conditions employed. In addition, although at this time the site of attachment of the glycosyl bond to the heterocyclic aglycon (7 *vs.* 9) cannot be established by mass spectrometry if only a single compound is available, the differentiation of isomers does appear feasible on the basis of the data obtained (Table I). It would further appear that CIMS may prove to be useful in predicting the relative rates of hydrolysis of closely related compounds in solution. Particularly advantageous are the speed and simplicity of data acquisition; moreover, much less material is required.

Further refinements in understanding the details of these reactions, as well as the prediction of substituent effects in both the vapor phase and in solution, will require more detailed knowledge of the site(s) of protonation and of the activation energies of the dissociation reactions.

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Structure and Reactivity Relationships in Chromium Carbonyl Photoassisted Hydrogenation of 1,3 Dienes

Sir:

We report herein product studies, relative rates, and selectivity experiments which implicate the importance of the s-cis conformation of 1,3 dienes which undergo hydrogenation under the conditions indicated in reaction 1. Further, our preliminary results reveal that the role of the uv light in reaction 1 is to generate a *thermally* active catalyst *via* photolysis of $Cr(CO)_6$ in the presence of H_2 and 1,3 dienes. The $Cr(CO)_6$ photoassisted hydrogenation of 1,3-cyclohexadiene and 2,3-dimethyl-1,3-butadiene has been reported to give, in synthetic yields, only cyclohexene and 2,3-dimethyl-2-butene, respectively.[1] Thermally catalyzed hydrogenation of 1,3 dienes using $(arene)Cr(CO)_3$[2] or $Fe(CO)_5$[3] requires both elevated temperatures and high H_2 pressure in marked contrast to the mild conditions of reaction 1.

$$\text{1,3 diene} \xrightarrow[\substack{\text{uv light} \\ Cr(CO)_6 \text{ (catalytic} \\ \text{amount), hydro-} \\ \text{carbon solvent} \\ 10^\circ}]{H_2\text{, 1 atm}} \text{alkene} \qquad (1)$$

That 2,3-dimethyl-1,3-butadiene yields only 2,3-dimethyl-2-butene reveals that 1,4 hydrogenation has been effected. The generality of this mode of addition is demonstrated by the products obtained from a series of 1,3 dienes:[4] *trans*-1,3-pentadiene yields *cis*-2-pentene, 2-methyl-1,3-butadiene yields 2-methyl-2-butene, and *trans,trans*-2,4-hexadiene gives *cis*-3-hexene. Additionally, when H_2 is replaced by D_2 in reaction 1 we find that *trans,trans*-2,4-hexadiene yields 2,5-dideuterio-*cis*-3-hexene as the exclusive product. The products indicated can be obtained in essentially quantitative yield. No gas chromatographically detectable isomers of the products are obtained with respect to either cis–trans or positional isomers nor does subsequent hydrogenation or isomerization of the alkenes occur under the conditions of reaction 1 using $Cr(CO)_6$.

All of the 1,3 dienes mentioned above have at least one structural feature in common, the ability to easily achieve the s-cis conformation, reaction 2. The significance of this observation is first demonstrated by considering the relative rates of hydrogenation of 2-methyl-1,3-butadiene, *trans*-1,3-pentadiene, and *cis*-1,3-pentadiene under identical conditions. Of these three 1,3 dienes only *cis*-1,3-pentadiene cannot easily achieve the s-cis conformation and it undergoes H_2 addition at an initial rate of less than one-tenth that of the other two. Even for *cis*-1,3-pentadiene, though, the product obtained is *cis*-2-pentene, consistent with 1,4 addition to an s-cis diene, and may actually be due to the selective hydrogenation of the *trans*-1,3-pentadiene which was present as a small impurity in the *cis*-1,3-pentadiene (*vide infra*). We observe that photoassisted *cis*- *to trans*-1,3-pentadiene conversion using $Cr(CO)_6$ does not occur on the same time scale under the hydrogenation conditions of reaction 1.

