sup>1</sup> A commercial product of 1,5-COD was distilled and stored under N<sub>2</sub>. Analysis of C<sub>8</sub>-hydrocarbons was performed on a Hewlett-Packard 5792A gas chromatograph equipped with an OV-1 capillary column (12 m × 0.20 mm). HPLC was performed on a Waters Associates HPLC system on μ-Porasil column and Model-440 UV detector at 254 nm. NMR spectra were recorded on a Bruker WM-400 spectrometer with a pulse width of 2 μs and two different offsets (01 = 2 177 and 1 000 Hz).

**ESR Spectroscopy.**—The method of irradiation and the recording of spectra are the same as those described.<sup>1</sup> The formation and decay curves, such as Figure 2, were obtained by setting the magnetic field at the peak of the first derivative signal and scanning against time at a cavity temperature of 24 ± 1 °C. Data points were obtained from decay curves and analysed as follows: (i) according to first- or second-order rate equations with the 'MINITAB program' (MTS Computing Centre, SFU) and (ii) according to double exponential decays as in equation (1) with the 'MINUIT program' (by Dr. P. Percival, SFU). The rate constants under various conditions are given in Table 2.

**Photohydrogenation of 1,5-COD.**—A solution of Ni(acac)<sub>2</sub>, xanthone, and an excess of 1,5-COD in benzene (200 cm<sup>3</sup>) was irradiated in a Hanovia photolysis apparatus with a 200 W Hg lamp. At proper intervals, samples (2 cm<sup>3</sup>) were withdrawn and passed through a small column of basic alumina (4 g). The filtrates and washings (with benzene) were combined together and were diluted to 5 cm<sup>3</sup> for GC analysis. The peaks of C<sub>8</sub>-hydrocarbons were identified by co-injection of authentic samples. 1,4-COD was prepared by the method of Moon and Gang<sup>49</sup> except that the product was isolated by preparative GC (OV-1, 4 ft × 0.2 in\*; 50 °C isothermal). The preparation of *cis,trans*-1,3-COD was carried out from *cis,cis*-1,3-COD according to the literature method.<sup>40</sup>

**Deuteration of 1,5-COD.**—A solution of Ni(acac)<sub>2</sub> (0.7 mmol), xanthone (1 mmol), and 1,5-COD (12 mmol) in benzene (120 cm<sup>3</sup>) was photolysed under an atmosphere of D<sub>2</sub> for 6 h. The photolysate was filtered through a basic alumina column and washed with benzene. The combined filtrates were analysed by GC-MS and contained 1,4-COD (5%), COE (50%), COA (7%), and 1,5-COD (17%). For 1,4-COD, the total MS was analysed for ion intensities at *m/z* 107.7–108.6 and *m/z* 108.7–109.6. This was performed using Option I, User's Guide for the answer software package for the HP5985 GC-MS system (Revision G, 1982) in order to manipulate the selected ion profiles, the so-called 'Mass Chromatogram.' For other C<sub>8</sub>-hydrocarbons and acetylactone, the intensities of the appropriate ions were read from the total MS obtained under identical conditions. The percentage of isotopomers was calculated with reference to the intensity ratio of (*M* + 1) to *M*<sup>+</sup> obtained from the MS of undeuterated compounds. The analytical details have been given.<sup>3</sup>

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\* 1 inch (in) =  $\frac{1}{12}$  foot (ft) ≈ 2.54 cm.

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