(2)

A set of selectivity experiments, Table I, lends even more impressive evidence supporting the implication that the s-cis conformation must be available for the $Cr(CO)_6$ photoassisted hydrogenation to occur. Hydrogenation of mixtures containing equal amounts of one diene which can easily achieve the s-cis conformation and one which cannot invariably yields selective hydrogenation of the s-cis diene. Particularly convincing is the fact that essentially total disappearance of *trans*-1,3-pentadiene to yield only *cis*-2-pentene is achieved in the presence of an equimolar amount of *cis,cis*-2,4-hexadiene, and little or no hexene products are formed.

The conformation effect established by the information in Table I is of practical value, and the product

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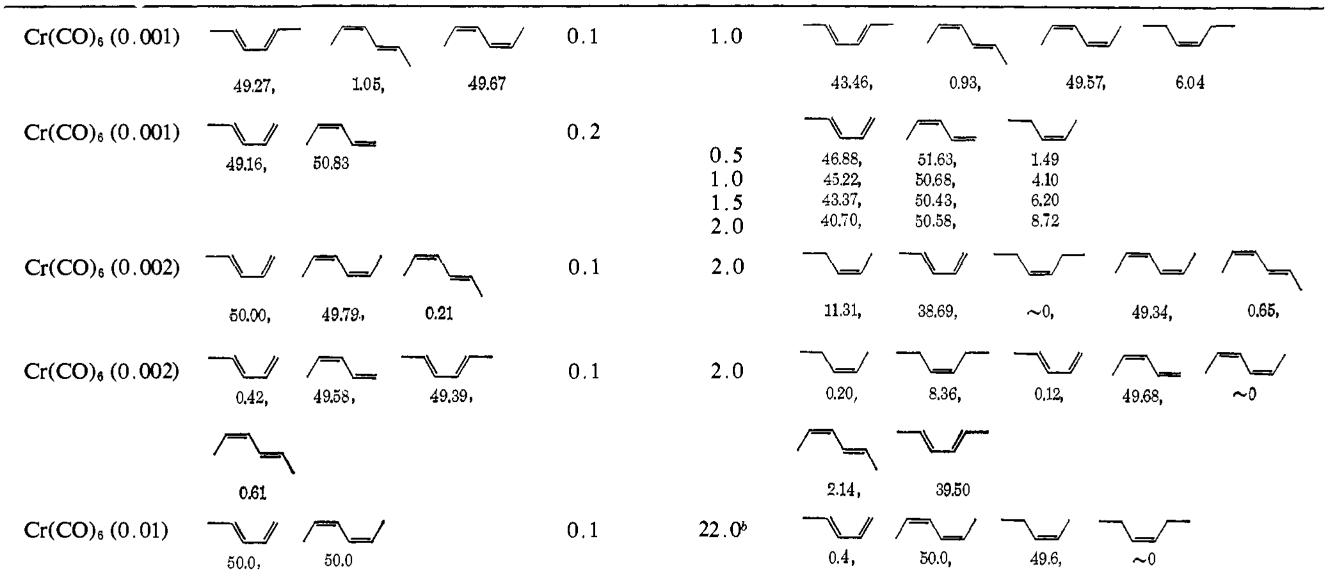
(4) The $Cr(CO)_6$ photoassisted hydrogenations were generally carried out in either benzene or isooctane solutions of the diene (~0.1 *M*) and $Cr(CO)_6$ (10^{-3}–10^{-2} *M*) at 10°. The solutions were thoroughly deoxygenated and then simultaneously stirred, exposed to uv light (300–380 nm), and subjected to 1 atm of H_2. Analysis of dienes and alkenes was by vpc where authentic samples of all C_5 and C_6 olefins could be separated; a 25 ft × 1/8 in. 25% $\beta\beta'$-ODPN column at 25° was used. The hydrogenation product of *trans,trans*-2,4-hexadiene has an nmr spectrum superimposable with an authentic sample of *cis*-3-hexene. The 2,5-dideuterio-*cis*-3-hexene was identified by its 100-MHz deuterium decoupled proton nmr.

Table I. Selective $M(CO)_6$ Photoassisted Hydrogenation of 1,3 Diene Mixtures



$M(CO)_6$ (*M*)	Starting mixture, %	Total diene, *M*	Reaction[a] time, hr	Mixture after reaction, %
$Cr(CO)_6$ (0.001)	49.27, 1.05, 49.67	0.1	1.0	43.46, 0.93, 49.57, 6.04
$Cr(CO)_6$ (0.001)	49.16, 50.83	0.2	0.5	46.88, 51.63, 1.49
			1.0	45.22, 50.68, 4.10
			1.5	43.37, 50.43, 6.20
			2.0	40.70, 50.58, 8.72
$Cr(CO)_6$ (0.002)	50.00, 49.79, 0.21	0.1	2.0	11.31, 38.69, ~0, 49.34, 0.65,
$Cr(CO)_6$ (0.002)	0.42, 49.58, 49.39, 0.61	0.1	2.0	0.20, 8.36, 0.12, 49.68, ~0 2.14, 39.50
$Cr(CO)_6$ (0.01)	50.0, 50.0	0.1	22.0[b]	0.4, 50.0, 49.6, ~0

[a] Reaction carried out at 10° with continuous uv irradiation in the presence of 1 atm of H_2, in benzene. [b] Reaction for first 2 hr at 10° then allowed to warm to 25°.

selectivity obtained here makes this system one of superlative specificity. In particular, none of the known[5] homogeneous hydrogenation catalysts have been shown to have the degree of selectivity exhibited by the $Cr(CO)_6$ photoassisted catalysis. Conformational effects in Diels–Alder reactions[6] of 1,3 dienes and in the triplet photosensitized dimerizations[7] and isomerizations[8] are known to involve the s-trans $\rightleftharpoons$ s-cis equilibrium, but this work represents the first report of a substantial conformational effect on diene reactivity in a metal photoassisted reaction. Preliminary results reveal that both $Mo(CO)_6$ and $W(CO)_6$ are effective as photocatalysts albeit with different rates, but they still yield selective H_2 addition to s-cis 1,3 dienes. However, both $Mo(CO)_6$ and $W(CO)_6$ suffer from the ability to assist isomerization of 1,3 dienes[9] and alkenes.[10]

While detailed mechanistic considerations may seem premature at this time we find that the role, in part, of the uv light in reaction 1 appears to be to generate a thermally active hydrogenation catalyst. This point was unequivocally established by several hours of dark reaction at 25° after an initial photolysis of 1 hr. Thermal hydrogenation proceeded, converting 2-methyl-1,3-butadiene to 2-methyl-2-butene, and the number of diene molecules hydrogenated is larger than the number of $Cr(CO)_6$ molecules initially present, Table II. Thus, the $[Cr(CO)_6–H_2–\text{light}]$ system represents a case of true *photocatalysis*, a situation where a catalytic reaction is triggered by light and the number of molecules ultimately undergoing reaction does not depend on the number of photons absorbed.

Table II. Chromium Carbonyl Photocatalyzed Hydrogenation of 2-Methyl-1,3-butadiene[a]

Time irradiated at 10°, hr	Time thermolyzed at 25°, hr	% hydrogenation
1	0	6.5
1	18	14.3
1	0	6.0
1	15	14.9

[a] $Cr(CO)_6$ initially 2×10^{-3} *M*, diene initially 10^{-1} *M*, and hydrogenation product from continuous photolysis and dark thermolysis is 2-methyl-2-butene.

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Cyclobutadiene as an Intermediate in the Oxidative Decomposition of Cyclobutadienyliron Tricarbonyl

Sir:

Rapid advances have been made recently in the study of the chemistry of cyclobutadiene. Although cyclobutadiene and its derivatives can be generated photochemically and observed at low temperature[1,2] the best potential precursors for cyclobutadiene remain the

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